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Synthesis and characterization of novel random copolymers based on PBN: Influence of thiodiethylene naphthalate co-units on its polymorphic behaviour

M. Soccio [a], M. Gazzano [b], N. Lotti [a,*], L. Finelli [a], A. Munari [a]

[a] Dipartimento di Chimica Applicata e Scienza dei Materiali, Università di Bologna, Via Terracini 28, 40131 Bologna, Italy
[b] Istituto per la Sintesi Organica e la Fotoreattività, CNR, Via Selmi 2, 40126 Bologna, Italy

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ABSTRACT

Poly(butylene/thiodiethylene naphthalate) copolymers (PBN-PTDEN) were synthesized in bulk according to the usual polycondensation procedure and examined by NMR, GPC, TGA, DSC and XRD techniques. At room temperature they appeared as semicrystalline materials; the copolymerization caused a lowering in the T_g value, a decrement of T_m and of the crystallization rate. Pure α- or β′-form was obtained at low and high TDEN unit content, respectively; crystalline form transition never occurred in the solid state, analogously to PBN. After cooling from the melt, the pure α-form was always evidenced in PBN-PTDEN10, whereas the pure β′ crystal phase develops in the copolymers containing 30 and 40 mol% TDEN units, independently on the cooling rate. In the case of PBN-PTDEN20 a pure α- or β′-form was obtained at low and high cooling rate, respectively.

1. Introduction

In order to improve the heat resistance of phenyl polyesters, some naphthyl polyesters have been developing, such as poly(ethylene 2,6-naphthalate) (PEN) and poly(butylene 2,6-naphthalate) (PBN). In particular, PBN is characterized by excellent mechanical, thermal, gas barrier and electrical properties, which permit its use as biaxially oriented films, fibres, connectors, switches, coil bobbins, ignition coils fuel sensors, fuel tanks and hoses. It is a linear aromatic polyester which consists of a flexible part, butylene, and a rigid one, naphthalate. PBN crystallizes very easily and consequently it is very difficult to obtain an isotropic glass, i.e. a frozen state of melt, by fast cooling. Probably, just due to the difficulty to obtain an isotropic glass, several values for the glass-transition temperature have been reported in the literature, ranging from 41 to 82 °C [1–6]. Up to the present, two crystalline structures, denoted as α- and β-forms, have been acknowledged and the transition between these two forms can take place reversibly by mechanical deformation. [7]. Ju et al. investigated the crystalline forms of PBN samples obtained by different thermal treatments in bulk: the α-form develops by annealing a quenched sample in the solid state or by crystallizing PBN from the static melt at temperatures lower than 250 °C. On the other hand, an exclusive β′-form is generated by performing non-isothermal crystallization from the melt at extremely low cooling rate (0.1 °C/min). This thermally prepared β′-form is characterized by WAXD profile similar to that of the β-form obtained by highly mechanical deformation, except for the substantial *d*-spacing deviation in (0 −1 1) and (0 1 0) planes [8]. Nevertheless, if PBN is melt crystallized at high T_c, both α- and β′-forms are obtained simultaneously, and their relative ratio is dependent on the adopted crystallization temperature. Additionally, crystalline form changes never occur in the solid state. Lastly, the main difference between the α and β′ crystal structures lies in the packing efficiency of the crystal chains, the β′-form being more tightly packed [8].

Taking into account that copolymerization represents an easy and efficacious way to favourably modify the characteristics of a polymer, recently we prepared a series of random poly(butylene/diethylene naphthalate) copolymers (PBN-PDEN) which were accurately characterized from the molecular, thermal and diffractometric point of view, with special attention devoted to the analysis of the effect of copolymerized DEN units on polymorphic behavior of PBN [9]. Beside the significant influence of ethero-oxygen containing comonomeric units on the final thermal properties of the material, the most relevant result of this study concerned the crucial importance of copolymer composition in determining the selective formation of one form. In particular, pure α-form was always evidenced in copolymers containing low amount of DEN units (10 and 20 mol%), whereas the pure β′ crystal phase develops in the copolymer containing 40 mol% DEN units, independently on the thermal treatment adopted. In the case of PBN-PDEN30, an effect of the thermal treatment has been on the

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* Corresponding author. Tel.: +39 051 2090354; fax: +39 051 2090322.
E-mail address: nadia.lotti@mail.ing.unibo.it (N. Lotti).

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contrary observed, a pure α- or β′-form being obtained at low and high cooling rate, respectively. Taking into account that the β′-form is more thermodynamically stable and more tightly packed, its selective formation in the copolymer with the highest content of DEN co-unit has been ascribed to the higher mobility and flexibility of the polymeric chains due to the presence of significant amount of ether-oxygen atoms [9].

Recently, we prepared samples of poly(thiodiethylene naphthalate) (PTDEN), a novel sulphur containing polyester based on 2,6-naphthalendicarboxylic acid. The comparison of its thermal and mechanical properties with those of the analogous homopolymer containing ether-oxygen atoms as well as of PBN evidenced an increase of chain flexibility [6].

In front of these considerations, it appeared very interesting to complete our previous work by synthesizing novel random copolymers of PBN and PTDEN with various composition, which have been subjected to thermal and X-ray diffraction characterizations. The main aim of this work is to elucidate the effect of copolymerized TDEN units on the polymorphic crystal structure of PBN, in order to prove that the selective formation of pure β′-form is strictly correlated to the macromolecular chains flexibility.

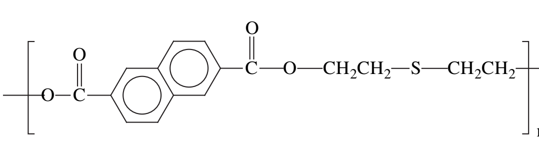
2. Experimental part

2.1. Products

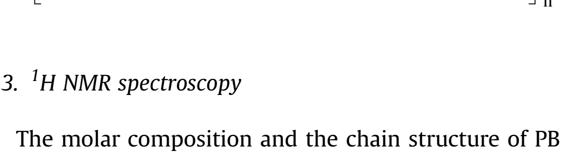
2,6-Dimethylnaphthalate (DMN), 1,4-butanediol (BD), thiodiethylene glycol (TDEG) and titanium tetrabutoxide ($Ti(OBu)_4$) (Aldrich) were reagent grade products; DMN, BD and TDEG were used as supplied, whereas and $Ti(OBu)_4$ was distilled before use.

