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Multi-oriented and fibrous liquid crystalline networks based on linear mesogenic polymers

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Abstract

Crosslinkable liquid crystalline co-polyesters based on substituted terephthalic acid moiety have been synthesised and their phase behaviour characterised. The network formation by thermally activated radical reaction has been examined on polymers with different amounts of monomer units bearing reactive acryloyloxy substituents at the terephthalic group. The relatively low melting temperatures allow fibre extrusion to be performed from a polymer matrix containing the crosslink reaction activator. Successive thermal curing produces a stabilisation of the macroscopic orientation of the liquid crystalline network. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Mesogenic polymers; Liquid crystalline networks; Fibrous networks

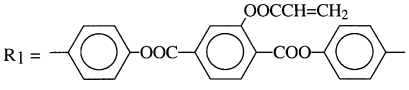
1. Introduction

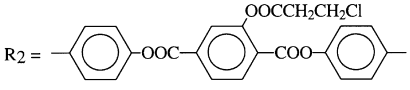
Liquid crystalline networks obtained by the crosslinking of either small molecules or pre-formed polymeric systems are known since many years [1–4]. The effect of crosslinking on the stability of the liquid crystalline phase depends essentially on two factors: (i) molecular structure of the network branches and (ii) crosslink density. Considering the extreme examples, dense crosslinking may lead to irreversible amorphous or liquid crystalline structures, according to whether the crosslinking process takes place in the amorphous or liquid crystalline state. On the contrary, low-density crosslinking operating in the isotropic state (e.g., in solution) on a mesogenic polymer having conformationally flexible chains may have only a small negative effect on the stability of the mesophase of the resulting network, allowing eventual enantiotropic mesomorphism to be preserved [5,6].

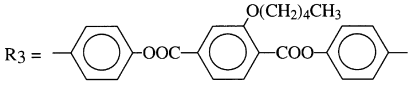
Stabilisation of the macroscopic orientation of liquid crystalline structures has also been obtained by crosslinking aligned samples [7–12]. Different alignment techniques have been employed, such as magnetic or electric field application, adhesion to a rubbed supporting surface or secondary crosslinking of a uniaxially stretched primary network [9]. Some of us have recently reported the formation of a stabilised macroscopic orientation in a nematogenic polymer by crosslinking a fibrous sample via thermally activated radical reaction [13]. As a result of the relatively high melting temperature of the polymer, the procedure followed was based on the use of an appropriate swelling solvent as the carrier of the radical initiator. The synthesis of linear mesogenic polymers, having the following general formula

$$Ln,m = \left((R_1\text{-}O(CH_2)_nO\text{-})_{m(eff)}\right)\text{--}(R_2\text{-}O(CH_2)_nO\text{-})_{m2}\text{-})\text{--}(R_3\text{-}O(CH_2)_nO\text{-})_{m3}\text{-})$$

$$n = 8,10,12;\quad m = m(eff) + m2\ ;\quad m3 = 100\text{-}m$$







and the network formation by radical crosslink reaction in the bulk, both on macroscopically non-oriented and oriented samples are reported here. The comparatively low melting temperature allows the extrusion of oriented fibres from a polymer matrix containing the radical initiator. Successive thermal curing completes the stabilisation of the oriented network structure.

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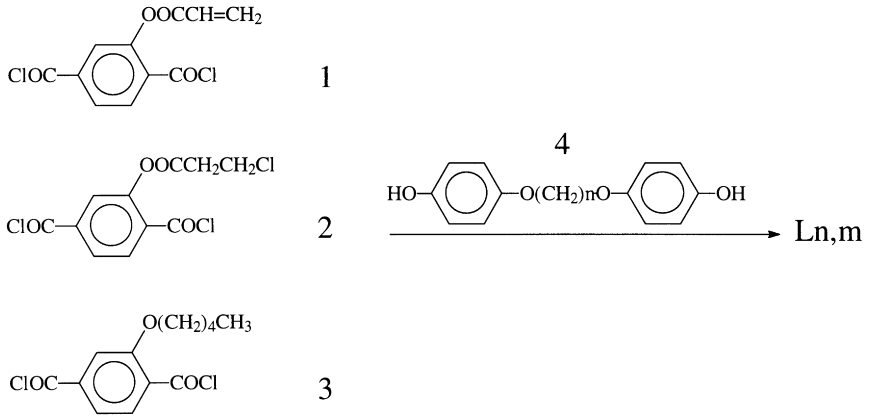

Scheme 1.

