Thermal and mechanical characterization of poly[bis(4-benzylphenoxy)phosphazene]

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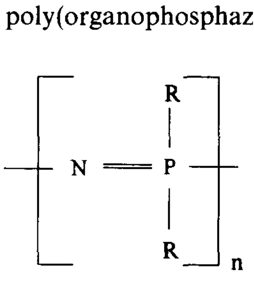
In this paper we report the thermal and mechanical characterization of poly[bis(4-benzylphenoxy)-phosphazene] (PBPP). Glass transition and melting temperatures of 13.8 and 88.2°C respectively, and heat of fusion of 7.0 J g^{-1} were measured by differential scanning calorimetry (d.s.c.) for the as-synthesized polymer. Crystallization studies from the melt, in both isothermal and dynamic regimes, showed a low crystallizability of PBPP, due to the high mobility and steric hindrance of lateral substituents, with a heat of fusion no higher than 9 J g^{-1}. Activation energies of about 70 kJ mol^{-1} were calculated both for the crystallization process and for the rubber–glass transition in the amorphous state. The highest crystallization rate in isothermal experiments occurred at a temperature of 45°C. Thermodegradation of PBPP in air was found to start with the probable formation of the hydroperoxide group on the methylene site at about 233°C, as demonstrated from both thermogravimetric and d.s.c. analyses. PBPP film behaved as an elastomeric polymer with a strain at break higher than 350%. A tensile modulus of 1.2 MPa and a stress at break of 4.8 MPa for the amorphous polymer were measured, whereas crystalline polymers exhibited higher tensile modulus and stress at break, ranging from 34 to 48 MPa and from 7 to 12 MPa, respectively.

(Keywords: polyphosphazenes; crystallization kinetics; mechanical properties)

INTRODUCTION

In the last three decades the continuous need for materials of high technological impact has stimulated scientists to develop new classes of polymers with special properties able to serve in applications where the usual organic macromolecules fail[1].

In this regard, poly(organophosphazenes) (POPs):



$$\left[N = \overset{R}{\underset{R}{P}} \right]_n$$

have proved to be of extreme interest, owing to the good skeletal characteristics of the –P=N– system (i.e. chain flexibility[2], oxidative stability[3], flame resistance[4], biocompatibility[5], spectral transparency[6]) and the great versatility of their synthesis[7,8], copolymerization[9] and functionalization[10–12].

Our interest in POPs has mainly been devoted to phosphazene materials that show photochemical interest[13]. For this aim we investigated first the basic photochemical behaviour of arylamino- and aryloxy-substituted POPs[14–17], and extended our research successively to polymer that show potential application as heterogeneous-phase photosensitizers[8,11], photoinitiators[18], photoresists[19], photochromic materials[20] and self-stabilized macromolecules[21].

In the frame of this work, we recently dedicated considerable effort to investigating poly[bis(4-benzylphenoxy)phosphazene] (PBPP), $[NP(O\text{–}C_6H_4\text{–}CH_2\text{–}C_6H_5)_2]_n$, a polymer whose synthesis has recently been reported in the literature[22].

The importance of this macromolecule is related basically to the high mobility of the secondary hydrogens of the methylene groups in the side phosphorus substituents, especially in the presence of molecular oxygen. Hydroperoxides, in fact, are easily formed in this material under oxidative conditions that are able to evolve eventually to carbonyl groups, so transforming the 4-diphenylmethane residues of PBPP into benzophenone chromophores[23,24].

Our investigation on poly[bis(4-benzylphenoxy)phosphazene] has been concerned up to now with the photochemical reactivity of the material under both direct irradiation[23] and photo-oxidative conditions[24], and the grafting reactions of organic macromolecules (e.g. poly(*N*,*N*′-dimethylacrylamide))[25] or maleic anhydride[26,27], by exploiting the easy formation of reactive radicals in the methylene site.

