Main-Chain Lyotropic Liquid-Crystalline Elastomers. 1. Syntheses of Cross-Linked Polyisocyanate Gels Acquiring Liquid-Crystalline Behavior in the Swollen State

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ABSTRACT: Copolymers of *n*-hexyl and allyl isocyanates were successfully synthesized using an organotitanium(IV) catalyst initiated polymerization. Viscosity measurements indicated that molecular weight increased with decrease in monomer/initiator ratio. Monomer reactivity ratios were calculated using the copolymer composition equation, and the resulting values indicated relative randomness in the copolymer. The liquid-crystalline behavior of these copolymers was studied with regard to their molecular weight, composition, and concentration. Radical cross-linking was extensively studied but yielded only very brittle gels. Consequently, hydrosilation cross-linking was investigated and did yield networks suitable for orientation in a novel technique for increasing the mechanical properties of polymer films. All the hydrosilation cross-linked gels exhibited brilliant mesomorphic birefringence under a cross-polarized microscope at low cross-link density. In addition, the glass transition temperatures of the hydrosilation cross-linked networks were found to be lower than those of their constituent polymers.

Introduction

During the past 40 years, the tremendous growth in the area of liquid-crystalline polymers (LCPs) has continued and has led to numerous developments in both new materials and applications. It was not until about 10 years ago, however, that cross-linked liquid-crystalline side-chain polysiloxanes were synthesized.[1] For the first time, the term "liquid-crystalline elastomer" was employed. Shortly afterward, the work on liquid-crystalline elastomers was extended to cross-linked side-group polymers with polyacrylate and polymethacrylate backbones and also to slightly cross-linked main-chain polymers and side-chain main-chain combined polymers.[2] Between the glass transition temperature and liquid-crystalline to isotropic phase transformation (clearing temperature), these materials exhibit both rubberlike elasticity (due to the cross-linked polymer backbones) and anisotropic liquid-crystalline behavior. Because of the interesting physical properties of these elastomers, this field has attracted increased attention.[3]

In contrast to the rapid development and extensive study of the above thermotropic liquid-crystalline networks, little was know about the phase behavior and physical properties of networks consisting of lyotropic LCPs. The term "lyotropic liquid-crystalline elastomers" was first introduced by Finkelmann describing polymeric networks from amphiphilic polymers (surfactants) that form micellar structures which aggregate into lyotropic liquid-crystalline phases.[4] The analysis of the phase behavior of such an elastomer in the swollen state using polarizing microscopy failed. Due to the strain-induced birefringence of the elastomer, contributions from mesophase birefringence were not distinguishable.[4]

Some theoretical work on lyotropic liquid-crystalline polymer networks was developed by Erman, Mark, and their co-workers in the early 1990s.[5,6] A modified version of the Flory lattice model was used in their theories to study the segmental orientation in deformed and swollen polymers of semirigid chains.[5,6] Their theoretical treatment clarified the molecular origin of the discontinuous stress−strain relationships associated with the isotropic−nematic transition phenomenon in networks of such chains. Several experimental observations were interpreted through this model, in particular the abrupt changes in the dimensions of liquid-crystalline networks subject to uniaxial deformation at constant force, the sharp minima in the dependence of the modulus on extension ratio, and discontinuities in the order parameter revealed by optical methods during deformations of the networks.[5,6]

In an effort to better understand the phase behavior and many other physical properties of main-chain lyotropic liquid-crystalline elastomers, novel types of networks consisting of main-chain liquid-crystalline polymers need to be synthesized. Among the many interesting classes, polyisocyanates are of particular importance. It had been reported that concentrated solutions of these isocyanate polymers exhibited liquid-crystalline behavior.[7] Traditional anionic polymerization had been a useful procedure to yield the desired polymers,[8] but it was mechanistically complicated and had little tolerance toward monomer functionality.[9] Previous efforts of making highly functionalized polyisocyanates using the anionic procedure failed due to the problematic side reactions between the functional side chains; *e.g.*, the polymerization of vinyl isocyanate yielded insoluble materials because the polymerization went through both the isocyanate moiety and the olefinic moiety.[10] The cross-linked polyisocyanates were briefly mentioned by Aharoni,[11] but due to the heavily cross-linked nature and inconvenience involved in producing the comonomer, his approach had little practical

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use. Thus, there is an obvious need to develop new synthetic methods to yield polyisocyanates with high functionalities, hopefully leading to the preparation of block copolymers, cross-linkable polymers or other interesting materials.

In 1991, Patten and Novak developed an organotitanium(IV)-based living polymerization of isocyanates.[12] By using an organotitanium initiator, they synthesized poly(*n*-hexyl isocyanate) (PHIC) with strict control over its molecular weight and polydispersity. In addition, they also controlled the end group on the initiating end of the polymer chain and manipulated the reactivity and selectivity of the active end group by changing the steric and electronic nature of the metal center.[13] Based on their methodology, we have synthesized polyisocyanates with highly functionalized side chains,[14,15] which produces cross-linked networks suitable for studying the phase behavior and other properties of main-chain lyotropic liquid-crystalline polymer networks.

Experimental Section

General Methods and Materials. All polymerizations and cross-linking reactions were performed under nitrogen or argon atmosphere, using standard Schlenck techniques or a Vacuum Atmosphere HE43 Dri Lab (with attached HE-493 Dri Train). ^{1}H NMR spectra were recorded at 250 MHz on a Bruker AM-250 spectrometer, and ^{13}C NMR spectra were recorded at 100 MHz on a Bruker AM-400 spectrometer. Chemical shifts were reported in δ values, with tetramethylsilane (TMS) as the internal standard. ^{1}H NMR data were tabulated by chemical shifts, multiplicity, number of protons, and coupling constants in hertz. All ^{13}C NMR spectra were proton decoupled. Infrared spectra were recorded on a Perkin-Elmer 1600 Series Fourier transform infrared spectrometer. Toluene, benzene, and petroleum ether (low boiling range) were distilled from potassium and degassed before use. Titanium(IV) tetrachloride and NMR grade 2,2,2-trifluoroethanol were purchased from Aldrich and used as received. Isocyanate monomers were purchased from Eastern Kodak and Carbolabs, Inc. and were vacuum distilled from CaH_2 under argon atmosphere. Syringe (0.5 μm) filter units were purchased from Millipore. Azobisisobutyronitrile (AIBN) was purchased from Fisher and recrystallized from methanol, and benzoyl peroxide (BPO) was purchased from Aldrich and used as received. α,ω-Dihydrooligo(dimethylsiloxane) with hydride terminal units (molecular weight MW = 400) and hexamethyltrisiloxane were purchased from Hüls America and used as received. *cis*-Dichloroplatinum(II) diethyl sulfide was purchased from Strem Chemical Co. and used as received.

