Thermotropic and Lyotropic Mesomorphism in a Polymeric Network with Low Cross-Link Density

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ABSTRACT: The synthesis and the phase properties of a cross-linked polymer obtained by reaction of a tricarboxylic acid chloride and an oligomeric derivative of the nematogenic polymer [–O-*p*-$C_6H_4O(CH_2)_{10}O$-*p*-C_6H_4OOC-*p*-$C_6H_4O(CH_2)_{10}O$-*p*-C_6H_4CO–]$_{dp}$ are reported. The cross-linked polymer exhibits thermotropic nematogenic behavior with isotropization temperature and enthalpy not very much lower than measured for the linear polymer. Swelling in *o*-dichlorobenzene produces an optically anisotropic material containing 73.7% (mass) solvent at room temperature. Its X-ray diffraction pattern is consistent with a noncrystalline structure. The swollen polymer undergoes a thermotropic transition (peaked around 84–87 °C) to an optically isotropic phase. If the phase transition takes place in the presence of free solvent, further swelling occurs. The transition enthalpy per unit mass of pure polymer is considerably larger than found for the isotropization of the pure polymer itself. Seemingly, some ordering of the solvent molecules is involved.

Introduction

Polymeric networks with liquid crystalline (LC) order have been investigated with the purpose of obtaining either elastomers[1–4] or highly rigid materials.[5,6] In the former case, the mesogenic groups are normally included as side-chain pendants of an elastomeric matrix with low cross-link density. In the latter, either extensive cross-linking of low molar mass mesogens[5] or inclusion of rigid-chain polymeric segments[6] has been utilized as a means to lock LC order in the cross-linked material.

Some cases have been reported also of LC networks obtained by cross-linking preformed segmented-chain LC polymers with short alkylsiloxane chains.[7] Seemingly, moderate cross-link density favors the permanence of thermotropic mesomorphism in the network polymer.

Networks are complicated systems. The relevance of some specific parameters concerning interchain ties (linear extension, flexibility, and density and distribution of cross-link groups) needs systematic evaluation. In this paper, we study the LC properties of a low cross-link density polymer network obtained by reaction of a conformationally flexible tricarboxylic acid with a LC segmented-chain oligomer having *p*-hydroxyphenylene terminal groups. The choice of using terminally functionalized oligomers (although not homogeneous by molecular weight) was designed to favor a more homogeneous distribution of cross-links in the network avoiding, in particular, the occurrence of successive cross-links separated by a single monomeric unit.

Experimental Section

The LC segmented-chain oligomer utilized is a low molar mass homologue of polymer 1:

[–O-*p*-$C_6H_4O(CH_2)_{10}O$-*p*-C_6H_4OOC-*p*-$C_6H_4O(CH_2)_{10}O$-*p*-C_6H_4CO–]$_{dp}$ (1)

Its preparation follows a chemical path equivalent to that utilized by Griffin and Havens,[8] who first prepared polymer 1 and gave account of its mesomorphic behavior. The *p*-C_6H_4-OH-terminated oligomer was synthesized by reaction of HO-*p*-$C_6H_4O(CH_2)_{10}O$-*p*-C_6H_4OH (**2**) and ClOC-*p*-$C_6H_4O(CH_2)_{10}O$-*p*-C_6H_4COCl (**3**) in *o*-dichlorobenzene solution at ~180 °C for 1 h under a nitrogen atmosphere. To obtain both low molar mass and prevalence of *p*-C_6H_4OH termination, a 50% molar excess of **2** was utilized. Oligomeric **1** (henceforth called **1**(ol)) precipitates from the reacted solution by addition of *n*-hexane. It was washed twice with boiling 95% ethanol and dried at ~110 °C. As a reference, polymer **1** was also prepared with the same procedure, but keeping **2** and **3** in equimolar amounts.

To obtain a cross-linked polymer (henceforth called **1**(cl)), oligomer **1**(ol) was made to react with $ClOCCH((CH_2)_2COCl)_2$ (**4**) in *o*-dichlorobenzene solution at 170 °C for 2 h. A 5% excess of **4** was utilized with respect to the stoichiometric molar proportion of 2(**4**)/3(**1**(ol)). The reaction product forms as a largely swollen gel. It was purified by three extractions with boiling *o*-dichlorobenzene and by two successive treatments with *n*-hexane. Finally, it was vacuum-dried at 110 °C for 8 h. Compound **4** was prepared by reaction of the corresponding acid with $SOCl_2$. To prevent anhydride formation, a small amount of $ZnCl_2$ was added to the reaction mixture. After removal of unreacted $SOCl_2$, **4** was purified by vacuum distillation.

