Main-Chain Lyotropic Liquid-Crystalline Elastomers. 2. Orientation and Mechanical Properties of Polyisocyanate Films

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ABSTRACT: Novel types of main-chain, lyotropic liquid-crystalline polymer networks consisting of polyisocyanate chains were prepared by hydrosilation cross-linking. The characteristic liquid-crystalline band texture generated by shearing these networks in the swollen state was found to persist much longer than in the case of solutions of the same polymer in the un-cross-linked state, suggesting preservation of increased chain orientation. A series of these gels were deformed by application of suitable stresses and then dried in the strained state, in an orientation technique developed to improve the properties of networks consisting of such semiflexible polymers. The mechanical properties of the oriented films were then carefully examined as a function of their processing history: curing temperature, curing time, sol fraction, equilibrium swelling ratio, cross-link length, and polymer concentration during deformation. In the case of uniaxial extension, the tensile strengths and moduli of these oriented films increased 5–7 fold in the orientation direction. As expected, however, their mechanical properties in the perpendicular direction were diminished. Equibiaxial extension was found to have the advantage of giving mechanical properties that were uniform in the plane of the films and gave more than 2-fold increases in tensile strength and modulus at extension ratios during drying as small as 20%! The conclusion that these improvements were due to long-range ordering of the chains was verified by birefringence measurements.

Introduction

Orientation has been a widely used method to improve the mechanical properties of polymers. Several processing methods have generally been used to induce segmental orientation of polymer chains, ranging from drawing at elevated temperatures to spinning from liquid-crystalline solutions or gels.[1–4] Liquid-crystalline polymers are ideal candidates for such processing techniques and have been extensively studied for the last several decades.[5,6] There is a natural tendency for the rigid segments in these polymers to self-align into ordered domains; in melts or in solutions, this enables liquid-crystalline polymers to be processed into ordered materials having excellent high-performance properties.[7,8] One disadvantage of these existing orientation methods is that the degree of segmental orientation is difficult to control. Also, the inevitable relaxation of the chains when the external field is removed results in losing some or all of the induced anisotropy.[1] There is therefore an obvious need for developing new orientation techniques for processing polymers into highly ordered, high-performance materials.

Liquid-crystalline polymer networks are extremely interesting from the orientation point of view.[9–12] In low molecular weight liquid-crystalline materials the director **n** can be easily oriented by the application of external electric or magnetic fields, giving rise to a fairly large field-induced monodomain. In liquid-crystalline polymers, however, orientation is much harder to achieve because of the high viscosity and polymer backbone conformation. Orientation is possible only in high magnetic or electric fields. On the other hand, liquid-

crystalline elastomers offer a distinct advantage over other liquid-crystalline polymers. They can be oriented by their liquid-crystalline nature and their network structure. This is simpler in the case of main-chain liquid-crystalline polymer networks than in their side-chain analogues.[9,10] Specifically, deformation (by a mechanical force) of networks of main-chain liquid-crystalline polymers leads to a direct deformation of the polymer backbones, which induces the corresponding orientation of the mesogenic groups. A mechanical field has the additional advantage that the resulting effects on the orientation order are several orders of magnitude larger than those induced by electric or magnetic fields.[12] The rigidity imparted on these main-chain liquid-crystalline polymers could allow these materials to be used in structural applications.

Based on the fact that rigid and semirigid liquid-crystalline chains have exceptional orientability and exhibit isotropic-to-anisotropic phase transitions under a mechanical force,[13,14] a novel orientation method for lyotropic main-chain liquid-crystalline polymer networks was proposed by Erman and Mark.[15,16] The technique consists of the following steps.

The first step consists of identifying polymeric systems of sufficient stiffness to give liquid-crystalline, anisotropic phases (either homopolymers or block copolymers consisting of stiff and flexible sequences). Such semiflexible chains undergo phase separation at all but the lowest concentrations. The anisotropic phases thus formed, however, consist of numerous small domains. The axes of the domains themselves are uncorrelated in direction, and a considerable amount of unoriented polymer is present as a second phase. This gives rise to various undesirable properties such as reduced mechanical strength and unpredictable absorption properties such as inhomogeneous swelling. This disadvantageous type of phase separation, however, can

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be avoided by the remaining steps in the procedure.

The next step consists of cross-linking the chains in a piece of polymer film, by either chemical reagents or high-energy radiation. This can be done in the presence of solvent, or the solvent can be introduced subsequently, by swelling. The cross-links confer sufficient solidity for the polymer to remain in a deformed state for any length of time, and the solvent prevents the premature ordering of the stiff chains or sequences. At this stage, the swollen network or gel can be deformed readily, in uniaxial or biaxial extension, to induce segmental orientation. The final step consists of removing the solvent, at constant length or at constant force, causing a first-order transition, and thus yielding a single-phase, homogeneous, and highly ordered material.

In the case of uniaxial extension, the chains should all be nearly perfectly oriented in the direction of stretching. Such a material would generally be weak in the directions perpendicular to the stretching direction, so this technique might be most useful when modified for the preparation of high-strength fibers. A biaxial extension procedure applied to a film could give an even more interesting material. Specifically, the described drying or solvent extraction procedure could give rise to layers that have chains that are not only entirely aligned into anisotropic phases but have their directions different in different layers. In a sense it would be a molecular analogue to the layered structure present in plywood. In any case, such a film should be extremely strong in all directions (except in the inconsequential one perpendicular to its plane).

