Flame-Resistant Polycaproamide by Anionic Polymerization of ε-Caprolactam in the Presence of Suitable Flame-Retardant Agents

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Synopsis

Poly(ε-caprolactam) (PCL) with improved flame-retardant (FR) properties can be easily obtained by activated anionic polymerization of the monomer, ε-caprolactam (C), in the presence of adequate amounts of red phosphorus (red P). Analogous results with reduced P content can be achieved by coupling red P with a synergistic compound such as a chlorinated hydrocarbon or magnesium oxide (MgO). A peculiar advantage of this method is the possibility of obtaining a very fine and homogeneous dispersion of the FR additive in the polymer matrix, meanwhile avoiding the typical compounding techniques, which are expensive, often unsafe, and require melt mixing of the ingredients. Molecular, thermal, and mechanical characterization, as well as morphology of the resultant products, have been determined: No significant properties change have been found when FR agents are present, apart from the relevant improvement of the flame-resistance. Thus, by this novel procedure it is possible to prepare FR poly-(ε-caprolactam) without any appreciable deterioration of its typical properties.

INTRODUCTION

In the last 20 or more years the technological and commercial developments in the field of materials science have emphasized the prominent role of polymer-based materials. Among the various polymer properties deserving adequate amelioration, fire resistancy has been considered an increasingly important problem to be solved. In particular, an eminent role, among molded and extruded materials, has been achieved by poly(ε-caprolactam) whose physical and mechanical characteristics enable us to classify it as an engineering plastics. Some of its properties can be enhanced or modified by the presence of suitable additives (e.g., glass-reinforcing agents, rubbers, flame-retardant agents, etc.). As far as flammability is concerned, all polyamides are usually said to be self-extinguishing because of their high nitrogen content; nevertheless, due to their relatively low melting point (for PCL, $T_m = 220°C$), they can easily melt in the flame and cause dangerous dripping and rapid spread of fire. Dripping can be reduced by using reinforcing agents, such as glass fibers, which also improve polymer mechanical properties, but may adversely affect some parameters related to fire resistance, for example, the limiting oxygen index (LOI).[1-3]

For these reasons, in order to obtain polyamides with increased flame resistance, it is necessary to add flame-retardant agents; many papers and patents dealing with this problem have appeared in the literature[1-12] in the last decade.

We have found that PCL-based materials with enhanced flame-resistance performances can easily be obtained *in situ* by using activated anionic polymerization of ε-caprolactam, in the presence of suitable amounts of various commercial FR agents, which do not adversely affect the polymerization reaction. Namely, among the many products normally used to improve the flame resistance of polymeric materials, adequately coated[13] red P, red P + Dechlorane plus, and red P + magnesium oxide have been found to behave as efficient FR agents for anionic PCL.

Synthesis, molecular characterization, thermal, and mechanical properties as well as morphology and flame resistance of the resultant products are here described. An explanation of the effectiveness of the flame retardants and of their mode of action on PCL is also given.

EXPERIMENTAL

Materials

A master batch of properly coated red P particle size < 40 μ) and ε-caprolactam (1:1 by weight) was kindly supplied by Saffa S.p.A. The master batch was always kept in a desiccator over $CaCl_2$ UV before using it for the polymerization. MgO was a pure chemical product from Carlo Erba. Dechlorane plus was a polyhalogenated cyclopentadiene derivative from Hooker Chemical Corp. Special grade CL monomer was kindly supplied by Enichimica. Its water content was lower than 100 ppm.

Polymerizations and Samples Preparation

Anionic polymerization of the lactam, containing the proper amount of dispersed FR agent, was initiated by Na or Li caprolactamate, activated by *N*-acetylcaprolactam (both 1 mol % referred to the monomer) and carried out in a quasiadiabatic reactor at the initial polymerization temperature of 155°C as previously described[14,15]

Stirring was obtained by vigorous bubbling of dry nitrogen through the mass. The as polymerized material was shaved at room temperature in inert atmosphere, compression-molded, and then kept at 110°C UV for 4 h in order to remove residual monomer and determine limiting conversion.