The phase behavior was examined by differential scanning calorimetric, optical, and X-ray diffraction means. An indium-calibrated Perkin-Elmer DSC-7 apparatus was utilized for the thermal analysis under a nitrogen atmosphere. A temperature scanning rate of 10 K/min was used in most cases. For the optical observations a Leitz polarizing microscope and a Mettler FP5 temperature controller were utilized. Cu Kα X-ray diffraction patterns were recorded by the photographic method utilizing a flat-film camera. A glass capillary was utilized to contain the sample under a nitrogen (*o*-dichlorobenzene vapor for swollen samples) atmosphere. Temperature was controlled within ±2 K by means of a microfurnace.

Results and Discussion

Oligomer 1(ol). The liquid crystalline properties of **1**(ol) have been examined utilizing two samples having moderately different molecular weights, 2400 and 3150, as measured by ^1H NMR spectrometry of acetylated derivatives. The only relevant difference between their thermal properties concerns the nematic–isotropic transition temperature: 185 °C for the sample having molecular weight 2400, and 191 °C for the other sample. For both samples, the melting behavior at the first DSC heating run is not entirely reproducible in the successive thermal cycles although the peak temperature is. A rather relevant difference distinguishing the two oligomers concerns the chain termination. For the lower molecular weight sample, chain termination with *p*-hydroxyphenylene groups is

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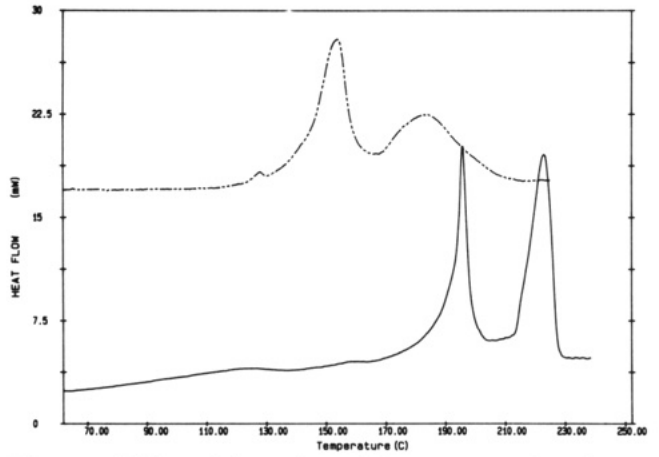

Figure 1. Differential scanning calorimetry curves for polymer 1 (full line), first heating run, and oligomer 1(ol) (broken line), second heating run.

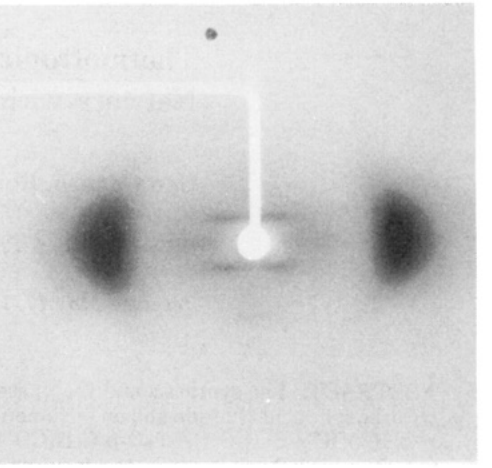

Figure 2. X-ray diffraction pattern of a fibrous sample of cross-linked polymer 1(cl) (room temperature).