Synthesis of Complex I: 2,2,2-Trifluoroethoxy Titanium(IV) Trichloride. $TiCl_3(OCH_2CF_3)$ was prepared according to the procedure of Paul *et al.*[17]

Homopolymerization of Hexyl Isocyanate. Poly(*n*-hexyl isocyanate) was synthesized according to the procedure of Patten and Novak.[12]

Attempts at Radical Cross-Linking of Poly(*n*-hexyl isocyanate) in Solution. In a 10 mL round-bottom flask, 100 mg of the homopolymer was dissolved in 2 mL of benzene to give a clear gel. Then 1 mg of AIBN was added, and the mixture was stirred before it was placed in a 60 °C oil bath and refluxed overnight. The resulting film readily dissolved in common organic solvents, indicating that no cross-linking occurred.

Attempts at γ-Ray Cross-Linking of Poly(*n*-hexyl isocyanate) in Bulk. A thin film of *n*-hexyl isocyanate homopolymer was obtained by casting a 5% polymer chloroform solution, followed by drying *in vacuo*. Strips cut from the films were placed into small vials and exposed to different dosages of γ-radiation. These irradiated films were also found to be soluble in chloroform or toluene, indicating failure to achieve cross-linking.

Homopolymerization of Allyl Isocyanate. In a drybox, 20 mg $TiCl_3(OCH_2CF_3)$ was added to a 10 mL round-bottom flask containing a magnetic stirring bar. A drop of toluene was added to ensure instant mixing. Allyl isocyanate (0.5 mL) was added *via* a syringe to give an orange-yellow solution. The flask was fitted with a rubber septum, and the solution was stirred for 45 min to 1 h at room temperature to give an orange solid. The flask was transferred out of the box, and several milliliters of cold methanol (−78 °C) were added to quench the polymerization. The resulting white polymer, poly(allyl isocyanate) (PAIC), was filtered and solvent removed *in vacuo*. The polymer was purified by filtering its chloroform solution through a 0.5 μm syringe filter. The polymer was recovered by reprecipitation from cold methanol. NMR: ^{1}H ($CDCl_3$) δ (ppm) 4.29 (br, 2H), 5.20 (m, 2H), 5.76 (m, 1H); ^{13}C ($CDCl_3$) δ (ppm) 49.59, 116.89, 131.89. (Due to the insufficient solubility of poly(allyl isocyanate) in chloroform, its carbonyl signal could not be detected.)

Copolymerization of *n*-Hexyl and Allyl Isocyanates. In a drybox, a premixed *n*-hexyl isocyanate and allyl isocyanate solution (with controlled composition) was added to a 50 mL round-bottom flask containing the catalyst−toluene solution. (The monomer/initiator ratio was varied to control the molecular weight.) The solution was stirred overnight to give an orange-yellow gel. Outside the drybox, cold methanol (−78 °C) was added to quench the polymerization. The resulting white polymer was filtered, and solvent removed *in vacuo*. The polymer was purified by filtering its solution using a 0.5 μm syringe filter. The polymer was recovered by reprecipitation from cold methanol and given the designation PHAIC. IR: 1697 cm^{-1} (ν_{CO}, s). NMR: ^{1}H ($CDCl_3$) δ (ppm) 0.85 (br), 1.25−1.56 (very br signals), 3.63 (very br); ^{13}C ($CDCl_3$) δ (ppm) 13.96, 22.53, 26.22, 28.36, 31.49, 48.53, 50.21, 118.61, 132.31, 156.66.

Determination of Molecular Weight of the Copolymer. Measurements of the intrinsic viscosity [η] of dilute polyisocyanate−toluene solutions were made using a Cannon-Ubbelohde viscometer at 30 °C.

The Mark−Houwink constants of poly(*n*-hexyl isocyanate) was obtained from Khatri amd Green as follows:[16]

$$\log K = -5.4219 \qquad \alpha = 1.1768$$

The K and α values of poly(allyl isocyanate) were unknown. The copolymer molecular weights (for lower allyl compositions) were estimated using the K and α values of the poly(*n*-hexyl isocyanate) and the standard relationship $[\eta] = KM^{\alpha}$.

Attempts at Solution Cross-Linking of Poly(*n*-hexyl and allyl isocyanates). A desired amount of copolymer was dissolved in solvent to give various ratios, after which a desired amount of BPO was added. The solution was heated at 80 °C overnight. No cross-linked materials were obtained for a starting concentration below 20 wt %.

Radical Solid-State Cross-Linking of Poly(*n*-hexyl and allyl isocyanates). A desired amount of copolymer was dissolved in sufficient amount of solvent (∼1 g of polymer/40 mL of solvent), after which a desired amount of BPO was added. The solution was stirred for at least 6 h to ensure homogeneity. It was then poured into a petri dish, and after 1 or 2 days, a smooth film resulted. Cross-linking occurred, and the procedure was completed in a vacuum oven at 70 °C overnight or on a hot-press for ∼1 h. Swelling tests were carried out in chloroform, benzene, and toluene.

Hydrosilation Cross-Linking of Poly(*n*-hexyl and allyl isocyanates). In a drybox, 0.5 g of the copolymer was dissolved in 11 mL of dry toluene. α,ω-Dihydrooligo(dimethylsiloxane) (70 μL) with hydride terminal groups (MW = 400) (or 50 μL of hexamethyltrisiloxane) was added via a syringe, followed by 0.1 mg of $PtCl_2(SCH_2CH_3)_2$ in 0.1 mL of toluene solution. The mixture was stirred for about 3−4 h before being transferred into a round Teflon pan (diameter 2 in.). The gelation was completed in the pan overnight (or 2−3 days) at 80 °C (or 40−50 °C), and the solvent was slowly evaporated. A smooth cross-linked film was obtained.

Determination of the Copolymer Composition and the Reactivity Ratios of the Isocyanates. The copolymerization composition was determined by integration of proton NMR spectra of the copolymers, *i.e.*, the ratio of the methylene protons (directly connected to the backbone) of both the *n*-hexyl and allyl side chains.

The reactivity ratios of the isocyanates were estimated using the above copolymer feed and composition data and the Fineman-Ross (FR) equation:[18,19]

$$G = r_1H - r_2 \tag{1}$$

where $G = (f_1/f_2)(1 - (F_1/F_2))$ and $H = (f_1/f_2)^2(F_2/F_1)$. The quantities f_1 and f_2 are the mole fractions of M_1 and M_2 in the feed, respectively, and F_1 and F_2 are the mole fractions of M_1 and M_2 in the copolymer.

