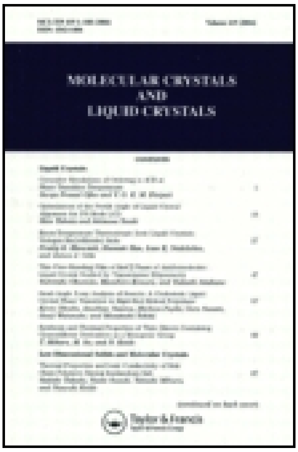

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Liquid Crystalline Behaviour of Polymer Networks Based on Segmented Chain Mesogenic Polymers

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LIQUID CRYSTALLINE BEHAVIOUR OF POLYMER NETWORKS BASED ON SEGMENTED CHAIN MESOGENIC POLYMERS

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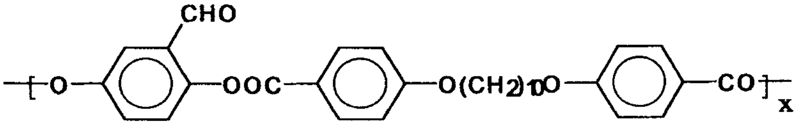
Abstract The synthesis of some crosslinked polymers based on a segmented-chain polymeric mesogen containing variable amounts of a side chain substituent is reported. The unswollen networks show thermotropic mesomorphism of nematic character whose stability decreases with increasing substitution and crosslink density. Depending on the same parameters, the swollen networks may show optical anisotropy at room temperature whose origin is attributed to phase separation

INTRODUCTION

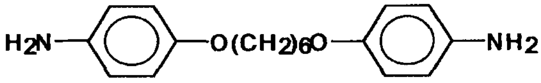
Polymer networks obtained from liquid crystalline materials have received attention for several and different reasons, e. g. : they may irreversibly fix and stabilize a liquid crystalline structure in a vitreous state[1] rising expectations for practical applications as thermosetting materials and composites[2,3] or in the manufacture of a particular class of optical displays[4,5]; they may constitute elastomeric materials whose state of internal order and macroscopic orientation may be reversibly influenced by a mechanical action[6]; they may afford anisotropic gel phases in the swollen state with theoretical implications which still need a complete understanding[7-9].

Liquid crystalline networks may be obtained both from low molar mass or polymeric molecules; we have reported in a previous article[10] the synthesis and the phase properties in the neat and swollen state of a network based on polymer **I**



I

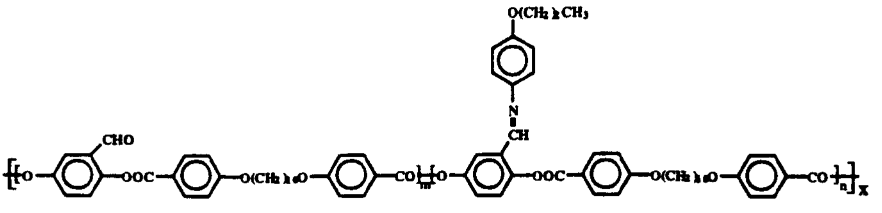
which was moderately (< 10%) crosslinked by reaction with diamine **II**:



II

The crosslink reaction was performed in isotropic solution phase (at 105 °C o-dichlorobenzene) . Two main features were discussed: a) The neat network shows enantiotropic nematic mesomorphism as its parent linear polymer **I** but the thermal stability of the mesopahse is decreased. A comparison with the mesogenic behaviour of a linear polymer of related structure **III** and of low molar mass model compounds **IV** and **V** suggests that this decrease may be largely associated to the intrinsic decrease of mesogenic potential of the monomeric unit bearing the branch point. b) The swollen network, which forms as an optically isotropic gel, becomes anisotropic at room temperature with polymer solvent weight ratio ranging between 0.065 and 0.080. The reverse transformation back to the isotropic state occurs in the range 50-90 °C, with an enthalpy change ranging between 2.4 to 2.8 J/g, . This phenomenon is not quantitatively reversible, at least within the time interval of an ordinary calorimetric cycle (< 1 h). On account of the substantial conformational mobility of polymer I and of the low polymer content found in the anisotropic swollen network, a straightforward interpretation of the feature in terms of a monophasic lyotropic system appeared rather unsafe and prompted further investigation. In fact, it should noticed that at comparable polymer concentrations a lyotropic mesophase is developed only for solutions of rigid-chain polymers such as poly(1,4-benzamide[11] or poly(1,4-phenylene terephthalamide)[12].

