Interpenetrating Liquid Crystalline Polymer Networks

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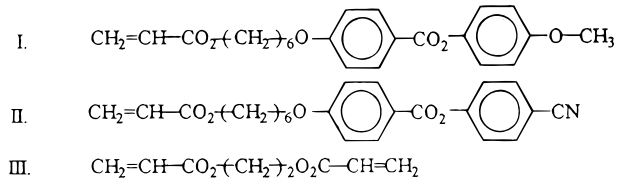
Introduction. Much effort has been made to explore novel liquid crystalline (LC) polymeric systems. An example is the studies on the LC block and graft copolymers[1] which combine the LC order with the immiscibility-induced microphase separation conferred on block and graft copolymers. Another system showing a great potential is the side-chain LC elastomers (SCLCEs)[2] prepared by cross-linking side-chain liquid crystalline polymers (SCLCPs). SCLCEs are attracting more and more attention since they allow a macroscopic and uniform orientation of the mesogenic groups to be achieved and controlled by a mechanical stretching, which is necessary for many applications of SCLCPs. Having been motivated by that research, recently we have begun investigations on a new system of liquid crystalline combination, namely, interpenetrating liquid crystalline polymer networks (ILCPNs). Here, an ILCPN is a combination of two liquid crystalline elastomers, or simply two LCPs in network form, whose networks are physically interlocked. On the basis of the extensive studies on the conventional IPNs,[3] we believe that extending the concept of IPNs to ILCPNs could offer new possibilities of making specialty materials. For instance, it is well-known that phase separation in IPNs might be restricted to different extents by the cross-links so that we could expect an ILCPN to bring together the important features of two LCPs while having a controlled morphology with finely divided phases or a dual phase continuity. This generally cannot be achieved by mixing two LCPs because of the immiscibility. Making IPNs can even result in miscible, one-phase systems of two components whose linear polymers are immiscible.[4] In this paper, to demonstrate the potential of ILCPNs we report some preliminary results of our investigations on some ILCPNs made from two polyacrylate-based SCLCPs.

Experimental Section. Sequential ILCPNs were prepared through the following procedure. A polyacrylate-based SCLCE (network I) was first obtained through copolymerization of a mesogenic monomer with a diacrylate monomer as the cross-linker.[5] Then, a sample of network I was immersed in a 20% toluene or chlorobenzene solution containing the other mesogenic monomer, the diacrylate monomer, and 1% AIBN as the initiator. After an overnight swelling by the reaction mixture, swollen network I was removed from the remaining solution and put into a closed small bottle under gentle circulation of nitrogen. The bottle was then placed in an oven for polymerization *in situ* at 60 °C for 20 h. With the formation of the second SCLCE (network II) interlocked with network I an ILCPN was obtained. Before characterization, in order to remove any unreacted monomers and un-cross-linked polymers each ILCPN sample was extracted several times in THF (the samples swelled) and finally dried in vacuum at 80 °C for 2 days. The mesogenic and diacrylate monomers used in this study have the following chemical structures:



Monomer III (ethylene diacrylate) was the cross-linker often used to prepare polyacrylate-based SCLCEs;[5] its concentration with respect to the mesogenic monomer determines the cross-link level. Monomer I differs from monomer II only by the end group ($-OCH_3$ instead of $-CN$). For the ILCPN samples reported in this paper monomer I was used for network I and monomer II for network II, and they will be referred to as netOCH_3−netCN. We found that netOCH_3 was suitable for network I since it could absorb a large volume of monomer II solution, making it possible to obtain ILCPNs containing a large amount of netCN. The presence of netCN in the ILCPNs was indicated by the characteristic $-CN$ infrared band at 2230 cm^{-1} which was absent for netOCH_3, and the content of netCN could easily be calculated from the 2230-cm^{-1} band by using the $-C{=}O$ band at 1734 cm^{-1} as a reference. Infrared analysis of the composition was confirmed by calculations based on the weight difference between the network I sample before swelling and the resulting ILCPN. A Leitz DMR-P polarizing microscope was used for observation of the liquid crystalline textures. The phase transitions were investigated by using differential scanning calorimetry (Perkin-Elmer DSC-7) with a heating rate of 10 °C/min and a sample weight of ca. 15 mg. All reported DSC curves were obtained from a second scan after retaining the samples at 140 °C for 10 min in order to remove any memory effects, and repeated measurements gave rise to the same results.