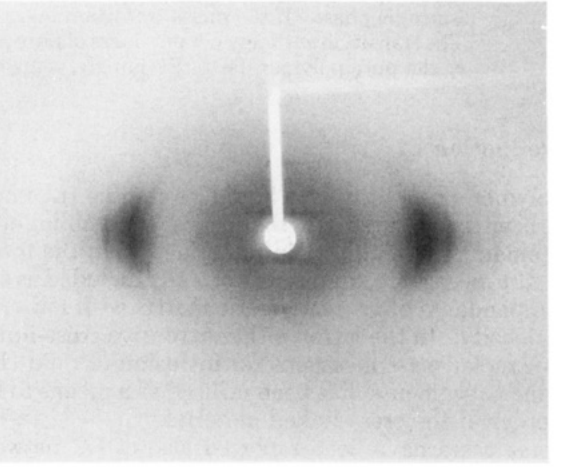

Figure 3. X-ray diffraction pattern of a fibrous sample of cross-linked polymer 1(cl) previously annealed 12 h at 120 °C (room temperature).

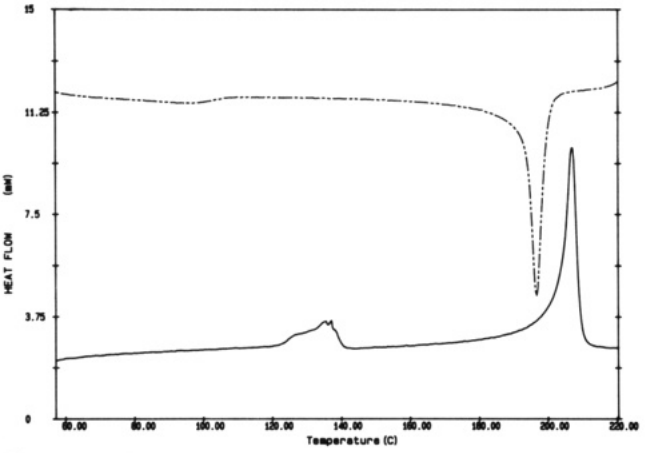

Figure 4. Differential scanning calorimetry curves for cross-linked polymer 1(cl): full line, first heating run; broken line, first cooling run.

virtually complete. In fact, the broad IR absorption band (3000–3700 cm^{-1}) that is connected with the presence of phenolic or carboxylic OH groups does not occur in the infrared spectrum of the acetylated derivative. On the contrary, about 10% of the chain terminations of the 3150 molecular weight oligomer are formed by p-C_6H_4COOH groups. This approximate evaluation is made by comparing the molecular weight of the oligomer measured by vapor pressure osmometry (*o*-dichlorobenzene as solvent, 120 °C), which is 2750, with that measured by NMR spectrometry of the acetylated derivative.

1(ol) with 2400 molecular weight was used to produce the network polymer. The DSC diagram relative to the second heating run is reported in Figure 1 superimposed on the diagram of polymer 1 (M_n = 14 000) prepared as indicated in the Experimental Section. The isotropization of the oligomer occurs within a broader temperature range and is peaked at a lower temperature compared to polymer 1. A lower value of the isotropization enthalpy (20.0 J/g compared to 25.4 J/g found for 1) is also a not unexpected feature. In fact, the dependence of T_i and ΔH_i on molecular weight for $M_n \lesssim 10^4$ is a well-known feature of nematogenic polymers with segmented-chain structure.[9]

Cross-Linked Polymer 1(cl). The cross-linked polymer as obtained is a biphasic material with poor crystallinity. This is documented both by the X-ray diffraction pattern and by the calorimetric behavior. Crystallinity may be almost completely suppressed by cold drawing (Figure 2). This action produces considerable macroscopic orientation in the sample. Successive premelt annealing enhances crystallinity with no negative consequence on macroscopic orientation (Figure 3).

The DSC behavior is shown in Figure 4. The endothermic transition peaked at ~135 °C occurs in correspondence to a complete loss of crystallinity (Figure 5). This "melting" does not produce any fluidity, in accordance with what is expected for a network structure. The "molten" sample is optically anisotropic. Isotropization occurs at temperatures above ~210 °C. This is consistent with the endothermic signal peaked at 207 °C shown in the DSC curve (Figure 4) and indicates that a phase transition takes place involving a liquid crystalline phase. Although no significant morphological feature was of any help to decide about the nature of the mesophase, the X-ray diffraction pattern recorded at 150 °C (Figure 5) should be sufficient to recognize its nematic structure.

In conclusion, the network structure does not impede the onset of thermotropic mesomorphism of the same nature shown by the linear polymer.