In this second part of the two-part study, poly(*n*-hexyl and allyl isocyanate) (PHAIC) networks were prepared using hydrosilation cross-linking. Their swollen gels were subjected to the orientation technique described above, and their phase behavior and mechanical properties documented.

Experimental Section

General Methods and Materials. All cross-linking reactions were performed under nitrogen atmosphere using a Vacuum Atmosphere HE43 Dri Lab with attached HE-493 Dri Train. Toluene was distilled from potassium and degassed before use. Samples of poly(*n*-hexyl and allyl isocyanate) were prepared as described in the preceding paper.[17] α,ω-Dihydrooligo(dimethylsiloxane) with hydride terminal groups (molecular weight MW = 400) and hexamethyltrisiloxane were purchased from United Chemicals and used as received. *cis*-Dichloroplatinum(II) diethyl sulfide was purchased from Strem Chemical Co. and also used as received.

Preparation of Thin Films of Hydrosilation Cross-Linked Poly(*n*-Hexyl and Allyl Isocyanates). 1. High-Temperature Curing, Using α,ω-Dihydrooligo(dimethylsiloxane) as Cross-Linker. In a drybox, 2.0 g of the copolymer was dissolved in 45 mL of dry toluene. α,ω-Dihydrooligo(dimethylsiloxane) (200 mL) with hydride terminal groups (MW = 400) was added via a syringe, followed by 0.4 mg of PtCl$_2$(SCH$_2$CH$_3$)$_2$ in 0.4 mL of toluene solution. The mixture was stirred for about 3–4 h before being transferred into a round Teflon pan (diameter 3 in.). The gelation was completed in the pan overnight at 80 °C, and the solvent was slowly evaporated. A smooth, cross-linked film was thereby obtained.

2. Low-Temperature Curing, Using α,ω-Dihydrooligo(dimethylsiloxane) as Cross-Linker. In a drybox, 2.0 g of the copolymer was dissolved in 45 mL of dry toluene. α,ω-Dihydrooligo(dimethylsiloxane) (280 mL) with hydride terminals (MW = 400) was added via a syringe, followed by 0.4 mg of PtCl$_2$(SCH$_2$CH$_3$)$_2$ in 0.4 mL of toluene solution. The mixture was stirred for about 36–48 h before being transferred into a round Teflon pan (diameter 3 in.). The semigelled mixture was heated at 40–50 °C until a form-retaining gel was obtained, usually in 1–2 days. The solvent was slowly evaporated for 2 more days, yielding a smooth cross-linked film.

3. Low-Temperature Curing, Using Hexamethyltrisiloxane as Cross-Linker. In a drybox, 2.0 g of the copolymer was dissolved in 45 mL of dry toluene. Hexamethyltrisiloxane (200 mL) was added via a syringe, followed by 0.4 mg of PtCl$_2$(SCH$_2$CH$_3$)$_2$ in 0.4 mL of toluene solution. The mixture was stirred for about 18–24 h before transferred into a round Teflon pan (diameter 3 in.). The semigelled mixture was heated at 40–50 °C until a form-retaining gel was obtained, usually in 1–2 days. The solvent was slowly evaporated for 2 more days, and a smooth cross-linked film was obtained.

Soluble Fraction Measurements. Representative samples from each of the above cross-linked PHAIC films were accurately weighed after drying the films *in vacuo* for 1–2 days. All the samples were then swollen in toluene and extracted for 2 days in order to remove any unreacted materials. The networks were then slowly deswollen with methanol and dried in air for 2 days, followed by *in vacuo* drying for 2 more days, and then reweighed. Values for the soluble fraction of polymer S$_f$ were then calculated from the original and final weights.

Equilibrium Swelling Measurements. The extent of maximum (equilibrium) swelling, characterized by the volume fraction of polymer v_{2m} in the swollen gel, was determined for each PHAIC network cross-linked by the various methods. Initial weights of extracted samples were accurately determined prior to swelling. The samples were weighed periodically until there was no further appreciable change in swollen weight as a function of time. These values for the maximum swollen weight were then used to calculate values of v_{2m} by assuming simple additivity of volumes.

Cross-Polarized Optical Microscopy. Samples for optical studies were studied between two cover glasses placed between two cross-polarizers. To generate the band textures, a shear force was applied to the sample by moving the cover glasses in opposite directions. The rate of shear was estimated to be 10 s^{-1}.

A Nikon polarizing optical microscope (Model DPTPHOT-PDL; Diagnostic Instrument, Inc.) equipped with an Olympus camera was used to study phase separations of the polyisocyanates and their networks. The magnifications of the lens used was 10 and 40, and the camera lens had an additional magnification of 2.5.

Orientation Procedures. The cross-linked polyisocyanate films were swollen overnight in chloroform or toluene to a desired swelling ratio (not necessarily the maximum extent). The swollen film was then uniaxially deformed to a desired extension by moving two clamps at both ends or simply stretching it by hand. The extension ratio was defined as

$$\text{extension (\%)} = 100(L - L_o)/L_o \tag{1}$$

where L is the final length of a stretched sample and L_o is its original length.

The stretched films were dried at constant length first under ambient conditions for 1–2 days followed by further drying *in vacuo* at 50 °C for an additional day. The resulting films were stored in a desiccator.

Biaxial orientation was performed by stretching the swollen networks simultaneously in two directions with the same extension ratio, as defined above. The films were dried while the two stretched sides were maintained at constant lengths.