Equilibrium Swelling Measurements. The extent of maximum (equilibrium) swelling expressed as the volume ratio of the swollen gel and dry polymer $\rho_m = (1/v_{2m}) = V_{sw}/V_{dry}$ was determined for each of the radical solid-state cross-linked polyisocyanate networks in chloroform, benzene, and toluene. Initial weights of the samples were accurately determined prior to each sample being placed into the solvent for 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 v_{2m} from

$$\rho_m = 1/v_{2m} = \frac{(W_p/\rho_p) + (W_s/\rho_s)}{(W_p/\rho_p)} \tag{2}$$

where W_p is the initial weight of the polymer and ρ_p is the density of the polymer (the PHAIC copolymer density used here was 1 g/cm^3). W_s is the weight of the solvent in the swollen specimen, and ρ_s is the density of the solvent.

Determination of Glass Transition Temperatures of the Polyisocyanates and Their Networks. Differential scanning calorimetry (DSC) experiments were performed using a Thermal Science DL series thermal analysis system equipped with a liquid nitrogen cooling apparatus. All the DSC scans were carried out under nitrogen purge at a heating and cooling rate of 10 °C/min. The aluminum sample pans for the glass transition measurements contained between 10 and 15 mg of sample.

Cross-Polarized Optical Microscopy. Samples for optical studies were studied between two cover glasses placed between two cross-polarizers. A Nikon polarizing optical microscope (Model DPTPHOT-PDL; Diagnostic Instrument, Inc.) equipped with an Olympus camera was used to study the phase separations of the polyisocyanates and their networks. The magnification of the lens used was 10 and 40, respectively, and the camera lens had an additional magnification of 2.5.

Results and Discussion

Preparation of Polymer. Poly(*n*-hexyl isocyanate) was successfully obtained by solution polymerization using organotitanium-initiated living polymerization, according to Novak's procedure.[12]

Radical and γ-Ray Cross-Linking Attempts on Poly(*n*-hexyl isocyanate). Cross-linking using radicals or γ-rays was performed on poly(*n*-hexyl isocyanate) immediately after its synthesis in hopes of preparing network structures. In this regard, it is well established that cross-linking of the polymers usually can be achieved by using chemical cross-linking reagents (such as peroxides) or high-energy radiation.[20] The peroxide-induced free radical reaction relies on the availability of C—H bonds, usually present in the side chains of polymers, and so does not add any additional organic groups. The main advantage of high-energy radiation is that cross-linking can be performed *in situ* on fabricated articles. Following each excitation—ionization, a polymer radical and a hydrogen atom are formed. Some of these hydrogens abstract in the immediate vicinity, yielding secondary polymer radicals. Pairs of adjacent radicals (one formed by radiation, the other by abstraction) can then cross-link readily, with minimum chance of interference by other molecules.

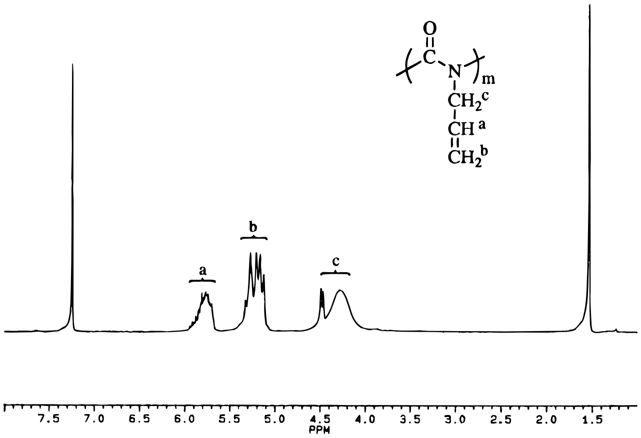
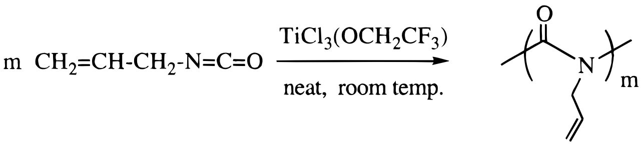


Figure 1. ^{1}H NMR spectrum of poly(allyl isocyanate) prepared using $TiCl_3(OCH_2CF_3)$.

Scheme 1. Synthesis of Poly(allyl isocyanate) Using $TiCl_3(OCH_2CF_3)$



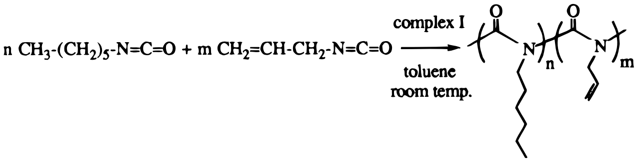
Unfortunately, this sequence of events did not occur in the case of this isocyanate polymer. All the resulting materials dissolved readily in many common organic solvents, indicating the absence of any network formation. The ^{1}H NMR spectra of those un-cross-linked materials were identical to the spectra before cross-linking.[15]

As in the polysiloxane and polyolefin industries,[20] replacing a small number of the alkyl chains by vinyl groups yields acceptable levels of cross-linking, even with a low level of peroxides. To facilitate cross-linking, therefore, attempts were made to incorporate small functional groups on the polyisocyanate backbones.

Polymerization of Allyl Isocyanate. The choices of comonomers were intentionally restricted to isocyanates, since other kinds of monomers might alter the living polymerization nature, probably complicate the reaction mechanism, and thereby disturb the regularity of the backbone structure (and suppress the liquid crystallinity which poly(*n*-hexyl isocyanate) itself exhibits). Allyl isocyanate was chosen for the above reason and because of its availability. The reaction, using the titanium catalyst $TiCl_3(OCH_2CF_3)$, is shown in Scheme 1. The only concern was that the polymerization could initiate from both the isocyanate moiety and the olefinic moiety, as was found in the polymerization of vinyl isocyanate using the NaCN anionic polymerization.[10]

The ^{1}H NMR spectra of PAIC prepared this way in a solution polymerization revealed no cross-link of the olefinic side chain. This is shown in Figure 1. The presence of olefinic protons and complete lack of extraneous methylene or methine protons that would indicate cross-linking or side reactions of the olefinic groups suggested the polymerization propagated only through the isocyanate moiety. The peak (~4.25 ppm) for CH_2 adjacent to the nitrogen was very broad, indicating some rigidity of the backbone. The olefinic proton peaks are

Scheme 2. Copolymerization of *n*-Hexyl and Allyl Isocyanates



broad and with less well resolved multiplicities, indicating the helical nature of polymer and the spacer interactions between the side chains, possibly due to the establishment of higher molecular weights. This showed that $\mathrm{TiCl_3(OCH_2CF_3)}$ can also polymerize isocyanate monomers containing olefinic unsaturation, in contrast to what was reported by Novak.[12,13] Complex **I** ($\mathrm{TiCl_3(OCH_2CF_3)}$), compared to complex $\mathrm{CpTiCl_2(OCH_2CF_3)}$ (which Novak used to obtain highly functionalized polyisocyanates), can polymerize isocyanate at a much faster rate. It was therefore particularly interesting for large-quantity syntheses. Poly(allyl isocyanate), synthesized using $\mathrm{TiCl_3(OCH_2CF_3)}$, was actually soluble at low molecular weights. This result was encouraging for copolymerizing allyl isocyanate with *n*-hexyl isocyanate.

