SYNTHESIS, CHARACTERIZATION AND APPLICATION OF POLYMERIC FLAME RETARDANT ADDITIVES OBTAINED BY CHEMICAL MODIFICATION

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Department of Analytical Chemistry and Organic Chemistry

Synthesis, characterization and application of polymeric flame retardant additives obtained by chemical modification

by

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Doctoral Thesis

Supervisor:
Dr. José Antonio Reina Lozano

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I CERTIFY that this thesis, entitled: "**Synthesis, characterization and application of polymeric flame retardant additives obtained by chemical modification**", presented by Silvana Saucă to receive the degree of Doctor, has been carried out under my supervision, in the Department of Analytical Chemistry and Organic Chemistry at the Universitat Rovira i Virgili, and qualifies to apply for the European Mention in the title.

Tarragona, February 2012

Supervisor of the doctoral thesis

Dr. José Antonio Reina Lozano

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Content

Apendixes

Chapter 1

General Introduction and Objectives

Synthetic and/or natural polymeric materials bring many advantages to society in daily life, but most of them in the presence of a heat source and oxygen are burned quickly and easily. This thesis presents a study of new polymeric systems that could act as flame retardant additives. This chapter shows their interest and outlines work objectives.

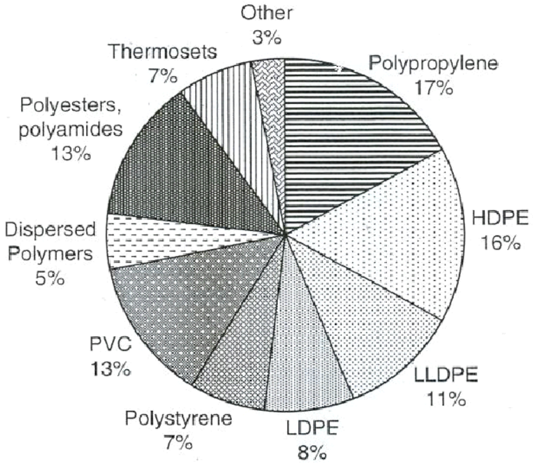
1. Introduction

1.1. Polymeric materials

The world production of polymers is about 260x10^6 Tons/year. Figure 1.1 shows the main polymers produced. As can be seen, thermoplastic polymers account the major part of the polymer market. Polyolefins, such as, low density polyethylene (LDPE) and linear low density polyethylene (LLDPE) are mostly used for film and sheet production, with smaller fractions devoted to pipe and conduits, wire and cable, and injection moulding. The main used applications of high density polyethylene (HDPE) are blow moulding, injection moulding, film and sheet, and pipe and conduit. Polypropylenes, such as, isotactic polypropylene (i-PP), high impact polypropylene (HIPP) and ethylene-propylene rubbers and elastomer (EPDM) are used for fibbers (commercial carpets, raffia, nonwoven fabrics, cordage), films (biaxial oriented and unoriented), injection moulding (appliances, general consumer products, rigid packaging, automotive parts) and wire and cable. Styrene polymers include general high impact polystyrene (HIPS), expandable polystyrene, and styrene-acrylonitrile (SAN) and acrylo(butadiene styrene) copolymers (ABS). Low viscosity (low M_w) HIPS are used for injection moulding whereas high M_w grades are used for melt mixing of films and sheets. The main markets are packaging, insulation, flotation and Geofoam. Most of SAN is used in manufacturing ABS resins that have a wide application in electrical and electronic equipments, houses and offices appliance and in the automotive industry. Poly(vinyl chloride) (PVC) is used in construction, domestic goods, packaging and clothing. Polyesters and polyamides, such as, poly(ethylene terephtalate) (PET), poly(buthylene terephtalate) (PBT), nylon 6 and nylon 6,6 have a large application in transportation, electrical and electronic industries as well as domestic appliances.

The most important thermosets are polyurethanes, phenol-formaldehyde resins and epoxy resins. Their main application is in coatings, adhesives and glass fibre insulation.[1] Because of their versatility and the fact that they are produced from cheap monomers, polyolefins compete with the rest of polymers in most of the markets.

Figure 1.1 World polymer market



Most of polymeric materials are easily fired in presence of a heat source and oxygen. This involves a series of problems such as loss of material properties, but also smoke and toxic gases that are formed during combustion could affect both human life and equipments. Because of that, fire hazards associated with the use of polymeric materials are of particular concern among government regulatory bodies, consumers and manufacturers alike.[2-4] This has led to the introduction of stricter legislation and safety standards concerning flammability, and extensive research into the area of flame retardants (FR) for polymeric materials has been the result.[4,5] Overall, world demand for FR is growing at

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[1] Asua, J.M. Polymer Reaction Engineering, Blackwell Publishing Ltd., **2007**, 1-28.

[2] Edbon, J.R.; Jones, M.S. In Concise Polymeric Materials Encyclopedia; Salamone, J.C., Ed.; CRC Press **1996**, 2397-2411.

[3] Hamerton, I.; Lu, S-Y. Prog Polym Sci **2002**, 27, 1661-1712

[4] Bourbigot, S.; Duquesne, S. J Mat Chem **2007**, 17, 2283-2300

[5] Anna, P.; Marosi, Gy.; Bertalan, Gy.; Márton, A; Szép, A. J Macromol Sci Part B **2002**, 41, 1321-1330.

nearly 5% per year and is expected soon to exceed annually 2 million metric tons, valued at $ 5 billon. Amongst the markets that require FR polymer compounds, industries related to construction, electrical and electronic components, transportation and textiles are the most important.[6-8] In terms of volume, FR used in ¨commodity¨ polymers, in special polypropylene (PP) and polyethylene (PE), surpasses the volumes used in all ¨non-commodity¨ polymers, according to year 2007 and 2008 market surveys.[8]

In order to understand the principle of flame retardants behaviour, it is first necessary to understand the thermal decomposition process of polymers.

1.2. Combustion of polymers

Polymeric materials combustion process is a highly complex process involving a series of related and/or independent steps that occur in condensed or gas phase, and also in the interphase between these two phases.

The most important step during the polymer combustion is fuel production, which takes place when a fire or external heat source produces an increment of temperature, resulting in the dissociation of chemical bonds and the evolution of volatile fragments. These compounds diffuse into surrounding atmosphere leading to a flammable mixture whose combustion is initiated when temperature exceeds the ignition. This combustion could be maintained or increased if exothermic reactions in gas phase involve enough heat flow that could arrive in condensing phase, decompounding polymeric material and producing more fuel, maintaining in this way the combustion cycle. (Figure 1.2)

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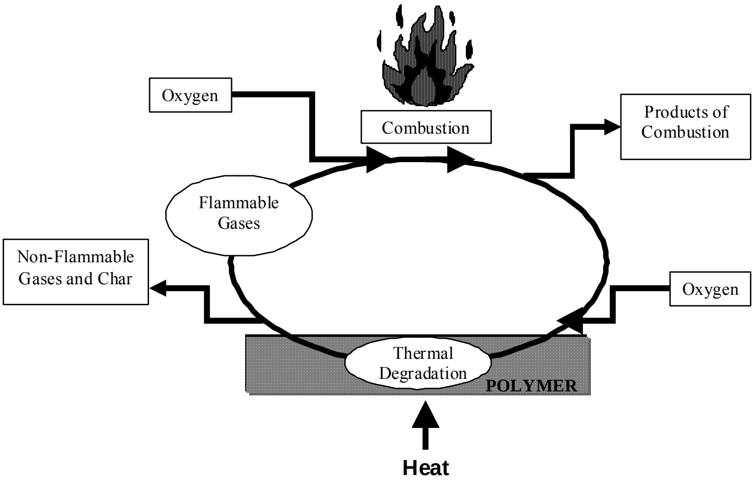
[6] Innes, J.D. Flame Retardants and Their Market Applications. Flame Retardants-101: Basic Dynamics, Past Efforts Create Future Opportunities, Fire Retardant Chemicals Associations: Baltimore **1996**, 61-69.

[7] Chen, L.; Wang, Y.-Z. Polym Adv Technol **2010**, 21, 1-26.

[8] Tolinski, M. Additives for Polyolefins, Elsevier Inc., 1st edition, **2009**, 61-62.

Figure 1.2 Combustion cycle of polymers



1.3. Flame retardants

A flame retardant may be defined as a substance built-in, or treatment applied to a material that suppresses or delays combustion thereof under specific conditions.

They interfere in the combustion process by physical or chemical action in the release of heat, decomposition, or spread of polymer flame. They may submit more than one mode of action depending on the chemical nature of the material, so it is difficult to ensure their operating way.[9]

Combustion process can be retarded by physical action in several ways, such as:

- **cooling**, when the endothermic reactions cool the polymeric material;
- **isolation**, when a protective char layer can be formed, isolating in this way polymeric material from heating source, oxygen and flames and preventing the volatile compounds to be transported to the flame;
- **dilution**, release of inert gases may dilute the volatile flammable compounds in the flame.

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[9] Lewin, M.; Weil, E.D. In Fire Retardant Materials; Horrocks, A.R. and Price, D., Eds.; CRC Press, **2001**, 31-68.

The chemical action of FR occur either in the vapour phase or the condensed phase, based in its interference in the reactions that maintain the combustion and/or in the reactions involved in the thermal degradation of the polymer.

In the gas phase FR activity is based on its interference in the combustion reaction. Burning polymeric materials produces species capable to react with atmospheric oxygen. As a result, the propagation of combustion occurs mainly through the following branching reactions (equations [1], [2] and [3]).

[1] $H\cdot + O_2 = HO\cdot + O\cdot$
[2] $O\cdot + H_2 = HO\cdot + H\cdot$
[3] $HO\cdot + CO = CO_2 + H\cdot$

Reaction related in the equation [3] is the main exothermic reaction and provides most energy to maintain the flame.

In the condensed phase, flame retardants or their thermal decomposition products catalyzes dehydration and condensation reactions that lead to cross-linking, forming a char layer over the polymer surface. This solid residue protects the polymer by isolating the non- burned material from the heat, oxygen and flames and prevents the volatile products to reach the flame and feed it.

Another major category of flame retarding mechanism is that known as ¨intumescent¨, in which materials swell when exposed to fire or heat to form a porous foamed mass, usually carbonaceous, which in turn act as a very effective barrier to heat, air and pyrolysis product.

Flame retardants are usually classified into two main categories, namely additives and reactives.[2,3] Additives are mixed with polymeric substrate and can be added at any stage of production and processing. Their use has some disadvantages, such as: they can be removed easily with water, detergents or solvents and can migrate altering the physical and chemical properties of material. In spite of this, they are widely used due to its low cost and easy

applicability.[3,10] Reactive FRs have the advantage to additive flame retardants on to be permanently bonded to the substrate. In fact, a relatively low amount of reactive flame retardants can have a comparable effect to that achieved with relatively high loads of additive flame retardants. In contrary, obtaining reactive systems are more expensive and time consuming, because they requires the development of a new polymer with chemical and physical specific properties.[3,6]
In order to combine additive and reactive flame retardant advantages, some researchers paid attention in polymeric and oligomeric structures to be used as additive flame retardants.[11-14] The case for the use of such flame retardant additives, rather than conventional non-polymeric species, is that they show better resistance to extraction, migration and volatile-loss, due to their high molecular weight. Thus, polymers with flame retardant properties can be used as blends to enhance the flame retardancy of other polymeric materials; the major criteria being compatibility.[3,7]

Additionally, flame retardant compounds can also be classified into halogenated and halogen-free flame retardants. For several decades, the polymer industry uses halogenated compounds (Cl and Br) combined to the polymer substrate as flame retardants.[15] Halogenated compounds may act in the condensed phase, but detailed research indicates that they are primarily vapour-phase flame retardants, interfering with the free radical reactions involved in flame propagation. Free HO• and H• radicals are responsible for propagation of combustion through chain branching (equations [1] and [2]). Halogenated FRs release hydrogen

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[10] Cullis, C.F.; Hirschler, M.M. The Combustion of Organic Polymers, Clarendon Press: Oxford, **1981**, p 300.

[11] Perez, R. M.; Sandler, J.K.W.; Altstädt, V.; Hoffmann, T.; Pospiech, D.; Artner, J.;Ciesielski, M.; Döring, M.; Balabanovich, A.I.; Schartel, B. J Mat Sci **2006**, 41, 8347-8351.

[12] Chung, Y.-J.; Kim, Y.; Kim, S.J. Ind Eng Chem **2009**, 15, 888-893.

[13] Wang, J.; Xin, Z. J Appl Polym Sci **2010**, 115, 330-337.

[14] Sundarrajan, S.; Kishore, K.; Ganesh, K. Indian J Chem Sect A **2001**, 40, 41-45.

[15] Morgan, A.B.; Tour, J.M. Macromolec **1998**, 31, 2857-2865.

halides during combustion, which effectively interfere with these branching reactions acting as flame inhibitors (equations [4] and [5]).

[4] $H\bullet + HX = H_2 + X\bullet$

[5] $HO\bullet + HX = H_2O + X\bullet$

Bromine compounds are generally more effective than chlorinated due to their labile C-Br bond, but they are more expensive and less thermally stable.

The use of halogenated compounds has the disadvantage of increasing quantities of smoke and toxic decomposition products that release during the combustion of the polymer. Moreover, they lead also the additional risk of formation of strong acid gases, such as HCl and HBr, which are released during combustion. Therefore, halogenated compounds represent a hazard environment pollution problem, which has been considered especially in recent years. The concept of sustainable development requires the use of flame retardant technologies with minimal impact on the environment. Thus, incorporation of different inorganic chemicals (metal hydroxides, antimony oxides or stannates) and flame retardants based on other heteroelements like phosphorus, nitrogen, boron or silicon in the polymer structure is described as one of the most efficient ways to obtain a set of environmentally friendly halogen free flame retardant polymers.[3,16] Recently, special interest has attracted the synergism obtained applying mixtures of flame retardant additives, which often have different mechanisms of action. The classic case is the antimony oxide interaction with halogenated compounds, although there are other examples such as halogens and peroxides, halogens and phosphorus, phosphorus and silicon and phosphorus and nitrogen compounds (intumescent systems).

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[16] Levchik, S.V.; Weil, E.D. J Fire Sci **2006**, 24, 345-364

Among environmentally friendly flame retardant systems, phosphorous-based flame retardants have been extensively studied and proven to act efficiently in the condensed phase. Moreover, some studies report their action also in the vapour phase. The use of phosphorous compounds as flame retardants in polymeric materials is well established.[17] Phosphorous can take many oxidation states, making the mechanisms of action of various phosphorous-based FR compounds difficult to summarize.[2,3] Generally, these FRs can be inorganic, organic or elemental (red phosphorous), they can act in the vapour phase or in the condensed phase, and some times may operate simultaneously in both phases.[2,18] Phosphines, phosphine oxides, phosphonium compounds, phosphonates, elemental red phosphorous, phosphites and phosphates are all used as flame retardants. Phosphine oxides[19] and phosphate esters[2,20,21] have been reported to act in the vapour phase through the formation of $PO\cdot$, $PO_2\cdot$, $HOPO\cdot$ and $HOPO_2\cdot$ radicals, which end the highly active flame propagation radicals ($HO\cdot$ and $H\cdot$). These radicals are formed after the parent compound decomposition and therefore, the flame inhibition does not depend on the form of the parent compound, provided that the parent breaks down in the flame.[20]

In the condensed phase action, the phosphorous FR decompose thermally producing phosphoric acid, which is further dehydrated to polyphosphoric acid, that reacts with polymeric material hydroxyl groups allowing condensation and dehydration reactions to take place in the polymeric surface; thus, giving rice to unsaturated carbonaceous species, that generate relative incombustible residues,

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[17] Edbon, J.R.; Price, D.; Hunt, B.J.; Joseph, P.; Gao, F.; Milnes, G.J.; Cunliffe, L.K. Polym Degrad Stab **2000**, 69, 267-277.

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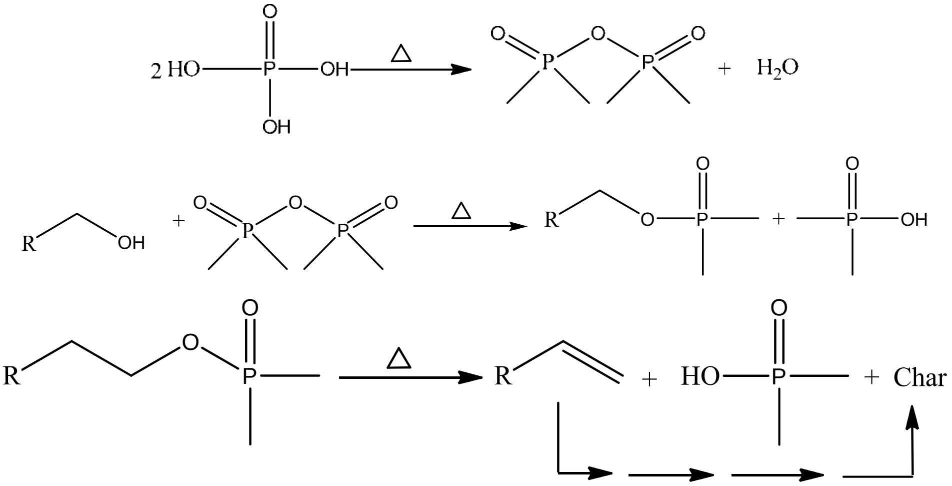
[21] Jayaweera, T.M.; Melius, C.F.; Pitz, W.J.; Westbrooka, C.K.; Korobeinchev, O.P.; Shvartsberg, V.M.; Shmakov, A.G.; Rybitskaya, I.V.; Curran, H. J. Comb Flame **2005**, 140, 103-115.

which act as a protective barrier that inhibits the degradation and protects the material of pyrolysis (see scheme 1.1)

Scheme 1.1



Increasing research is now being directed to the synthesis of phosphorous-based flame retardant polymers. Some recently published examples include polyphosphonates,[22] phosphonate-based polyurethanes,[23] epoxy resins,[24-27] poly(ether-ester)s,[24,28-34] polyacrylates[35-37] phosphate containing nylon and

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[22] Ranganathan, T.; Zilberman, J.; Farris, R.J.; Coughlin, E.B.; Emrick, T. Macromolec **2006**, 39, 5974-5975.

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[27] Lligadas, G.; Ronda, J.C.; Galià, M.; Cádiz, V. J Polym Sci Part A: Polym Chem, **2006**, 44, 6717-6727.

[28] Canadell, J.; Mantecón, A.; Cádiz, V. J Polym Sci Part A: Polym Chem, **2007**, 45, 1980-1992.

[29] Canadell, J; Hunt, B.J.; Cook, A.G.; Mantecón, A.; Cádiz, V. J Polym Sci Part A: Polym Chem, **2006**, 44, 6728-6737.

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silk,[38,39] modification of cotton fabric with phosphoric acid,[40] polybenzoxazines,[41,42] poly(ether-ketone)s,[43] polyphosphorinanes,[44] and styrene polymers and copolymers.[45]

On the other hand, many researchers have shown that the addition of relatively small amounts of silicon compounds to different polymeric materials can significantly improve their flame retardancy, which could be due to both, char forming in the condensed phase and the trapping of free radicals in the vapour phase.

Some recently published examples include the synthesis of silicon-containing epoxy resins[46,47] and polybenzoxazines[48] and the synthesis of one alkoxysilane functionalized polycaprolactone / polysiloxane modified epoxy resin through sol-gel process.[49] Furthermore, silicon-based nanocomposites have been

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[31] Hoffman, T.; Pospiech, D.; Häuβler, L.; Komber, H.; Voigt, D.; Harnisch, C.; Kollann, C.; Ciesielski, M.; Döring, M.; Graterol, R.P.; Sandler, J.; Altsädt, V. Macromol Chem Phys **2005**, 206, 423-431.

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[46] Spontón, M.; Mercado, L.A.; Ronda, J.C.; Galià, M.; Cádiz, V. J Polym Sci Part A: Polym Chem **2005**, 43, 6419-6430.

[47] Wu, K.; Song, L.; Hu, Y.; Lu, H.; Kandola, B.K.; Kandare, E. Prog Org Coating **2009**, 65, 490-497.

[48] Spontón, M.; Ronda, J.C.; Galià, M.; Cádiz, V. Polym Degrad Stab **2009**, 94, 145-150.

[49] Liu, P.; Song, J.; He, L.; Liang, X.; Ding, H.; Li, Q. Eur Polym J **2008**, 44, 940-951.

prepared via sol-gel method,[50] using polyhedral oligomeric silsesquioxane (POSS),[51] polymer-layered silicates[52] and other silicon-containing materials.[53]

Also boron compounds are widely used as flame retardants in textile area and some plastic formulations.[54] Borates and boric acid have been well established as flame retardants for a long time.[55,56] Boron compounds act in the condensed phase favouring carbon formation rather than CO and CO_2, leading in this way to the formation of a charred protective layer, which acts as a barrier.3 above

Some examples of boron-based flame retardants in recent literature include the synthesis of boron-containing epoxy-novolac resins,[57] boron-modified phenol-formaldehyde resins,[58] boron-containing phenolic resins,[59,60] boron-based styrenic systems,[3,61] boron-containing nanocomposites[62] and polyurethane-zinc borate composites.[63]

Nitrogen-based flame retardants are environmentally friendly because they are less toxic and do not have additional elements to those already presented in polymers. There are no dioxin and halogen acids by-product, but there are low evolution of smoke during combustion. Materials based on nitrogen containing

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[52] Pavlidou, S.; Papaspyrides, C.D. Prog Polym Sci **2008**, 33, 1119-1198.

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[61] Martín, C.; Hunt, B.J.; Edbon, J.R.; Ronda, J.C.; Galià, M.; Cádiz, V. J Polym Sci Part A: Polym Chem **2005**, 43, 6419-6430.

[62] Gao, J.; Jiang, C.; Ma, W. Polym Composite **2008**, 29, 274-279.

[63] Yildiz, B.; Seydibeyoglu, M.O.; Güner, F.S. Polym Degrad Stab **2009**, 94, 1072-1075.

flame retardant are also suitable for recycling.[64] More interestingly, novel nitrogen containing polymers with inherent flame retardant properties are being developed.[65] Various phosphorus-nitrogen (P–N) containing compounds have shown to impart flame retardancy to polymers.[66] Moreover, showing a synergistic behaviour the P–N compounds have greater thermal stabilities and lower toxic smoke evolution when compared to phosphorus based FR.

Many P-N systems can be classified as intumescent systems. In recent years, intumescent flame retardant (IFR) additives have been widely used in the flame retardation of many flammable polymers, especially in polyolefins.[4] The following three critical components are typically required in each IFR:

- an acid source which usually forms, during the pyrolysis (often poly (phosphoric acid))
- a char promoter which is dehydrated by the acid released from acid source and forms an insulating cellular carbonaceous layer between the polymer and flame
- a blowing agent which expands the cellular char foam, often nitrogen compounds will release ammonia on decompounding.

1.4. Flame retardancy tests

The fire behaviour of polymeric materials cannot be fully evaluated by the simple determination of some parameters in the laboratory. Fire and combustion process are very complex and it should at least take into consideration four aspects, which are interrelated in the overall process of combustion. These aspects are ignition, the flame propagation speed, the rate of heat release and formation of fumes and gases, which all contribute in the burning process and hazards associated with fire.

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[64] Lomakin, S. M.; Zaikov, G. E. Ecological aspects of polymer flame retardancy. Utrecht: VSP; **1999.**

[65] Schreiber, H.; Saur, W. Makromol Chem Macromol Symp **1993**, 74, 165-171.

[66] Hsiue, G.-H.; Liu, Y.-L.; Tsiao, J. J Appl. Polym. Sci. **2000**, 78, 1-7.

As a result of complex nature and poor reproducibility of a fire, there are many techniques to estimate the flammability of polymeric materials, each one focusing in certain characteristic of the combustion process. There are three main categories of tests procedure: small-scale, in which a small amount of sample is burnt and the combustion behaviour observed; medium-scale techniques, including tunnel tests and radiant panel tests; and the large-scale, with experiments carried out in rooms and corridors that provides the best reproduction of a real fire situation. Although the large-scale tests are very comprehensive and give the closest representation to a real fire, they are expensive and difficult to control, and thus the small and medium-scale tests are often more practical.[67]

Among the techniques most widely used in laboratory could be reported:

- **Limiting oxygen index (LOI)**, defined as the minimum concentration of oxygen in a flowing oxygen/nitrogen mixture, required to just support candle-like downward burning of a vertically mounted test specimen. Hence, higher LOI values represent better flame retardancy. This test method is generally reproducible to an accuracy of ±0.5%, and although originally designed for testing plastics, the method has been used extensively for evaluating the relative flammability of the rubbers, textiles, paper, coatings and other materials. LOI tests can be performed in accordance with international standards, including ASTM D2863 and ISO 4589-2.
- **UL-94 test** (ASTM D3801), is a standard applied for testing the flammability and fire safety of materials used specially for manufacture of electric and electronic components. Its action is based on firing time, the flame propagation speed and the dripping during the burning. Usually a vertical burn test is carried out and the flammability is rated

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[67] Grassie, N.; Scott, G. Polymer Degradation and Stabilisation Cambridge University, **1985**

from V0 to V2. To achieve the best flame retardancy rating of V0, the burning must stop within 10 s after two applications of 10 s each of a flame to a test bar and no flaming drips are allowed.

- **Thermogravimetric analysis (TGA)** is one of the most popular methods for characterizing the thermal stability of polymers. It determines the thermal behaviour and the amount of char formed during the thermally decomposition of polymeric material in nitrogen or air atmosphere. The char yield can serve as an indirect indication of flame retardancy. Thick char becomes a better thermal insulating layer, which undergoes slow oxidative degradation and prevents heat reaching the remaining polymer. Lewin[68], pointed that the chars obtained in the intumescent systems are different. They are prepared at lower temperatures and are not fully pyrolysed or oxidised, their rate of formation is high and involves thermo-oxidation; though, they serve the same purpose, namely acting as barriers to the passage of molten polymer and decomposition gases. The starting temperature of the weight loss process can be an indication of how the flame retardant acts. Low onset temperature of weight loss process is associated to flame retardants which act by formation of protective barriers, such as already explained for intumescent systems, delaying the mainly weight loss process and leading to significant char yield at high temperature. High onset temperature of weight loss process is usually characteristic for systems that are more thermal stable.
- **Cone calorimeter** represents an important advance at laboratory scale as flame retardancy test of polymeric materials and composites, based in principle of oxygen consumption calorimetry. This test not only provides

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[68] Lewin, M. Physical and chemical mechanisms of flame retarding of polymers. In: Le Bras M.; Camino G.; Bourbigot S; Delobel R. Fire retardancy of polymers-the use of intumescence. Cambridge: The Royal Society of Chemistry; **1998**, 1-32.

an idea of the risk of fire, it gives also the possibility to evaluate the rate of heat release (HRR), total heat released (THR), the ignition time (TTI), mass loss rate (MLR), and the smoke and toxic gases production. Generally, the heat of combustion of any organic material is directly related to the amount of oxygen required for combustion in which 13.1 MJ of heat is released per kg of oxygen consumed. The cone calorimeter brings quantitative analysis to materials flammability research. The HRR measurements can be interpreted by looking at average HRR, peak HRR and time to peak HRR. Heat release rate is the key measurement required to assess the fire hazard of materials and products as it quantifies fire size, rate of fire growth and consequently the release of associated smoke and toxic gases. The cone calorimeter can also measure and quantify smoke output as well as CO/CO_2 release rates.[69] Cone calorimeter tests can be conducted in accordance with national and international standards including BS 476, ASTM E1354 and ASTM E1474, and ISO 5660-1.

Since cone calorimeter measures flammability in different manner than LOI and UL-94 fire tests, one should not be surprised by the poor correlation between the methods. Morgan and Bundy[69] tried to explain differences among LOI, cone calorimeter and UL-94 test. LOI is a small-scale test that uses a variable percentage oxygen atmosphere to maintain a candle-like burn, and UL-94 V applies a small calibrated flame twice under the sample (configured vertically) for 10 s followed by measuring time to extinguishment after each flame application. Cone calorimetry, on the other hand, uses a forced combustion in which radiant heat is projected onto a sample before ignition and during burning of the sample. The sample is usually in a horizontal configuration, thus

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[69] Morgan, A.B.; Bundy, M. Cone calorimeter analysis of UL-94 V-rated plastics. Fire Mater **2007**, 31, 257–283.

eliminating any physical effects of polymer burning (dripping away from the flame, for example) that are sometimes used to pass the UL-94 V test, especially under the V2 rating. Further, the sample in the cone calorimeter exposed to continuous heat during the test is well ventilated, whereas UL-94 is not. In effect, cone calorimeter measures the material response to constant fire threat by time, whereas UL-94 measures the material response to remove a fire threat and its time to self-extinction. Therefore, some studies have been conducted to show correlations between UL-94, LOI and cone calorimeter tests.

2. Objectives

The general objective of this doctoral thesis is to develop new halogen-free polymeric flame retardant additives and to study their action in ¨commodity¨ polymers.

To achieve this goal, the experimental work was divided into two parts.

- Synthesis and characterization of polymeric flame retardant additives; this part, focused on the chemical modification of polymers with phosphorous-based compounds known to be good flame retardant promoters. In some cases, nitrogen-containing moieties were also introduced to see the synergistic effect between phosphorous and nitrogen actions on the flame retardancy.
- Blending of some of the synthesised polymeric flame retardant additives with ¨commodity¨ polymers, to study their effect on the flame retardancy behaviour and on the mechanical properties of the final polymeric materials in order to envisage their applicability.

Chapter 2

Flame retardant phosphorous-containing polymers obtained by chemically modifying poly(vinyl alcohol)

A new family of polymeric flame retardant additives that could be blended by thermoplastic polymers for improve their thermal stability and flame resistance was synthesized. Polymeric flame retardant additives were performed through the chemical modification of poly(vinyl alcohol) by phosphorous-containing compounds reported as good flame retardant moieties, where the phosphorous compound act as a catalyst and poly(vinyl alcohol) as a carbon char formation source.

1. Introduction

As already discussed in chapter 1, polymeric materials that become widely used for many different applications are inherently combustible. Their combustion process and problems that this involves have been developed in the general introduction. Thus, the use of flame retardants, which help to reduce the inherent combustibility of polymers and the production of smoke and toxic gases, has become a key part of new polymeric materials development.[4,5]

On the basis of all mentioned above, we intended to synthesise a new set of flame retardant phosphorous-containing polymers suitable to be applied as environmentally friendly flame retardant additives by blending with thermoplastic ¨commodity¨ polymers. These flame retardant polymeric additives have been obtained by chemically modifying poly(vinyl alcohol) (PVA) through reaction with phosphorous-containing reagents.

As phosphorous source we used a phosphate, a phosphite and a phosphine oxide derivative compound which have been reported to be good flame retardancy promoter structures.[3,4,7,16,70-72] The choice of different phosphorous derivative classes was in order to get widely compatibility with many ¨¨commodity¨ polymers¨ and different char forming, respectively.

The choice of PVA as starting pre-formed polymer is due to its high availability, low cost, and high reactivity, but mostly to its high char forming character, which in turn is due to the presence of free hydroxyl groups (unmodified). On heating, they can easily lead to dehydration reactions which give rice to unsaturated materials, especially in the presence of phosphorous-containing moieties which can act as a dehydration catalyst source. Moreover, dehydration reactions obviously involve water vapour release, which contribute to dilute the

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[70] Zhang, S.S; Xu, K.; Jow, T.R. J Power Sources **2003**, 113, 166-172.

[71] Xie, F.; Wang, Y-Z.; Yang, B.; Liu, Y. Macromol Mater Eng **2006**, 291, 247-253.

[72] Peng, H.-Q.; Zhou, Q.; Wang, D.-Y.; Chen, L.; Wang, Y.-Z. J Ind Eng Chem **2008**, 14, 589-595.

flammable gases on the flammable mixture and to cool the pyrolysis zone due to the high evaporation latent heat of water.[3,73]

In this chapter, we focus on the synthesis and characterization of the above mentioned flame retardant PVA derivatives. Furthermore, a detailed study on the thermal degradation of some of them is also reported, since it can be useful to envisage whether (and how) they can act as a flame retardant polymeric additive on blending with thermoplastic ¨commodity¨ polymers.

2. Experimental Part

2.1-Materials

Commercial materials

Poly(vinyl alcohol) (degree of polymerization = 300) was supplied by Fluka and dried, prior to use, at 60 ºC for 24 h under vacuum. Its degree of hydrolysation (percentage of free hydroxyl groups) is 88 mol% as determined by ^{1}H NMR spectroscopy.

Benzoyl chloride (Sigma-Aldrich, 99%), valeroyl chloride (Sigma-Aldrich, 98%), 4-(dimethylamino)-pyridine (DMAP, Fluka, 99%), thionyl chloride (Sigma-Aldrich, 97%), oxalyl chloride (Fluka, 96%) and hexane (Scharlau, synthesis grade) were used as received.

1-Methyl-2-pyrrolidinone (NMP, Sigma-Aldrich, 99.5%), chloroform ($CHCl_3$, Panreac, 99%) and pyridine (Py, Sigma-Aldrich, 99%) were purified prior to use. NMP was first dried by removing water as benzene azeotrope (Dean-Stark apparatus) and then fractionally distilled, collecting the desired fraction (78-79 ºC/12 mmHg) over Linde type 4Å molecular sieves. Pyridine was first pre-dried over KOH pellets and then fractionally distilled from sodium hydride over Linde type 5Å molecular sieves. Chloroform was extract from water several times in order to eliminate ethanol traces, dried over anhydrous calcium chloride and

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[73] Wang, D.-L.; Liu, Y.; Wang, D.-Y.; Zhao, C.-X.; Mou, Y.-R., Wang, Y.-Z. Polym Degrad Stab **2007**, 92, 1555-1564.

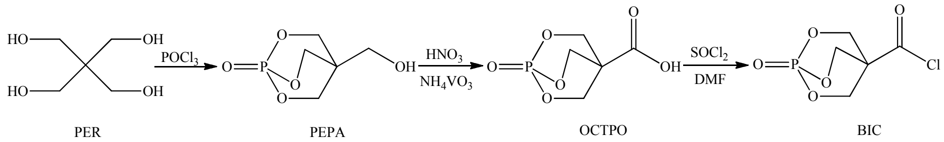
then refluxed with calcium chloride, fractionally distilled over Linde type 4Å molecular sieves and stored under argon atmosphere with 4Å molecular sieves in a dark flask.[74]

Linde type 4Å and 5Å molecular sieves were previously activated by heating them in an oven at 200 ºC for 24 h, and then leaved to cool and kept under argon atmosphere in a well-dried flask.

Synthesized materials

4-Chloroformyl-1-oxo-2,6,7-trioxa-1-phosphabyciclo[2.2.2]octane (BIC) was synthesized from pentaerythritol according to a published three steps procedure (scheme 2.1).[71] The overall yield was 44 %. The characterization data are as follows: melting point (°C): 243-245; IR (cm^{-1}): 1780 (C=O); 1312 (P=O); 1170 (C-O); 987 (P-O); 860 (skeleton vibration of caged bicyclic phosphate) ; ^1H NMR (acetone-d_6, 400 MHz, δ(ppm)): 5.1 (d, 6H, $^3J_{H-P}$=6.9 Hz); ^{13}C NMR (acetone-d_6, 100.6 MHz, δ(ppm)): 43.6 (s), 75.5 (t), 165.8 (s); ^{31}P NMR (acetone-d_6, 161.9 MHz, δ(ppm)): -7.9 (s).

Scheme 2.1



2-chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane (CDDP) (scheme 2.2) was obtained from ice-cooled ether solution of phosphorous trichloride with 2,2-dimethyl-1,3-propandiol according to a published procedure.[75,76] Yield was 78 %. Characterization data are as follows: melting point (ºC): 42-45; IR (cm^{-1}):

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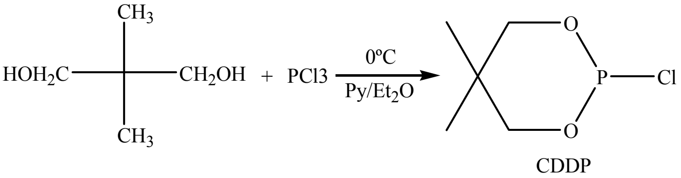
[74] Armarego, W.L.F.; Perrin, D.D. Purification of Laboratory Chemicals, 4th edition, **1996**, pp. 275, 317, 143.

[75] White, D.W.; Bertrand, R.D.; McEwen, G.K.; Verkade, J.G. JACS **1970**, 92, 24, 7125-7135.

[76] Muthiah, C.; Praveen Kumar, K.; Aruna Mani, C.; Kumara Swamy, K.C. J Org Chem **2000**, 65, 3733-3737.

1288 (C-O); 1003 (P-O); 835 (skeleton vibration of cycle); ^{1}H NMR ($CDCl_3$, 400 MHz, δ(ppm)): 3.4-4.2 (m, 4H), 0.8-1.2 (d, 6H); ^{13}C NMR ($CDCl_3$, 100.6 MHz, δ (ppm)): 22.7-22.8 (d), 33.2-33.3 (d), 71.2-71.3 (d); ^{31}P NMR ($CDCl_3$, 161.9 MHz, δ (ppm)): 146.

Scheme 2.2



4-carboxyphenyl-diphenyl-phosphine-oxide (CDPO) was synthesized from 4-bromotoluene through a three steps procedure, according to literature (scheme 2.3a)[77]. The overall yield was: 68%. Melting point (ºC) was 256-260. IR (cm^{-1}): 3060; 1120 (OH); 1700 (C=O); 1249 (P=O); 1436 (P-Ar); 860 (C-C); 709 (C-H); ^{1}H NMR (DMSO-d_6, 400 MHz, δ(ppm): 13.2 (s, 1H); 8.1 (d, 2H); 7.7 (t, 2H); 7.6-7.7 (m, 10H); ^{13}C NMR (DMSO-d_6, 100.6 MHz, δ(ppm)): 166.6 (s); 133.8-128.8 (m); ^{31}P NMR (DMSO-d_6, 161.9 MHz, δ(ppm): 25.7.

4-(diphenyl-phosphinoyl)-benzoyl chloride (DPBC) was obtained from the corresponding acid (CDPO) using two different methods (scheme 2.3b):

a) by treatment with thionyl chloride ($SOCl_2$) following the same method used for BIC preparation[71] (see scheme 1). Yield was 38%;
b) by treatment with oxalyl chloride ($(COCl)_2$)[78]

In a well dried two necked round bottom flask of 250 ml equipped with additional funnel under argon atmosphere were introduced 32.2 g (0.1 mol) CDPO with 100 ml $CHCl_3$. In the mixture was dropped, under stirring at room temperature, oxalyl chloride 17.5 g (11.43 ml; 0.135 mol). After the addition was completed the mixture was heated at reflux. The reaction was

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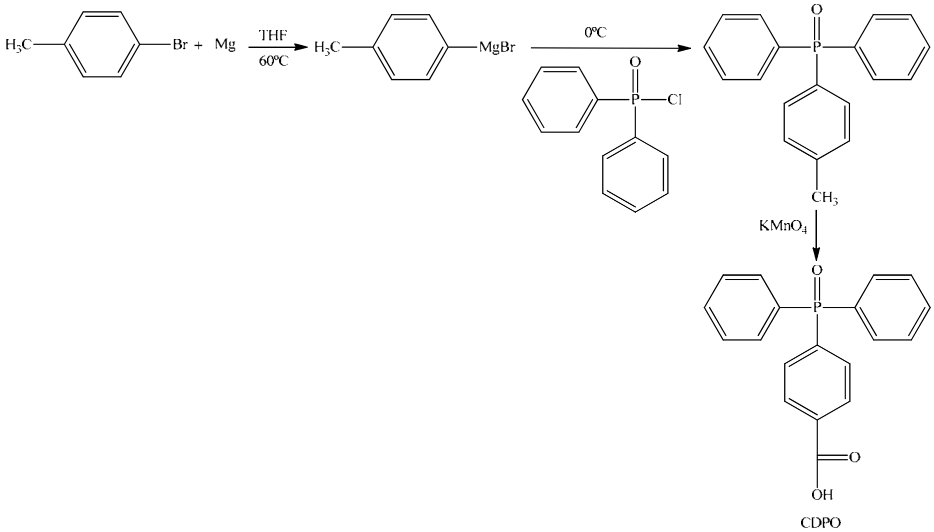
[77] Lin, Q.; Unal, S.; Fornof, A.R.; Armentrout, R.S.; Long, T.E. Polymer **2006**, 47, 4085-4093.

[78] Ward, D.E.; Rhee, C.K. Tetrahedron Lett **1991**, 32, 49, 7165-7166.

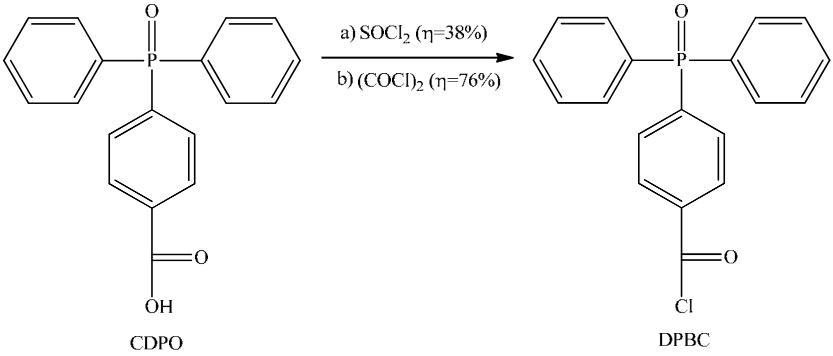
fallowed by TLC and stopped after 48 h. Reaction mixture was concentrated by solvent rota evaporation and 100 ml of hexane were added. Light brown oil was obtained through solvent decantation and dried under vacuum for 24 h. Overall yield was 76%.

The characterization data are as follows: melting point range (ºC) was: 254-258; IR (cm^{-1}): 1701 (C=O); 1249 (P=O); 860 (C-C); 708 (C-H); ^{1}H NMR (TCE-d_2, 400 MHz, δ(ppm)):8.2 (d, 2H); 7.8 (t, 2H); 7.6-7.5 (m, 10H); ^{13}C NMR (TCE-d_2, 100.6 MHz, δ(ppm)):132.8-128.9 (m); 168.1 (s); ^{31}P NMR (TCE-d_2, 161.9 MHz, δ(ppm)): 29.0

Scheme 2.3a



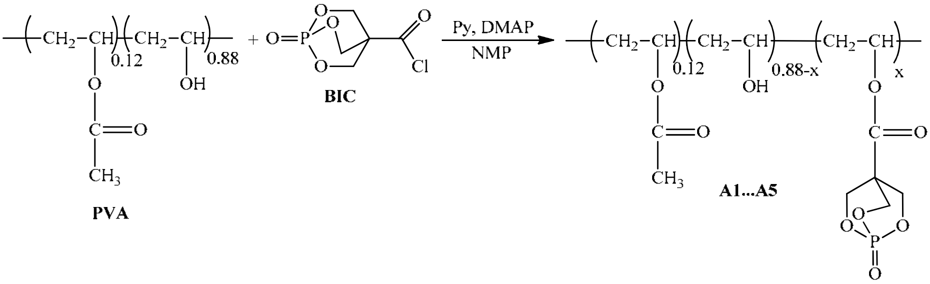
Scheme 2.3b



2.2- Chemical modification reactions

2.2.1-Poly(vinyl alcohol) chemically modified with 4-chloroformyl-1-oxo 2,6,7-trioxa-1-phosphabicyclo-[2,2,2]-octane (polymers A1-A5, scheme 2.4)

Scheme 2.4



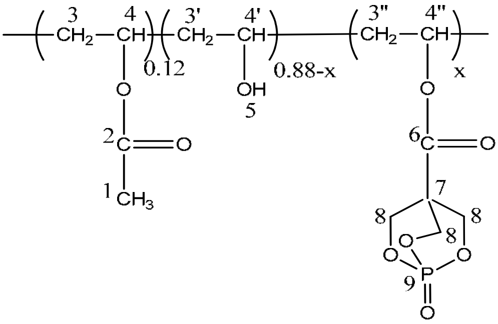
In a well-dried 50-ml two-necked round-bottom flask equipped with magnetic stirrer, reflux condenser, and dry argon inlet, 20 ml of 1-methyl-2-pyrrolidinone and 1.00 g of PVA (0.018 mol of hydroxyl group) were introduced. The mixture was stirred and heated at 80 ºC under argon flow until PVA was completely dissolved. Thereafter, it was left to cool down to room temperature. Then, 0.22 g (0.0018 mol) of DMAP, 1.45 ml (0.018 mol) of pyridine, and 3.67 g (0.018 mol, for polymers A1-A4) or 1.84 g (0.009 mol, for polymer A5) of BIC was added. The mixture was kept magnetically stirred in an argon atmosphere at the selected temperature for the selected time (Table 2.1). The white powdered modified PVA was obtained after the precipitation of the reaction mixture in 1 l of cold water, vacuum filtration, washing with water and drying under vacuum at 70 ºC. The yield was 70-98%. Modification degree=36-57%. The ^{1}H (DMSO-d_6, 400 MHz, δ(ppm)), ^{13}C (DMSO-d_6, 100.6 MHz, δ (ppm)), and ^{31}P (DMSO-d_6, 161.9 MHz, δ(ppm)) NMR data are collected in Table 2.2. The IR data (cm^{-1}) are as follows: 3453; 1121 (OH); 1726 (C=O); 1313 (P=O); 1168 (C-O); 998 (P-O); 852 (skeleton vibration of caged bicyclic phosphate).