Mechanical Property Measurements. The tensile strengths and moduli of dried samples having dimensions of $30 \times 3 \times 0.3$ mm^3 were measured with an Instron mechanical tester (Model 1122). The cross-head speed was 0.1 in./min with an initial gauge length of 0.7 in. The force and deformation were recorded on an x–y recorder.

Birefringence Measurements. The birefringence of some of the oriented films was measured using a compensation method, with a Babinet-Soleil compensator (Karl Lambert
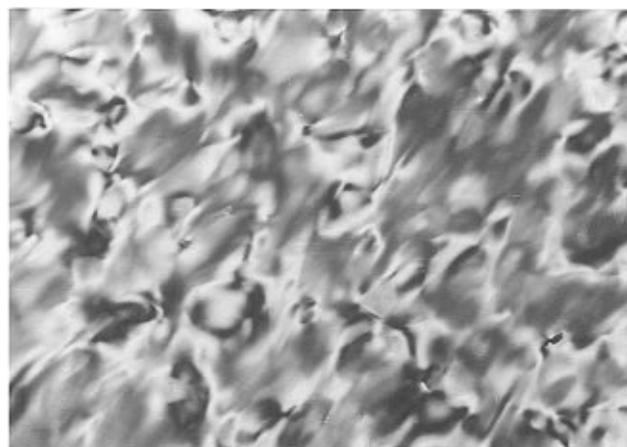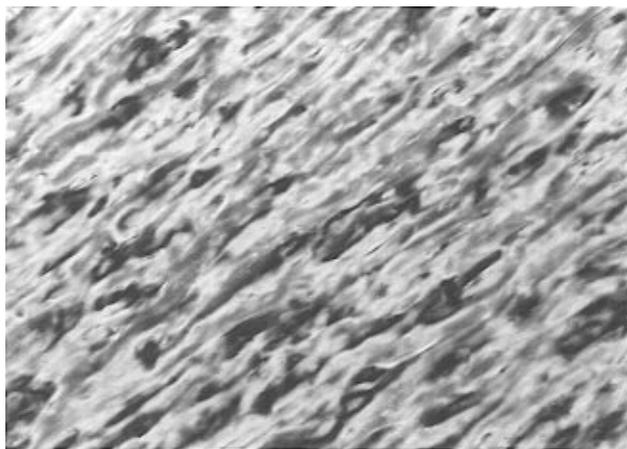
⊢————⊣ 50 μm

Figure 1. (a, top) Band texture of 37 wt % PHIC (MW = 40 000) in chloroform, immediately after shearing. Original magnification 350×. (b, bottom) Band texture disappearing, 30 s after shearing. Original magnification 350×.

Corp.). The light source was a He−Ne laser beam (Oriel Corp.) with a wavelength of 632.8 nm.

Results and Discussion

Cross-Linking Effects on the Band Textures of the Polyisocyanate Gels. As already mentioned, the novel feature of the proposed orientation technique is use of the cross-links to suppress irrecoverable polymer chain motions, so that their orientation in the swollen state can be preserved under deformation. One of the characteristics of liquid-crystalline polymer solutions or melts is the formation of a band texture during shearing or shear relaxation, for both thermotropic and lyotropic systems.[18−23] The band texture consists of alternating dark and bright bands under a cross-polarized microscope, and these dark and bright bands are aligned perpendicular to the shear direction. The band can appear during continuous shear or after cessation of the shear. For all the polyisocyanate samples studied, the band texture appeared after the shear cessation. The decay rate of these polyisocyanate band textures induced by a shear force depended not only on the molecular weight but also on the copolymer composition. Figure 1a shows the band texture of a solution of poly-(*n*-hexyl isocyanate) (MW = 40 000) in chloroform. The photograph was taken immediately after cessation of shear. It was reported that the band texture of these liquid-crystalline polymers decays as a result of chain relaxation, which restores their original less-ordered
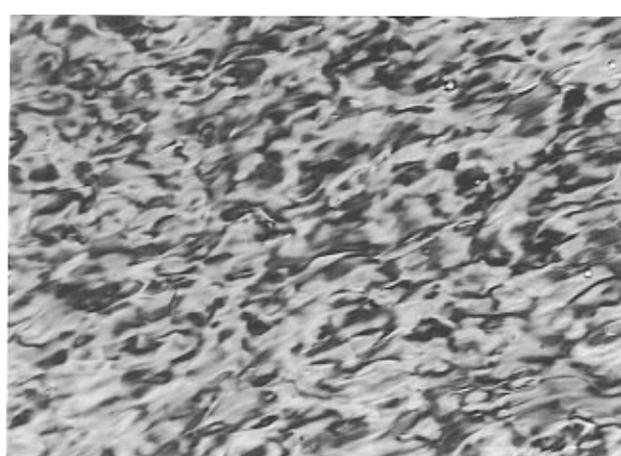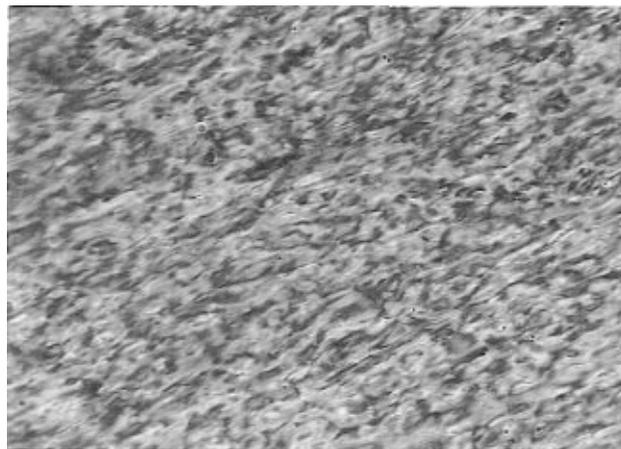
⊢————⊣ 50 μm

