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Crosslinking liquid crystalline polyesters with allyl group as lateral substituent: thermal and UV activation

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Abstract

The synthesis of networks from liquid crystalline polyesters bearing allyl groups as lateral substituents is reported. Crosslinking is performed both by thermally activated radical reaction and by UV irradiation of film samples containing the suitable activator. Moreover, fibrous samples have been crosslinked in the solid state by UV irradiation, "quenching" the nematic organisation on a macroscopic scale and resulting in a macro-oriented network. Crosslinking does not hamper molecular mobility. As a consequence, the degree of orientation and the length of crosslinked fibres change continuously and reversibly upon heating and cooling through the isotropisation transition. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Liquid-crystalline polymers; Macro-oriented network; X-ray diffraction

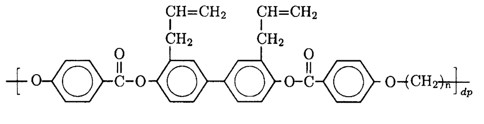
1. Introduction

Liquid crystalline networks oriented on a macroscopic scale (MONs) have been extensively investigated mainly for their promising application in those fields were macro-alignment of material is sought (for instance high mechanical performance and non-linear optical properties).

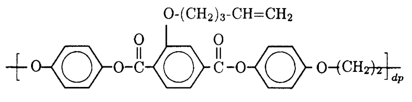
Several authors have shown that MONs may be prepared starting from low molecular weight, not necessarily mesogenic, monomers [1–11]. According to Finkelman [3,4] and Ober [5], taking advantage of the unique anisotropy of monomers, MONs with different molecular structure are obtained by "locking in" either the nematic or the smectic order. The synthetic route is an improvement of the pioneering approach followed by Zentel [1] and Hikmet [2], the main difference being the possibility to synthesise macro-oriented samples. The adopted strategy is to apply a stress to samples during the crosslinking reaction when the viscosity is rather high to avoid mechanical collapse. In this way, oriented samples with an order parameter S up to 0.35 was obtained [5].

Recently it has been also shown that MONs may be synthesised by starting directly from polymers which may be first processed and then crosslinked to the final shape, thus very well oriented and organised samples may be prepared. For instance Wegner et al. [10] reported the synthesis of an anisotropic network, with application in micro-litography, starting from a polymer bearing the cinnamic ester moiety as pendant group. Polymer is processed to give a multi-layers film using the Langmuir–Blodgett technique. Finally, crosslinking was performed by photo-induced cycloaddition of the cinnamic acid derivatives.

In previous papers we have reported the synthesis and the characterisation of MONs obtained from liquid crystalline polymers (LCPs) with formula [12,13]:



PA(n) n=6,8,10,12



P'(2,5)

These polymers are thermotropic and they can be easily extruded to form fibrous samples with a high degree of

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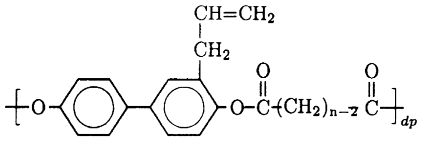
orientation. **P′(2,5)** polymers can be processed in the nematic phase at temperatures low enough to prevent crosslinking. On the contrary, this is not completely true in the case of **PA(n)**, due to the higher reactivity of the allyl group compared to the pentenyl moiety, and due to the higher melting temperature (in the range 144–216°C) which promotes a limited crosslinking [12]. After extrusion, fibres can be crosslinked obtaining MONs which retains good tensile properties when heated at high temperature (150°C). Two different crosslinking procedures were followed in the solid state: Thermally activated crosslinking by peroxide activators and crosslinking by exposure to γ-radiation. Thermal decomposition of peroxides during processing of material de facto limits the application of thermally activated crosslinking. The peroxide should be added via diffusion from a suitable solution. For **P′ (2,5)** this was achieved by immersing fibres in a dichloremethane solution of *t*-butyl peroxibenzoate as the activator, but this cannot be considered a general procedure [13]. In fact, the choice of an appropriate solvent, which should swell but do not dissolve the polymer, is not an easy task. Moreover, relaxation of orientation may occur to some extent due to reduction of glass transition temperature induced by the presence of solvent. The latter procedure was successfully tested on fibres of **PA(n)** which, after an irradiation of about 100 kGy, retain the oriented morphology even after heating at temperature higher than the clearing point of virgin material or after immersion in boiling *o*-dichlorebenzene, which is a good solvent for the untreated polymers [14]. Of course, the use of γ-radiation might have a negative effect on the tensile performance if chain breakage takes place, although this was not observed for **PA(n)**.

