Phase Behavior of a Network Polymer Based on a Segmented-Chain Polymeric Mesogen

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ABSTRACT: The phase behavior of a polymer network obtained by moderately cross-linking a segmented-chain liquid crystalline polymer is presented. The network was formed by reacting $H_2NC_6H_4$-*p*-$O(CH_2)_6O$-*p*-$C_6H_4NH_2$ with an *o*-dichlorobenzene solution of a polyester previously prepared by reaction of 2,5-dihydroxybenzaldehyde with $ClOCC_6H_4$-*p*-$O(CH_2)_{10}O$-*p*-C_6H_4COCl. The network shows thermotropic nematic behavior of a cybotactic type as observed for the linear polymer. However, the mesophase stability is significantly reduced. The origin of this reduction is discussed and related to the intrinsic decrease of the mesogenic potential of the linear chains forming the network. The phase behavior of the swollen network is also examined. The formation of a noncrystalline anisotropic gel at temperatures lower than ~80 °C is observed with a polymer/solvent ratio ranging between 0.065 and 0.080. Isotropization takes place on heating and is accompanied by an enthalpic increase. The ^{1}H-NMR spectrum of the anisotropic gel suggests that the gel has a biphasic structure rather than a lyotropic single structure.

Introduction

Liquid crystalline networks are remarkable systems. Following with some delay an isolated early theoretical attention to the mechanical properties of the elastomers and specifically to the relationships between mechanical action and nematic order,[1] liquid crystalline networks have become the subject of increasing experimental[2-8] and theoretical[9,10] research as well as applicative interest.[11-13] One specific problem in the field concerns the phase structure and the properties of a swollen network. The most common examples (among the few) of such a system are the lyotropic mesophase of cross-linked cellulose derivatives[14,15] or of cross-linked poly(γ-benzyl L-glutamate).[16] In both cases, liquid crystallinity is related to the presence of rigid molecular segments of considerable length.

Quite recently, a concise theoretical treatment of the phase equilibria that may occur in swollen nematic elastomers based on intrinsically nematogenic semiflexible chains has been formulated by Warner and Wang.[17] Conditions for the coexistence of a nematic gel with the solvent or with an isotropic gel are outlined.

In an article[18] appearing simultaneously in the same journal, we reported the phase behavior of a network polymer with moderate cross-link density obtained by reaction of a mesogenic terminally *p*-C_6H_4OH-functionalized segmented-chain oligomeric homologue of polymer 1 and a tricarboxylic acid chloride. It was shown that the

$$[\text{-O-}p\text{-}C_6H_4O(CH_2)_{10}O\text{-}p\text{-}C_6H_4OOC\text{-}p\text{-}C_6H_4O(CH_2)_{10}O\text{-}p\text{-}C_6H_4CO\text{-}]_n$$
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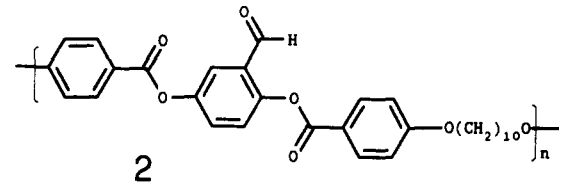
cross-linked polymer, although formed in an isotropic medium, preserves the thermotropic mesogenic behavior of the same nature as found for the linear oligomer. The swollen network is optically anisotropic at room temperature. Anisotropy fades out or is recovered as a thermally detectable transformation takes place reversibly around a temperature considerably lower than measured for the isotropization of the unswollen polymer. To further investigate the nature of the phenomenon and to explore to what extent it may be dependent on specific chemical and structural features, we have examined the phase properties of a network obtained by low-density cross-linking in an isotropic medium of a mesogenic polymer bearing a reactive group in each monomeric unit



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and diamine $H_2NC_6H_4$-*p*-$O(CH_2)_6O$-*p*-$C_6H_4NH_2$ (**3**).

Experimental Section

Polymer Synthesis. Polymer **2** was prepared by interfacial reaction of 2,5-dihydroxybenzaldehyde with the appropriate dicarboxylic acid chloride. The benzaldehyde derivative (Aldrich; Fluka) was previously purified by sublimation; the carboxylic acid chloride was obtained by standard methods from the corresponding dicarboxylic acid whose preparation was performed according to a method already described.