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In the light of these results, and given also the potential of applicability of this polymer in several technological domains (photochemistry, photoresist technology, compatibilization and blends), we thought it useful to start systematic investigations on PBPP. In this paper we present our findings on the thermal and mechanical properties of this macromolecule, while results concerning its sensitized photochemistry[28] and grafting processes[29] will be reported elsewhere.

EXPERIMENTAL

Materials

Hexachlorocyclophosphazene $(NPCl_2)_3$ (Shin Nisso Kako) was purified by multiple vacuum sublimations to a constant melting point of 113°C[7]. Polychlorophosphazene $(NPCl_2)_n$ was prepared by bulk thermal polymerization of $(NPCl_2)_3$ at 250°C in vacuum[30,31], and purified from the residual unreacted trimer under reduced pressure[32]. 4-Hydroxydiphenylmethane (Aldrich) was purified by vacuum sublimation. Poly[bis-(4-benzylphenoxy)phosphazene] $[NP(O{-}C_6H_4{-}CH_2{-}C_6H_5)_2]_n$ (PBPP) was prepared[22] and characterized[23] according to the literature.

All solvents were Carlo Erba RPE Analytical Grade; when needed, they were purified with standard procedures[33] or dried by refluxing over Na–benzophenone complex prior to use.

PBPP polymer in the shape of flakes was used for thermal characterization and treatments. Dynamic mechanical thermal analysis (d.m.t.a.) and mechanical analysis were performed on PBPP films as obtained from solution casting, then as quenched, and finally as annealed. PBPP films crystallized from chloroform solution (about $10\,g\,l^{-1}$) in Petri dishes were detached from the glass by using methanol. By melting at 110°C in an oven for 10 min in a nitrogen atmosphere and quenching in ice–water, amorphous polymer films were prepared.

Thermal treatments and analysis

Thermal treatments were performed with polymer samples weighing about 50 mg in a differential scanning calorimeter (Mettler DSC 30) under nitrogen, flushed at $100\,ml\,min^{-1}$.

Treatment cycles comprising specific combinations of heating, melting, cooling and crystallization were applied as follows. *Slow-cooling crystallization:* The polymer was heated at $10°C\,min^{-1}$ until 110°C, at which it was retained for 5 min, and then cooled to $-50°C$, at different rates ranging from -0.3 to $-20°C\,min^{-1}$. *Isothermal crystallization:* Molten polymer samples were quenched to a selected crystallization temperature, T_c, in the range 20–70°C, where it was retained for a crystallization period ranging from 1 to 4 h, followed by quenching to room temperature. Each sample after thermal treatment was characterized by a final d.s.c. scan from -50 to $+200°C$ at a heating rate of $10°C\,min^{-1}$, and the data were analysed by a Mettler TA72 program. Glass transition temperature displayed by samples during heating or cooling was determined as the inflection point of d.s.c. curves. Thermal transitions at high temperature were also studied in d.s.c., flushing nitrogen and air at $100\,ml\,min^{-1}$ until 500°C.

A Mettler MT5 microbalance equipped with a TG50 oven was used for thermogravimetric analysis on approximately 10 mg of sample heated at $10°C\,min^{-1}$ from 30 to 700°C, in air at a flowing rate of $200\,ml\,min^{-1}$.

Specific annealing treatments of amorphous PBPP films were also performed in an oven at 45°C corresponding to the maximum of crystallization rate as determined by d.s.c.

Mechanical analysis

Dynamic mechanical thermal analysis (d.m.t.a.) was performed in tensile mode (specimen size $20 \times 4 \times 0.45\,mm^3$) at a frequency of 5 Hz with 16 μm of deformation, from -30 to $+60°C$ at a heating rate of $2°C\,min^{-1}$ under a nitrogen atmosphere, by using a Polymer Laboratories DMTA Mk II (Loughborough, UK).

