

Macro-oriented network of liquid-crystalline polyesters: crosslinking induced by γ -irradiation and thermally activated reaction

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Abstract

The synthesis of a macro-oriented network from liquid-crystalline polymers, bearing pendant groups with unsaturations, is reported. Virgin polymers are processable to obtain oriented samples, e.g. fibres, which may be crosslinked through thermal activation and/or exposure to γ -radiation. The liquid-crystalline state is “frozen” and the macroscopic anisotropy is preserved even at high temperatures. Compared to virgin fibres, irradiated samples show an enhancement of tensile performances, thus indicating that the main effect of irradiation is crosslinking without significant degradation phenomena. © 2000 Elsevier Science Ltd. All rights reserved.

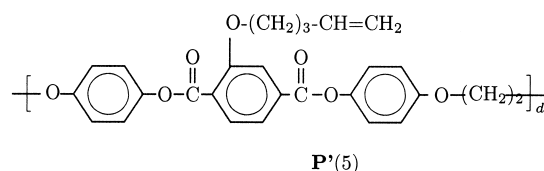
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1. Introduction

In the last two decades new polymeric materials have been developed in order to improve the mechanical performance [1,2]. A significant role has been played by main-chain liquid-crystalline polymers (LCPs) because of their processability and the high degree of chain orientation that may be obtained during extrusion. LCPs have been tested not only as pure materials but also as reinforcing agents in the preparation of new composites, as well as minor components in polymeric blends, usually in quantities of a few percent.

Several synthetic routes to prepare liquid-crystalline networks (LCNs) have been reported, in order to study the effect of crosslinking on sample properties [3–14], with particular emphasis on the mechanical performance and optical properties. For example Finkelman and co-workers [4] have shown that LC networks (side-chain type) may be obtained in a two-step curing process. First, a weak network is synthesized and a constant load is applied to induce anisotropy, then a second crosslinking reaction is applied to “quench” the initial network anisotropy. Recently, Shiota and Hober [10] have reported the synthesis of a smectic network prepared from a LC epoxy monomer; the reaction

with a diamine compound gives rise to the formation of samples which can be aligned by applying an external stress in the rubbery regime. In this way they prepared samples with a value of the order parameter S of up to 0.35. In a previous paper [14], some of us have shown that the LCP with formula



may be thermally processed to give a macro-oriented sample (e.g. fibres) and then crosslinked to an anisotropic network in which the liquid-crystalline order is “frozen”. Crosslinking is carried out in two steps: first the fibres are immersed in a solution of radical activator (dichloromethane as solvent, *t*-butylperoxybenzoate as activator) allowing its diffusion in the bulk of sample, then thermal activated radical crosslinking (TARC) is performed by annealing at a temperature lower than the melt. It is important to choose a solvent that may swell the LCP and allow the diffusion of the radical activator, but also this should not lead to polymer solubilization. The occurrence of these two conditions is indeed very rare, thus this procedure is not a general one. Moreover, solvent–polymer interaction may also cause loss of orientation and sample deformation to some extent.

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Table 1
Thermodynamic DSC data concerning virgin fibres of PA (*n*)

Polymer	T_m^a	ΔH_m^b	T_i^c	ΔH_i^d	η^e
PA(8)	188.2	11.2	274.2	7.9	1.43
PA(10)	157.2	10.8	235.3	9.8	1.26
PA(12)	143.8	11.0	212.1	9.1	2.36

^a T_m (°C) melting temperature. Temperatures are measured at the maximum of the transition endotherm.

^b ΔH_m (J g⁻¹) melting enthalpy.

^c T_i (°C) isotropization temperature.

^d ΔH_i (J g⁻¹) isotropization enthalpy.

^e Intrinsic viscosity, $[\eta]$ (dl g⁻¹) measured at 25.0°C in chloroform.

It is well known that ionising radiation, like γ -rays, gives rise to radicals which may modify the chemical structure of polymeric materials, causing chain scission, branching or crosslinking [15–17]. The relative amount of these phenomena depends on chemical composition and molecular structure (both molecular packing and morphology) of the investigated polymer as well as on the γ -radiation dose and the dose rate, when the kinetics of the different phenomena are quite different in scale. For instance, low γ -radiation doses (50–200 kGy) induce mainly degradation processes in polypropylene while high dose (300 kGy and higher) promotes crosslinking and branching [18]. In the case of polyethylene, branching and crosslinking take place even at low doses [16,17].