A ^{13}C NMR study[13] of the anisotropic swollen state suggests for it a biphasic structure with a fraction of the polymer matrix arranged as a liquid-like, highly mobile phase and a second fraction of quasi-solid, non crystalline structure. To this phase would be associated the optical anisotropy which characterises the swollen network at room temperature. This result suggests that the formation of the anisotropic phase on cooling the isotropic gel is equivalent to a "precipitation" which, therefore, might be prevented by increasing the solubility of the polymer matrix. On the other hand, it had already been observed that copolymer **III** (n=10) [n = molar percent of branched monomer units] is more soluble in o-dichlorobenzene than polymer **I**. Therefore, it has been assumed that an increased solubility, caused by a progressive increase of n, might either allow to reach polymer concentrations high enough to produce



(III)

true lyotropic solutions or prevent the formation in the swollen network of the anisotropic segregates outlined above. On this grounds we have studied copolymers III and some networks based on them.

EXPERIMENTAL SECTION

Polymer synthesis. Synthesis of polymer I was performed by interfacial reaction in water chloroform solution of 2,5-dihydroxybenzaldheyde with 1,10-bis(decandioxy)benzene dicarboxylic acid chloride in stoichiometric ratio, in the presence of tetrabutyl-ammoniumhydrogensulphate as interfacial agent and potassium hydroxide as acid acceptor. A detailed description of the adopted procedure was reported in a previous article[10]. Different polymer samples have been prepared whose isotropization temperatures range between 298 and 304 °C. For all of them the ^1H NMR spectrum (deuterated o-dichlorobenzene solution at 100 °C) is in accordance with t he formula. Solution viscosities (o-dichlorobenzene at 100°C) were measured using an Ubbelohde viscosimeter. Intrinsic viscosities range between 1.52 and 2.10 dLg^{-1}.Diamine II and monoamine $H_2N\text{-}C_6H_4\text{-}O(CH_2)_2CH_3$ were prepared by reduction of the corresponding nitro compounds in ethanol solution with hydrated hydrazine utilizing Palladium/carbon as a catalyst. ^1H NMR spectra (deuterated chloroform solution) are in accordance with the formulas.

Copolymer synthesis. Copolymers were prepared by reaction of polymer I, dissolved in hot o-dichlorobenzene solution under nitrogen atmosphere, with the appropriate quantity of monoamine, as reported in ref. 10. ^1H NMR spectrometry (deuterated o-diclorobenzene solution at 100 °C) is utilised to determine the percentage of imine formation, by the analysis of the intensity ratio of -CHO and -CH=N- proton resonance.

Networks. Crosslinking was performed with a procedure analogous to that reported in ref. 10 utilizing a polymer/solvent weight ratio of 0.038. An appropriate quantity of **III** was dissolved in o-dichlorobenzene at 180°C. At this solution, cooled at 105°C, was added an appropriate quantity of diamine **II** dissolved in 0.5 mL of o-dichlorobenzene. The reaction vessel was sealed to prevent solvent evaporation and kept at 105°C for a period of 30 minutes. The polymer network was than cooled, extracted from the reaction vessel and stored 20 days at room temperature in a large excess of solvent before any characterisation is performed. This delay time is sufficient to allow swelling equilibrium to be attained.

Experimental methods. The phase behavior of all compounds was examined by differential scanning calorimetry utilising an indium calibrated Perkin-Elmer DSC7 apparatus. Samples were examined under dry nitrogen atmosphere, (in a sealed vessel for swollen networks), with a temperature scanning rate of 10 K/min. Temperature controlled polarising microscopy (Zeiss microscope with Mettler FP5 micro furnace) was also utilised for the analysis of the texture of the mesomorphic phase. X-ray diffraction patterns (Ni filtered CuKα radiation) were recorded at room temperature utilising a photographic flat-film camera. ^{1}H NMR spectra were recorded utilising either a Varian 200 MHz or a Bruker 270 MHz apparatus. Thermogravimetric analysis using a Mettler TG50 apparatus was utilised to evaluate the solvent content of the swollen crosslinked samples. IR spectra were recorded using a Bruker IFS66 Ft spectrometer.

RESULTS AND DISCUSSION

Linear copolymeric system (III).

All polymers synthesised show a low degree of crystallinity. This is by no means surprising. Actually, even polymer **I** shows poor crystallinity due to the regioirregular sequence of polar -CHO groups along the main chain. For copolymers **III**, an obvious additional factor is the constitutional disorder related to the random copolymeric structure. Some crystallinity may be recovered by annealing . Figure 1 shows the DSC heating curve for copolymer III(n=21). The endothermic signal peaked at 100 °C is only observable because the sample was previously annealed for 2 h at 80 °C.