The isotropization temperature of 1(cl) is intermediate between that measured for full polymer 1 and oligomer 1(ol) and its isotropization enthalpy is somewhat smaller than measured for 1 (Table I). A similar, small decrease of the isotropization temperature in network polymers with low, cross-link density has also been found by Zentel et al.[7] and it does not appear to be related to the nature of the mesophase. In a simple hypothesis, it may be taken

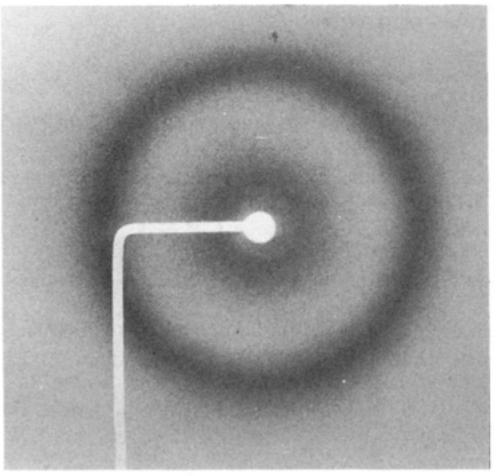

Figure 5. X-ray diffraction pattern of a macroscopically unoriented sample of cross-linked polymer 1(cl) at 150 °C.

Table I
Thermodynamic Data Concerning Phase Transitions[a]

	T_m	T_i	ΔH_i
polymer 1[b]	195	223	25.4
oligomer 1(ol)[c]	154	185	20[e]
polymer 1(cl)	130	207	20.0
swollen 1(cl)[d]		84–87	36

[a] T_m/°C = melting temperature; T_i/°C = isotropization temperature; $\Delta H_i/(J\,g^{-1})$ = isotropization enthalpy. Temperatures are taken at the maximum of the transition DSC endotherm. [b] Polymer (M_n = 14 000) synthesized by solution polycondensation. [c] Data refer to the oligomer with M_n = 2400. [d] The two values for T_i refer to measurements made with or without excess (at room temperature) of swelling agent. ΔH_i is reported per gram of dry polymer. [e] Measured on heating the supercooled liquid crystalline phase before crystallization takes place.

as the obvious consequence produced on the liquid crystalline properties of a linear polymer when a small amount of a nonmesogenic component is copolymerized according to a random sequence. On the other hand, the higher value of T_i found for 1(cl) with respect to 1(ol) may be seen as the consequence of the chain extension produced by the cross-linking reaction.

The phase properties of 1(cl) swollen in *o*-dichlorobenzene are noteworthy. Swelling occurs readily at temperatures above ~100 °C. On cooling, a considerable fraction of the solvent is expelled. The swollen polymer kept at room temperature for a sufficiently long time (>48 h) reaches a fairly constant composition with 73.7% (by weight) content of solvent. In this condition, it is optically anisotropic and its X-ray diffraction pattern, which is hardly distinguishable from that of the pure solvent, indicates that no crystallinity is present. The calorimetric behavior of a swollen sample in the presence of free solvent is shown in Figure 6. The endothermic signal peaked at ~84 °C corresponds to the optical isotropization of the sample, and, in coincidence with the broader exotherm on cooling, optical birefringence is restored. In the isotropization transition the degree of swelling increases. The reverse occurs on cooling. However, it is apparent that supercooling of the isotropic phase is relevant. No complete reversibility is attained unless the sample is cooled to a sufficiently low temperature or enough time is allowed for the original phase to be restored at room temperature.

It is apparent that the swollen polymer may exist as a lyotropic liquid crystalline phase, presumably of nematic structure. The isotropization of this mesophase is not necessarily connected to the possibility for the system to

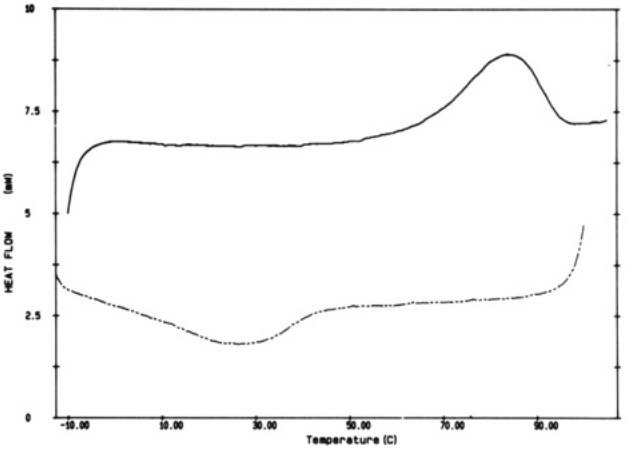

Figure 6. Differential scanning calorimetry curves for a swollen sample of cross-linked polymer 1(cl) in the presence of free solvent (*o*-dichlorobenzene): full line, heating run; broken line, cooling run.