2.2. Synthesis of copolymer samples

Poly(butylene/thiodiethylene naphthalate) copolymers (PBN-PTDEN) were synthesized in bulk starting from different ratios BD/TDEG and from DMN (using a 50% glycol excess on respect of DMN), employing titanium tetrabutoxide as catalyst (about 0.2 g of $Ti(OBu)_4$/kg of polymer). The syntheses were carried out in a 200 mL stirred glass reactor, with a thermostatted silicon oil bath; temperature and torque were continuously recorded during the polymerization. The polymers were prepared according to the usual two-stage polymerization procedure. In the first stage, under pure nitrogen flow, the temperature was raised to 215 °C and maintained there for until more than 90% of the theoretical amount of methanol was distilled off (about 1 h). In the second stage the pressure was reduced, in order to facilitate the removal of the glycol excess and the temperature was kept at 250 °C until a torque constant value was measured. The chemical structures of the parent homopolymers are the following:



PBN



PTDEN

2.3. ^{1}H NMR spectroscopy

The molar composition and the chain structure of PBN-PTDEN copolyesters were determined by means of ^{1}H NMR spectroscopy. Polymer samples were dissolved (15 mg/mL) in a 20/80 (v/v) mixture of trifluoroacetic acid/chloroform-d solvent with 0.03% (v/v) tetramethylsilane added as an internal standard. The measurements were carried out at room temperature, employing a Varian INOVA 400 MHz instrument.

2.4. Gel-permeation chromatography

Molecular weight data were obtained by gel permeation chromatography at 30 °C using a 1100 HP Series system with an UV spectrophotometer (at 254 nm wavelength) as detector, equipped with PL gel 5μ MiniMIX-C column (250/4.6 length/i.d., in mm). A mixture of chloroform/1,1,1,3,3,3-hexafluoro-2-propanol ($CHCl_3$/HFIP) (95/5 v/v) was used as diluent with a 0.3 mL/min flow, and sample concentrations of about 2 mg/mL were applied. A molecular weight calibration curve was obtained with several monodisperse polystyrene standards in the range of molecular weight 2000–100,000.

2.5. Thermal analysis

2.5.1. TGA measurements

Thermogravimetric analysis was carried out both in air and under nitrogen atmosphere using a Perkin Elmer TGA7 apparatus (gas flow: 40 mL/min) at 10 °C/min heating rate up to 900 °C. The procedure suggested by the supplier was followed for the temperature calibration of the equipment. This method is based on the change of the magnetic properties of two metal samples (Nickel and Perkalloy) at their Curie points (354.0 and 596.0 °C, respectively). The T_{onset} at which the weight loss starts was taken as temperature of initial decomposition (T_{id}).

2.5.2. DSC measurements

Calorimetric measurements were carried out by means of a Perkin Elmer DSC7 instrument equipped with a liquid subambient accessory and calibrated with high purity standards (indium and cyclohexane). The external block temperature control was set at −40 °C. Weighed samples (c.a. 10 mg) were encapsulated in aluminum pans and heated to about 40 °C above fusion temperature at a rate of 20 °C/min (first scan), held there for 3 min, and then rapidly quenched to −10 °C. Finally, they were reheated from −10 °C to a temperature well above the fusion one of the sample at a heating rate of 20 °C/min (second scan). The glass-transition temperature T_g was taken as the midpoint of the heat capacity increment Δc_p associated with the glass-to-rubber transition. The melting temperature (T_m) and the crystallization temperature (T_c) were determined as the peak value of the endothermal and exothermal phenomena in the DSC curve, respectively. The specific heat increment Δc_p, associated with the glass transition of the amorphous phase, was calculated from the vertical distance between the two extrapolated baselines at the glass-transition temperature. The heat of fusion (ΔH_m) and the heat of crystallization (ΔH_c) of the crystal phase were calculated from the area of the DSC endotherm and exotherm, respectively.

In order to determine the crystallization rate under non-isothermal conditions, the samples were heated at 20 °C/min to about 40 °C above fusion temperature, kept there for 3 min and then cooled at 10 °C/min. The temperature corresponding to the maximum of the exothermic peak in the DSC-cooling curve (T_{cc}) can be correlated to the crystallization rate.

Repeated measurements on each sample showed excellent reproducibility.

2.5.3. Wide-angle X-ray measurements

X-ray diffraction patterns were collected with Cu K_α radiation by means of an X'Pert PANalytical diffractometer equipped with a fast

X'Celerator detector. Variable temperature measurements were carried out in an Anton Paar TTK450 heating device mounted into the diffractometer.

In order to perform a "second scan" (on heating), the samples were melted at 280 °C, kept there for 3 min, put into liquid nitrogen, then transferred in the TTK450 heating device. The samples were analyzed at 25 °C then heated at 20 °C/min. The heating ramp was stopped for about 1.4 min at each pre-selected temperature to collect diffraction data.

3. Results and discussion

At room temperature the as-synthesized copolyesters appear as opaque white solids. Their solubility was checked in various solvents: all the samples were found to be fully soluble at room temperature only in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) or in a mixture of chloroform/1,1,1,3,3,3-hexafluoro-2-propanol, showing a behavior similar to PBN and PTDEN. Before molecular, thermal and diffractometric characterization, all the polymers were carefully purified by dissolution in a mixture of $CHCl_3$/HFIP (80/20 v/v) and precipitation in methanol. After that, they were recovered by filtration and again dissolved and reprecipitated twice. Finally, the samples were kept under vacuum at room temperature for several days in order to remove the residual solvent. The purified polymers appear as white powders and their characteristics are collected in Table 1.

First of all, it can be noted that all the copolymers are characterized by high molecular weights, comparable to those of the parent homopolymers, proving that appropriate polymerization conditions were adopted and a good polymerization control was obtained.

The chemical structure of all the copolyesters was determined by ^{1}H NMR spectroscopy. As an example, the ^{1}H NMR spectrum of PBN-PTDEN40 is shown in Fig. 1, together with the chemical shift assignments. In all cases, the spectra were found to be consistent with the expected structures. The copolymer composition was calculated from the relative areas of the ^{1}H NMR resonance peak of the **e** aliphatic protons of the butanediol sub-unit located at 2.13 ppm and of the **g** protons of the thiodiethylene diol sub-unit at 3.13 ppm. The data, collected in Table 1, show that the final copolymer composition is slightly different from the feeding one. This result can be ascribed to differences in reactivity of the glycols as well as in their vapour pressures [10].