In a typical polymer preparation 5.67998 g of the dicarboxylic acid chloride dissolved in 108 mL of anhydrous chloroform was added, under a nitrogen atmosphere, to a solution containing 1.73793 g of 2,5-dihydroxybenzaldehyde, 2.600 g of tetrabutylammonium hydrogen sulfate, and 2.084 g of potassium hydroxide in 235 mL of deaerated distilled water. The reaction mixture was strongly stirred for 4 min, and then 250 mL of *n*-hexane was added. The polymer was filtered and carefully washed according to the sequence water, chloroform-*n*-hexane (50% vol mixture), 95% ethanol, 50% ethanol-water, water. Finally, the polymer was dried at 70 °C for 180 min at 20-mmHg pressure; yield 86%. The elemental analysis is in accordance with the formula $(C_{31}H_{32}O_7)_x$: % C, 71.92 (72.08 calcd); % H, 6.33 (6.24 calcd), % O, 21.81 (21.68 calcd).

The ^{1}H-NMR spectrum (deuteriated bromoform solution at 50 °C) shows all expected resonances in the correct intensity ratios.

The FT-IR spectrum recorded utilizing a polymer film cast from o-dichlorobenzene solution shows carbonyl bands typical of the ester group (1733 cm^{-1}) and the aldehyde (1696 cm^{-1}).

Solution viscosities (*o*-dichlorobenzene solution, 100 °C) were measured using an Ubbelohde viscometer.

Cross-Link Agent and Model Compounds. Diamine **3**, utilized as the cross-link agent, was prepared by reduction of the corresponding dinitro compound. The synthesis of the latter was performed by standard methods from 4-nitrophenol and 1,6-dibromohexane, and its purification was achieved by recrystallization from ethanol solution. To obtain **3**, 2.958 g of the dinitro compound was dissolved in 200 mL of boiling 95% ethanol, and 32 mg of catalyst (5% Pd on carbon) in ethanol suspension was added. Hydrated hydrazine (2.65 mL) was then added dropwise

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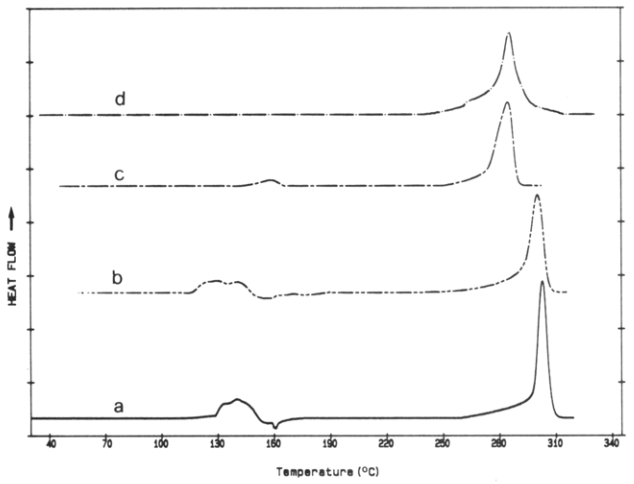
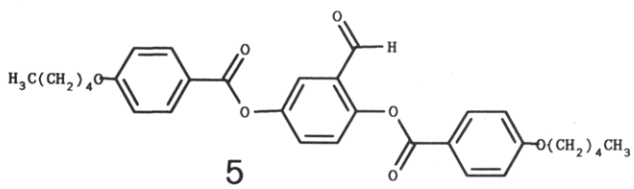


Figure 1. Heating DSC curves for linear polymer **2** with no previous thermal treatment (curve a), linear polymer **2** previously annealed at 110 °C for 30 min (curve b), model polymer **8** with no previous thermal treatment (curve c), and network polymer with no previous thermal treatment (curve d). Temperature scanning rate 10 K/min.

and, successively, a further 32 mg of catalyst. The reaction mixture was refluxed for 12 h and then filtered. Hot water (100 mL) and 2 g of sodium hydrosulfite were then added to the solution. Diamine **3** crystallizes on cooling. Purification was achieved by crystallization from ethanol–water (40%) solution in the presence of a very small amount of sodium hydrosulfite. The ^{1}H-NMR spectrum is in accordance with the formula.