Figure 2. (a, top) Band texture of 40 wt % PHAIC (10% allyl composition, MW = 15 000) in chloroform, immediately after shearing. Original magnification 350×. (b, bottom) Band texture disappearing, 30 s after shear. Original magnification 350×.

texture.[23] The time required for total decay ranges from a few seconds to several days, depending on the mobility of the polymer chains. It is therefore of special interest to study the relaxation of chain segments, particularly when they are subject to an external mechanical force. The band texture observed for the poly(*n*-hexyl isocyanate) solution was highly mobile, having disappeared only seconds after the cessation of shear, returning to its original Schlieren texture (Figure 1b). The PHAIC copolymer (10% allyl composition, MW = 15 000) in chloroform displayed a similar behavior, and the band texture disappeared only 30 s after the shear. This indicated high chain mobility for the copolymer at low molecular weight (Figure 2), but increase in molecular weight had a considerable effect on the decay rate. Figure 3 shows the band texture of the copolymer (10% allyl composition) with a much higher molecular weight (MW = 120 000). The band texture now persisted for 2 min after the cessation of shear. This is understandable since increase in molecular weight increased the viscosity and this restricted the chain mobility, thus preventing it from quickly returning to its original texture. Increase in the allyl composition in the copolymer had a similar effect on the decay rate. Figure 4 shows the band texture of the PHAIC at 20% allyl composition (MW = 120 000). The band texture was preserved for a much longer time (~10 min) before decaying, which
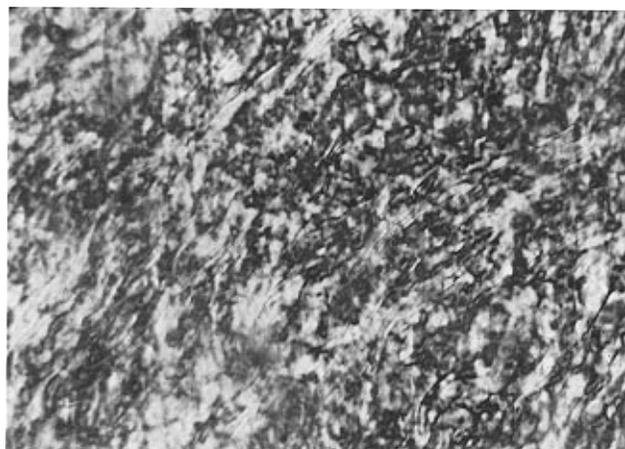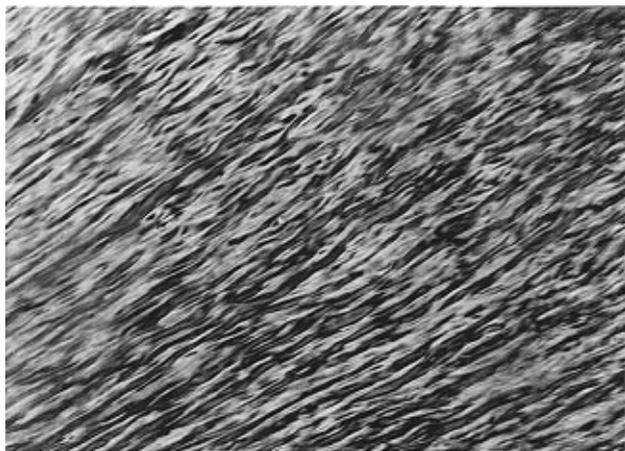
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Figure 3. (a, top) Band texture of 40 wt % PHAIC (10% allyl composition, MW = 120 000) in chloroform, immediately after shearing. Original magnification 350×. (b, bottom) Band texture disappearing, 2 min after shear. Original magnification 350×.
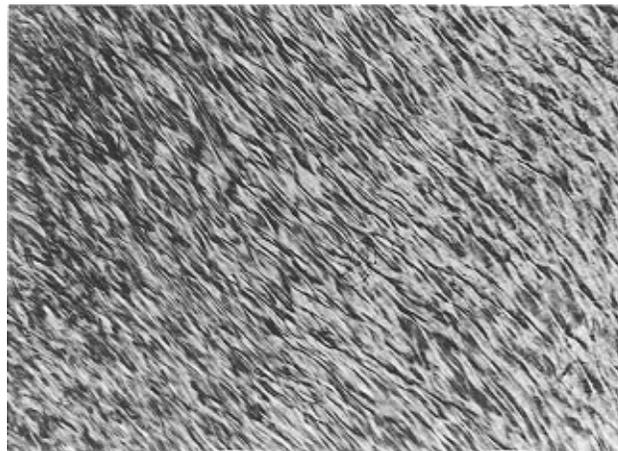
└──────┘ 50 μm

Figure 4. (a, top) Band texture of 40 wt % PHAIC (20% allyl composition, MW = 120 000) in chloroform, immediately after shearing. Original magnification 350×. (b, bottom) Band texture disappearing, 10 min after shear. Original magnification 350×.

was also due to the increased viscosity of the copolymer at higher allyl compositions.