Table 2.1 Conditions of PVA modifying with BIC

Polymer	**Time (days)**	**T (ºC)**	**Molar Ratio (PVA/BIC/AL/AR)****
A1	2	*	1/1/0/0
A2	5	*	1/1/0/0
A3	10	*	1/1/0/0
A4	2	40	1/1/0/0
A5	2	*	1/0.5/0/0
B	2	*	1/0.5/0.5/0
C	2	*	1/0.5/0/0.5

- *= 25±2ºC;
- ** PVA/BIC/AL/AR= poly(vinyl alcohol) / 4-chloroformyl-1-Oxo-2,6,7-trioxa-1-phosphabicyclo-[2,2,2]-octane/ valeroyl chloride/ benzoyl chloride.

Table 2.2 NMR data of polymer A1-A5



^{1}H NMR data		^{13}C NMR data		^{31}P NMR data	
Resonances	**Assignment**	**Resonances**	**Assignment**	**Resonances**	**Assignment**
1.2-2.0	1, 3, 3’ 3’’	20.8	1	(-6.8)-(-6.6)	9
3.5-4.1	4’	37.0-42.0	3, 3’’		
4.3-4.7	5	43.1	7		
4.8-5.2	4, 4’’, 8	44.0-46.0	3’		
		62.0-74.0	4, 4’, 4’’		
		74.7	8		
		164.0-164.9	6		
		169.0-169.8	2		

2.2.2- Poly(vinyl alcohol) chemically modified with 4-chloroformyl-1-oxo-2,6,7-trioxa-1-phosphabicyclo-[2,2,2]-octane and valeroyl chloride (polymer B, scheme 2.5)

Scheme 2.5

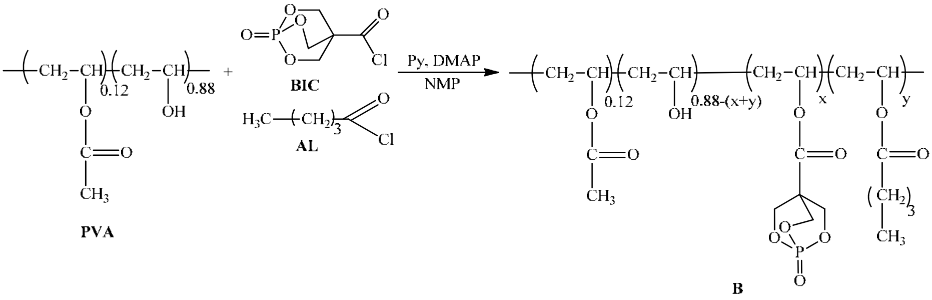
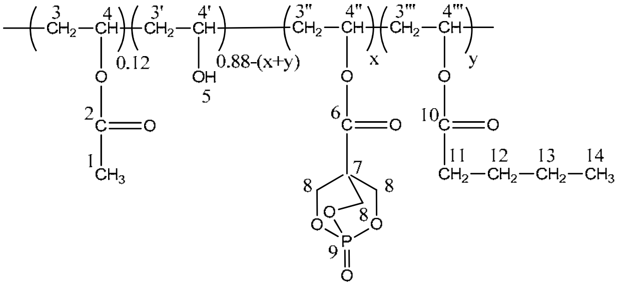


Table 2.3 NMR data of polymer B.



^{1}H NMR data		^{13}C NMR data		^{31}P NMR data	
Resonances	**Assignment**	**Resonances**	**Assignment**	**Resonances**	**Assignment**
0.9	14	13.6	14	-6.7	9
1.2-2.0	1, 3, 3’, 3’’, 3’’’, 12, 13	20.8	1		
2.2	11	21.7	13		
3.5-4.1	4’	26.5	12		
4.3-5.2	4, 4’’, 4’’’, 5, 8	33.4	11		
		37.0-42.0	3, 3’’, 3’’’		
		43.1	7		
		44.0-46.0	3’		
		62.0-74.0	4,4’, 4’’,4’’’		
		74.9	8		
		164.0-164.9	6		
		169.9	2		
		172.8	10		

The polymer B was synthesized following the same procedure as for polymers A1-A5 using 1.84 g (0.009 mol) of BIC and 1.09 g (0.009 mol) of valeroyl chloride (Table 2.1). The yield was 87 %. The ^{1}H (DMSO-d_6, 400 MHz, δ(ppm)), ^{13}C (DMSO-d_6, 100.6 MHz, δ(ppm)) and ^{31}P (DMSO-d_6, 161.9 MHz, δ(ppm)) NMR data are collected in Table 2.3. The IR data (cm^{-1}) are as follows:

3489; 1122 (OH); 1726 (C=O); 1326 (P=O); 1170 (C-O); 1001 (P-O); 852 (skeleton vibration of caged bicyclic phosphate).

2.2.3- Poly(vinyl alcohol) chemically modified with 4-chloroformyl-1-oxo-2,6,7-trioxa-1-phosphabicyclo-[2,2,2]-octane and benzoyl chloride (polymer C, scheme 2.6)

Scheme 2.6

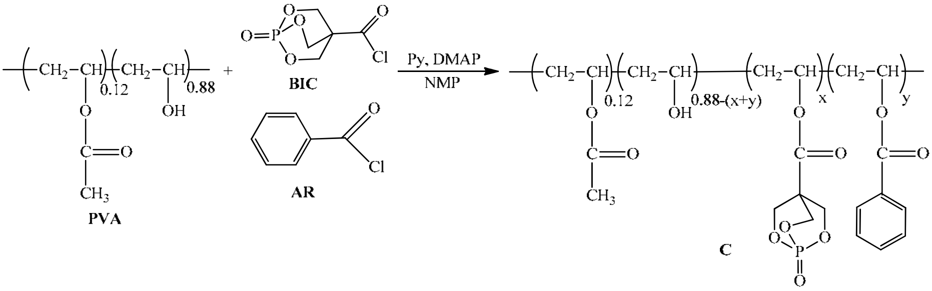
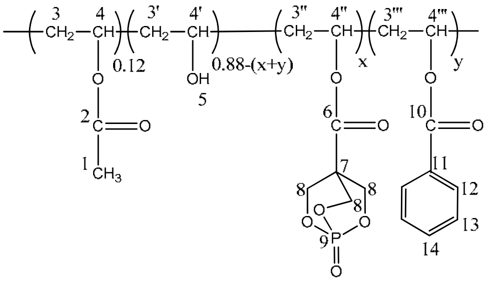


Table 2.4 NMR data of polymer C.

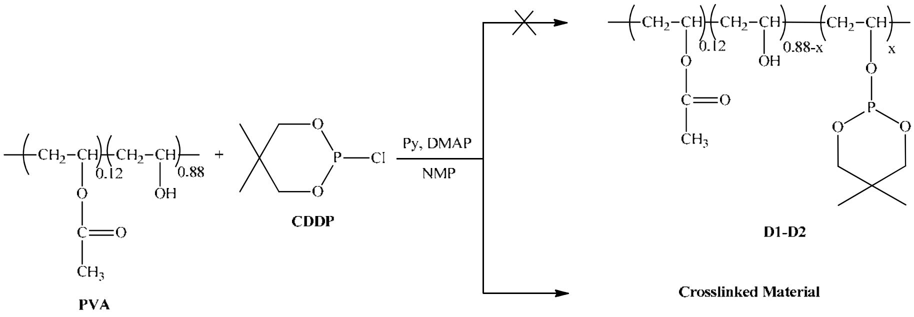


^1H NMR data		**^{13}C NMR data**		**^{31}P NMR data**	
Resonances	**Assignment**	**Resonances**	**Assignment**	**Resonances**	**Assignment**
1.2-2.1	1, 3, 3’, 3’’, 3’’’	20.9	1	-6.7	9
3.4-4.0	4’	37.0-42.0	3, 3’’, 3’’’		
4.4-5.3	4, 4’’, 4’’’, 5, 8	43.1	7		
7.4-8.1	12, 13, 14	44.0-46.5	3’		
		62.0-74.0	4, 4’, 4’’, 4’’’		
		74.9	8		
		128.2-130.0	11, 12, 13		
		133.0-134.0	14		
		164.8	6		
		167.6	10		
		169.8	2		

Polymer C was prepared by the same procedure reported above for polymer B, but using 1.26 g (0.009 mol) of benzoyl chloride instead of valeroyl chloride (Table 2.1). The yield was 60 %. The ^{1}H (DMSO-d_6, 400 MHz, δ (ppm)), ^{13}C (DMSO-d_6, 100.6 MHz, δ (ppm)), and ^{31}P (DMSO-d_6, 161.9 MHz, δ (ppm)) NMR data are collected in Table 2.4. The IR data (cm^{-1}) are as follows: 3454; 1119 (OH); 1724 (C=O); 1257 (P=O); 999 (P-O); 854 (skeleton vibration of caged bicyclic phosphate); 712 (aromatic C-C-H out of plane deformation).

2.2.4- Poly(vinyl alcohol) chemically modified with 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane (polymers D1-D2, scheme 2.7)

Scheme 2.7



The preparation of polymers D1 and D2 was tested following the same procedure as for polymers A1-A5, using CDDP in equivalent molar ratio at different conditions. In all cases a crosslinked material was obtained, in site of expected polymers.

2.2.5- Poly(vinyl alcohol) chemically modified with 4-(diphenyl-phosphinoyl)-benzoyl chloride (polymers E1-E5, scheme 2.8)

Polymers E1-E5 were prepared using the same procedure as for previously families (scheme 2.8). Instead of BIC (or CDDP) was used DPBC in excess of 20%. The polymers were recovered via precipitation in cold water. The light yellow to dark brown powdered polymers were obtained and dried at 60ºC under vacuum until constant weight. Overall yield was 48-93%. Reaction conditions are summarized in Table 2.5. The ^{1}H (DMSO-d$_6$, 400 MHz, δ (ppm)), ^{13}C (DMSO-d$_6$, 100.6 MHz, δ (ppm)), and ^{31}P (DMSO-d$_6$, 161.9 MHz, δ (ppm)) NMR data are collected in Table 2.6. The IR data are as follows (cm^{-1}): 3363 (OH); 1716 (C=O); 1188 (P=O); 694 (aromatic C-C-H out of plane deformation).

Scheme 2.8

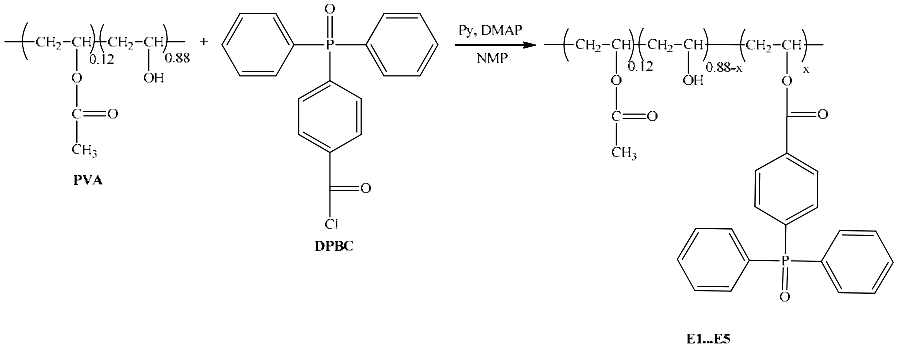
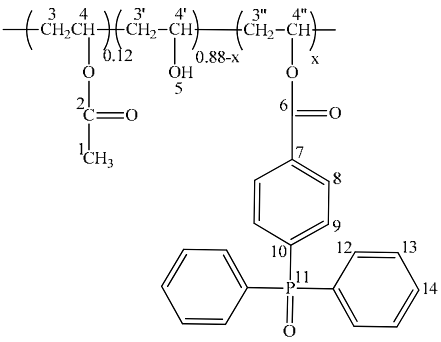


Table 2.5 Conditions of PVA modifying with DPBC

Polymer	Time (days)	T (ºC)	Molar Ratio PVA/DPBC’
E1	2	rt.’’	1/1.2
E2	2	60	
E3	2	80	
E4	7	80	
E5	2	100	

’ PVA/DPBC=poly(vinyl alcohol) / 4-(diphenyl-phosphinoyl)- benzoyl chloride
’’ rt.= 25±2ºC

Table 2.6 NMR data of polymer E2-E5



^{1}H NMR		^{13}C NMR		^{31}P NMR	
Resonances	**Assignment**	**Resonances**	**Assignment**	**Resonances**	**Assignment**
1.0-2.2	3,3’,3’’	21.2	1	25.3	11
1.7	1	40.7-47.6	3,3’,3’’		
3.5-4.0	4’	62.4-72.3	4,4’,4’’		
4.1-4.8	5	128.8-130.5	8,13		
4.8-5.5	4,4’’	131.4-134.2	7,9,12,14		
7.3-7.5	13	137.0-139.0	10		
7.5-7.7	12,14	164.9	6		
7.7-7.8	9	170.1	2		
7.9-8.2	8				

2.3- Characterization techniques

^{1}H, ^{13}C and ^{31}P NMR spectra were recorded at room temperature with a Varian Gemini 400 MHz spectrometer using acetone-d_6, $CDCl_3$, TCE-d_2 or DMSO-d_6 as solvents. For ^{1}H and ^{13}C NMR spectra tetramethylsilane was used as a reference, while for ^{31}P NMR spectra phosphoric acid was used as an internal standard: a closed capillary tube containing this acid was introduced in the NMR tube together with the solution to be analysed. In the case of the spectra of polymers, a pulse delay time was used: 5 s for ^{1}H NMR spectra and 10 s for ^{13}C NMR spectra.

Fourier transform infrared spectra were recorded on a FT-IR 680 PLUS spectrophotometer from JASCO with a resolution of 4 cm^{-1} in the absorbance mode. This device is equipped with an attenuated total reflection accessory (ATR) with thermal control and a diamond crystal (Golden Gate heated single reflection diamond ATR from Specac-Teknokroma). The spectra were recorded at room temperature from the solid / liquid state pure compounds.

Phosphorous contents were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on a Perkin Elmer Plasma 400 device. Solutions to be analyzed were prepared by submitting *ca.* 40 mg of polymer to acidic attack (2-2.5 ml HNO_3 65%) on an Anton Paar Q M627 PMD 750W microwave system and, then, diluting with water to several concentrations. In the case of polymer C and polymers E2-E5 the acidic attack was performed by using 2 ml HNO_3 65% + 2 ml HCl 37%. The samples were compared by check solutions of 0, 25, 50, 75 and 100 ppm of phosphorous obtained by diluting an ICP multielement standard solution XII (Merck).

Inherent viscosities ($\eta_{inh.}$) were measured in dimethyl sulfoxide (DMSO) solutions (*ca.* 2 g/l) at 30±0.05 ºC in an Ubbelohde capillary viscosimeter on a Schott Geräte AVS 310 automatic appliance provided with a Schott Geräte CT 050/1 thermostatic bath and a Selecta 6000382 external cryoscopic unit.

Differential scanning calorimetry (DSC) studies were performed on a Mettler DSC822e thermal analyzer with samples of about 5 mg in covered 40 μl aluminium standard crucibles. The heating/cooling rate was 10 ºC/min, nitrogen was used as a purge gas (100 ml/min) and liquid nitrogen was used in the cooling system. The device was previously calibrated with indium (156.6 ºC) and zinc (419.6 ºC) pearls.

Thermogravimetric analyses (TGAs) were carried out in 70 μl aluminium oxide crucibles on a Mettler TGA/SDTA851e/LF/1100 device at a heating rate of 10 ºC/min up to 800 ºC. Each experiment was performed under a nitrogen or air flux (100 ml/min) using *ca.* 10 mg of sample. The equipment was previously calibrated with indium (156.6 ºC) and aluminium (660.3 ºC) pearls.

TGA combined with mass spectrometry (TGA-MS) studies were performed on a Mettler TGA/SDTA851e/LF/1600 device coupled with Pfeiffer Vacuum Thermostar quadrupolar mass spectrometer covering a mass range from 0 to 300 a.m.u. The equipment was previously calibrated with In (156.6ºC), Al (660ºC) and Pd (1554ºC) pearls. Platinum cresols of 150 µl were used. Samples were heated from 30 ºC to 240 ºC at a heating rate of 10 ºC/min and then this latter temperature was kept for 30 minutes. Studies were performed in nitrogen or air atmosphere (50 ml/min).

Pyrolisis studies were performed in a Carbolite TZF 12/38/400 pyrolytic oven connected to a condenser cooled by liquid nitrogen. Samples were heated from room temperature to 240ºC and then this temperature was kept for 3 hours. The studies were performed in an air atmosphere (100 ml/min). All volatiles evolved during the above process were analyzed.

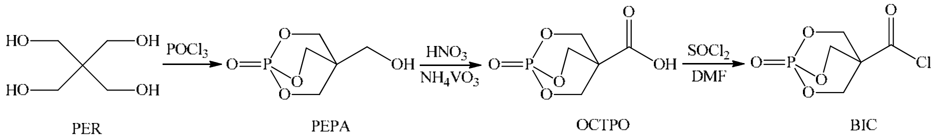
Gas Chromatography- Mass Spectrometry (GC-MS) analyses were carried out in an HP 6890 gas chromatograph provided with a 5973 mass selective detector from Hewlett Packard and with an Ultra 2 capillary column HP5MS using He as carrier gas. Samples of 1µl were analyzed in split mode with a split ratio of 50:1, inlet temperature of 180 ºC and inlet pressure of 6.47 psi. The program of temperatures used in the oven includes tree isotherms and two dynamics scans: 35 ºC (10 min), 35 ºC→100 ºC (5 ºC/min), 100 ºC (20 min), 100 ºC→250 ºC (30 ºC/min), 250 ºC (40 min); The overall time of analysis was 88 min. Acquisition occurred by SCAN mode in a range of m/e from 43 to 600 a.m.u.

3. Results and discussion

3.1- Polymers preparation and chemical characterization

In this chapter we report the synthesis of new halogen free polymeric flame retardant additives obtained by chemical modification of commercially poly(vinyl alcohol) (PVA) (88 mol% free hydroxyl groups) with different phosphorous containing moieties, such as phosphates, phosphites and phosphine oxides. All this classes were mentioned by Hamerton et al., Zhang et al. and others as good flame retardants. [3,4,7,16,70-72] Particularly, phosphine oxide structures have been described by Levchik et al. as proposed structure to impart flame retardancy to curing agents, due their thermally and hydrolytically high stability.[16] Phosphites are mentioned by many authors as good flame retardants[3,16,70], some of them relate them as good thermal stabiliser, also.[79] Phosphates are widely reported as good flame retardants although they present the problem of hydrolysis.[3,7]

First, we tackle the chemical modification of PVA with 4-chloroformyl-1-oxo-2,6,7- trioxa-1-phosphabicyclo-[2,2,2]-octane (BIC). The cyclic caged phosphate structure of BIC has been used by several authors due to its good flame retardant action.[71,72,80] Moreover, this structure seems to suffer hydrolysis slower than common phosphate groups, probably due to the high stability of the six-membered cyclic structure.[7,72,80] BIC was synthesized according to a three steps published procedure.[71]



First of all phosphorous oxychloride ($POCl_3$) was condensed with pentaerythritol (PER) to give 1-oxo-4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo(2.2.2)octane (PEPA), and subsequent oxidation with concentrated nitric acid catalysed by ammonium vanadate, provided the corresponding acid (OCTPO). Further reaction with thionyl chloride using N,N-dimethylformamide

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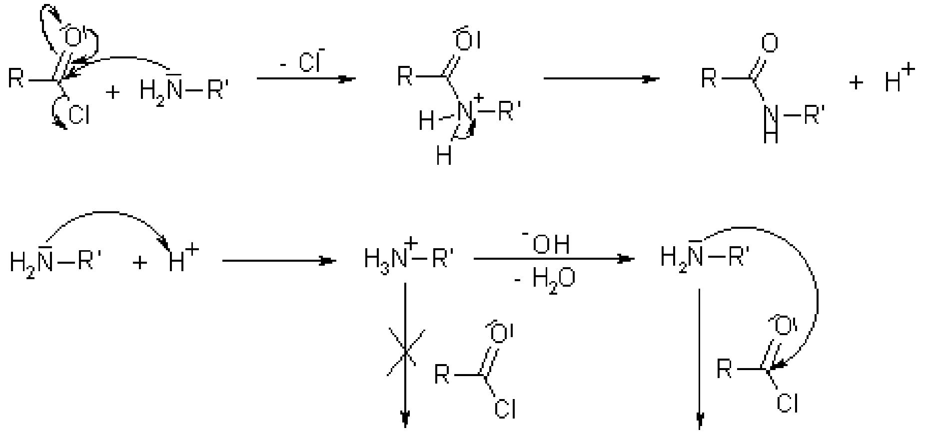
[79] Stevenson, D.R; Harr, M.E.; Jakupca, M.R. J Vinyl Addit Techn **2002**, 8, 1, 61-69.
[80] Li, X.; Ou, Y.; Shi, Y. Polym Degrad Stab **2002**, 77, 383-390.

(DMF) as a catalyst yielded the acyl chloride (BIC). The reactions were followed by TLC and stopped when limiting reactant has been completely consumed. The overall yield was 90%.

The synthesized acid chloride was then used as an acylating agent for PVA chemical modification. One of the most commonly used method for alcohols esterification with acylating agents is Schotten- Baumann reaction[81], related in scheme 2.9. The Schotten –Baumann reaction is a method to synthesize amides from amines and acid chlorides. Sometimes the name of this reaction is also used to indicate the reaction between an acid chloride and an alcohol to form an ester. In the first step an acid chloride reacts with an amine (alcohol) so that an amide (ester) is formed, together with a proton and a chloride ion. Addition of a base is required to catch this acidic proton. Often, an aqueous solution of a base is slowly added to the reaction mixture. The name ¨Schotten-Baumann reaction ¨ is often used to indicate the use of a two-phase solvent system, consisting of water and an organic solvent. A base within the water phase neutralizes the acid, generated in the reaction, while the starting materials and product remain in the organic phase, thus avoiding acyl chloride hydrolysis.

Scheme 2.9



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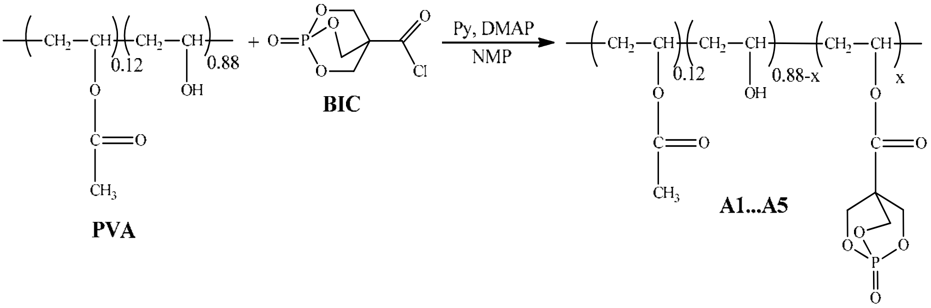
[81] Tsuda, M. Makromol. Chem **1964**, 72(1), 174-182.

This method was not applicable in this case because of particularly easy hydrolization of the phosphorous acylating agent in aqueous medium. For this reason chemical modifications of PVA were carried out in homogenous phase using dry NMP as solvent and stoichiometric quantities of pyridine.[82,83] The pyridine acted as base in order to capture evolved hydrochloric acid (HCl), forming pyridinium salt, easily removed by washing. 4-(Dimethylamino)-pyridine, pyridine derivative, acted as catalyst.[84] The reactions were carried out using different molar ratios of acylating agent under different reaction conditions (Table 2.1) following a procedure previously used in our laboratory[85] (see scheme bellow).



First, the synthesis was performed at room temperature for two days using BIC in stoichiometric ratio respect to PVA hydroxyl groups (polymer A1) obtaining the expected structure with a degree of modification of *ca.* 0.55 (see Table 2.7). The structure has been characterized and confirmed by FT-IR and NMR techniques. From FT-IR spectrum (figure 2.1) a diminution of OH vibration band around 3500 cm^{-1} coming from PVA[82,86] have been seen and also appearance of phosphorous characteristic bands about 1300 cm^{-1} (P=O) and

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[82] Arranz, F.; Sanchez-Chaves, M.; Gill, F. Angew Makromol Chem **1980**, 92, 121-131.
[83] Fernandez, M.D.; Fernandez, M.J. J Appl Polym Sci **2008**, 107, 2509-2519.
[84] Mormann, W; Wagner, T. Macromol Chem Phys **1996**, 197, 3463-3471.
[85] Gimenez, V.; Reina, J.A., Mantecon, A.; Cadiz, V. Polymer **1999**, 40, 2759-2767.
[86] Xiao, S.; Huang Y.M., R.; Feng, X. J Membr Sci **2006**, 286, 245-254.

1000 cm^{-1} (P-O), respectively, coming from bicycle caged phosphate group[71,72] which confirm that PVA chemical modifications occurred.

Figure 2.1. FT-IR spectrum of polymer A1

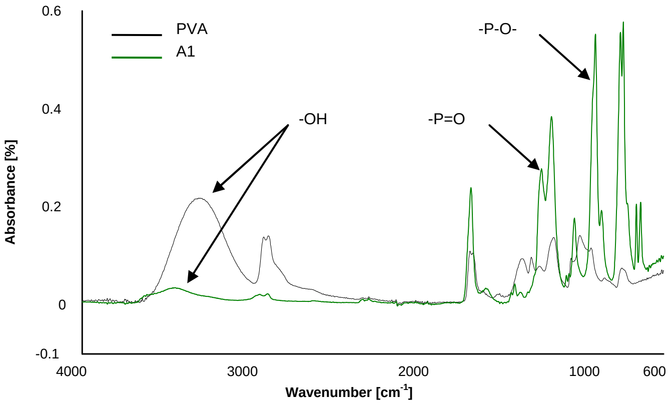

Figure 2.2 illustrates ^{1}H and ^{31}P NMR spectrum for PVA modified with BIC. In ^{1}H NMR signal around 4.8-5.0 ppm is characteristic for methylene protons of the bicycle caged phosphate.[71] The signals between 3.5-4.1 ppm and around 5.0-5.2 ppm were attributed to methine protons of unmodified PVA chain and esterified units, respectively. OH groups gave the signal around 4.5 ppm.[87] The signals coming from methylene protons of main chain and methyl protons from acetyl units were observed at 1.2-2.0 ppm. As can be seen only one sharp signal around -7 ppm appears in the ^{31}P NMR spectrum.[72]

^{13}C NMR spectrum for PVA modified with BIC is presented in figure 2.3. Signals at 164.0-165.0 ppm and 169.0-170.0 ppm can be attributed to the carbonylic carbons from BIC and acetyl groups, respectively. The singlet that appears at 20.8 ppm corresponds to methyl carbons from acetylated unit. The strong sharp signal 74.7 ppm was attributed to methylene carbons from caged bicycle phosphate. Signal at 43.1 ppm corresponds to quaternary carbon coming from caged bicycle phosphate ($^3J_{P\text{-}C}$=48.62 Hz) Signals corresponding to the

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[87] Gimenez, V.; Reina, J.A., Mantecon, A.; Cadiz, V. J Polym Sci Part A: Polym Chem **1996**, 34, 925-934.

methine and methylene carbons of PVA chain appear between 62.0-74.0 ppm and 37.0-46.0 ppm respectively.[87] All these are broad and/or split due to stereo and comonomer sequences.

Figure 2.2. ^{1}H and ^{31}P NMR of polymer A1 recorded in DMSO-d_6

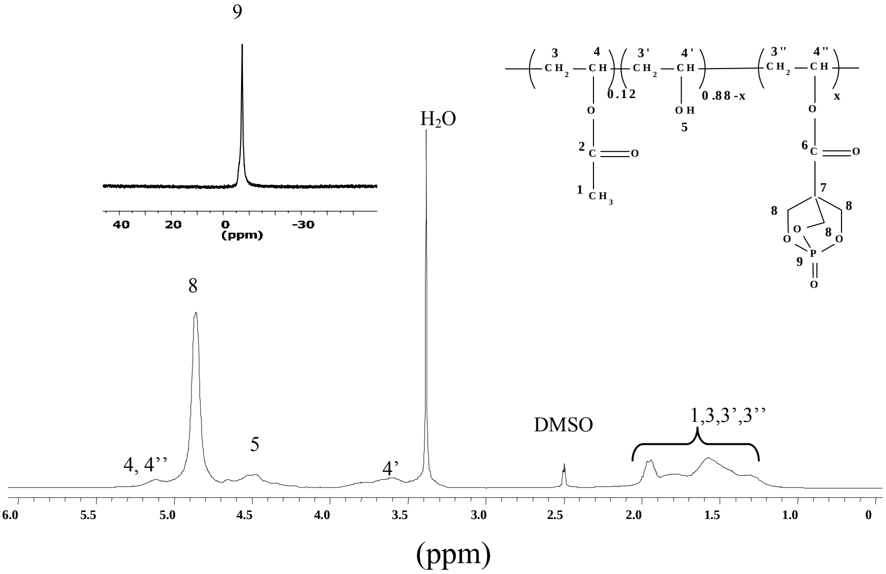
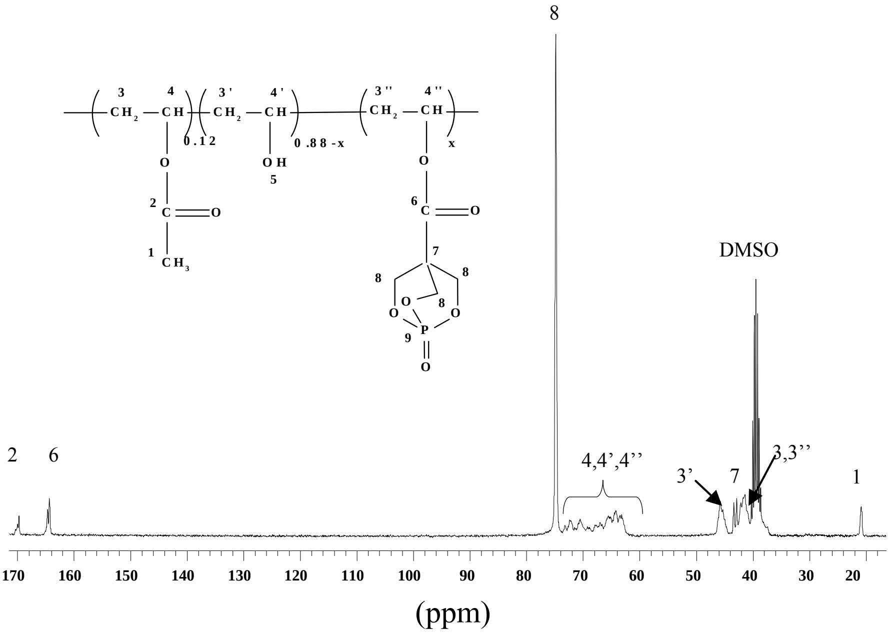


Figure 2.3. ^{13}C NMR of polymer A1 recorded in DMSO-d_6



The degree of modification was estimated from the ^{13}C NMR spectrum recorded under quantitative conditions using the intensity of carbonyl signals which appears resolved, and considering that acetylated units does not suffer any transformation. The quantification was performed over a night (30000 scans) using a delay time of 10 seconds which was previously established by determination of relaxation time for carbonyl carbons.

In order to get higher degree of modification the synthesis has been carried out at room temperature for 5 and 10 days (polymers A2 and A3) and 40ºC (polymer A4), 60ºC and 80ºC for two days, using also a stoichiometric molar ratio of acylating agent and base. At temperature higher than 40ºC crosslinked polymers were obtained, that was associated with PVA dehydration tendency on heating, which lead to ether bridges.[88]

At longer reaction time and/or 40ºC the degree of modification rises slightly and a ¨ plateau ¨ seems to be reached (± 60%), probably due to group size and the steric hindrance. In no case total modification was reached. PVA was also modified by using PVA: BIC in 1:0.5 molar ratios at room temperature for two days (polymer A5), leading to a degree of modification of 23%.

Table 2.7 Results of PVA modified with BIC

Polymer	**%P Obtained from**		**Degree of modification**			**Yield (%)**	**$\mu_{inh.}$ (dl/g)**
	ICP-AES	**^{13}C NMR**	**x^a**	**x^b**	**y^b**		
PVA							0.52
A1	11.5	11.8	0.52	0.57		90	0.19
A2	11.8	-	0.57	-		70	0.16
A3	12.1	11.0	0.61	0.47		98	0.24
A4	12.2	11.9	0.63	0.58		98	0.23
A5	8.0	10.0	0.23	0.36		91	0.42
B	5.7	6.3		0.27	0.44	87	0.24
C	7.6	10.0		0.48	0.16	60	0.27

a)Obtained from %P determined by ICP-AES
b)Obtained from ^{13}C NMR considering 12% of acetylated part

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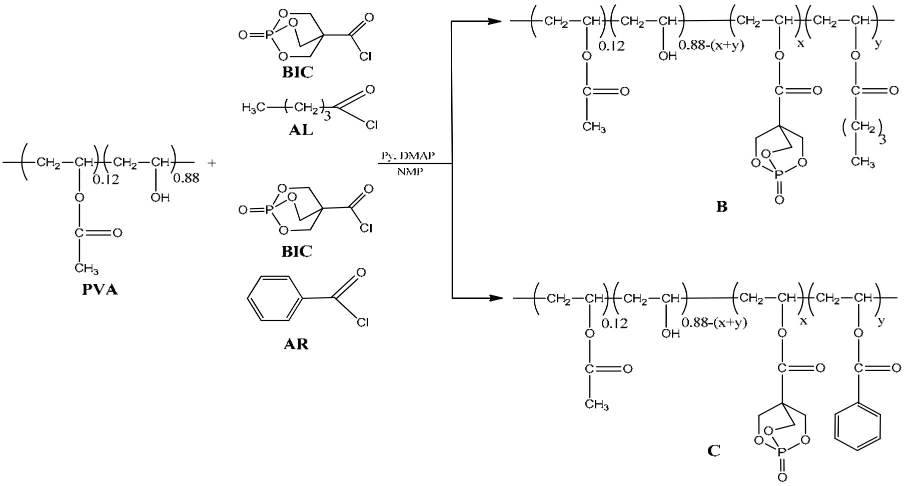
[88] Pritchard, J.G. Polyvinyl Alcohol. Basic proprieties and uses, McDonald Technical & Scientific, London, **1970**, p. 83.

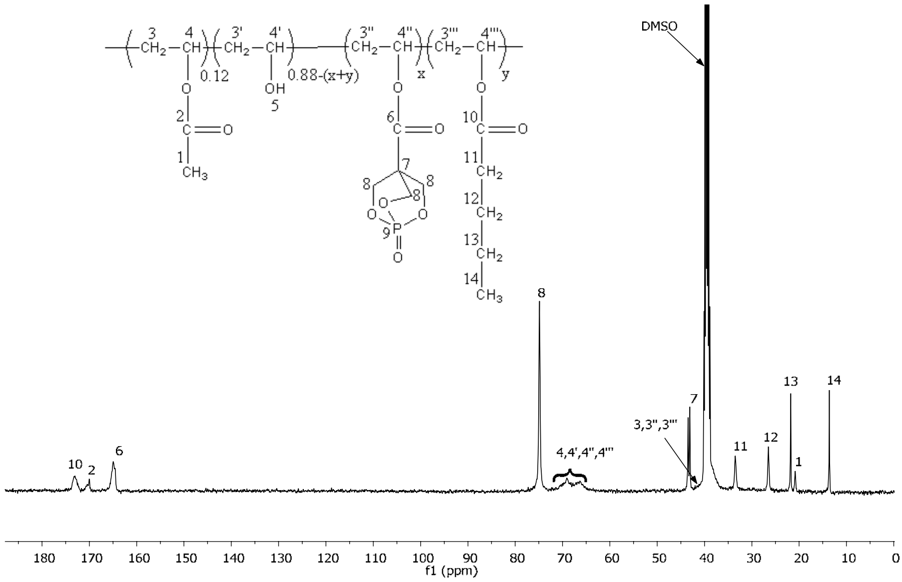
Once determined the degree of modification, the phosphorous content was calculated and compared with the value obtained from ICP-AES. In most of the cases a good agreement between these values was obtained (see table 2.7).

Since the obtained polymers are highly polar and we propose to use them as additives for apolar ¨commodity¨ polymers, we introduced more non-polar groups such as, an aliphatic and an aromatic moiety, in order to increase the compatibility. The synthesis was therefore carried out using valeroyl chloride as aliphatic moiety (polymer B) and benzoyl chloride (polymer C) as an aromatic moiety, at room temperature for two days. The selected molar ratios were PVA: BIC: valeroyl chloride/benzoyl chloride in 1:0.5:0.5 (see scheme below).



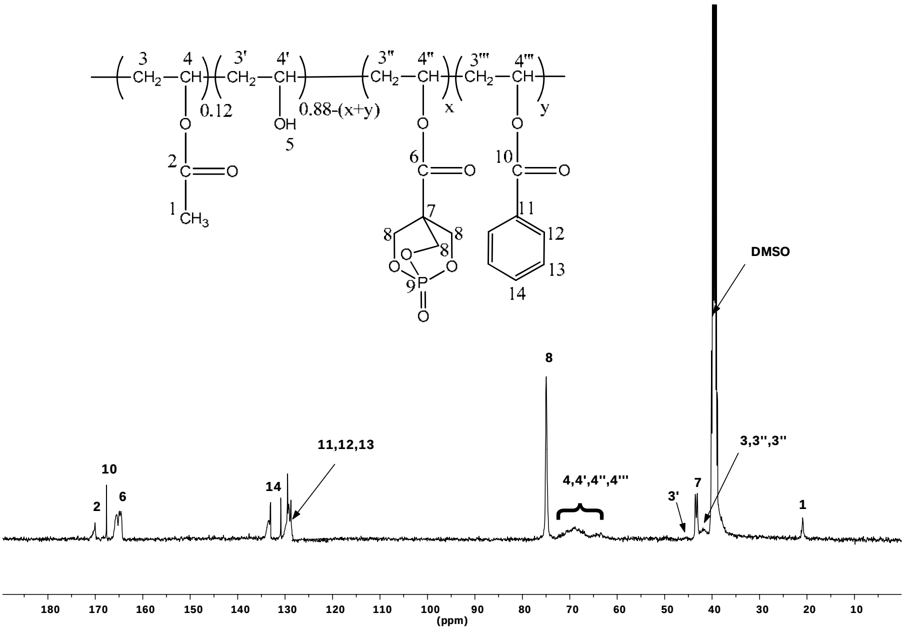
The structures of the modified polymers were confirmed by FT-IR and NMR characterization. Also in these cases, in FT-IR we observed diminution of OH band at 3489-3454 cm^{-1} and appearance of phosphorous characteristic bands at 1326-1257 cm^{-1} (P=O) and at 1001-999 cm^{-1} (P-O). In case of polymer C, we also observed C-C-H out-of-plane deformation band at 712 cm^{-1}. From NMR spectra apart from the already explained signals for polymers A1-A5, coming from the PVA main chain and cyclic caged phosphate, we also observed new signals characteristic for the aliphatic chain coming from valeroyl chloride units and aromatic ring from benzoyl units introduced. Thus, we observed for polymer B in ^{1}H NMR spectrum, a signal at 2.2 ppm which was assigned to methylene protons next to carbonyl group and a signal at 0.9 ppm, attributed to methyl protons, both coming from valeroyl units. The other methylene protons from valeroyl units overlapped with methylene protons from the main chain and methyl protons from the acetylated units. In ^{13}C NMR spectrum (Figure 2.4) we observed carbonyl carbon coming from valeroyl units at 172.8 ppm. Also, all methylenes and methyl carbons coming from valeroyl units appeared resolved. Signals at 33.4 ppm, 26.5 ppm and 21.7 ppm were attributed to methylene carbons, whereas signal at 13.6 ppm was associated to methyl carbons.

Figure 2.4 ^{13}C NMR of polymer B recorded in DMSO-d_6



In case of polymer C, ^{1}H NMR spectrum shows signals at 7.4-8.1 which are due to the aromatic protons coming from the benzene ring. In ^{13}C NMR spectrum (Figure 2.5), we observed carbonyl carbon next to aromatic ring at 167.6 ppm. The region of 128.2-134.0 ppm was assigned to methine and quaternary carbons from the benzene ring. In both, polymer B and polymer C, ^{31}P NMR spectrum shows a singlet in the same region as polymers A1-A5 (*ca.* -7 ppm). All these signals confirmed that the desired structures were obtained.

Figure 2.5 ^{13}C NMR of polymer C recorded in DMSO-d_6

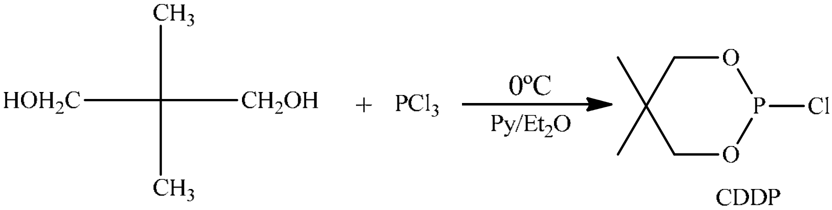


Also in these cases carbonyl signals appeared resolved, which permit us to calculate the degree of modification by ^{13}C NMR quantification, as already described for previous polymers. The phosphorous content estimated from ^{13}C NMR spectra was in agreement with the phosphorous content calculated by ICP-AES (Table 2.7).

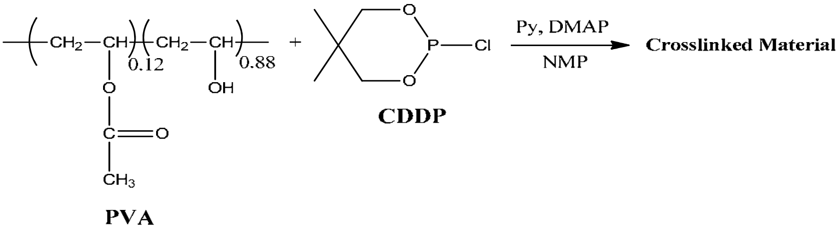
The overall yields of all synthesized polymers were calculated from the weight of the pure product by taking into account the degree of modification. The obtained yields ranged from 60% to 98% (see Table 2.7).

The inherent viscosity measurements were performed for all prepared polymers using DMSO as solvent for samples of 0.2 g/dl at 30 ºC. Obtained results show that viscosity of all polymers exhibit the same order of magnitude, with values slightly smaller than the virgin PVA. This is probably due to changes in the hydrodynamic volume of the modified polymers due to the bulky side groups introduced, since it seems that cleavage and branching side reactions did not occur, at least in high extension.

Then we try the chemical modification of PVA with 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane (CDDP), a six-membered ring which should confer a certain stability to obtained phosphite. CDDP has been synthesised following a published procedure.[75] The synthesis occurs very fast through a direct condensation of phosphorous trichloride with 2,2-dimethyl-1,3-propanediol in ice-cooled ethylic ether in pyridine presence.



The PVA chemical modification with CDDP was based in method reported by Said et. al. in which they react i-propanol, a secondary alcohol, with CDDP in presence of triethylamine as a base.[89]



First we tested the preparation of PVA modified with CDDP under the same conditions used in case of BIC derivatives. Thus, the chemical modification has been tried at room temperature in dried NMP using CDDP and pyridine in stoichiometric ratio with respect to PVA free hydroxyl groups and DMAP in

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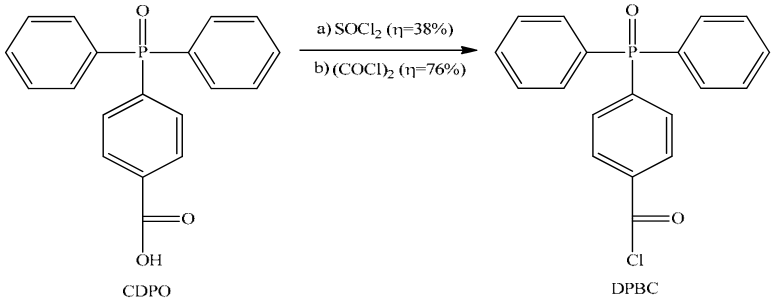
[89] Said, M.A.; Kumara Swamy, K.C.; Veith, M.; Huch, V. J Chem Soc Perkin Trans 1 **1995**, 2945-2951.

catalytic amount. A reaction took place very fast and a crosslinked material was obtained instead of desired polymer. The obtained material was not possible to be characterised.

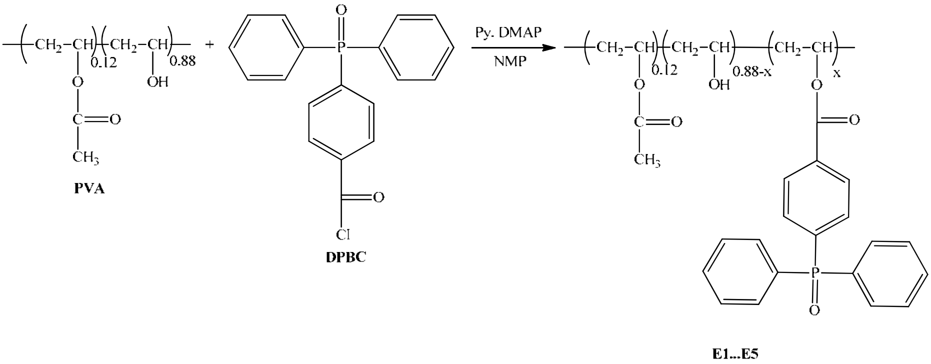
Then, the synthesis of desired polymer has been tested at low temperature (0ºC) using the same system, but also in this case a crosslinked material was obtained. This can be perhaps due to the nucleophilic attack of the free OH groups to phosphite group, leading to the opening of the six-membered ring and the formation of phosphite group bridge chains, which give rise to the formation of a crosslinkable material.[89] It seemed difficult to eliminate the problem of these side reactions and therefore a further study of this polymer was not performed and our attention has been redirected to other families.