The rate of polymerization of allyl isocyanate was slightly faster relative to that of hexyl isocyanate under similar conditions. Because of the limited solubility of poly(allyl isocyanate) in toluene, the homopolymer precipitates from the reaction mixture as the polymerization progresses (*i.e.*, at higher conversions).

Copolymerization of n-Hexyl and Allyl Isocyanates. Copolymerization of *n*-hexyl isocyanate and allyl isocyanate proceeded at a rate similar to that for homopolymerization of *n*-hexyl isocyanate at low allyl isocyanate concentration. (This is shown in Scheme 2.) Usually, the *n*-hexyl and allyl isocyanates were premixed first to facilitate the random copolymerization. The concern here was that if the polymerization of these two isocyanates proceeded at very different rates, a physical mixture of the two homopolymers, or block copolymers, might be obtained. The ^{1}H and ^{13}C NMR spectra obtained from the reaction mixture excluded this possibility (see Figure 2). There was clearly a difference between the olefinic protons (around 5.10−5.40 ppm, $\mathrm{CH_2CH{=}}$$CH_2$) in the homopolymer of the allyl isocyanate and the same protons in the copolymer. The olefinic group in the pure PAIC had a clear multiplicity, due to its coupling with the neighboring proton and the nonequivalent nature of those two protons. On the other hand, the olefinic groups ($\mathrm{CH_2CH{=}}$$CH_2$) in the copolymer gave peaks that were much broader, suggesting higher molecular weight. Also, this peak was split into two signals, suggesting the enhanced nonequivalent nature of those two olefinic protons. This observation indicated that a significant interaction existed between the allyl side groups and the neighboring hexyl side chains. The methylene protons adjacent to nitrogen ($>\mathrm{N}CH_2$) for both the allyl and the hexyl side chains gave peaks that were remarkably broader than those in the homopolymers, further suggesting some sort of side-chain interactions along the backbone. This information confirmed production of chemical copolymers (poly(allyl and *n*-hexyl isocyanates), PHAIC), although it revealed very little about their blockiness. In addition, the absence of any extraneous methylene or methine protons (upper portion of Figure 2) and the excellent solubility of the copolymer in common organic solvents excluded the possibility of side-chain reactions or cross-linking during polymerization. The ^{13}C NMR spectrum (lower portion of Figure 2) gave 10 carbon signals, which was consistent with the copolymer constitution.

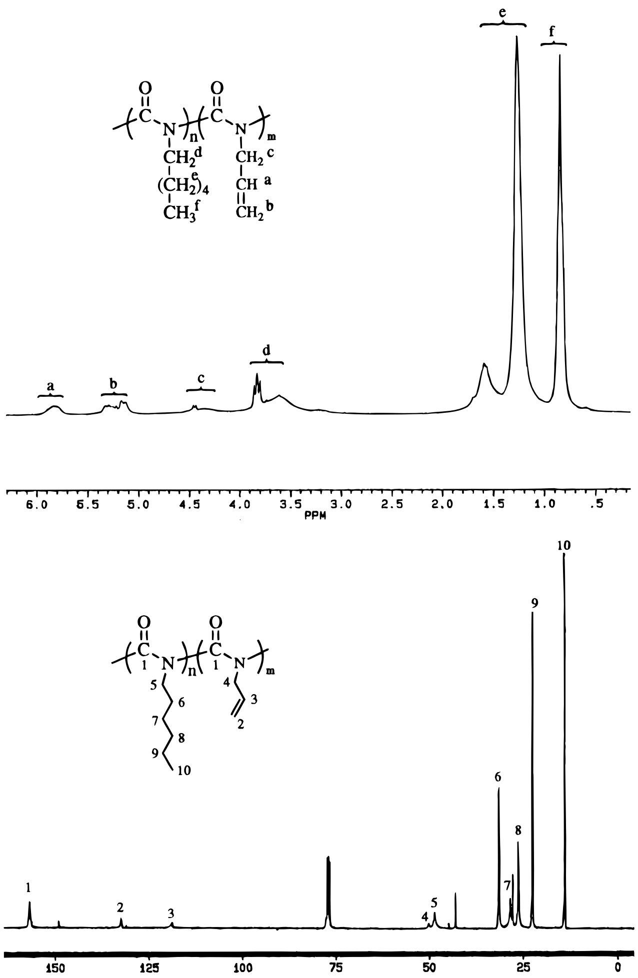


Figure 2. ^{1}H (upper portion) and ^{13}C (lower portion) NMR spectra of PHAIC.

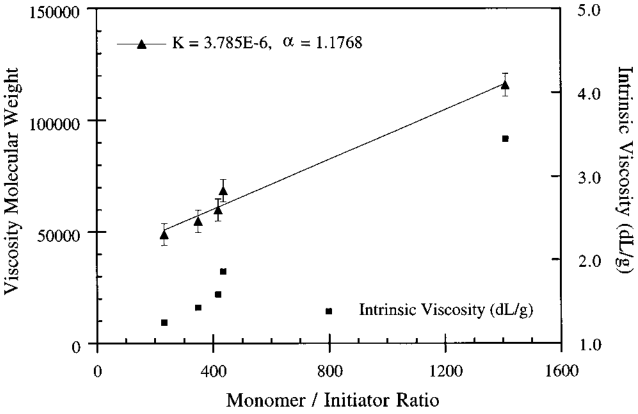


Figure 3. Intrinsic viscosity (■) and molecular weight (▲) dependence on monomer/initiator ratio.