Analogous results on a typical gel obtained from hydrosilation cross-linking are given in Figure 5. It shows the band texture of a PHAIC gel at a concentration of 40 wt % in chloroform immediately after shearing and demonstrates that the texture of the band structure was essentially the same as that of un-cross-linked PHAIC, in spite of the network structure. Figure 5b is a microphotograph taken 2 h after the cessation of shear and clearly shows that the desired stability of this texture over a considerable period of time has been attained.

Orientation of Main-Chain Lyotropic Liquid-Crystalline Polymer Networks Using the Novel Orientation Technique. The initial stages of the mechanical properties characterization were carried out on polyisocyanate networks which had been prepared from the high-temperature curing with α,ω-hydridooligo(dimethylsiloxane) (MW = 400). These gels can usually be swollen to 25−30 times their original volume in chloroform. The high values of the maximum swelling ratios ($1/v_{2m}$) indicated low cross-link density, which would allow high chain deformability.

These high-temperature, oligo(dimethylsiloxane)-cured PHAIC gels were oriented in the manner schematically represented in Figure 6. First, the cross-linked samples were swollen in chloroform to the desired

ratio. In the case of these specimens, the polymer concentration was 0.20−0.25 vol %. Within this swelling range, the gels were soft and flexible, and they could easily be stretched to 250% of their original length without premature cracking. In the second step, these swollen specimens were stretched uniaxially either using two clamps or simply by hand. The deformed films were kept at constant length using Scotch tape attached to their ends. They were dried in air, but slowly to avoid any inhomogeneous shrinkage. The extension ratio during drying (a parameter to be used to describe the orientation degree) was defined as the ratio of the increased length of the stretched dried sample relative to the length of the original (dried) sample. This ratio ("extension ratio during drying") will be used throughout this part of the study to characterize the degree of orientation.

For biaxial orientation, the swollen films were stretched equally and simultaneously in two perpendicular directions, with all four ends held fixed during the drying. The extension ratio during drying was defined in the same way as that in the uniaxial deformation.

Figure 7 shows some microphotographs taken during the actual orientation process. A cross-linked PHAIC specimen was swelled to a certain degree ($v_2 = 0.2−0.25$) in chloroform. At this stage, the specimen was birefringent as observed under a cross-polarized micro-

⊢———⊣ 50 μm
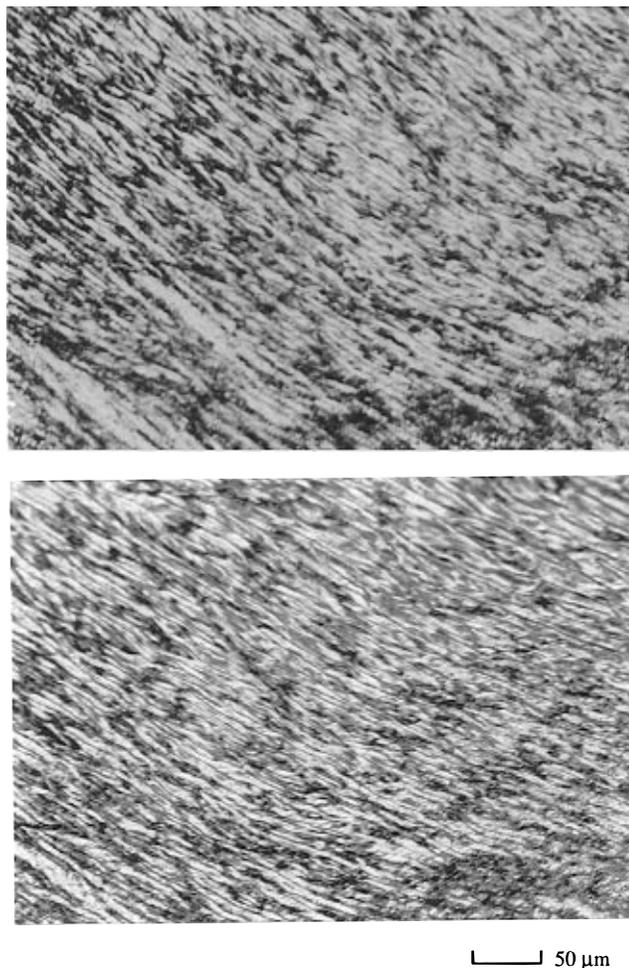
Figure 5. (a, top) Band texture of hydrosilation cross-linked PHAIC gel in chloroform, immediately after shearing. Original magnification 350×. (b, bottom) Band texture of hydrosilation cross-linked PHAIC gel in chloroform, 2 h after shearing. Original magnification 350×.

scope. The absence of the Schlieren texture in this particular specimen was probably due to the specimen being too thick. The sample was then stretched uniaxially to the desired length and kept at this length during drying. The specimen dried in this way was highly birefringent with a similar band texture (with directions perpendicular to the stretching direction), indicating the preservation of ordering.