In the effort of synthesising new polymeric materials with good reactivity to give MONs by a single step reaction, we have recently reported on a new class of LCPs with formula [15]:



P(n) n=6,8,10,12,14

In this article we report the preparation and the characterisation of MONs obtained from **P(n)** by both thermally activated radical reaction and UV irradiation.

2. Experimental

2.1. Sample preparation

P(n) were synthesised by interfacial polycondensation according to Ref. [15]. Films of **P(n)** were prepared by casting from chloroform solution containing the required amount of activator (3–5% weight percentage with respect to the polymer). The final thickness of samples is about 100–200 μm. The fibres were extruded from the anisotropic molten phase and cooled to room temperature. The averaged diameter of fibres is 200–300 μm. The activators used were *t*-butyl peroxibenzoate or benzoyl peroxide for thermally activated crosslinking, and 2,2-dimethoxy-2-phenylacetophenone for UV crosslinking.

2.2. Characterisation

Thermal measurements were carried out on fibre samples by means of a DSC-7 Perkin–Elmer calorimeter under nitrogen flow at 10°C/min rate. Polarised optical microscopy was performed by means of a Jenapol microscope fitted with a Linkam THMS 600 hot stage. Fibre diffraction spectra were recorded under vacuum by means of a cylindrical camera with a radius of 57.3 mm and the X-ray beam direction perpendicular to the fibre axis (V-filtered CrK_α radiation). The high temperature X-ray diffraction patterns were collected using a flat camera and a modified Linkam THMS 600 hot stage. The imaging plate Fujix BAS-1800 system was used to record the diffraction patterns. The infrared measurements were performed with a Bruker IFS 66 spectrometer. Tensile analysis was carried out by means of TA Instruments TMA 2940 analyser. The measurements were performed under nitrogen flow at 10°C/min. UV experiments were carried out by means of a 125 W mercury lamp (mod. GR.E.—Helyos Italquartz, Italy) with a 10 cm sample to lamp distance. Solubility was evaluated by immersing samples in refluxing chloroform for 30 min.

3. Discussion

3.1. Thermally activated crosslinking

P(n) are nematic [15]. Films of **P(n)** were prepared according to Section 2. Calorimetric data related to DSC first heating runs of cast films are shown in Fig. 1. The endothermic peaks at high temperature correspond to the isotropisation transition. The details of thermal characterisation are summarised in Table 1. All samples contain the activator, but are not yet crosslinked. The small amount of activator used in the film preparation produces only a slight reduction of transition temperature of the pure polymers [15]. The films containing the activator were thereafter treated for 30 min at 130°C to induce crosslinking. Hereinafter, samples crosslinked by benzoyl peroxide as activator are referred to as samples **A**, samples **B** being those containing *t*-butyl peroxibenzoate. The melting transition in the first heating run disappears after annealing, while the isotropisation is still observed only for samples **A**, even though transition enthalpy is smaller than that of virgin material being related to a different crosslinking density (and solubility) (see Table 2 and Fig. 2). In previous works we found that residual isotropisation enthalpy is

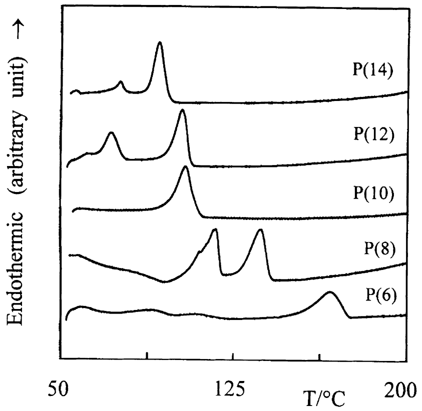


Fig. 1. DSC first heating run of film samples of **P(n)** containing activator.