Another synthesis that we approach in this chapter is PVA chemical modification with 4-(diphenyl- phosphinoyl)- benzoyl chloride (DPBC). The phosphine oxide derivative has an interest, because it is not a hydrolyzable group and is aromatic, which implies more carbon residue, lower polarity and higher compatibility with ¨commodity¨ polymers of low polarity. In order to get DPBC first of all was synthesised its corresponding carboxylic acid (CDPO) following a three steps published procedure (scheme 2.3a).[77] First the Grignard reagent was obtained from 1-bromo-4-toluene and react with biphenyl phosphinic chloride in order to get 4-methylphenyl biphenyl phosphine oxide which was later oxidized with excess of $KMnO_4$ to corresponding carboxylic acid.

The corresponding acyl chloride, which is not reported in the literature, was first synthesised from CDPO by treatment with $SOCl_2$ in presence of DMF, but the resulting yield was low (38%). In order to improve the yield we applied a treatment with oxalyl chloride to CDPO in $CHCl_3$.[78] The obtained product was isolated from hexane in satisfactory yield (76%).



Once that DPBC has been synthesised PVA chemical modification was carried out. The synthesis was tested using as model PVA chemical modification with BIC derivatives.



First it was performed at room temperature for two days in NMP system using an excess of 20 % -mol of DPBC as acylating agent with report to PVA hydroxyl groups, pyridine as a base in soichiometric ratio with DPBC and a catalytic amount of DMAP in order to get completely esterification of PVA hydroxyl groups. After polymer isolation and characterization was concluded that reaction did not occurred in that conditions; i.e. unreacted PVA was recovered combined with the corresponding carboxylic acid.

Then this synthesis has been repeated increasing reaction temperature at 60 ºC and keeping the other conditions unchanged (polymer E2). In order to reach higher modification degree, the synthesis has been performed also at 80 ºC and 100 ºC for two days (polymers E3 and E5) and 80 ºC for a week (polymer E4). In all this cases the expected modification reactions occurred. Summarized reaction conditions and results are related in table 2.5 and table 2.8. It was observed that increasing temperature and/or increasing reaction time, higher modification degree was obtained.

The degree of modifications were estimated comparing the intensities of characteristic aromatic signals of triphenilphosphine oxide and intensities coming from the methyl and methylene signals from the polymeric main chain using quantified ^{1}H NMR spectra with a delay time (d1) of 5 seconds.

The phosphorous content estimated from the modification degrees shows concordance with the phosphorous content calculated from the ICP-AES analysis (Table 2.8).

Obtained polymers were characterised and confirmed by FT-IR and NMR techniques. Figure 2.6 shows FT-IR spectra of neat PVA and polymer E2.

As can be observed, a strong diminution of OH characteristic band occurred in case of polymer E2 which shows that PVA chemical modification with DPBC tacked place. In the same figure could be seen presence of phosphorous characteristic bands P=O (*ca.* 1188 cm^{-1})[77] and aromatic carbons out of plane deformation bands (*ca.* 697 cm $^{-1}$), respectively.

Figure 2.6 FT-IR spectra of PVA and E2

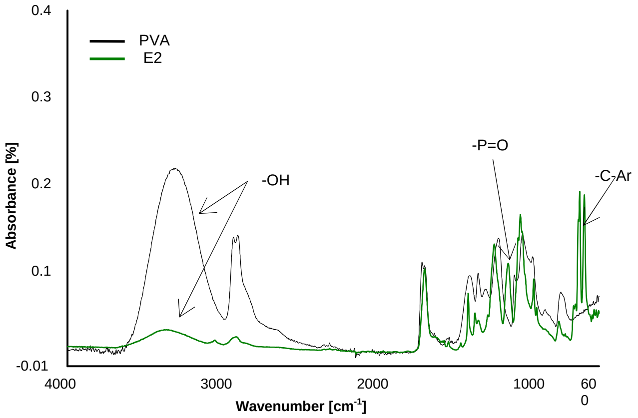
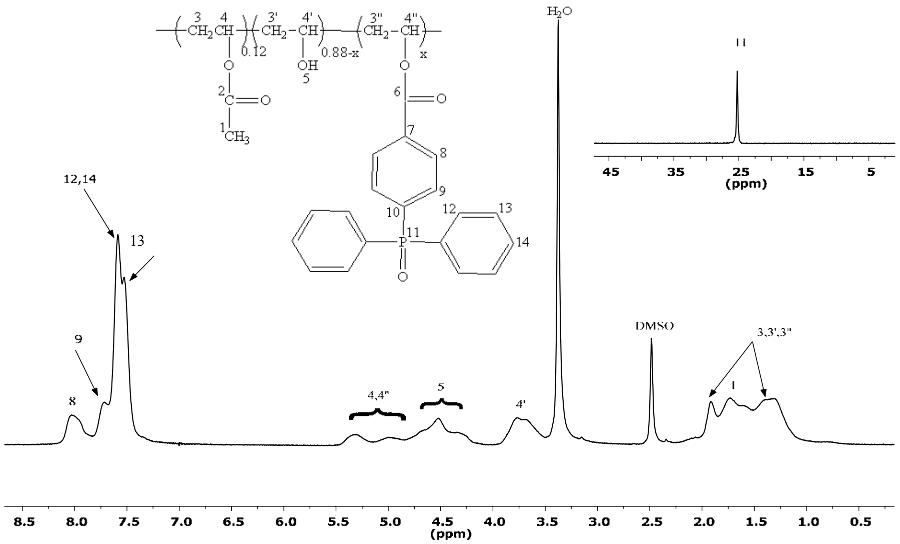


Figure 2.7 shows ^{1}H and ^{31}P NMR spectra of polymer E2. A single sharp peak in the ^{31}P NMR spectrum confirmed that pure polymer was obtained. The absence of multiplicity of this signal may be due to the distance of the phosphorus to the backbone, so there is no stereo or regiosecvences and tacticity. By ^{1}H NMR were observed signals between 7.5-8.0 ppm that corresponds to aromatic region coming from triphenyl phosphine oxide groups. Methyne protons coming from acetylated units and PVA modified with phosphine oxide groups appeared together between 4.7-5.5 ppm. Methyne protons of unmodified PVA appear between 3.5-4.0 ppm.

PVA hydroxyl proton appears just between unmodified PVA methyne protons and modified PVA methyne protons at 4.5 ppm. Methylene and methyl protons appear all together between 1.4-2.1 ppm.[77,87]

Figure 2.7 ^{1}H and ^{31}P NMR of polymer E2 recorded in DMSO-d_6

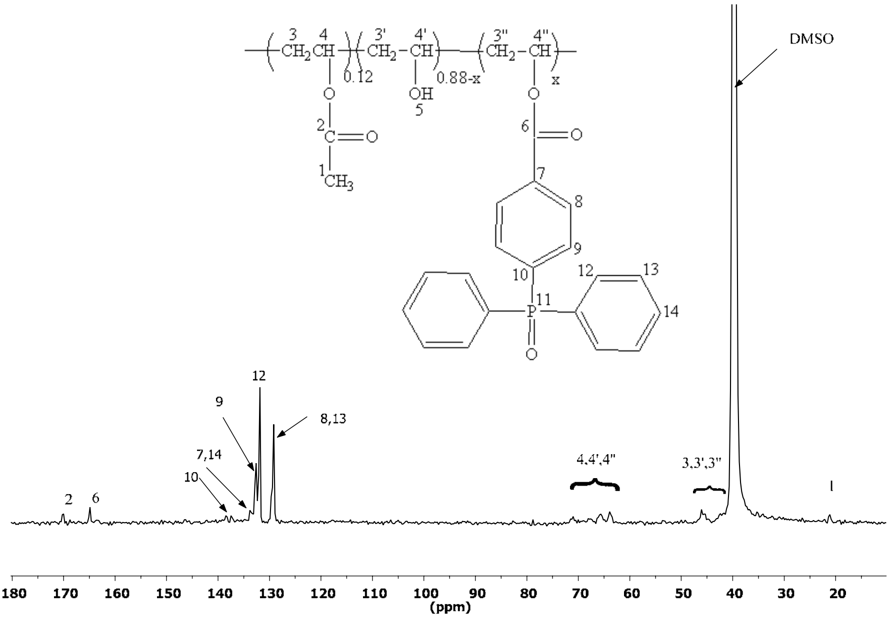


^{13}C NMR spectrum related in figure 2.8 shows signals at 164.6 ppm and 169.7 ppm that were attributed to carbonylic carbons coming from modified PVA with phosphine oxide groups and PVA acetylated units, respectively.

Signals between 128.8-138.1 ppm which are in characteristic area of aromatic carbons were associated to triphenyl phosphine oxide units. Methyne and methylene carbons from PVA chain were found between 63.6-71.0 ppm and 45.8 ppm, respectively. A weak signal has been found at 20.8 ppm which was due to methyl carbons from PVA acetylated units.

All the evidences mentioned above and absence of unexpected signals shows that the target products were synthesized successfully.

Figure 2.8 ^{13}C NMR of polymer E2 recorded in DMSO-d_6



The inherent viscosity measurements were performed in DMSO for samples of 0.2 g/dl at 30 ºC. Obtained values presented in table 2.8 are lower than in case of virgin PVA and they decrease with modification degree increment. The decrease in viscosity is probably due to a more globular conformation adopted by the polymer since bulky groups are introduced.

All viscosity values present the same order of magnitude, which indicates there are not ruptures or branching of polymeric structure at least in an important extent. The overall yields were calculated from the weight of well dried pure product taking into account the modification degree values obtained in each case and that acetylated units remained unchanged.

Table 2.8 Results of PVA modifying with DPBC

Polymer	**%P Determined from**		**Degree of modification**	**Yield (%)**	**$\mu_{inh.}$ (dl/g)**
	ICP-AES	**^{1}H NMR**	**x^a**		
PVA					0.72
E2	5	6	0.23	93	0.49
E3	6	6.8	0.33	93	0.35
E4	7	8.1	0.66	48	0.32
E5	8	8.3	0.87	89	0.26

[a] Obtained from ^{1}H NMR considering 12% of acetylated part

3.2- Polymers thermal characterization

Thermal characterization of resulted polymers was carried out by DSC and TGA analysis. The results are summarized in table 2.9 and table 2.10.

In some cases, an annealing of the samples was necessary in order to get clearly visible their glass transitions. Thus, samples were isothermally heated at the convenient temperature for two hours in order to cancel their thermal history, previously to the dynamic scans.

In case of neat PVA a glass transition temperature (Tg) at about 60 ºC and an endotherm peak at about 190 ºC due to the polymer melting were found. Such a high Tg is due to hydroxyl groups that contribute, by hydrogen bonding, to the stiffness of the linear polymers.[90] When the number of hydroxyl groups is reduced by esterification, hydrogen bonding interactions decrease which

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[90] Champetier, G.; Monnerie, L. Introduction à la Chimie Macromoléculaire, Ed. Masson & cie, Paris, **1969**, p.426.

produces a diminution in the stiffness. The new moieties introduced can affect Tg in a different way depending on their structure and the degree of modification. As can be seen in table 2.9 and table 2.10, most of modified polymers showed higher Tg values than starting PVA, in spite of their low trend to establish hydrogen bonds; this is probably due to chain mobility restrictions produced by the bulky groups that were introduced. In case of the BIC derivatives Tg slightly increased, whereas in case of phosphine oxide derivatives Tg strongly increased, that could be explained on the bases of high rigidity and size of aromatic moiety introduced. An exception was observed for polymer B, where a lower glass transition temperature was detected, due to flexible aliphatic chain introduced. None of the polymers prepared showed melting endotherms, as expected for such irregular structures. Therefore, the new synthesized polymers are all amorphous.

Table 2.9 Thermal data of BIC derivatives

Polymer	DSC	TGA					
	Nitrogen	Nitrogen		Air		Char yield, 790°C (%)	
	Tg (°C)	Tonset[a] (°C)	Tmax.[b] (°C)	Tonset[a] (°C)	Tmax.[b] (°C)	Nitrogen	Air
PVA	60	289	322	281	321	4	0
A1	85	242	247	235	242	29	3
A2	75	239	249	237	246	32	3
A3	70	238	241	232	244	30	2
A4	72	236	244	235	240	28	4
A5	70	222	239	218	230	35	4
B	44	240	247	234	248	24	10
C	Not detected	226	242	221	232	34	12

[a] Onset temperature of weight loss
[b] Temperature of maximum rate of weight loss

Table 2.10 Thermal data of phosphine oxide derivatives

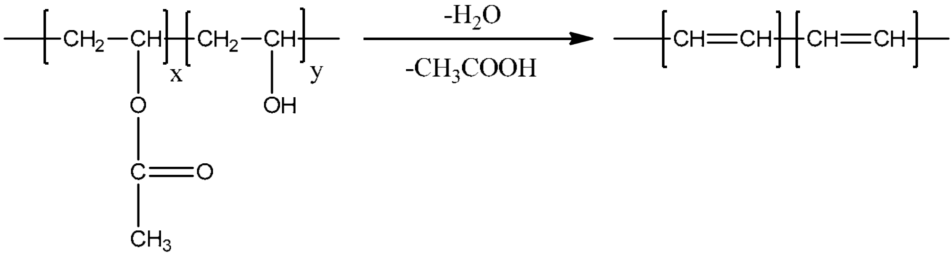
Polymer	DSC	TGA					
	Nitrogen	Nitrogen		Air		Char yield, 790°C (%)	
	Tg (°C)	Tonset[a] (°C)	Tmax.[b] (°C)	Tonset[a] (°C)	Tmax.[b] (°C)	Nitrogen	Air
PVA	60	278	322	278	320	4	0
E2	142	280	405	278	395	17	11
E3	137	293	397	288	436	18	17
E4	131	292	406	286	415	22	21
E5	143	300	419	297	420	27	20

[a] Onset temperature of weight loss
[b] Temperature of maximum rate of weight loss

All polymers were analyzed by TGA using air and nitrogen atmospheres. TGA can serve as a useful indicator of polymer flammability.[91] Particularly, char yields are an indication of trend to form protective barriers, which act as bumpers between polymeric material and flame. Table 2.9 and 2.10 lists the data from the curves including the onset weight loss temperature (Tonset), temperature of maximum rate of weight loss (Tmax) and the char yields at 790ºC in nitrogen and synthetic air atmosphere.

The thermal degradation of PVA starts with the loss of water and acetic acid. (Scheme 2.10)[92] It is evident that this degradation involves in a first stage a considerable weight loss. As PVA always contains a small quantity of free water, the first part of TGA curve (up to about 150 ºC) represents evaporation of this kind of water. Growing weight loss from approximately 280 to 320 ºC is related to the first stage of degradation and elimination of volatile products. Thus, virgin PVA is relatively thermally stable below 280 ºC with a weight loss of approximately 5%, mostly due to the free water. When the temperature further increases, weight loss increases rapidly and a lot of volatiles are produced, leading to a very low char yield (4%) at about 600 ºC in nitrogen and no char yield in air.

Scheme 2.10.



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[91] Wang, D.-Y.; Liu, Y.; Wang, Y.-Z.; Perdomo Artiles, C.; Richard Hull, T.; Price, D. Polym Degrad Stab **2007**, 92, 1592-1598.

[92] Alexy, P.; Káchová, D.; Kršiak, M.; Bakoš, D.; Šimková, B. Polym Degrad Stab **2002**, 78, 413-421.

As can be seen from TGA curves (Figure 2.9) and data presented in table 2.9, all BIC derivatives present a similar thermal behaviour. The modified polymers start to lose weight at lower temperatures than precursor PVA, probably due to the presence of phosphate group, which can be partially hydrolyzed at the beginning of weight loss process, and leads to phosphoric acid groups, able to promote dehydration, further cross-linking and carbonization on the surface of polymer. This leads to a charcoal protective barrier. The formation of this char is associated with the strong weight loss between 220-250 ºC, when approximately 50% of polymer weight is lost. This charred barrier remains more or less unchanged in nitrogen atmosphere and a high amount of char yield is obtained at 790ºC, while the presence of a very oxidant medium facilitates its oxidation at high temperatures in air, leading in most cases to a very small char yield.

In case of PVA modified with phosphine oxide derivative, data from table 2.10 and TGA curves (Figure 2.10) show that weight loss process starts at higher temperatures than in case of starting PVA. In fact, the weight loss process delays as the degree of modification increase, while the char yield at 790 ºC also increase. This behaviour, which is observed both in nitrogen and air, can be explained by taking into consideration that aromatic moieties are introduced, which are thermally stable and trend to lead to charcoal residues.

All TGA curves showed more than one weight loss step. The first one, corresponding to at least 40% of polymer weight loss, starts around 280-300 ºC and reaches a maximum rate of weight loss about 400 ºC, and is the most significant. A second process, taking place at about 480 ºC, was also observed and is associated with the thermal oxidative decomposition of already formed char residue. It can be observed that the weight loss process occurs similarly, in both, nitrogen and air atmosphere.

Figure 2.9. TGA curves in nitrogen and air atmosphere of PVA modified with BIC

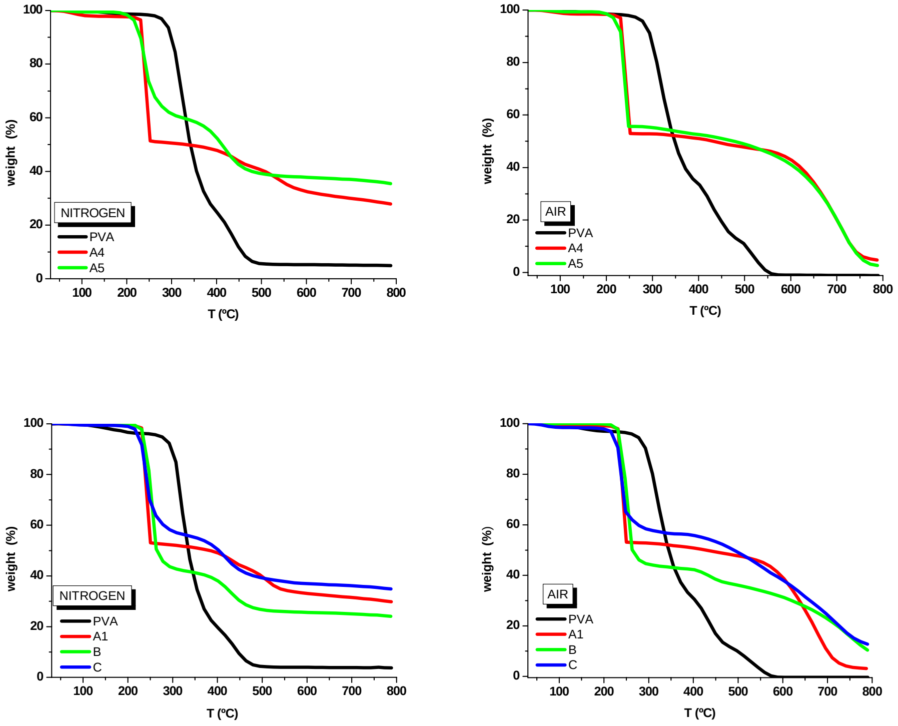
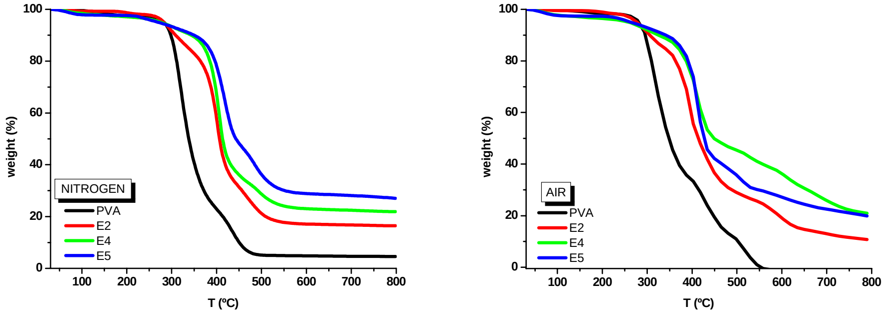


Figure 2.10 TGA curves of PVA modified with DPBC in nitrogen and air

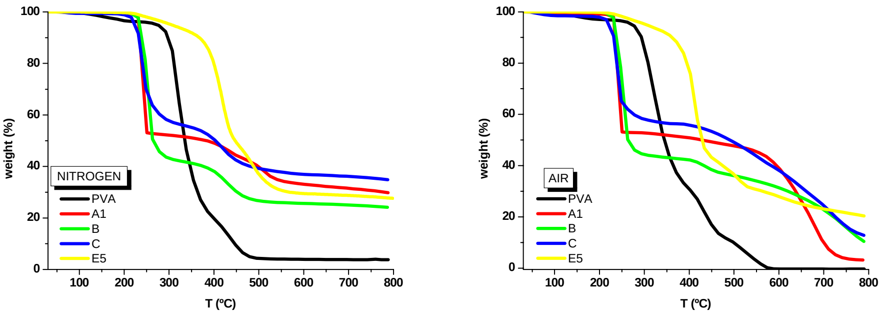


A comparison between BIC and DPBC modified PVA derivatives can be taken from TGA curves (Figure 2.11) and tables 2.9 and 2.10.

It can be observed that in case of PVA modified with BIC derivatives the weight loss process starts at lower temperatures than of neat PVA, whereas in case of modification with DPBC it starts at higher temperatures than of neat polymer. In the case of BIC derivatives, as already mentioned, a phosphate group is present, which can be partially hydrolyzed at the beginning of weight loss process, leading to phosphoric acid groups, able to further catalysed dehydration, and subsequently all weight loss process. This can explained that the weight loss starts earlier than in PVA. In the case of DPBC derivatives, the phosphine oxide group leads to phosphoric acid derivatives with more difficulty, and thus the process is delayed.

It must be noted, that both, BIC and DPBC derivatives, lead to a significant char yields at 790ºC in nitrogen atmosphere. Therefore, in the rich on nitrogen atmosphere of a fire, they would presumably lead to the formation of protective barriers, when they mixed with ¨commodity¨ polymers, thus acting as flame retardant additives.

Figure 2.11 TGA curves of PVA modified with BIC and PVA modified with DPBC in nitrogen and synthetic air



At that point we intended to perform a deeper investigation on polymers degradation process of one of these polymers. If we are able to understand how polymers degrade, we will probably also envisage how this degradation can affect the degradation and flammability of the blends obtained by mixing these polymers with ¨commodity¨ polymers. We decided to perform these studies on one of the BIC derivatives (A1). This polymer was submitted to thermogravimetry coupled with mass spectrometry studies (TGA-MS) and also to pyrolisis studies; in the latter volatile degradation products and non-volatile residues were afterwards analysed.

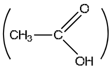
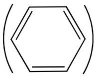
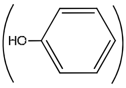
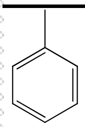
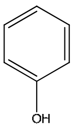
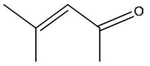
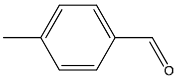
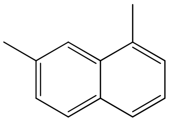
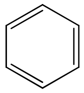
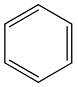
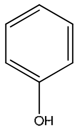
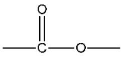
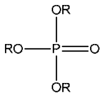
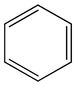
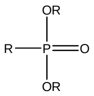
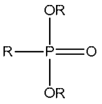
TGA-MS is a simultaneous technique that combines measurements of weight loss on heating with a spectrometric detector. This analysis is giving more than weight loss information, since it allows analyses in real time of volatile compounds evolved during the thermal decomposition of polymeric materials.

In this study we were able to identify some volatiles and gases evolved during the thermal degradation process of polymer A1. In the experiments the sample was heated from 30 ºC up to 240 ºC at heating rate of 10 ºC/min and then it was kept at this temperature for 30 minutes in nitrogen or air atmosphere. The mass spectrometer, coupled with thermobalance through a quartz capillary tube, takes volatiles from the emission point and analyzes them. The results are reported in table 2.11.

In both, nitrogen and air atmospheres, we observed peaks in the mass spectra products attributable to water (m/e=18), unsaturated products such as ethylene (m/e=28), propine (m/e=40) and acetaldehyde (m/e=44), acetic acid (m/e=60). There were also observed m/e peaks corresponding to aromatic compounds (m/e=78, benzene and m/e=94, phenol). The m/e= 28 and m/e= 44 can be associated, also to CO and CO_2 formation.

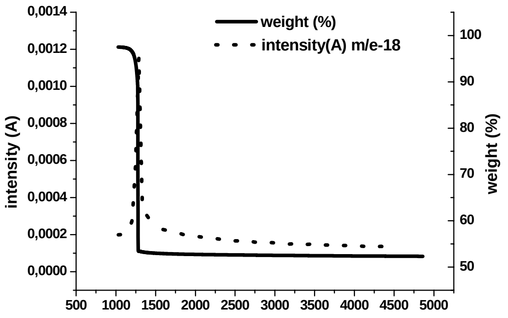
In Figure 2.12 we can see the TGA curve versus time overlapped with the curve showing the intensity of the peaks at m/e=18 (corresponding to water) versus time. As can be seen the highest amount of water detected by MS, coincides with the most important weight loss, indicating that the loss of water is probably crucial to start the decomposition process. The figure refers to the process performed under nitrogen. A similar behaviour was observed under air atmosphere.

Table 2.11. Mainly detected degradation products.

TG-MS [a]	**Volatiles**			**Residue**	
	GC-MS [b]	**FT-IR** [c]	**NMR** [d]	**FT-IR** [e]	**NMR** [f]
m/e=18 (H_2O) m/e=28 ($CH_2{=}CH_2$; CO) m/e=40 ($CH\equiv C-CH_3$) m/e=44 (CH_3-CHO; CO_2) m/e=60  m/e=78  m/e=94 	    	OH C-O C=O  P-O P=O	$-CH_3$ R—CHO    	$-C\equiv C-$  aryl or unsaturated ketones 	

a) structures attributed to m/e peaks detected by TG-MS
b) evolved volatile products formed by pyrolisis and identified by GC-MS
c) functional groups recognized by FT-IR to be present on the evolved volatile products formed by pyrolisis
d) moieties recognized by NMR to be present on the evolved volatile products formed by pyrolisis
e) functional groups recognized by FT-IR to be present on carbonaceous residue obtained by pyrolisis
f) moieties recognized by solid state ^{31}P NMR on carbonaceous residue obtained by pyrolisis

Figure 2.12 TGA curve versus time and intensity of the peaks at m/e=18 versus time in nitrogen



As already mentioned, another technique used for investigation of polymers thermal degradation process was pyrolisis. Thus, polymer A1 was heated in a pyrolytic oven at 240 ºC for 3 hours in a synthetic air atmosphere. The volatile compounds evolved in this process were condensed, collected and analyzed by FT-IR, NMR and GC-MS. The remained solid residue was characterized by FT-IR and solid state ^{31}P NMR. The results of these characterizations are listed in table 2.11.

In the ^{1}H NMR spectrum of the collected mixture of volatiles we observed signals between 1.2-2.2 ppm which can be due to methyl groups of acetaldehyde, acetic acid, acetate esters and other alkyl groups (i.e. ethyl).

We also observed protons coming from aromatic ring in region of 6.8-7.3 ppm. Moreover a small broad signal between 5.2-5.3 ppm is associated to protons coming from phenolic OH groups and another small signal at about 9.5 ppm was attributed to aldehyde protons. The ^{13}C NMR confirmed the presence of aromatic moieties, methyl groups and carbonyl ester groups. A signal at 158.3-158.4 ppm was observed, which can be attributed to the quaternary carbon linked to OH phenol. A phosphorous signal was detected by ^{31} P NMR at about -0.5 ppm and was associated to phosphate derivatives.

The FT-IR spectrum of the collected mixture of volatiles showed a broad signal between 3600-3100 cm^{-1} that was attributed to OH groups. The region of 1734-1700 cm^{-1} show peaks attributed to carbonyl groups (acid, ester, ketone, aldehyde). We also observed signals characteristic for C-O group (ester, phenol) at about 1230-1150 cm^{-1} and signals characteristic for alkenes at 1650 cm^{-1} (C=C vibration band). Aromatic groups were observed in region of 1603 cm^{-1} and 1583 cm^{-1} characteristic for C=C vibration and at 756-690 cm^{-1} characteristic for deformation out-of-plane. Some characteristic signals of phosphorous were also detected at about 1291 cm^{-1} (P=O) and 1000 cm^{-1} (P-O).

The mixture of volatile compounds was finally analyzed by GC-MS: in this way, this mixture was separated and some of the peaks identified by comparing with reported mass spectra. Most of these compounds are aromatic derivatives and some also contains phenol or aldehyde groups. There was also observed a structure corresponding to aldol condensation product of acetone.

The charcoal residue obtained after pyrolisis was analyzed by solid state ^{31}P NMR and FT-IR. The results are reported in table 2.11 as well. In the NMR spectrum we observed a signal at about 9 ppm which was attributed to aromatic phosphonate derivatives.

FT-IR analyses of the charcoal residue shows signals between 2000-2300 cm^{-1} characteristic for C-C triple bonds and signals at 1577 cm^{-1}; 1448 cm^{-1} and 870 cm^{-1} which are attributable to aromatic C-C absorptions and out-of-plane deformation bands. A signal attributable to carbonyl group from aromatic ketones was found at 1675 cm^{-1}; signals at 1100 and 960 were attributed to P=O and P-O bonds.

It must be noted that PVA thermal degradation process was studied by Gillman et al. and by other researchers[93-96] and they propose that this process starts by dehydration reactions. The initially formed unsaturated products further react in a variety of ways; the most important are shown in scheme 2.10.

Thus, dehydration reactions can lead to the formation of conjugated polyenes or, by chain-scission of the partially degraded products, they can lead to the methyl-terminated polyene structures. Moreover, conjugated polyenes can cyclise through Diels-Alder reaction or electrocyclic rearrangement to cyclohexenes or cyclohexadienes, respectively, which further aromatize by dehydrogenation. Polyenes can also add free radicals formed by chain-scission leading to aliphatic products or substituted olefins.

As expected, water is one of the important products evolved during the degradation process. This suggests us that the degradation process starts by

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[93] Gillman et al. Thermal Decomposition Chemistry of Poly(vinyl alcohol). Char Characterization and Reactions with Bismaleimides. BFRL, NIST. Proceedings of ACS Symp. Ser. 599 (Fire and Polymers II), Gaithersburg **1995**, 161-185.

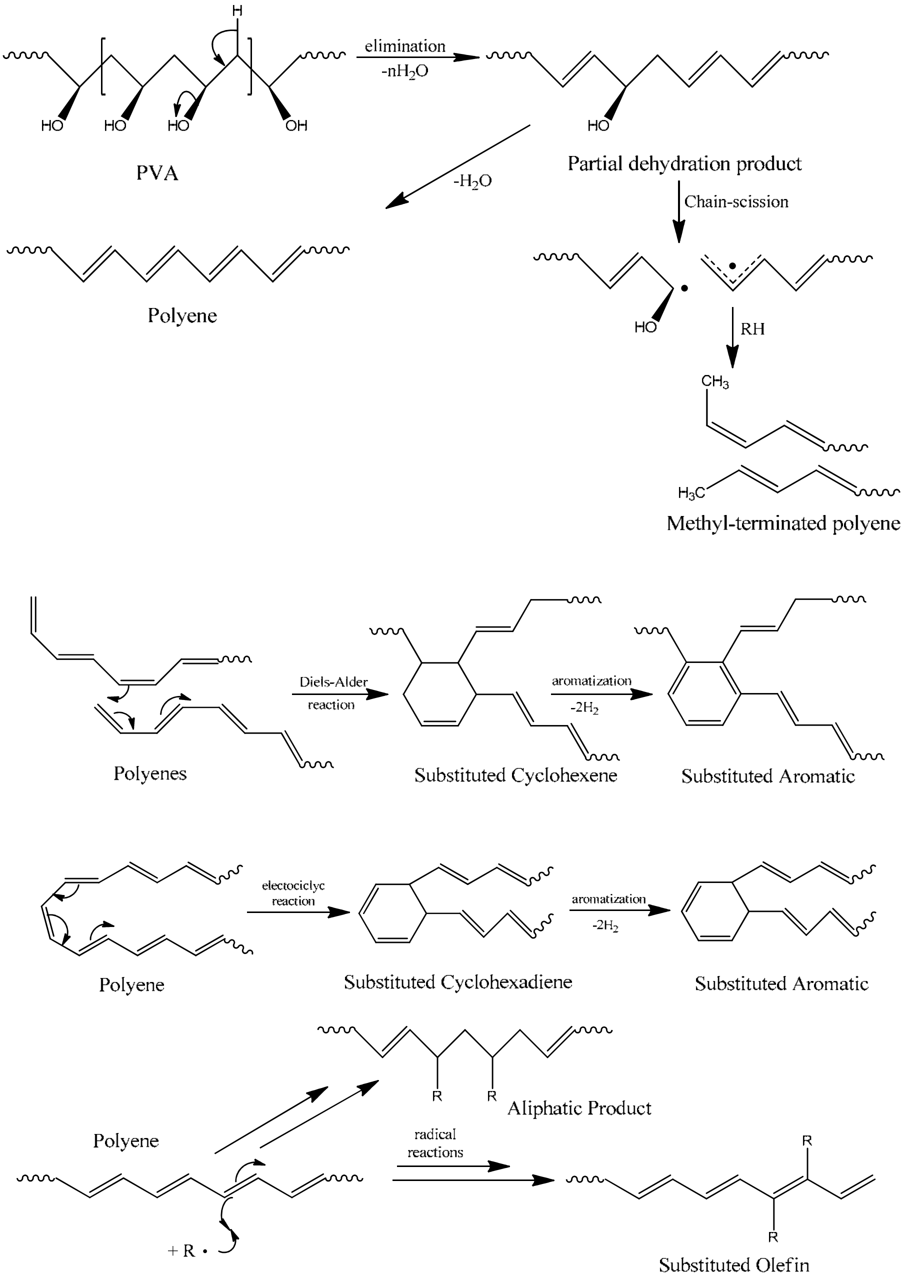
[94] Shaulov, A. Yu.; Lomakin, S. M.; Zarkhina, T. S.; Rakhimkulov, A. D.; Shilkina, N. G.; Muravlev, Yu. B.; Berlin, Al. Al. Dokl Phys Chem **2005**, 403, 2, 154-158.

[95] Zhao, C.-X.; Liu, Y.; Wang, D.-Y.; Wang, D.-L.; Wang, Y.-Z. Polym Degrad Stab **2008**, 93, 1323–1331.

[96] Zaikov, G. E.; Lornakin, S. M. Polym Degrad Stab **1996**, 54, 223-233.

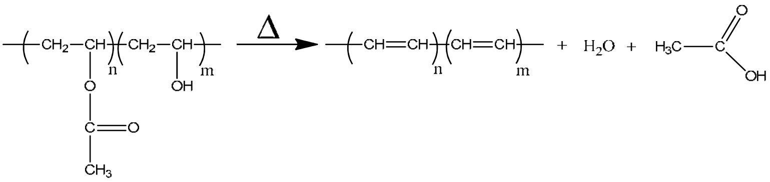
dehydration reactions, as it was already related for PVA; all the reactions depicted in scheme 2.10 are expected to take place also in polymer A1.

Scheme 2.10

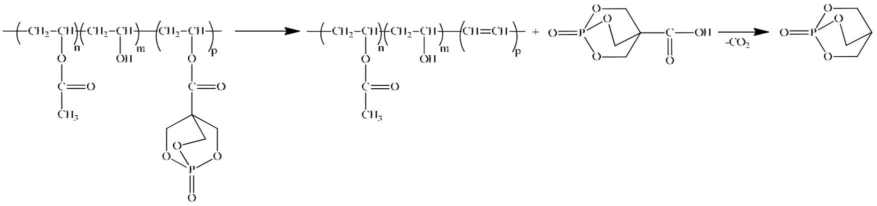


To sum up, from the analyses of compounds formed during thermal decomposition of A1, the following can be point out:

- Water and acetic acid formed, probably through dehydration and acetic acid pyrolitic elimination.

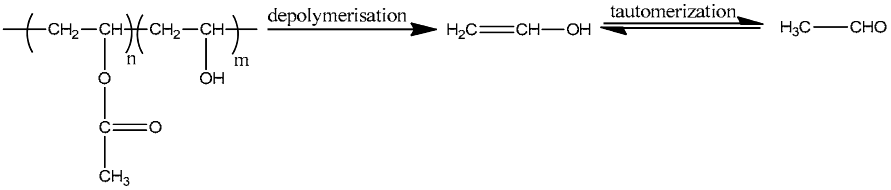


- Some phosphate volatile compounds evolved, probably formed from the pyrolitic elimination reaction of the corresponding bicyclic acid (4-carboxy-1-oxo-2,6,7-trioxa-1-phosphabicyclo-[2,2,2]-octane), which could further decarboxylate.



- Formation of aromatic compounds occurs as already described for neat PVA, through the aromatization of polyene structures by an electrocyclic cyclization and/or a Diels-Alder condensation. A part of them is lost as volatile molecules (in some case partially oxidized). Another part is retained and gives rise to condensed aromatic systems and finally to charcoal (see scheme 2.10).
- Alkenes and alkanes, like in PVA, can be formed through radical addition reaction on polyenes.
- The alkynes formed, probably come directly from depolymerisation process of polyenes.
- Esters (probably acetates) are formed through the vinyl acetate chains scission.

- Acetaldehyde is probably resulting from enol-ketone tautomerization of enol formed by depolymerisation.



- The phosphorous present in carbonaceous residue corresponds, as mentioned, to aromatic phosphonate. Therefore, probably it was formed from the reaction of phosphoric acid derivatives, which act as electrophiles, on aromatic moieties, through a process similar to a Friedel-Crafts acylation.
- The formation of CO and CO_2 is also generally expected, particularly under air degradation conditions.

By considering the results of the thermal degradation study of polymer A1 and the degradation mechanism reported for neat PVA in the literature, we conclude that polymer A1 and PVA degrade in a similar manner, but with some differences. As mentioned above, polymer A1 start to lose weight at temperatures lower than PVA, indicating that some catalytic effect is provided by phosphorous. Thus, the water evolved through the incipient dehydration process probably hydrolyzes the phosphate groups and leads to phosphoric acid derivatives. These later derivatives can, in turn, catalyze the dehydration process, leading to more water evolution and formation of polyene structures. Polyene, as in PVA, will lead to the formation of aromatic and unsaturated structures. However, if we consider that in polymer A1 a higher char yield is observed, this process, leading to aromatic structure, takes place in a higher extent in our case. This could be related to the presence of phosphoric acid derivatives, which, as indicated above, catalyze dehydration reactions and make easier the formation of aromatic compounds and then charcoal. It must be noted that phosphorous seems to show a dual action in polymer A1. First, it acts in the condensed phase, catalyzing dehydration reaction, thus leading a charred layer formation on the polymer surface. This layer acts as a barrier to difficult volatile products from diffusing to the flame and to shield the polymer surface from heat and air. Second, the presence of phosphate derivatives on the evolved gas phase, suggests that phosphorous could also act in the gas phase, since it was reported that phosphorous compounds can trap the radicals in the flame, thus interrupting the exothermic reactions that take place and suppress the combustion of flammable mixture.[3,80]

For these reasons, polymer A1 is in principle a good candidate to act as a flame retardant polymeric additive on ¨commodity¨ polymers, since it can be expected to act both on the gas and the condensed phase. The observed effect on blending it with polypropylene will be discussed in Chapter 5.

4. Conclusions

As a summary of this chapter, we can indicate that most of the polymeric structures, that we intend to prepare, were successfully synthesized and characterized. Thus different sets of polymers which were obtained shows different polarities associated to phosphorous functional groups. These polymers should show a different compatibility with ¨commodity¨ polymers.

All synthesized polymers led to high char yields on TGA curves. Therefore, they are good candidates to act as flame retardant additives through the formation of charred barriers on the condensed phase. Moreover, the BIC set of polymers can be envisaged also to act in the gas phase, since phosphate volatile derivatives have been identified in the volatile mixture after the degradation process study.

Chapter 3

Flame retardant phosphorous or phosphorous- nitrogen containing polymeric additives obtained by chemical modification of polyketones

In this chapter we intend to prepare a set of polymeric flame retardant additives based on chemical modification of polyketones. These chemical modifications have been performed through a nucleophilic addition reaction of phosphorous and/or nitrogen containing compounds on polymeric carbonyl groups. As starting polyketones we used poly(methylene ketone) and alternating CO- 4-tert-butylstyrene copolymer.

1. Introduction

In this chapter we intend to prepare a set of polymeric flame retardant additives, based in polyketones modified with phosphorus and/or nitrogen containing derivatives. As already mentioned in detail, phosphorus containing derivatives are widely used as flame retardants. They exist in many phosphorous oxidation states and could act in both, condensed or vapour phase. Depending of phosphorous functional group they should confer to the polymers different compatibilities with ¨commodity¨ polymers.

As mentioned in the general introduction, various phosphorus-nitrogen (P–N) containing compounds have shown to impart flame retardancy to polymers. Moreover, showing a synergistic behaviour the P–N compounds have greater thermal stabilities and lower toxic smoke evolution when compared to phosphorus based FR.[97]

Many P-N systems can be classified as intumescent systems. Intumescent flame retardants are well known as a new generation of flame retardants for polyolefins,[4] especially polypropylene and polyethylene.[98] As already described in the chapter 1, intumescent system is mainly composed of inorganic acid sources (e.g. polyphosphate), charring sources (e.g. pentaerythritol, sorbitol etc.) and foaming agents (e.g. melamine)[98,99] its behaviour resulting from a combination of charring and foaming of the surface of the burning polymer. The acid source first breaks down to yield a mineral acid (usually polyphosphoric acid), which then dehydrates the carbon compound to produce a char. The foaming agent then decomposes generating gaseous products that cause the char to swell to form the insulating layer.[100] Often, the foaming agent is based on a nitrogen moiety, which developed on burning ammonia vapours.

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[97] Nguyen, C.; Kim, J. Polym Degrad Stab **2008**, 93, 1037-1043.

[98] Li, B.; Xu, M. Polym Degrad Stab **2006**, 91, 1380-1386.

[99] Fontaine,G.; Bourbigot, S.; Duquesne, S. Polym Degrad Stab **2008**, 93, 68-76.

[100] Estevão, L. R.M.; Nascimento, R. S. V. Polym Degrad Stab **2002**, 75, 517–533.

Polyketones are partially crystalline engineering thermoplastics that can be used at high temperatures, provided from cheap and abundant raw materials and easily to synthesize. They also have excellent chemical resistance, high strength, and excellent resistance to burning.[101-103] A wide variety of synthetic methods are available for polyketones modification in order to convert them to other functional polymers.[102,104,105] Polyketones used in this study are poly (methylene ketone) obtained by the chemical oxidation of PVA[106] and a polyketone obtained by the copolymerization of carbon monoxide and an olefin, tert-butyl styrene.[107,108]

The first aim of this chapter is to modify the starting polyketones with phosphorus containing compounds, which acts as nucleophiles into carbonyl groups of the polyketones leading to corresponding polyalcohols.[105,106]

The presence of free hydroxyl groups in the final polymer is interesting, since these groups can easily lead to a charred layer.

The chosen nucleophilic reaction was phosphorilation. As nucleophiles, a cyclic phosphinic acid ester, 9,10-dihydro-9-oxa-10-phosphaphenantrene-10-oxide (DOPO) and a cyclic hydrogen phosphite derived from 2,2-dimethyl-1,3-propandiol have been used. Thus, the polymers that we intend to synthesize will contain phosphoryl-oxygen bonds, which are easily hydrolysable groups. In this way, these groups lead to phosphoric acids, which catalyze dehydration reactions. This will lead to unsaturated systems, which further aromatize giving rise to high carbonaceous residue, which probably will act as a protective barrier

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[101] Lagarona, J.M.; Vickersb, M.E.; Powella, A.K.; Davidsona, N.S. Polymer **2000**, 41, 3011-3017.

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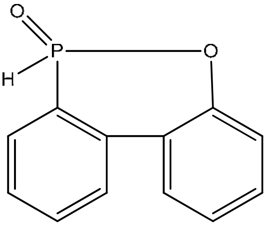
[105] Zhang, Y.; Broekhuis, A.A.; Stuart, Marc C. A.; Picchioni, F. J Appl Polym Sci **2008**, 107, 262–271

[106] Liu, Y.-L.; Chiu, Y.-C. J Polym Sci Part A: Polym Chem **2003**, 41, 1107-1113.

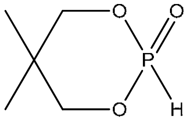
[107] Giménez-Pedrós, M.; Tortosa-Estorach,C.; Bastero,A.; Masdeu-Bulto, A.M.; Solinas, M; Leitner, W. Green Chem **2006**, 8, 875–877.