Mechanical Properties of Oriented Polyisocyanate Films Using Oligo(dimethylsiloxane) as Cross-Linker. Typical values of mechanical properties of these oriented PHAIC (high-temperature, oligo(dimethylsiloxane)) films after drying are shown in Figure 8. It shows the tensile strength as a function of the uniaxial extension maintained during drying, as well as the corresponding dependence for the tensile modulus. These results should be compared with those of PHAIC films themselves, which are brittle plastics, and their hydrosilation cross-linked films are rubberlike with glass transition temperatures at ∼−15 °C. On this basis, both the tensile strength and modulus increased monotonically and substantially with increase in extension ratio during drying. The increase was ∼6-fold for an extension ratio of 100%, for both tensile strength and modulus. This observation of dramatically increased mechanical properties after orientation is consistent with similar observations on oriented cellulose derivatives.[18−20]

Despite this dramatic increase in mechanical properties compared to those in the unoriented state, the maximum tensile strength and modulus of films oriented from the above curing method were relatively low (see Table 1). Compared to un-cross-linked PHAIC film, the improvement can be describe as 2-fold at best. Because of the very flexible nature of the oligo(dimethylsiloxane) linkages present, the tensile strengths and moduli of the hydrosilation cross-linked networks were substantially decreased, although the elongation at break was significantly increased. Nonetheless, these results demonstrated the utility of the orientation techniques applied and encouraged further experiments. Considering the fact that these high-temperature cured films had a very high sol fraction, there appeared to be great potential for further improvements in mechanical properties, if the sol fraction were reduced or a shorter cross-linking agent employed.

Several efforts were therefore introduced to improve cross-linking conditions so as to lead to films with smaller sol fractions. It was found that decrease in curing temperature and increase in curing time did result in a more homogeneously cross-linked films with smaller sol fractions, similar to that found in some other studies.[24,25] Table 2 summarizes the cross-linking and orientation conditions used for these studies. The films were oriented as already described, in chloroform. They exhibited maximum swelling ratios of 15−20, lower than those of the high-temperature cured films, which is consistent with their smaller sol fractions. The maximum values obtainable for the extension ratio during drying were also lower (∼100% compared to 150% for the high-temperature cured networks). This was attributed to the higher polymer concentrations used during stretching ($v_2 = 0.33−0.4$ compared to $v_2 = 0.2−0.25$ for the high-temperature cured samples). As is generally observed, the higher the polymer concentration during stretching, the lower the extensibility.[26−29]

The mechanical properties of these low-temperature cured PHAIC films are summarized in Figure 9. The tensile strengths and tensile moduli increased monotonically with increase in extension ratio during drying (from 0 to 100%). A 6-fold increase in tensile strength and a 7-fold increase in modulus were obtained for an extension ratio during drying of 100%. The increases in mechanical properties were attributed to increases in chain alignment resulting from the described orientation technique. Figure 10 shows the correlation between the extension ratio during drying and the birefringence. As can be seen, the birefringence was found to increase significantly with increase in extension ratio during drying. Thus, the extension ratio during drying can indeed be used as a parameter to described the degree of orientation. The increases in mechanical properties were paralleled by increases of birefringence, *i.e.,* increases in ordering. In comparison to films oriented in the high-temperature curing process, the maximum values of the tensile strength and tensile modulus obtained from the low-temperature curing were substantially increased. Useful ranges of tensile strengths (9.72−24.13 MPa) and tensile moduli (83−310 MPa) were obtained. Thus, what were originally liquid-crystalline elastomers having very low strengths and moduli were transformed into tough plastics.

There was an important disadvantage in the uniaxially oriented PHAIC samples. Although their mechanical properties had been greatly improved in the direc-

Uniaxial Orientation:

L_0 Solvent Stretching L

Biaxial Orientation:

L_0 Solvent Stretching L

Extension (%) = (L - L_0) X 100 / L_0
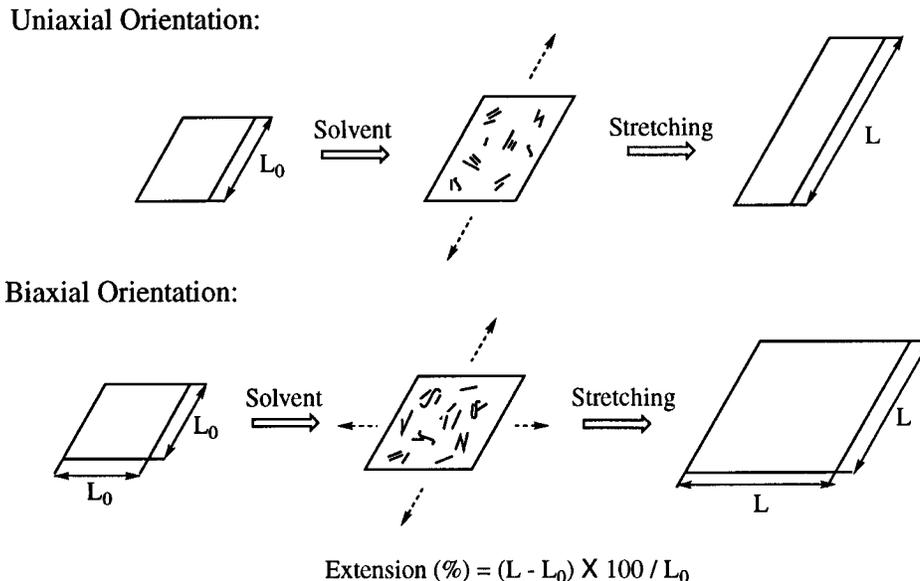
Figure 6. Schematic representation of the orientation procedures.