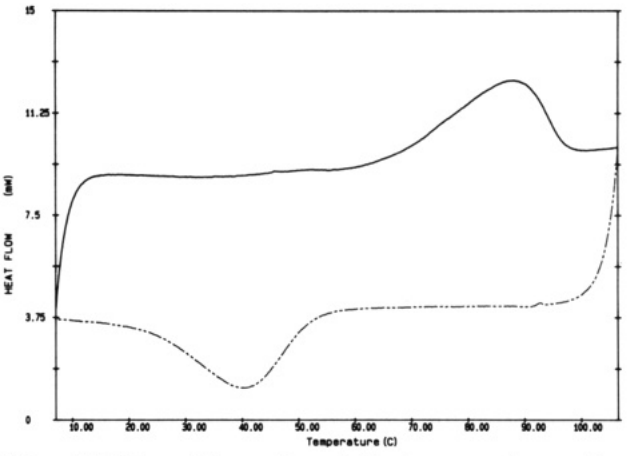

Figure 7. Differential scanning calorimetry curves for a swollen sample of cross-linked polymer 1(cl) with no excess of swelling agent (at ~20 °C): full line, heating run; broken line, cooling run.

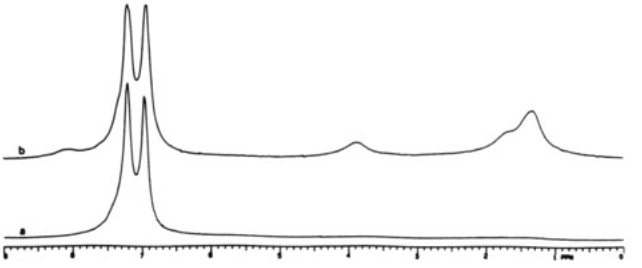

Figure 8. ^{1}H NMR spectra at 28 °C (curve a) and at 105 °C (curve b) for a sample of cross-linked polymer 1(cl) swollen with an excess of swelling agent (70% fully deuterated *o*-dichlorobenzene).

increase its solvent content. In fact, the phase transition shown in Figure 6 is exhibited in its basic features by a swollen sample also in the absence of free solvent (Figure 7). Seemingly, a small increase of the peak temperature of the transition endotherm and a significant reduction of the supercooling of the isotropic phase are the only detectable differences.

Some variation of the molecular mobility of the polymeric matrix taking place at the phase transition is detectable by ^{1}H NMR spectrometry. Figure 8 reports the NMR spectra recorded at 28 and 105 °C for 1(cl) swollen in *o*-dichlorobenzene containing 70% of the fully deuterated homologue. An XL-200 Varian NMR spectrometer was utilized with *o*-dichlorobenzene (same par-

tially deuterated mixture used as swelling agent) as external standard. Resonance signals pertaining to the polymeric matrix are detectable in the high-temperature spectrum (curve b).

The isotropization enthalpy of swollen 1(cl) is relatively high (9.5 J/g). It is definitely larger than measured for the nematic to isotropic phase transition of low molecular weight mesogens whose molecular structure is similar or homologous to that of the polymer (e.g., for nematogenic compounds with formula $CH_3(CH_2)_nO$-*p*-C_6H_4COO-*p*-C_6H_4-$O(CH_2)_mCH_3$, ΔH_i = 4.07 J/g for n = 4, m = 6; ΔH_i = 3.7 J/g for n = 5, m = 6).[10] If referred to unit mass of pure polymer, ΔH_i of swollen 1(cl) is significantly larger than that measured for the pure polymer itself (Table I). An even larger difference separates the respective entropy values because of the considerably lower isotropization temperature of the swollen polymer. This feature indicates that some ordering of solvent molecules occurs in the lyotropic phase.

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Registry No. **2–3** (copolymer), 70856-66-5; **2–3** (SRU), 70857-27-1; **2–3–4** (copolymer), 136827-43-5.