[108] Campos-Carrasco, A. Doctoral Thesis: Universitat Rovira i Virgili, Carbon dioxide as solvent and C1 building block in catalysis **2011**, ISBN:/DL:T. 1023-2011.

in burning, when blended with ¨commodity¨ polymers. Both structures were reported by many researchers as good flame retardant promoters. [3,7,16,109-111]

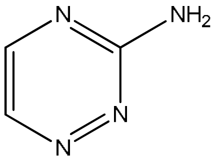


DOPO



Pcyc

A second aim of this chapter was to introduce nitrogen on the phosphorous containing polyketones derivatives, in order to obtain intumescent systems. Nitrogen can be introduced before or after the modification with phosphorous moieties. As a first approach, we intend to prepare imines from the reaction of carbonyl groups with primary amine, and then add phosphorous nucleophiles to the C=N double bonds. The selected primary amine was 3-amino-1,2,4-triazine (Tz), since its structure is similar to melamine and its high nitrogen content can make it prompt to easily develop ammonia on decomposing.[105,112]



Tz

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[109] Schäfer, A.; Seibold, S.; Lohstroh, W.; Walter, O.; Döring, M. J Appl Polym Sci **2007**, 105, 685-696.

[110] Joseph, P.; Tretsiakova-Mcnally, S. Polym Adv Technol **2011**, 22, 395-406.

[111] Chen, L.; Wang, Y.-Z. Materials **2010**, 3, 4746-4760.

[112] Gaan, S.; Sun, G.; Hutches K.; Engelhard, M.H. Polym Degrad Stab **2008**, 93, 99-108.

2. Experimental section

2.1- Materials

Commercial materials

PVA used in this work, supplied by Fluka, was already described in previous chapter. Potassium permanganate ($KMnO_4$) 99% Probus, aniline (An) 99% Sigma-Aldrich, triethylamine (Et_3N) 99% Sigma-Aldrich, erbium(III) trifluoromethanesulphonate ($Er(OTf)_3$) 98% Sigma-Aldrich, lanthanum(III) trifluoromethanesulphonate ($La(OTf)_3$) 99.9% Sigma-Aldrich, phenyl acetone (PhAc) 99% Sigma-Aldrich, acetyl acetone (AcAc) 99% Sigma-Aldrich, 3-amino-1,2,4-triazine (Tz) 97% Sigma-Aldrich, manganese (II) chloride ($MnCl_2$), 99% Merck, ethanol (EtOH) 96.9% Scharlau, glacial acetic acid (AcOH) 99.5% Scharlau were used without previous purification. 9,10-dihydro-9-oxa-10-phosphaphenantrene-10-oxide (DOPO) was kindly provided as a gift from Schill & Seilacher and used as received. Tetrahydrofyrane (THF) 99.5% Scharlau was used freshly distilled from sodium- benzophenone. Toluene (TOL) 99.5%, Panreac was fractionally distilled from sodium previous to use.[113]

Synthesized materials

Alternating CO- 4-tert-butyl styrene copolymer (COTBS) was prepared as reported below by the researchers of Inorganic Section of our Faculty. 5,5-dimethyl-1,3,2-dioxaphosphinan-2-one (Pcyc) and poly(methyl ketone) (OPVA), were synthesized as follows.

5,5-dimethyl-1,3,2-dioxaphosphinan-2-one (Pcyc) has been synthesized from 2,2-dimethyl-1,3-propanediol (DPD) following a published procedure (scheme 3.1).[114] The yield was 50%. Melting point was 53-55ºC.

IR (cm^{-1}): 2890-2975 (C-H); 2432 (P-H); 1258 (P=O); 1054 (C-O). ^1H NMR ($CDCl_3$, 400 MHz, δ (ppm)): 0.9 (s, 3H); 1.31 (s, 3H); 4.0-4.1 (m, 4H); 7.0 (s,

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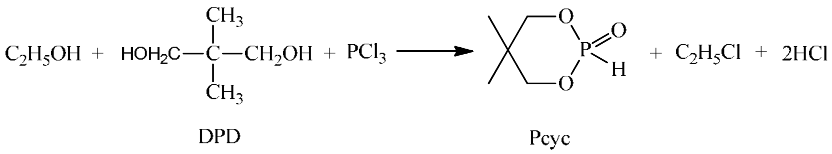
[113] Armarego, W.L.F.; Perrin, D.D. Purification of Laboratory Chemicals, 4th edition, **1996**, pp. 334, 342.

[114] McConnell, R.L.; Coover Jr, H.W. J Org Chem **1959**, 24, 630-635.

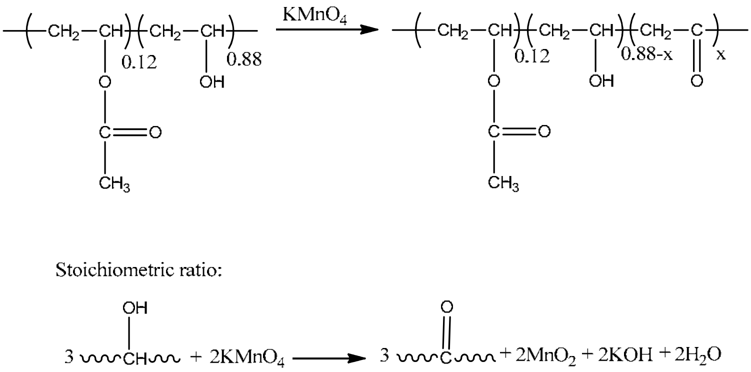
1H). ^{13}C NMR ($CDCl_3$, 100.6 MHz, δ (ppm)): 20.7(q); 21.9 (q); 32.2-32.3 (s); 76.1-76.2 (t). ^{31}P NMR ($CDCl_3$, 161.9 MHz, δ (ppm)): 5.8.

Scheme 3.1



Poly(methylene ketone) (OPVA) was obtained from the chemical oxidation of PVA with $KMnO_4$. Synthesis process was launched based in a published method related in scheme 3.2.[106] A general method is as follows.

Scheme 3.2



In a three necked round bottom flask was introduced a 10 wt% aqueous polymeric suspension of 2.0 g of PVA (0.036 mol of OH groups). The flask was provided with a reflux condenser, a magnetic stirrer and a thermometer. The well stirred suspension was taken to 80-90 ºC for completely solubilisation of PVA. Then the polymeric solution was left to cool to room temperature and the necessary amount of $KMnO_4$ was added in small portions during 1-2 h. After the addition of oxidizing agent was completed, the mixture was heated and kept to different temperatures for different times. The reaction mixture was diluted with a large amount of H_2O. Then, the formed MnO_2 was filtered off and the resulted polymer was isolated by rotary evaporation of water and drying under vacuum at 70 ºC. Reaction conditions and weight of isolated oxidized polymer are related in table 3.1. IR (cm^{-1}): 3229 (OH); 1560 (enol C=C). The NMR data collected in D_2O in solution and in solid state (using benzene- d_6 as humectant to lock the signal) are related in table 3.2.

Table 3.1 Reaction conditions for synthesis of poly (methylene ketone)

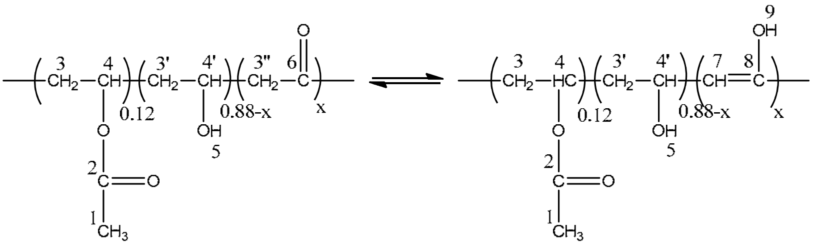
Assay	**Time*** **(h)**	**T (ºC)**	**Molar ratio**** **OH groups :$KMnO_4$**	**Weight of obtained polymer*** (g)**
R1	12	90	1:0.33	1.9
R2	12	50	1:1	1.7
R3	12	70	1:1	1.8
R4	24	75	1:2	1.9

* Time after complete addition of $KMnO_4$

** The stoichiometric ratio is OH: $KMno_4$/ 1:0.67

*** The amount of starting PVA was 2.0 g

Table 3.2 NMR data of poly (methylene ketone)



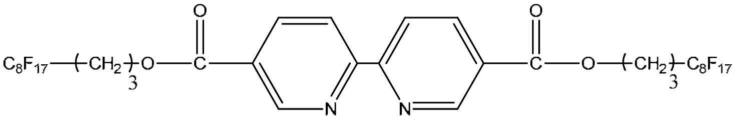
Compound	**^{1}H NMR data**		**^{13}C NMR data**	
	Resonances	**Assignment**	**Resonances**	**Assignment**
OPVA (D_2O)			23.9-24.3	1
	1.5-2.0	1,3,3’	43.3	3
	2.3	3’’	43.8-44.0	3’
	3.7	4’	44.7	3’’
	4.0-4.3	5	64.6-66.1	4’
	4.7-5.1	4	67.6	4
	6.4	7	162.0	8
	8.4	9	173.2	2
			181.3	6
OPVA (solid state)			25.5	1
	1.3-2.3	1, 3, 3’	35.0-37.0	3, 3’
	2.8	3’’	46.0-48.0	3’’
	3.5	4’	67.0-69.0	4’
	4.2-4.8	4, 5	70.0	4
	5.6	7	112.0	7
	9.0	9	164.0	8
			171.0-172.0	2
			179.0-183.0	6

Alternating CO-4-tert-butylstyrene copolymer (COTBS) was synthesized as follows. The copolymerization reaction was performed in an 11 ml stainless steel autoclave. $2.2*10^{-3}$ mmol (5.3 mg) of catalyst (palladium (II) complex, $[Pd(N\text{-}N)_2][BArF]_2$) (see structure below) was weight and introduced into the purged autoclave. Then a solution of 2.2 ml (12 mmol) of 4- tert-butyl styrene and 52 µl of 2,2,2-trifluoroethanol (TFE) was added under argon atmosphere. The autoclave was pressurized with CO (30 atm) and CO_2 (up to 70 atm) and heated to 60 ºC for 24h. After reaction time, the autoclave was cooled down and depressurised. The product was dissolved in 5 ml of dichloromethane (CH_2Cl_2) and precipitated by dropping the solution into 70 ml of stirred methanol. The polymer was filtered, washed with methanol and dried under vacuum.

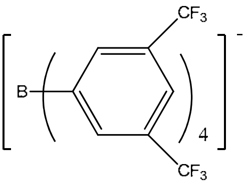
^{1}H NMR ($CDCl_3$, 400 MHz, δ (ppm)): 1.1-1.5 (q, 9H); 2.4-3.2 (t, 2H); 3.8-4.2 (d, 1H); 6.5-6.8 (d, 1H); 7.0-7.2 (d, 1H). ^{13}C NMR ($CDCl_3$, 100.6 MHz, δ (ppm)): 31.8 (q); 34.8 (s); 43.5-44.0 (t); 53.0 (d); 125.8-126.3 (d); 128.5 (d); 134.5-134.8 (s); 150.0 (s); 207.1-208.0 (s).

$Pd(N\text{-}N)_2][BArF]_2$

N-N:



BArF:



2.2- Chemical modification reactions

Reactions on model compounds

Reaction 1-AcAcPcyc. The reaction takes place between acetyl acetone (AcAc) and 5,5-dimethyl-1,3,2-dioxaphosphinan-2-one (Pcyc) as related in scheme 3.3. Reaction conditions are summarised in table 3.3.

Table 3.3. Reaction conditions of AcAcPcyc

Assay	T (ºC)	Solvent	$Er(OTf)_3$
R1	rt.*	Toluene	No
R2	60	Toluene	No
R3	rt.	THF	Yes

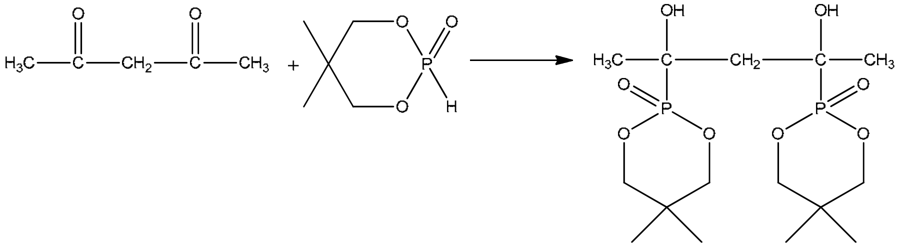
* rt.= 23±2 ºC

In a round bottomed two necked flask of 50 ml well dried and previously purged with argon we introduced 0.01 mol (1.0 g) of AcAc, 0.02 mol (3.0 g) of Pcyc, 20 ml of fresh distilled toluene (R1; R2) or THF (R3) and eventually 0.001 mol (0.61 g) of $Er(OTf)_3$ (R3). The flask was provided with a reflux condenser, magnetic stirrer and an addition funnel and kept under argon flow. Through the addition funnel 0.01 mol (1.0 g) of Et_3N were added dropwise into the reaction mixture under stirring at room temperature. After all Et_3N was added, the reaction mixture was held at 60 ºC (R2) or at room temperature (R1; R3) until the reaction was completed. The reaction was followed by TLC using as eluent acetone: methanol / 1:2. The product was recovered by successive washing with hexane and diethyl ether. The solvent was removed through decantation and vacuum drying. The overall yield was 43% (R3). R1 and R2 did not give to the desired product.

^1H NMR (DMSO- d6, 400 MHz, δ ppm): 1.1-1.2 (4s, 12H); 1.3 (s, 3H); 2.1 (s, 3H); 3.0; 3.2 (2s, 2H), 3.3-3.4 (d, 8H); 5.4 (s, 1H); ^{13}C NMR (DMSO- d6, 100.6

MHz, δ ppm): 21.7 (q); 24.5 (q); 36.9 (s); 48.8 (t); 66.5 (s); 67.7 (t); ^{31}P NMR (DMSO- d6, 161.9 MHz, δ ppm): 20.9; 24.1(2s).

Scheme 3.3



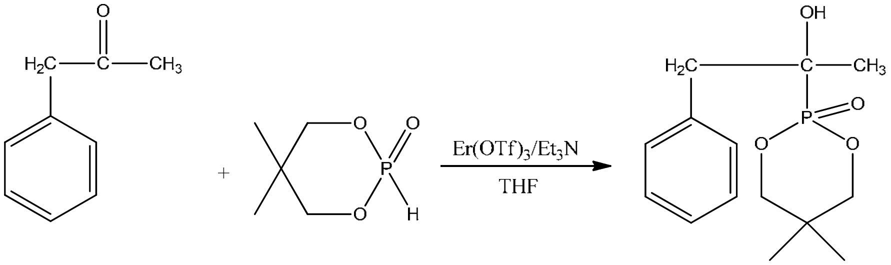
AcAc Pcyc AcAcPcyc

mixture of diastereoisomers

<u>Reaction 2- PhAcPcyc.</u> The reaction of phenylacetone with 5,5-dimethyl-1,3,2-dioxaphosphinan-2-one, presented in scheme 3.4, was carried out following the same procedure used for reaction 1 (assay R3). In a round bottomed two necked flask of 50 ml we introduced 0.01 mol (1.3 g) of PhAc, 0.0125 mol (1.88 g) of Pcyc and 0.001 mol (0.61 g) of Er(OTf)3. The flask was provided with a magnetic stirrer and an addition funnel and kept under argon. Then 0.01 mol (1.0 g) of Et_3N were added dropwise into the reaction mixture and stirred at room temperature until the reaction was completed. The reaction was followed by TLC using as eluent ethyl acetate: hexane/ 10:1. The product was obtained after successive washing with hexane and diethyl ether, decantation and dried under vacuum. The yield was 20 %.

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 1.0 (s, 3H); 1.1 (s, 3H); 1.3-1.4 (d, 3H); 2.5 (s, 1H); 2.9-3.3 (m, 2H); 4.0-4.2 (m, 4H); 7.2-7.3 (m, 5H), ^{13}C NMR ($CDCl_3$, 100.6 MHz, δ ppm): 21.1-21.8 (q); 22.0 (q); 32.5-32.6 (s); 42.1-42.2 (t) 72.5 (t); 74.2 (t); 76.8 (s); 126.9 (d); 128.2 (d); 131.1 (d); 134.6-134.7 (s); ^{31}P NMR ($CDCl_3$, 161.9 MHz, δ ppm): 21.1 (s).

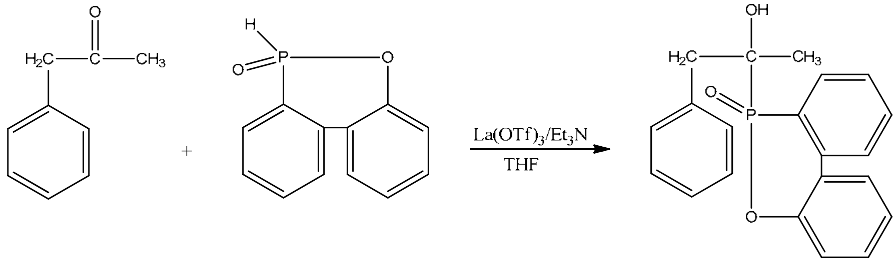
Scheme 3.4



PhAc Pcyc PhAcPcyc

Reaction 3- PhAcDOPO. The reaction between phenyl acetone (PhAc) and 9,10-dihydro-9-oxa-10-phosphaphenantrene-10-oxide (DOPO) was performed in the same conditions as reaction 2 but using La(OTf)$_3$ instead of Er(OTf)$_3$ (Scheme 3.5). The reaction was followed by TLC using as eluent dichloromethane: methanol / 20:1 and stopped when a single product was observed. The resulted product was well washed with hexane and diethyl ether and dried under vacuum. The yield was 80%. ^{1}H NMR (DMSO- d6, 400 MHz, δ ppm): 1.0 (d, 3H); 3.0-3.1 (m, 2H); 5.6-5.7 (m, 1H); 7.1-8.3 (m, 13H); ^{13}C NMR (DMSO- d6, 100.6 MHz, δ ppm): 20.1 (q); 40.5 (s); 73.2 -74.4 (t); 119.5-135.2 (m); 150.2 (s); ^{31}P NMR (DMSO- d6, 169.1 MHz, δ ppm): 36.7 (s).

Scheme 3.5

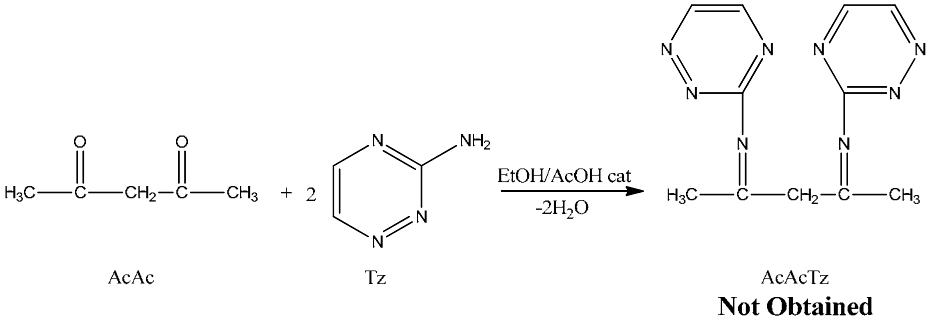


PhAc DOPO PhAcDOPO

Reaction 4- AcAcTz. The synthesis of this compound was tackled according to scheme 3.6 from acetyl acetone and 3-amino-1,2,4-triazine.

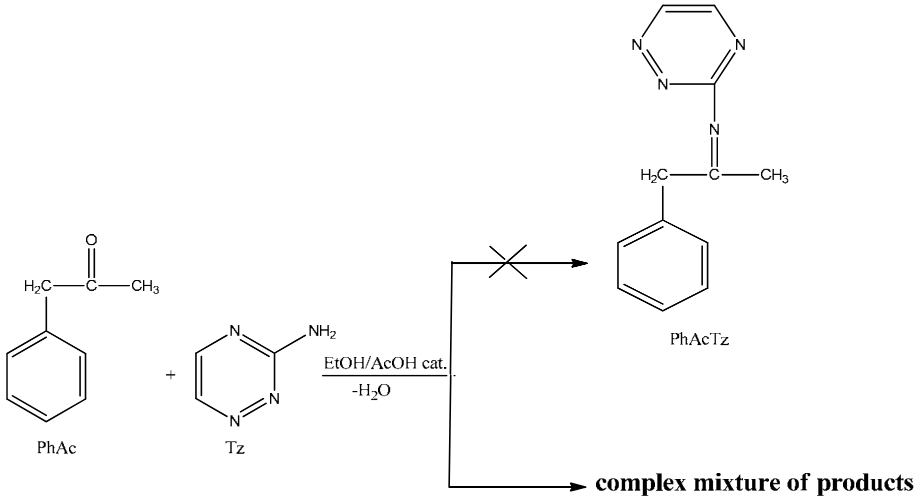
In a 25 ml two necked round bottom flask we introduced 0.01 mol (1.0 g) of AcAc, 0.025 mol (2.4 g) of Tz, 10 ml of EtOH and a catalytic amount of acetic acid (2-3 drops). The system was closed with $CaCl_2$ guard tube and kept under stirring at room temperature (R1) or reflux (R2). The reaction was followed by TLC using as eluent dichloromethane: methanol/ 10:1. In assay R1, unreacted product was recovered. In assay R2, an untreatable mixture of product was obtained.

Scheme 3.6



Reaction 5- PhAcTz (Scheme 3.7).

Scheme 3.7

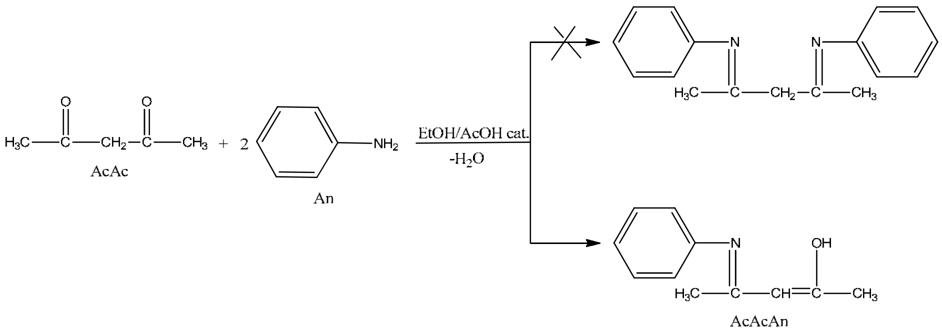


The synthesis of PhAcTz was tested following the procedure used for AcAcTz (Reaction 4) on the conditions of assay R1. An untreatable mixture of products was obtained as indicated by NMR spectra.

Reaction 6- AcAcAn. This reaction was tackled according to scheme 3.8. In a bottomed round two necked flask of 50 ml we introduced 0.01 (1.0 g) of acetyl acetone, 0.025 mol (1.98 g) of aniline and 20 ml of ethanol. Then 2-3 drops of acetic acid were introduced into the reaction mixture. The reaction was kept under stirring at room temperature until it was completed. The reaction was followed by TLC using as eluent dichloromethane: methanol/ 10: 1. The product was isolated by washing with hexane and diethyl ether and dried under vacuum. The obtained yield was 29 %.

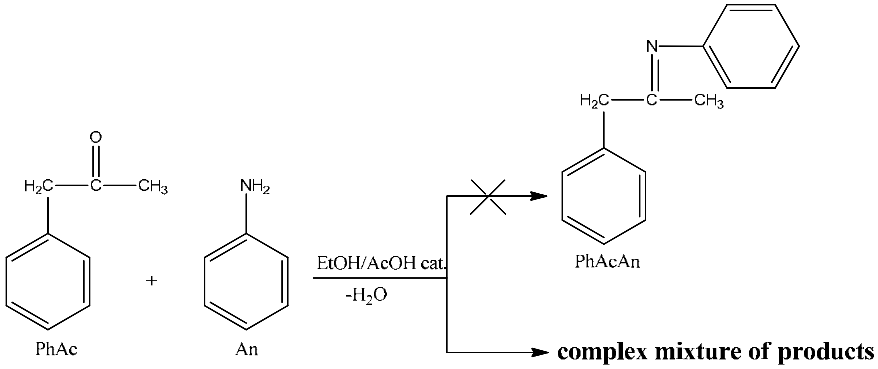
IR (cm^{-1}): 1594; 1502-1491 (C=C); 1567 (enol C=C); 742; 695 (C-C-H out of plane deformation); ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 2.0 (q, 3H); 2.2 (q, 3H); 5.2 (s, 1H); 7.0-7.4 (m, 5H); 12.5 (s, 1H) ^{13}C NMR ($CDCl_3$, 100.6 MHz, δ ppm): 19.9 (q); 29.3 (q); 97.7 (d); 124.6-138.8 (m); 160.4 (s); 196.2 (s).

Scheme 3.8



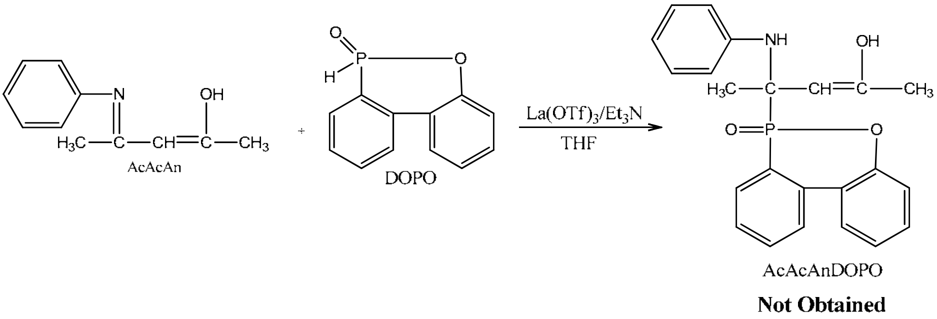
Reaction 7- PhAcAn. The reaction was tested under the same conditions as for reaction 6 (scheme 3.9). An untreatable mixture of products was obtained as indicated by NMR spectra.

Scheme 3.9



Reaction 8- AcAcAnDOPO. The synthesis was tested as shown in scheme 3.10. In a round bottomed two necked flask of 50 ml we introduced 0.30 g (0.0017 mol) of AcAcAn, 0.0021 mol (0.46 g) of DOPO and 0.00017 mol (0.1 g) of $La(OTf)_3$. The flask was provided with a magnetic stirrer and an addition funnel and kept under argon. Then 0.0017 mol (0.17 g) of Et_3N were added dropwise into the reaction mixture and stirred at room temperature until the reaction was completed. The reaction was followed by TLC using as eluent dichloromethane: methanol / 20:1. The product was well washed with hexane and diethyl ether and dried under vacuum. Mixture of starting products was recovered as indicated by NMR spectra.

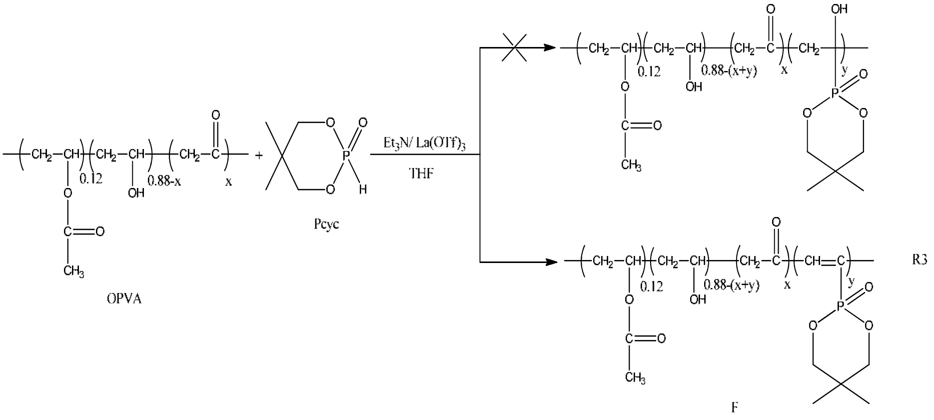
Scheme 3.10



Chemical modification reactions of polyketones with phosphorous containing compounds.

2.2.1- Poly(methylene ketone) chemically modified with 5,5-dimethyl-1,3,2-dioxaphosphinan-2-one (polymer F, scheme 3.11)

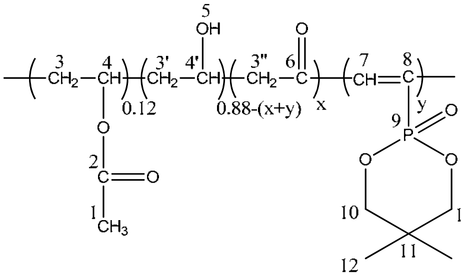
Scheme 3.11



In a well dried round bottomed two necked flask of 20 ml previously purged with argon and provided with a reflux condenser we introduced 0.50 g of OPVA (0.010 mol of ketone groups considering a complete oxidation of OPVA, x=0.88), 0.0125 mol (1.88 g) of Pcyc, 0.0010 mol (0.59 g) of La(OTf)$_3$ and 10 ml of freshly distilled THF. Then 0.01 mol (1.0 g) of Et$_3$N were added dropwise into the reaction mixture. The reaction mixture was kept under stirring at room temperature for 3 days (R1), at 65 ºC for 3 days (R2) and at 45 ºC for 5 days (R3). In none of the reactions the desired product was obtained. In reaction R3 the eliminated polymer F was recovered by precipitation in cold water, filtration and drying under vacuum at 60ºC. The yield was 64% (R3).

IR (cm^{-1}): 3580-3030 (OH); 2956-2877 (C-H); 1560 (enol C=C); 1179 (P=O); 1049-977 (C-O).

Table 3.4 NMR data of polymer F recorded in DMSO-d_6

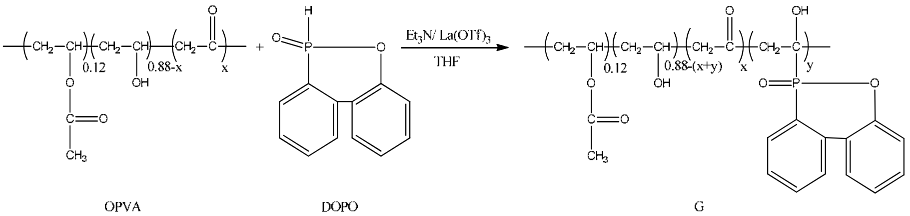


^{1}H NMR		^{13}C NMR		^{31}P NMR	
Resonances	**Assignment**	**Resonances**	**Assignment**	**Resonances**	**Assignment**
0.7 2.1 3.1-3.3 3.4- 3.7 5.8; 7.2	12, 12’ 1 3, 3’, 3’’ 4, 4’, 10 7	20.7 21.5 36.6 38.0-44.0 66.2 67.6 122.2 141 174 188	1 12, 12’ 11 3, 3’, 3’’ 10 4, 4’ 7 8 2 6	2.7; 9.8*	9

* Intensity ratio is 1: 0.1 respectively (This splitting is probably due to comonomer sequences)

2.2.2- Poly(methylene ketone) chemically modified with 9,10-dihydro-9-oxa-10-phosphaphenantrene-10-oxide (polymer G, scheme 3.12)

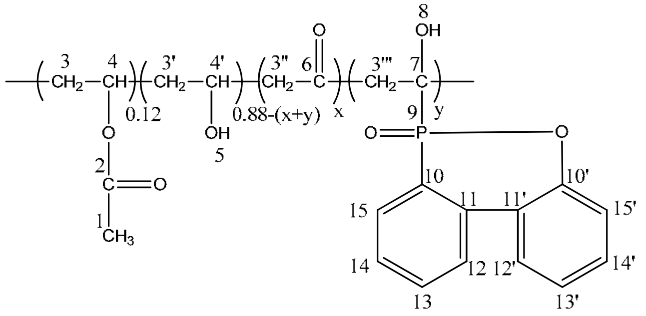
Scheme 3.12



In a well dried round bottomed two necked flask of 20 ml provided with a reflux condenser and previously purged with argon we introduced 1.0 g of OPVA (0.019 mol of ketone groups considering a complete oxidation of OPVA, x=0.88), 0.024 mol (5.2 g) of DOPO, 0.0019 mol (1.11 g) of La(OTf)$_3$ and 10 ml of freshly distilled THF. Then 0.019 mol (1.9 g) of Et$_3$N were added dropwise into the reaction mixture. The reaction mixture was heated to 45 ºC and kept under stirring at this temperature for a week. The resulting polymer was recovered after precipitation in cold water, filtering and drying under vacuum at 60 ºC. The yield was 24%.

IR (cm^{-1}): 3620-3090 (OH); 1580 and 1470-1430 (C-C, aromatic) 1560 (enol C=C), 1137-1097 (P=O); 1051-980 (C-O); 750-680 (C-C-H out of plan deformation)

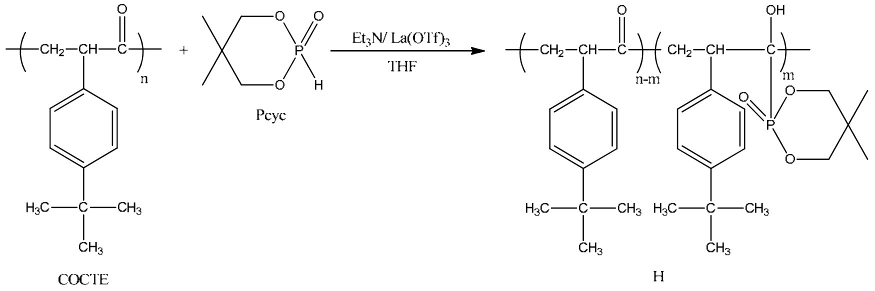
Table 3.5 NMR data of polymer G recorded in DMSO-d$_6$



^{1}H NMR		^{13}C NMR		^{31}P NMR	
Resonances	Assignment	Resonances	Assignment	Resonances	Assignment
		20.0	1		
2.0-2.4	1, 3, 3’	44.0-45.0	3, 3’, 3’’, 3’’’		
2.6-3.2	3’’, 3’’’	51.0	7		
3.6-4.2	4, 4’, 5	60.0-62.2	4, 4’		
6.6	13’, 15’	115.0-119.0	10, 12, 15’		
6.8	14’	120.3	11, 13’		
6.9	14	126.5	12’	8.9	9
7.1	13	128.4-131.4	14, 14’		
7.4	12’	136.0-138.4	15		
7.9	15	140.5	11’, 13		
8.2	12	155.0	10’		
10.3	8	175.0	2		
		206.7	6		

2.2.3- Alternating CO- 4-tert-butylstyrene copolymer chemically modified with 5,5-dimethyl-1,3,2-dioxaphosphinan-2- one (polymer H, scheme 3.13)

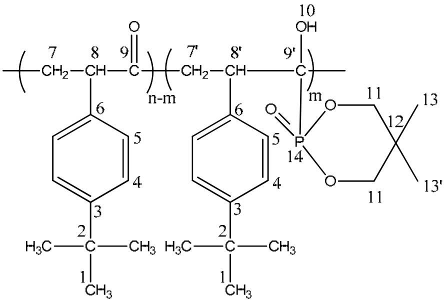
Scheme 3.13



In a well dried round bottomed two necked flask of 20 ml previously purged with argon, provided with a reflux condenser we introduced 0.10 g ($5.3*10^{-4}$ mol of ketone groups) of COTBS, $9.3*10^{-4}$ mol (0.14 g) of Pcyc (R1) or $6.6*10^{-4}$ mol (0.08 g) of Pcyc (R2), $5.3*10^{-5}$ mol (0.033 g) of Er(OTf)$_3$ (R1) or $5.3*10^{-5}$ mol (0.031 g) of La(OTf)$_3$ (R2) and 5 ml THF. Then we added $5.3*10^{-4}$ mol (0.05 g) of Et_3N dropwise into the reaction mixture. The reaction mixture was stirred at room temperature for 3 days (R1) and at 45ºC for a week (R2). The resulted polymer was recovered by precipitation in cold water, filtration and drying under vacuum at 60ºC. The yield was 78% (R2). In the case of assay R1 starting polymer was recovered.

IR (cm^{-1}): 3640-3130 (OH); 1710 (C=O); 1500-1460 (C-C aromatic) 1157 (P=O); 1060 (C-O); 760-640 (C-C-H out of plane deformation).

Table 3.6 NMR data of polymer H recorded in $CDCl_3$



^{1}H NMR		^{13}C NMR		^{31}P NMR	
Resonances	**Assignment**	**Resonances**	**Assignment**	**Resonances**	**Assignment**
		21.5	13, 13’		
		31.8	1		
		34.2	2		
0.8	13, 13’	38.7	12		
1.2	1	43.0-44.0	7, 7’		
2.3-3.1	7, 7’	46.0	9’		
3.7-4.1	8, 8’, 11	52.5	8, 8’	-3.4; 6.7; 11.7*	14
6.3-6.8	4	75.4	11		
6.9-7.2	5	126.0	4		
		128.1	5		
		134.1	6		
		150.0	3		
		207.0	9		

* Intensity ratio is 2:20.1. This splitting is probably due to comonomer sequences

2.2.4- Alternating CO- 4-tert-butylstyrene copolymer chemically modified with 9,10-dihydro-9-oxa-10-phosphaphenantrene-10-oxide (polymer I, scheme 3.14)

Scheme 3.14

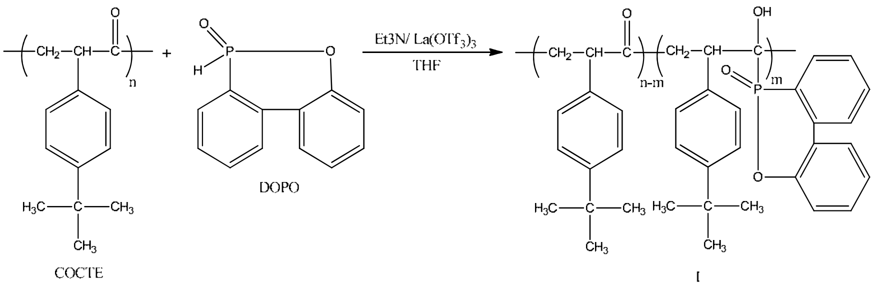


Table 3.7 Reaction conditions for the preparation of polymer I

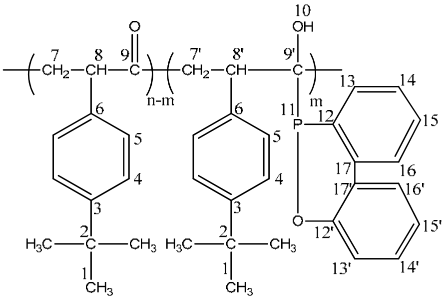
Assay	T (ºC)	Time (days)	M(TfO)$_3$
R1	rt.*	3	Er(OTf)$_3$
R2	rt.*	5	La(OTf)$_3$
R3	rt.*	10	
R4	60	3	
R5	45	7	
R6	60	7	
R7	50	7	
R8	45	10	

* rt.= 23±2

In a well dried round bottomed two necked flask of 20 ml previously purged with argon, provided with a reflux condenser we introduced 0.50 g of COTBS ($2.7*10^{-3}$ mol ketone groups), $3.4*10^{-3}$ mol (0.73 g) of DOPO, $2.7*10^{-4}$ mol (0.17 g) of $Er(OTf)_3$ (R1) or $2.7*10^{-4}$ mol (0.16 g) of $La(OTf)_3$ and 10 ml of THF. Then we added $2.7*10^{-3}$ mol (0.27 g) of Et_3N dropwise into the reaction mixture. The reaction mixture was stirred at the desired temperature for the desired time and resulting polymer was precipitated in cold water, filtered and dried under vacuum at 60ºC. The yield was 47% (R5). The other assays reported in table 3.7 did not give the desired product.

IR (cm^{-1}): 3600-3100 (OH); 1707 (C=O); 1510 and 1460-1410 (C-C, aromatic); 1161 (P=O); 921 (C-O); 756 (C-C-H out of plane deformation).

Table 3.8 NMR data of polymer I recorded in $CDCl_3$



^{1}H NMR		^{13}C NMR		^{31}P NMR	
Resonances	**Assignment**	**Resonances**	**Assignment**	**Resonances**	**Assignment**
		31.6	1		
1.2-1.4	1	34.6	2		
2.4-3.2	7, 7’	43.3	7, 7’		
3.8-4.2	8, 8’	44.6	9’		
6.5-6.8	4	52.8	8, 8’		
7.0-7.1	5	124.0-127.5	12, 13, 15, 15’,16’,17’		
7.2	13’	125.6	4		
7.3	15’	128.2	5	34.8; 38.6*	11
7.4	14’	130.6	16		
7.5	15	133.0	14, 14’		
7.6	14, 16	134.3	6		
7.8-8.1	13, 16’	136.7	17		
10.6-10.7	10	143.2	12’		
		150.0	3		
		206.4-207.5	9		

* Intensity ratio is 2:1. This split is probably due to comonomer sequences.

Chemical modification reactions of polyketones with nitrogen containing compounds.

2.2.5- Poly(methyl ketone) chemically modified with aniline (polymer J, scheme 3.15).

Scheme 3.15

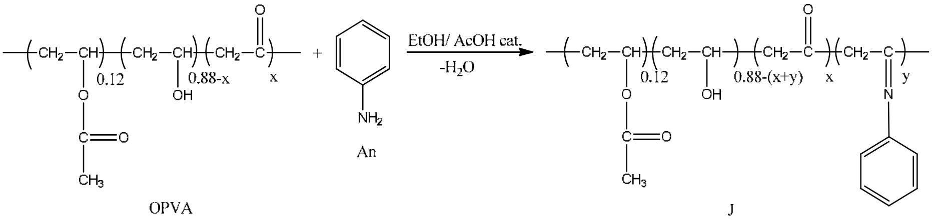
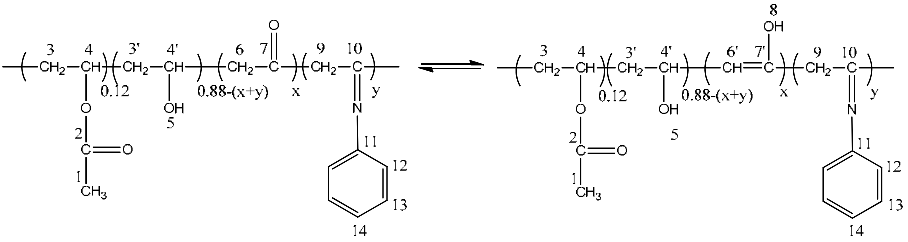


Table 3.9 NMR data of polymer J



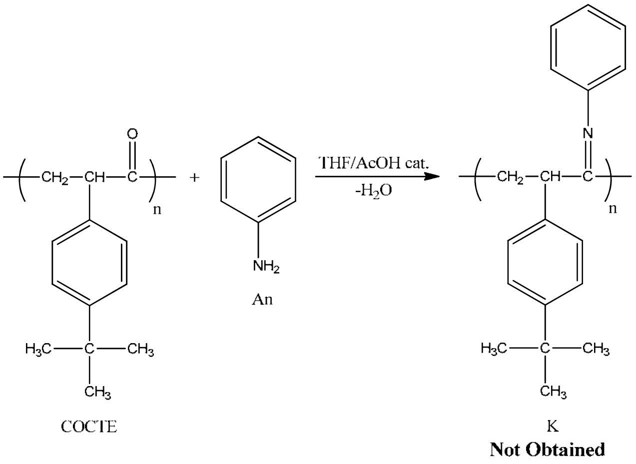
^{1}H NMR (D_2O)		^{13}C NMR (solid)	
Resonances	**Assignment**	**Resonances**	**Assignment**
		23.8	1
1.6-2.0	1, 3, 3’	47.0-51.0	3, 3’, 6, 9
2.3-2.6	6, 9	65.2-70.4	4, 4’
3.5	4’	112.0	6’
4.0	4	121.8	12, 14
4.3	5	136.0	13
6.1	6’	147.0	11
7.2	12, 14	160.2	7’
7.4	13	175.0	2
10.4	8	180.0	10
		192.3	7

In a round bottomed flask of 50 ml, provided with a reflux condenser, we introduced 1.0 g of OPVA (0.019 mol of ketone groups considering a complete oxidation of OPVA, x=0.88), 0.023 mol (2.14 g) (R1) or 0.029 mol (2.70 g) (R2) of aniline, 2-3 drops of acetic acid and 20 ml of ethanol. The reaction mixture was stirred at 60ºC for 5 days (R1) or at room temperature for 4 days (R2). Then the solvent was eliminated on the rotary evaporator, washed with hexane and diethyl ether and dried under vacuum at 60ºC. In case of assay R1 a mixture of untreatable products was obtained according to NMR spectra. In case of assay R2, 0.5 g of the desired polymer was obtained.

IR (cm^{-1}) 3550-2990 (OH); 1690 low intensity (C=O); 1610 (C-C aromatic and C=N); 1560 (enol C=C); 1400 (C-C aromatic); 700-650 (C-C-H aromatic out of plane deformation)

2.2.6- Chemical modification of alternating CO- tert-butyl styrene copolymer with aniline (polymer K, scheme 3.16).

Scheme 3.16

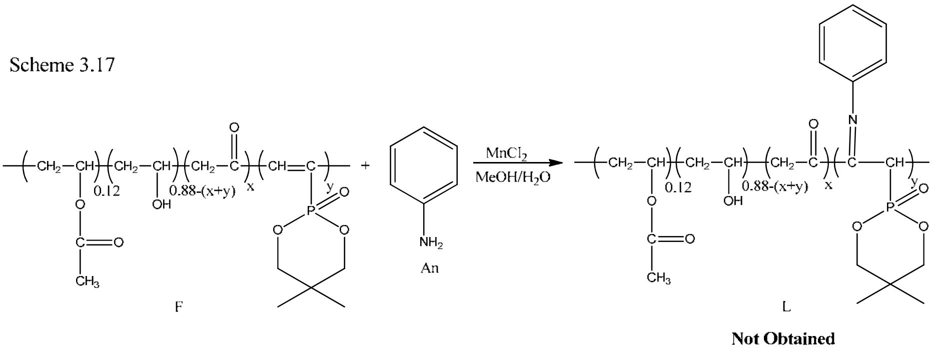


In a round bottomed flask of 20 ml we introduced 0.5 g of COTBS ($2.7*10^{-3}$ mol of C=O groups), $3.3*10^{-3}$ mol (0.31 g) of aniline, 2-3 drops acetic acid and 10 ml of THF. The reaction mixture was stirred at room temperature for 6 days.