Molecular Characterization

Molecular mass distribution was evaluated by GPC on PCL *N*-trifluoroacetyl derivatives, using well-established procedures.[16,17] Double filtration of the CH_2Cl_2 solution in order to remove red P solid particles completely was performed using 0.2 μm filters.

Thermal and Mechanical Properties

These properties have been measured with a Perkin-Elmer DSC-2 scanning calorimeter and an Instron Model 1122 tensile machine, respectively. Experimental conditions were as described in Ref. 18.

Morphology

The morphology of the resultant polymers has been observed by a Cambridge Stereoscan 250 MK2 Scanning Electron Microscope, on Au-coated fracture surfaces obtained at liquid nitrogen temperature. Phosphorus distribution was detected by using a Silicon X-Ray Spectrometer (Link System 2010 Pulse Processor).

Limiting Oxygen Index and Underwriters Laboratory Test UL-94

These tests were performed according to LOI ASTM 2863 method[6] and UL-94 method,[6] respectively.

RESULTS AND DISCUSSION

Synthesis and Characterization

Virtually all flame-resistant thermoplastics are produced by compounding techniques. Thus, in order to obtain fire-retardant grades, many problems must be solved due to the severe technical difficulties of processing, mostly related both to the handling of dangerous and toxic products and to the thermal stability of the polymeric materials.

By using the *in situ* mixing procedure by polymerization it is possible to bypass this problem; the only stringent condition is that the FR agent must not adversely affect kinetics, thermodynamics, and mechanisms of the polymerization. In this respect, successful results have been recently attained,[19,20] in the framework of our research project on activated anionic polymerization of CL in the presence of various additives.[21-23]

Indeed, the activated anionic polymerization of CL requires a careful control on some parameters such as initiator and activator concentrations, which strongly affect both reaction kinetics and polymer properties. Namely, not only the absolute concentrations of these active species, but also their relative ratios determine residual monomer content, the amount of side products, the high polymer yield, and its whole molecular mass distribution.[15]

The optimum conditions and results found for the polymerization of neat CL should be mantained, when the FR agent is added, also in order to apply the new RIM (reaction injection molding) technology to this system. As is well known, RIM requires both very fast polymerization and very high conversion.

Flame-retardant systems currently used for polyamides are mainly of three types: halogenated organic compounds, usually in association with a metal oxide as synergist, red phosphorus, and nitrogen-containing organic compounds (such as melamine and its derivatives). All of them have been

tested in order to find their suitability for the anionic polymerization. Interesting results have been obtained by using red P, red P + MgO, and red P + Dechlorane plus; on the contrary, polymerization is strongly inhibited by the presence of melamine derivates as well as by other compounds such as stannous chloride ammonium polyphosphate and other halogenated commerical compounds. The tested additives and their influence on the anionic polymerization of ϵ-caprolactam are shown in Table I.

The better performance of the specific red P used in our experiments as compared to other commercial types is due to its special coating,[13] which minimizes the possibility of phosphine formation and allows us to reach an extremely low moisture content, both phosphine and moisture negatively affecting anionic reactions. In fact, high conversions in very short times have been obtained for systems up to 10% of P content. By using higher percentages of this additive, conversion yield decreases and polymerization time increases as clearly appears in Figure 1. Anyhow, due to the great effectiveness of red P, it is possible to obtain V-0 rating in the UL-94 test, at relatively low levels of flame-retardant concentration, as well be shown further on.

Similar, even better results have been obtained by using red P with MgO and, in part, also for the system red P–Dechlorane plus. Both magnesium oxide and Dechlorane plus, when associated with red P, show a relevant synergistic effect; indeed, improved fire performance of the resultant products has been achieved with lower phosphorus concentrations. However, while red P itself or red P + MgO practically do not affect the reaction kinetics, Dechlorane plus clearly interferes with the anionic polymerization of ϵ-caprolactam by lowering the limiting conversion and by increasing the polymerization time (Fig. 1).