One of the most valuable performances of ionising radiations is that they allow to process polymer materials in the solid state and in their final shape. This was applied to fix, through crosslinking reactions, thermodynamically unstable

Table 2
Thermodynamic DSC data after thermal crosslinking of fibres of PA(*n*) (crosslinking is performed by annealing for 30 minutes at 145°C for *n* = 8, 10 and 130° for *n* = 12)

Polymer	% ^a	T_m^b	Δ_m^c	T_i^d	ΔH_i^e
PA(8)	0	188	11.0	273	7.9
	5.2	189	14.5	272	8.6
	2.1	189	14.1	268	8.6
PA(10)	21.7	189	7.2	268	6.0
	0	156	11.2	236	9.8
	5.2	156	5.7	235	3.3
PA(12)	12.1	156	4.9	234	2.7
	21.7	156	3.7	234	1.8
	0	145	10.8	214	9.1
	5.2	146	11.5	211	5.3
	12.1	145	4.3	209	2.4
	21.7	146	8.5	208	4.9

^a Weight percentage of *t*-butylperoxide as thermal activator in dioxane solution.

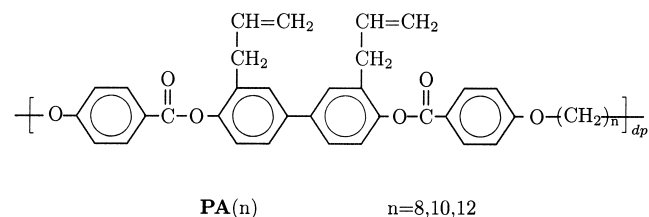
^b T_m (°C) melting temperature.

^c ΔH_m (J g⁻¹) melting enthalpy.

^d T_i (°C) isotropization temperature.

^e ΔH_i (J g⁻¹) isotropization enthalpy. Temperatures are measured at the maximum of the transition endotherm.

morphologies, for instance in incompatible polymer blends [19]. In this article the use of γ -radiation to crosslink thermotropic polymers with formula [20]



is studied and a comparison with the TARC approach is also presented.

2. Experimental section

PA(*n*) polymers were synthesized by the interfacial polycondensation of 3,3'-diallyl-4,4'-dihydroxybiphenyl and the chlorinated derivative of the appropriate 4,4'-dicarboxy-1,*n*-diphenoxy-alkane, as already reported [20]. Fibres were extruded from the anisotropic liquid phase and cooled in air without temperature control.

Before irradiation, virgin fibres were carefully dried and degassed by a vacuum pump for at least 2 h. Irradiation was done under vacuum at room temperature (about 25°C) by the IGS-3, a panoramic ⁶⁰Co irradiator [18]. The dose rate, measured by a PTW Universal Dosimeter, was 4.1 kGy/h and the total absorbed doses were in the range of 20–350 kGy, a variance of 5% in the radiation absorption was accepted.

Thermal measurements were carried out on fibre samples by means of a DSC-7 Perkin–Elmer calorimeter under a nitrogen flow rate of 10°C/min. Optical microscopy was performed by means of a Jenapol microscope fitted with a Linkam THMS 600 hot stage.

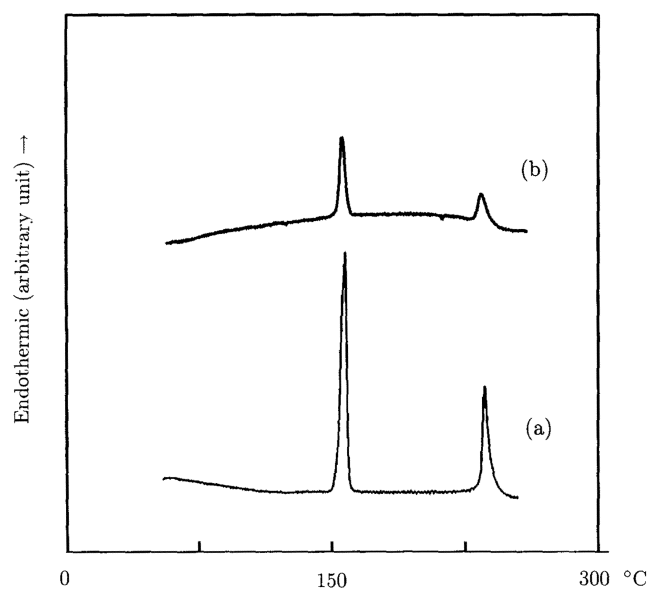


Fig. 1. DSC heating traces (10°C/min) of PA(10) (fibres): (a) before; and (b) after TARC, previous immersion in sol. III.