Table 2
DSC data concerning annealed films of **P(n)**, containing approx. 5% weight of benzoyl peroxide (temperatures are measured at the maximum of the transition endotherm. All samples have been annealed for 30 min at 130°C)

Polymer	T_m[a]	ΔH_m[b]	T_i[c]	ΔH_i[d]	S[e]
P(6)	n.o.	n.o.	168	2.5	Insoluble
P(8)	n.o.	n.o.	156	1.5	8
P(10)	n.o.	n.o.	98	9.7	8
P(12)	n.o.	n.o.	92	13.0	7
P(14)	n.o.	n.o.	83	7.8	7

[a] T_m (°C), melting temperature.
[b] ΔH_m (J g^{-1}), melting enthalpy.
[c] T_i (°C), isotropisation temperature.
[d] ΔH_i (J g^{-1}), isotropisation enthalpy.
[e] S (% weight), solubility in boiling chloroform.

somewhat proportional to the amount of non-crosslinked volumetric fraction of the sample [13,19]: networks are not homogenous indeed, and should be regarded as "two-phases" systems. The non-crosslinked fraction of samples was reduced by increasing carefully the activator concentration or by extracting the non-crosslinked polymer with boiling solvent. Following to the previous procedure, isotropisation transition disappears in the heating trace. In our case, the residual isotropisation enthalpy of samples **A** does not change significantly after prolonged immersion in boiling chloroform, thus suggesting that networks should be regarded as homogeneous systems.

According to theoretical predictions by de Gennes [16] and Warner et al. [17], samples of **P(10)**, **P(12)** and **P(14)** crosslinked at 130°C while exhibiting an isotropic phase show an isotropisation temperature T_i lower, whereas detectable, than those corresponding to virgin material. In fact, inter-chain connections "quench" the disordered molecular organisation of the isotropic phase, thus destabilising the nematic order. Consequently, if molecular mobility in the crosslinked sample allows the transition to be observed, the isotropisation occurs at a lower temperature [18]. On the other hand, crosslinking **P(6)** and **P(8)** samples in the nematic phase at 130°C stabilises the ordered molecular organisation, resulting in increased or substantially unchanged isotropisation temperature with respect to virgin polymers. In any case, both samples **A** and **B** show a rubbery behaviour above 80°C.

Polarised optical microscopy is in agreement with DSC measurements. Samples **A** are anisotropic at room temperature and their isotropisation is completely reversible. In the case of samples **B**, **P(6)** and **P(8)** are anisotropic up to about 200–220°C, even though a continuous decrease of brightness can be observed in the viewing field starting from 140–150°C. This continuous loss of anisotropy, which is reversible in character, corresponds to a continuous decreasing of the structural organisation of samples at molecular level according to the absence of a first order transition in the DSC heating trace. The structural defects in the matrix induced by crosslinking, coupled with a higher degree of crosslinking with respect to samples **A**, may be responsible for this phenomena. On the other hand, the samples of **B** type [**P(10)**, **P(12)** and **P(14)**] are isotropic in the whole range of their thermal stability. In the present work, we have not investigated whether these networks are in thermodynamic equilibrium or their phase behaviour is under kinetic control. In the latter case, annealing at the appropriate temperature might induce phase modifications including, for instance, the anisotropisation. During optical

Table 1
DSC data concerning virgin films of **P(n)** (temperatures are measured at the maximum of the transition endotherm)

Polymer	T_m[a]	ΔH_m[b]	T_i[c]	ΔH_i[d]
P(6)	n.o.	n.o.	167.1	12.7
P(8)	117.2	14.4	136.7	12.7
P(10)	n.o.	n.o.	103.9	12.0
P(12)	71.7	7.3	102.5	15.0
P(14)	75.5	2.0	92.3	12.6

[a] T_m (°C), melting temperature.
[b] ΔH_m (J g^{-1}), melting enthalpy.
[c] T_i (°C), isotropisation temperature.
[d] ΔH_i (J g^{-1}), isotropisation enthalpy.