The synthesis of 4-(propyloxy)benzenamine (**4**) was performed following a similar procedure. The only relevant difference concerns the recovery of the product from the reaction mixture. The solvent was evaporated and the residue dissolved in benzene. The resulting solution was washed several times with water and dehydrated with Na_2SO_4, and the benzene was removed by evaporation. Oily amine **4** was finally distilled under vacuum. The ^{1}H-NMR spectrum is in accordance with the formula.

Model compound **5** was prepared by reaction of 4-(pentyloxy)-



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benzoyl chloride (previously prepared following standard procedures) and 2,5-dihydroxybenzaldehyde. The carboxylic acid chloride (3.07 g) dissolved in 10 mL of anhydrous dioxane was added dropwise within 5 min to a solution containing 0.89 g of 2,5-dihydroxybenzaldehyde in 30 mL of pyridine. The reaction mixture was stirred for 14 h at room temperature. Compound **5** was precipitated by pouring the reacted solution in ice water. It was recovered and dissolved in CH_2Cl_2. After dehydration with Na_2SO_4, the solution was concentrated by evaporation, and hot *n*-hexane was added. The resulting solution, showing some opalescence, was treated with basic alumina, filtered, and concentrated by evaporation at boiling temperature. White needles of crystalline **5** separated on cooling. The ^{1}H-NMR spectrum is in accordance with the formula.

Model compound **6** was prepared by reacting **4** and **5**. **5** (0.491 g) was dissolved in 30 mL of hot absolute ethanol, and 0.286 g of **4** was added. The solution was kept boiling for 3 min. Microcrystalline **6** separated on cooling. Purification was achieved by further crystallization from ethanol solution.

Model compound **7** was synthesized by reacting **3** and **5** following the same procedure utilized to prepare **6**. For both compounds, the ^{1}H-NMR spectrum is in accordance with the formula.

Model Polymer 8 and Polymer Network. To obtain model polymer **8** with 10% of the aldehyde groups involved, 0.729 g of

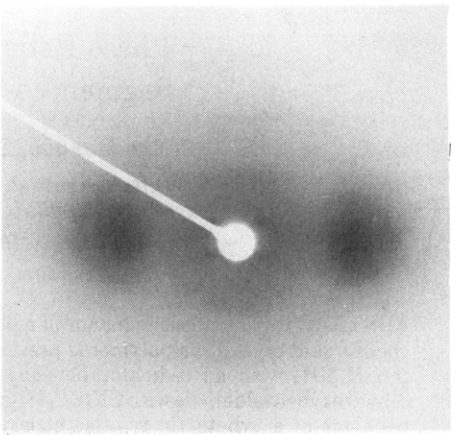


Figure 2. X-ray diffraction pattern of a fibrous sample of polymer **2** recorded at room temperature.

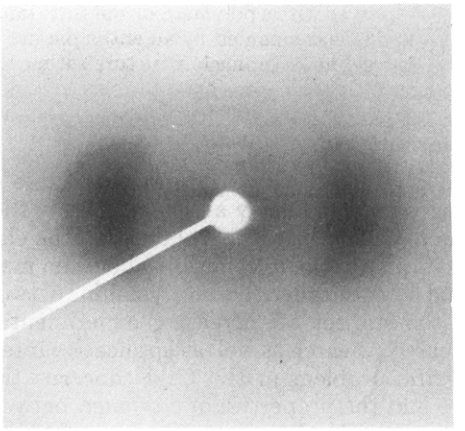


Figure 3. Room temperature X-ray diffraction pattern of a network sample previously stretched above the melting temperature and then quenched under load.