LJ 50 μm

50 μm
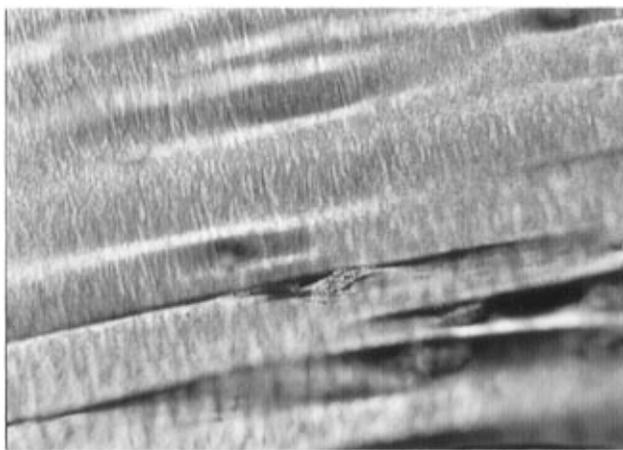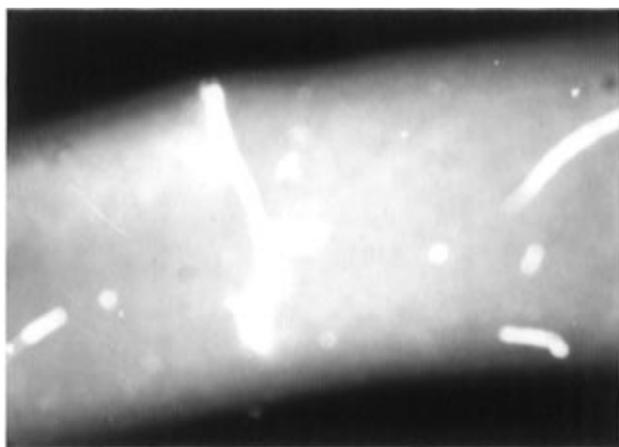
Figure 7. (a, top) Microphotograph of a hydrosilation cross-linked PHAIC specimen in chloroform. Original magnification 90×. (b, bottom) Band texture on the oriented PHAIC specimen after drying. Original magnification 350×.

Figure 8. Tensile strength (○) and modulus (□) as a function of extension ratio during drying for oriented PHAIC films prepared by high-temperature, oligo(dimethylsiloxane) curing.

Table 1. Mechanical Properties of PHAIC Films Prepared by High-Temperature Curing Using α,ω-Hydridooligo(dimethylsiloxane) as Cross-Linker

	tensile strength (MPa)	tensile modulus (MPa)	elongation at break (%)
PHAIC un-cross-linked (10% allyl concn)	10.6	140	11.0
PHAIC cross-linked (high-temp, hydrosilation)	2.6	30	46.0
oriented PHAIC (high-temp, hydrosilation)	15.6	260	12.5

tion parallel to the stretching direction during drying, there were no improvements, and even decreases, in the mechanical properties in the perpendicular direction. This is demonstrated in Figure 11, which shows the stress–strain behavior of the oriented films prepared

by low-temperature, oligo(dimethylsiloxane) curing. The unsymmetrical nature of the changes can readily be seen. Tensile strengths and moduli were greatly improved in the orientation direction, and the improvements increased with increase in extension ratio during drying. The toughness of these uniaxially oriented samples also increased with increase in extension ratio during drying, although the elongations at break were found to decrease with increase in orientation. In the direction perpendicular to the orientation, however, the tensile strengths and moduli showed no improvements; on the contrary, the strengths, for example, decreased with increase in extension ratio during drying (from 20 to 50%). More specifically, a 30% decrease in strength in the perpendicular direction was observed for the films

Table 2. Cross-Linking and Orientation Conditions for the PHAIC Films

cross-linker	curing temp (°C)	curing time (h)	max swelling[a]	sol fraction (%)	polym conc at stretching (v_2)[b]
hydridooligo-(dimethylsiloxane)	80	12	25–30	15–20	0.2–0.25
hydridooligo-(dimethylsiloxane)	40–50	36–48	15–20	10	0.33–0.40
hexamethyltrisiloxane	40–50	36–48	25	7–10	0.25–0.30

[a] The maximum swelling ratio was measured in chloroform, and it is a volume ratio. [b] The polymer concentration at stretching was measured in chloroform, and it is a volume ratio.
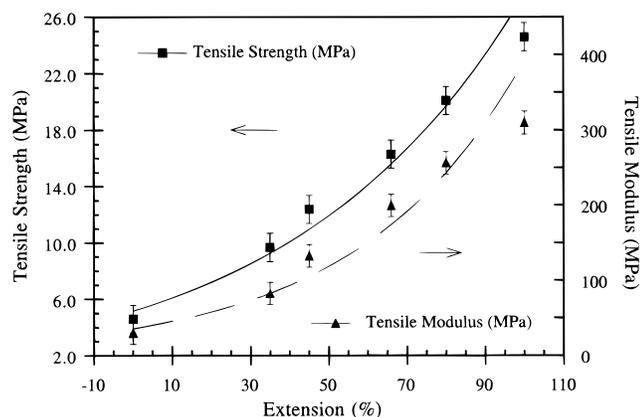
Figure 9. Tensile strength (■) and modulus (▲) as a function of extension ratio during drying for oriented PHAIC films prepared by low-temperature, oligo(dimethylsiloxane) curing.

Figure 11. Stress−strain behavior of uniaxially and biaxially oriented PHAIC films prepared by low-temperature, oligo-(dimethylsiloxane) curing.