The resulting polymer was precipitated in water, filtered and dried under vacuum at 60ºC. The NMR spectra showed that starting polymer was recovered.

2.2.7- Chemical modification of polymer F with aniline (polymer L, scheme 3.17).

Scheme 3.17



In a round bottomed flask of 10 ml we introduced 0.15 g ($2.5*10^{-4}$ mol of P=O) of polymer F, $2.5*10^{-4}$ mol (0.023 g) of aniline, $2.5*10^{-5}$ mol (0.0032 g) of $MnCl_2$, 2.5 ml of methanol and 2.5 ml of water. The reaction was kept at room temperature for two days. The resulted polymer was isolated by extraction with hexane and dried under vacuum at 60ºC. The NMR spectra indicated that virgin starting polymer was recovered.

2.3- Characterization techniques

^1H, ^{13}C and ^{31}P NMR performed in solution were on a Varian Gemini 400 MHz. The samples were analysed at room temperature in $CDCl_3$, DMSO-d_6 or D_2O. HR-MAS solid spectra were recorded on a Bruker Avance III 500 Spectrometer operating at a proton frequency of 500.13 MHz. The instrument was equipped with a 4-mm triple resonance (^1H, ^{13}C, ^{31}P) gradient HR-MAS probe. Samples conveniently prepared with benzene-d6 were spun at 7 kHz in order to keep the rotation sidebands out of the spectral region of interest. One-dimensional (1D) ^1H spectra were acquired adding 16 scans in 0.5 min, with a 30000 Hz (60 ppm) of spectral width, and a 1.0 s of relaxation delay. One-dimensional (1D) ^{13}C spectra were acquired adding 200000 scans in 16h, with a 37500 Hz (300 ppm) of spectral width, and a 0.5 s of relaxation delay.

Fourier Transform Infrared spectra were recorded on a FT-IR 680 plus spectrophotometer from JASCO connected to an ATR device as well described in previous chapter. The analyses were performed at room temperature in absorbance mode using samples in solid state.

Phosphorous contents were determined by ICP-AES analysis following the same procedure previously detailed for samples of polymer C.

Inherent viscosities were measured in 1-methyl-2-pirrolidinone (NMP) or dimethyl sulfoxide (DMSO) following the procedure described for previous set of polymers.

TGAs and DSC studies were performed in Mettler equipments under the same conditions as already related in previous chapter.

3. Results and discussion

In this chapter we intend to develop a set of polymers, based on chemical modification of polyketones, by introducing different heteroatoms, such as phosphorous or nitrogen that could improve their thermal stabilities and make them useful as flame retardant additives for ¨commodity¨ polymers.

In order to develop this study we used as starting polyketones a poly (methylene ketone), which was synthesized in our laboratory, and an alternating CO-4-tert-butylstyrene copolymer, which was synthesized in Inorganic Chemistry of our Faculty.

First we discuss the syntheses of these polyketones. Poly (methylene ketone) (OPVA) was synthesized following a published procedure[106] by the PVA oxidation with $KMnO_4$ (see the scheme below). Reaction was carried out under different conditions as specified in the experimental part, in order to get a high degree of oxidation (see table 3.10).

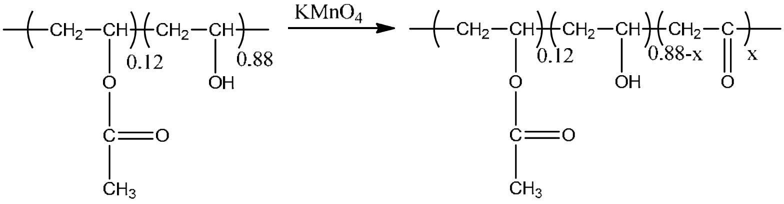


Table 3.10 Reaction conditions of poly (methylene ketone) syntheses

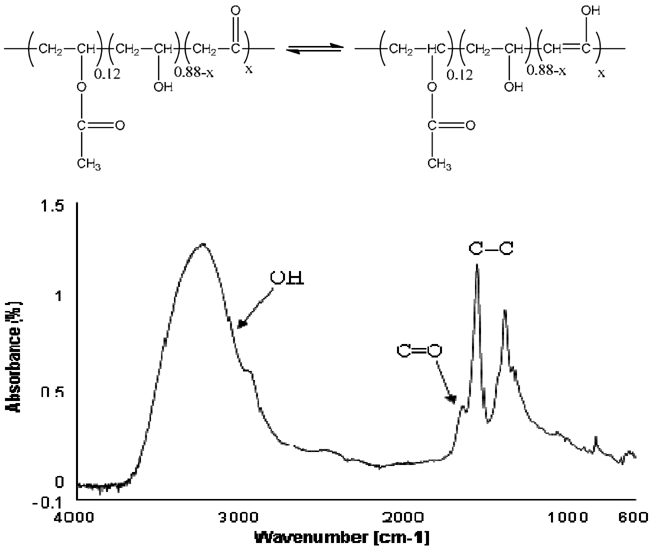
Assay	**Time (h)**	**T (°C)**	**Molar ratio***
			OH groups :$KMnO_4$
R1	12	90	1:0.33
R2	12	50	1:1
R3	12	70	1:1
R4	24	75	1:2

* The stoichiometric ratio is OH: $KMno_4$/ 1:0.67

First, the reaction was performed reproducing the published reaction conditions (R1), but the ^1H NMR spectrum of the obtained polymer recorded in D_2O shows signals attributable to C=C groups coming from elimination reactions (probably dehydration). Because of that, we performed the reaction at lower temperature in order to reduce the elimination reactions and we increased the molar ratio of oxidizing agent to make the reaction not to slow (R2, R3 and R4).

Figure 3.1 shows FT-IR spectrum of OPVA (R4), from which could be observed that ketone groups appeared mainly in enol form. Broad signal between 3620-2990 cm^{-1} was attributed to OH groups coming from enol and unmodified OH groups and the signal at 1560 cm^{-1} was attributed to enol C=C bonds. A small carbonyl signal appears at 1650 cm^{-1}, which can be due to acetate or ketone groups.

Figure 3.1 FT-IR spectrum of poly (methyl ketone) (R4)



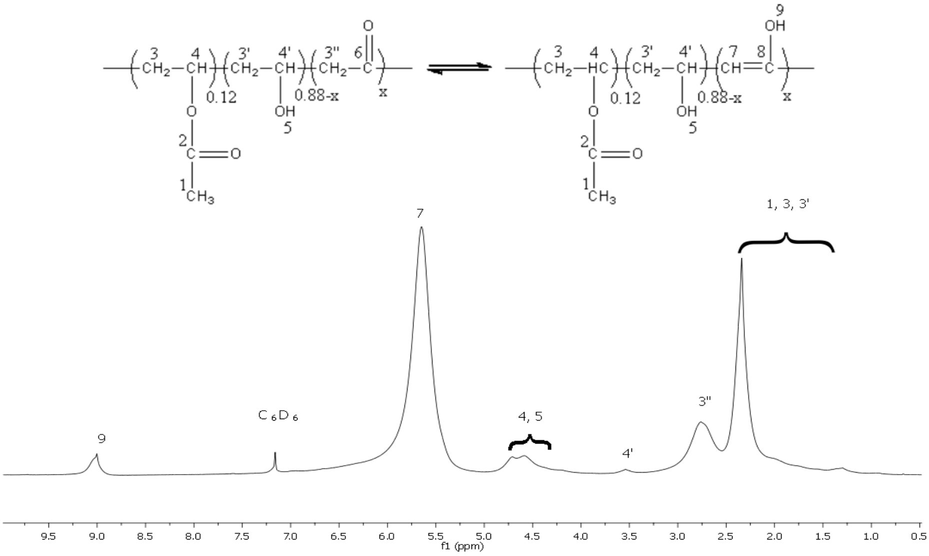
In the case of R2 and R3 the expected signals were observed by ^1H and ^{13}C NMR in D_2O. These signals are summarized in table 3.2. In the case of R2, the signal at 4.0-4.3 ppm in the ^1H NMR spectrum, which is due to PVA alcohol groups, was quite intense; while in R3, it was visible but smaller. Therefore, a high degree of oxidation can be assumed to be achieved in R3 with respect to R2.

In the case of R4 only signal arising from vinyl acetate units could be detected. Moreover a strong broad signal due to HDO was also observed at 4.7-4.8 ppm. The appearance of this signal indicates that a fast proton interchange occur between α protons in ketone or enol groups with the solvent; this avoid the corresponding methylene or methine signals to be detected by NMR of D_2O solution. It must be noted that in the cases of R2 and R3, this signal due to HDO also appears but it showed less intensity.

Therefore, it seems that in the case of R4 a high degree of oxidation was achieved, which facilitate the proton interchange due to the formation of a conjugated polyenol system. In order to confirm this, we recorded the ^1H and ^{13}C NMR spectra of this polymer on solid state. Figure 3.2 shows the solid state

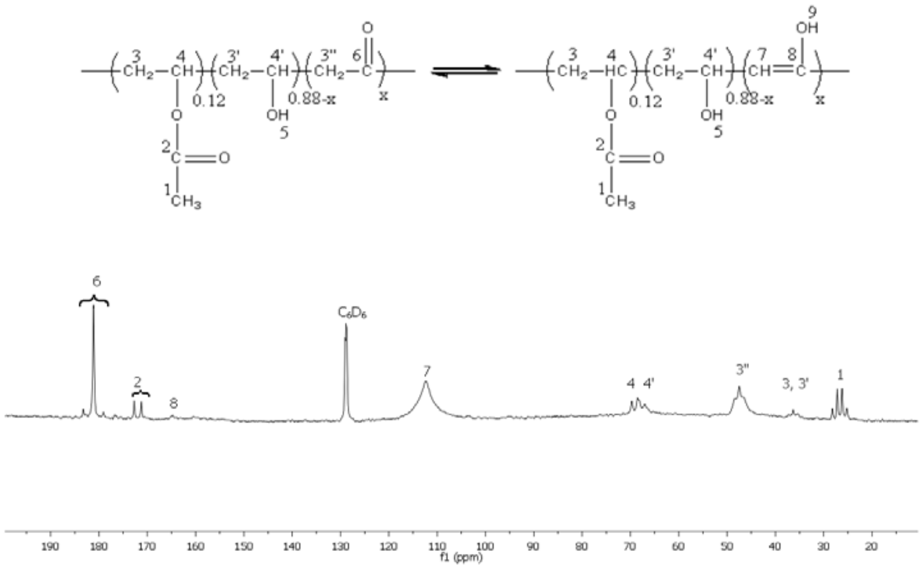
^{1}H NMR spectrum of this polymer. The signals at 1.3-2.3 ppm are due to methyl and methylene protons coming from acetylated and vinyl alcohol units. The signal at 2.8 ppm was attributed to methylene protons directly bonded to carbonyl ketone groups. Signal at about 3.5 ppm was assigned to methine protons from unmodified alcohol units. Methine protons from the acetylated units appeared together with OH protons from unmodified PVA alcohols at 4.2-4.8 ppm. Signal at 5.6 ppm was attributed to enol methine protons. Enol OH appears at 9.0 ppm.

Figure 3.2 ^{1}H NMR spectrum of poly (methylene ketone) (R4) in solid state swollen in C_6D_6



Solid state ^{13}C NMR spectrum showed methyl carbons at 25.5 ppm. Methylene carbons of acetyl and unmodified alcohol units appeared at 35.0-37.0 ppm and methylene carbons of ketone units appeared at 46.0-48.0 ppm. Methine carbons of acetylated and unmodified units appeared in the region of 67.0-70.0 ppm. Carbons from enol units appeared at 112.0 ppm and 164.0 ppm. The region of 171.0-183.0 was attributed to carbonyl groups coming from acetate and ketone units.

Figure 3.3 ^{13}C NMR spectrum of poly (methylene ketone) (R4) in solid state swollen in C_6D_6

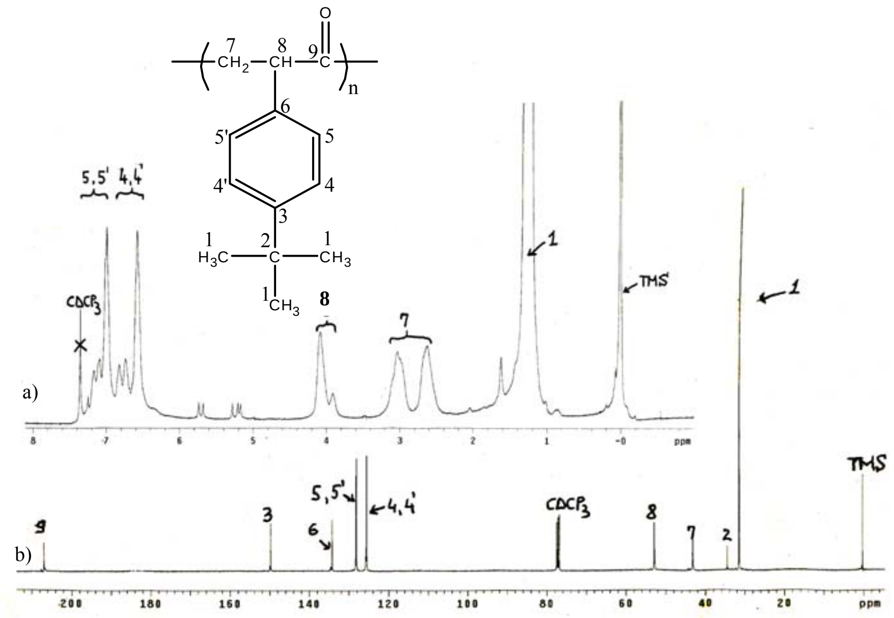


A quantification of oxidation degree was not possible to be performed from NMR spectra. In the case of NMR spectra recorded in solution this was due to the fast proton interchange with solvent already discussed, while the solid state NMR spectra are not quantitative. If we consider that the oxidation does not lead to an important change of the molecular weight of the repeating unit, an estimation of the yield can be calculated from the obtained polymer weight and assuming a complete oxidation of the polymer. For these estimations we also assumed that no hydrolysis of the acetate groups take place. In all cases (R1-R4) the yield estimated was over 90%.

As mentioned above, the degree of oxidation of R4 can be assumed to be high, since small signals attributable to unmodified vinyl alcohol units were observed by NMR (solution or solid state). In the modification reactions of OPVA to be reported later, R4 was always used as starting material.

Alternating CO-4-tert-butylstyrene (COTBS) was synthesised by our colleagues of the Inorganic Chemistry Section by a catalytic copolymerization of 4-tert-butylstyrene with CO. The copolymerization was carried out in a reactor under 30 atm pressure of CO using as a catalyst a bipyridine palladium complex derivative. ^{1}H and ^{13}C NMR spectra are shown in figure 3.4.

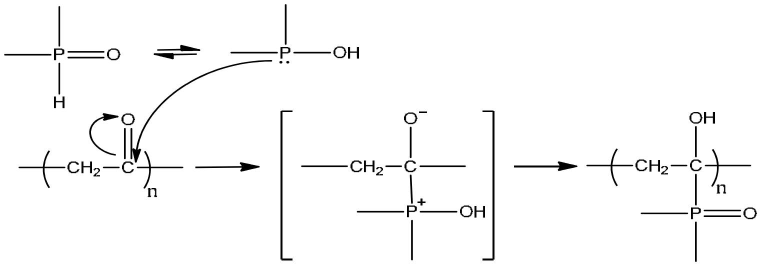
Figure 3.4 ^{1}H (a) and ^{13}C (b) NMR spectra of COTBS recorded in $CDCl_3$



^{1}H NMR spectrum showed signals at 1.1-1.5 ppm due to methyl protons from 4-tert-butylstyrene units. Methylene protons from the main chain appeared at 2.4-3.2 ppm and methine protons at 3.8-4.2 ppm. The region between 6.5-7.2 ppm was assigned to aromatic protons. ^{13}C NMR spectrum showed a signal at 31.8 ppm which was attributed to methyl groups from 4-tert-butylstyrene. Signal at 34.8 was attributed to quaternary carbon from tert-butyl group. Signals between 43.5-44.0 ppm and 53.0 ppm were attributed to main chain methylene and methine groups, respectively. The region between 125.8-150.0 ppm was assigned to aromatic carbons. Signals at 207.1-208.0 ppm were attributed to ketone carbonyl groups. This polymer was recognised to be syndiotactic.

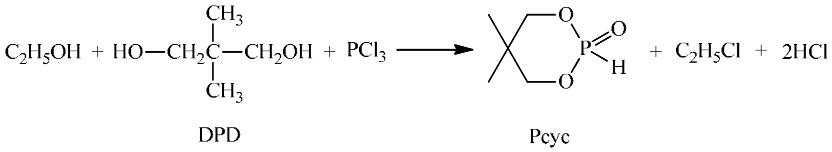
Once that we have got starting polyketones, as a first aim of this work we intend to react the carbonyl groups with phosphorous containing compounds in order to obtain phosphorus containing polymers with OH groups. As commented above the presence of free hydroxyl groups in the final polymer is interesting, since these groups can easily lead to a charred layer. Therefore the chemical modification reactions were first tackle by a nucleophilic addition reaction as showed in scheme 3.18.

Scheme 3.18



As already mentioned in the introduction of this chapter, phosphorous containing nucleophiles that we used in this work were 9,10-dihydro-9-oxa-10-phosphaphenantrene-10-oxide (DOPO) and 5,5-dimethyl-1,3,2-dioxaphosphinan -2-one (Pcyc), reported by many researchers as good flame retardant promoters. DOPO was already used in the literature as nucleophile to react with polyketone carbonyl groups. This reaction was performed in bulk between DOPO and OPVA, and polymers with improved thermal stabilities and excellent flame retardant properties were obtained.[106]

The cyclic hydrogen phosphite (Pcyc) was reported to be a good flame retardant by several authors and probably due to its six-membered ring it is not very easy to hydrolyse. Because Pcyc is not a commercial product, it was previously synthesized from 2,2-dimethyl-1,3-propandiol (DPD) through a condensation reaction with phosphorous trichloride (PCl_3) and ethanol in stoichiometric ratio, following a published procedure (see scheme below).[114]

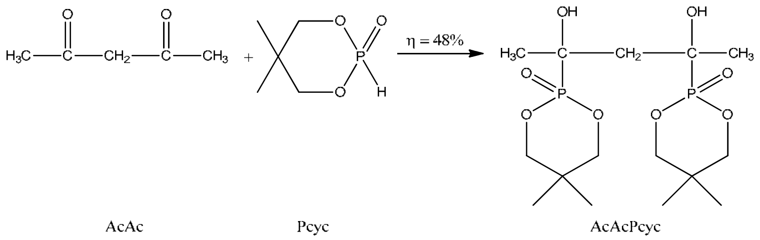


Thus, we proposed to perform the reaction of COTBS and OPVA with Pcyc and DOPO in solution.

In order to find appropriate reaction conditions for polyketone modification reactions with phosphorous containing compounds, model compound reactions were performed, using acetyl acetone (AcAc) as pattern model for OPVA and phenyl acetone (PhAc) as pattern model for COTBS.

First based in some procedures described for aldehydes,[76,115] we tried to react acetyl acetone with Pcyc at room temperature using toluene as a solvent and Et_3N in stoichiometric amount, but the reaction did not occurred (starting material was recovered).

Then, we increased temperature at 60 ºC; again the starting material was recovered. Finally, we performed the reaction at room temperature but increasing the system polarity (using THF as a solvent) and using a catalytic amount of $Er(OTf)_3$ to increase the carbonyl electorfilicity. In this way the desired product was obtained in satisfactory yield, 48% (see scheme below).



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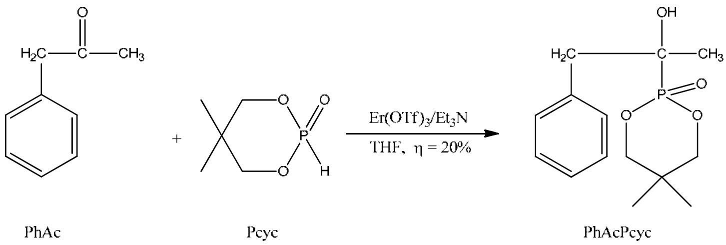
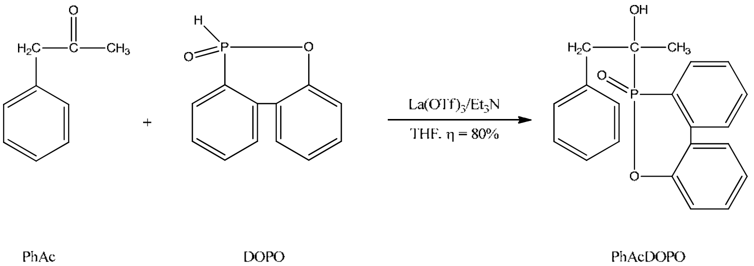
[115] Kumaraswamy, S.; Senthamizh Selvi, R.; Kumara Swamy, K.C. Synthesis **1997**, 207-212.

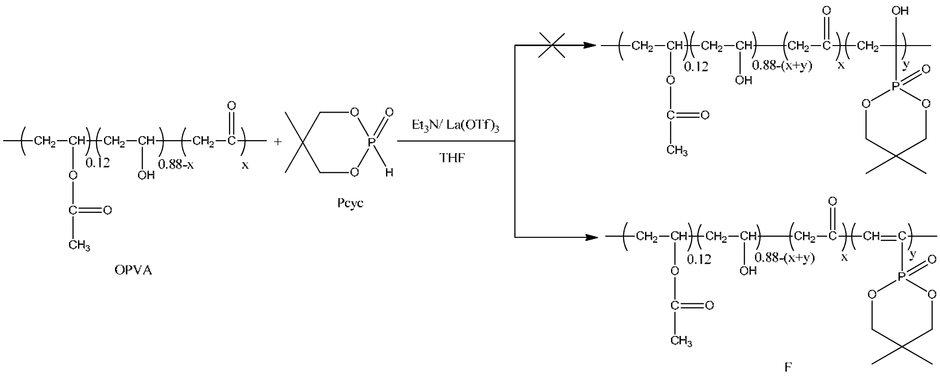
These conditions were then tested in case of reaction of phenyl acetone with Pcyc and DOPO, respectively (see schemes below).





In the later case, La(OTf)$_3$ was used instead of Er(OTf)$_3$ in order to eliminate problems associated to the paramagnetic character of Er(III) whose traces difficult the recording of NMR spectra of the purified products. The obtained yields were 20% and 80% for Pcyc and DOPO reaction, respectively.

Polyketone modifications were performed on the basis of these results. First, the reaction of OPVA with Pcyc (polymer F) was performed following the corresponding model compound reaction (AcAcPcyc, see scheme below).



First, it was tested at room temperature in THF using La(OTf)$_3$ and Et$_3$N, but the unmodified starting polymer was recovered. Then we increased temperature at 65 ºC and an untreatable mixture of products was obtained. Finally, we decreased temperature at 45 ºC and addition reaction occurred together with subsequent elimination, giving rice to the corresponding unsaturated product. All reaction conditions of polyketones modification with phosphorous containing moieties are summarized in table 3.11. As can be seen a 25 % excess of Pcyc was used; but it must be considered that as mentioned at above we do not know the actual degree of oxidation of OPVA (x). This excess was calculated by considering a quantitative oxidation degree (x=0.88) and assuming that acetate groups present in PVA were not altered during oxidation. Table 3.12 shows results of chemical modification reactions of polyketones with phosphorous containing compounds

Table 3.11 Reaction conditions of polyketones modification with phosphorous compounds

Polymer	**Assay**	**Time (days)**	**T (ºC)**	**Molar ratio**
				PK[a]/ PC[b]/ Et$_3$N/ La(OTf)$_3$
F[c]	R1	3	65	1/1.25/1/0.1
	R2	5	45	
G[d]	R1	7	45	1/1.25/1/0.1
H[e]	R1	3	rt.[g]	1/1.75/1/0.1
	R2	7	45	1/1.25/1/0.1
I[f]	R1	3	rt.[g]	1/1.25/1/0.1
	R2	5	rt.[g]	
	R3	10	rt.[g]	
	R4	3	45	
	R5	3	60	
	R6	7	60	
	R7	7	50	

a) polyketone carbonyl groups
b) phosphorous compound
c) OPVA modified with Pcyc
d) OPVA modified with DOPO
e) COCTE modified with Pcyc
f) COCTE modified with DOPO
g) rt.= 23±2 ºC

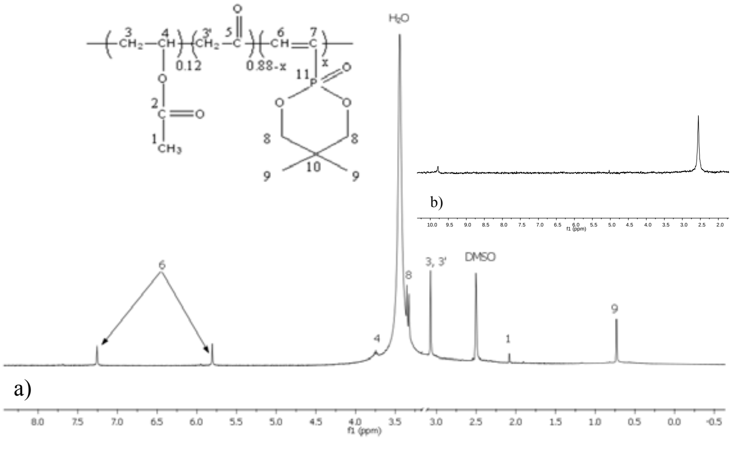
Table 3.12 Results of chemical modification reactions of polyketones with phosphorous compounds

Polymer	**%P Determined from ICP-AES**	**Degree of modification***	**Yield (%)**	**μinh. (dl/g)**
OPVA	-	-	-	0.72
F	11	0.30	44	0.65
G	9	0.42	41	0.62
COTBS	-	-	-	0.37
H	3	0.21	78	0.32
I	2	0.14	47	0.23

* Obtained from %P determined by ICP-AES
For OPVA derivatives it is ¨y¨ and for COTBS derivatives it is ¨m¨

The structure of polymer F was confirmed by FT-IR and NMR analyses. FT-IR spectrum shows signal between 3580-3030 cm^{-1} which was attributed to OH groups from unmodified alcohol units. The absorption band at 1560 cm^{-1} was attributed to C=C bonds. The band at 1180 cm^{-1} was attributed to P=O. The absorption bands observed at 1050 cm^{-1} and at 980 cm^{-1} were assigned to C-O groups.

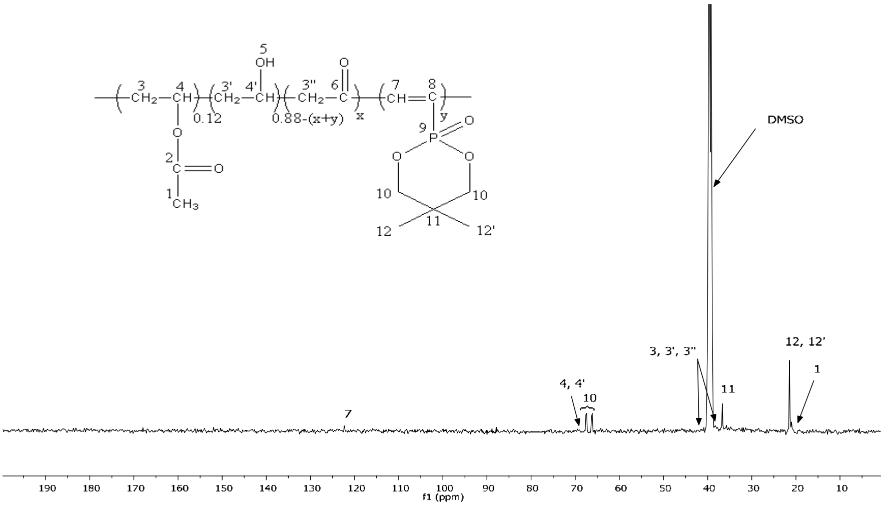
Figure 3.5 ^{1}H and ^{3}1P NMR spectrum of polymer F recorded in DMSO-d$_6$



^{1}H and ^{31}P NMR spectra are related in figure 3.5. In ^{1}H NMR we observed a signal at 0.7 ppm which corresponds to methyl protons from Pcyc and a signal at 2.1 ppm which corresponds to methyl groups from acetylated units. Signals at 3.1-3.3 ppm were attributed to methylene protons from main chain. Signals at

3.4 ppm and 3.7 ppm overlapped with water signal and were attributed to methylene protons from Pcyc and methine protons from main chain, respectively. Signals at 5.7 ppm and 7.2 ppm were attributed to methine proton of double bond which appeared spleated due to proton-phosphorous coupling. ^{31}P NMR showed an important signal at 2.5 ppm and a secondary signal at 9.8 ppm in 1:0.1 intensity ratios. This split is probably due to comonomer regiosequences.

Figure 3.6 ^{13}C NMR spectrum of polymer F recorded in DMSO-d$_6$

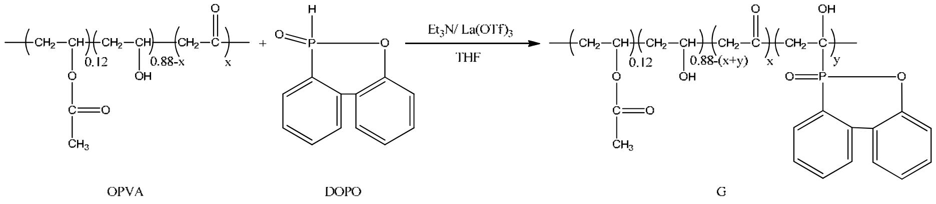


In the ^{13}C NMR spectrum (figure 3.6) signals that appear at 20.7 ppm and 21.5 ppm were attributed to methyl groups from OPVA acetylated units and Pcyc units, respectively. Signal at 36.6 ppm was attributed to quaternary carbon from cyclic units. Small signals at 38.0-41.0 ppm which overlapped with DMSO-d$_6$ signal were attributed to methylenes from main chain. Signals at 66.2-67.4 ppm were attributed to methylene carbons from Pcyc. This signals appeared split due to phosphorous coupling. Signals due to methine carbons from main chain which appear around 70.0 ppm are confused with the noise. The signal that appears at 122.2 ppm was attributed to carbon double bond. The poor quality of this spectrum and the missing of some signals (2, 6, 8 and maybe 3, 3’, 3’’ and 4, 4’) even after a long acquisition time (*ca*. 20000 scans) can be explained by the low solubility of this polymer. No other solvent than DMSO has been found better for polymer solubilisation.

The degrees of modification were not possible to be calculated from NMR spectra due to their low quality and overlapping with solvent signals; they were estimated from phosphorous content obtained by ICP-AES analysis, assuming that the oxidation of OPVA was complete and acetylated units remained unchanged (12% of acetylated units). The obtained values are collected from table 3.12.

The yields were calculated from the weight of well dried pure product taking into account the modification degree values obtained for each polymer.

Then, OPVA modification with DOPO (polymer G) was tested, following previous polyketone modification (assay R3), in THF with $La(OTf)_3$ and Et_3N at 45 ºC for a week. The modified polyketone was obtained through the precipitation in water and dried under vacuum to constant weight (see scheme below).

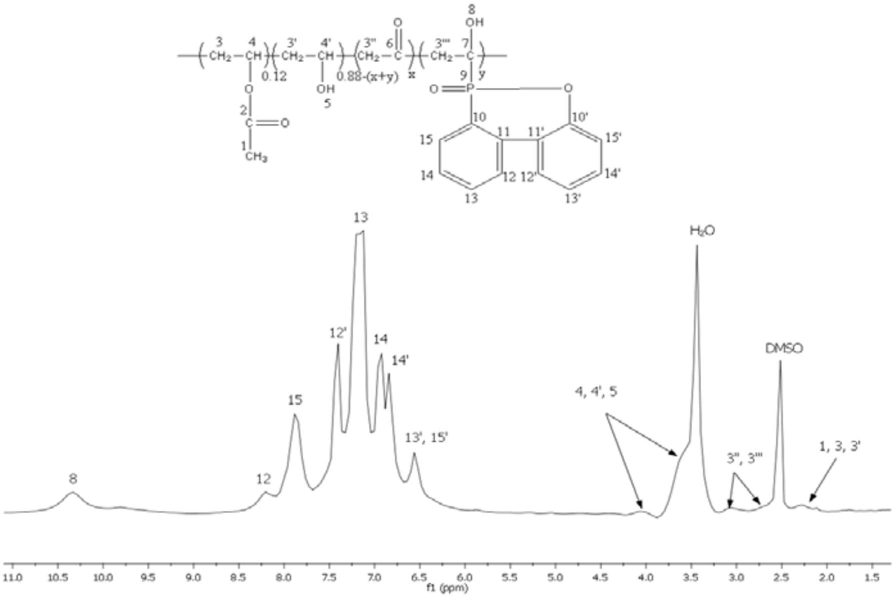


The FT-IR and NMR spectra confirmed the desired structure. One of these spectra is showed in the figure 3.7. FT-IR spectrum shows a broad band between 3620-3090 cm^{-1} which was attributed to OH groups and absorption bands at 1580 cm^{-1} and 1470-1430 cm^{-1} which were assigned to aromatic C-C bonds. An absorption band that appeared at 1280 cm^{-1} was assigned to P=O. The absorption bands at 1137-1097 cm^{-1} and 1051-980 cm^{-1} were due to P-O and C-

O groups. At 750-680 cm^{-1} aromatic out-of-plane deformation bands were observed.

^{1}H NMR spectrum related in figure 3.7 shows signals between 2.0-3.2 which overlapped with DMSO-d_6 signal that were attributed to methylene protons of main chain and methyl protons from acetylated units. Signals which appear at about 3.6-4.2 ppm overlapped with water signal were attributed to methine protons from the main chain and to unmodified OH groups. Region from 6.6-8.2 ppm was assigned to aromatic protons from DOPO. The signal at around 10.3 ppm was due to OH group neighbour to phosphorous which appeared down-fields, probably due to the formation of an intramolecular hydrogen bond with phosphoryl group.

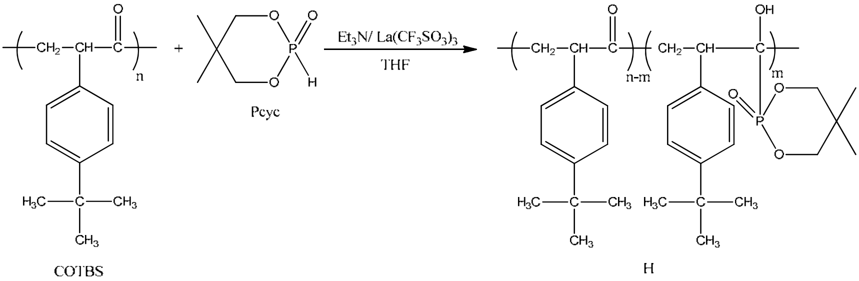
Figure 3.7 ^{1}H NMR spectrum of polymer G recorded in DMSO-d_6



From ^{13}C NMR spectrum, we observed a signal at 20.0 ppm which was attributed to methyl group from acetylated units. Signals between 44.0-45.0 ppm were attributed to methylene groups from main chain and signal at 51.0 ppm was assigned to quaternary carbon directly bonded to phosphorous. Methine carbons from the main chain were observed between 60.0-62.2 ppm. Aromatic signals appeared in region 120.0-155.0 ppm. At 175.0 ppm was observed carbonyl group from acetylated units and at 206.7 ppm carbonyl groups from ketone units. ^{31}P NMR spectrum presents a single signal at 8.9 ppm.

As for polymer F the degree of modification was estimated from % P (see table 3.12) obtained by ICP-AES with the same assumption already mentioned for polymer F. Also in this case the degree of modification could not be obtained from NMR. This degree was 42 % and the yield was 41%.

Now we will proceed to discuss the chemical modification of COTBS. First, COTBS modification with Pcyc (polymer H) was performed following the corresponding model compound reaction (PhAcPcyc) (see scheme below).

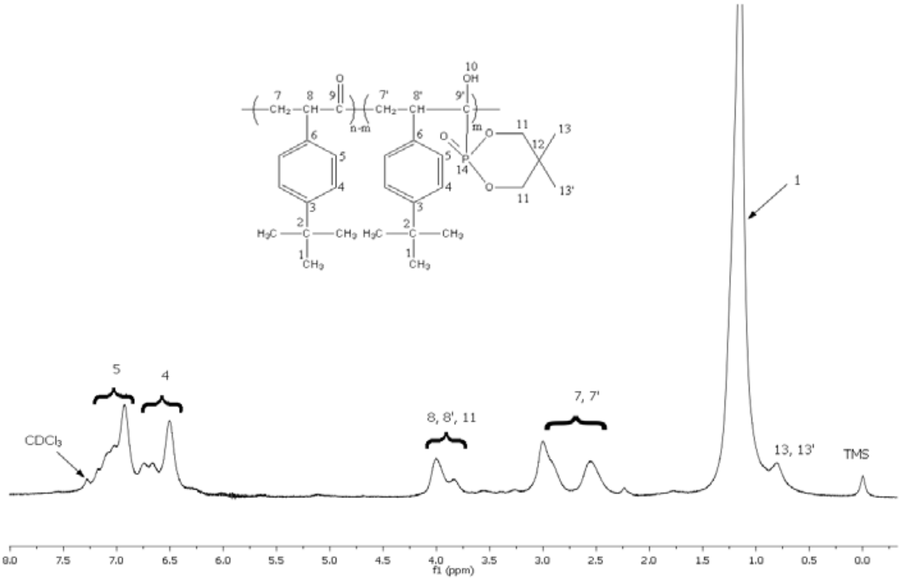


The reaction was tested in THF using La(OTf)$_3$ and Et$_3$N at room temperature for 3 days and 45 ºC for a week. Again the reaction did not take place at room temperature. From the reaction at 45 ºC modified polyketone was isolated in high yield (78%) and with a moderate degree of modification (21%).

FT-IR and NMR spectra show that the desired structure was obtained. By FT-IR an absorption band at 3640-3130 cm^{-1} corresponding to OH groups was observed, wile ketone carbonyl was observed at 1710 cm^{-1}. The region of 1600-1460 cm^{-1} was assigned to aromatic C-C bands. The absorption band from 1270 cm^{-1} was attributed to P=O groups and the band from 1060 cm^{-1} to C-O groups. Region 760-640 cm^{-1} was assigned to aromatic out-of-plane deformation bands.

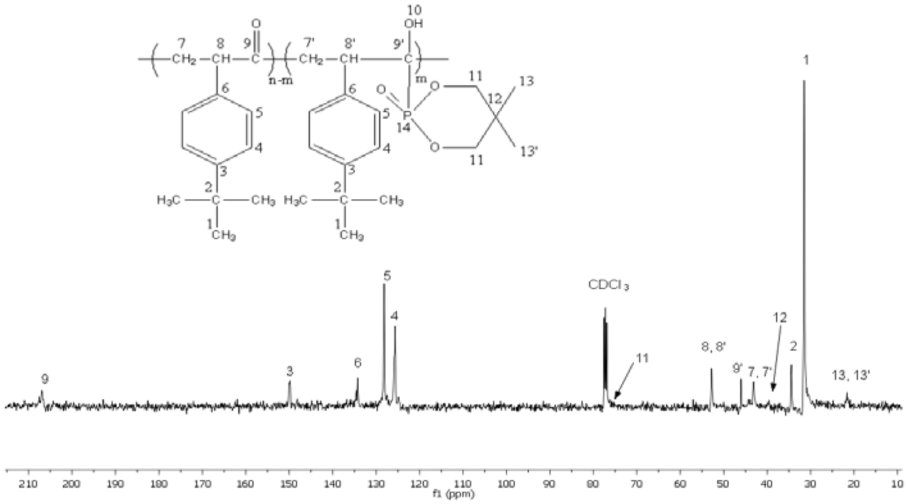
By ^{1}H NMR (figure 3.8) a small signal at 0.8 ppm was observed and attributed to methyl protons from cyclic units. The signal at about 1.2 ppm was attributed to methyl protons from 4-tert-butylstyrene units. Signals from 2.3-3.1 ppm were attributed to methylene protons from main chain and signals from 3.7-4.1 ppm were attributed to methine protons from main chain and methylene protons from Pcyc. Signals from 6.3-7.2 ppm were due to aromatic protons from the 4-tert-butylstyrene units.

Figure 3.8 ^{1}H NMR spectrum of polymer H recorded in $CDCl_3$



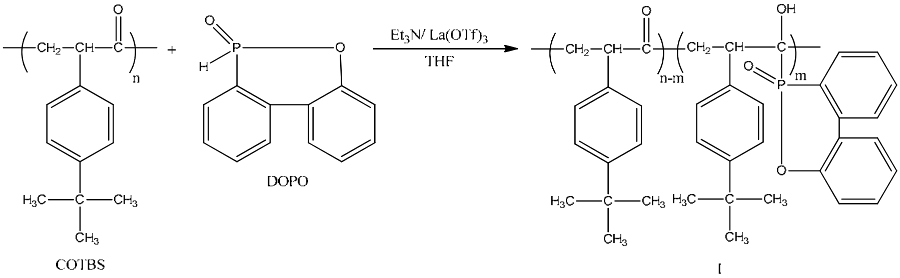
^{13}C NMR spectrum (figure 3.9) shows a small signal at 21.5 ppm which was attributed to methyl group from Pcyc. The significant signal that appears at 31.8 ppm was attributed to methyl groups from COTBS. Signals at 34.2 ppm and 38.7 ppm were attributed to quaternary carbon from 4-tert- butyl groups and quaternary carbon from cyclic units, respectively. Signals at 43.0-44.0 ppm were attributed to methylene groups from main chain and signal around 46.0 ppm was attributed to quaternary carbon directly joined to phosphorous. Signal at 52.5 ppm was attributed to methine groups from main chain. The signal due to methylene groups from cyclic units overlapped with solvent signal at about 77.0 ppm. The region from 126.0-150.0 ppm was attributed to aromatic carbons. The signal at about 207.0 ppm was attributed to carbonyl group from ketone units. ^{31}P NMR spectrum showed tree signals at -3.4 ppm; 6.7 ppm and 11.7 ppm in ratio of 2:20:1, probably due to comonomer regiosequences.

Figure 3.9 ^{13}C NMR spectrum of polymer H recorded in $CDCl_3$



The degree of modification was not possible to be calculated from NMR spectra due to broadening of the signals and overlapping between them; but in this case was possible to make a calculation from the phosphorous content obtained by ICP-AES analyses. The obtained value is collected in table 3.12 (m=0.21) .This degree of modification can be considered as an acceptable value if we take into account the steric hindrance produced by tert-butyl-phenyl groups. The yield (78%) was calculated from weight of well dried polymer by taking into consideration the degree of modification archived.

Then, COTBS was modified with DOPO (polymer I) in THF in the presence of $La(OTf)_3$ and Et_3N (see scheme below).



The reaction was tested under different temperature and time conditions, such as summarized in table 3.11. Starting polymer was recovered when the reaction was performed at room temperature, even after 10 days of reaction. When the reaction was performed at 45ºC (7 days) the expected polymer was obtained, but with a moderate degree of modification (m=0.14, calculated from phosphorous content). However, when the temperature was further increased, the unmodified COTBS was again recovered (assays R5-R7). Therefore it seems that this addition is reversible, and that the addition product is not thermodynamically stable, probably due to the high steric hindrance.

The structure was confirmed by FT-IR and NMR analysis. IR absorption bands between 3600-3100 cm^{-1} were attributed to OH groups. A band at 1707 cm^{-1} was observed and was assigned to carbonyl groups from ketone units. Region of 1600-1410 cm^{-1} was assigned to aromatic C-C bands. At 1161 cm^{-1} appeared P=O groups. The absorption at 921 cm^{-1} was assigned to C-O groups. At 756 cm^{-1} aromatic out-of-plane deformation bands were observed.

^{1}H NMR spectrum related in figure 3.10 shows, signals at 7.2-8.1 ppm which are due to aromatic protons from DOPO moiety and at 10.6-10.7 ppm that was assigned to OH group bonded to phosphorous; this later appeared down-fielded due to intramolecular hydrogen bonding. The other signals appeared as expected in the same region than in polymer H (4-tert-butyl-phenyl group and the main chain).