The behavior of the aforementioned additives can be explained by their differences both in thermal stability and in ease of drying. In fact, while in red P and MgO the water content can be easily reduced below 50 ppm, by keeping them under vacuum at high temperature, Dechlorane plus is not stable enough to be held under vacuum at high temperatures for a long

TABLE I
Influence of Some FR Agents on the Anionic Polymerization of ϵ-Caprolactam

FR agent	Inhibition[a]
Melamine cyanurate	+
Ammonium polyphosphate	+
Stannous chloride	+
Red phosphorus	−
Velsicol 935[b]	+
DE 83 R[b]	+
Dechlorane plus[b]	−
Antimonium trioxide	−
Magnesium oxide	−

[a] (+) reaction inhibited; (−) noninhibited.
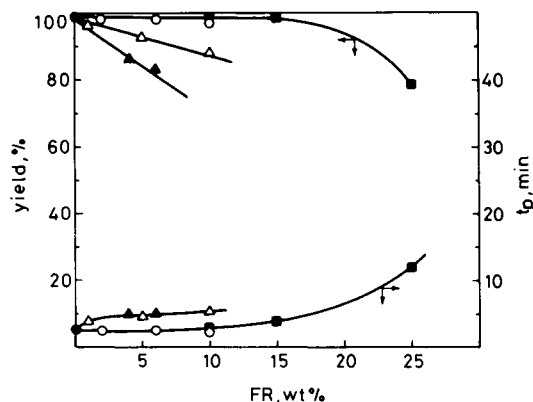[b] Commercial FR agents based on halogenated hydrocarbons.

Fig. 1. Influence of the FR agents on overall polymerization time and conversion yield (initiator : Na-caprolactamate) (■) red P; (○) red P + MgO; (△) Dechlorane plus; (▲) red P + Dechlorane plus.

time. Moreover, the major problem when halogenated hydrocarbons are used arises from the dehalogenation and dehydrohalogenation reactions which can easily be placed in the basic medium at high temperatures.

Molecular masses and their distribution of PCL samples synthesized in presence of FR additives do not exhibit any appreciable modification as compared to the values found for neat PCL obtained in the same experimental conditions. Thus, the specimen containing 5 wt % red P is characterized by $M_w = 42,850$ and $M_n = 20,250$ ($Q = 2.12$) and with 5 wt % of red P plus 5 wt % of MgO shows M_w 48,650 and M_n 28,600 ($Q = 1.70$). A typical set of molecular mass values for neat PCL is as follows: 29,000 < M_w < 71,000; 14,000 < M_n < 27,000 (2.0 < Q < 2.6).[15]

Melting and glass transition as well as crystallization temperatures do not show significant variations in presence of the FR agents independently of their concentration. The corresponding values are quoted in Table II. The chemical inertia of the above additives towards the polymerization reaction manifests itself leaving unchanged also the degree of crystallinity, the crystal structure, and crystallization kinetics as well as the morphology of PCL.

As a consequence, the stress–strain behavior does not show any relevant variation in the examined range of FR additives %. Initial modulus and tensile strength are given in Table III. The slight variations can be considered within the experimental error, mainly associated with the moisture uptake, typical of polyamides. The distribution of the FR agents in the polymer matrix is homogeneous, as evidenced by XR-fluoresence analysis.

In Figure 2 a typical distribution of the additives, for a sample containing both P and MgO (5 + 5 wt %) is given. The homogeneous dispersion is indicative of no coarse segregation of the additives, during the polymerization. This is due to an adequate stirring at the initial stages of polymerization and to the rapid increase of the medium viscosity, which prevents particle settling.

TABLE II
Thermal Transitions of PCL Synthesized in the Presence of Different FR Agents

FR agent	FR[a] (wt %)	T_g (°C)	T_m (°C)	T_c (°C)
None	0	49	217	187
Red P	1	47	219	186
	5	48	219	186
	10	47	220	187
Red P + MgO	1+1	48	217	186
	3+3	47	217	186
	5+5	48	217	186
Dechlorane plus	1	50	219	186
	5	48	217	186
	10	51	220	186
Red P + Dechl. plus	4[b]	51	220	186
	6[b]	49	217	186
	4[c]	n.d.[d]	n.d.	n.d.
	6[c]	n.d.	n.d.	n.d.

[a] Referring to the initial monomer concentration.
[b] Overall wt % (Cl/P atomic ratio = 3/1).
[c] Overall wt % (Cl/P atomic ratio = 2/1).
[d] Not determined.