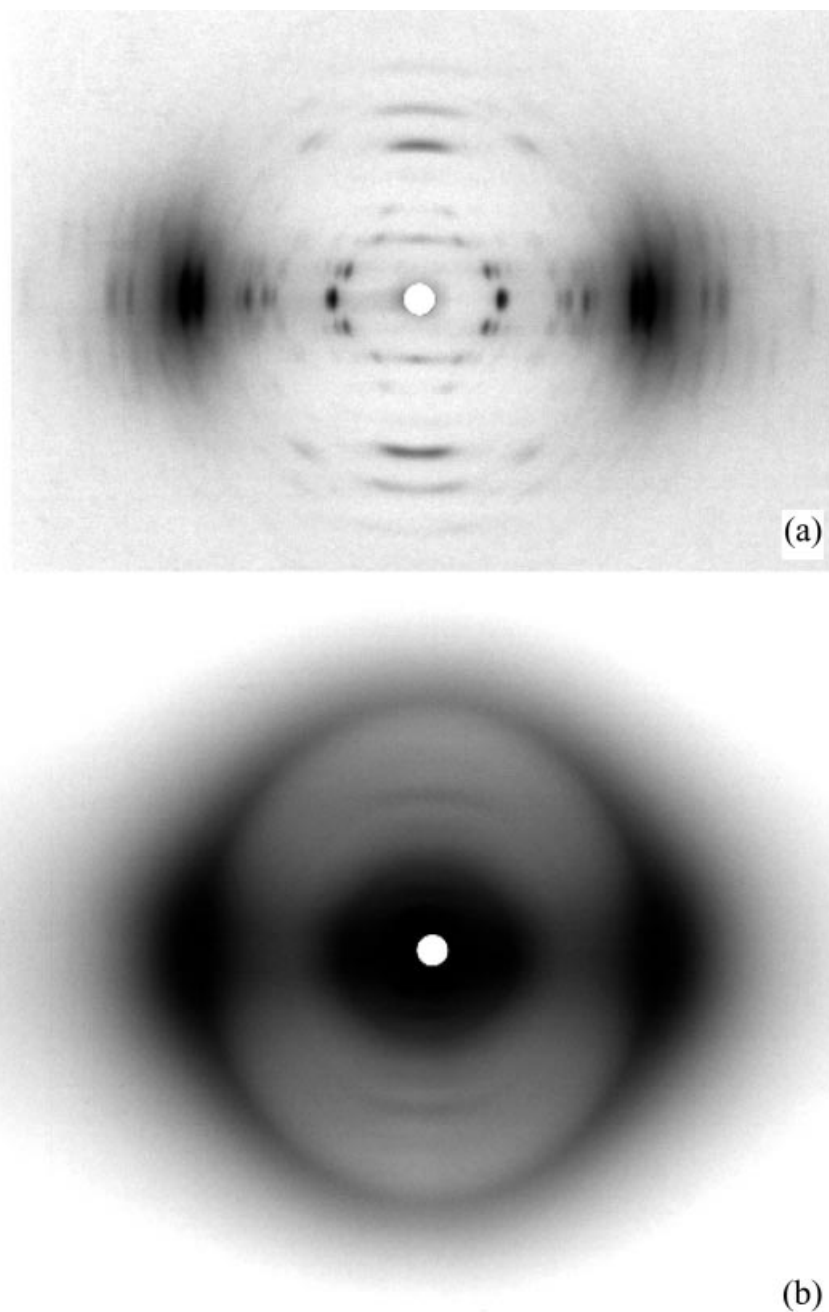


Fig. 2. X-ray diffraction patterns of **PA**(10) (fibres) after TARC, previous immersion in sol. III: (a) immediately after TARC; and (b) after the DSC first heating run until 300°C.

Fibre diffraction spectra were recorded under vacuum on photographic film (Kodak DEF-5), by means of a cylindrical camera with a radius of 57.3 mm with the X-ray beam direction perpendicular to the fibre axis. V-filtered Cr-K α radiation was employed to ensure high spectral resolution.

Solubility tests were made by means of a Soxhlet extractor, using *o*-dichlorobenzene as solvent. Samples were exposed in refluxing *o*-dichlorobenzene for at least 72 h.

Tensile measurements were performed with an Instron 4301 instrument on fibres of 60.0 mm length and 0.25 mm diameter (average of 15 fibres). Grip distance and cross-

head speed were set at 10 mm and 30 mm/min, respectively. Tests were done both at room temperature and 150°C.