2. Experimental

2.1. Synthetic procedures

All linear polymers Ln,m were obtained by interfacial synthesis utilising the components shown in Scheme 1. The key point is the preparation of 2-acryloyloxy terephthalic acid dichloride (**1**). Actually, the synthesis of this compound by reaction of the corresponding acid with α,α' dichloromethylmethylether in the presence of pyridine and successive vacuum distillation, leads to an unreliably impure product with a high content (25%–30%) of 3-chloropropanoyloxyterephthalic acid chloride (**2**) and partial polymerisation. A better, although not entirely satisfactory result, could be obtained by vacuum distillation of pure 3-chloropropanoyloxy terephthalic acid chloride according to the reaction **2** = **1** + HCl. Following this procedure, which requires preliminarily the synthesis of **2**, a mixture of compounds **1** and **2** containing 84 mol% of **1** could be prepared in a fairly reproducible way. This mixture was utilised for polymerisation. The synthesis of the acid precursor of **2** was performed by standard procedures from 2-hydroxyterephthalic acid and 3-chloropropanoylchloride with a good yield (83%). It melts with decomposition at 235°C. Compound **2** was finally obtained by reaction with refluxing $SOCl_2$ in the presence of traces of pyridine. The procedures already described were followed in the synthesis of 2-hydroxyterephthalic acid [14], 2-pentyloxyterephthalic acid and its chloride (**3**) [14] and 4,4′-dihydroxy-1,ω-diphenoxyalkanes (**4**) [15]. All synthesised compounds were monitored by ^{1}H NMR spectroscopy.

The synthesis of polymer L8,8 is reported in detail, as an example. 2.03656 g of **4**(8) and 0.711 g of tributylammonium hydrogensulfate, as the surfactant, are dissolved in 125 ml water in a high-speed blender. Twenty millilitre of an alkaline water solution containing 0.950 g KOH are then added under stirring, followed by 66.4 ml of a chloroform solution containing 0.14596 g of **1** + **2** and 1.63495 g of **3**. The reaction is allowed to continue for 5 min under stirring, then 200 ml of *n*-hexane is added. The precipitated polymer is first washed with 95% ethanol, then with a 1/2 (vol) mixture of chloroform/*n*-hexane, and finally with water and 95% ethanol again. Drying is operated at room temperature giving a yield of 83%. Mutatis mutandis, analogous procedures were followed in the synthesis of all the other polymers.

Crosslinking of linear polymers was performed by thermally activated radical reaction in the bulk. Polymer samples containing the radical initiator (*t*-butylperoxybenzoate) were prepared from CH_2Cl_2 solutions by room temperature solvent evaporation. The initiator content in the solid polymer was limited to 0.3–0.5 wt.%.

2.2. Characterisation techniques

^{1}H NMR spectrometry was performed by means of a Varian XL 200 MHz apparatus at the Centro Interdipartimentale di Metodologie Chimico-Fisiche of the Naples University. Intrinsic viscosity of chloroform solutions of linear polymers was measured at 25.0°C utilising an Ubbelohde viscometer. The phase behaviour of all the synthesised polymers was investigated by differential scanning calorimetry (DSC) under nitrogen flow (Indium calibrated Perkin Elmer DSC7 apparatus), optical microscopy (Zeiss Axioscop polarising microscope, FP5 Mettler temperature heating stage), and X-ray diffraction (flat film camera, CuKα radiation) on non-oriented and fibrous samples.