It is well known that the random or alternate or block nature of copolymers is an important factor which can influence strongly their final properties. Information on the arrangement of the comonomeric units in the chain can be deduced by the degree of randomness *b*, which can be determined by ^{1}H NMR spectroscopy. The calculation of *b* has been carried out taking into consideration the resonance peaks of the **a** aromatic protons of the naphthalate sub-unit, so that it can be expressed as [11]

$$b = P_{BTDG} + P_{TDGB} \tag{1}$$

where P_{BTDG} and P_{TDGB} are the probability of finding a *B* unit next to a *TDG* unit and the probability of finding a *TDG* unit next to a *B* unit, respectively.

The two probabilities can be expressed as

$$P_{BTDG} = \frac{(I_{BTDG} + I_{TDGB})/2}{(I_{BTDG} + I_{TDGB})/2 + I_{BB}} \tag{2}$$

$$P_{TDGB} = \frac{(I_{TDGB} + I_{BTDG})/2}{(I_{TDGB} + I_{BTDG})/2 + I_{TDGTDG}} \tag{3}$$

where I_{BTDG}, I_{TDGB}, I_{BB} and I_{TDGTDG} represent the integrated intensities of the resonance signals of *BTDG*, *TDGB*, *BB*, and *TDGTDG* sequences, respectively. It has to be emphasized that *b* is equal to 1 for random copolymers, equal to 2 for alternate copolymers and $0 < b < 1$ for block copolymers.

As it can be seen from Fig. 1, the resonance peaks due to mixed sequences are partially overlapped. In order to perform an accurate calculation of the two probabilities, a nonlinear fitting was performed with multiple Gaussian curves. Fig. 1 also shows the resolved curves and the results obtained demonstrate the correctness of the deconvolution method employed.

Table 1 lists the value of *b* obtained for all the samples investigated. In all cases, the degree of randomness was found very close to 1, indicating the random nature of the copolyesters synthesized.

The polyesters were afterwards examined by thermogravimetric analysis and differential scanning calorimetry. The investigation on the thermal stability was carried out both in air and under nitrogen atmosphere. Fig. 2 shows the thermogravimetric curves of the samples under nitrogen atmosphere, from which the temperature of initial decomposition (T_{id}) and the temperature corresponding to the maximum weight loss rate (T_{max}), collected in Table 2, were determined. In the same figure the TGA curves of the parent homopolymers are also reported for comparison [6].

As it can be seen, in all the copolymers under investigation the weight loss takes place in one-step, analogously to PBN and PTDEN, and the residue appears to depend on composition, increasing as the amount of TDEN co-units is increased. The thermal stability was found to depend on composition, being lower as TDEN unit content increases. However, all the samples are characterized by good thermal stability, the temperature of initial decomposition T_{id} ranging from 355 to 396 °C (see Table 2). An analogous dependence on composition of the thermal stability was observed in air, even though in this case all the samples are characterized by a weight loss of 100% and the thermal degradation process takes place in two steps.

3.1. As-prepared samples

As regards calorimetric results, being the samples characterized by high M_ns, an influence of molecular weight on the glass transition and melting of the polymers synthesized can be excluded.

It is well established that the melting behavior of a polymer is affected by its previous thermal history and therefore, in order to provide the same heat treatment to all the samples investigated, prior to thermal analysis the specimens have been aged for a very long time (about 6 months) at room temperature in desiccators. The DSC traces of such samples are reported in Fig. 3 and the data obtained in Table 2, together with the data concerning pure PBN and PTDEN, for comparison.

The DSC traces of all the samples are typical of semicrystalline materials, being characterized by the presence of a conspicuous melting endotherm. Both melting point and heat of fusion of the copolymers are found to be affected by composition, regularly decreasing as the amount of TDEN co-units is increased, as usually

Table 1
Molecular characterization data of PBN-PTDEN random copolymers.

Sample	TDEN (mol %)		b	M_n	M_w/M_n
	Feed	^{1}H NMR			
PBN[a]	0	0	–	23,000	2.1
PBN-PTDEN10	10	9.5	0.99 ± 0.01	36,400	2.8
PBN-PTDEN20	20	16.5	1.00 ± 0.01	30,500	3.2
PBN-PTDEN30	30	30	1.00 ± 0.01	31,000	2.7
PBN-PTDEN40	40	35	1.00 ± 0.01	31,400	3.1
PTDEN[a]	100	100	–	35,000	1.9

[a] From ref. [6].