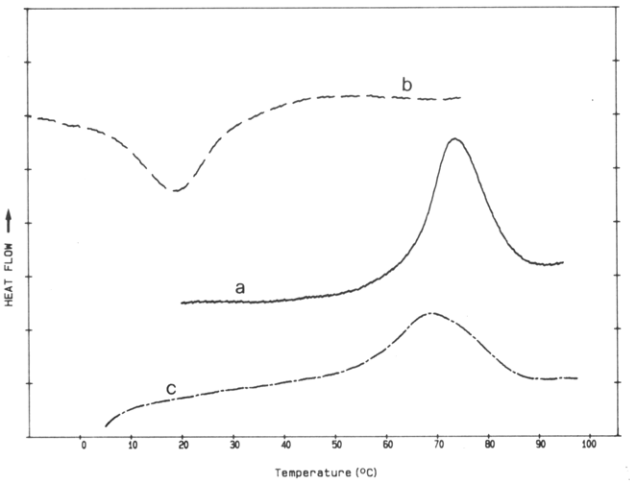
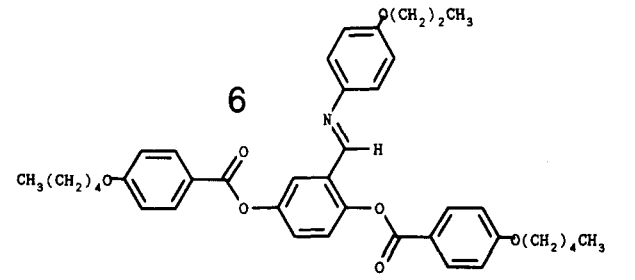


Figure 4. DSC curves for a swollen network sample in the absence of excess solvent: first heating (curve a); first cooling (curve b); second heating (curve c).

polymer **2** was dissolved in 20 mL of hot *o*-dichlorobenzene under a nitrogen atmosphere. The solution was brought to 100 °C and, with rapid stirring, 1 mL of *o*-dichlorobenzene solution containing 0.02116 g of amine **4** was added. After 30 min the reacted mixture was poured into 200 mL of *n*-hexane kept at room temperature. Precipitated polymer **8** was washed at room temperature with *n*-hexane and, successively, with absolute ethanol. It was dried at 70 °C under 20-mmHg pressure. The ^{1}H-NMR spectrum (deuteriated bromoform solution at 50 °C) indicated that the imine formation was quantitative. The intensity ratio between CHO and CH=N proton resonances has the expected value. Significant is also the presence of the signal characterizing the



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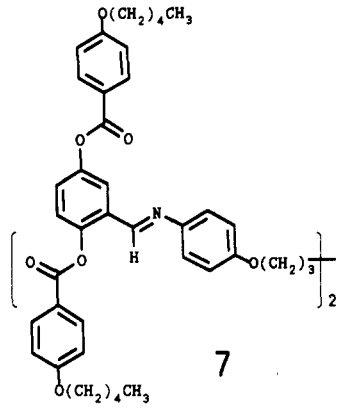

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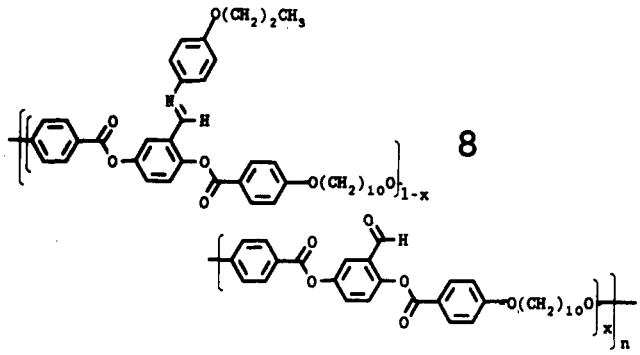

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OCH_2 protons of the reacted amine distinguished from those pertaining to the OCH_2 groups of the main chain.

Network Polymer. In the cross-link reaction, polymer 2 and diamine 3 were combined in the weight ratio corresponding to 10% of the aldehyde groups theoretically involved. In a typical reaction, 0.418 g of polymer 2 was dissolved in 7.5 mL of *o*-dichlorobenzene under a nitrogen atmosphere at 180 °C. The solution was cooled to 105 °C, and 0.01215 g of diamine 3 dissolved in 0.5 mL of *o*-dichlorobenzene was added under swift stirring. The reaction vessel was sealed to prevent evaporation, and the reaction was allowed to proceed for 30 min at 105 °C. No stirring was applied at this stage. The cross-linked polymer was then cooled and extracted from the reaction vessel in the swollen state. In the same state it was stored in the presence of a large excess of *o*-dichlorobenzene for at least 30 days before any characterization of the cross-linked samples was performed.