3. Results and discussion

3.1. Linear polymers

The structural features, common to all synthesised polymers are: (i) the presence of a fairly long flexible spacer between two consecutive rigid (mesogen) segments; (ii) the presence of a flexible substituent at the mesogen; (iii) the constitutional (regio) inhomogeneity caused by the random orientation of the substituted terephthalic group along the backbone chain. For all polymers, but L8,0, further constitutional inhomogeneity is produced by the

Table 1
Thermodynamic data for linear polymers Ln,m[a]

n,m	*m*(eff)	[ν](dl/g)	T_g (°C)	Ti(I)[b] (°C)	ΔHi(I)[b] (J/g)	Ti(II)[b] (°C)	ΔHi(II)[b] (J/g)
8,100	84.0	0.52	58	188	4.0	188	4.8
8,25	20.7	2.00		180	3.0	178	5.5
8,18	14.9	2.19		182	4.7	182	6.9
8,13	11.0	2.67	35	178	3.9	177	6.0
8,8	6.9	2.59		180	5.5	179	7.0
8,0	0			180	5.4	180	6.8
10,18	14.4	3.36		161	4.2	160	5.8
10,13	10.5	2.40	30	159	6.1	158	7.6
10,8	6.4	2.51		164	3.7	162	5.2
12,13	10.7	0.94	28	148	8.1	148	8.0

[a] *n*(eff) = effective % molar fraction of acrylic substituent; $m - m$(eff) = % molar fraction of 3-chloropropyloyloxy substituent; $100 - m$ = % molar fraction of pentyloxy substituent.
[b] (I), (II) = first and second DSC heating run.

presence of different substituents according to a random sequence. Therefore, it is not surprising that the as-prepared polymers are non-crystalline materials, and crystallisation is not observed for samples cooled from the molten state. All polymers exhibit thermotropic liquid crystalline behaviour, as ascertained by DSC, optical and X-ray diffraction means. Some relevant DSC data concerning the liquid crystal phase are reported in Table 1. With an exception for polymers L12,13 and L8,0, samples previously brought above isotropisation temperature are less soluble. This feature, which indicates that some crosslinking has taken place, does not hamper the enantiotropic character of the liquid crystal-isotropic liquid transition, as clearly evident from the data reported in Table 1. The thermal stability of some polymers, as may be inferred from dynamic thermogravimetric measurements under nitrogen atmosphere, was examined for homologous polymers L8,13; L8,18 and L8,25 having increasing content of acrylic substituent. The thermal stability appears to be influenced by this parameter. The 5% weight loss temperature decreases from 400°C to 380°C and 340°C with increasing content of the acrylic moiety. In any case, it is high enough to allow polymer melting and fibre extrusion (although some crosslinking may take place).

The phase behaviour of the linear polymers is quite simple in most cases. Fig. 1 shows the DSC curves for polymer L12,13. No melting or crystallisation signals are observed, while glass transition and isotropisation (curves a, c) and anisotropisation (curve b) are quite evident. Absence of crystallisation allows the formation, by melt extrusion, of polymer fibres preserving the liquid crystalline structure at room temperature. The X-ray diffraction pattern of a fibrous sample of L12,13 is characterised by an equatorially polarised halo peaked at $\sin\theta/\lambda = 0.118$ Å^{-1} and by a diffuse "four spot pattern" at $\sin\theta/\lambda = 0.027$ Å^{-1}, consistent with a cybotactic nematic structure. Only the latter structural parameter appears to be moderately dependent on the length of the flexible segment of the polymer backbone: $\sin\theta/\lambda = 0.029$ Å^{-1} for $n = 10$, and 0.032 Å^{-1} for $n = 8$. With a partial exception for L8,100, the phase

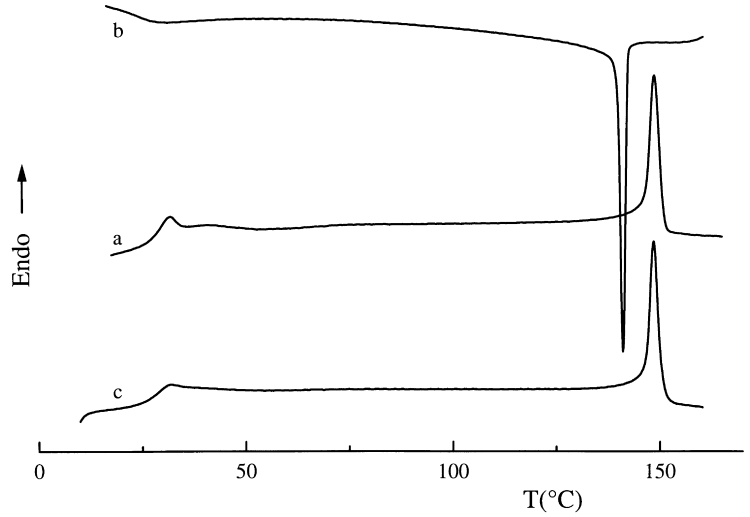

Fig. 1. DSC behaviour of polymer L12,13. First heating (curve a), cooling (curve b) and second heating (curve c).