Figure 3.10 ^{1}H NMR spectrum of polymer I recorded in $CDCl_3$

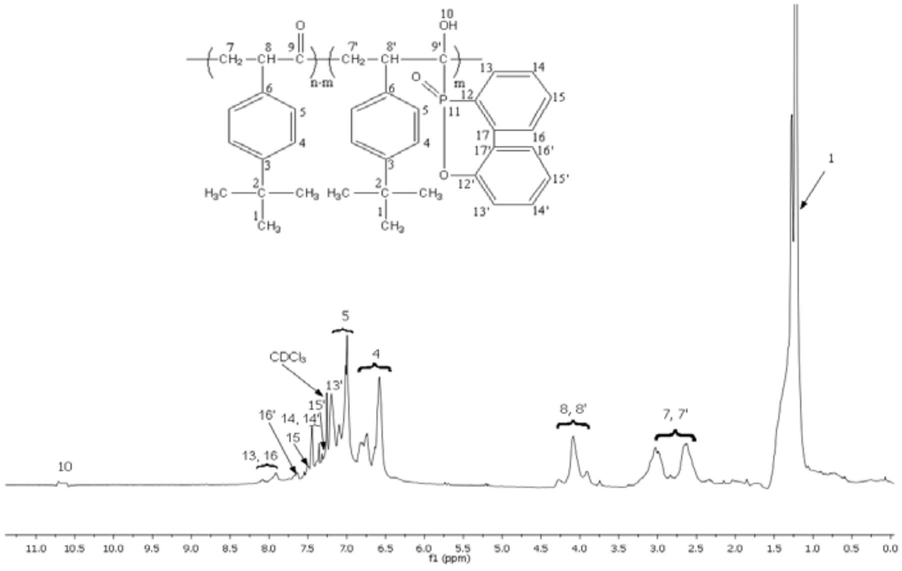
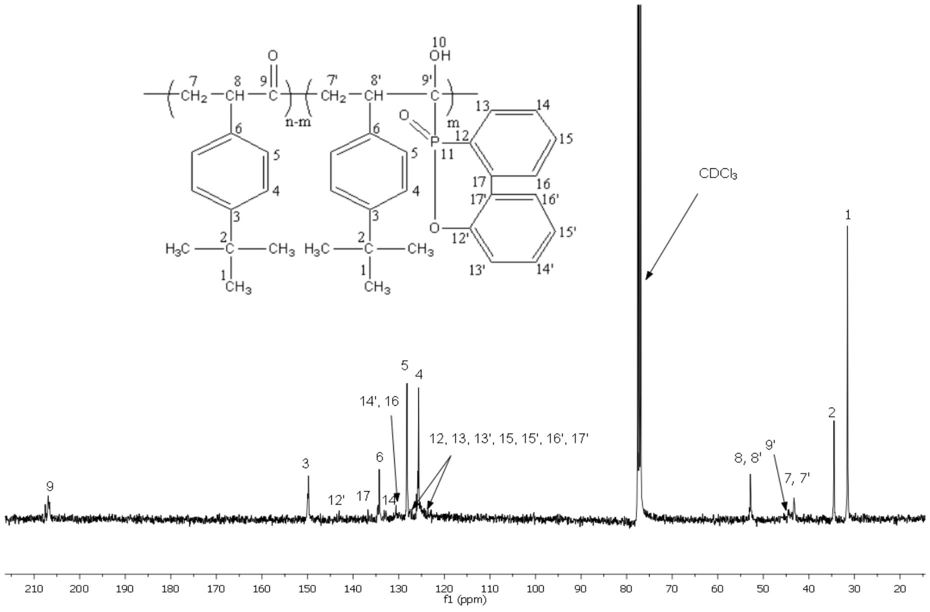


Figure 3.11 ^{13}C NMR spectrum of polymer I recorded in $CDCl_3$



In the ^{13}C NMR spectrum related in figure 3.11, main chain carbons and carbons of 4-tert-butyl groups appears at the same chemical shift than in polymer H. The small signal at about 45.0 ppm was assigned to quaternary carbon directly bonded to phosphorous. Signals of DOPO moiety appeared with low intensity, overlapping with aromatic carbons of 4-tert-butyl-sturene units at 124.0-150.0 ppm. Carbonyl signals of ketone groups appeared split at 206.4-207.5 ppm. ^{31}P NMR spectrum shows two signals at 34.8 ppm and 38.6 ppm. The intensity ratio was 2:1, respectively. This split is probably due to comonomer regiosequences.

As for polymer H, the degree of modification was calculated from the phosphorous content. It was low (m=0,14), but taking into account the high steric hindrance produced by 4-tert-butyl-phenyl groups and DOPO moiety it can be considered reasonable. The yield (calculated by taking into account this degree of modification) was 47%.

Then, inherent viscosities were determined for all synthesized OPVA and COTBS derivatives. These viscosities were performed in DMSO for OPVA derivatives and in NMP for COTBS derivatives at 30 ºC. Obtained values presented in table 3.12 are slightly lower than in case of virgin polymer. The decrease in viscosity is probably due to a more globular conformation adopted by the polymer since bulky groups are introduced. All viscosity values present the same order of magnitude, which seems to indicate that no cleavage or branching side reactions occurred, at least in an important extent.

As mentioned in the introduction section, a second aim of this chapter was to introduce nitrogen on the phosphorous containing polyketone derivatives, in order to obtain intumescent systems. First, we intend to prepare imines by reacting carbonyl groups with primary amine, and then add phosphorous nucleophiles to the C=N double bonds (scheme 3.19). As commented before the selected primary amine was 3-amino-1,2,4-triazine (Tz), due to its ability to easily develop ammonia on decomposing.[105,116]

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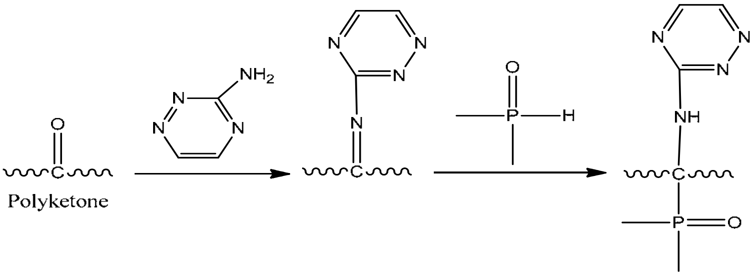
[116] Gaan, S.; Sun, G.; Hutches K.; Engelhard, M. H. Polym Degrad Stab **2008**, 93, 99-108.

Scheme 3.19



As already done for polyketone modification reactions with phosphorous containing compounds, in order to find appropriate reaction conditions model compound reactions were performed, using acetyl acetone (AcAc) as pattern model for OPVA and phenyl acetone as pattern model for COTBS.

First, acetyl acetone (AcAc) was reacted with 3-amino-1,2,4-triazine (Tz) in ethanol using acetic acid in catalytic amount at room temperature by following a reported procedure, already performed in our laboratory between an aldehyde and an aminophenol[117], but the starting materials were recovered. Afterwards, the reaction was tested at reflux maintaining the other conditions unchanged and an untreatable mixture of products was obtained. Then, we used the same reaction conditions but using PhAc as a reagent; again in this case an untreatable mixture was obtained. On the view of these results, we decided to use aniline as primary amine, since its reaction will probably be easier to perform and, although it presents a low content of nitrogen, can also act as good ammonia promoter by heating.

Thus, AcAc was reacted with aniline in ethanol at room temperature using acetic acid as catalyst. Even if an excess of aniline was used (25%-mol) the isolated product corresponds to the monoimine indicated in the scheme shown below, and none diimine was detected. This is probably due to the intramolecular hydrogen bond established between enol and imine nitrogen, which stabilizes enol tautomer and avoid it to act as electrophile. This product was isolated in a

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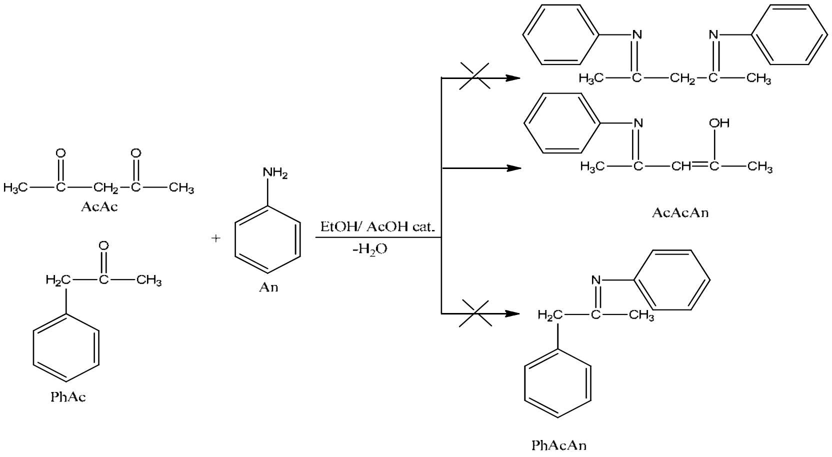
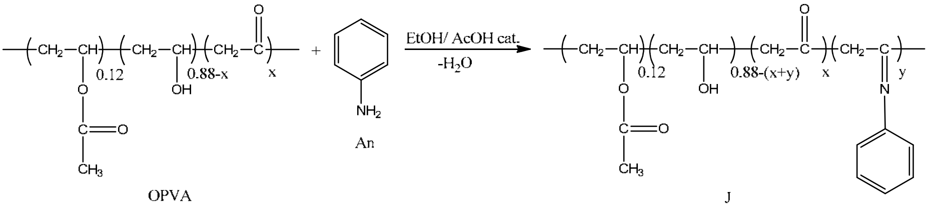
[117] Furniss, B.S.; Hannaford, A.J; Smith, P.W.G; Tatchell, A.R. Vogel's Textbook of Practical Organic Chemistry, 5th edition, Pearson Education, **1989**, p.782.

satisfactory yield (59 %) after 2 days of reaction. The reaction was then tested with phenyl acetone and aniline under the same conditions, but an untreatable mixture of products was obtained (see scheme below).



Then, we proceed with the modification reactions of polyketones with nitrogen containing compounds. First we performed the modification of OPVA with aniline (polymer J, see scheme below).



The reaction was tested in ethanol, using an excess of aniline and acetic acid as catalyst at 60 ºC for 5 days, but a mixture of untreatable products was obtained. Then, the reaction was performed at room temperature for 4 days and the modified polymer was obtained.

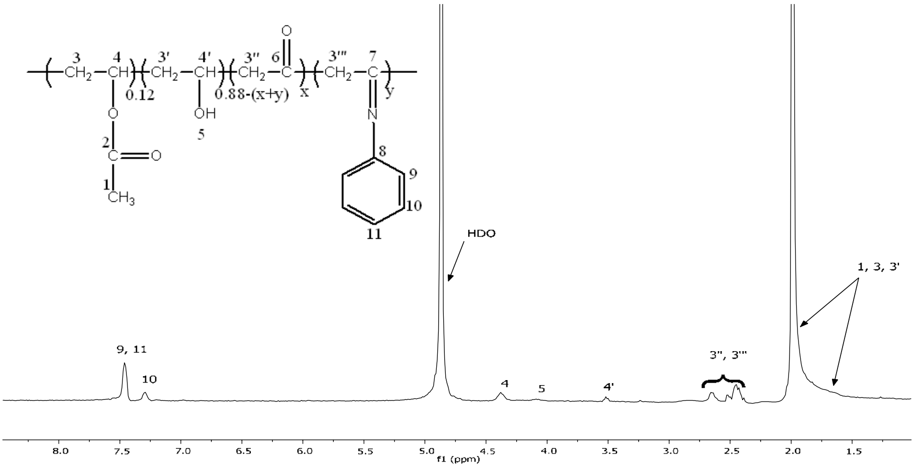
The structure was confirmed by FT-IR and NMR techniques. By FT-IR spectrum a wide band at 3550-2990 cm^{-1} was observed and attributed to OH groups coming from enol and unmodified alcohol units. A low intensity signal at

1690 cm^{-1} was assigned to C=O groups from ketones. The bands at 1640-1570 cm^{-1} were associated to C-C aromatic, C=C from enol and C=N from imine units. Signals at 1400 cm^{-1} and 700-650 cm^{-1} were attributed to aromatic groups. The low intensity of C=O band indicates that unmodified ketones exist mainly in the enol form, probably due to the formation of the intramolecular hydrogen bond discussed on model compound AcAcAn.

^{1}H NMR spectrum (figure 3.12) shows signals at 1.6-2.0 ppm which were attributed to methyl and methylene protons from acetylated and unmodified alcohol units. Methylene protons from ketone and imine units appeared at 2.4-2.7 ppm. Signals at 3.5 ppm and 4.1 ppm were attributed to methine protons and OH protons from unmodified alcohol units. Signal at 4.4 ppm was assigned to methine protons of acetylated units. Region of 7.2-7.5 ppm was attributed to aromatic protons from aniline. This spectrum was recorded in D_2O but the low solubility of the polymer avoid recording of the ^{13}C NMR spectrum in this medium. Thus it was recorded in solid state. It must be noted that no enol proton signals were observed in the ^{1}H NMR spectrum recorded in D_2O; this is probably due to interchange with deuterated solvent.

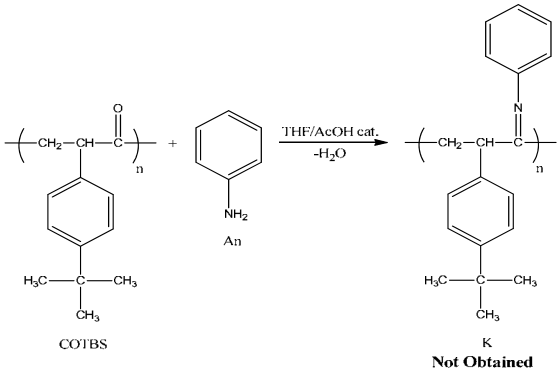
Solid state ^{13}C NMR spectrum (swollen in C_6D_6) presents a signal at 23.8 ppm which was attributed to methyl groups from the acetylated units. Signals at 47.0-51.0 ppm were due to methylene groups from the main chain. Between 65.0-70.0 ppm were observed methine signals from the main chain. Signal at 112 ppm was assigned to enol methine. Signals at 121.8-147.0 ppm were attributed to aromatic carbons from aniline units. At 160.0 ppm appeared quaternary carbon from enol units. The signals at 172.0 ppm and 191.0 ppm were assigned to carbonyl groups from acetylated and ketone units, respectively. Signal at 180.0 ppm was attributed to C=N groups from imine units. Signal at 112 ppm, due to enol group as indicated above, showed the highest intensity of all signals, indicating that probably a high content of enol units occurred in this polymer.

Figure 3.12 ^{1}H NMR spectrum of polymer J recorded in D_2O



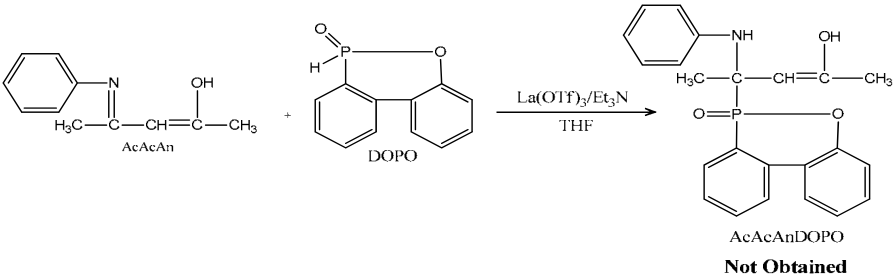
For this polymer, we could not determine the degree of modification by NMR. As mentioned above, in the ^{1}H NMR spectrum interchange with solvent (D_2O) occurred, which avoid quantification. As known, solid state ^{13}C NMR is also not quantitative. This polymer was very insoluble in all tested solvents; actually it was only slightly soluble in water: therefore, no other deuterated solvent could be used to record the NMR spectra. The inherent viscosity was not determined due to low solubility of synthesized polymer in all tested solvents.

Then, we tested the modification of COTBS with aniline (polymer K, see scheme below).

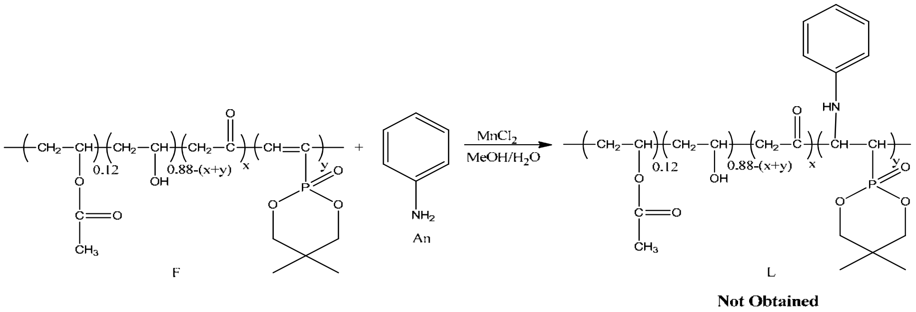


The reaction was tested at room temperature in THF, using an excess of aniline and acetic acid as catalyst. The reaction did not occur, even after 6 days. NMR spectra showed that starting polymer was recovered.

As mentioned above, one of the aims of this work was to obtain intumescent systems by introducing phosphorous and nitrogen in the same polymer. Thus, we intended to prepare imines and then react them with phosphoryl groups. Therefore, we first tested the addition reaction between AcAcAn and DOPO (see scheme below), in order to serve as model reaction for polymeric imine (polymer J) modification. This reaction was performed at room temperature in THF using La(OTf)$_3$ and Et$_3$N for 4 days, but a mixture of starting products was recovered.



On the view of the negative results obtained in the formation of imines and its reaction with phosphorous compounds, we decided to give up this approach to obtain intumescent systems. Considering the successful preparation of phosphorous polymer F, we decided to use it as starting material and modified it with a nitrogen compound. This polymer contains C=C double bonds conjugated to a phosphoryl group. Therefore, we can introduce nitrogen by the conjugated addition of primary amines to these systems. Thus, we tested this reaction between polymer F and aniline (polymer L, see scheme below).



The reaction was tested at room temperature for two days, using methanol-water as a solvent, aniline in a stoichiometric amount and $MnCl_2$ as Lewis-acid catalyst. This reaction was done on the basis of a study developed by Roy et. al.[118] in which different electron deficient alkenes, such as α,β-unsaturated nitrile, carboxylic ester, ketone and amides, were reacted with amines. The NMR spectra indicated that the virgin starting polymer was recovered.

As can be seen, all our attempts to obtained phosphorous-nitrogen containing polymers were unsuccessful. Therefore, we decided to approach the preparation of intumescent systems by a completely different strategy that will be disscused in the next chapter.

To conclude this chapter, we will discuss the thermal characterization of all the polymers successfully prepared (polyketones and phosphorous containing derivatives).

Thermal studies were performed with DSC and TGA techniques. Tg's were obtained from second heating dynamic scans performed at a heating rate of 10ºC/ min in a nitrogen atmosphere. The results are summarized in table 3.13.

In case of starting OPVA was observed a glass transition temperature (Tg) at about 80 ºC. The new moieties introduced can affect Tg in a different way, depending on their structure and the degree of modification.[119] As can be seen in

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[118] Roy, A.; Kundu, D.; Kumar Kundu, S.; Majee, A.; Hajra, A. Open Catalysis Journal, **2010**, 3, 34-39.

[119] Gimenez, V.; Reina, J.A.; Mantecon, A.; Cadiz, V. Acta Polym **1999**, 50, 187-195.

table 3.13, modified OPVA polymers showed slightly higher Tg values than starting OPVA. The Tg is higher in case of polymer G, probably due to the stiffness of aromatic moiety introduced. In the case of polymer F, the presence of C=C double bonds on the main chain can be responsible of the observed increase in Tg.

In case of COTBS a high Tg was observed at 148ºC. Such a higher value is due to its aromatic structure. As showed in table 3.13, this Tg decreased slightly when the polymer is modified with phosphorous containing moieties. In this case, the introduction of bulky groups in a quite stiff chain which already contains bulky groups, will probably led to a less organized chain, and therefore to a reduction of Tg. In no case melting endotherms were observed. Hence, these polymers are all amorphous.

Table 3.13 Thermal data of polyketones and phosphorous derivatives

Polymer	**DSC**	**TGA**					
	Nitrogen	**Nitrogen**		**Air**		**Char yield, 790ºC (%)**	
	Tg (ºC)	**Tonset[a] (ºC)**	**Tmax.[b] (ºC)**	**Tonset[a] (ºC)**	**Tmax.[b] (ºC)**	**Nitrogen**	**Air**
OPVA	81	187	219	184	218	69	68
F	86	274	303	257	294	43	48
G	93	202	320	185	311	52	54
COTBS	148	340	397	318	377	3	0
H	141	307	340	261	347	18	8
I	140	335	384	296	357	14	3

a) onset temperature of weight loss

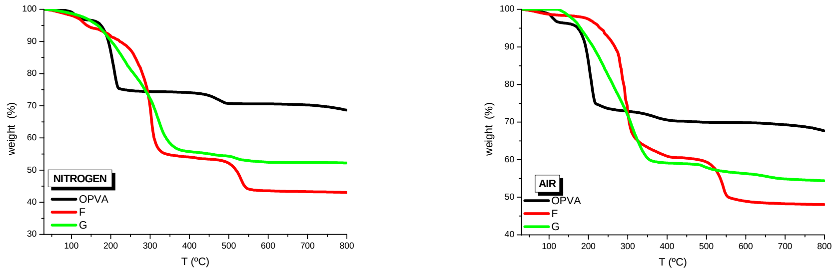
b) temperature of maximum rate of weight loss

Then, all these polymers were characterized by TGA under air and nitrogen atmospheres.

As already mentioned, TGA, particularly char yields, are a useful indication of polymer flammability and their trend to form protective barriers.[91] Table 3.13 shows the data from the TGA curves including the onset temperature of weight loss (Tonset), temperature of maximum rate of weight loss (Tmax) and the char yields obtained at 790ºC in both, nitrogen and synthetic air atmosphere. Figure

3.13 and figure 3.14 shows TGA curves of starting and modified polyketones in nitrogen and synthetic air atmospheres.

Figure 3.13 TGA curves in nitrogen and air atmospheres of OPVA derivatives



a) b)

In case of starting OPVA (figure 3.13 a and b), first part of TGA curve (up to about 150ºC) can be attributed to loss of hydration water. This polymer, due to the presence of a high proportion of enol groups, contains a certain amount of this kind of water, since these groups tend to form hydrogen bonds with water (coming also from ambient). The weight loss starting at approximately 200ºC is related to the thermal degradation and elimination of volatile products. In this case, degradation process probably starts by enol groups dehydration lading to alkynes. Due to the high ratio of enol groups, conjugated alkynes will form, which easily can lead to aromatic rings through trimerization.[120,121] In both, nitrogen and air atmosphere OPVA degradation process, leads to a very high char yield (approximately 70%) at 790ºC. This is in agreement with the trimerization reaction already mentioned and with the formation of a graphitic structure. As can be seen from the TGA curves and thermal data related in table 3.13, polymer F and polymer G start to lose weight at higher temperature than precursor OPVA, in both, nitrogen and air atmospheres. This is probably due to the lower polarity of the polymer which reduces the content of water of

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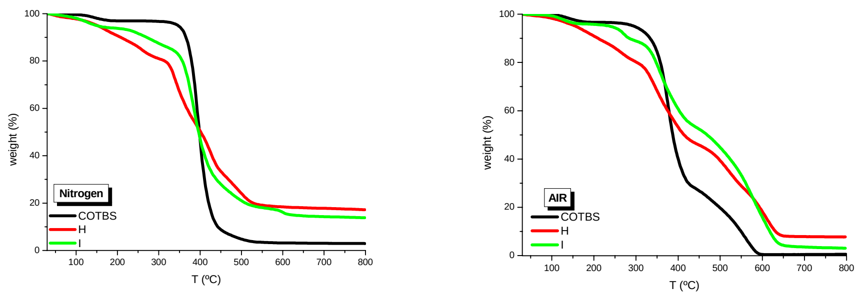
[120] Saaby, S; Baxendale, I.R.; Ley, S.V. Org Biomol Chem **2005**, 3, 3365- 3368.

[121] Saito, S.; Yamamoto, Y. Chem Rev **2000**, 100, 2901-2915.

hydration. Both polymer F and polymer G show a delay of thermal degradation process and present a high char yield at 790ºC, although it must be noted that the char yield is lower than of starting OPVA. Since, a lower ratio of enol groups is present in the modified polymers, the dehydration process is more difficult (a less conjugated system is formed); in this way, the degradation is delayed. On the other hand, the formation of a graphitic structure is easier when a high conjugated polyine is formed; and this is not the case in modified polymers.

In case of unmodified COTBS, it can be observed, from TGA curves (figure 3.14 a and b) and thermal data from table 3.13, that weight loss process starts at about 400ºC and is almost finished at about 600ºC, when a constant low char yield was observed both in nitrogen and air atmospheres. It was also observed a small weight loss up to 200ºC, which was associated to evaporation of hydration water.

Figure 3.14 TGA curves in nitrogen and air atmospheres of COTBS derivatives


a) b)

Modified COTBS with Pcyc and DOPO show a similar behaviour in TGA as the already discussed for PVA modified with BIC derivatives in chapter 2 (table 2.7). They start to lose weight at lower temperatures than starting COTBS, but they lead to higher char yields at high temperatures than COTBS. This behaviour can be explained as for PVA modified with BIC polymers from chapter 2: a phosphoryl-oxygen bond is present, which can easily be hydrolyzed at the beginning of weight loss process (due to water formed), leading to formation of phosphoric acid groups, able to further catalysed dehydration, and subsequently to launch all other stages of degradation process. The dehydration reactions could be related to the presence of hydroxyl groups introduced in the polymer and can take place at the beginning of the degradation process. Water formed can react with phosphoryl-oxygen bonds lading to phosphoric acids which further facilitate the dehydration; This will lead to unsaturated systems, which further will cross-link and will led to a carbonaceous barriers on the surface of polymer, which can difficult volatile products from diffusing to the flame and will shield the polymer surface from heat and air. This explanation is in agreement with the high amount of char yield at 790º C.

4. Conclusions

In summary, in this chapter we report the preparation and characterization of a set of phosphorous containing polyketone derivatives with several structures. However, the preparation of all the proposed phosphorous-nitrogen containing polymers was unsuccessful, although different approaches were tested. All phosphorous containing polymers lead to high char yield on TGA curves, which allow us to think that they are good candidates to act as flame retardant additives through the formation of charred barriers on the condensed phase.

As mentioned above, the preparation of intumescent systems will be tackled with a completely different approach in the next chapter.

Chapter 4

Flame retardant phosphorous-nitrogen containing polymers obtained by chemical modification of poly[1-(2-hidroxyethyl)aziridine]

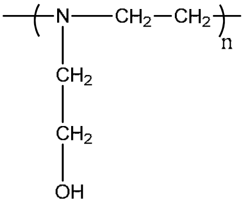
In this chapter we propose to synthesize and characterize phosphorous-nitrogen containing polymers obtained by chemically modifying poly[1-(2-hidroxyethyl)aziridine] with phosphorous containing moieties (BIC and DPBC), which are expected to be useful as flame retardant intumescent systems by blending with ¨commodity¨ polymers.

1. Introduction

On the view of the negative results obtained in chapter 3 concerning the preparation of intumescent systems, in this chapter we intend to prepare polymeric flame retardant additives, which contain phosphorous-nitrogen moieties in their structure, through a completely different synthetic approach. As described in previously chapters, phosphorous compounds are widely used as flame retardants, due to their possible action in both, condensed or vapour phase. As mentioned before, various phosphorus-nitrogen (P-N) containing compounds have shown to act as flame retardants for polymeric systems. Furthermore, featuring a synergistic behaviour the P-N compounds present better thermal stabilities and less toxic smoke evolution when compared to phosphorus based FR.[97]

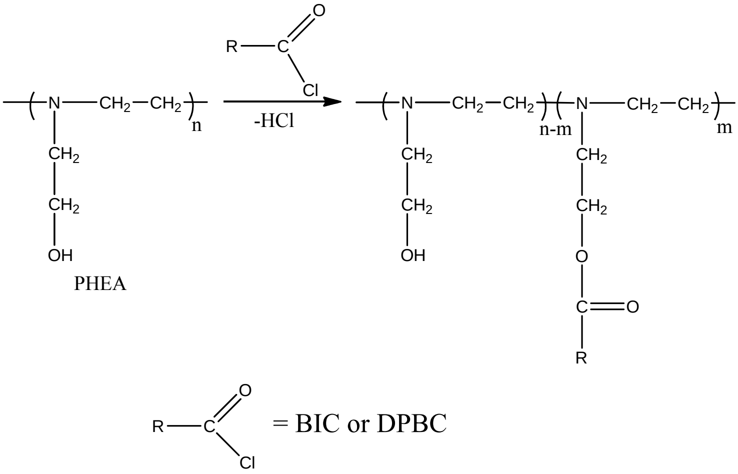
Many P-N containing systems are classified as intumescent systems, well known as a new generation of flame retardants for polyolefins, especially polypropylene and polyethylene.[98] As already described in the general introduction and previous chapter, intumescent system have to contain an inorganic acid source, a charring source and a foaming agent,[98,99] its behaviour resulting from a combination of charring and foaming of the surface of the burning polymer. In previous chapter we intend to obtain intumescent systems, preparing imines from the reaction of polyketone's carbonyl groups with primary amine, and then add phosphorous nucleophiles to the C=N double bonds. Unfortunately, these attempts have not achieved the goal.

Therefore, in this chapter we intend to chemically modify a hydroxylated polyaziridine with phosphorous containing moieties. Actually, as starting material, we choose poly[1-(2-hidroxyethyl)aziridine] (PHEA). This polymer is interesting because it already contains nitrogen and hydroxyl groups, which facilitate its chemical modification through esterification reactions. This polymer is not commercially available, and its synthesis was described in the literature by Rivas et. al.[122] through cationic polymerization of the corresponding aziridine in the presence of $BF_3 \cdot Et_2O$. This polymerization reaction has been recently improved by other colleagues from our group.[123]



PHEA

As phosphorous containing reagents, we choose 4-chloroformyl-1-oxo-2,6,7-trioxa-1-phosphabyciclo[2.2.2]octane (BIC) and 4-(diphenylphosphinoyl) benzoyl chloride (DPBC), already used in chapter 2, which can react easily with alcohol groups of PHEA by forming esters.



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[122] Rivas, B. L.; Geckeler, K. E.; Bayer, E. Eur Polym J **1991**, 27, 1165-1169.

[123] Šakalytė, A.; Giamberini, M.; Lederer, A.; Reina, J. A. J Polym Sci Part A: Polym Chem Submitted.

Thus, a polymer containing phosphorous, nitrogen and free hydroxyl groups will be obtained. Phosphorous moiety could act as an inorganic acid source; unmodified hydroxyl groups would act as charring source and nitrogen moieties as a foaming agent. In this way an intumescent system could be obtained.

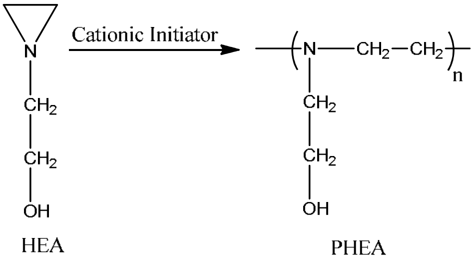
2. Experimental section

2.1- Materials

4-chloroformyl-1-oxo-2,6,7-trioxa-1-phosphabyciclo[2.2.2]octane (BIC) and 4-(diphenylphosphinoyl)benzoyl chloride (DPBC) were synthesized as shown in the chapter 2. 4-(Dimethylamino)pyridine (DMAP, Fluka, 99%) was used as received. 1-Methyl-2-pyrrolidinone (NMP, Sigma-Aldrich, 99.5%) and pyridine (Py, Sigma-Aldrich, 99%) were purified prior to use according to literature[56] as related in chapter 2.

Poly[1-(2-hidroxyethyl)aziridine] (PHEA) (scheme 4.1) was synthesized as follows. The monomer (1-(2-hydroxyethyl)aziridine, HEA; 2.17 g, 0.02 mol) and initiator ($BF_3 \cdot EtNH_2$; 1 mol%) were placed in a round-bottom glass flask with an argon inlet tube. The mixture was heated at 45 ºC under stirring. After 24 hours 2-3 ml of methanol were added to dissolve the polymer; this was then reprecipitated twice from methanol in diethyl ether and dried under vacuum to constant weight. Conversion was 75%. ^1H NMR ($CDCl_3$, 400 MHz, δ ppm): 2.6 (m, 6H); 3.6 (t, 2H); 4.8 (broad, 1H); ^{13}C NMR ($CDCl_3$, 100.6 MHz, δ ppm): 53.0 (t); 56.6 (t); 60.0 (t). Inherent viscosity (DMSO, dl/g) =0.75.

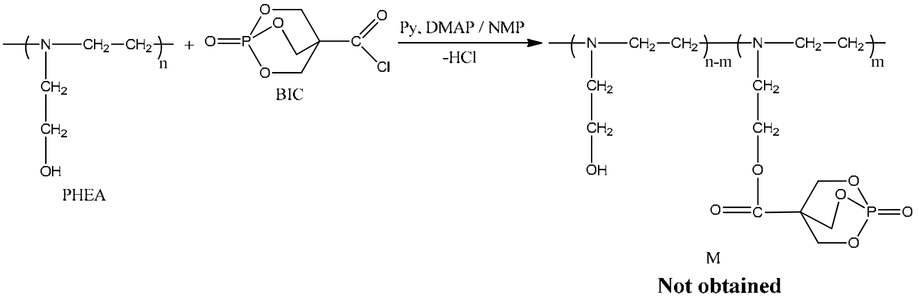
Scheme 4.1



2.2- Chemical modification reactions

2.2.1- Chemical modification reaction of poly[1-(2-hidroxyethyl)aziridine] with 4-chloroformyl-1-oxo-2,6,7-trioxa-1-phosphabycicl [2.2.2] octane (polymer M, scheme 4.2)

Scheme 4.2



Not obtained

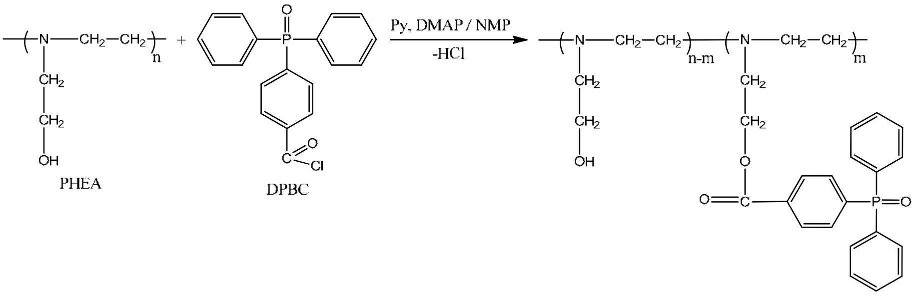
In a round bottomed flask, well dried and purged previously with argon, we introduced 0.80 g (0.009 mol) of PHEA and 10 ml of NMP. The mixture was stirred at room temperature until the polymer was completely dissolved. Then, we add into the reaction mixture 0.009 mol (0.71 g) of pyridine, 0.0009 mol (0.109 g) of DMAP and 0.011 mol (2.34 g) of BIC. The reaction was kept under stirring at room temperature for 2 days. The resulting material was recovered through the precipitation in THF, washed with THF and dried under vacuum at 60ºC to constant weight. The NMR spectra showed that the desired polymer was not obtained.

2.2.2- Chemical modification reaction of poly[1-(2-hidroxyethyl)aziridine] with 4-(diphenylphosphinoyl)benzoyl chloride (polymer N, scheme 4.3)

In a round bottomed flask, well dried and purged previously with argon, we introduced 0.44 g (0.005 mol) of PHEA and 10 ml of NMP. The mixture was stirred at room temperature until the polymer was completely dissolved. Then, we added into the reaction mixture 0.005 mol (0.40 g) of pyridine, 0.0005 mol

(0.061 g) of DMAP and 0.006 mol (2.04 g) of DPBC. The reaction was kept under stirring at room temperature for 3 days. The resulting material was recovered through the precipitation in water from the reaction mixture, washed with water and dried under vacuum at 60º C until constant weight. The yield was 78%. IR (cm^{-1}): 3400 (OH); 1717 (C=O); 1630-1390 (C-C aromatic); 1270-1000 (C-O and C-N); 1180 (P=O); 724-690 (aromatic C-C-H out of plane deformation); ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 2.5-3.5 (m); 3.6 (t); 4.4 (t); 4.8 (broad); 7.3-7.8 (m); 7.9-8.1 (m); ^{13}C NMR ($CDCl_3$, 100.6 MHz, δ ppm): 51.3-52.6 (t); 59.5 (t); 61.5(t); 128.8 (d); 129.7 (s); 131.2 (s); 132.0 (d); 132.6 (d); 137.4-138.4 (s); 165.5 (s); ^{31}P ($CDCl_3$, 161.9 MHz, δ ppm) 28.2 (s). Inherent viscosity (DMSO, dl/g) =0.69.

Scheme 4.3



N

2.3- Characterization techniques

Polymers were characterized by ^{1}H, ^{13}C and ^{31}P NMR which were performed using chloroform ($CDCl_3$) as a deuterated solvent with a Varian Gemini 400 MHz spectrometer (^{1}H- 400 MHz, TMS; ^{13}C- 100.6 MHz, TMS; ^{31}P- 161.9 MHz, H_3PO_4) at room temperature.

Fourier Transform Infrared spectra were recorded on a FT-IR 680 plus spectrophotometer from JASCO, connected to an ATR device, at room temperature in absorbance mode using samples in solid state.

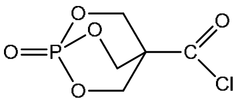
Phosphorous contents were determined by ICP-AES analysis under the same conditions as detailed for previously reported polymers.

Inherent viscosities were measured in dimethyl sulfoxide (DMSO) solutions (*ca.* 2 g/l) at 30ºC as described for first set of polymers (chapter 2).

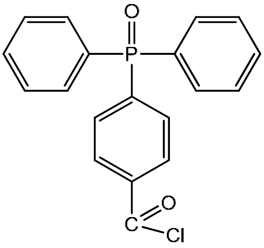
TGA curves were recorded, using samples of about 10 mg, in a Mettler TGA equipment at temperature range from 30-800ºC at 10ºC/min. DSC curves were recorded at the heating rate of 10°C/min using about 5 mg of sample with a Mettler DSC822e thermal analyzer. The Tg's were determined from the second heating scans.

3. Results and discussion

As mentioned in the introduction part, in this chapter we intend to synthesize new flame retardant phosphorous-nitrogen containing polymers potentially useful to act as intumescent systems by blending with thermoplastic ¨commodity¨ polymers. These polymers have been obtained by chemically modifying a hydroxylated polyaziridine with phosphorous containing compounds. The choice of this kind of polymer as starting material was due, as mentioned above, to the fact that it contains nitrogen and hydroxyl groups. The hydroxyl groups, which can easily be reacted to get different functional groups, are very interesting to be present in the final polymer, due to their char forming character. They can easily lead on heating to dehydration reactions giving to unsaturated materials; especially in the presence of phosphorous-containing moieties, which can act as a dehydration catalyst source. Nitrogen moiety will probably act as a foaming agent, due to free ammonia developed by heating. As phosphorous reagents we choose two acid chlorides (BIC and DPBC), since they can react with polymeric OH groups by forming esters. The chosen structures, shown below, present different polarity and therefore they will confer to the final modified polymer different compatibility behaviour with selected ¨commodity¨ polymers.



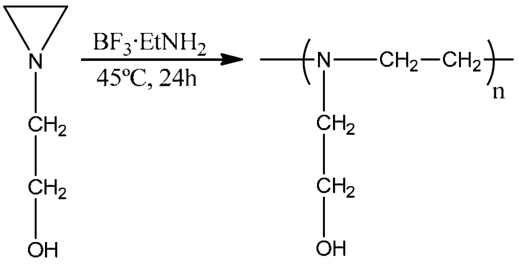
BIC



DPBC

BIC moieties would lead on burning to phosphoric acid derivatives quite easily, and these groups tend to catalyze hydroxyl dehydration reactions. On the other hand, DPBC moieties would in principle lead to a high char yield, due to its aromatic character.

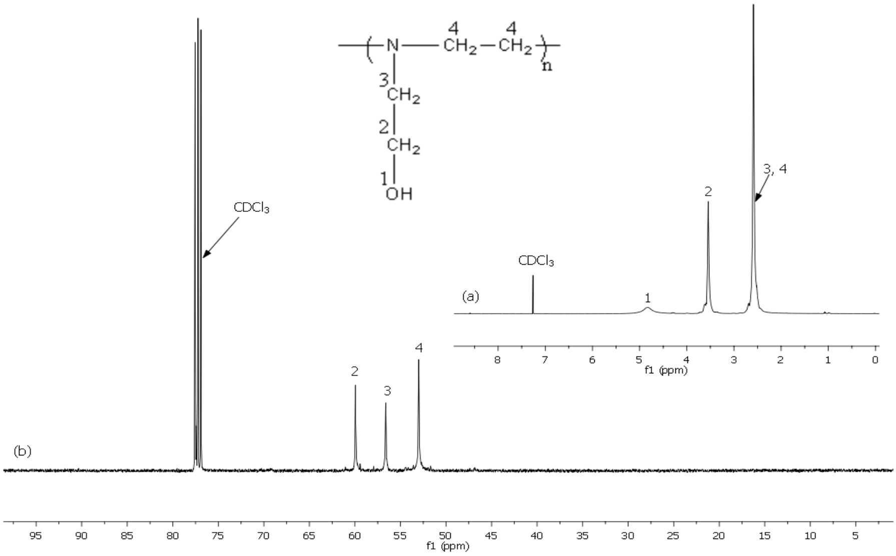
As mentioned above, PHEA is not commercially available. This polymer was reported on the 90's by Rivas at. al.[122] Its synthesis was performed by cationic polymerization of the corresponding monomer HEA on the presence of $BF_3{\cdot}Et_2O$ (1.5 mol %) in solution (acetonitrile, dimethylformamide, dichloromethane and toluene) at 25-45ºC. This procedure has been recently reviewed and improved by colleagues on our group, and they have seen that a good polymer with a degree of polymerization *ca.* 44 is obtained when the monomer is reacted in bulk using $BF_3{\cdot}EtNH_2$ as initiator at 45º C for 24 hours, according to the scheme below.



HEA PHEA

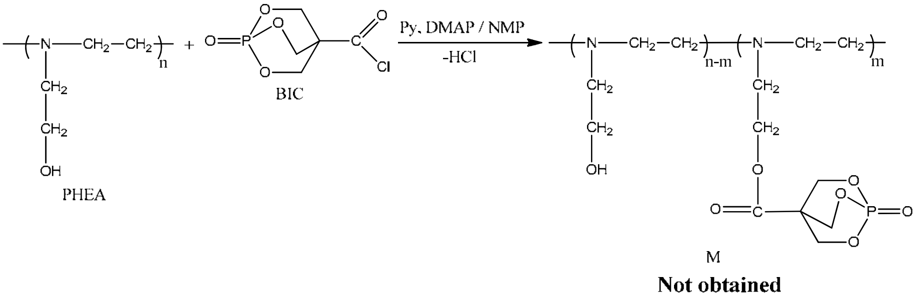
The polymer structure was characterized by ^1H and ^{13}C NMR spectrometry. The figure 4.1 shows the ^1H and ^{13}C NMR spectra of synthesized polymer.

Figure 4.1 ^1H (a) and ^{13}C (b) NMR spectra of PHEA recorded in $CDCl_3$



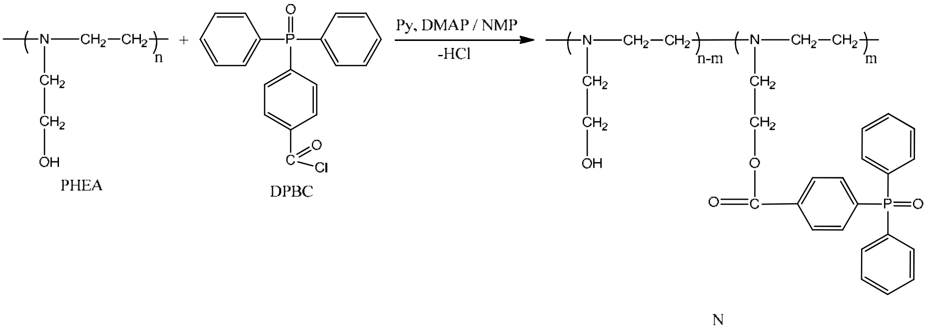
In ^1H NMR spectrum, figure 4.1 (a), a signal at 2.6 ppm was observed, which was assigned to protons from the main chain methylene and those methylene directly bonded to nitrogen. Signal at 3.6 ppm was attributed to methylene protons next to OH group and at 4.8 ppm was observed a broad signal which is due to hydroxyl protons. ^{13}C NMR, figure 4.1 (b), spectrum shows signals coming from the main chain at 53.0 ppm. Signals at 56.6 ppm and 60.0 ppm were assigned to methylene carbons directly bonded to nitrogen and to OH groups, respectively.

Then, we tried to chemically modify PHEA with phosphorous containing compounds (BIC and DPBC), which were already synthesized and characterized as described in chapter 2. The modification reactions were tested following the method used in chapter 2 for PVA chemical modification reactions. Thus, they were carried out in a homogenous system at room temperature in NMP, using pyridine as a base, in a stoichiometric amount with respect to acylating agent, and DMAP as catalyst, for two-three days. First, we tested the reaction of PHEA with a cyclic caged phosphate (BIC), according to the scheme shown below.