Mechanical tests were carried out at room temperature on five specimens for each sample by using an Instron 4502 tensile tester equipped with a 10 N load cell. PBPP films cast from chloroform solution were cut to obtain strip-shaped specimens with a uniform width of 5 mm and an overall length of 60 mm. The thickness of specimens was located in the range 30–90 μm.

As recommended by the Standard Test Methods ASTM D882-88 for Tensile Properties of Thin Plastic Sheeting, modulus measurements were performed at a strain rate of $0.1\,min^{-1}$ whereas stress and strain at break determinations were carried out at a strain rate of $10\,min^{-1}$ as suggested for materials having a strain at break higher than 100%.

RESULTS AND DISCUSSION

Thermal treatment and d.s.c. analysis

PBPP was previously described as an opaque crystalline polymer[34]. Our d.s.c. thermogram of the as-synthesized material, reported in *Figure 1a*, revealed that the polymer has a glass transition temperature, T_g, of 13.8°C (measured in the heating cycle) in good correspondence with the value reported in the literature[22], and a melting temperature T_m of 88.2°C, and heat of fusion of $7.0\,J\,g^{-1}$. The molten and quenched polymer was found to be completely amorphous, with a glass transition temperature of 12.8°C, as reported in the second d.s.c. scan of *Figure 1b*, without crystallization or melting phenomena. These results seem to indicate a low crystallinity and crystallizability of the polymer, which could be attributed to the high mobility and steric

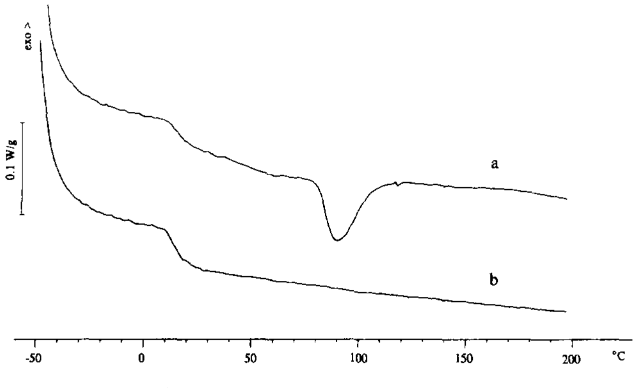

Figure 1 D.s.c. thermograms of PBPP as synthesized (a) and after melting and quenching (b)

hindrance of the benzylphenoxy phosphorus substituents present in PBPP that hardly allow the development of ordered structure. More favourable conditions for crystallization were shown from different phosphorus substituents, such as the more flexible group in poly[bis(trifluoroethoxy)phosphazene][35,36], or the less hindered aromatic one in poly[bis(methoxyphenoxy)-phosphazene][37], which showed a heat of fusion of about 20–30 J g^{-1}. Moreover, Sohoni and Mark[38], analysing several crosslinked poly(organophosphazene) equimolar copolymers with varied *meta-* and *para*-substituted phenoxy repeat units, reported melting energies up to about 16 J g^{-1}.

In order to investigate the capability of increasing crystallinity of PBPP, specific thermal treatments were performed. The molten polymer was cooled in the d.s.c. chamber at different cooling rates from -20.0 to -0.3°C min^{-1}, and crystallization temperature (T_c), heat of crystallization (H_c) and glass transition temperature (T_g) were registered. Data are summarized in *Table 1*. No crystallization occurred at cooling rates faster than -2.0°C min^{-1}, and the slower the cooling process the higher the crystallinity gain. For cooling rates of -2.0 and -1.5°C min^{-1}, crystallization peaks of 2.1 and 3.3 J g^{-1} respectively were obtained, whereas for the slower process values of about 7 J g^{-1} were measured. Assuming that the temperature of the highest crystallization rate, T_c, expressed in K, defined as the temperature of the maximum of the crystallization peak in each cooling thermogram, is related to the cooling rate, v, by an Arrhenius type equation, the activation energy of crystallization, E_a, can be worked out for each crystallization from the equation[39]:

$$\ln v = \ln v_0 - (E_a c/R)(1/T_c) \qquad (1)$$

where v_0 is a pre-exponential factor (*a priori* unknown expressed in °C min^{-1}) and $c = 1.052$ is the constant reported in the literature[39]. *Figure 2* presents a plot of the experimental values of $\ln v$ against $1/T_c$, the inverse of the temperature of highest crystallization rate. From the slope of the best-fit straight line, an activation energy of 73 kJ mol^{-1} for the crystallization process was obtained.