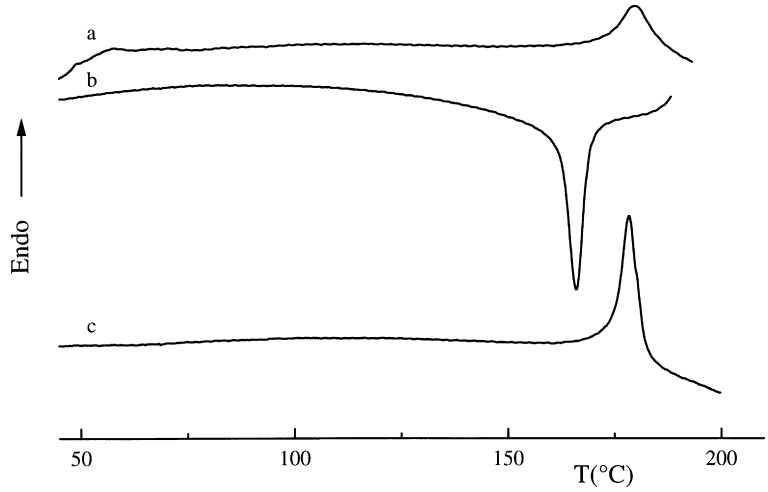

Fig. 2. DSC behaviour of polymer L8,25. First heating (curve a), cooling (curve b) and second heating (curve c).

behaviour of the other polymers is analogous to that outlined for L12,13, notwithstanding the occurrence of some crosslinking on isotropisation. To take polymer L8,25 as an example, the DSC behaviour of a previously untreated sample and the X-ray diffraction pattern recorded at room temperature for an as extruded fibre are shown in Figs. 2 and 3, respectively.

Polymer L8,100 exhibits some peculiarity. The X-ray diffraction pattern of the as-prepared polymer is indicative of a very poor crystallinity, if any. It is characterised by a diffuse halo peaked at $\sin\theta/\lambda = 0.118$ Å^{-1} and a second sharper diffraction at $\sin\theta/\lambda = 0.031$ Å^{-1}. The first DSC heating run of such a polymer (Fig. 4, curve a) shows an endothermic signal at $\backsim 110$°C, preceded by an exothermic phenomenon. The successive cooling and heating runs (Fig. 4, curves b, c) show that the thermal feature is reversible and possibly indicative of a structural change taking place. The X-ray diffraction recorded at room temperature for a polymer sample previously recorded at 130°C still shows no evidence of crystallinity but the lower angle diffraction moved at $\sin\theta/\lambda = 0.035$ Å^{-1}. Consistently, the room temperature X-ray diffraction pattern of a fibrous sample obtained by extrusion at ~ 150°C (therefore, subjected to a thermal treatment analogous to that corresponding to curves a and b of Fig. 4) shows a "four spot pattern" at $\sin\theta/\lambda = 0.035$ Å^{-1}. In contrast, the diffraction pattern recorded at 140°C for a fibrous sample shows that the orientation is completely lost and the low-angle, rather feeble, diffraction is centred around $\sin\theta/\lambda = 0.030$ Å^{-1}. A merely tentative conclusion is that the DSC signal at ~ 110°C might indicate the occurrence of a structural transition from a twisted smectic phase to a cybotactic nematic. The latter should be present in the metastable state as-prepared polymer. Its transition to the smectic phase would take account of the exothermic signal detected along the first DSC heating run and preceding the smectic-nematic change (Fig. 4, curve a). Some crosslinking takes place for samples brought above isotropisation temperature (solubility is lost). This is probably the reason why the smectic-nematic transition is almost cancelled from the successive DSC curves (Fig. 4, curves d, e).