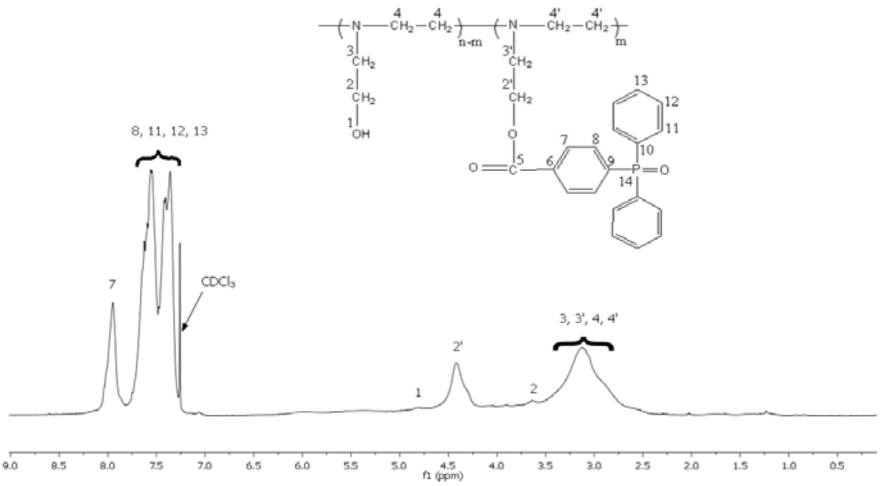
The NMR spectra showed that a mixture of unmodified alcohol groups and eliminated (unsaturated) groups were present in the recovered polymer. Thus, we observed in ^{1}H NMR spectrum signals at 4.0-4.2 ppm and 6.0 ppm and in ^{13}C NMR spectrum at 108.0 ppm and 140.0 ppm which were attributed to double bonds directly linked to nitrogen (enamine groups). These groups probably formed due to the presence of traces of phosphoric acid which catalyze dehydration reactions. In this case, it seems that BIC cage is partially cleaved, probably as a result of some attack from the nucleophilic nitrogen atoms present in the polymer, leading to phosphoric acid derivatives.

Then we tried to perform the reaction, using DPBC as acylating agent. This reaction was performed for 3 days in NMP, using pyridine in a stoichiometric amount with respect to acylating agent, and DMAP as catalyst (see scheme below). In this case the desired polymer was isolated in high yield (78%).



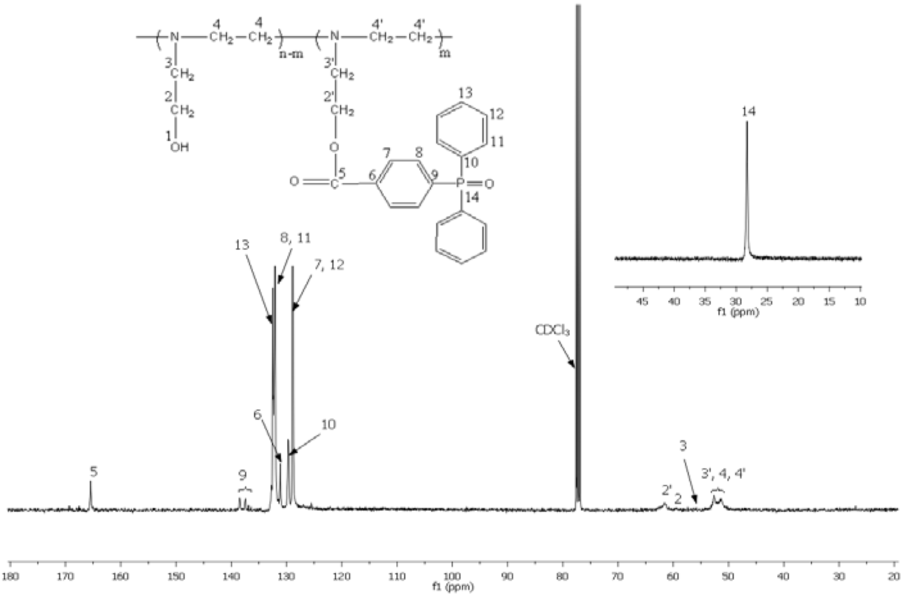
The polymer structure was confirmed by NMR characterization. ^{1}H NMR spectrum (figure 4.2) shows signals at 2.5-3.5 ppm which were assigned to methylenes coming from main chain and methylenes directly bonded to nitrogen from both, modified and unmodified units. Methylenes which are directly linked to oxygen atoms appeared at 3.6 ppm for the unmodified units and at 4.4 ppm for the modified units. The small broad signal at 4.8 ppm was attributed to OH groups. The region of 7.3-8.1 ppm was assigned to aromatic protons coming from DPBC units introduced.

Figure 4.2 ^{1}H NMR spectrum of polymer N recorded in $CDCl_3$



^{13}C and ^{31}P NMR spectra are shown in figure 4.3. There were observed signals at 51.3-52.6 ppm which were attributed to methylenes from the main chain and to methylenes directly bonded to nitrogen from modified units; methylenes directly linked to nitrogen, coming from unmodified units, which should appear at about 56.0 ppm can not be observed and probably appear confused with the noise. Signals at 59.5 ppm and 61.5 ppm were assigned to methylenes directly bonded to oxygen from unmodified OH groups and formed ester groups, respectively. The region 128.8-138.4 ppm was associated to aromatic methines and quaternary carbons from DPBC units; the signal at 165.5 ppm was attributed to carbonyl group. It must be noted that signal at 138.0 ppm appeared split into two signals, due to coupling with phosphorous nuclei ($^{1}J_{C\text{-}P}$=92.0 Hz). ^{31}P NMR spectrum shows a singlet at 28.2 ppm.

Figure 4.3 ^{13}C and ^{31}P NMR spectra of polymer N recorded in $CDCl_3$



The degree of modification achieved was determined from the ^{1}H NMR spectrum, by integration of suitable signals. The phosphorous content (%P) calculated from the degree of modification obtained from the NMR was in agreement with the value determined by ICP-AES analysis, performed as already described for the PVA modified polymers (chapter 2). All results are shown in the table 4.1.

The yield (78%) was calculated from the weight of dried polymer, taking into account the obtained modification degree.

The inherent viscosities were measured for both, starting and modified polymer. The measurements were carried out in DMSO at 30ºC. The obtained values are shown in table 4.1; modified polymer present a slightly lower viscosity, probably due to a more globular conformation, conferred to the polymer by the bulky groups that are introduced. They present the same order of magnitude, which suggests that no scission or ramification side reactions were observed, at least in an important extent.

Table 4.1 Results of chemical modification of PHEA

Polymer	**Degree of modification[a] (m)**	**% P determined from**		**Inherent viscosity, $\eta_{inh.}$ (dl/g)**
		ICP-AES	**^{1}H NMR**	
PHEA				0.75
N	0.60	6.7	7.1	0.69

[a] obtained by ^{1}H NMR

Polymer N and the starting PHEA were then thermally characterized by DSC and TGA analysis. By DSC analysis glass transition temperatures (Tg) were determined from the dynamic second heating scan at a rate of 10ºC/min in nitrogen atmosphere (see table 4.2). As can be observed, the starting polymer (PHEA) presents a low Tg value (-35ºC), whereas the phosphorous modified polymer shows a higher Tg (85ºC). This increment is certainly due to bulky groups introduced, restricting the chain mobility and therefore increasing the stiffness of the polymer. Moreover both, virgin and modified PHEA are amorphous materials since no melting endotherm was observed.

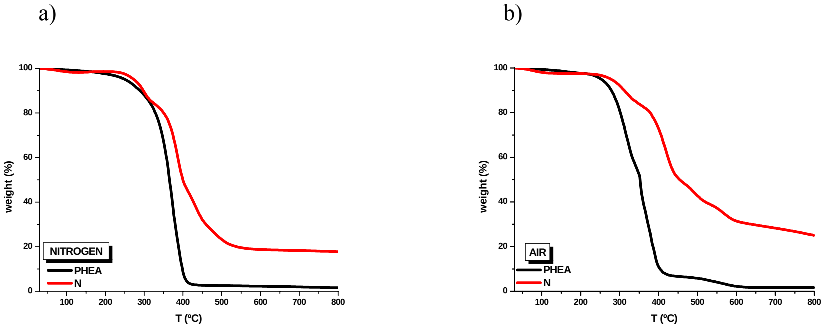
Then, these polymers were analysed by TGA. Table 4.2 displays the data from the curves including the onset temperature of weight loss (Tonset), temperature of maximum rate of weight loss (Tmax) and the char yields at 790ºC in both, nitrogen and synthetic air atmospheres.

Table 4.2 Thermal data of PHEA and polymer N in nitrogen and air atmospheres

Polymer	**DSC**	**TGA**					
	Nitrogen	**Nitrogen**			**Air**		
	Tg (ºC)	**Tonset[a] (ºC)**	**Tmax.[b] (ºC)**	**Char yield, 790ºC (%)**	**Tonset[a] (ºC)**	**Tmax.[b] (ºC)**	**Char yield, 790ºC (%)**
PHEA	-35	251	371	2	253	353	2
N	85	274	388	18	272	418	26

a) onset temperature of weight loss
b) temperature of the maximum rate of weight loss

Figure 4.4 TGA curves in nitrogen (a) and air (b) atmospheres of PHEA and polymer N



Starting PHEA starts to lose weight at about 250ºC and present a maximum rate of weight loss at about 370ºC, in nitrogen atmosphere (figure 4.4 a). The weight loss process show similar behaviour in air atmosphere (figure 4.4 b). In both cases, nitrogen and air atmospheres, the polymer shows a low char yield that is almost steady from 600 ºC. In case of modified PHEA the weight loss process starts at higher temperatures than in virgin polymer. Their TGA curves show more than one steps of weight loss in both, nitrogen and air atmospheres. The weight loss from approximately 270 ºC to 400 ºC is associated to the first step of thermal degradation process. In that range of temperature, it is generally accepted that the intumescent process develops.[99] When the temperature further increases, a second step is observed at about 450 ºC and is associated to oxidative degradation of already formed intumescent layer. It must be noted, that polymer N not only starts to lose weight later than starting polymer, but also it leads to a markedly higher char yield. This behaviour was already observed in chapter 2 for PVA modified with DPBC polymers (E2-E5). As for those polymers this behaviour can be explained by taking into account that aromatic moieties are introduced, which are thermally stable and trend to lead to charcoal residues. Moreover, the delay in the beginning of the weight loss process can be understand if we consider the lower content of hydroxyl groups presents in polymer N, which are responsible of dehydration reactions that initiate the degradation process. Also, in this case, it should be considered that a nitrogen moiety is present, which can release ammonia by heating, therefore acting as a foaming agent and giving rise in this way to a swollen material which acts as a protective layer. Thus, the TGA behaviour of modified PHEA seems to indicate that in the fire, this polymer will probably act as an intumescent system when mixed with ¨commodity¨ polymers.

4. Conclusions

To sum up, in this chapter we reported the preparation and characterization of a phosphorous-nitrogen containing polymers. This polymer leads to a significant char yield on TGA curves and a delay of the thermal degradation process is observed (with respect to starting material). Its thermal behaviour allows us to observe this polymer as a promising intumescent system on mixing with ¨commodity¨ polymers.

Chapter 5

Application of synthesized polymeric flame retardant additives

In this chapter we report the behaviour as flame retardant additives of the polymers obtained through the PVA chemical modification with BIC derivatives. Thus, we prepared and characterized polypropylene blends with these flame retardant additives. Their fire resistances as well as their thermal and mechanical properties were studied.

1. Introduction

Polymeric materials find growing applications in various fields of everyday life because they offer a wide range of relevant properties. As already mentioned in the general introduction, most of them are easily combustible involving a series of problems in their use.[2,3,4] To reduce their flammability a solution is to incorporate flame retardants in the polymer structure. [2,3] As well described in the chapter 1, FRs can be introduced in the polymer matrix trough a chemical modification of polymer (reactive FRs) or by blending (additive FRs).[4,5] Such as mentioned in the beginning of this thesis, our objective was to synthesize polymeric flame retardant additives, which, on blending with ¨commodity¨ polymers, can confer to them flame retardant properties. As already mentioned, the advantage of using polymeric additives, rather than conventional non-polymeric species, is that they show better resistance to extraction, migration and volatile-loss due to their high molecular weight.[3,7]

In this work various sets of polymers, which show promising action as flame retardant additives, were synthesized. In this chapter we propose to study the behaviour as polymeric flame retardant additives of one set of them; we choose for this study the set of polymers obtained by chemically modifying PVA with BIC derivatives (polymers A1, A5, B and C), synthesized and characterized in chapter 2. Below are shown the chemical structures of these polymers (scheme 5.1). Their degrees of modification are listed in table 5.1.

The choice of these structures is motivated by the different polarity expected to be shown by them, which should confer different compatibilities on blending with ¨commodity¨ polymers. PVA main chain is quite polar and also the BIC moieties. On the other hand, the aliphatic and aromatic ester groups will lead to a reduction of the polarity of the polymer. In this way, these polymers show a range of polarity.

Scheme 5.1

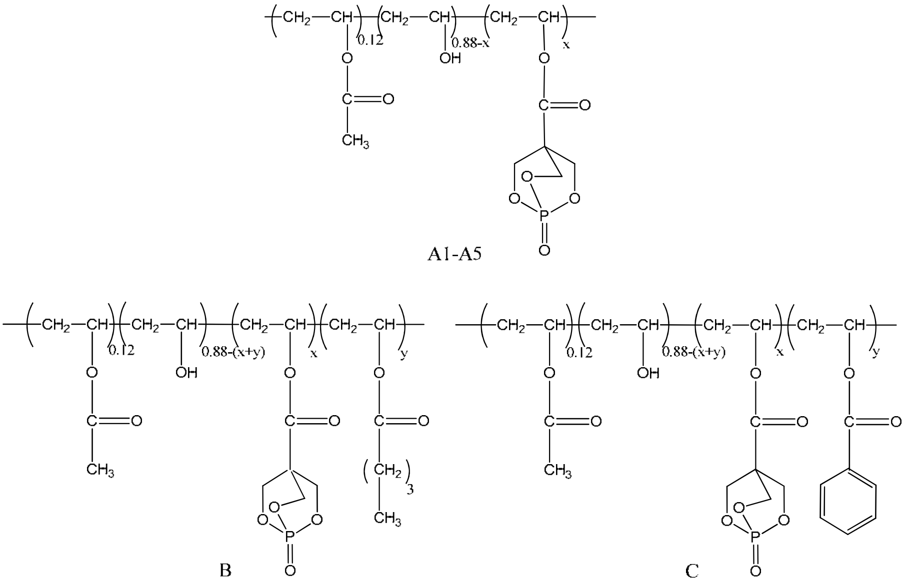


Table 5.1 Degrees of modification and phosphorous content of additives

Additive	% P Obtained from		Degree of modification		
	ICP-AES	^{13}C NMR	x[a]	x[b]	y[b]
A1	11.5	11.0	0.52	0.57	
A5	8.0	10.0	0.23	0.36	
B	5.7	6.3		0.27	0.44
C	7.6	10.0		0.48	0.16
A1'	11.0	11.0	0.47	0.46	
A5'	9.3	9.2	0.32	0.31	
B'	8.6	9.1		0.44	0.27
C'	8.7	10.6		0.51	0.1

[a] Obtained from %P determined by ICP-AES
[b] Obtained from ^{13}C NMR considering 12% of acetylated part

In this work we chose polypropylene (PP) as thermoplastic material to be ignifugated on blending with the above mentioned polymers. PP is one of the most used polymers in industrial area because of its low cost, ease of processing, as well as, high water and chemical resistance. It is used in several applications, for example housing, electronic pieces, wire and cables, automotive industry, and so on. For most of these uses the flame retardation is needed, since the virgin PP is high combustible. [124-127]

Thus, we prepared blends with PP and studied their flame retardancy by TGA and LOI techniques. Also, their compatibility and mechanical properties were studied by using several techniques, such as DSC, X-Ray diffraction, SEM, impact tests and tensile tests.

2. Experimental Section

2.1- Materials

Amorphous polypropylene (APP, M_w=14000, softening point= 155 ºC), low molecular weight isotactic polypropylene (LIPP, M_w=12000, mp= 157 ºC, softening point= 163 ºC), high molecular weight isotactic polypropylene (HIPP, M_w=580000, $T_m$onset= 160-165 ºC) and maleic anhydride grafted polypropylene (PP-g-MAH, containing ~0.6 wt. % of maleic anhydride) were purchased by Aldrich. Moplen type polypropylene EP1X30F (MPP, containing 2% wt. ethylene, M_w= 250000, melt flow at 230ºC= 7.00 - 10.0 g/10 min) was provided by Montell. All these polymers were used as received. Thermoplastic hydrocarbon resin (Necirès TR100, based on cycloaliphatic monomers with hydroxyl value 40 and acid value 7) was provided by Neville Chemical Europe BV, Netherlands. Polymeric flame retardant additives A1, A5, B and C, used for the preparation of the blends by dissolution, were synthesized as described in chapter 2. Polymeric flame retardant additives A1', A5', B' and C' were synthesized analogue to A1, A5, B and C, respectively but using a higher amount of reagent (5 g of PVA). Their degrees of modification and phosphorous contents are shown in table 5.1. Toluene (TOL, 99.5%, Scharlau) and 1,1,2,2-tetrachloroethane (TCE, 97 %, Aldrich) were used without further purification.

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2.2- Blends preparation

2.2.1- Blends prepared by dissolution

Preparation method: In a round bottomed flask provided with magnetic stirrer, we introduced selected polypropylene (PP) and appropriate solvent (100 ml). The mixture was heated under stirring up to 100 ºC for completely solubilise PP. Then, it was cooled down at 80ºC and corresponding amount of selected additive was added. The mixture was further driven to reflux and stirred for two hours. After that, the solvent was removed by rotary evaporation and the resulting material was dried under vacuum at 70ºC for 1h, and afterwards at room temperature for 24 h. In all cases, the amounts of PP and polymeric additive used were selected to prepare 5 g of blend. *Ca.* 1 g of blend was pressed in a preheated press at 165ºC and 2.5 atm for 1 hour in order to get bars (70 x 6 x 3 mm). Table 5.2 shows the blends prepared in this way.

Table 5.2 Blends prepared by dissolution

Blend	Polypropylene	Additive	Solvent	Additive content (% wt.)	Phosphorous content (% wt.)
B1	APP	A1	TOL	8.6	1
B2		A1		4.3	0.5
B3		A5		6.2	0.5
B4		B		8.8	0.5
B5		C		6.6	0.5
B6	LIPP	A1	TOL	8.6	1
B7		A1		4.3	0.5
B8		A5		6.2	0.5
B9		B		8.8	0.5
B10	HIPP	A1	TCE	8.6	1
B11		A1		4.3	0.5
B12		A5		6.2	0.5

2.2.2- Blends prepared by melt mixing

In order to establish the blend preparation conditions, a preliminary study was carried out by using a small scale extruder, namely Thermo Haake MiniLab (5 g capacity). Thus, the more convenient conditions were set out and applied to a conventional batch mixer of 50 g of capacity.

<u>Preparation method:</u> Blends preparation was carried out in a twin screw Brabender Plastograph EC mixer (Brabender GmbH & Co. KG, Germany) at 175 ºC with a screw rate of 40 rpm. The flame retardant additives and, in case, the compatibilizer (PP-g-MAH), were added after the polypropylene (MPP) melted, and the resulting blend was mixed additionally for 5 minutes. Then, the material was removed, left to cool and cut in pellets. The amounts of PP, compatibilizer and polymeric additive used were selected to prepare 50 g of blend. The pellets were hot-pressed under a pressure of 100 bar at 165 °C for 3 minutes, to obtain thin films (average thickness 150 μm), or at 175 ºC for 5 minutes, to obtain plates of 3 mm thickness. Thin films samples were used to perform FT-IR, TGA, DSC, X-Ray and tensile tests, while the plates were cut in bars and used for Charpy impact tests and LOI measurements. Blends prepared in this way are related in table 5.3.

Table 5.3 Blends prepared by melt mixing

Blend	**Additive**	**Additive content**[*] **(% wt.)**	**Compatibilizer content** [**] **(% wt.)**
B13	A1’	9.0	-
B14	A5’	10.8	
B15	B’	11.6	
B16	C’	11.6	
B13’	A1’	9..0	9.1
B14’	A5’	10.8	8.9
B15’	B’	11.6	8.8
B16’	C’	11.6	8.8

[*] In all cases the amount of polymeric additive used corresponds to a 1 % wt. of phosphorous in the final blend

[**] This amount corresponds to a relation of 10% wt. compatibilizer/ PP

2.3- Characterization techniques

Transmission FT-IR analysis was performed using a Nicolet Nexus FT-IR spectrophotometer. Spectra were collected using 32 scans at 4 cm^{-1} resolution, in the 400–4000 cm^{-1} range.

The number-average (M_n) and weight-average (M_w) molecular weights and intrinsic viscosity were estimated by a Gel Permeation Chromatography (GPC) in a Waters Alliance GPC V2000 system, equipped with a Refractive Index and viscosimetric detectors, using two consecutive Polymer Laboratories mixed columns with 1,2-dichlorobenzene (DCB) at 145ºC as eluent (0.8 mLmin^{-1}). The equipment was calibrated with polystyrene standards.

Thermogravimetric analysis (TGA) were carried out for blends prepared by dissolution on a Mettler TGA/SDTA851e/LF/1100 device at a heating rate of 10 ºC/min up to 800 ºC under nitrogen atmosphere (flow rate= 100ml/min). For the blends prepared by melt mixing, TGA analysis were performed on a Perkin Elmer Pyris Diamond TG-DTA thermogravimetic analyzer under the same conditions, but in this case prior to the heating ramp the samples were subjected to a 30 minutes isotherm at 80 ºC to remove the moisture that could be absorbed after the melt processing. The TGA analyses for compatibilized blends were performed under the same conditions as for the melt mixing blends but using a Mettler TGA/SDTA851e/LF/1100 device.

Differential scanning calorimetric (DSC) analysis were performed on a Mettler Toledo DSC Star 822e calorimeter at a heating/ cooling rate of 10 ºC/ min in a nitrogen atmosphere. T_g’s and melting enthalpies were calculated from second heating scans.

X-ray diffraction (XRD) experiments were performed using a Philips PW 1710 diffractometer with a rotating anode generator and a wide-angle power goniometer. The used radiation was not filtered Cu Kα, with 40 kV voltage and 20 mA intensity. The scan rate was 1°/min over a diffraction angle 2θ ranging between 2 and 40°. The estimation of degree of crystallinity for each sample was obtained from the ratio between the area under the crystalline peaks and the total area under the diffraction curve, with the different contribution of the crystalline and amorphous regions considered. The crystalline peaks separation from the amorphous part was made by the fitting of the curve through a program using Gaussian funtions.

Charpy impact tests were performed on a CEAST 6545 apparatus according to ASTM standard test method D256-06. A standard notch (3.5 mm long) was applied to the rectangular shaped rod sample with dimensions of 60 x 10 x 3 mm. The notch is in the opposite direction to the striking hammer.

Scanning electron microscope (SEM, Philips XL20) and environmental scanning electron microscope (ESEM-FEI Company, QUANTA 600) were used to examine the morphology of the cross-section of specimens subjected to impact tests. Samples were metallised before the observation with a gold–platinum mixture by means of a BalTec MED020 coater.

Tensile tests were performed on an Instron 5564 dynamometer equipped with a 100N load cell on test specimens prepared according to ASTM D882-02 standard test method. The samples of L_0 length = 22 mm, width 4 mm, present a ¨dog-bone¨ shape to make the necking of failure to occur in the centre of the specimen. The thickness (0.1-0.2 mm) of the samples was measured at different points for each sample and its average was introduced in the Instron Merlin calculation software. The tests were performed using 5-8 specimens for each sample. The measurements were carried out by a separation rate of 20 mm/min at room temperature after the samples were conditioned for 24 hours at 50% relative humidity (RH).

Limiting Oxygen Index (LOI) measurements were performed in vertical tests on a Stanton Redcroft FTA flammability unit provided with an oxygen analyzer, previously calibrated with polystyrene standard bars. The dimensions of the polymer bars were 70 x 6 x 3 mm prepared by hot pressing.

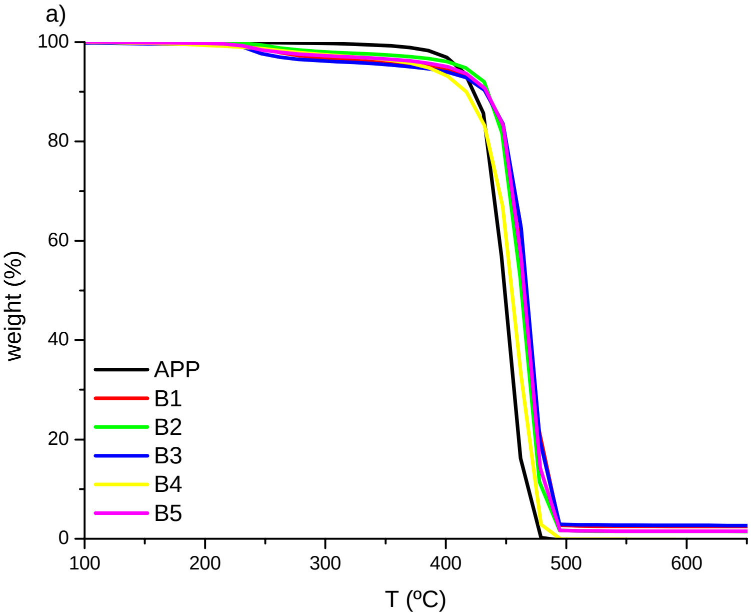
3. Results and discussion

As mentioned in the introduction part, in this chapter we intend to test the ignifugation of polypropylene with several phosphorous-containing PVA based flame retardant additives prepared in chapter 2. PP was chosen because of its wide range of application and high combustion character. The choice of BIC derivative polymeric additives (A1, A5, B and C), as flame retardants, was due to the different compatibility with PP expected to be shown by them.

As a previous study, we prepare blends of PP with flame retardant additives by dissolution, using commercially available polypropylenes with different characteristics.

First, we choose two low molecular weight polypropylenes, one amorphous (APP, M_w= 14000, softening point= 155 ºC) and one isotactic (LIPP, M_w= 12000, mp= 157 ºC, softening point= 163 ºC). The blends were prepared by dissolution in hot toluene (see table 5.2). The additive/PP ratio was chosen avoiding incorporating more than 10 % of additive, since high proportion of the additive will certainly negatively affect the mechanical properties of PP. This ratio was then chosen to obtain blends which contain 1% or 0.5% of phosphorous, in order to compare them. The resulting blends were first studied by TGA analysis under nitrogen atmosphere. The obtained results are shown in table 5.4 and figure 5.1 (a and b), which displays TGA curves of blends prepared from APP and LIPP, respectively. It can be seen that, in all cases, the blends show a small loss of weight at *ca.* 250 ºC. This loss of weight can be associated to the decomposition of the polymeric additives (mainly dehydration), by comparing these curves with TGA curves of virgin A1, A5, B and C (chapter 2). Moreover, in most of the blends, the main loss of weight process is slightly delayed with respect to starting PP. Also, in general terms, the blends present a small residue at high temperatures (600 ºC), while starting PP does not show residue at all from 500 ºC. Therefore, it seems that initial degradation of polymeric additives confer some flame retardancy to the PP blends, since the weight loss process delays and a certain char yield is formed at high temperature. It must be noted that blends based on polymer B (B4 and B9) those not completely follow these general trends. The blend B4 shows a Tonset close to virgin APP and a Tmax. close to the one shown by the other blends (B1, B2, B3 and B5), whereas blend B9 shows both, Tonset and Tmax, similar to those shown by the other blends. It must be also mentioned that, although TGA curves of B4 and B9 are quite reproducible in general (leading to the same Tonset and Tmax in different experiments), they are not reproducible when we consider char yield. In fact, they led to a range of char yield when we repeat the experiment. This results seems to indicate that a heterogeneous blend is formed, indicating that a low compatibility exists between polypropylene and additive B. Actually, in figure 5.1 only one of the TGA curves obtained for blends B4 and B9 is shown.

Figure 5.1 TGA curves of neat APP (a) and LIPP (b) and their blends in nitrogen atmosphere



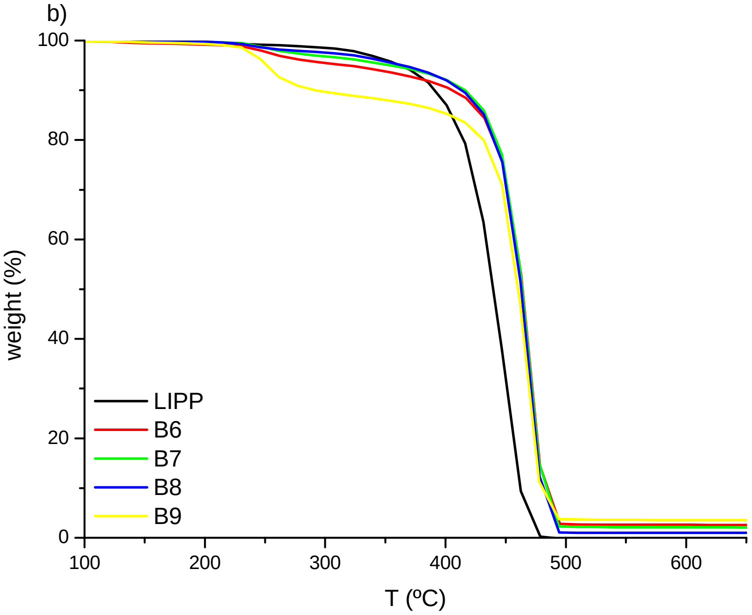


Table 5.4 Thermogravimetric data of virgin APP, LIPP and their blends

Sample	Additive	Phosphorous content (% wt.)	Tonset [a] (ºC)	Tmax. [b] (ºC)	Char yield at 600 ºC (%)
APP			403	446	0
B1	A1	1	421	462	2.4
B2	A1	0.5	419	461	1.5
B3	A5	0.5	422	463	2.7
B4	B	0.5	403	462	0-0.7
B5	C	0.5	420	463	1.5
LIPP			364	446	0
B6	A1	1	403	463	2.7
B7	A1	0.5	402	461	2.2
B8	A5	0.5	396	462	1.2
B9	B	0.5	405	462	1.4-3.5

[a] Onset temperature of main weight loss process
[b] Temperature of the maximum rate of weight loss

To test the flame retardancy of the obtained blends, it was necessary to carry out LOI measurements. As already mentioned in the introduction, LOI measures the ease of extinction of materials as the minimum percentage of oxygen in an oxygen/nitrogen atmosphere that will just sustain the combustion in a candle-like configuration of a top-ignited vertical test specimen. Therefore, bars of 70x 6x 3 mm suitable for LOI measurements were prepared from virgin APP, LIPP and their blends by hot pressing. Unfortunately, in no case was possible to obtain a LOI value. This was due to the fact that all these bars melted easily in contact with the flame. Those, the specimens were not able to initiate the combustion, because they dripped heavily, not supporting the flame and leading to its quenching.

Taking into account this inconvenience, we decided to prepare blends using a polypropylene with a higher molecular weight and melting point (HIPP, M_w= 580000, melting range (onset)= 160-165ºC), which should show less dripping on burning. The HIPP blends were prepared by dissolution in hot 1,1,2,2-tetrachloroethane (table 5.2). In this case, 1,1,2,2-tetrachloroethane was used instead of toluene due to HIPP insolubility in the latter solvent. As for previous set of blends, the additive/PP ratio was chosen avoiding incorporating more than 10 % of additive, obtaining in this way blends which contain 1% or 0.5% of phosphorous. The obtained blends were studied by TGA and LOI techniques.

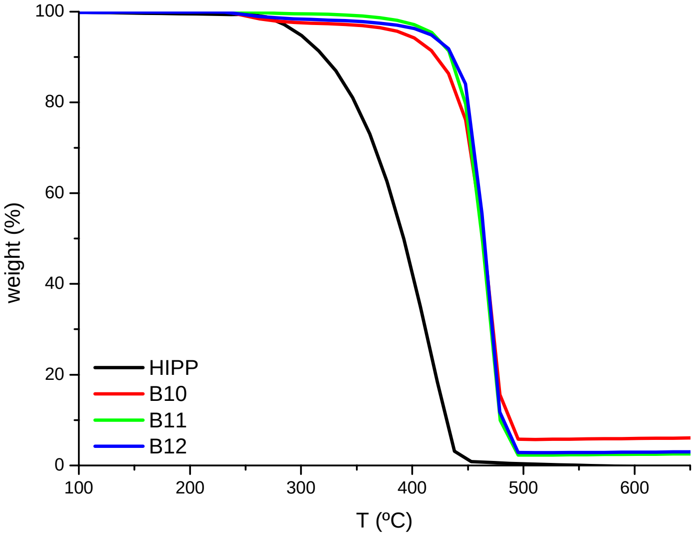
The TGA curves, performed in nitrogen atmosphere, are shown in figure 5.2. and the TGA data are collected in table 5.5. Also in this case, it was observed the small loss of weight at *ca.* 250 ºC, that was associated to polymeric additives decomposition. Moreover, in the obtained blends the main weight loss process is also delayed (›100 ºC) with respect to virgin HIPP, and the blends also show char residue at high temperature, while the starting HIPP is almost exhausted from less than 500 ºC. However, in this case there exists some differences with respect to previously studied blends (table 5.4). First, loss of weight at *ca.* 250 ºC is smaller than for previous set of blends. Also, as indicated above, the delay of weight loss process is higher and also the char yield at 600 ºC; for example, compare the blend B10 with blends B1 and B6. Therefore, in this case it seems that the flame retardancy conferred by the additive is greater, may be due to a better compatibility.

Table 5.5 Termogravimetric results of neat HIPP and its blends

Sample	Additive	Phosphorous content (% wt.)	Tonset[a] (ºC)	Tmax.[b] (ºC)	Char yield at 600 ºC (%)
HIPP			297	415	0
B10	A1	1	408	463	6.0
B11	A1	0.5	416	463	2.5
B12	A5	0.5	421	463	2.9

[a] Onset temperature of main weight loss process
[b] Temperature of the maximum rate of weight loss

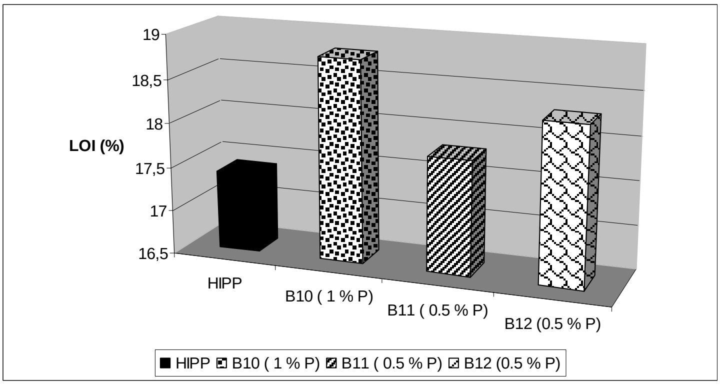
Figure 5.2 TGA curves of neat HIPP and its blends in nitrogen atmosphere



In case of these blends, LOI measurements were possible to be performed. As can be seen in figure 5.3, LOI values increased slightly in all these blends with respect to non-additivated HIPP. Therefore, also LOI values indicate that certain flame retardancy is conferred by additive A1 and A5 to HIPP.

The highest LOI value was obtained for the blend containing the highest phosphorous content (B10). Also, it can be observed that, using the same content of phosphorous, but two different additives, the LOI value is higher when the blend contains more hydroxyl groups (B12). This result is in agreement with TGA data (see table 5.5): B12 shows a higher Tonset and also a higher char yield with respect to B11. All these observations can be understood if we consider that the first step of weight of loss of the polymeric additives is dehydration.

Figure 5.3 LOI values of neat HIPP and its blends obtained by dissolution



Based in all these results, we proceed with the PP ignifugation by melt mixing. The melt processing is a blending technique which, in principle, could lead to a better dispersion of the polymeric flame retardant additive into the PP matrix; therefore, homogeneous blends can easier be obtained. First, we choose as a polypropylene to ignifugate HIPP, which was already used in the preparation of blends by dissolution. In this case we used polymeric additives A1', A5', B' and C' which have an analogue structure as A1, A5 B and C respectively, but different comonomer composition (see scheme 5.1 and table 5.1). These additives have been prepared as reported for A1, A5, B and C in chapter 2 but using a higher amount of reagents. The additive/PP ratio was chosen to obtain blends which contain 1% of phosphorous in order to compare them. To establish the blending conditions, a preliminary study was carried out by using a small scale twin screw extruder (5 g capacity). Blends preparation was tested by using different temperature, screw rotation rate and time. Unfortunately, we could not obtain a suitable blending, due to the high viscosity of melted HIPP at the used temperature (170-180 ºC). When we increased the temperature, in order to get a more fluid sample, it seems that the polymer started to degrade. Therefore, we tried to improve the processability by adding 5-10% by weight of a hydrocarbon resin (TR 100), which can act as both compatibilizer and softener; but the viscosity of the mixture was still very high.

Taking into account this inconvenience, we decided to prepare blends by using a less viscous polypropylene. The polymer chosen was a Moplen type polypropylene (MPP, M_w= 250000), which has a lower molecular weight and contain 2 % wt ethylene, thus showing a higher flexibility than HIPP. Moreover, Moplen type PPs have been used in different application in automotive industry.[128-131]

For the preparation of the blends with the small scale extruder, different temperature (165-200 ºC), screw rotation rate (10-50 rpm) and time (5-10 min) were tested. It was observed that at low temperature, low screw rotation rate and short time highly heterogeneous blends were obtained, which show the presence of portions of not well dispersed additive. On the other hand, at high temperature, high screw rotation rate and long time we got an apparently homogenous blend, but the polymer appeared starting to degrade. Thus, as the best conditions we choose a medium temperature (175 ºC), short time (5 min) and high screw rotation rate (40 rpm) and then a suitable blend seemed to be obtained.

Once the best blending conditions were established with the small scale extruder, we applied them to a conventional batch mixer (50 g capacity). Thus, the MPP was blended with A1’, A5’, B’ and C’ at 175 ºC, 40 rpm for 5 min. The obtained blends were removed and cut in pellets after cooled down. The pellets were then hot pressed, in order to obtain thin films or plates, useful for further characterization. As mentioned above, for each blend, the amount of the

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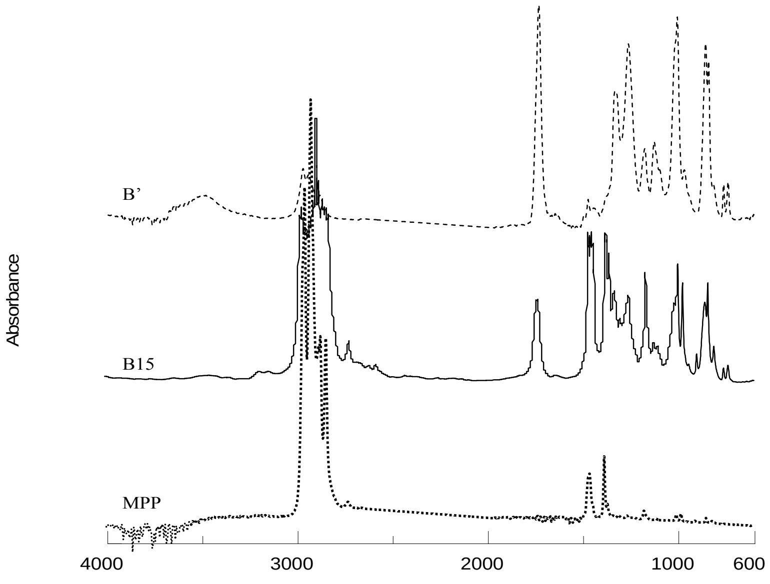
polymeric additive was selected in order to get a phosphorous content of 1% wt. In the table 5.3 the blends formulations are listed.

In order to explore the possibility that MPP and/or the polymeric additives partially degrade during the blending process, the obtained blends were characterized by FT-IR and GPC.

The FT-IR spectra of all these blends show signals coming from MPP and the corresponding additive. The main MPP bands appear at 3000-2850 cm^{-1} (C-H stretching) and 1500-1350 cm^{-1} (C-C stretching). All the blends show signals due to additive at 3600-3400 cm^{-1} (OH), 1730 cm^{-1} (C=O) and 856 cm^{-1} (skeleton vibration of caged bicyclic phosphate). It must be noted that no additional bands appear in the blend with respect to virgin MPP and additive. This suggests that no degradation occurred during the blending process, at least in an important extent. As an example, figure 5.4 shows the spectrum of virgin MPP, one of the blends (B15) and the corresponding polymeric additive (B').

Figure 5.4 FT-IR spectrum of virgin MPP, one of the blends (B15) and the corresponding additive (B')



GPC analysis were performed in 1,2-dichlorobenzene (DCB) at 145 ºC. The obtained data are collected in table 5.6. For the sake of comparison, GPC analysis was also performed on an unprocessed (virgin) MPP and a sample of MPP that was processed analogously to the blends, but that contains no additive. The polydispersity (M_w/M_n, where M_w is weight-average molecular weight and M_n is number-average molecular weight) of the unprocessed MPP is rather high, typical of a PP synthesized in the presence of Ziegler-Natta catalysts.[132] As can be seen the molecular weight, as well as the polydispersity of processed MPP are lower than that of unprocessed polymer pellets. Thus, melt-mixing processing of neat MPP brought about slight degradation of the polymer. This is consistent with ‘‘controlled PP degradation’’ principles, where the highest molecular weight chains are statistically more likely to undergo radical-mediated scission.[133]

Although the polymeric additives were rather insoluble in DCB, when they were incorporated into the blends, a small fraction seems to be dissolved in the solution subjected to GPC characterization. Nevertheless, as can be observed from figure 5.5 and table 5.6, the GPC curves of most of the blends are similar to that of neat processed MPP, leading to similar *Mw* and polydispersity. Moreover, in general, neither peaks related to the presence of the additive, nor bimodal patterns of the molecular-mass curves were observed. This finding suggests that the polymeric additives could interact with the polypropylene phase, forming physical or chemical associates having a hydrodynamic volume similar to that of plain MPP, which are not separated during the elution run. Blend B16 is an exception to this general behaviour, since its GPC chromatogram shows a minor portion of higher molecular weight chains.

These findings suggest that the polymeric additives could interact with the polypropylene phase, forming physical or chemical associates having a slightly

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[132] Rodionov, A.G.; Domareva, N.M.; Baulin, A.A.; Ponomareva, Ye.L.; Ivanchev, S.S. Polym Sci USSR **1981**, 23, 1724-1732.

[133] Tzoganakis, C.; Vlachopoulos, J.; Hamielec, A.E. Polym Eng Sci **1989**, 29, 390-396.

larger hydrodynamic volume than that of plain MPP, which are not separated during the elution run. This could also explain the increase in M_w observed for B16, in which the bulky pendant substituent can modify the size of the dissolved polymer adduct, thus yielding increased values of molecular weight.[134]

Table 5.6 GPC data of the neat MPP and its blends

Sample	Additive	M_w[a]	M_w/M_n[b]	M_{peak}[c]
Unprocessed MPP	-	254000	6.8	159000
Processed neat MPP	-	218000	4.5	136000
B13*	A1’	218000	4.8	139000
B14*	A5’	229000	5.2	144000
B15*	B’	235000	4.8	145000
B16*	C’	278000	4.6	159000

* All these blends contain 1% of phosphorous
[a] weight- average molecular weight
[b] polydispersity of polymer
[c] peak of GPC curve

A further confirmation of this hypothesis can be obtained by the Mark-Houwink-Sakurada (MHS) plots, Fig. 5.5(b), in which the intrinsic viscosity *versus* M_w is reported. MHS plots are widely used for the analysis of polymer structure, as they reflect structural changes in the polymer, such as branching and chain rigidity[135] The slope, described by the Mark-Houwink exponent, can vary between 0 for solid spheres and 2 for rod-shaped structures.

From the figure, it is observed that while all samples showed comparable curve slope values of about 0.71 (typical of linear flexible chains in good solvents), processed neat PP sample displayed higher values of viscosity throughout the range of M_w values analyzed. This suggests that polypropylene molecules in the blends present chain branching[136], due to the interaction of MPP with the modified PVAs. This can be due to some radical reactions that may occur between them. Usually, the radical formation occur in the presence of an

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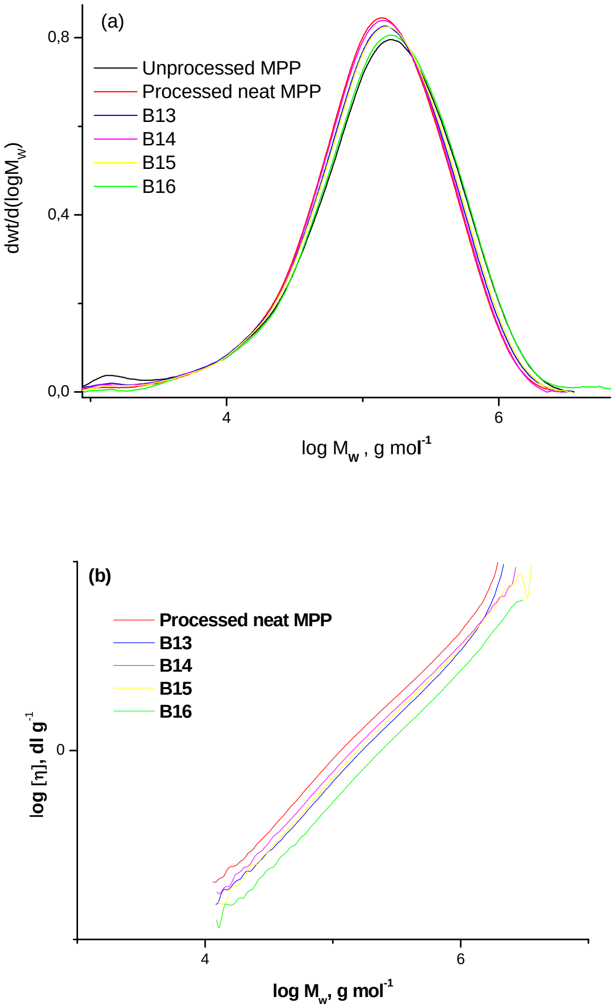
[134] Parent, J.S.; Bodsworth, A.; Sengupta, S.S.; Kontopoulou, M.; Chaudhary, B.I.; Poche, D.; Cousteaux, S. Polymer **2009**, 50, 85–94.