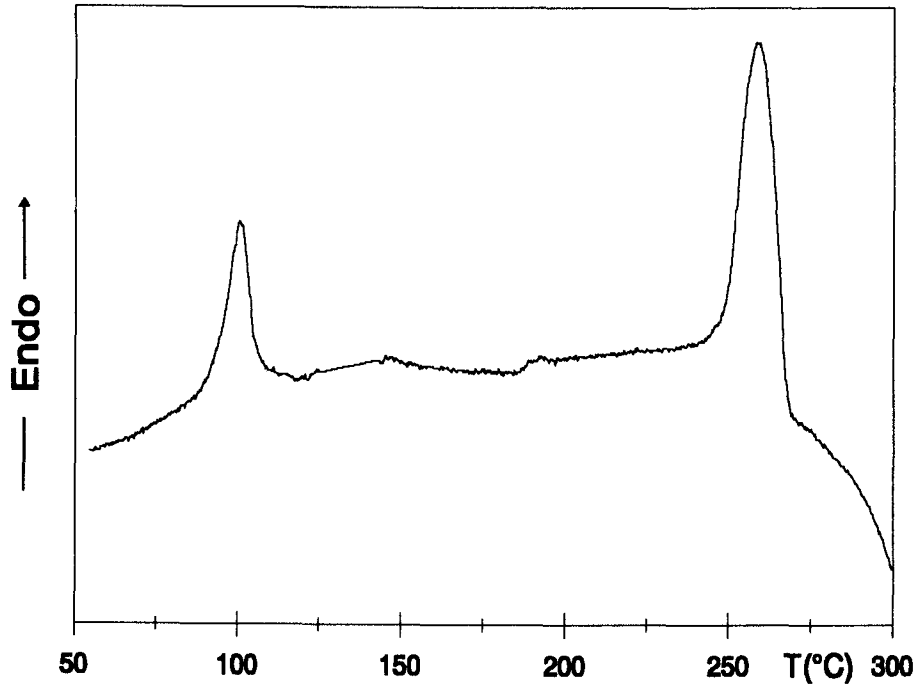
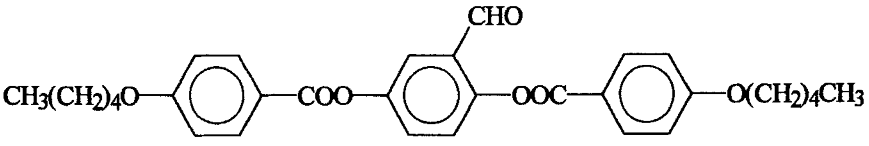


FIGURE 1 Heating DSC curve for copolymer III, n=21. Temperature scanning rate 10 K/min

No crystallisation endotherm is detectable on cooling and the liquid crystalline phase is quenched at room temperature. The endothermic signal peaked at 263°C corresponds to the isotropization of the liquid crystalline phase, as confirmed by polarising microscopy. The nematic nature of the mesophase is suggested by the X-ray diffraction pattern recorded at room temperature utilising a fibrous sample obtained by melt extrusion and quenched in the mesomorphic state. The X-ray diffraction spectrum is essentially characterised by an equatorially polarised halo centred at $\sin(\theta)/\lambda = 0.115$ Å^{-1}.

The phase behaviour of polymer III(n=21) is qualitatively similar to that found for all the homologues. However, as shown in table 1, the thermal stability of the mesophase and the isotropization enthalpy is strictly related to the chemical composition of the polymer decreasing with increasing values of n. This result was expected and appears to be imputable to the presence of an increasing amount of monomer unities having a lesser mesogenic capability as evidenced by the comparison of the mesogenic properties of compounds IV and V (ref. 10).

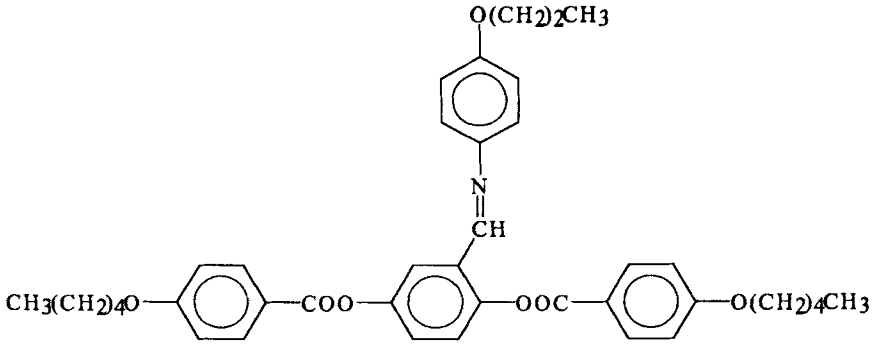


IV

TABLE 1 Isotropization temperatures and enthalpies of copolymers III

n	Ti(°C)	ΔHi(Jg^{-})
7	287	14.4
10	280	13.6
11	277	12.6
21	263	10.8
23	250	10.4
29	243	8.1
32	241	8.1
44	222	5.5