Fire-Retardant Action and Synergism

The original assumption[24] that red P would show FR properties only in the presence of oxygen-containing polymeric substrates (polyesters, polyamides, polyurethanes, etc.) suggested that its specific role involves the scavenging of the chain carriers, i.e., oxygen-containing radicals, active in the secondary pyrolisis step that induces the formation of gaseous fuel species.[24]

Indeed, the effectiveness of red P as FR agent also for some nonoxygenated polymers, such as polyacrylonitrile (PAN),[25,26] polyethylene,[6] and other sub-

TABLE III
Initial Modulus and Tensile Strength of PCL Samples Obtained in the Presence of
Different FR Additives

FR agent	FR (wt %)	E (GPa)	σ (MPa)
None	0	1.9	67
Red P	1	1.7	60
	5	1.7	58
	10	2.1	56
Red P + MgO	1+1	1.8	67
	3+3	1.9	66
	5+5	2.1	65
Dechlorane plus	1	1.8	60
	5	2.1	60
	10	2.1	60
Red P + Dechl. plus	4[a]	2.0	67
	6[a]	1.9	60
	4[b]	1.9	65
	6[b]	1.9	63

[a] Overall wt % (Cl/P atomic ratio = 3/1).
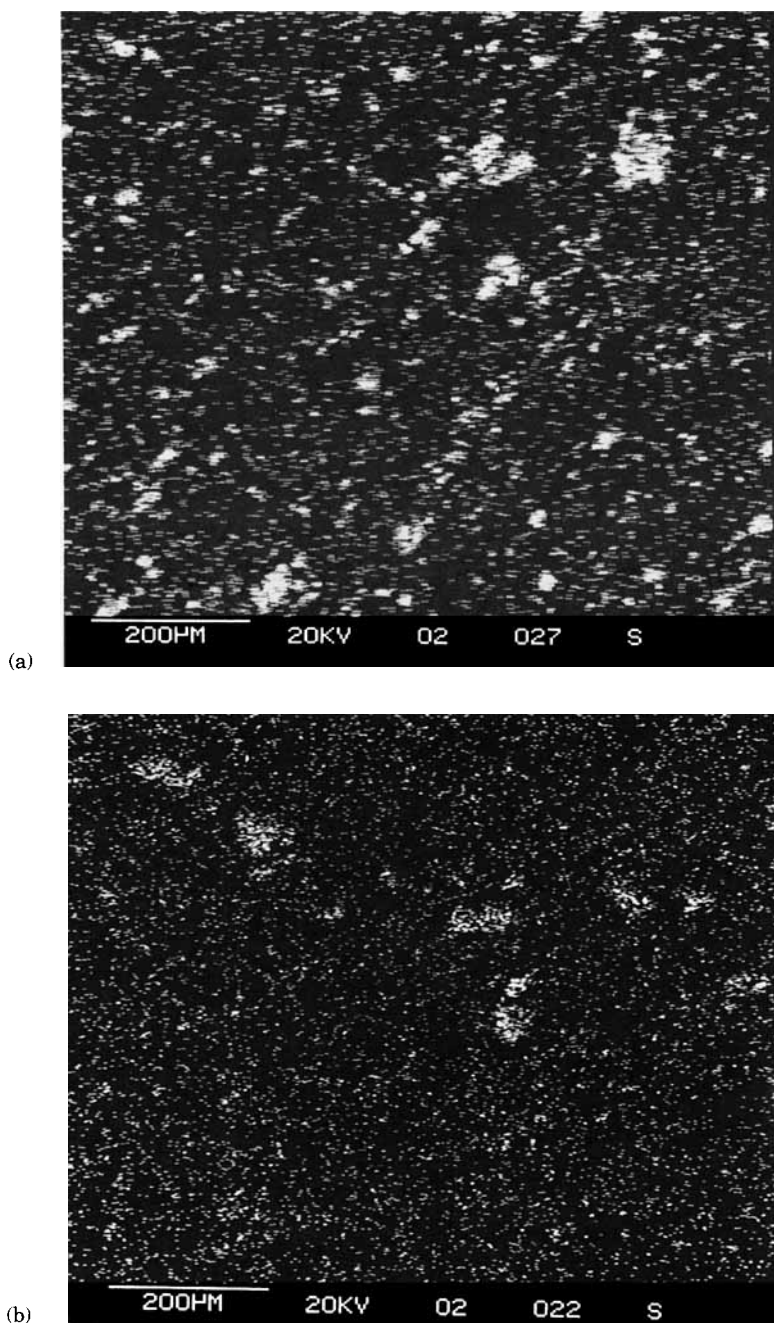[b] Overall wt % (Cl/P atomic ratio = 2/1).