[135] Mendrek, B.; Trzebicka, B. Eur Polym J **2009**, 45, 1979–1993.

[136] Zhang, C.; Zhou, Y.; Liu, Q.; Li, S.; Perrier, S.; Zhao, Y. Macromolec **2011**, 44, 2034-2049.

initiator[137,138], which in this case may be played by metallic parts of the equipments used for the processing. Also, we should take into account, that a small part of PVAs additives may undergo dehydration reactions, leading to double bond formation, which can add polypropylene free radicals that could be formed by heating.

Figure 5.5 GPC chromatograms (a) and Mark-Houwink-Sakurada plots (b) of the neat MPP and its blends



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[137] Kaur, I.; Gautam, N.; Deepika Khanna, N. J Appl Polym Sci **2008**, 107, 2238–2245.
[138] Jang, J.; Lee D.K. Polymer **2004**, 45, 1599–1607.

In order to study the compatibility of the blends, DSC, X-Ray diffraction and SEM analysis were carried out.

The DSC (see table 5.7) thermogram of starting processed MPP (melt mixed analogously to the blends) shows a melting endotherm at 143-161 ºC and a Tg at -10 ºC. The DSC curves of blends revealed that the Tg and melting process of virgin polypropylene is not apparently affected so much with the addition of flame retardant additives, indicating the absence of interactions such as co-crystallization within the polypropylene phase.[139] All this seems to indicate a poor compatibility of flame retardants with polypropylene. In principle, if the blend is rather incompatible, the Tg of polymeric additives is expected to be seen at the temperature collected in table 5.7; however, the small proportion of additive added into the blend, probably avoid the observation of these Tg's.

Table 5.7 Differential scanning calorimetry data[*]

Sample	Tonset[b] (ºC)	Tpeak[c] (ºC)	[d]ΔH_1(J/g)	[e]ΔH_2 (J/g)	Tg[f] (ºC)	$Tg_{aditive}$[g] (º C)
MPP[a]	144	154	83	83	-10	
B13	142	153	73	80	-9	83
B14	144	154	70	78	-13	71
B15	143	154	81	89	-10	45
B16	143	155	73	80	-9	Not observed

[*] The calorimetric data were recorded from the second heating scan
[a] This sample was extruded analogously to the blends, but contains no additive
[b] Onset temperature of melting endotherm
[c] Peak temperature of melting endotherm
[d] Melting enthalpy per gram of blend
[e] Melting enthalpy per gram of MPP
[f] glass transition temperature
[g] glass transition temperature of neat polymeric additives

The degree of crystallinity of MPP and its blends was calculated by using $\Delta H^{o}_{melting}$ =209 J/g, reported as the melting enthalpy of 100 % crystalline PP (see table 5.8).[140] As can be seen, the degree of crystallinity of MPP remained unaltered when blended with polymeric flame retardant additives, with the exception of blend B15 where a slight increase in crystallinity was observed.

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[139] Kontopoulou, M.; Wang, W.; Gopakumar, T.G.; Cheung, C. Polymer, **2003**, 44, 7495-7504.

[140] Avella, M; Martuscelli, E.; Raimo, M.; Partch, R.; Gangolli, S. G., Pascucci, B. J Mater Sci **1997**, 32, 2411-2416.

Table 5.8 Degree of cristallinity of MPP and its blends

Sample	Degree of cristallinity determined by DSC	Degree of cristallinity determined by X-Ray
	X_c (%)*	X_c (%)
MPP**	40	37
B13	38	43
B14	37	37
B15	43	46
B16	39	41

* Degree of cristallinity obtained from ΔH_2.
** This sample was extruded analogously to the blends, but contains no additive.

X-ray diffraction analysis was performed on standard samples of virgin polypropylene and samples blended with polymeric flame retardant additives under the conditions described in the experimental section. The results, as seen in figure 5.6, show that only the monoclinic α form was present in all cases, because there are no peaks at 2θ=16.1° associated with β form (hexagonal).[141] This is in agreement with the fact that the commercial samples of isotactic polypropylene, prepared with the traditional heterogeneous Ziegler-Natta catalysts, generally are in the stable α form.[142]

The degree of crystallinity for each sample was obtained also by X-Ray diffraction as detailed in the experimental part. In this approach, the amorphous contribution to the scattering was taken into account through a broad diffraction band. From the table 5.8, where are related the degrees of crystallinity obtained from X-Ray diffraction and DSC analysis, respectively, it could be observed, that the results obtained by both techniques are comparable. Moreover, the blends do not present significant changes compared to virgin PP, with the exception of blend B15, already mentioned. It could be that the aliphatic additive, while being not miscible, had little bit more compatibility with the matrix than the others, so that the additive particle could act as heterogeneous nucleating agents for the PP molecules.

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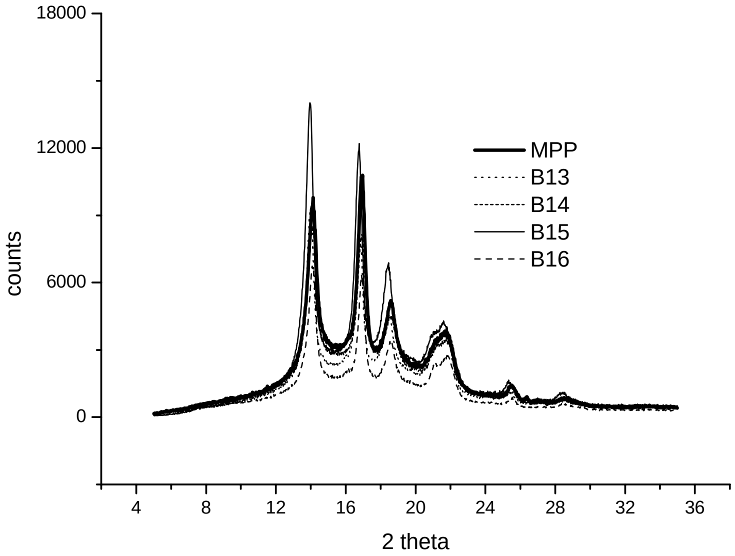
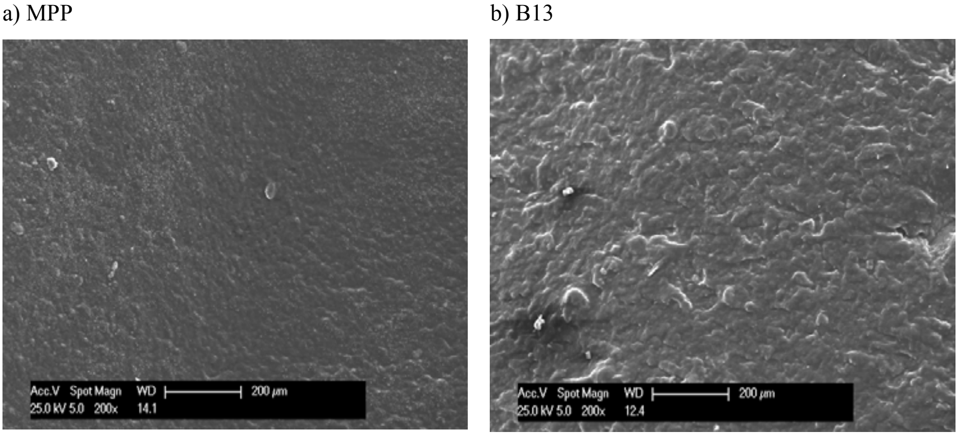
[141] Yamaguchi, M.; Miyata, H.; Nitta, K-H. J Appl Polym Sci **1996**, 62, 87-97.
[142] De Rosa, C.; Auriemma, F.; Spera, C. Macromol Symp **2004**, 218, 113-123.

Figure 5.6 X-Ray diagrams of virgin MPP and its blends

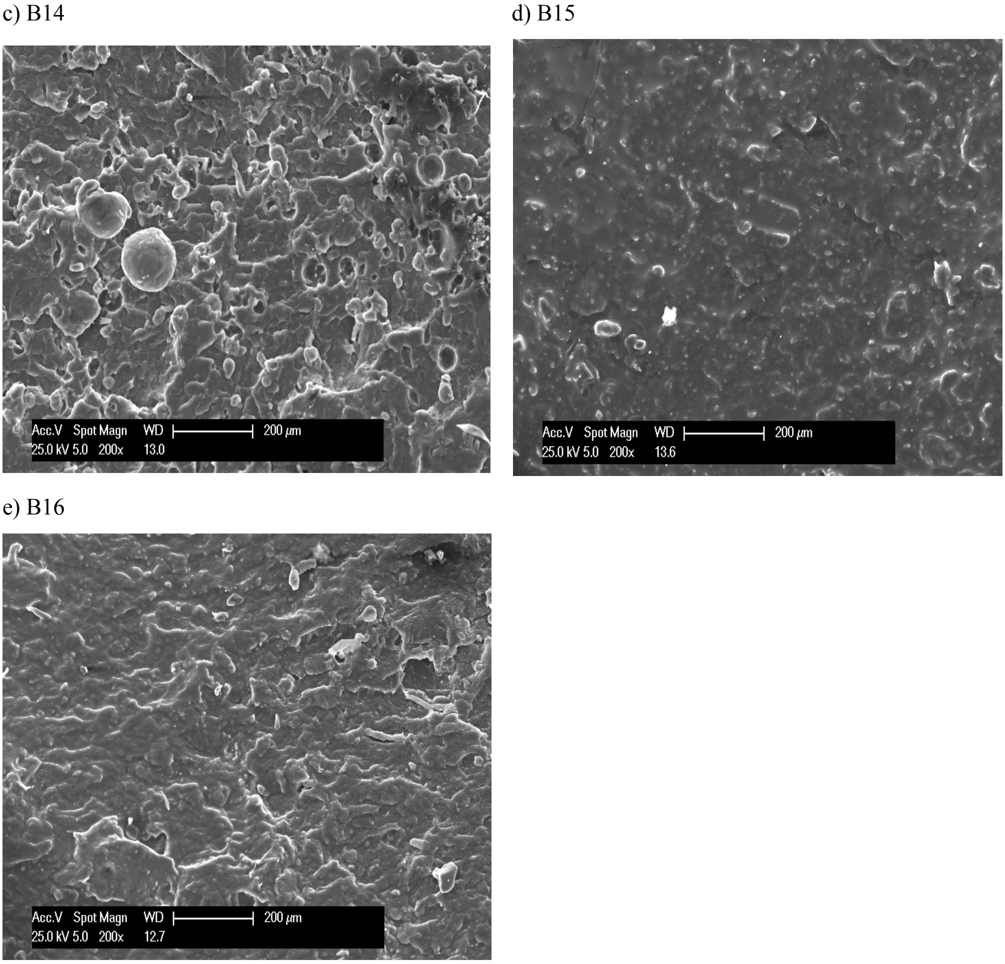


The morphology of the blends and virgin MPP (melt mixed analogously to the blends, but that contains no additive) was studied by SEM observation of the fracture surfaces of samples subjected to impact tests. The results are presented in figure 5.7.

Figure 5.7 SEM micrograph of the fracture surface of virgin MPP and its blends


a) MPP

b) B13



c) B14

d) B15

e) B16

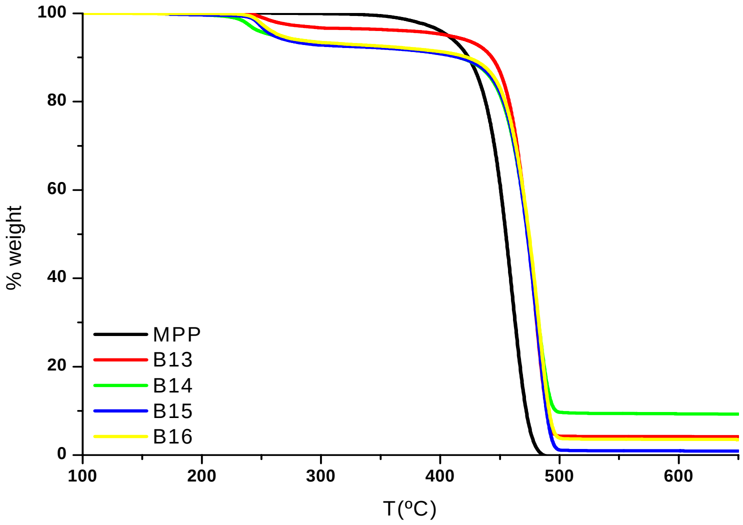
As seen in figure 5.7 a), the virgin MPP presents a smooth and homogenous surface, evidencing a britle fracture of the sample. Figure 5.7 b) and d) are similar to virgin MPP, however small particles of additives well dispersed and covered by a layer of the polypropylene matrix could be observed. In figure 5.7 c) and e) the additive particles are poorly dispersed into the MPP matrix, thus indicating a strong incompatibility between the polymers. Therefore, it must be concluded that although all the blends are incompatible the dispersion of polymeric additives is acceptable in blends B13 and B15 and not in blend B14 and B16. However, it should be noticed that the latter samples showed a more ductile fracture, as evidenced by the appearance of multiple fracture planes.

It must be noted that, regarding the flame retardancy of a blend in general the low compatibility is not a problem; however, this can negatively affect the mechanical properties of the final blend.

Further, we will discuss the flame retardancy behaviour of the prepared blends. This study was performed by TGA and LOI measurements.

Figure 5.8 shows the thermogravimetric curves of neat MPP (melt mixed analogously to the blends, but contains no additive) and its blends in nitrogen atmosphere. These curves were obtained by heating the samples at 10ºC/min. From the curves it can be observed that the neat MPP showed one step of weight from 400 to 500ºC, while all the blends displayed an additional degradation step in the range 200-300ºC. This additional weight loss process can be attributed to the decomposition of the additives, starting by dehydration reaction.

Figure 5.8 Thermogravimetric thermograms of virgin MPP and its blends



This step appears at slightly lower temperature in B14 with respect to the other blends, probably due to its higher content in –OH groups. Table 5.9 shows the onset temperature of weight loss and the temperature of the maximum rate of weight loss for both steps. Also the char yield at 600 ºC is indicated.

As can be seen in figure 5.8 and table 5.9, the second weight loss step of the blend, which is related to MPP degradation, is slightly delayed with respect to virgin MPP. Therefore, it seems that the dehydration of additives leads to a charred layer which can protect polypropylene from the degradation. From this point of view, no differences can be observed between the different additives used.

At the end of the second degradation step neat MPP was completely volatilized at 500 ºC, whereas all the blends lead to a certain residue at 600 ºC. The highest amount of residue was associated to B14, as higher content of -OH groups favoured charring. Due to lower amount of -OH groups, B13, B15 and B16 lead to a lower char yield. B15 shows a very low char yield, probably due to the aliphatic nature of some of the side groups introduced.

Therefore, it seems that, as already discussed for the blends prepared by dissolution, also in this case the polymeric additives confer flame retardancy to the blends prepared by melt mixing.

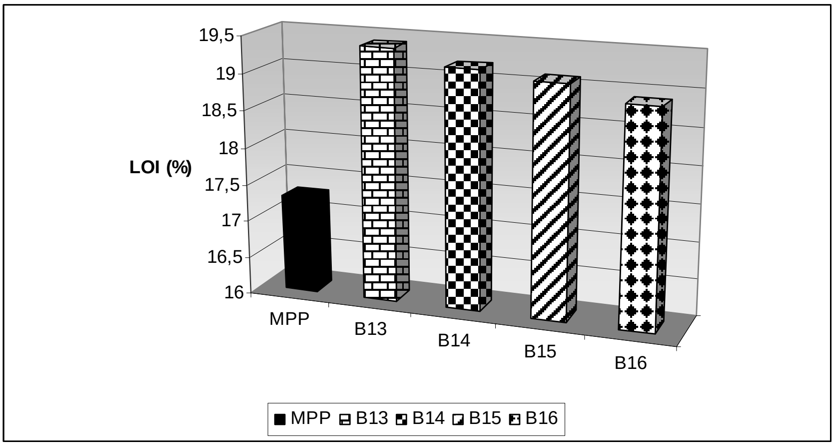
Table 5.9 Thermogravimetric results of neat MPP and its blends[*]

Sample	**Additive**	**Step 1**		**Step 2**		**Char yield at 600 ºC (%)**
		Tonset[a] (ºC)	**Tmax.[b] (ºC)**	**Tonset[a] (ºC)**	**Tmax[b] (ºC)**	
MPP				403	460	0
B13	**A1'**	237	246	432	480	4.2
B14	**A5'**	225	240	429	481	9.3
B15	**B'**	236	249	431	481	0.9
B16	**C'**	233	249	432	483	3.5

[*] All these blends contain 1 % wt. of phosphorous
[a] Onset temperature of weight loss process
[b] Temperature of the maximum rate of weight loss

In figure 5.9 LOI value of neat MPP and its blends are shown. As can be seen, even with a small content of phosphorous (1% wt.), LOI values increased (to some extent) comparing with the virgin polypropylene. It was also observed a reduction of dripping during the burning for additivated polypropylene. Thus, also LOI value indicate that flame retardancy is conferred by additive A1', A5', B' and C' when they are melt mixed with MPP.

Figure 5.9 LOI values of neat MPP and its blends obtained by melt mixing



Finally, studies of the mechanical properties of the blends prepared by melt mixing were performed. This is interesting in order to see whether the mechanical properties can be negatively affected by the addition of flame retardant additives, especially if we consider that the blends seem to be poorly compatible. For this study, tensile tests and impact tests were carried out.

Tensile test is a fundamental materials test in which a sample is subjected to uniaxial stress until failure. These tests were performed in a single tension mode at an elongation rate of 20 mm/min. The results, collected in table 5.10, display the tensile modulus, the yield point, the rupture stress and the rupture strain. The tensile modulus is a measure of the stiffness of an elastic material; it is defined as the ratio of the uniaxial stress over the uniaxial strain in the range of stress in which Hooke's law holds. The yield point is the stress at which a material begins to deform plastically. The rupture stress and the rupture strain correspond to these magnitudes, when a sudden complete failure of the specimen occurs.

Table 5.10 Tensile tests results

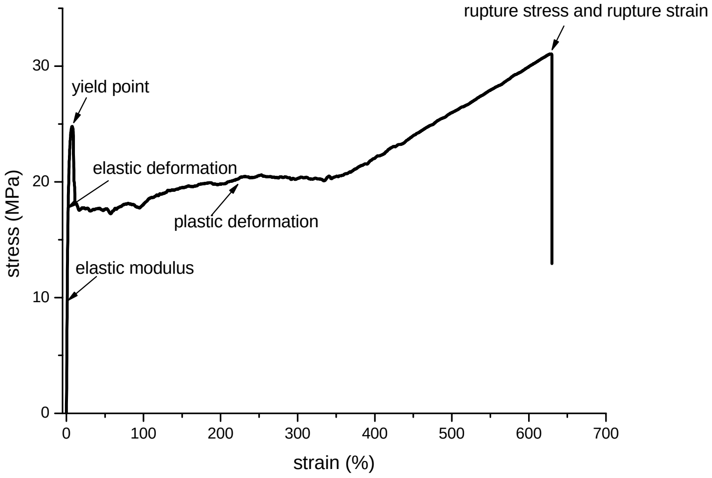
Sample	Additive content (% wt.)	Modulus (MPa)	Yield point (MPa)	Rupture stress (MPa)	Rupture strain (%)
MPP		970±0.2	25±1.9	32±5.8	625±166.7
B13	9.0	1063±0.3	26±1.0	21±1.1	12±2.5
B14	10.8	1135±0.2	21±1.3	19±1.2	5±0.8
B15	11.6	1027±0.2	22±0.9	19±0.5	16±3.9
B16	11.6	1032±0.2	17±2.9	16±2.4	4±1.2

Regarding the modulus and the yield point, the values obtained in case of blends do not vary significantly with respect to the one of the starting MPP. Thus, the blends show a similar behaviour as MPP and it seems that the addition of the flame retardant does not affect so much these mechanical properties. On the other hand, the rupture stress and mainly the rupture strain decrease respect to the starting polypropylene. Therefore, the elastic behaviour is not observed to be altered by the addition of flame retardant, whereas the plastic behaviour is markedly altered. It can be mentioned that the blends B13 and B15 show a slightly better rupture strain respect to the other blends, which is probably due to a better compatibility between the corresponding additive and the matrix, as observed by SEM micrographs.

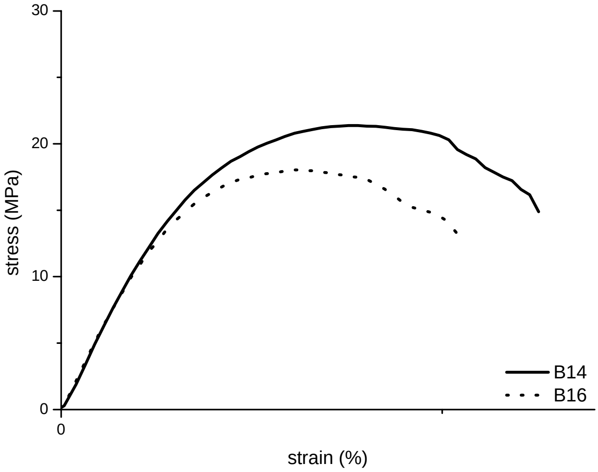
In figure 5.10 tensile stress–strain curves of the virgin MPP and two of its blends are shown. Virgin MPP was elongated up to 625 % of the tensile strain without fracturing (figure 5.10.a), and its behaviour showed the typical characteristics for ductile polymers: stress whitening followed by necking and drawing. Brittle behaviours were observed in the blends; here, the tensile specimens failed right after the linear elastic region of the stress–strain curves (figure 5.10.b). This behaviour can be due to the poor interfacial interaction between matrix and flame retardant additives, while GPC results showed that polypropylene molecular weight was not affected by the presence of the additives. In order to explain this result, it must be pointed out that the flame retardant additives are not well blended, but only simple dispersed on the matrix. It is known that strength and elongation at break for filled systems depend on the state of the polymer-particle interface, because when the adhesion between filler and matrix is poor, a reduced stress transfer occurs at the interface, facilitating void opening and crack propagation.[143,144]

Figure 5.10. Tensile stress–strain curves

a) MPP



b) B14 and B16



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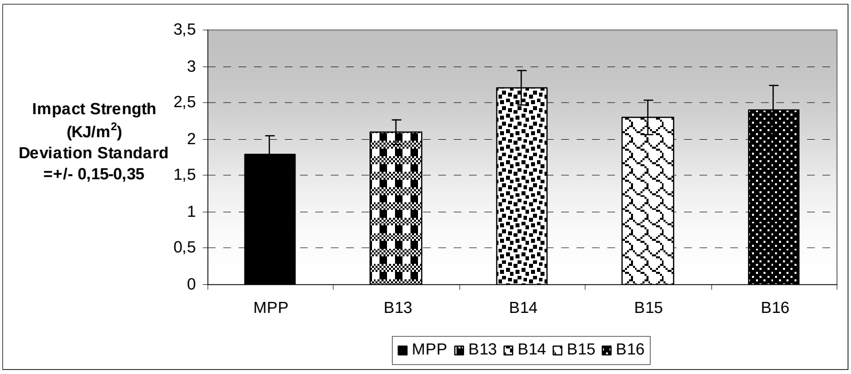
[143] Ratanakamnuan, U.; Aht-Ong, D. J Appl Polym Sci **2006**, 100, 2717-2724.

[144] Persico, P.; Ambrogi, V.; Carfagna, C.; Cerruti, P; Ferrocino, I.; Mauriello, G. Polym Eng Sci **2009**, 49, 1447–1455.

In summary it can be concluded that from the point of view of the elastic behaviour of the material, the properties are not affected on adding the flame retardant additives, while the plastic behaviour of the material is observed to be markedly altered. It must be noted that in most applications where PP must be ignifugated, like for example automotive industry, the elastic behaviour of the material is crucial, while the plastic behaviour is not. Therefore, used additives do not affect so negatively the applicability of PP, while they increase slightly its flame retardancy. However, the poor compatibility between matrix and additives is a problem from the point of view of plastic behaviour and would be desirable to improve it.

As mentioned the PP- based blends are widely used. In many cases a good resistance to physical impulsive shocks is needed. For example, in automotive industry, where the PP forms part of many items, the impact resistance is very important (especially in the vehicle crashes). Thus, it is convenient to perform the study of the impact tests for the materials where the toughness is required. The Charpy impact test is an ASTM standard method of determining impact strength. Generally a notched sample is used to determine it. The sample is placed on a support that holds extremities and is struck by a hammer on the opposite side of the notch that makes his swing in the plane of the same notch. From the energy absorbed by the sample, its impact strength is determined. The results are reported as energy lost per cross-sectional area unit at the notch. The impact strength of starting MPP and its blends are related in figure 5.11. In all blends slightly higher values of the impact strength were obtained. This can be associated with the poor compatibility. For example, as can be seen from the figure 5.11, the blends B14 and B16 shows the highest impact strength which is in concordance with the SEM micrograph, which showed a more ductile fracture, even though the worst compatibility was observed in case of these blends. As already mentioned for the tensile tests, this can be explained by considering that the polymeric additives are only dispersed into the matrix on lengthscales of tenths of microns, which make the additive particles acting as fillers, and conferring greater toughness to the matrix even with poor filler-to-matrix interaction. In fact, the impact energy is partly dissipated in a mechanism, where the crack advancement is hindered by the presence of the stiffer additive particles. Crack deflection and twisting occur as a growing crack encounters the matrix-particle interfaces, which act primarily ahead of the crack tip to impede crack advance.[145]

Figure 5.11 Impact results of MPP and its blends



Therefore, the obtained blends do not affect the properties of starting MPP from elastic point of view of the material; actually the elastic modulus is slightly improved. Also the flame retardancy is slightly improved. The main limitation is that the samples are not compatible.

Thus, we intend to compatibilize these systems by adding into the blending some compatibilizing agents. Regarding them, maleic anhydride (MAH), diethyl maleate (DEM), acrylic acids (AA) grafted systems were reported by several researchers to act as compatibilizers for thermoplatics.[146-148] E. Passaglia et. al. showed that by grafting diethyl maleate and maleic anhidryde onto styrene-*b*-(ethylene-*co*-1-butene)-*b*-styrene triblock copolymer (SEBS) a good

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[145] Ritchie, R.O. Nat Mater **2011**,10, 817–822.

[146] Passaglia, E.; Ghetti, S.; Picchioni, F.; Ruggeri, G. Polymer **2000**, 41, 4389–4400.

[147] Ma, Z-L.; Zhao, M.; Hu, H-F.; Ding, H-T.; Zhang, J. J Appl Polym Sci **2002**, 83, 3128–3132.

[148] Chiang, W-Y.; Hu, C-H. Eur Polym J **1996**, 32, 3, 385-390.

compatibilizer was obtained for polyamide blends. Z.-L. Ma et. al showed that α-methacrylic acid grafted polypropylene (PP-g-MAA) can act as compatibilizer for polypropylene systems. The polypropylene grafted by maleic anhidryde (PP-g-MAH) was also reported, by K. Oksman et. al.[149] and many others[150-152] as a good compatibilizer between PP and polar fillers. Thus, we chose the PP-g-MAH as compatibilizer for the blends, since our additives are very polar. As it is well known, a compatibilizer affects the compatibility between two phases by interacting with both the filler and the matrix, thus forming physical or chemical links between the components. It is shown that PP-*g*-MAA had an excellent compatibilizing effect on intumescent flame retarded PP (IFR/PP) composites; as for the essence of the compatibilization of this type, probably the PP segments of PP-*g*-MAA formed miscible blends with the bulk PP through cocrystallization. On the other hand, considering the abundant NH_2 groups on the surfaces of IFR (melamine in excess) and the polar part of PP-*g*-MAA (MAA), probably the PP-*g*-MAA can react with IFR through an amino link.[147] A similar behaviour should occur when we treat the PP-based blends with the PP-g-MAH. The PP segments from the PP-g-MAH will interact with the bulk PP by cocrystalization, while the polar part of PP-g-MAH (MAH), will probably react with the OH groups coming from the additives.

Therefore, the blends were melt mixed analogously to the blends without compatibilizing agent, as described in the experimental section (see table 5.3), but adding compatibilizer in a 10% wt. with respect to the amount of polypropylene. A sample which contains the compatibilizer, but contains no additive, was also mixed in order to compare (MPP’). Also in these cases, the blends contain all 1% wt. of phosphorous. The new blends were also hot

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[149] Oksman, K.; Clemons, C.J Appl Polym Sci **1998**, 67, 1503-1513.

[150] Yuan, X; Zhang, Y.; Zhang, X. JAppl Polym Sci **1999**, 71, 333-337.

[151] Henry, G.R.P.; Drooghaag, X.; Rousseaux, D.D.J.; Sclavons, M.; Devaux, J.; Marchand- Brynaert, J.; Carlier, V. J Polym. Sci Part A: Polym Chem **2008**, 46,2936–2947.

[152] Kandola, B. K.; Smart, G.; Horrocks, A. R.; Joseph, P.; Zhang, S.Hull, T.R.; Ebdon, J.; Hunt, B.; Cook, A J Appl Polym Sci **2008**, 108, 816-824.

pressed, to obtain thin films and plates necessary for the characterization. Then, the mechanical properties (tensile tests and Charpy impact tests) were performed. The results are collected in table 5.11.

Table 5.11 Mechanical properties of virgin MPP and its blends containing compatibilizer.

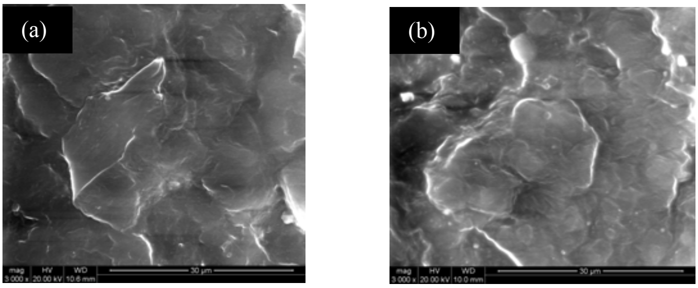
Sample	**Tensile tests**				**Impact test**
	Modulus (MPa)	**Yield point (MPa)**	**Rupture stress (MPa)**	**Rupture strain (%)**	**Impact strength (KJ/m^2)**
MPP	970±0.2	25±1.9	32±5.8	625±166.7	1.81±0.2
MPP'*	1051±0.2	28±0.7	28±4.8	513±4.8	1.84±0.2
B13'	1161±0.3	26±2.3	21±1.8	7±2.0	1.79±0.2
B14'	1211±0.3	23±1.5	21±1.0	6±1.3	2.18±0.3
B15'	1114±0.3	24±1.5	20±1.2	9±4.0	1.92±0.1
B16'	1142±0.1	21±0.8	17±3.0	4±0.9	1.57±0.4

* This sample contains compatibilizer, but contains no additive.

It can be observed from tensile tests, that also in these cases the elastic behaviour of the material is maintained more or less unaltered, but maybe it is even slightly improved respect to the samples without compatibilizer. The plastic behaviour is also strongly affected. On the other hand, the impact strength is lower in all cases respect to the samples without compatibilizer.

ESEM observation of the fracture surfaces of samples subjected to impact tests showed that the blends present similar morphology to the starting MPP'. There was not observed significant separation of additives, such as in the case of blends without compatibilizing agent. As an example, figure 5.12 shows the ESEM micrographs of the starting MPP' and the blend B14', which was one of less compatible in the case of blends without compatibilizer.

Figure 5.12 ESEM micrograph of MPP' (a) and one of its blends, B14' (b)



The calorimetric behaviour was also studied. As can be seen from the table 5.12, Tg and melting temperatures are not altered with respect to the blends without compatibilizer (see table 5.7). On the other hand, the melting enthalpy and the degree of crystallinity decreased significantly with respect to the non compatibilized samples (table 5.7 and 5.8). Also this suggests an improvement in compatibility when the PP-g-MAH is added to polypropylene. Thus, PP-g-MAH disturbs polypropylene crystallization, but the addition of additives did not change this behaviour too much.

Table 5.12 Calorimetric data of MPP' and its blends[*]

Sample	Tonset[b] (ºC)	Tpeak[c] (ºC)	[d]ΔH_1 (J/g)	[e]ΔH_2 (J/g)	Tg[f] (ºC)	Degree of cristallinity[g] x_c (%)
MPP'[a]	144	151	58	58	-12	28
B13'	144	151	58	63	-10	30
B14'	142	150	55	61	-9	29
B15'	142	151	57	64	-9	31
B16'	140	151	55	61	-11	29

[*] The calorimetric data were recorded from the second heating scan
[a] This sample contains the compatibilizer, but contains no additive
[b] Onset temperature of melting endotherm
[c] Peak temperature of melting endotherm
[d] Melting enthalpy per gram of blend
[e] Melting enthalpy per gram of PP (MPP and PP-g-MAH)
[f] Glass transition temperature
[g] This was calculated as the ratio of ΔH_2 and $\Delta H^{\circ}_{melting}$ of 100% crystalline PP (209 J/g)

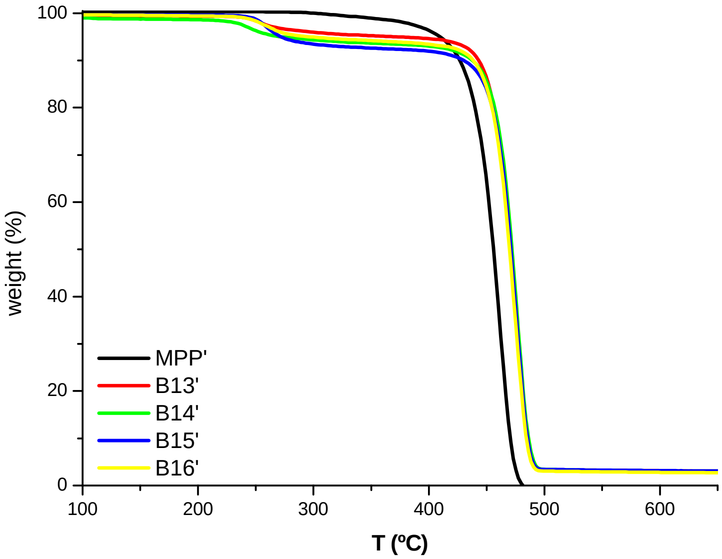
From the point of view of the flame retardancy, the compatibilized blends present similar behaviour to the non compatibilized additivated PP blends. The TGA data (see table 5.13 and figure 5.13) show a certain char residue at elevated temperatures. The blends loss weight process begins earlier than that of starting polypropylene, probably due to dehydration reactions taking place on the additives during heating, but the main process of weight loss is delayed. They also show a small but detectable increase in LOI.

Table 5.13 Thermogravimetric data of MPP' and its blends

Sample	**Additive content (% wt.)**	**Step 1**		**Step 2**		**Char yield at 600 ºC (%)**	**LOI (%)**
		Tonset[a] (ºC)	**Tmax.[b] (ºC)**	**Tonset[a] (ºC)**	**Tmax.[b] (ºC)**		
MPP'				402	462	0	17.4
B13'	9.0	236	256	431	476	3.0	19.2
B14'	10.8	223	242	429	476	3.3	19.0
B15'	11.6	238	258	429	476	3.0	19.3
B16'	11.6	231	259	431	475	2.7	18.8

[*] All these blends contain 1 % wt. of phosphorous
[a] Onset temperature of the weight loss process
[b] Temperature of the maximum rate of the weight loss

Figure 5.13 TGA curves of MPP' and its blends



All the results above mentioned show that the used compatibilizer (PP-g-MAH) seems to confer a certain improvement of the compatibility between the polymeric additives and the polypropylene matrix, as expected; but it affect negatively the impact resistance of the material, probably due to the flame retardant additives behave less as filler. Compatibilization leads to a reduction of the additive particle dimensions, likely reducing the probability of crack deflection and twisting during crack propagation. Regarding the elastic modulus and the flame retardancy, no remarkably differences were detected.

4. Conclusions

To end this chapter, we can report that the prepared blends show as an essential limitation a poor compatibility. It seems that the polymeric additives are only dispersed into the polypropylene matrix, and no interaction between them occurs. Even so, the flame retardancy improvement was reached in certain extent, confirming that the used polymeric additives could act as flame retardants where the phosphate moiety introduced presumably act as a carbonization promoter. The mechanical properties of the starting MPP were not affected so much from the elastic point of view of the material, but they were significantly altered from the plastic point of view. We must pointed out, that in the automotive industry, were the PP-based blends consist the major used thermoplastic, a great importance represent the elastic behaviour of the material, which in our case is not affected negatively, even improved slightly, thus permitting a properly use of the obtained blends.

The compatibilization attempt with the PP-g-MAH, showed a slightly improvement into the compatibility, but worsens some of the mechanical properties that are very important for the use of the material.

Chapter 6

General Conclusions

Conclusions

- Novel polymeric flame retardant additives have been prepared by chemically modifying PVA with different moieties containing phosphorous, reported as good flame retardant promoter structures.
- The synthesis of novel polymeric flame retardant additives based on polyketones, containing phosphorous and/or nitrogen in their structure, was studied in order to obtain intumescent systems.
- A novel polymeric flame retardant additive has been obtained by chemical modification of a hydroxylated polyaziridine with phosphorous containing moiety.
- All synthesized polymeric additives lead to high char yield on TGA curves and a delay of the thermal degradation process is observed (with respect to starting material). Therefore, they are good candidates to act as flame retardant additives through the formation of charred barriers on the condensed phase.
- From the thermal degradation study performed for one of the BIC (1-oxo-2,6,7-trioxa-1-phosphabicyclo[2.2.2]-octane) derivatives, it can be concluded that the additive acts mainly as a flame retardant by formation of a carbonaceous layer, produced from dehydration reactions.
- BIC derivatives can be envisaged also to act in the gas phase, since they evolved on burning volatile phosphate derivatives.
- Polypropylene blends with BIC derivatives have been prepared. Although a poor compatibility has been observed, LOI measurements showed that a certain improvement in their flame retardancy was reached.
- The mechanical properties of the starting PP were not affected so much from the elastic point of view of the material, but they were significantly altered from the plastic point of view. This does not limit so much the

most common application of PP where the toughness is required, such as automotive industry.

- The compatibilization attempt with the PP-g-MAH, showed a slightly improvement into the compatibility, but not for the mechanical properties.

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Appendixes

Appendix A. List of abbreviations

ABS- Acrylonitrile butadiene styrene
AcAc- Acetyl acetone
AcOH- Acetic acid
An- Aniline
APP- Amorphous polypropylene
ATR- Attenuated total reflection accessory

$BF_3 \cdot Et_2O$- Boron trifluoride diethyl ether
$BF_3 \cdot EtNH_2$- Boron trifluoride ethyl amine
BIC- 4-Chloroformyl-1-oxo-2,6,7-trioxa-1-phosphabyciclo[2.2.2]octane

Ca.- Approximately
$CaCl_2$- Calcium chloride
cat.- Catalyst
$CDCl_3$- Deuterated chloroform
CDDP- 2-Chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane
CDPO- 4-Carboxyphenyl-diphenyl-phosphine-oxide
CH_2Cl_2- Dichloromethane
$CHCl_3$- Chloroform
CO- Carbon monoxide
CO_2- Carbon dioxide
$(COCl)_2$- Oxalyl chloride
COTBS- Alternating CO- 4-tert-butyl styrene copolymer
^{13}C NMR- Carbon magnetic nuclear resonance

d1- Delay time
D_2O- Deuterated water
DMAP- 4-(Dimethylamino)-pyridine
DMF- N,N-dimethylformamide
DMSO- Dymethyl sulfoxide
DMSO-d_6- Deuterated dymethyl sulfoxide
DOPO- 9,10-Dihydro-9-oxa-10-phosphaphenantrene-10-oxide
DPBC- 4-(Diphenyl-phosphinoyl)-benzoyl chloride
DPD- 2,2-Dimethyl-1,3-propanediol
DSC- Dynamic scanning calorimetry

EPDM- Ethylene-propylene rubbers and elastomer
$Er(OTf)_3$- Erbium(III) trifluoromethanesulphonate
ESEM- Environmental scanning electron microscope
Et_2O- Diethyl ether
Et_3N- Triethylamine

EtOH- Ethanol
EVA- Ethyl(vinyl alcohol)

FR- Flame retardant
FT-IR- Fourier transform infrared

GC-MS- Gas chromatography-mass spectrometry
GPC- Gel permeation chromatography

HBr- Hydrobromic acid
HCl- Hydrochloric acid
HDPE- High density polyethylene
HEA- 1-(2-Hydroxyethyl)aziridine
HIPP- High molecular weight isotactic polypropylene
HIPS- High impact polystyrene
^{1}H NMR- Proton magnetic nuclear resonance
HNO_3- Nitric acid
H_3PO_4- Phosphoric acid
HRR- Heat release
HRR- Rate of heat release

i.e.- That is to say
ICP-AES- Inductively coupled plasma atomic emission spectroscopy
IFR- Intumescent flame retardant
i-PP- Isotactic polypropylene

$KMnO_4$- Potassium permanganate

$La(OTf)_3$- Lanthanum(III) trifluoromethanesulphonate
LDPE- Low density polyethylene
LIPP- Low molecular weight isotactic polypropylene
LOI- Limiting oxygen index
LLDPE- Linear low density polyethylene

MeOH- Methanol
MLR- Mass loss rate
$MnCl_2$- Manganese (II) chloride
MnO_2- Manganese (IV) oxide
MPP- Moplen type polypropylene EP1X30F

NH_4VO_3- Ammonium metavanadate
NMP- 1-Methyl-2-pyrrolidinone
OPVA- Poly(methyl ketone)

PBT- Poly(buthylene terephtalate)
PCl_3- Phosphorous trichloride
Pcyc- 5,5-Dimethyl-1,3,2-dioxaphosphinan-2-one
PE- Polyethylene
PEPA- 1-Oxo-4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo(2.2.2)octane
PER- Pentaerythritol
PET- Poly(ethylene terephtalate)
PhAc- Phenyl acetone
PHEA- Poly[1-(2-hidroxyethyl)aziridine]
P-N- Phosphorus-nitrogen
^{31}P NMR- Phosphorous magnetic nuclear resonance
$POCl_3$- Phosphorous oxychloride
PP- Polypropylene
PP-g- MAH- Maleic anhydride grafted polypropylene
PVA- Poly(vinyl alcohol)
PVC- Poly(vinyl chloride)
Py- Pyridine

RH- Relative humidity

SAN- Styrene-acrylonitrile
SEM- Scanning electron microscope
$SOCl_2$-Thionyl chloride

TCE- 1,1,2,2-Tetrachloroethane
TCE-d_2- Deuterated 1,1,2,2-tetrachloroethane
TFE- 2,2,2-Trifluoroethanol
Tg- Glass transition temperture
TGA- Thermogravimetric analysis
TGA-MS- Thermogravimetric analysis combined with mass spectrometry
THF- Tetrahydrofyrane
THR- Total heat released
TLC- Thin layer chromatography
Tmax- Temperature of maximum rate of weight loss
TMS- Tetramethylsilane
TOL- Toluene
Tonset- Onset weight loss temperature
TR- Thermoplastic hydrocarbon resin
TTI- Ignition time
Tz- 3-Amino-1,2,4-triazine

XRD- X-Ray diffraction

Appendix B. List of tables and figures

Appendix C. Stages, meeting contributions and publications

Stages

Three months stay (1st February- 2nd May 2009) at the Institute of Polymer Chemistry and Technology of CNR, Pozzuoli (Italy) under the supervision of Dr. Mario Malinconico.

Meeting contributions

- PVA Modificado con 4-Cloroformil-1-Oxa-1-Fosfa-2,6,7-Trioxabiciclo [2.2.2]-Octano: Un Nuevo Aditivo Polimérico Potencialmente Retardante a la Llama.
  S. Saucă, J.A. Reina.
  Poster.
  X Raunión del Grupo Especializado de Polímeros (RSEQ y RSEF).
  Avances en Materiales Poliméricos, Sevilla, 16-20 September, 2007, Spain.

- Polímeros Fosforados Retardntes a la Llama Obtenidos por Modificación Química del Alcohol Polivinílico.
  S. Saucă, J.A. Reina.
  Prezentación oral.
  IV Congreso de Jóvenes Investigadores en Polímeros (JIP2008)
  Nuevos Retos en Materiales Poliméricos, Peñíscola (Castellón), 15-19 June, 2008, Spain

- Flame Retardant Phosphorous-Containing Polymers Obtained by Chemical Modification.
  S. Saucă, J.A. Reina.
  Poster.
  International Symposium Celebrating the 50th Anniversary of the Journal polymer.
  Frontiers in polymer science, Mainz, 7-9 June, 2009, Germany.

Publications

Flame Retardant Phosphorous-Containing Polymers Obtained by Chemically Modifying Poly(Vinyl Alcohol).
Saucă, S; Giamberini, M; Reina, J.A. Polym. Degrad. Stab., Submitted.