Compound IV shows an enantiotropic nematic phase with Ti = 172.8°C while compound V exhibits a monotropic nematic phase with Ti = 63.8°C. Of course, the behaviour of the low molecular weight "monomeric" model compounds affords a plausible explanation only on a qualitative ground. No quantitative extrapolation to polymers is possible.



V

Polymer networks. All networks were formed as isotropic gels from o-dichlorobenzene solutions of III . For some compositions optical anisotropy developed on cooling at room temperature. Samples were examined only after at least 20 days permanence in large excess of solvent at room temperature. They were first characterised by the measure of the apparent swelling ratio by use of a TGA apparatus. In all cases, the content of neat polymer in the swollen network does not exceed 5% by weight. The phase properties of these systems will be discussed as a function of two parameters, n and r.

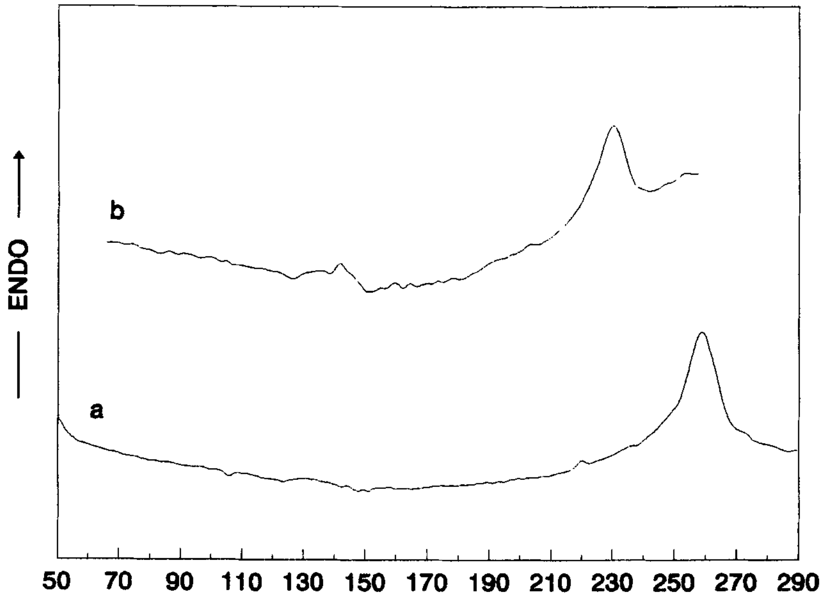


FIGURE 2 DSC behaviour of unswollen networks: n=8,r=20 (curve a); n=32,r=10 (curve b). Heating scan, dT/dt = 10 °C/min.

Parameter n is an experimentally measured quantity that has been used to quantify the composition of copolymer III used in the crosslink reaction. Parameter r is the percent ratio between the amine functions utilised for the crosslink reaction and the amount of monomeric units of the polymer utilised. It is quite clear that, since in the crosslink reaction some diamine molecules may be linked to the polymer via a single amine group or even be left totally unreacted, parameter r only indicates a nominal crosslink density . The phase properties of the unswollen network are not qualitatively different from those of the linear polymer III utilised for the crosslink reaction. Melting is hardly detectable by DSC means while the isotropization is quite evident both in the DSC thermogram and under the polarising microscope. (Fig. 2 shows the DSC heating curvefor two unswollen samples characterised by n = 8 and r = 20 (curve a) and n = 32, r = 10 (curve b). Table 2 reports isotropization temperature and enthalpy for a set of crosslinked polymers. For easy of comparison, the isotropization temperature of the starting polymer III is also reported.

This feature is not unreasonable on account of the expectation that the fraction of diamine molecules that may be linked to the network utilising both amine groups should decrease as n and r increase.