3. Discussion

3.1. Thermally activated radical crosslinking

Thermodynamic properties of virgin **PA**(*n*) fibres are given in Table 1. Solubility of **PA**(*n*) in common polar organic solvents (e.g. chloroform, dichloromethane) is

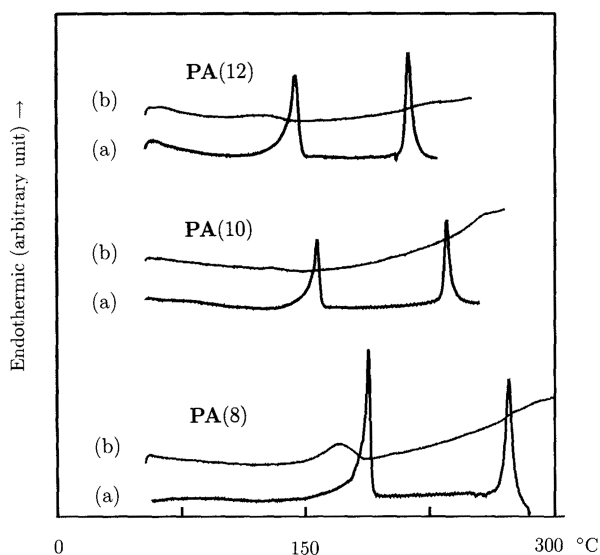


Fig. 3. DSC first heating traces (10°C/min) of **PA**(*n*) (fibres): (a) before; and (b) after γ -irradiation.

very high compared to **P'**(5), as expected for the longer aliphatic spacer in the chain. Dioxane was found to be an adequate solvent, swelling the polymers with weight increases of about 15% after 24 h of immersion. After immersion, fibre orientation, checked by X-ray diffraction, was preserved, thus all the required conditions for TARC were fulfilled. Three solutions of *t*-butylperoxybenzoate radical activator were prepared in dioxane (solutions I, II, and III, with 5.2, 12.1, and 21.7 wt%, respectively) in which the fibre samples were immersed. After 24 h, fibres were

Table 3

Thermodynamic DSC data (first heating run, 10°C/min) and solubility after γ -irradiation of fibres of **PA**(*n*)

Polymer	D^a	% ^b	T_m^c	ΔH_m^d	T_i^e	ΔH_i^f
PA (8)	0	0	188.2	11.2	274.2	7.9
	24	Some	191.2	9.3	277.7	6.7
	57.6	22.5	183.0	10.1	281.8	6.2
	96	60.2	169.1	2.4	n.o.	n.o.
PA (10)	214.4	88.4	154.3	3.9	n.o.	n.o.
	0	0	157.2	10.8	235.3	9.8
	48	59.1	146.7	2.8	239.8	2.0
	96	75.3	n.o.	n.o.	n.o.	n.o.
	214	77.5	n.o.	n.o.	n.o.	n.o.
PA (12)	348	84.5	n.o.	n.o.	n.o.	n.o.
	0	0	143.8	11.0	212.1	9.1
	24	Some	146.3	9.1	217.1	6.2
	57.6	68.5	147.3	2.5	n.o.	n.o.
	96	81.8	n.o.	n.o.	n.o.	n.o.
	214.4	85	n.o.	n.o.	n.o.	n.o.

^a D (kGy), γ -irradiation dose.

^b Insoluble percentage of sample in boiling *o*-dichlorobenzene.

^c T_m (°C) melting temperature. Temperatures are measured at the maximum of the transition endotherm.

^d ΔH_m (J g⁻¹) melting enthalpy.

^e T_i (°C) isotropization temperature.

^f ΔH_i (J g⁻¹) isotropization enthalpy.

taken out, placed on an adsorbing paper, and left in air for 60 min. Subsequently, crosslinking, by solid state annealing, was performed in a calorimeter at 145°C ($n = 8, 10$) and 130°C ($n = 12$) for 30 min. This was followed by a heating run in order to check the fraction of “frozen” nematic phase. The lower the isotropization enthalpy, the higher the amount of the frozen nematic phase. Thermodynamic data given in Table 2 show that crosslinking takes place, but that complete reaction is never reached: in the most favourable case [**PA**(10), sol. III] a residual $\Delta H_i = 1.8$ J/g is measured.

The major features of LCNs obtained through TARC are summarised as follows:

- Optical observations show all fibres are anisotropic up to thermal decomposition. The fibre shape of samples is retained for $n = 10, 12$ while the $n = 8$ fibres collapse to a viscous state at higher temperatures than the melting temperature of the virgin material. This is in agreement with the lower degree of crosslinking found for **PA**(8) corresponding to the higher residual isotropization enthalpy (Table 2). As an example, the DSC first heating traces of virgin and crosslinked **PA**(10) fibres, after immersion in solution III, are compared in Fig. 1. The X-ray diffraction pattern of the crosslinked sample, after the DSC heating scan, shows a residual orientation (see Fig. 2).
- Isotropization temperatures are independent of activator concentration, probably being related to that part of the sample in which crosslinking does not occur. The anomalous trend of isotropization enthalpies for **PA**(12) (Table 2) may be explained by keeping in mind that increasing the activator concentration may decrease the polymer-solution compatibility and, consequently, may reduce the absorption of the activator. For instance, **PA**(12) fibres treated in solution III gives rise to a less