Characterization Techniques. The phase behavior of all compounds was examined by thermal, optical, and X-ray diffraction means. Differential scanning calorimetry was performed using an indium-calibrated Perkin-Elmer DSC7 apparatus. Samples were examined under a nitrogen atmosphere or in sealed containers with a temperature scanning rate usually set at 10 K/min. For the optical observations a Leitz polarizing microscope and a Linkam temperature-controlled microfurnace (nitrogen atmosphere) were utilized. The X-ray diffraction patterns (Cu Kα) were recorded by the photographic method utilizing a flat-film camera. The sample was contained under a nitrogen atmosphere (swelling agent vapor for the swollen samples) inside sealed glass capillaries. Its temperature was controlled within ±2 °C by means of a microfurnace. IR spectra were recorded using a Bruker IFS 66 FT spectrometer. ^{1}H-NMR spectra were recorded utilizing either a Varian 200-MHz or a Bruker 270-MHz apparatus.

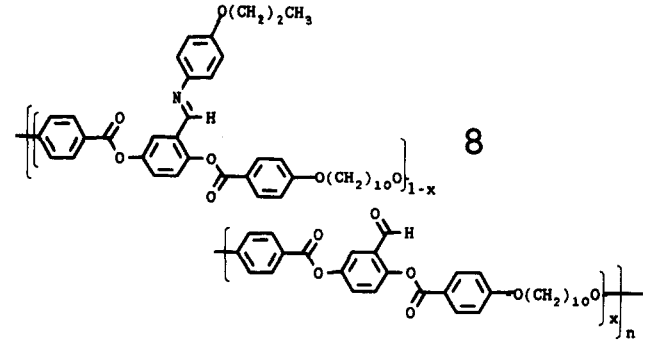
Thermogravimetric analysis using a Mettler TG 50 apparatus was utilized to evaluate the solvent content of swollen cross-linked samples.

Results and Discussion

Polymer 2 without any previous thermal treatment has very poor crystallinity. A significant fraction of crystal phase is only observed with samples annealed at temperatures close to melting. The reason for this behavior is probably the constitutional disorder characterizing the random sequence of the polar aldehyde groups along the polymer chain. Polymer 2 melts at ~145 °C to a nematic liquid which can be quenched at room temperature with virtually no crystallinity. The cybotactic structure of the nematic phase is clearly shown in the X-ray diffraction spectrum of a quenched fibrous sample (Figure 2). Isotropization occurs at a temperature ranging between 297 and 304 °C for polymers with intrinsic viscosity between 1.25 and 2.31 dL g^{-1}. The DSC thermogram of a sample with no previous thermal treatment (curve a) and that of a sample of the same polymer previously annealed at 110 °C for 30 min to enhance crystallinity (curve b) are shown in Figure 1.

Because of the low cross-link density the phase properties of the dry network polymer are not very different. "Melting" (of course, no fluidity is possible) is hardly detectable by DSC means. For networks vacuum dried at ~100 °C it occurs at ~140 °C. The isotropization temperature, ~285 °C, is significantly depressed as compared to the un-cross-linked polymer (Figure 1, curve d). The X-ray diffraction pattern recorded at room temperature for a sample stretched above the melting temperature and successively quenched under load (Figure 3) shows that the cybotactic nematic nature of the liquid crystalline phase is not changed.

Some relationship between the isotropization temperatures of homologous linear and network polymers and the cross-link density is theoretically expected.[1,10] If cross-linking occurs in the liquid crystalline phase, the stability of the latter should be increased because elastic forces oppose its deformation. On the contrary, if the network is obtained in the isotropic state (as in our case), elastic forces contrast the successive formation of the ordered phase, increasing its free energy and depressing its stability. This effect has been qualitatively confirmed by experiment. However, its quantitative relevance also with reference to the specific chemical nature of the cross-linking group has received very little attention. For a better understanding of the origin of the quantitative differences between linear polymer and network, the structure of the latter may be envisaged as an assembly of polymer chains of random copolymeric structure



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connected to each other through the flexible oligomethylene terminals. The insertion of $=NC_6H_4OR$ groups,