Determination of Molecular Weights, Copolymer Compositions, and Reactivity Ratios. The molecular weights of the copolymers were estimated using viscosity measurements. The known K and α values of the poly(*n*-hexyl isocyanate) were used to estimated the molecular weight of the copolymers at the lower allyl composition. Figure 3 indicates that the molecular weight of the copolymers increased with increase in monomer/initiator ratio. By carefully controlling the anhydrous and anaerobic conditions, co-

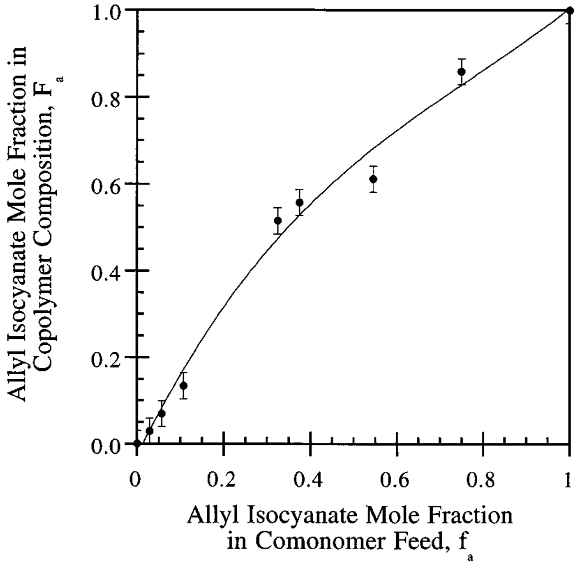


Figure 4. Copolymer composition (●) vs monomer feed.

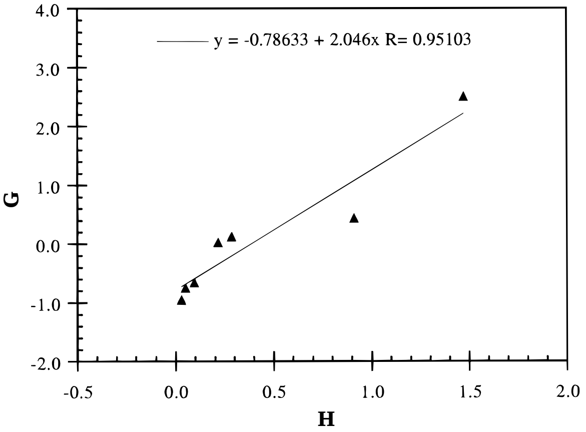


Figure 5. Calculation of monomer reactivity ratios using the copolymer equation.

polymers having very high molecular weight (~120 000) were obtained for cross-linking, orientation, and property studies. Copolymer composition was determined by NMR analysis.[21] It was found that at lower allyl concentration the copolymer was relatively brittle, but with increase in allyl concentration, it became tougher. An allyl concentration of 10 mol % was typically used to synthesize these cross-linkable polyisocyanates. Polymer film having very high allyl compositions demonstrated exceptional selectivity between organic solvents and water, which is described elsewhere.[15]

Clearly, a knowledge of reactivity ratios and the sequence distribution in a chain is of immense benefit for obtaining a homogeneously cross-linked film. NMR spectroscopic analysis indicated that the copolymer composition was essentially the same as the monomer feed (see Figure 4). The reactivity ratios of the polyisocyanates were estimated using the above data and the Fineman–Ross equation derived from the copolymer composition equation.[18,19]

By plotting G against H, as indicated in Figure 5, the reactivity ratios of the comonomers could be estimated. From the resulting graph, the r_1 for n-hexyl isocyanate was found to be 2.05, and r_2 for allyl isocyanate to be 0.79. Since $r_2 < 1$, this was a good indication that the allyl isocyanate was more likely to cross-propagate with n-hexyl isocyanate than to self-propagate. This excluded the possibility of having large blocks of the allyl functional groups in the copolymer.

Table 1. Attempts at Peroxide Cross-Linking of PHAIC in Dilute Solution[a]

allyl group conc in copolymer (wt %)	polymer conc (wt %)	BPO conc (wt %)
1	10	1
	5	5
10	5	5
	5	10
20	10	5
30	10	5

[a] All reactions were carried out at 80 °C in toluene under nitrogen.

Table 2. Copolymer Composition Effect on the Swelling Ratio ($1/v_{2m}$)[a]

solvent	10% allyl	33% allyl	50% allyl
chloroform	3.4	1.7	1.5
benzene	2.5	1.2	1.4
toluene	3.7	1.6	2.0

[a] All films had been cast from chloroform, and cross-linking was carried out in a 110 °C hot press, using a BPO concentration of 1 wt %. The quantity v_{2m} is the volume fraction of polymer present in the network at maximum (equilibrium) swelling.

Table 3. Effect of BPO Concentration on the Swelling Ratio ($1/v_{2m}$)[a]

	BPO conc (%)				
solvent	0.02	0.1	0.2	0.4	1
chloroform	13.2	7.4	3.8	2.9	3.4
benzene	15.1	5.8	3.5	2.8	2.5
toluene	11.4	7.1	3.7	3.0	3.7

[a] All films had been cast from chloroform, and cross-linking was carried out in a 110 °C hot press. The copolymer composition was 10% allyl isocyanate.

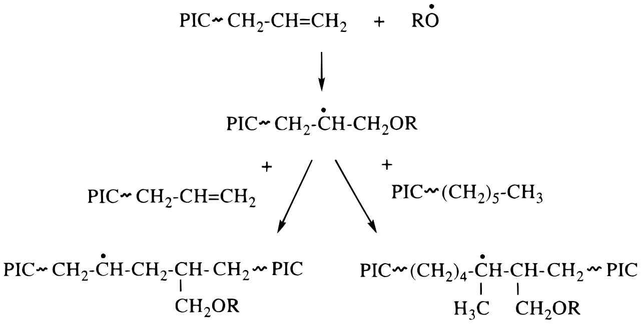
Attempts at Radical Cross-Linking of Poly(n-hexyl and allyl isocyanates). Solution cross-linking of PHAIC was attempted in both dilute and concentrated solutions. Dilute solution cross-linking was attempted in benzene or toluene, but it failed at all BPO concentrations and allyl compositions (see Table 1). This was probably due to the polymer secondary radicals being too far apart to combine or due to the stability of the allyl radicals. Concentrated solution cross-linking could succeed only if the initial polymer concentration was above 20 wt % and the peroxide concentration was above 5 wt %. The resulting materials from solution cross-linking were very brittle in the swollen state and irregular in shape and were thus not suitable for the planned orientation procedures.

Consequently, solid-state radical cross-linking was investigated to achieve a thin film with uniform thickness and no defects. The peroxide was first stirred with a PHAIC toluene solution overnight to ensure homogeneous mixing. The films were obtained by casting the above solution on glass or Teflon sheet. They were heated in a hot-press at 110 °C for ~1 h.