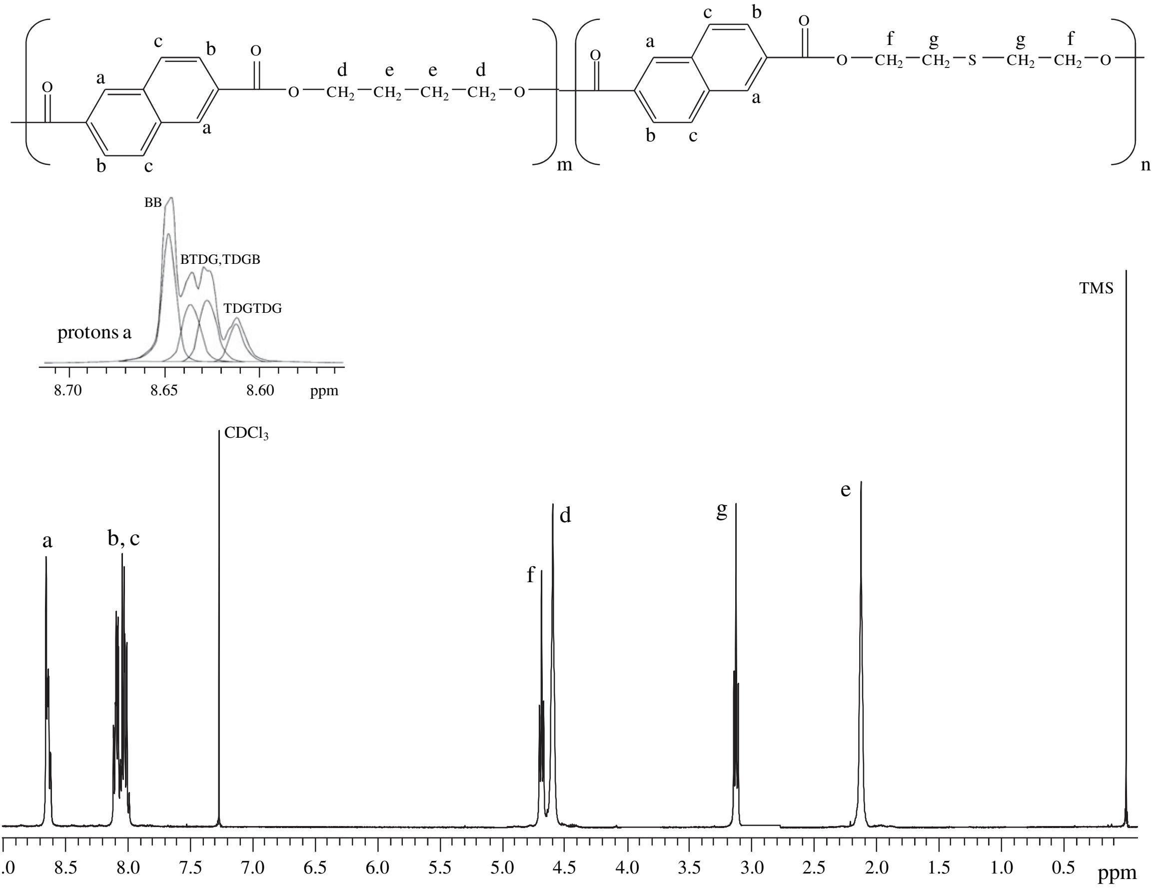


Fig. 1. 400 MHz ^{1}H NMR spectrum of PBN-PDEN40 copolymer and resonance assignments with the expansion of region of protons **a** between 8.30 and 8.70 ppm.

found in random copolymers with the comonomeric units present in minor amount completely rejected from the crystalline phase or partially incorporated in it [12,13]. Furthermore, in the copolymers the endotherm region is broader, suggesting the presence of a larger distribution of crystallites with different degree of perfection. As is well known, in the case of copolymers, a "natural" or "inbuilt" limit to the lamellar thickness as a result of non-crystallizable chain segments occurs [14,15]. In fact, in the presence of these ones, the envisaged mode of chain attachment does affect the driving force term as well as the barrier. Consequently, the formation of very thick crystallites is prevented.

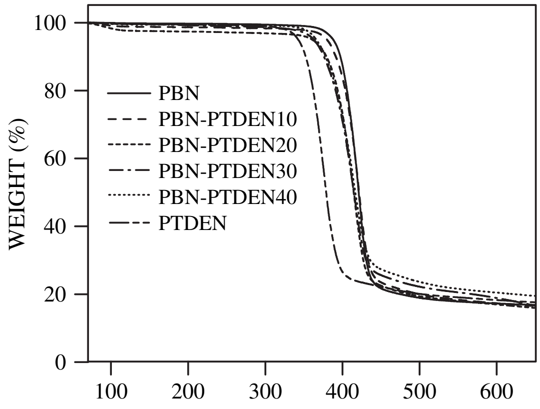


Fig. 2. Thermogravimetric curves of PBN, PTDEN (from ref. [6]) and of their random copolymers under nitrogen atmosphere (heating rate: 10 °C/min).

As is well known, PBN is characterized by two crystal forms, α and β. As can be appreciated from the sketches and from the data reported in Fig. 4, the molecular packing appears to be very similar for the two phases. The aromatic rings lye in planes almost parallel to the *ab* one, the major difference being the conformation of the butylene sub-unit, which is more extended in the β-form. This causes a larger period along the *c*-axis (fibre axis). Reversible transition between these two forms can be obtained by mechanical deformation. By slow cooling from the melt state (0.1 °C/min), a crystalline form, denoted as β′, characterized essentially by the same X-ray diffraction profile of β one, i.e. has the same structure, is obtained [8]. α and β′ crystal phases can be distinguished on the basis of their X-ray diffraction patter [16] and therefore all the samples under investigation were submitted to X-ray analysis. The data collected for the "as-prepared" PBN-PTDEN copolymers and for PTDEN are reported in Fig. 5.

The profiles are typical of semicrystalline samples: a crystalline component embedded in an amorphous medium. On the basis of the profile shapes, it can be deduced that only one crystalline phase is present in each sample. However, the patterns can be subdivided into two groups, according to TDEN content: the samples containing up to 20 mol% of TDEN units are characterized by X-ray patterns very similar to that of the α-form of PBN [16], indicating that the crystal structure which develops in these copolymers has the characteristics of the α lattice. On the contrary, the copolymers with TDEN unit content higher than 20 mol% crystallize assuming the lattice of the PBN β′-form.

The reflections of PTDEN were not detected in the copolymers, but the increase of PTDEN amount causes a moderate shift in the interplanar distances as can be appreciated for d_{010} and d_{100} in the

Table 2
Thermal characterization data of PBN-PTDEN random copolymers.

Sample	T_{id} (°C)	T_{max} (°C)	"As-prepared"		"Melt-quenched"						T_{cc} (°C)
			T_m (°C)	ΔH_m (J/g)	T_g (°C)	Δc_p (J/g °C)	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)	
PBN[a]	396	422	240	57	79	0.104	–	–	240	50	210
PBN-PTDEN10	393	420	229	39	72	0.068	83	14	227	58	197
PBN-PTDEN20	389	415	221	35	66	0.038	80	39	219	41	190
PBN-PTDEN30	384	414	200	32	61	0.073	75/88	37	199	38	168
PBN-PTDEN40	381	413	191	24	58	0.087	73/94	32	189	32	157
PTDEN[a]	355	377	160	40	47	0.343	136	3	160	3	–

[a] From ref. [6].

inset of Fig. 5. A discontinuity is evident in the lines connecting the points between PBN-PTDEN20 and PBN-PTDEN30 samples, confirming the variation in the crystal phase type at this value of composition.

In the case of PBN-PTDEN copolymers too, analogously to what found in the case of PBN-PDEN [9], composition plays a crucial role in determining the selective formation of pure α- or β′-phase, this last exclusively obtained in pure PBN by performing non-isothermal crystallization from the melt at an extremely low cooling rate (0.1 °C/min). Moreover, it is worth remembering that usually copolymerization affects the polymorphic behavior of the parent homopolymer by changing the relative ratio between the two forms and rarely the growth of a unique phase is overall favored at the other's expense.