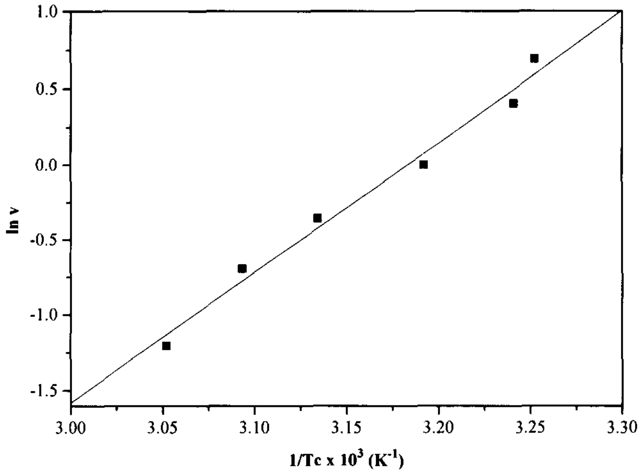

Figure 2 Arrhenius plot for crystallization of PBPP. The cooling rate, v (°C min^{-1}), from the molten state is reported as a function of $1/T_c$, where T_c is the temperature of the higher crystallization rate, measured during the d.s.c. scan. The slope of the straight line allows the calculation of the activation energy for the crystallization process (see text)

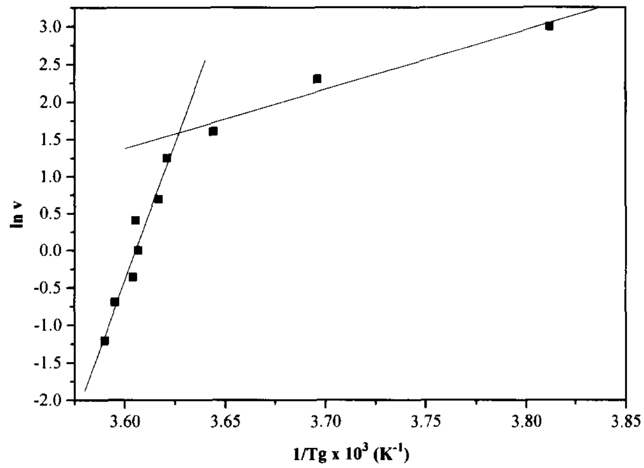

Figure 3 Arrhenius plot for rubber–glass transition of PBPP. The cooling rate, v (°C min^{-1}), from the molten state is reported as a function of $1/T_g$, where T_g is the glass transition temperature measured during the cooling d.s.c. scan. The slopes of the two best-fit lines represent activation energies of rubber–glass transition for completely amorphous and semicrystalline polymer, respectively

The same procedure can be applied for calculation of the relaxation activation energy, the energy involved in the rubber–glass transition during cooling at different controlled rates[40]. By plotting the logarithm of the cooling rate *versus* T_g a straight-line fit can normally be obtained[41]. However, introducing in equation (1) the T_g values of *Table 1* expressed in K, the data of the Arrhenius-type plot reported in *Figure 3*, can be fitted with two straight lines that intersect at 0.003 62 K^{-1}, which corresponds to a cooling rate of -4.2°C min^{-1}. The different slopes are related to different mechanisms, and activation energy values of 70 and 570 kJ mol^{-1} were respectively found for cooling rates formally faster and slower than -4.2°C min^{-1}, the intersection point of the two best-fit lines. This value is quite in agreement with the experimental results reported in *Table 1*; in fact, for cooling rates equal to or faster than -3.5°C min^{-1}, no crystallization was detected in d.s.c. The increase of about eight times observed in the relaxation activation energy for the lower cooling rates can be attributed to the different morphology of the polymers. Amorphous PBPP obtained at higher cooling rate showed the lower relaxation energy, whereas the semicrystalline polymers developed during slow cooling processes revealed the higher activation energy. Moreover, about the same activation energies were found for the rubber–glass