Results and Discussion. Before discussing the obtained ILCPNs, it should be mentioned that we made a number of unsuccessful attempts to make ILCPNs. We found several factors which are important and need careful consideration. First, in contrast to the preparation of a conventional sequential IPN, for which the monomer swollen into the first network for subsequent polymerization is generally a liquid, here the mesogenic monomer is dissolved in a solvent before being swollen into network I and polymerized. The monomer concentration should be high enough to expect a significant amount of network II in the resulting ILCPN, but should not be too high because the monomer molecules must be kept in a mobile, liquid phase during the polymerization. The 20% monomer concentration was found to be appropriate. Also, keeping in mind that the solvent evaporates as the polymerization progresses, the reaction temperature and the choice of the solvent affect the results. For this reason chlorobenzene is a better solvent than toluene because of a higher boiling point. On the other hand, factors like monomer concentration and temperature determine the rate of the polymerization inside the swollen samples, which was revealed to be important. We did not know precisely how the cross-link level of network II changed wth the advancement of the polymerization, but it was likely that with a slow polymerization a certain time was needed to reach an effective cross-link level that was necessary to ensure gelation or physical interlocking between the two net-

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Table 1. Phase Transition Temperatures and Enthalpies of the Samples

sample	composition	T_g (°C)	T_{sn} (°C)	ΔH_{sn} (J/g)	T_{ni} (°C)	ΔH_{ni} (J/g)
1	polyOCH$_3$	25	94	2.67	119	2.08
2	polyCN	30			122	0.92
3	netOCH$_3$(20%)	34	69	0.74	102	1.13
4	48/52 netOCH$_3$(20%)−netCN(10%)	35	68	0.14	106	1.06
5	netCN(10%)	34			113	0.80
6	netOCH$_3$(10%)	32	80	2.11	111	1.99
7	44/56 netOCH$_3$(10%)−netCN(20%)	39	79	0.38	109	1.02
8	netCN(20%)	43			100	0.71
9	51/49 netOCH$_3$(20%)−netCN(20%)	37	69	0.26	104	0.48

works. As is known for IPNs, phase separation tends to occur once the second polymer is formed. If the polymerization *in situ* is not fast enough, the early-formed linear and slightly cross-linked polymer chains could be phase-separated and extracted in the purification process; and meanwhile, the swollen sample becomes drier and drier, which prevents the polymerization from occurring at a later time. This seems to explain some unsuccessful experiments by swelling a network I sample in a 10% (or less) monomer solution and using a low reaction temperature (55 °C). Finally, another crucial factor we found is the size of the network I sample used for the experiments. Under the same conditions and with the same weight of the network I sample, e.g. 0.2 g, it was necessary to have a single or a couple of big pieces which led to successful preparation of ILCPNs, while the attempts starting with fine granules (ca. <1 mm) for swelling and polymerization ended in failure or resulted in ILCPNs containing only a very small amount of network II. This observation can be explained by a different evaporation rate of the solvent once the polymerization *in situ* starts. The solvent evaporates much more rapidly with small swollen granules of network I because of a much larger surface; consequently, the swollen sample loses most solvent and is dried shortly after being placed in the oven, and no effective polymerization *in situ* occurs.