Subsequently, the as-prepared samples were submitted to variable temperature XRD analysis, in order to investigate if crystalline structure changes occur in the solid state (see Fig. 6 for PBN-PTDEN10 and PBN-PTDEN40, as examples): in this view, we choose temperature scans that reproduce the thermal treatment performed in the DSC analysis (see 1st scan), the only difference being the need of keeping the sample at the selected temperature for about 1.4 min in order to collect the diffraction data. In both cases, a sharpening of the peaks of the developed phase was observed as the temperature is increased, indicating an improved crystallinity and crystal perfection: however, whereas for PBN-PTDEN40 crystalline form transformations never occur in the solid state, confirming the stability of the β′-form, in the case of PBN-PTDEN10, obtained as α-phase, the heating induces significant changes in the sample. In fact, as evidenced by the Fig. 6A, new peaks appear in the XRD profile over 200 °C, whose position proves the presence of the β′-form, which at high temperature coexists with the α one. At 230 °C, it is evident that most of the α-form was transformed in the β′ one. As regards PBN-PTDEN20 and PBN-PTDEN30, they were found to be characterized by a behavior analogous to PBN-PTDEN10 and PBN-PTDEN40, respectively.

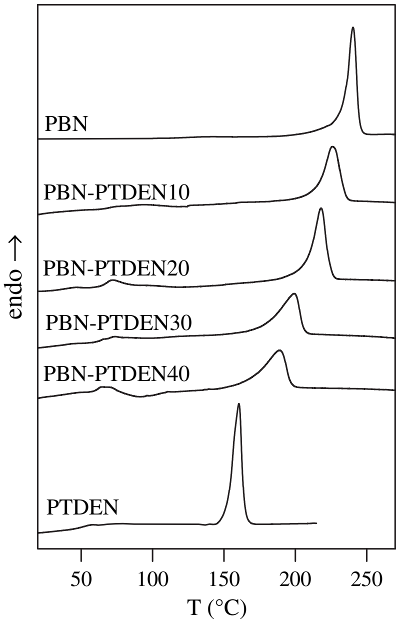
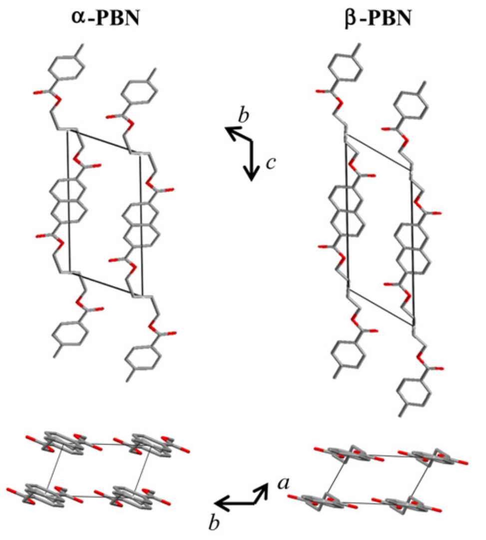


Fig. 3. Calorimetric curves of PBN, PTDEN (from ref. [6]) and their random copolymers (1st scan, heating rate: 20 °C/min).

3.2. Melt-quenched samples

As a further study, the transformations of melt-quenched samples were investigated. Preliminary, PBN-PTDEN copolymers, rapidly cooled from the molten state were examined by differential scanning calorimetry, in order to get information both on the glass-transition and fusion phenomena. The DSC curves of the so-treated samples are shown in Fig. 7, together with those concerning pure PBN and PTDEN, for the sake of comparison.

As it can be seen, the DSC trace of PBN is characterized by a small endothermal baseline deviation, associated with the glass-transition phenomenon, followed by a conspicuous melting endotherm



	α-form	β-form
a (nm)	0.487	0.455
b (nm)	0.622	0.643
c (nm)	1.436	1.531
α (°)	100.78	110.1
β (°)	126.90	121.1
γ (°)	97.93	100.6

Fig. 4. Arrangement of the polymer chains in the α-form (left) and β-form (right) of PBN: a view along the *a*-axis (top) and a projection along *c*-axis (bottom). Crystallograpic data of PBN from ref. [16] are reported in the box.

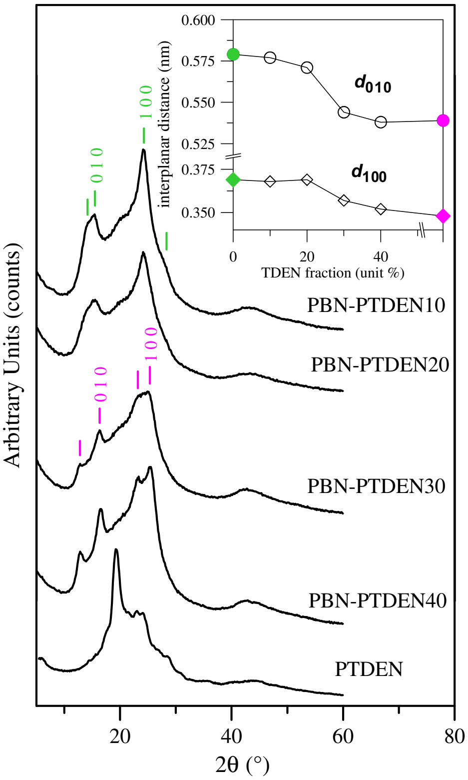


Fig. 5. XRD patterns of the "as-prepared" PBN-PTDEN copolymers and PTDEN homopolymer. The sticks in green and pink colors indicate the positions of the four main reflections in the PBN α- or β-form, respectively. The position of the (0 1 0) and (1 0 0) peaks are highlighted. Inset: plot of the (0 1 0) and (1 0 0) interplanar spacings *versus* TDEN unit content for PBN-TDEN copolymers. For comparison the values reported in the literature for the α- and β-phases of the PBN are shown as filled symbols. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

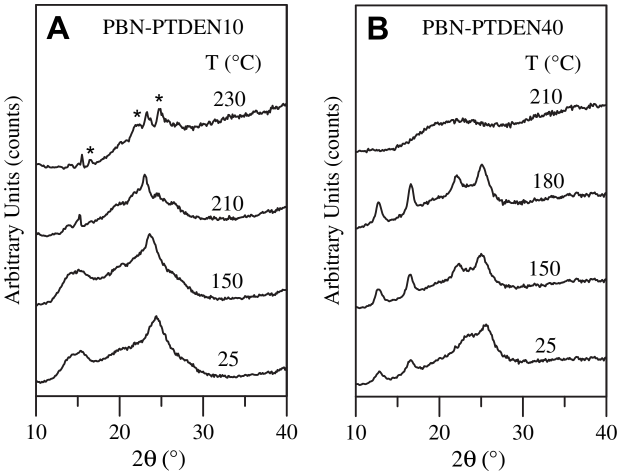


Fig. 6. XRD measurements collected at the indicated temperatures for: A) PBN-PTDEN10 and B) PBN-PTDEN40. The asterisks indicate the most intense reflections of β′-phase.