TABLE 2 Isotropization temperatures and enthalpies of unswollen networks

n	r	Polymer III Ti (°C)	Unswollen network Ti (°C)	Unswollen network ΔHi(J/g)
10	10	280	259	14.0
8	20	276	260	11.9
8	35	276	256	10.7
20	10	263	242	10.3
20	20	262	234	8.8
23	35	260	238	3.3
32	10	241	230	6.7
31	20	243	235	3.0
32	20	241	235	5.2

Crosslinking does not suppress liquid crystallinity but reduces its thermal stability. The isotropization temperature appears to be a decreasing function of n+r, that is, of the overall fraction of monomer units bearing a branch point. However, the nominal character of the crosslink density does not allow more strict correlations. For the same reason no quantitative conclusions can be drawn from the observation that for compositions having comparable values of n+r, the isotropization temperature is lower for higher values of n

The phase behaviour of swollen networks depends on parameter n+r. For n+r < 40 , transparent isotropic swollen network as it forms as the crosslink reaction takes place slowly develops optical anisotropy on cooling at room temperature. Isotropy may be recovered on heating and in both senses the phenomenon is detectable also by calorimetry. Figure 3 shows the DSC curves for a sample characterized by n = r = 10. At least in the time scale of the experiment, no quantitative reversibility is attained. Actually, at 10 °C/min temperature scanning rate, anisotropy is developed on cooling well below room temperature (curve b).

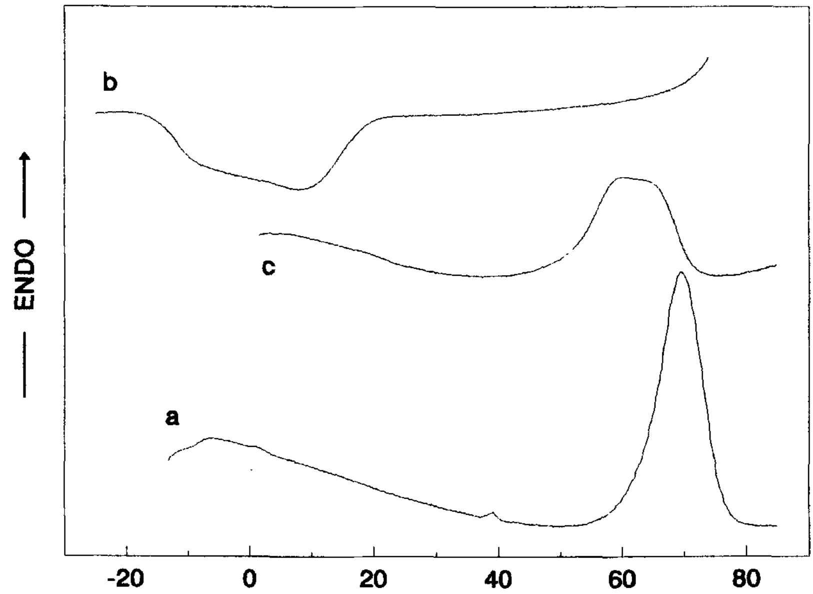


FIGURE 3 DSC behaviour of a swollen network (n = r = 10) ; curve a : first heating run. dT/dt = 10 °C/min.

Table 3 reports some relevant data for the same set of polymers reported in table 2. For those compositions showing anisotropic behaviour at room temperature, temperatures and enthalpy changes associated to the transformation to the isotropic gel phase are given. Temperatures correspond to the maximum of the DSC endothermic signal recorded during the first heating run of wollen samples in the absence of excess free solvent. Although the differences are of scarce statistical significance , the decreasing trend for increasing values of n+r is not unreasonable. The same trend is observed for the polymer content in the swollen samples reported in the last column. A clear relationship between this parameterand the absence of optical anisotropy at room temperature is also detectable.

TABLE 3 Swollen networks

n	r	Polymer III Ti (°C)	Swollen network Ti (°C)	Swollen network ΔHi (J/g)	Optical behaviour	w% dry polym.
10	10	280	69	2.2	anisotr.	4.8
8	20	276	67	1.4	anisotr.	4.4
20	10	263	65	2.0	anisotr.	4.3
20	20	262	53	1.2	anisotr.	4.2
23	35	260			isotr.	3.8
32	10	241			isotr.	1.0
31	20	243			isotr.	1.7
32	20	241			isotr.	1.8

In conclusion, the behaviour of the swollen networks supports the view that the results of the ^{13}C NMR study performed on the polymer characterised by n = 0, r = 13 (ref. 13) may be extended to the present case. This means in particular that the optical isotropy characterising networks with n+r > 40 (which is accompanied by the highest values of swelling solvent content) should be attributed to their increased solubility in o-dichlorobenzene which prevents the segregation of microphases of nematic structure having high polymer content.

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