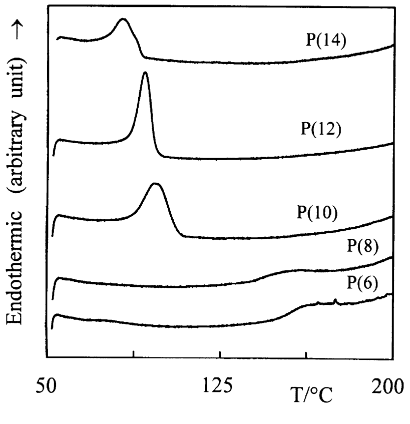


Fig. 2. DSC first heating run of crosslinked film samples of **P(n)** by thermally activated reaction, benzoyl peroxide as activator.

Table 3
DSC data concerning films of **P(n)** exposed to UV for 60 min. Films contain approx. 5% weight of 2,2-dimethoxy-2-phenylacetophenone (temperatures are measured at the maximum of the transition endotherm)

Polymer	T_m[a]	ΔH_m[b]	T_i[c]	ΔH_i[d]
P(6)	82.0	4.4	168	1.3
P(8)	82.6	8.2	134	1.0
P(10)	n.o.	n.o.	100	3.9
P(12)	n.o.	n.o.	104	Residual
P(14)	n.o.	n.o.	97	5.6

[a] T_m (°C), melting temperature.
[b] ΔH_m (J g^{-1}), melting enthalpy.
[c] T_i (°C), isotropisation temperature.
[d] ΔH_i (J g^{-1}), isotropisation enthalpy.

observation all samples, both **A** and **B** types, retain their shape and do not undergo evident modification.

The possibility of preparing uniformly oriented crosslinked samples (MONs) by the use of thermally activated crosslinking of **P(n)** was tested without success. The reasons are the following: (i) a solvent suitable for activator diffusion in oriented samples (fibres) was not found; and (ii) the crosslinking temperature is higher than melting or softening temperatures of virgin material, resulting in structure collapse. The attempt to extrude **P(n)** previously mixed with the activator, following a procedure recently described by Caruso et al. [20], failed because crosslinking takes place suddenly and viscosity increases very much.

3.2. Crosslinking by UV irradiation

Films suitable to be exposed to UV radiation were prepared by casting from chloroform solution according to Section 2. The calorimetric data of UV irradiated samples are given in Table 3. Samples containing the activator are anisotropic at room temperature and almost insoluble in chloroform after UV irradiation, that in the case of **P(8)** and **P(12)** was quite short (only few minutes) (see Table 4). Isotropisation enthalpy decreases significantly after 60 min of UV irradiation (Table 3 and Fig. 3), except for **P(10)** and **P(14)** samples.

Table 4
Solubility (% weight, solubility in boiling chloroform) of UV exposed films of **P(n)**, containing approx. 5% weight of 2,2-dimethoxy-2-phenylacetophenone

Polymer ⇓	t[a] ⇒			
	5	15	60	240
P(6)	33	27	8	6
P(8)	21	15	Insoluble	Insoluble
P(10)	59	41	25	9
P(12)	26	17	Insoluble	Insoluble
P(14)	71	53	17	8

[a] t (min.), time of exposition to UV radiation.

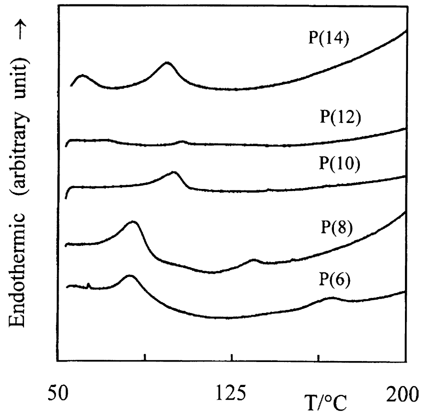


Fig. 3. DSC first heating run of crosslinked film samples of **P(n)** after 60 min of UV irradiation.