Table 4

Tensile properties of fibres of **PA**(*n*) before and after γ -irradiation

Polymer		T^a	E^b	σ_b^c	ϵ_b^d
PA (8)	Before	25	7.0 (1.0)	330 (50)	8.0 (2.5)
	After	25	7.6 (1.1)	320 (25)	5.5 (1.5)
	After	160	2.5 (0.8)	80 (28)	7.0 (1.0)
	After ^e	25	7.4 (1.0)	320 (60)	5.9 (1.0)
	After ^f	25	5.5 (1.0)	270 (50)	9.5 (1.5)
PA (10)	Before	25	6.5 (1.0)	330 (120)	8.0 (3.5)
	After	25	8.6 (1.2)	350 (100)	6.0 (2.0)
	After	160	0.5 (0.1)	40 (13)	8.0 (2.5)
PA (12)	Before	25	4.6 (1.0)	300 (80)	9.0 (3.0)
	After	25	8.4 (1.2)	340 (75)	6.5 (2.0)
	After	160	0.2 (0.1)	20 (8)	10.0 (1.5)

^a T (°C) temperature at which tensile measurements are performed.

^b E (GPa) elastic modulus.

^c σ_b (MPa) stress at break.

^d ϵ_b (%) strain at break. Standard deviations are given in parenthesis. All the data are the average of 15 independent measurements.

^e Fibrous samples previously annealed 5 min at 150°C.

^f Fibrous samples previously annealed 5 min at 200°C.