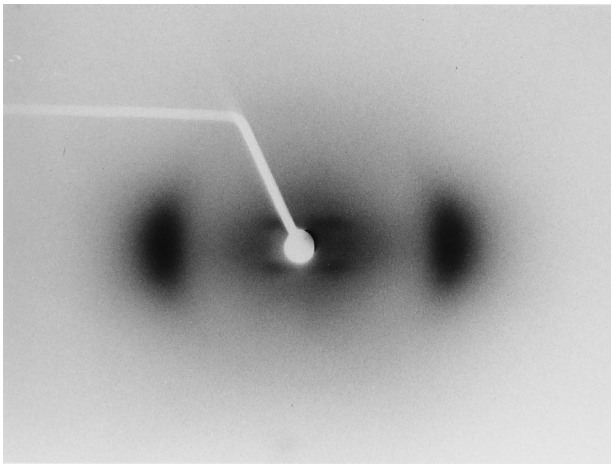

Fig. 3. Polymer L8,25. X-ray diffraction pattern of an as-extruded fibrous sample. Room temperature, CuKα radiation.

3.2. Crosslinked polymers

Crosslinking in the presence of a radical activator was operated both on non-oriented and fibrous samples. Polymer samples containing 0.3–0.5 wt.% of *t*-butylperoxy-benzoate as radical initiator were prepared by room temperature solvent evaporation of CH_2Cl_2 polymer solutions. The transparent non-oriented material thus obtained was utilised to prepare samples for DSC analysis, and as the feed for fibre extrusion at ~ 100°C. Some relevant data concerning the crosslinked materials as obtained from DSC experiments on non-oriented samples are reported in Table 2. All samples undergo crosslinking along a large temperature range, starting from temperatures below 100°C. Fig. 5 shows the DSC behaviour of N8,18. Curve a corresponds to the first heating run and shows the exothermic signal around $\sim$110°C

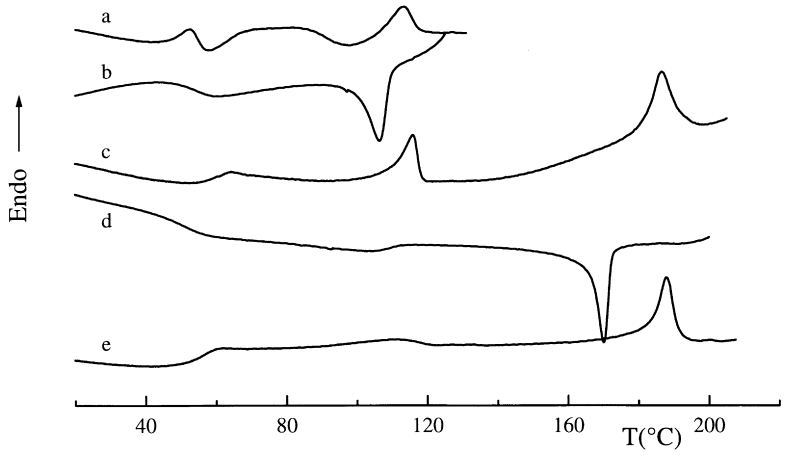

Fig. 4. DSC behaviour of polymer L8,100. Temporal sequence a–e; curve a: first heating run of a previously untreated sample.

relative to the network formation. Both curve b (cooling run) and c (2° heating run) are featureless. No isotropisation or anisotropisation transitions are detectable below ~230°C. Polarising microscopy confirms that the liquid crystalline phase was largely stabilised by crosslinking. No isotropisation will be detected below ~300°C (maximum observation temperature). All polymers with $m(\text{eff}) > 14$ exhibit analogous behaviour. For lower values of m(eff), the enantiotropic behaviour is not cancelled out by crosslinking, although some stabilisation of the liquid crystalline phase still does occur. Fig. 6 shows the DSC behaviour of N8,8 as an example. The isotropisation transition is observed around ~197°C along the first heating run (curve a) and at ~188°C along the second one (curve c). This feature, that is qualitatively observable for the other polymers also with $x(\text{eff}) < 14$, requires some comment. As the crosslinking process starts and takes place mostly within the thermal stability range of the liquid crystal phase of the linear polymer, the stabilisation of this phase is to be expected. The extent of stabilisation should depend on the intrinsic conformational mobility of the linear polymer chains and the crosslink density. This, in turn, must bear some relation to the molar fraction of unsaturated sites, m(eff), present in the original polymer. Lower m(eff) values, leading to crosslink densities compatible with a large structural mobility, allow the permanence of a thermotropic phase transition, although with reduced enthalpy change. The higher value of Ti(I) over Ti(II) observed for these polymers might be traced to two, possibly concomitant factors: (a) the occurrence of some crosslinking at temperatures higher than the isotropisation during the first DSC heating run, and (b) the kinetically based incomplete reversibility of the isotropisation transition.