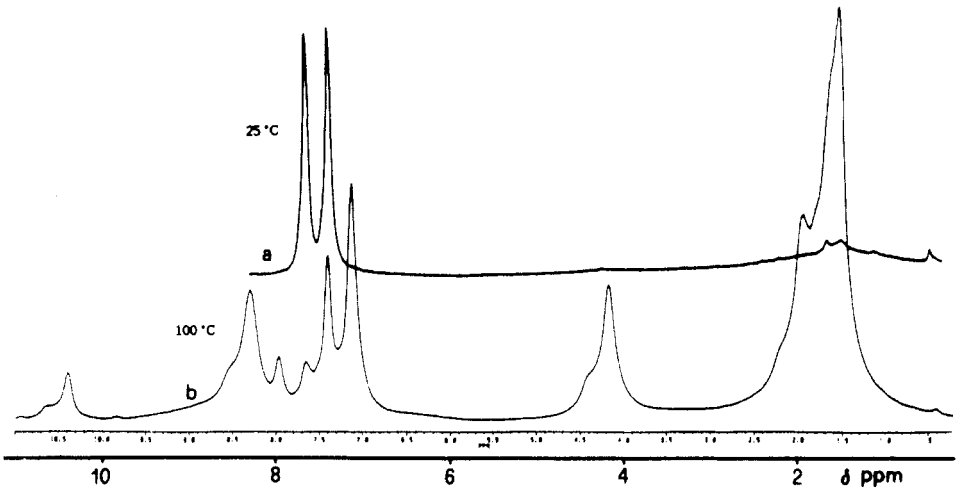

Figure 5. ^{1}H-NMR spectrum of a network sample swollen in 99.5% *o*-dichlorobenzene-d_4: (a) 25 °C (anisotropic phase); (b) 100 °C (isotropic phase).

although in a relatively small proportion and according to a random distribution, modifies the intrinsic mesogenic properties of the original linear polymer. This has been checked by examining the properties of model polymer 8. The nematogenic character is preserved but the thermal stability of the mesophase undergoes a substantial reduction (T_i = 285 °C, Figure 1, curve d). The reason for this becomes apparent if the mesogenic behavior of model monomeric units 5 and 6 is compared. Both compounds are nematogenic, but while 5 shows enantiotropic mesomorphism with T_i as high as 172.8 °C, 6 has a monotropic isotropization at 63.8 °C. The lateral insertion of a rigid and bulky atomic group has a dramatic effect on the mesophase stability.

Connecting "ideally" two units like 6 produces compound 7, that is, a model for the couples of connected monomer units formed as cross-linking of polymer 2 takes place. Like 6, compound 7 is nematogenic in a monotropic way. Its mesophase stability is about 10 °C higher (T_i = 73.1 °C) than for 6. This result is not surprising. The dimeric structure of 7 favors an increasing of the mesophase stability, but the lateral position of the flexible connecting segment provides an orientational coupling of the two "monomers" weaker than what is usually found for dimeric nematogens connected along the main elongation axis.

Going back to polymer 8, it should be considered as a binary random copolymer whose monomer units have a different intrinsic mesogenic potential. Its isotropization temperature should be to some extent negatively influenced by an increasing amount of the "less mesogenic" monomer containing the cross-link. This temperature should be taken as the reference in the comparison with the cross-linked polymer rather than the isotropization temperature of polymer 2. Taking this view, it is apparent that, for a low cross-link density, the depression of the isotropization temperature observed for the network may be attributed to the reduced intrinsic mesogenic potential of the cross-linked polymer chain more than to the interchain constraints produced by the cross-linking.

The Swollen Network. The cross-linking reaction was performed at 105 °C in *o*-dichlorobenzene solution with a polymer/solvent weight ratio ranging between 0.036 and 0.048 according to the polymer preparation used (this feature was essentially related to the necessity of having a gentle stirring of the polymer solution). Under these conditions no stir opalescence is detectable, and the network forms in the isotropic state. The solvent is entirely included in the cross-linked gel. Cooling at room temperature produces partial deswelling and onset of optical anisotropy. The equilibrium degree of swelling is attained slowly for bulky samples (>10 days at 26 °C) at a polymer/solvent weight ratio ranging between 0.065 and 0.080 according to the polymer preparation utilized. Better reproducibility (<4%) was obtained for networks prepared from the same polymer sample.