The IR spectra of **P(n)** films show several weak peaks, which may be assigned to the allyl unit (Fig. 4). The most suitable one for the qualitative evaluation of the crosslinking degree is the weak but well resolved stretching band of the carbon–carbon double bond at about 1640 cm^{-1}. As an internal reference for quantitative analysis the plane deformation of the phenyl ring at about 1600 cm^{-1} has been used. As an example, the two bands are shown for **P(12)** at different irradiation times in the inset in Fig. 4. The intensity at 1640 cm^{-1} quickly decreases with increasing exposure time, but does not disappear completely even after longer exposures. Values of fractional conversion α of about 0.33, 0.36 and 0.51 for irradiation times of 5, 15 and 60 min, respectively, are obtained, using as internal reference the peak at 1600 cm^{-1}. The presence of molecular constraints and crosslinks results in unreacted allyl groups, due to a strongly reduced diffusion through the network. The reason for the greater reactivity of **P(8)** and **P(12)** with respect to the homologues polymers in the same family is not clear at the present stage of investigation and it requires an “ad hoc” analysis of molecular structure present during crosslinking.

Oriented fibres of **P(n)** containing 2,2-dimethoxy-2-phenylacetophenone as the UV activator were obtained extruding the polymer at a temperature about 20°C lower than the isotropisation temperature. The samples were subsequently irradiated with UV light at room temperature to induce crosslinking. Room temperature is required in order to avoid the loss of fibre orientation because of the low melting or softening temperature of material. The DSC analysis performed on UV irradiated fibres and films show the same thermal behaviour. A strong contraction of fibre length (Fig. 5) can be observed as a result of phase transition from nematic to isotropic phase during heating of samples. A similar behaviour has been reported by Caruso et al. [20] and by Finkelman et al. [21].

The fibre contraction upon heating is related to the loss of order and uniform orientation of rigid molecular moieties due to the phase transition from nematic to isotropic. This

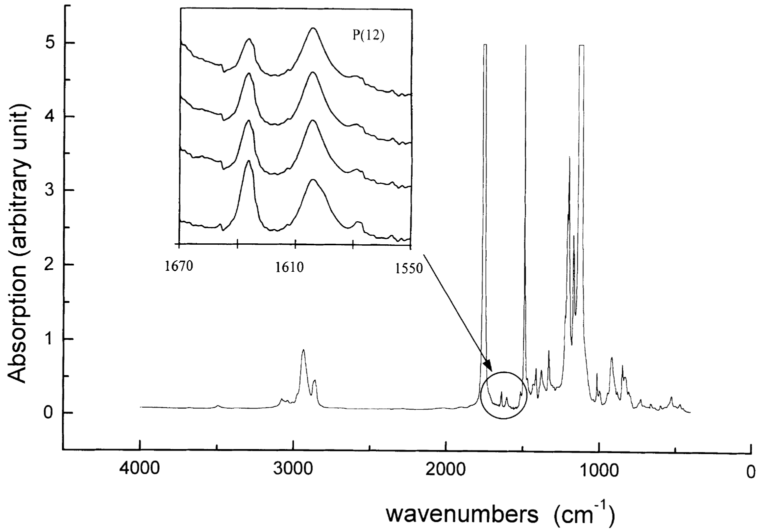


Fig. 4. FTIR spectra of a film sample of **P(12)** containing 2,2-dimethoxy-2-phenylacetophenone. In the inset the FTIR spectra is referred to samples of **P(12)** irradiated with UV: irradiation time increases from the bottom to the top (0, 5, 15, and 60 min, respectively).

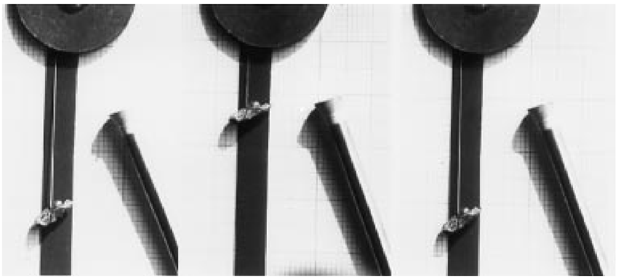


Fig. 5. UV crosslinked fibre of **P(12)**: (a) at room temperature; (b) heated up to about 150°C; and (c) cooled at room temperature (scaled background smaller subdivision length is 1 mm).

phenomenon is completely reversible during cooling. In fact, the fibre recovers the initial length on cooling.