Table 2
Crosslinked polymers Nn,m[a]

n,m	m(eff)	Ti(I)[b] (°C)	Ti(II)[b] (°C)	ΔHi(II)[b] (J/g)	$R(L)$[d]
8,100	84.0	–[c]	–[c]		1.0
8,25	20.7	–[c]	–[c]		1.7
8,18	14.9	–[c]	–[c]		2.2
8,13	11.0	195	187	5.2	2.5
8,8	6.9	197	188	3.4	2.9
10,18	14.4	–[c]	–[c]		2.4
10,13	10.5	177	165	3.0	2.5
10,8	6.4	177	163	3.7	2.8
12,13	10.7	161	160	2.8	2.2

[a] n(eff) = effective % molar fraction of acrylic substituent; $m - m$(eff) = % molar fraction of 3-chloropropyloyloxy substituent; $100 - m$ = % molar fraction of pentyloxy substituent.

[b] (I), (II) = first and second DSC heating run, non-oriented samples.

[c] – = decomposes before isotropisation.

[d] $R(L)$ = crosslinked fibres, fibre length ratio $L(T\text{amb})/L(190°\text{C})$, $\sigma(R)/R = 0.1$.

Extrusion at moderate temperatures (~100°C) of polymer samples containing the radical activator produces well-oriented fibres in the liquid crystalline state. Crosslinking of these fibres has the same consequences on the phase behaviour as described for non-oriented samples. In order to obtain macroscopically oriented crosslinked fibres, a special procedure had to be developed to avoid two negative effects, namely: (i) the crosslink reaction is scarcely effective at temperatures lower than ~100°C, and (ii) at higher temperatures than that, macroscopic orientation of free standing fibres relaxes too quickly to be preserved during the crosslink process. Therefore, the following procedure was followed. The as-extruded fibre is sealed under nitrogen atmosphere (to eliminate the well-known negative effect of molecular oxygen on the radical reaction) inside a glass capillary having an internal diameter slightly larger than that of the fibre. Temperature is rapidly brought to ~100°C. A sharp shortening of the fibre takes place (but for L8,100) with a concomitant increase of its cross-section, accommodating the internal size of the container. Temperature is kept at ~ 100°C for 10 min, allowing crosslinking to take place to a considerable extent, then brought at ~ 10 K/min rate up to 190°C (at this temperature, all linear polymers are in the isotropic liquid phase), and kept there for ~ 20″. Finally, the temperature is lowered to ambient again and the glass container broken to free the fibre. Fibres subjected to

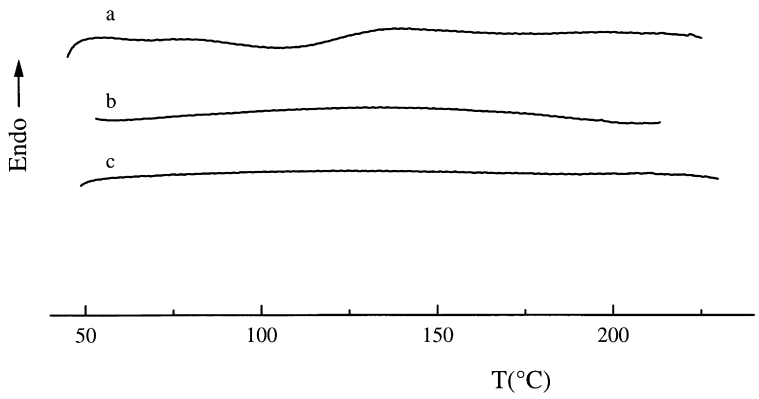

Fig. 5. DSC behaviour of N8,18. First heating run of L8, 18% + 0.3% activator (curve a); cooling run (curve b); second heating (curve c).