Table 1 Crystallization temperature (T_c), heat of crystallization (H_c) and glass transition temperature (T_g) for PBPP during cooling from the molten state at different cooling rates

Cooling rate (°C min^{-1})	T_c (°C)	H_c (J g^{-1})	T_g (°C)
0.3	54.7	6.7	5.6
0.5	50.3	7.2	5.2
0.7	46.1	7.7	4.5
1.0	40.3	6.1	4.3
1.5	38.4	3.3	4.3
2.0	34.5	2.1	3.5
3.5	–	–	3.2
5.0	–	–	1.5
10	–	–	−2.4
20	–	–	−10.6

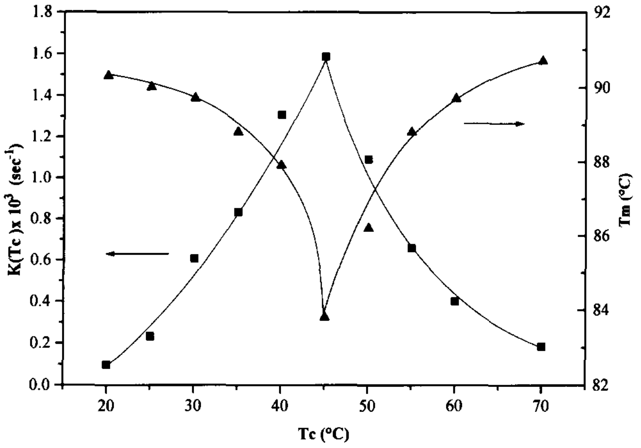

Figure 4 Bulk crystallization kinetic factor, $K(T_c)$, and corresponding melting temperature of crystallized polymer, T_m, as functions of the crystallization temperature T_c

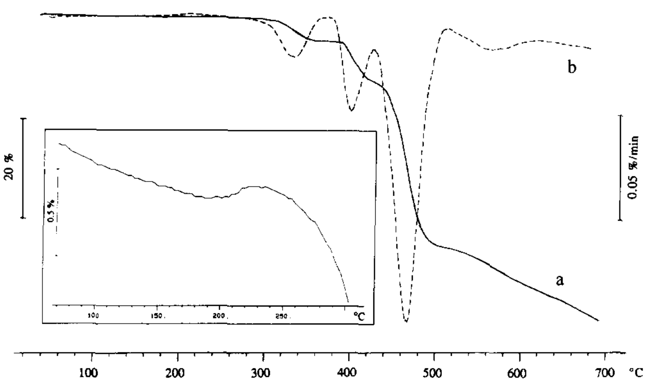

Figure 5 T.g.a. thermograms of PBPP in air flow of 200 ml min^{-1} with a heating rate of 10°C min^{-1} until 700°C. Percentage of mass loss (a) and derivative function (b) are reported

transition (70 kJ mol^{-1}) and for the crystallization process from the melt (73 kJ mol^{-1}). These results suggest that in both cases the same energy is required to activate the transition of the polymer chain from a completely amorphous rubbery state to a glassy or semicrystalline state.

Kinetics of isothermal crystallization can provide further information on structure and morphology. The molten PBPP polymer was quenched to different crystallization temperatures (T_c) and then isothermally treated at these temperatures. At temperatures lower than 20°C and higher than 70°C the process is so slow that the signal is comparable with the noise of the equipment. The time, t_c, expressed in seconds[42], required to reach half of the final crystallinity amount as determined in d.s.c., defines the bulk crystallization kinetics factor $K(T_c)$, where $K(T_c) = 1/t_c$. *Figure 4* presents a plot of $K(T_c)$ as function of T_c, where two regions are evident, below and above 45°C (318 K), the temperature of the highest crystallization rate. Moreover, the lower the crystallization rate of PBPP isothermally crystallized, the higher the melting temperature and the more ordered the crystalline structure.