Swelling tests of the resulting cross-linked films were performed using chloroform, benzene, or toluene, and the results were recorded in Tables 2 and 3. As can be seen, the cross-link density increased with increase of the allyl composition at constant peroxide level. It also increased with peroxide loading at constant allyl composition.

The classical involvement of side-chain unsaturated groups in organic polymer cross-linking reactions (*e.g.*, the 1,2 units in polybutadiene) involves initiation by the addition of the peroxide free radical to the unsaturated groups. This is followed by a propagation step of

Scheme 3. Mechanisms Operating in Radical Curing of Polyisocyanates



addition to a further unsaturated group, a mechanism analogous to free radical polymerization:

initiation

$$\mathrm{CH{=}CH_2 + \dot{O}R \rightarrow \dot{C}HCH_2OR}$$

propagation

$$\mathrm{CH{=}CH_2 + \dot{C}HCH_2OR \rightarrow \dot{C}HCH_2\underset{|}{C}HCH_2OR}$$

Termination occurs by combination or disproportionation of the propagating radicals.

This mechanism (vinyl–vinyl addition) did operate in the radical cross-linking of poly(*n*-hexyl and allyl isocyanates), since without the olefinic side groups, the homopolymer of *n*-hexyl isocyanate failed to cross-link. Also, the cross-link density was highly dependent on the allyl composition (Table 2). But vinyl–vinyl addition was not the only operating mechanism, since the cross-link density was also highly dependent on the peroxide loading (Table 3). Vinyl–vinyl addition and vinyl–hydrogen abstraction are both suggested to be operative in radical curing of polyisocyanates, as illustrated in Scheme 3.

Unfortunately, all the solid-state cross-linked films were found to be very brittle and had very limited extensibility in the swollen state. The resulting cross-linked films were not suitable for phase behavior and orientation study of the main-chain lyotropic liquid-crystalline networks.

Hydrosilation Cross-Linking of Poly(*n*-hexyl and allyl isocyanates). Because of the ineffectiveness of peroxide curing, other possible cross-linking reactions were extensively studied, one example being hydrosilation cross-linking. The hydrosilation reaction has been widely used in the synthesis of organofunctional siloxanes and in the cross-linking of siloxane polymers.[20] The hydrosilation reaction most frequently used is that between a hydridosilane group (SiH) and a silicon vinyl group ($\mathrm{SiCH{=}CH_2}$). In practice it is possible to synthesize an extensive range of polymers with the SiH and $\mathrm{SiCH{=}CH_2}$ reactive groups included in a variety of positions in the polymer chain. More important, virtually any polymer with pendant olefinic groups can undergo hydrosilation cross-linking with certain hydridosilanes. Since this reaction involves the specific interaction of SiH and a carbon–carbon double bond, the position of these reactive groups effectively defines the matrix that can be formed.

First, α,ω-dihydrooligo(dimethylsiloxane) with hydride terminal groups (MW = 400) was chosen as the cross-linker. It is miscible with toluene and stays miscible with the PHAIC–toluene solution. The hydrosilation was first attempted using chloroplatinic acid ($\mathrm{H_2PtCl_6}$) as the catalyst. This was quickly abandoned, however, since the chloroplatinic acid–2-propanol solution was not miscible with the polyisocyanate toluene solution and this prevented its use as a homogeneous catalyst. *cis*-Dichloroplatinum diethyl sulfide was then chosen, because of its solubility in common organic solvents.

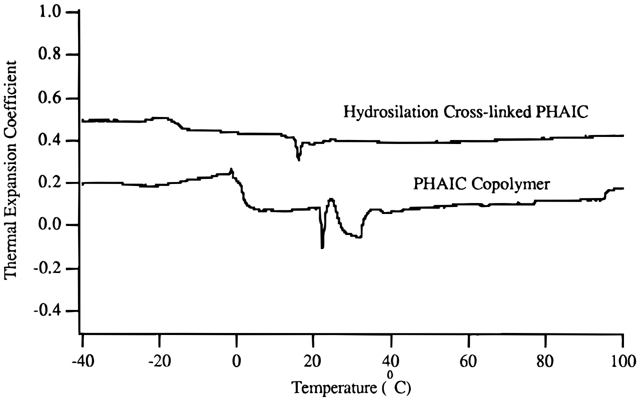


Figure 6. DSC curves for PHAIC and its hydrosilation cross-linked network.

To obtain an optimal degree of cross-linking, there should be control of reaction variables such as reaction temperature, time, hydridosilane/$\mathrm{CH{=}CH_2}$ ratio, $\mathrm{PtCl_2(SCH_2CH_3)_2}$ concentration, polymer/solvent ratio, copolymer composition, and cross-linker length.

In the case of copolymers with very low allyl concentrations, the films cast from the chloroform solution were relatively brittle. For mechanical property studies, all the copolymers used contained higher concentrations (~10 mol % allyl groups) and had excellent film-forming ability and reasonable toughness.

For copolymers with 10 mol % allyl concentration, it was found that the starting copolymer/toluene ratio of 2–2.5 wt/vol % gave a moderately viscous homogeneous solution without generating air bubbles. The hydrosilation catalyzed by $\mathrm{PtCl_2(SCH_2CH_3)_2}$ was very slow at room temperature, and higher temperatures were therefore used to ensure gelation within reasonable times. The mixture was usually stirred for about 6–8 h at room temperature before transferring it to a Teflon tray. The optimal level of hydridosilane/$\mathrm{CH{=}CH_2}$ was ~20%. The catalyst concentration usually is effective between 10^{-4} and 10^{-6} of the concentration of double bonds. As indicated in Table 4, high-temperature curing (80 °C) usually generates films with higher sol fractions, although the curing usually took overnight. Lower temperatures (40–50 °C) and longer curing time (1–2 days) usually decreased the sol fraction.