The swollen polymer has a rubbery consistency. The X-ray diffraction spectrum photographically recorded at room temperature shows no evidence of crystallinity. Actually, the diffraction pattern is not distinguishable from that of pure *o*-dichlorobenzene. No textural features of particular significance have been observed by polarizing microscopy that might help to recognize a specific mesophase. The absence of macroscopic orientation, also detected by polarizing microscopy, indicates the polydomain structure of the network.

The DSC thermogram of a swollen sample in the absence of excess solvent is shown in Figure 4. An endothermic transformation occurs in the temperature range 50–90 °C with an enthalpic change ranging between 2.4 and 2.8 J g^{-1} corresponding to 37–39 J per unit mass of unswollen polymer. In correspondence with that, isotropization takes place as detectable by polarizing microscopy. Both phenomena are reversible, although quantitative reversibility of the thermal effect is not completely attained in the time scale of the experiment (temperature scanning rate 10 °C/min). The stability of the anisotropic state at ambient temperature is complete. Portions of the same polymer sample examined after 10 months exhibit indistinguishable behavior.

In the presence of excess solvent the behavior is qualitatively analogous. Only small variations of the DSC thermal quantities are observed together with an increased swelling of the sample.

The crucial point is about the origin of this behavior. As far as the birefringence is concerned, it should not be ascribed to a coarsely inhomogeneous internal stress pattern. The isotropic swollen sample undergoes a uniform volume contraction with no shape deformation as deswelling occurs and uniform optical anisotropy develops. Seemingly, thermal and optical phenomena are not only simultaneous but also mutually related. Two basic hypothesis have been examined: (i) The swollen polymer is a monophasic nematic gel and the endothermic DSC signal corresponds to the isotropization of the mesophase. In the presence of excess solvent, the equilibrium between solvent and nematic gel should be considered and the

temperature-driven phase transformation is accompanied by further solvent intake. (ii) The swollen network, even in the absence of excess solvent, is a biphasic system. Optical anisotropy is due to a phase of liquid crystalline "solid" structure microdispersed in the solvent and the endothermic DSC signal corresponds to the solution of this condensed phase to form a monophasic isotropic gel. In the presence of excess solvent, further swelling may occur.

Any hypothesis assigning to the swollen network (including free solvent) a three-phase structure (e.g., solvent + nematic gel + isotropic gel or solvent + "solid" + isotropic gel) implies the invariance of the system at constant pressure. Hypothesis i has its awkward point in the small value of the polymer weight fraction that characterizes the swollen network. This smallness would be particularly surprising on account of the relatively low cross-link density of the network and of the conformation flexibility of its constitutive chains. Although the behavior of linear LCP's cannot be extrapolated to networks without using some caution, only for solutions of rodlike polyaromatics such as poly(1,4-benzamide)[19] or poly(1,4-phenyleneterephthalamide)[20] have comparably low (or even lower) critical concentrations for the onset of lyotropic mesomorphism been measured.

Hypothesis ii assumes that as the isotropic swollen network is cooled and deswelling occurs a collapse of the cross-linked gel takes place in a quasi-discontinuous way in qualitative analogy with what was reported by Tanaka and Hirokawa[21] for nonionic isotropic gels and discussed by Erman and Flory.[22] The main problem with this hypothesis is that if a large portion of the polymeric matrix is collapsed into a "solid" phase (ref 22 reports the reasons why this "solid" phase cannot have expelled all the solvent molecules; in our case, it may be considered as a concentrated lyotropic phase), the high overall degree of swelling found cannot be justified unless a very peculiar morphology (e.g., of the polymicellar type) is associated to the "solid" phase.

Although the available experimental data do not allow a definite choice between these two hypotheses, the proton NMR spectra as well as the smallness of the polymer concentration characterizing the anisotropic swollen network indicate hypothesis ii as the most likely.

The high-resolution ^{1}H-NMR spectrum of the network swollen in 99.5% *o*-dichlorobenzene-d_4 shows only very feeble and broadened signals pertaining to the polymer matrix in the anisotropic state at 25 °C (Figure 5, curve a). The poor resolution of the solvent resonances indicates that a significant fraction of the solvent cannot be considered in the free state. At 100 °C, in the isotropic state, the resonances of the polymer matrix are much better detectable, although resolution is not complete and a moderate line broadening is still present (Figure 5, curve b).

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