High-temperature analysis (t.g.a. and d.s.c. results)

Thermogravimetric analysis, reported in *Figure 5*, showed degradation of PBPP in air. Four different ranges can be identified with transformation temperatures of 331, 400, 467 and 550°C respectively, as measured from the minima of the derivative function. At 700°C a residual mass of 39% was detected, exactly the same value as for thermodegradation in nitrogen atmosphere (not reported).

Further information can be collected from differential scanning calorimetry. PBPP heated in air showed several exothermic peaks above 200°C, as shown in *Figure 6*. The first exothermic peak at 233°C is associated with a slight mass increase (see t.g.a. thermogram reported in *Figure 5*), and the formation of hydroperoxide groups on methylene sites can easily explain the phenomenon. A deeper investigation concerning the thermodegradation mechanism of PBPP is in progress. Other peaks located at 336, 386°C and above correspond quite well to those registered during t.g.a. analysis, and at these temperatures thermo-oxidation processes proceed with degradation and mass loss of benzylphenoxy substituents.

Dynamic mechanical and mechanical analysis

PBPP film samples were cast from chloroform solution for mechanical characterization. Three different types of film were considered, i.e. amorphous, crystallized from solution, and crystallized from annealing process. The polymer directly obtained from the casting process was analysed by d.m.t.a. and the thermogram is shown in *Figure 7*. A glass transition temperature can be seen

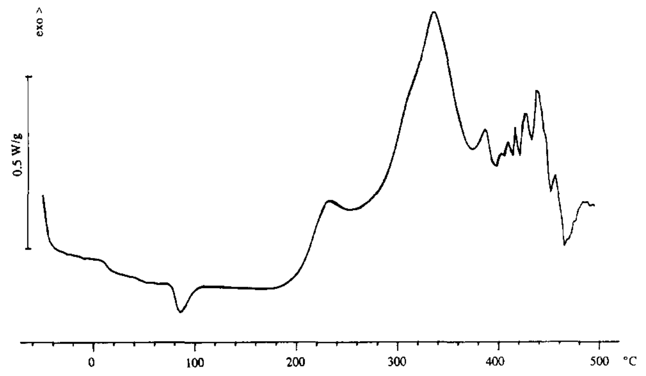

Figure 6 D.s.c. thermograms of PBPP in air flow of 100 ml min^{-1} with a heating rate of 10°C min^{-1} until 500°C

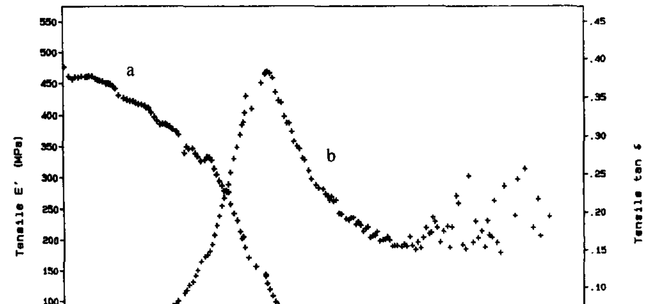

Figure 7 D.m.t.a. thermogram of PBPP film directly obtained from solution. Tensile storage modulus (a) and damping factor (b) are reported as functions of temperature

Table 2 Average values of tensile modulus, stress at break and strain at break, measured on five specimens of three different types of PBPP films

Sample	Heat of fusion ($J g^{-1}$)	Tensile modulus (MPa)	Stress at break (MPa)	Strain at break (%)
Quenched	0	1.2	4.8	425
Crystallized from annealing	7.3	34.2	7.8	347
Crystallized from solution	8.8	48.0	11.7	381