this treatment, largely preserve the original macroscopic orientation and the geometrical dimensions acquired at 100°C at room temperature. Besides, for these polymers having $m(\text{eff}) < 14$, macroscopic orientation may be substantially cancelled and reversibly restored by thermal treatment, following the corresponding liquid phase transitions. Figs. 7 and 8a show respectively the DSC behaviour of a previously crosslinked fibre of N8,13, and the X-ray diffraction pattern recorded at room temperature for a crosslinked fibre of the same polymer, previously subjected to repeated thermal cycles including nematic-isotropic-nematic transitions. This pattern contains, although in a somewhat blurred shape, the signals corresponding to the cybotactic character of the nematic phase which are more neatly present in the diffraction pattern of the uncrosslinked fibre (Fig. 8b).

Fibres crosslinked under geometrical constraint, as described before, and eventually freed from the glass container, undergo a remarkable shrinking along the fibre axis when brought to isotropisation temperature (or to ~190°C, for $14 < m(\text{eff}) < 100$). This geometrical collapse is reversible. Table 2 reports the fibre length ratios $R(L) = L(\text{room temperature})/L(190°\text{C})$ averaged over several experiments. Not unexpectedly, as a general trend, $R(L)$ decreases with increasing $m(\text{eff})$, that is, approximately, with increasing crosslink density. Consistently, no measurable effect was observed ($R(L) = 1$) for N8,100. This feature may be qualitatively explained as follows.

(1) The shrinking of the original fibre under geometrical constraint at ~ 100°C corresponds to a possibly partial relaxation of the macroscopic orientation of the as-extruded fibre. No qualitative modification of the liquid crystalline phase takes place, however, some decrement of its intrinsic order parameter (i.e., the order parameter connected to the liquid crystalline structure of the polymer) is to be expected as a consequence of the increased temperature.

(2) Crosslinking under geometrical constraint, the liquid crystalline sample produces a topologically fixed set of branch points which are distributed in space according to an elongated morphology following the actual shape of the fibre. The rigidity of this morphology should increase with increasing crosslink density.

(3) Bringing the crosslinked and unconstrained fibre to isotropisation conditions (which is feasible for low-crosslink densities), produces the collapse of the intrinsic orientational order and favours the space rearrangement of the branch points toward a less anisometric morphology. This, necessarily requires the occurrence of some shrinking along the original elongation direction. The topological rigidity of the branch points set involves the substantial reversibility of the phenomenon.

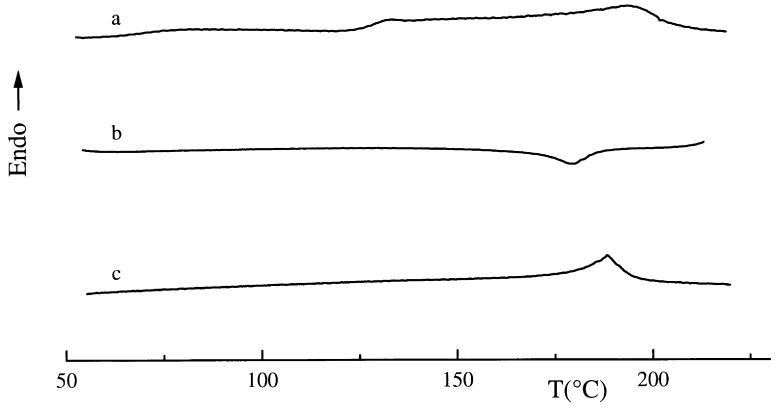

Fig. 6. DSC behaviour of N8,8. First heating run of L8, 8% + 0.3% activator (curve a); cooling run (curve b); second heating (curve c).