Fig. 2.   Distribution of additives particles as evidenced by XR-Fluoresence: (a) red P; (b) MgO.

strates,[6] has been proven. Consequently, a different mode of action of red P has been proposed.[26] On heating, red P is depolymerized almost quantitatively to volatile white phosphorus (P_4), which diffuses from the bulk of the polymer to the burning surface, where it is oxidized to phosphoric

acid derivatives that can eventually come in close contact with the flame. At the burning polymer surface the formed phosphoric acid acts as a char-forming agent, thus physically limiting oxygen access and fuel volatilization.

Although this mode of action of red P was proposed for a nonoxygenated substrate (PAN),[26] we believe that it is also active in the case of PCL. Indeed, the synergism observed here for the mixtures red P–MgO can be explained according to the above mechanism.

A specimen containing 5% of red P + 5% of MgO has a LOI value of 28.5 (Table IV). This value is higher than that calculated by adding the increments caused by the two additives taken separately. In fact, a specimen with 5% of red P alone has a LOI value of 23, while a specimen with 5% of MgO alone has a LOI value of 22 (Table IV).

The synergistic effect is also observed in the combustion experiments, where a great increment in the char yield is noted with respect to the amounts of char formed when the two additives act separately. It is known[27] that some metals are able to catalyze the reaction of red P with oxygen in presence of moisture, to yield phosphoric acid and its derivatives. The action of MgO at the combustion temperature can be similar, so that the synergistic FR effect on PCL combustion can be explained by the ability of MgO to induce a higher rate of phosphoric acid formation and, therefore, a higher charring rate on the burning polymer surface.

Analogous synergistic effects, although reduced with respect to that shown with MgO, are observed when a chlorinated hydrocarbon is added to red P (Table IV). In this case, the synergistic action is better evidenced considering the UL-94 test. A specimen containing 1% of red P + 5% of Dechlorane plus is rated V-0. This rating is better than one could expect by the values obtained from the specimens containing each additive. In fact, both the specimen with 1% of red P and that with 5% of Dechlorane plus are rated FB (free burning, Table IV).

In this case, besides the mode of action in condensed phase caused by red P as charring agent, one has to consider a concomitant activity in gaseous phase. In fact, P_4 species, deriving from the thermal decomposition of red

TABLE IV
Effect of Red P and Red P Mixed with Dechlorane Plus or MgO on the LOI
and UL-94 for PCL

Red P (wt %)	Dechlorane plus (wt %)	MgO (wt %)	LOI	UL-94[a]
—	—	—	21	FB
—	1	—	21	FB
—	5–15	—	22–23	FB
1	—	—	23	FB
1[b]	5[b]	—	24	V-0
5	—	—	23	V-1
8–15	—	—	25–27	V-0
—	—	5	22	FB
5	—	5	28.5	V-0

[a] Free burning.
[b] Cl/P atomic ratio = 3/1.

P,[25] can react in the presence of O_2 and HCl, originating from the hydro-clorinated hydrocarbon, to yield PCl_3, a well-known flame poison.[28]

CONCLUSIONS

The activated anionic polymerization of CL in the presence of some FR agents has been proved to be an efficient method for the preparation of the corresponding FR polyamide. Namely, red P and its mixture with MgO do not adversely affect both kinetics and thermodynamics of CL polymerization. Their presence in the PCL matrix is not detrimental to the molecular, thermal, and mechanical properties of the resultant polymer.

The fire performance is enhanced by the thorough distribution of the additives which, on the other hand, do not alter the typical morphology of PCL.

The relevant synergistic effect observed when MgO or Dechlorane plus are added to red P has been interpreted on the basis of recent reaction pathways.[26]

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