The hydrosilation curing was also conducted using hexamethyltrisiloxane; the hydrosilation took place considerably faster than the reaction when α,ω-dihydridooligo(dimethyl siloxane) was used. The hexamethylenetrisiloxane cross-linked PHAIC gels usually had lower sol fractions.[14]

Glass Transition Temperatures T_g of Polyisocyanates and Their Networks. The DSC measurements indicated that the hydrosilation cross-linked PHAIC network had a lower T_g compared to that of the linear copolymer, as illustrated in Figure 6. The copolymer with 10 mol % allyl composition had a T_g of 0 °C. The hydrosilation cross-linked film had a T_g of −15 °C. Usually the cross-links increase the glass transition temperature due to their suppressing chain mobility. However, due to the presence of very flexible

Table 4. Hydrosilation Cross-Linking Conditions for PHAIC Using α,ω-Hydridosilane as the Cross-Linker

allyl composition (%)	polymer conc (g/mL)[a]	PHMS (μL)	temp (°C)	max swelling ratio[b]	comments
10	0.5/10	n/a[c]	n/a	n/a	too viscous to stir
10	0.5/11	20	80	n/a	not CL[d]
10	0.5/11	30	80	n/a	not CL
10	0.5/11	40	80	n/a	not CL
10	0.5/11	50	80	25−30	high sol fraction
10	0.5/15	50	80	n/a	not CL
10	0.5/11	50	40−50	n/a	not CL after 2−3 days
10	0.5/11	70	40−50	25	smaller sol fraction
1	0.54/10	50	80	16	polymer is brittle
2.5	0.5/10	50	80	10	polymer is brittle
10	0.5/11	50	40−50	25	good for orientation

[a] The solvent used was toluene. [b] Represented as a volume ratio. [c] n/a, not available. [d] CL, cross-linked.

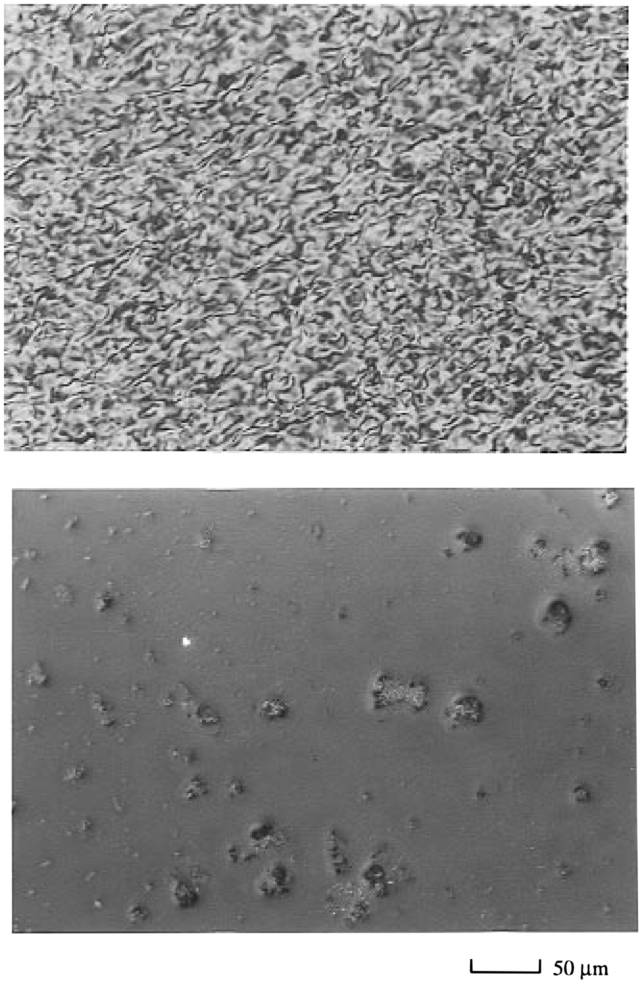


Figure 7. (a, top) Schlieren texture of 37 wt % PHIC (MW = 40 000) anisotropic phase in chloroform; original magnification 350×. (b, bottom) Microphotograph of 5 wt % PAIC (MW = 15 000) in chloroform; original magnification 350 ×.

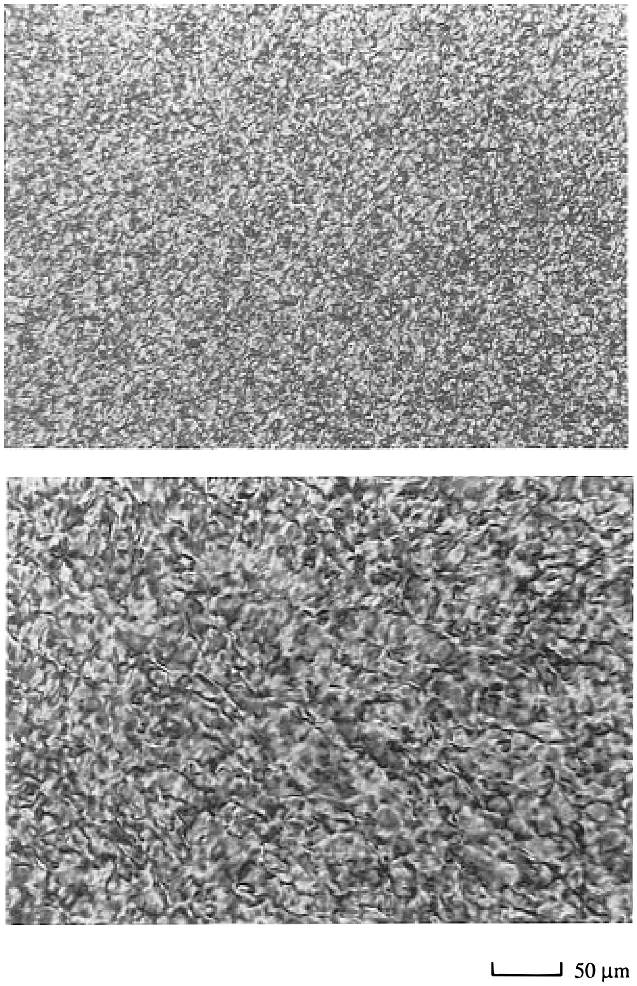


Figure 8. (a, top) Schlieren texture of 40 wt % PHAIC (5% allyl composition, MW = 120 000) anisotropic phase in chloroform; original magnification 350×. (b, bottom) Schlieren texture of 40 wt % PHAIC (10% allyl composition, MW = 120 000) anisotropic phase in chloroform; original magnification 350×.

siloxane oligomers, the glass transition temperatures of the PHAIC networks were actually decreased. Similar behavior was found in the thermotropic liquid-crystalline networks prepared from the hydrosilation reaction using low molecular weight hydridosilanes.[1,2]

Liquid-Crystalline Behavior of Isocyanate Copolymers and Their Networks. As is well-known, lyotropic liquid-crystalline polymers exhibit phase separation above a certain critical concentration v_2*. Below this concentration, the solutions are isotropic; at this concentration and above, an anisotropic phase appears.

Poly(*n*-hexyl isocyanate) homopolymers in chloroform exhibit brilliant Schlieren textures above concentrations of 37 wt % (see Figure 7a), similar to those reported for PHIC by Aharoni.[7] This clearly demonstrates their liquid-crystalline character. The homopolymer of allyl isocyanate, however, was only sparingly soluble in organic solvents and yielded only an isotropic dilute solution (Figure 7b). The failure of the PAIC to show liquid-crystalline behavior is probably due to its low solubility, precluding it from exceeding v_2*, and thus forming mesomorphic structures. The microparticles seen in Figure 7b were actually the insoluble part of the poly(allyl isocyanate).