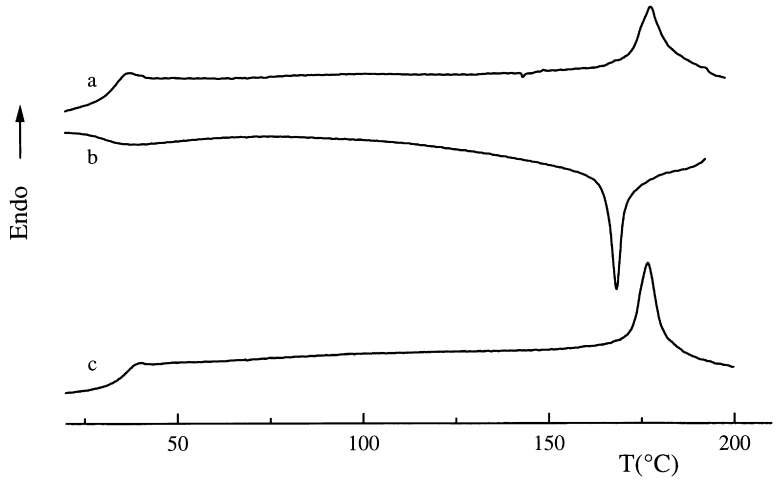

Fig. 7. DSC behaviour of fibrous N8,13. Sample previously subjected to two thermal cycles. Heating run (curve a); cooling (curve b); second heating run (curve c).

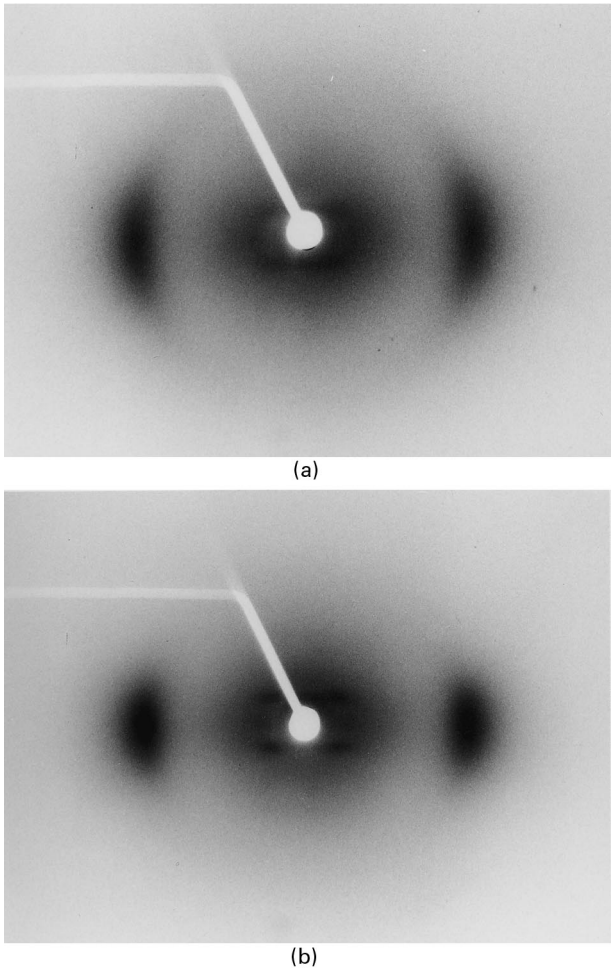

Fig. 8. X-ray diffraction patterns of fibrous samples of: (a) N8,13 (sample previously subjected to several thermal cycles), (b) L8,13 (as-extruded). Room temperature, CuKα.

4. Conclusions

We have shown that liquid crystalline linear polymers, containing acrylic groups as lateral substituents, may be crosslinked by thermally activated radical reaction without disruption of the mesomorphic structure. For moderate crosslink densities, isotropisation of the liquid crystal phase is still reversibly observable. Crosslinking of fibrous samples under a geometrical constraint limiting the fibre diameter, produces macroscopically oriented liquid crystalline networks. Orientation may be reversibly destroyed or restored by a thermal treatment across the liquid crystal-isotropic liquid phase transition. Correspondingly, a remarkable dimensional change occurs. Isotropisation is accompanied by a shrinking along the fibre axis, while the original extension is restored as the reverse phase transition takes place.

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