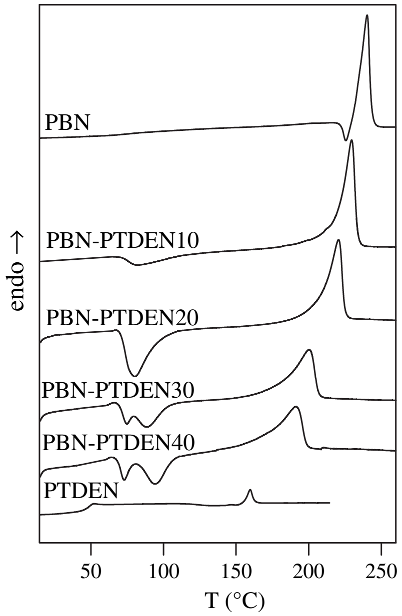


Fig. 7. Calorimetric curves of PBN, PTDEN (from ref. [6]) and PBN-PTDEN random copolymers after melt quenching (2nd scan, heating rate: 20 °C/min).

at a much higher temperature, indicating that the sample cannot be frozen into a completely amorphous state by quenching and therefore is partially crystalline. On the contrary, PTDEN reveals to be completely amorphous, the corresponding calorimetric curve being characterized by an intense baseline deviation associated to the glass-transition phenomenon, followed by small exotermic and endotermic peaks of comparable heats. As far as the copolymers under investigation are concerned, the corresponding calorimetric traces are characterized by a glass transition followed by an exothermal "cold-crystallization" peak and a melting endotherm at higher temperature. In the case of PBN-PTDEN10, the enthalpy associated with the crystallization phenomenon is lower than that of fusion endotherm, indicating that this sample cannot be frozen into a completely amorphous state by quenching, analogously to PBN. On the contrary, for PBN-PTDEN20, PBN-PTDEN30 and PBN-PTDEN40, the enthalpy of crystallization very well compares with the corresponding heat of fusion, indicating that these polymers after melt quenching are completely amorphous, similarly to PTDEN. As to the glass-transition phenomenon, the values of the glass-transition temperature collected in Table 2 show a clear dependence on composition, decreasing as the content of TDEN units is increased. The flexibility of the chain is undoubtedly the most important factor influencing T_g, being a measure of the ability of a chain to rotate, and therefore the more flexible chains are, the lower the T_g. The decrease in the glass-transition temperature on introducing thiodiethylene naphthalate co-units can be correlated to the higher flexibility induced in the polymer chain by sulphur atoms. As mentioned above, a cold-crystallization process is always evident, except in the case of PBN, indicating that a portion of amorphous material, once T_g is exceeded, acquires enough mobility to rearrange and crystallize. Looking into more detail the cold-crystallization phenomenon, it can be noted that its nature is quite complex, the corresponding exotherm being formed by two partially overlapped peaks which become better separated as TDEN co-unit content increases. A single melting phenomenon appears at higher temperatures: the melting point decreases with increasing the co-unit content, due to the formation of less perfect crystals; moreover the width of the endothermic peak increases as the amount of thiodiethylene naphthalate unit is increased because of the presence of a larger distribution of crystallites with different degree of perfection. Lastly, a decrement of the heat of fusion of the copolymers with respect to that of the homopolymer PBN is observed. Afterwards, variable temperature X-ray diffraction experiments were carried out on PBN-PTDEN copolymers subjected to melt quenching. As examples, the results obtained for PBN-PTDEN10 and PBN-PTDEN20 are shown in Fig. 8. PBN-PTDEN10 is

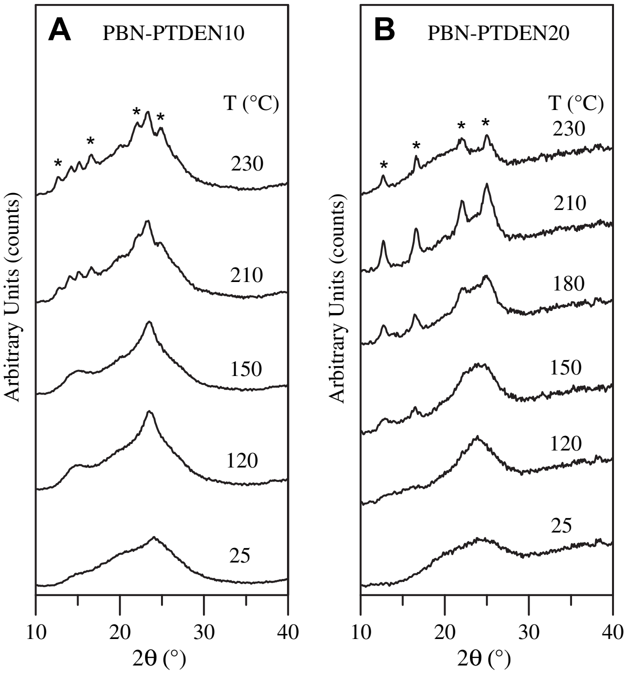


Fig. 8. XRD patterns of PBN-PTDEN10 (A) and PBN-PTDEN20 (B) after melt quenching recorded during a second heating at the indicated temperatures. The asterisks indicate the most intense reflections of the β′-phase.

characterized at 25 °C by a very small order degree reminiscent of the α-phase, as can be seen from the corresponding XRD profile. By heating, an improvement of crystal size (a reduction of the peak width was indeed observed) and crystallinity was displayed. The position of such diffraction peaks was practically identical to those of α-form. At 210 °C, the appearance of new diffraction peaks was observed. Their position proves the presence of the β′-form, which at high temperature coexists with the α one. The appearance of the β′-form at a so high temperature, as well as the fact that α-form is kinetically whereas β′-form is thermodynamically favorite, indicate a possible α → β′ transformation, which have been never observed previously in pure PBN [8].