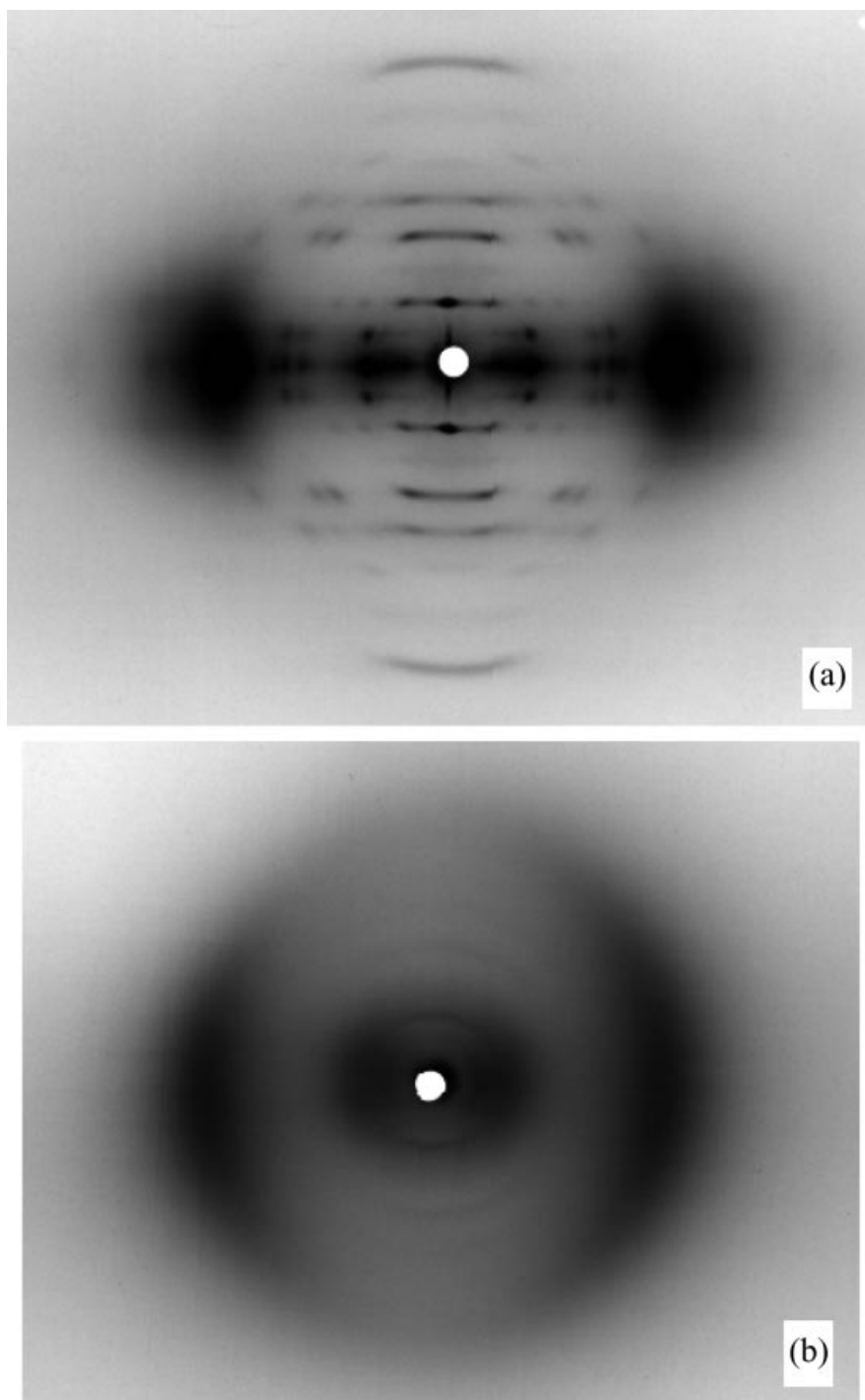


Fig. 4. X-ray diffraction patterns of **PA(8)** (fibres) after γ -irradiation: (a) immediately after irradiation treatment; and (b) after the DSC first heating run until 300°C.

crosslinked sample than that obtained from solution II. About **PA(8)**, the high isotropization enthalpy is quite independent of the activator concentration. This may be accounted for by a low activator–polymer compatibility (the weight increase after immersion is comparable to that of **PA(10)** and **PA(12)** showing that the solvent–polymer interaction is much the same). In this case a

new thermal activator or activator/solvent couple should be tested.

3. The crystalline phases of the three polymers are different. This makes it difficult to compare sample behaviour, because of the expected correlation between the molecular structure and the crosslinking reaction in the solid state.

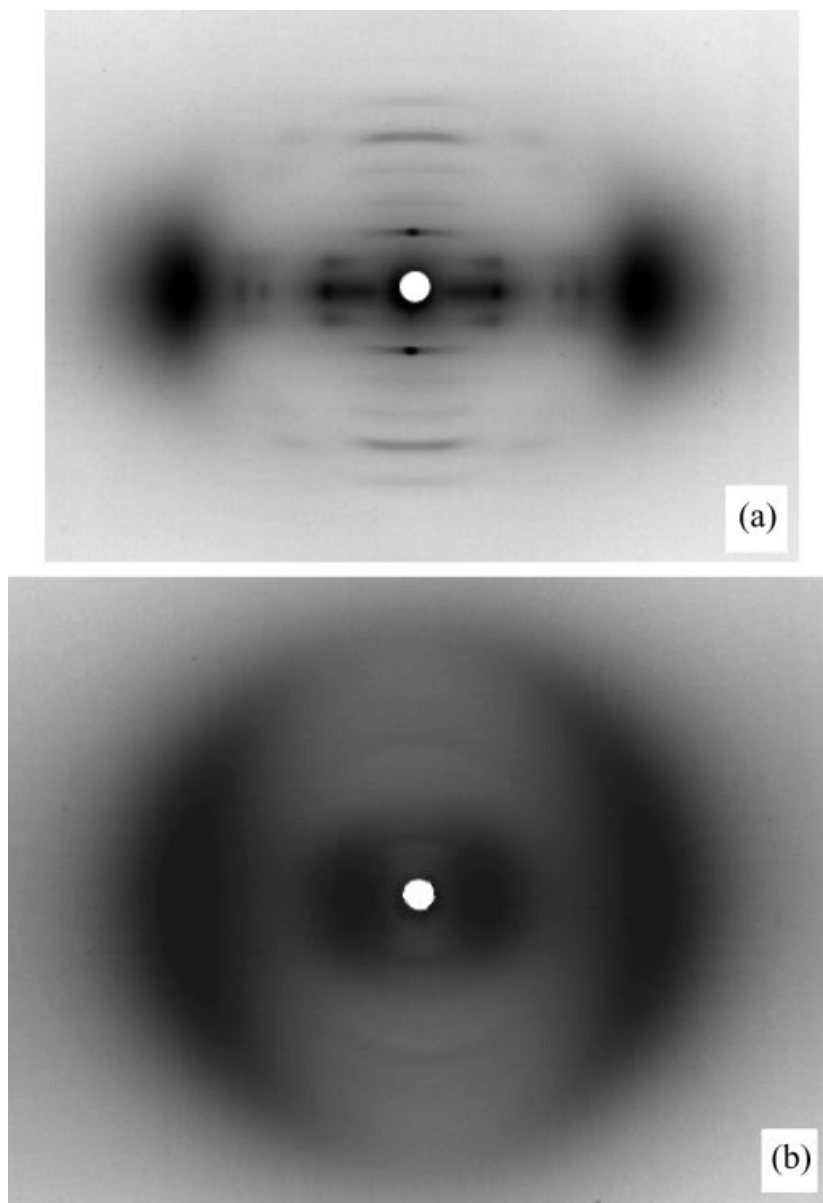


Fig. 5. X-ray diffraction patterns of PA(10) (fibres) after γ -irradiation: (a) immediately after irradiation treatment; and (b) after the DSC first heating run until 270°C.