Figure 10. Birefringence as a function of extension ratio during drying for oriented PHAIC films prepared by low-temperature, oligo(dimethylsiloxane) curing.
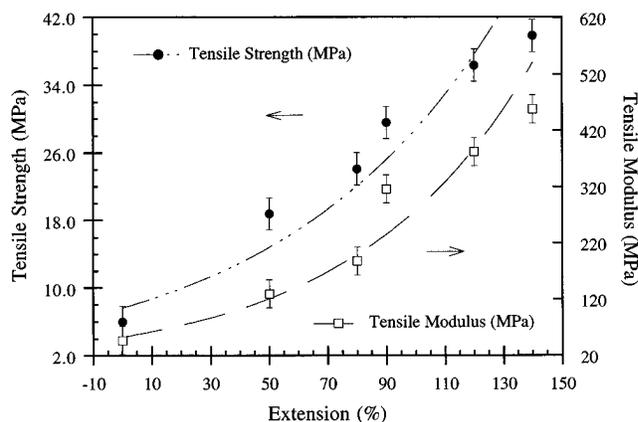
Figure 12. Tensile strength (●) and modulus (□) as a function of extension ratio during drying for oriented PHAIC films prepared by low-temperature, hexamethyltrisiloxane curing.

at an extension ratio of 50%. Elongations at break in the perpendicular direction also decreased with increase in extension ratio.

As can be seen from some of the other curves in Figure 11, the equibiaxial orientation was strikingly successful in producing materials with good mechanical properties in all directions within the plane of the films. For example, in this case, the tensile strengths and moduli were increased ∼3-fold at an extension ratio of only 20%!

Mechanical Properties of Oriented Polyisocyanate Networks Prepared Using Hexamethyltrisiloxane as Cross-Linker. In these experiments, the α,ω-dihydrooligo(dimethylsiloxane) (MW = 400) was replaced by hexamethyltrisiloxane in additional studies on the effect of cross-linker length on swelling behavior, orientability, and mechanical properties. Unexpectedly, shortening the cross-linker did not affect the orientability at all (see Table 2). Indeed, the swollen networks having hexamethyltrisiloxane linkages showed high equilibrium swelling ratios ($1/v_{2m} = 25$) and small sol

fractions (7−10 wt %). They could easily be stretched by 140% of their original lengths without rupture, at polymer concentrations of 0.25-0.3 vol %. As shown in Figure 12, the mechanical properties of these uniaxially extended samples were improved, with tensile strengths and tensile moduli increasing monotonically with increase in extension ratio during drying, from 0 to 140%. This is similar to the results obtained in the other two cases. More specifically, a 5.6-fold increase in tensile strength and a 24-fold increase in modulus were obtained for an extension ratio during drying of 140%. These absolute values of the mechanical properties were substantially higher than the maximum values obtained from the networks prepared using the other two curing processes. In fact, much higher ranges of strengths (23.60−39.82 MPa) and moduli (103−394 MPa) were thus obtained. This may be related to changes in the packing of the chains.

Figure 13 shows the stress−strain behavior of the uniaxially oriented PHAIC films prepared by the low-
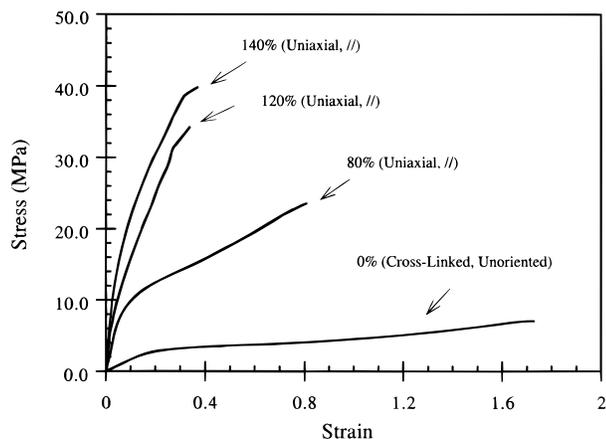
Figure 13. Stress–strain behavior of uniaxially oriented PHAIC films prepared by low-temperature, hexamethyltrisiloxane curing.

temperature, hexamethyltrisiloxane curing. The elongations at break decreased considerably with increase in extension ratio during drying. The unoriented film had an elongation at break of 157%, which was typical for a rubbery material. After the orientation treatment, the materials became stronger, harder, and tougher.

Comparisons among the complete set of results on the mechanical properties[29] indicated that the oriented films prepared by low-temperature, hexamethyltrisiloxane cure were the strongest of all the oriented samples investigated.

Conclusions

Novel main-chain lyotropic liquid-crystalline polymer networks were successfully prepared using hydrosilation cross-linking of isocyanate copolymers. The characteristic liquid-crystalline band texture was formed for both polyisocyanate copolymers and their networks, indicating little effect of the cross-links on this anisotropic behavior. The decay rate of these band textures was found to depend not only on the molecular weight of the copolymer but also on its composition. For the polyisocyanates in the form of gels, the band texture remained for a much increased length of time, suggesting preservation of the orientation. An orientation procedure was applied to the cross-linked polyisocyanate films, either uniaxially or biaxially, to induce segmental orientation. The orientation was studied with regard to the sol fraction, polymer concentration at stretching, and cross-linker length. Under all circumstances, the mechanical properties of the oriented films exhibited dramatic improvements compared to their unoriented state, suggesting sufficient chain alignment from the orientation technique. In addition, it was found that the shorter the cross-linker the higher the mechanical property values of the oriented films. This may be related to changes in the packing of the chains. It was thus demonstrated that these main-chain lyotropic liquid-crystalline polymers have exceptionally good orientability under an external mechanical force in the swollen state. The dramatically improved tensile properties and the anisotropic nature of their oriented films could be very useful in some types of structural applications.

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