Tensile tests were performed by means of TMA in order to characterise the fibre deformation as a function of temperature and of applied stress. A typical tensile experiment is shown in Figs. 6 and 7 for **P(12)** crosslinked fibre (60 min UV irradiated). The sample is heated at 10°C/min from 50–170°C under a load of 2.0 g. After load removal (a residual load of 0.3 g was imposed to retain fibre alignment during cooling) the sample is cooled to 50°C, and subsequently the load is applied again. The testing cycle is illustrated in Figs. 6 and 7 vs. temperature and time, respectively. During

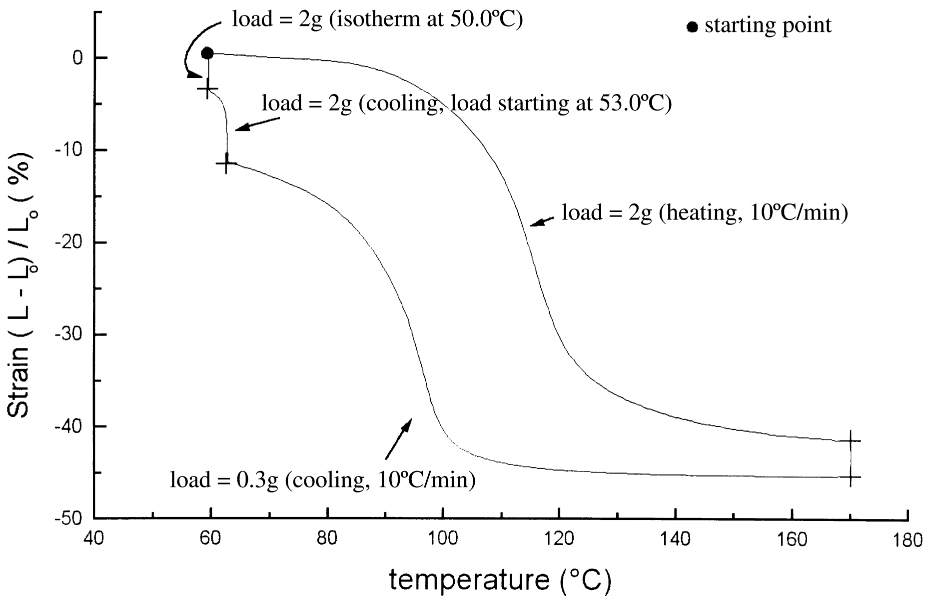


Fig. 6. Strain vs. temperature of a UV crosslinked fibre of **P(12)** at constant load (2 g in the heating run and 0.3 g in the cooling run).