3.2. γ -irradiation induced radical crosslinking

The influence of γ -radiation on the molecular structure and the thermodynamic behaviour of the polymers is reported in Table 3. Irradiation causes crosslinking with formation of insoluble fractions increasing with the dose and this effect is enhanced with the chain length of the LCP. Accordingly, a generalised decrease of both melting and isotropisation temperature and enthalpy is observed. In particular, for radiation doses causing about 60–70% of insoluble fractions neither melting nor isotropization phenomena occur. This is evidenced in Fig. 3, where DSC traces for LCPs unirradiated and irradiated at 96 kGy are shown.

In Figs. 4–6 the X-ray diffraction patterns for all irradiated polymers before and after the DSC heating runs are reported. It is evident that after the heating run the crystalline phase disappears completely and in the subsequent cooling run only the mesophasic structure is preserved (see Figs. 4b, 5b, and 6b). Moreover, X-ray analysis performed on irradiated fibres of PA(8) annealed at 150°C for 90 min (see Fig. 7) gives evidence that thermal treatment at this temperature does not destroy the crystalline phase. We can conclude that the heating process over the isotropization temperature is responsible for the destruction of the crystalline phase. This is not accompanied by a sharp endothermic peak in the heating trace because of the constraints and of the structural defects in the network

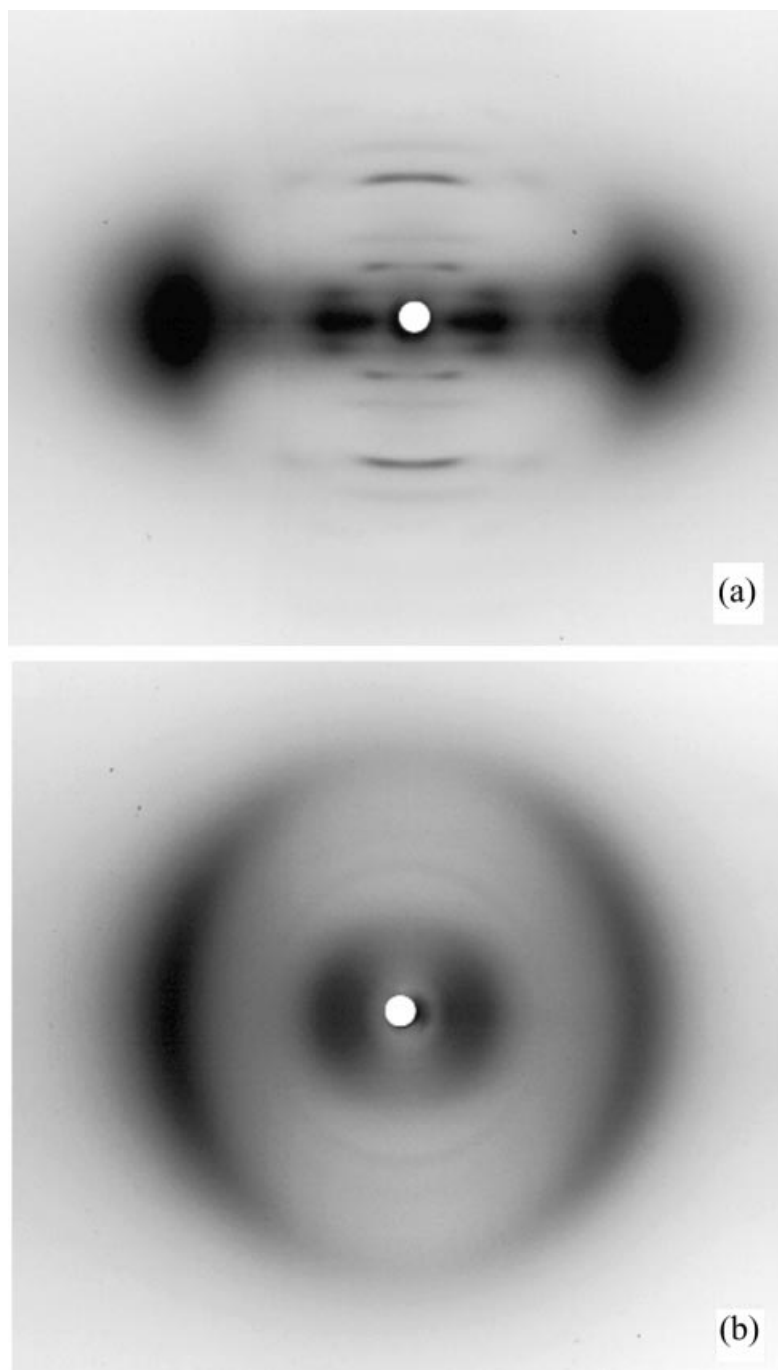


Fig. 6. X-ray diffraction patterns of **PA**(12) (fibres) after γ -irradiation: (a) immediately after irradiation treatment; and (b) after the DSC first heating run until 250°C.

matrix after crosslinking. The consequence is broadening of the melting transition and the loss to some extent of the first order character of the transition itself. Fibre shape and molecular orientation are partially preserved even after the DSC heating treatment, as shown in Figs. 4–6.