As concerns PBN-PTDEN20 sample, the amorphous sample obtained by fast cooling from the melt develops directly the β′-phase during the subsequent heating scan when the temperature reaches the value of 150 °C; as the temperature is further increased, only an improvement of a such crystalline phase can be observed. An analogous behavior was found for PBN-PTDEN30 and PBN-PTDEN40 copolymers, the only difference being the lower value of temperature at which the melting process occurs. In conclusion, the XRD results obtained at different temperatures on the copolymeric samples after melt quenching indicate a marked effect of composition on the polymorphic behavior of PBN: in the case of PBN-PTDEN10 copolymer, the α-phase formation is favorite and only at high temperature a partial α → β′ transformation occurs; for TDEN unit content ranging from 20 to 40 mol%, the selective formation of β′-form takes place and, as expected, no polymorphic changes are observed. Consequently, the double crystallization peaks, which appear in the 2nd calorimetric scan, have to be ascribed to melting/recrystallization processes occurring during the DSC scan and not to the formation of different crystal phases within the samples.

To evaluate the effect of the cooling rate from the molten state on the crystalline phase that the polymer develops after re-heating, each sample was subjected also to the following procedure: cooling from the melt at a controlled cooling rate (20 °C/min) and subsequent re-heating at 20 °C/min. As examples, the results obtained for PBN-PTDEN10 and PBN-PTDEN20 are shown in Fig. 9.

At 25 °C the pattern of both samples shows the contemporary presence of the α- and β′-form peaks. As the temperature is increased, the peaks of β′-form grow to the detriment of α-form ones. The transformation of α → β′-phase becomes appreciable over 200 °C. It appears complete for the PBN-PTDEN20, whereas in the case of PBN-PTDEN10 a little amount of α-phase is detectable up to melting. The presence of a crystalline form even at 25 °C proves that the cooling rate adopted is lower than the crystallization rate of the polymer and probably crystalline nuclei generate during the cooling step. Different results have been obtained for PBN-PTDEN30 and PBN-PTDEN40. First of all, the lower cooling rate applied appears to be however higher than the crystallization rate of both samples and therefore after cooling they are into a completely amorphous state. By heating, β′-form develops at 120 °C, and as temperature raises, the diffraction peaks grow and sharpen, indicating an increased crystallinity and perfection of crystals.

3.3. Slow cooled samples

In order to get an idea on the effect of composition on the crystallization rate of PBN, non-isothermal experiments were also carried out, subjecting the samples to the thermal treatment described in the Experimental Section. It is worth remembering that the half-time of primary crystallization in isothermal measurements correlates with the temperature corresponding to the maximum of the crystallization peaks in non-isothermal experiments (T_{cc}) [17], which is more easily obtainable. The exothermic crystallization peaks of the samples under investigation are reported in Fig. 10. From the inset, where T_{cc} values are reported as a function of composition, it can be observed that the temperature corresponding to the maximum of the exothermal

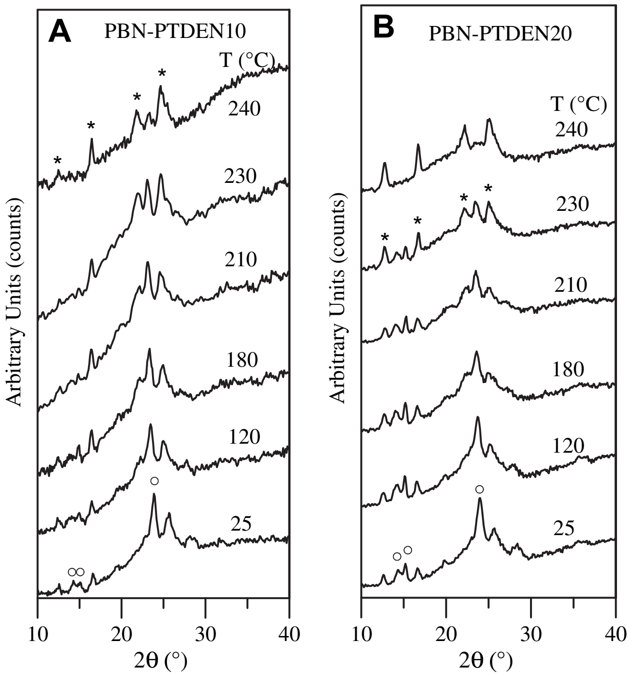


Fig. 9. XRD patterns of PBN-PTDEN10 (A) and PBN-PTDEN20 (B) after melting and slow cooling (20 °C/min), recorded while re-heating at the indicated temperatures. The asterisks indicate the most intense reflections of β′-phase, circles the most intense of α-phase.

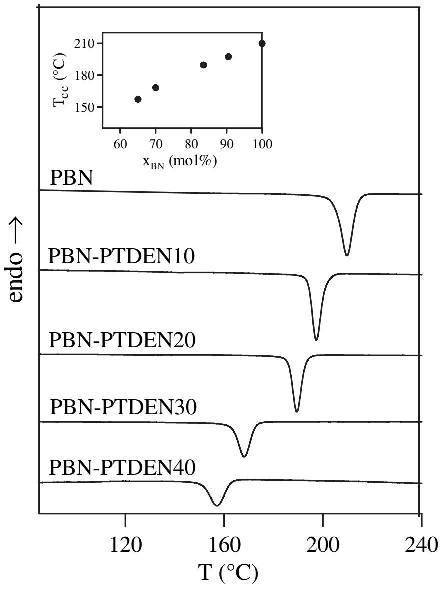


Fig. 10. DSC crystallization exotherms of PBN and PBN-PTDEN random copolymers cooled from the melt at 10 °C/min. In the inset: T_{cc} as a function BN unit content.

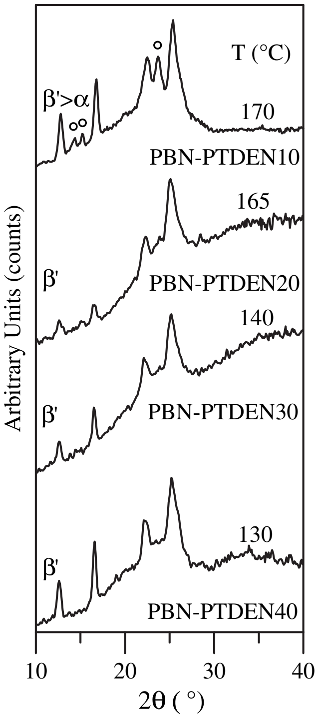


Fig. 11. XRD results of the samples cooled from the melt at 10°/min up to the indicated temperature ($T_{meas} = T_m - 35$ °C,); circles mark the most intense reflections of α-phase.

crystallization peak regularly decreases as the TDEN unit content is increased.