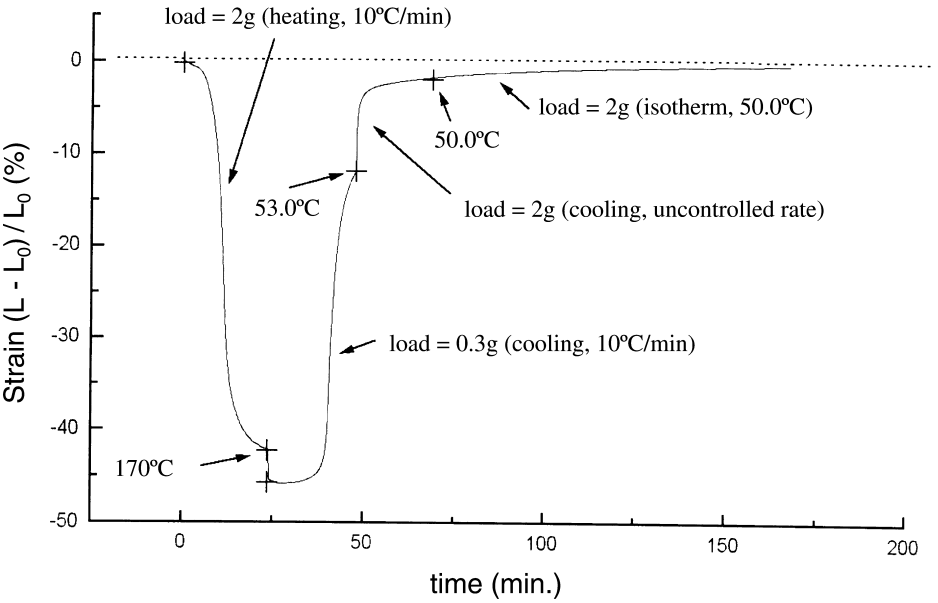


Fig. 7. Same experiment of Fig. 7 but with strain vs. time.

the heating ramp the fibre length reduces by about 40% of the original length: when load is removed at 170°C, further contraction takes place up to about 45%. In the following cooling ramp under a reduced load the length increases but the initial dimension is not restored completely; at 53°C there is still a 12% of residual contraction compared to the original sample. When the load of 2.0 g is applied again, the original dimension is recovered over the interval of 120 min (Fig. 7). The effect of applied stress ranging from 101 kPa to 1.31 MPa is shown in Fig. 8 and summarised in Table 5. As can be evidenced, the fibre shrinkage decreases with increasing the applied stress. Moreover, temperatures of flexes increase with increasing stress. This effect is not unexpected: applied load stabilises the oriented state of macromolecules. As a consequence, the "isotropisation" temperature (flex temperature) increases with load.

X-ray measurements are in agreement with the proposed

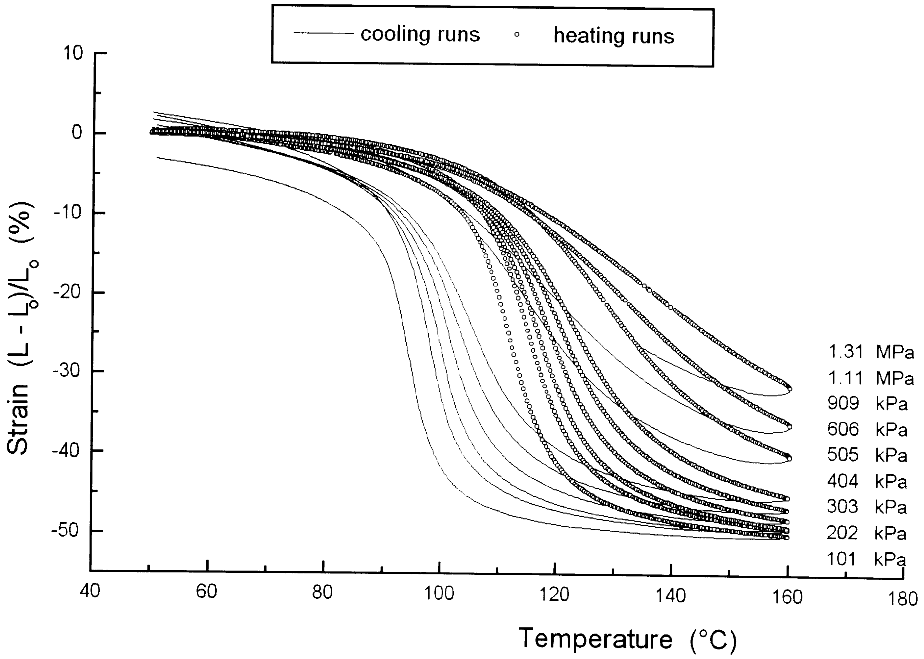


Fig. 8. Strain vs. temperature for an UV crosslinked fibre of **P(12)** at different loads.

Table 5
Flex temperature and contraction of fibre samples of **P(12)** at different load

Stress[a]	C[b]	$T_{\mathrm{f,heat}}$[c]	$T_{\mathrm{f,cool}}$[c]
101	50.3	111.6	94.3
202	49.4	114.6	98.0
303	49.2	116.6	100.4
404	48.2	118.5	101.2
505	46.9	120.5	102.5
606	45.3	122.2	103.9
909	40.2	128.9	114.9
1110	36.3	131.4	118.3
1310	31.5	136.6	Break

[a] Stress (kPa), load applied to fibre.