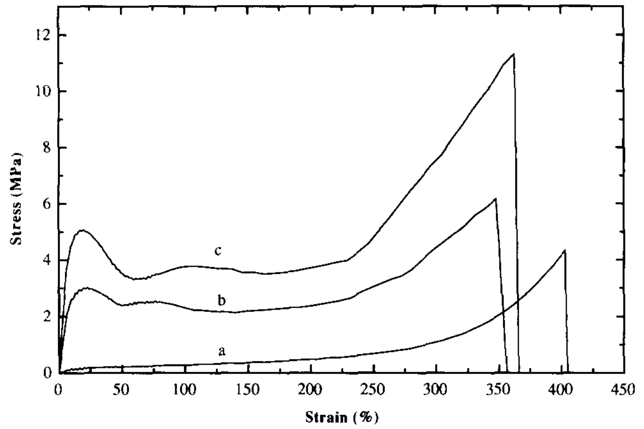

Figure 8 Stress–strain curves of a single specimen of PBPP films: amorphous (a), crystallized from annealing (b) and crystallized from solution (c)

in the range 0–20°C with a maximum of the damping factor peak at 8°C. The corresponding glass transition temperature of PBPP film measured at 13.8°C by d.s.c. was in good agreement with dynamic mechanical thermal analysis. Below the transition zone, PBPP behaves as a stiff and brittle polymer, with a tensile storage modulus having a value (400 MPa at −20°C) of about one order of magnitude higher than the corresponding value at room temperature (50 MPa at 25°C).

Annealing of amorphous PBPP film at 45°C for 30 min produced a heat of fusion of 7.3 $J g^{-1}$, whereas PBPP crystallized from solution showed a value of 8.8 $J g^{-1}$. Examples of stress-strain curves for the three types of film are reported in *Figure 8*. All polymers, amorphous and crystalline, exhibited elastomeric behaviour, having a strain at break higher than 350%, as reported in the literature for other polyphosphazene materials[35]. On the other hand, both modulus and stress at break showed a direct correlation with morphology, as reported in *Table 2*. The higher the crystallinity content, the higher the mechanical properties. Whereas amorphous polymer showed low tensile modulus and stress at break, of 1.2 and 4.8 MPa respectively, polymers crystallized from annealing or from solution exhibited higher mechanical properties. Tensile moduli ranging from 34 to 48 MPa, and stress at break of 7–12 MPa, were registered, showing a direct dependence on the crystallinity content. Finally, crystallization from solution appears to be the more promising method to obtain crystallinity, as shown elsewhere for poly[bis(phenoxy)-phosphazene][43].

CONCLUSIONS

Poly[bis(4-benzylphenoxy)phosphazene] showed behaviour of a semicrystalline polymer with a glass transition temperature of 13.8°C. Notwithstanding the high mobility of the chain at room temperature, PBPP was shown to be unable to develop a highly crystalline structure. Differential scanning calorimetry experiments in both dynamic and isothermal crystallization treatments resulted in polymers with heat of fusion less than about 8 $J g^{-1}$. Almost the same activation energy of 70 $kJ mol^{-1}$ was calculated both for the crystallization process and for the rubber–glass transition in the amorphous state. The temperature of the highest crystallization rate in isothermal experiments was found to be 45°C, and below and above this temperature crystallized polymers showed higher melting temperature (about 90°C).

The formation of hydroperoxide group on the methylene site starting at about 200°C seems to be the first step of thermodegradation of PBPP in air, as demonstrated from both t.g.a. and d.s.c. analyses.

Mechanical properties of PBPP films depend strictly on crystallinity content. Tensile modulus and stress at break, ranging from 34 to 48 MPa and from 7 to 12 MPa, were found for PBPP crystallized from annealing and from solution respectively. Both crystalline and amorphous polymers showed elastomeric behaviour, with strain at break higher than 350%.

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