This trend indicates a decrement of the overall crystallization rate of PBN, due to the presence of the non-crystallizable TDEN co-units, which slow down the crystallization process, being rejected in the amorphous state. Also in this case, it's important to obtain information on the nature of crystalline phase which develops during the cooling at 10 °C/min. In this view, we performed XRD experiments which reproduce the thermal treatment employed in the DSC measurements: in particular, each sample was melted and subsequently cooled at 10 °C/min to a temperature of 35 °C lower than the corresponding melting point. The adopted experimental procedure permits to investigate by means of X-ray diffraction the crystalline phases whose formation was observed in the DSC-cooling curves reported in Fig. 10. The results obtained are shown in Fig. 11.

As it can be seen, in the case of PBN-PTDEN10 both phases are evidenced, the β′ one being the main phase; in all other cases, only the β′-form is detected.

It can be concluded that also this thermal treatment confirms that the selective formation of the more thermodynamically stable β′-form is favorite as the TDEN unit content is increased.

By further slow cooling of the copolymers at 10 °C/min to room temperature, no changes of the kind of crystalline phase were observed, the only difference consisting in a general improvement of the crystal perfection as the temperature decreases.

In conclusion, the pure β′-phase can be obtained at TDEN unit content ≥30 mol%, independently on the thermal treatment applied to the sample. As proved by the DSC results, the flexibility of the chains and therefore their mobility increases as the amount of co-unit content is increased and this should help the more tightly packing of the macromolecules in the crystalline phase characteristic of the β′-form. In order to confirm such hypothesis, the diffractometric results of the copolymeric system under investigation can be compared with those of poly(butylene/diethylene naphthalate) copolymers (PBN-PDEN) previously reported [9] (see Table 3).

As far as the "as-prepared" samples are concerned, no difference can be observed between the two copolymeric systems, since they display the same dependence of crystal form on composition, independently on the nature of the ethero atoms introduced. When the "as-prepared" samples of the two copolymeric systems are subjected to variable temperature XRD analysis, one significant difference appears: in the case of all the PBN-PDEN copolymers no crystalline structure changes occur in the solid state, whereas for PBN-PTDEN10 and PBN-PTDEN20 the transformation of most of the α-form into the β′ one takes place. A different behavior between PBN-PDEN and PBN-PTDEN can be also evidenced analyzing the XRD profiles of samples melt quenched and reheated at 20 °C/min. In fact, the β′-phase formation is favorite at TDEN unit content ≥20 mol%, whereas in the case of PBN-PDEN copolymers amounts ≥30 mol% of DEN co-units are needed. When the XRD profiles are collected on heating after slow cooling from the melt, several differences are observed between the two copolymeric systems: first of all, the contemporary presence of α- and β′-forms is already detected at 25 °C in PBN-PTDEN10 and in PBN-PTDEN20, whereas in PBN-PTDEN30 and PBN-PTDEN40 in the same conditions only the β′-phase develops. Lastly, the analysis of the crystal phase which develops after cooling from the melt at 10 °C/min indicates that in the case of PBN-PTDEN copolymers the β′ formation is significantly more favorite, being this phase present in abundant amount already in PBN-PTDEN10.

In conclusion, as a general outline, it can be pointed out that the substitution of PDEN co-units with PTDEN ones gives rise to a pronounced increment of the stability of the β′-form on respect to the α one. This result can be explained on the basis of two reasons:

1. The presence of sulphur atoms in place of ether-oxygen ones makes the polymer chains more flexible;
2. The sulphur atoms are characterized by a Van der Waals radius which is very similar to that of neighbor CH_2, whereas the ether-oxygen atoms have a lower Van der Waals radius.

Both factors favor a higher packing efficiency, which undoubtedly help the formation of the more tightly packed β′-form.

Table 3
Crystalline phases evidenced performing *on site* X-ray diffraction.[a,b]

conditions used	PBN-PDEN10	PBN-PDEN20	PBN-PDEN30	PBN-PDEN40
	PBN-PTDEN10	PBN-PTDEN20	PBN-PTDEN30	PBN-PTDEN40
as obtained	α	α	β’	β’
	α	α	β’	β’
1st scan	α	α	β’	β’
	α → α + β’	α → α + β’	β’	β’
2nd scan after melt quenching	α → α + β’	α → α + β’	*Am* → β’	*Am* → β’
	α → α + β’	*Am* → β’	*Am* → β’	*Am* → β’
2nd scan after melt and slow cooling	α → α + β’	α → α + β’	α → α + β’	β’
	α + β’ → β’ + α	α + β’ → β’	β’	β’
isot. cryst. from the melt at $T=T_m$-35°C	α >> β’	α + β’	β’ > α	β’
	β’ + α	β’	β’	β’

[a] *Am* means amorphous phase. The arrow means a phase transformation that occurs during the heating process.
[b] When two phases are indicated, the one on the left of the + sign is the most abundant.

4. Conclusions

The introduction along the PBN polymer chain of sulphur atoms lead to significant variations in the final properties and copolymer composition appears to be the prominent parameter in determining the characteristics of the samples under investigation. In particular:

- the thermal stability slightly decreases, even though keeps good for all the samples under investigation;
- the glass-transition temperature decreases, due to the higher flexibility of the sulphur containing TDEN co-units;
- the crystallization rate decreases, due to the rejection in the amorphous phase of the non-crystallizable co-units.
- the most relevant result concerns the influence of sulphur containing co-units on the polymorphic behavior of PBN. This latter is substantially altered by the introduction of thiodiethylene naphthalate comonomeric unit and composition reveals to be a crucial factor in favoring one crystalline form. In particular, the presence in the copolymer of increasing amount of TDEN units favors the β′-form over the α one, and for TDEN unit content equal to 30 mol% the α-form can never be obtained, irrespective of the thermal treatment adopted. An effect of the thermal treatment has been on the contrary observed for PBN-PTDEN20. In this case it also play a role in favoring one form with respect to the other: when the sample is slowly cooled from the melt, a mixture of α- and β′-forms is observed, whereas, after melt quenching, the formation of the β′-form takes place.

  Lastly, an analysis of the effect of substitution of ether-oxygen atoms (present in the PBN-PDEN copolymeric system previously investigated) with sulphur ones point out that the formation of the β′-form is favorite in PBN-PTDEN copolymers due to the higher packing efficiency. This latter can be ascribed to the larger dimensions of sulphur atoms, very similar to those of neighbor methylene groups, and to the higher chain flexibility due to the longer C–S–C bonds.

In conclusion, a new route has been found in order to obtain a pure α or β′ crystalline form of PBN: each of them can indeed be selectively obtained simply by switching copolymer composition.

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