Collected in Table 1 are the data on the glass transition temperature, T_g, the smectic−nematic transition temperature, T_{sn}, and the transition enthalpy, ΔH_{sn}, and the nematic−isotropic transition temperature, T_{ni}, and the transition enthalpy, ΔH_{ni}, for the samples investigated. Each sample is numbered, and information such as the amount of each component in an ILCPN and the cross-link level for each network is given in the abbreviations of the samples listed in the composition column. For instance, sample 4 is abbreviated as 48/52 netOCH$_3$(20%)−netCN(10%), where 48/52 is the weight ratio of the two components in the ILCPN, while 20% and 10% are the mole percentages of the diacrylate monomer used to obtain netOCH$_3$ and netCN, respectively. The two un-cross-linked polymers (samples 1 and 2) made from monomers I and II are denoted as polyOCH$_3$ and polyCN, respectively.

Figure 1 displays the DSC heating curves for samples 3−8 and for a 50/50 blend of samples 1 and 2. The mesophases of the two starting SCLCPs are well-known;[6] the DSC curve of the blend is a simple addition of the curves of samples 1 and 2 (not shown for the sake of clarity). The first two peaks centered at 94 and 119 °C are due to, respectively, the smectic−nematic and nematic−isotropic transitions of polyOCH$_3$, while the peak at 122 °C, indicated by the arrow, characterizes the nematic−isotropic transition of polyCN. Figure 2 shows a polarizing photomicrograph of the blend at 80 °C. Two distinct liquid crystalline textures are clearly seen in the phase-separated blend; the polyCN phase

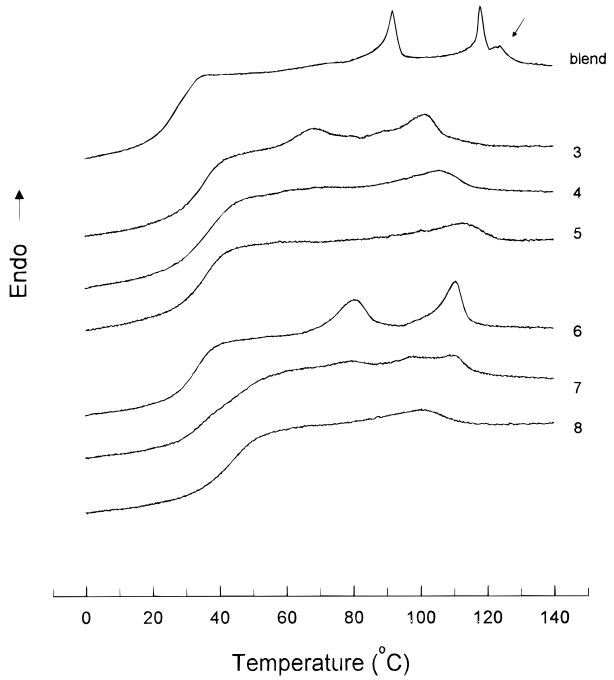

Figure 1. DSC heating curves for samples 3−8 and for a 50/50 blend of samples 1 and 2 (see Table 1 for sample assignments).

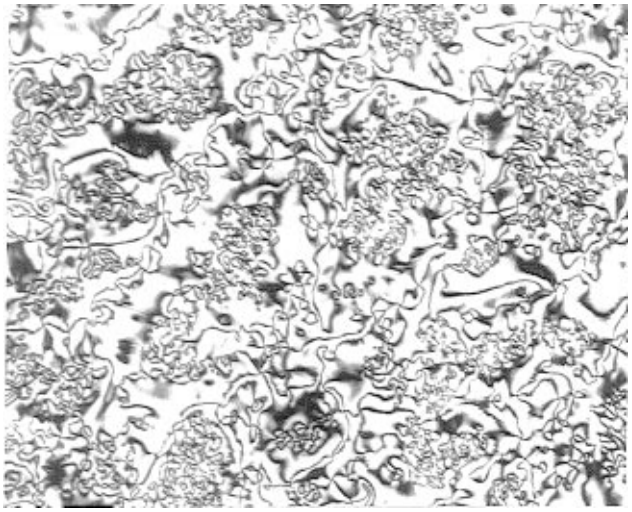

Figure 2. Polarizing optical micrograph of the 50/50 blend of samples 1 and 2 at 80 °C. Magnification: 170×.

exhibits a threaded nematic texture, whereas the smectic polyOCH$_3$ displays a Schlieren texture with four brushes. The sizes of the two phases are of the order of 50 μm. Unfortunately, for network samples we did not succeed, till now, in preparing the thin films necessary for microscope observation; but as the mesophases of the starting polymers are evident, and on the basis of a large number of experimental results,[2] it

is reasonable to assume that cross-links essentially have the effects of reducing the transition temperatures and broadening the transition regions. These changes can readily be seen from DSC observations.