In Table 4 the tensile properties of both unirradiated and irradiated fibres are reported. It is well known that the mechanical performances can be affected by irradiation in two opposite ways: they can be improved when crosslinking

occurs and stiffness is increased, or they can be decreased if chain scission is induced. Data relative to tests performed at room temperature indicate that the elastic modulus and stress at break are improved by irradiation for **PA**(10) and **PA**(12), while no difference is detectable for **PA**(8). Moreover, strain at break after irradiation always decreases in agreement with the enhanced rigidity of fibres. At 160°C the tensile response is still good for **PA**(8), comparable to that observed for a crosslinked fibre sample of **P'**(5) via

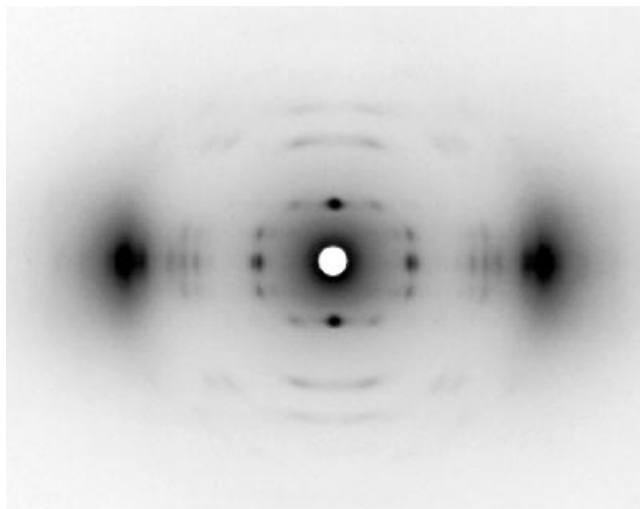


Fig. 7. X-ray diffraction pattern of an irradiated fibre of PA(8). The sample has been annealed at 150°C for 90 min after irradiation.

TARC [14] (at $T = 150^\circ\text{C}$ $E = 3.5(0.3)$, $\sigma_b = 144(30)$, $\epsilon_b = 12.2(1.7)$), while only a residual tensile performance is observed for PA(10) and PA(12).

The occurrence of radiation damage at a temperature higher than the melt temperature, caused by some trapped reactive radicals, is not a remote event. In fact the molecular mobility and, consequently, the radicals reactivity in the non crystalline phase are higher than those in the crystalline phase. To check the behaviour of our samples, some fibres of PA(8) were annealed for five minutes at 150°C and 200°C at which temperatures correspond the preservation and the disappearing of the crystalline phase, respectively. Tensile measurements performed at room temperature (see Table 4) show that thermal treatments do not cause evident damage to fibres. In fact annealed fibres at 150°C has the same tensile performances of fibres immediately after irradiation whilst annealed fibres at 200°C show a little different tensile performance which may be ascribed to the disappearing of crystalline phase and the loss of orientation to some extent (the strain at break increases up to 9.5%).

4. Conclusions

We have shown that LC polymers bearing side groups with unsaturations may be crosslinked by exposure to γ -radiation. Less significant effects have been observed for samples subjected to thermal treatment. When crosslinking is performed on fibre samples, a macro-oriented network is obtained showing good tensile performance even at 160°C [PA(8)].

The mechanism of crosslinking has not been investigated, but according to a previous contribution on thermally activated crosslinking of P'(5) [14] molecular structure of the polymer in the solid state might play a relevant role. For

instance, due to the molecular packing, unsaturations may stand close to each other thus increasing both the rate and the density of crosslinking. Of course mobility of pendant groups is also important and higher temperatures should promote reaction. In previous investigations [20,21], we have shown that PA(n), at room temperature, possess hexagonal or quasi-hexagonal packing, accommodating 6 or 12 chains per unit cell. Chains are aggregated to form "bundles" with allyl groups placed inside the bundles and close to each other. This seems a good condition for promoting crosslinking in the solid state.

The synthesis of new processable LCPs, bearing unsaturations in the pendant groups, as well as a new approach for their crosslinking to give macro-oriented LCNs are now in progress.

Acknowledgements

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