[b] C (%), fibre contraction referred to the heating run and defined as $100 \times (L_{160°\mathrm{C}} - L_0)/L_0$. L_0 is taken at room temperature from the heating run with the lowest load (101 kPa).

[c] T_{f} (°C), flex temperature of the correspondent heating and cooling run.

scheme. In Fig. 9 X-ray diffraction patterns of the **P(12)** UV crosslinked fibre are shown. The effect of applied stress in stabilising the nematic phase is evidenced comparing images (b) and (d). In fact, as the temperature is increased at 150°C the fibre shrinks due to the transition from the oriented nematic to the disordered isotropic phase (Fig. 9(b)). If the fibre length is fixed at room temperature and then the sample is heated at 150°C, the dimensional constrain results in an axial tensional state. The sample under load is still oriented, according to the polarisation of the diffraction halo in Fig. 9(d). Cooling the unconstrained (Fig. 9(c)) and the constrained sample (Fig. 9(e)) results in the complete recovery of the initial dimension and, as a consequence, in the relaxation of the tensional state. The diffraction images are in agreement with oriented nematic structures for both constrained and unconstrained samples.

4. Conclusion

In the present paper we have shown that MONs can be prepared from LCPs by UV activated crosslinking. This procedure offers the possibility of preparing samples that can be quenched in their final shape by chemical crosslinking. The pendant allyl group seems to be a suitable choice, due to the careful balance achieved between the thermal stability of material and reactivity of crosslinking groups. The characterisation of the crosslinking density of **P(n)** is beyond the limit of the present study. This topic is very important indeed and, in our opinion, deserves ad hoc investigation. Moreover, MONs based on rigid moiety with a higher axial ratio should be synthesised as a model compound, in order to verify the possibility of obtaining anisotropic networks in the whole range of thermal stability.

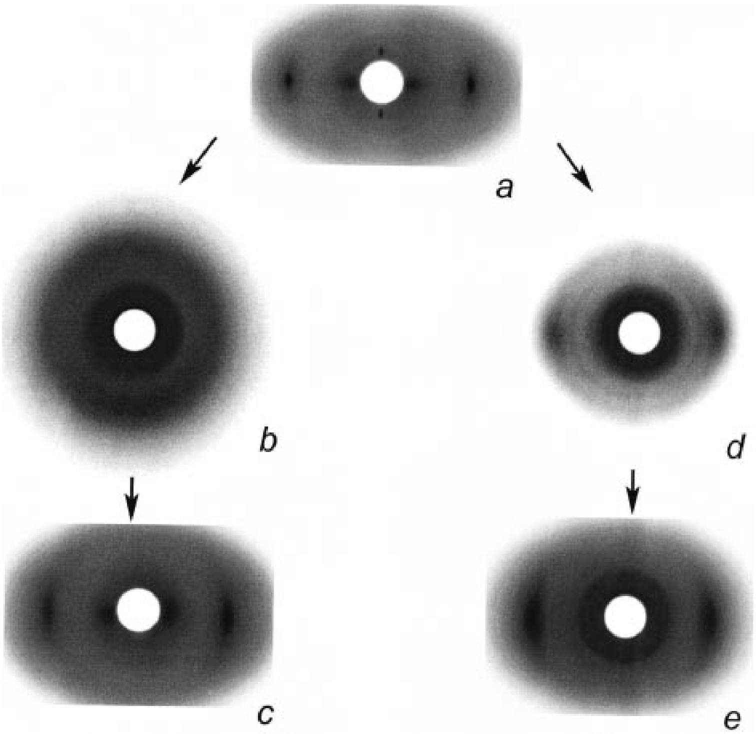


Fig. 9. X-ray diffraction pattern of a UV crosslinked fibre of **P(12)**: (a) fibre at room temperature; (b) fibre without constraint at 150°C and then (c) cooled at room temperature; and (d) constrained fibre (fixed at tips) at 150°C and then (e) cooled at room temperature.

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