Now, let us take a closer look at the DSC curves of samples 3−8 in Figure 1. An interesting feature of ILCPNs can be revealed by comparing sample 4 with samples 3 and 5, the two corresponding pure network polymers. As compared with the un-cross-linked polymers, sample 3 still exhibits both transitions, but as expected, owing to the cross-linking effects, both T_{sn} and T_{ni} are shifted to lower temperatures, with $T_{sn} = 69$ °C and $T_{ni} = 102$ °C, and the transition peaks are broadened and the transition enthalpies lowered, whereas its T_g increases to 34 °C. The same observation can be made for sample 5 which has a T_{ni} lowered to 113 °C. Now, for sample 4, i.e., the ILCPN, its T_g is almost unchanged with respect to both pure networks, but only a very weak low-temperature transition seems to persist at temperatures around 68 °C, and the drastic decrease of the transition enthalpy from 0.74 J/g for sample 3 to the estimated 0.14 J/g for the ILCPN sample obviously cannot be accounted for only by the dilution effect arising from the presence of netCN which has no smectic phase. This result clearly indicates much interaction between the mesogenic side groups of both networks which leads to a severe perturbation effect on the smectic ordering of sample 3. More interesting is the nematic−isotropic transition peak of the ILCPN sample which appears at 106 °C that is intermediate between T_{ni} of sample 3 and that of sample 5, i.e., 4 deg higher than the former and 7 deg lower than the latter. This change of the nematic−isotropic transition implies a single nematic phase formed by both mesogenic groups, or two nematic phases whose T_{ni}'s approach each other. In one way or another, this can only result from an intimate interlocking of both networks in the ILCPN sample. Similar results were obtained for sample 9, an ILCPN having a higher network II density. These results strongly suggest a miscibility, apparently to a great extent, between the two components in these ILCPNs using netOCH_3(20%) as network I. This miscibility is revealed, most significantly, by a nematic−isotropic transition occurring at intermediate temperatures as compared to the corresponding pure networks.

Investigations on the conventional IPNs[3] indicate that the domain sizes in IPNs are mostly determined by the cross-link levels, especially that of network I. Sample 7 is an ILCPN having a lower cross-link level of network I. Comparing sample 7 with samples 6 and 8 reveals another situation. Although the apparent low-temperature transition of sample 7, appearing at 79 °C, is also severely weakened, which indicates a strong interlocking of the two networks, some significant differences can be noticed. The glass transition region is broadened, and the nematic−isotropic transition peak clearly is composed of two superimposed peaks at around 109 and 98 °C, respectively. They apparently correspond to the peaks of the two pure networks. All this indicates a lesser miscibility between the two components in this sample, which should result in larger domain sizes. This is likely to be due to the lower cross-link level of network I which restricts less efficiently the phase separation during the polymerization *in situ*.

To summarize, we have shown that the concept of IPN can be used to prepare ILCPN which is a combination of two interlocked liquid crystalline elastomers. Several polyacrylate-based sequential ILCPNs were successfully prepared. Phase transitions in the ILCPNs were modified to different extents depending on the miscibility between the two components in the samples. We believe that the potential of ILCPNs as a new system of liquid crystalline combination needs to be explored in search of the ways of making new specialty materials. More detailed studies are being undertaken in our laboratory, which include (1) preparation of ILCPNBs with two SCLCPs having very different T_g's and mesophase transition temperatures and (2) investigation of the morphology control and the effects on the phase transition behavior.

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References and Notes

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