At lower allyl compositions (<20%) (Figures 8−10), the copolymer (PHAIC) still exhibited liquid-crystalline

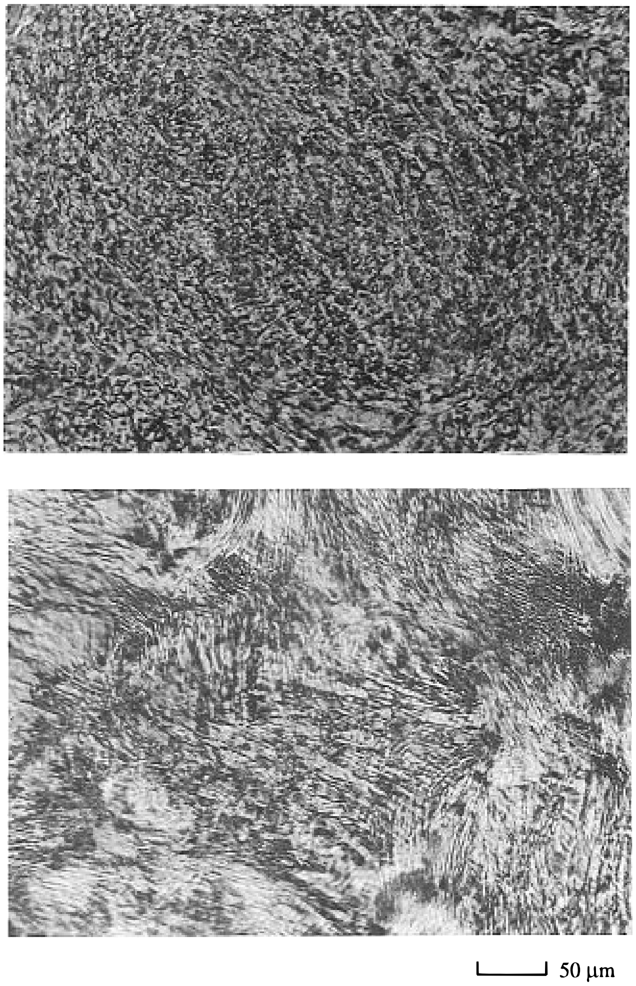


Figure 9. (a, top) Schlieren texture of 40 wt % PHAIC (20% allyl composition) anisotropic phase in chloroform; original magnification 350×. (b, bottom) Microphotograph of 40 wt % PHAIC (33% allyl composition) in chloroform; original magnification 350×.

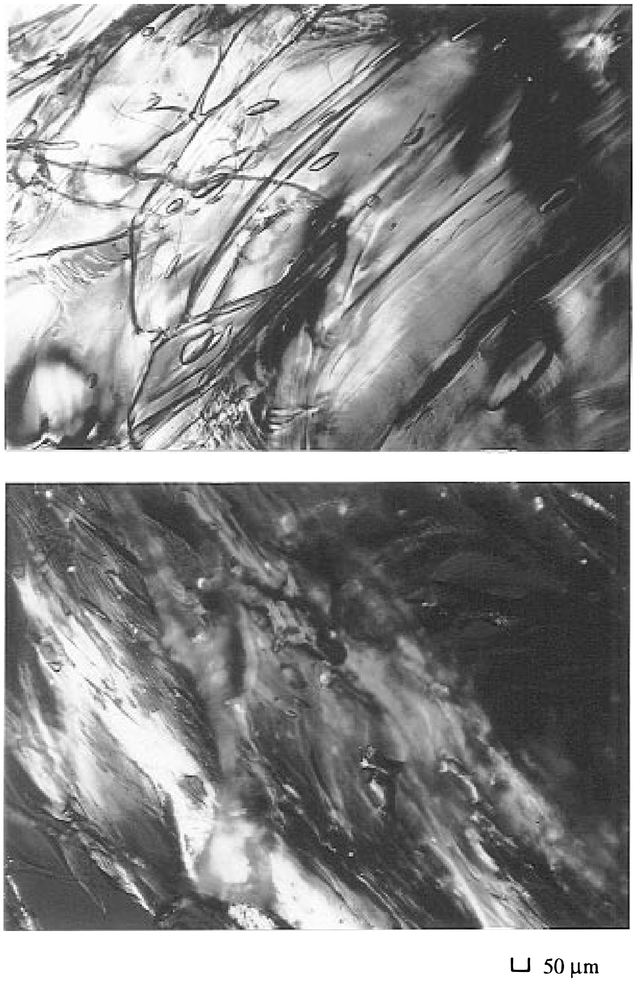


Figure 10. (a, top) Schlieren texture of 40 wt % PHAIC (50% allyl composition) anisotropic phase in chloroform; original magnification 90×. (b, bottom) Schlieren texture of 40 wt % PHAIC (75% allyl composition) anisotropic phase in chloroform; original magnification 90×.

behavior similar to that of PHIC. Thus, relatively small concentrations of these comonomeric groups did not suppress the formation of the desired anisotropic phases. Figures 8a,b, and 9a are microphotographs of 40 wt % PHAIC with allyl concentrations of 5, 10, and 20 wt %, respectively. They all exhibited brilliant mesomorphic birefringence. At higher allyl compositions (>33%), however, mesophase birefringence was not distinguishable. Both strain-induced birefringence and mesomorphic birefringence were observed. (See Figure 9b). Beyond 50% allyl composition, only strain-induced birefringence was observed (Figure 10a,b), although these polymers still displayed fair solubility in chloroform. These observations were in support of Aharoni's argument[7] on the side-chain length effect on the liquid-crystalline behavior of the polyisocyanates.

Little was known about the liquid-crystalline behavior of networks consisting of polyisocyanate chains. Lucht *et al.*,[22] however, prepared networks generated *in situ* by polymerization of *n*-hexyl isocyanate and hexamethylene diisocyanate, and they briefly mentioned that the resulting network was highly birefringent.

The radical cross-linked PHAIC film exhibited similar behavior. Figure 11a is a microphotograph of 0.4% BPO-cured PHAIC network, in which the brilliant birefringence was shear induced. Compared to Figures 8–10, there is a significant difference between the shear-induced birefringence and the self-assembled nematic Schlieren texture. The absence of mesomorphic birefringence probably is due to the very rigid linkages in radical-cured systems and the high cross-link density. Figure 11b is a microphotograph of a lightly cross-linked PHAIC thin film (10% allyl composition, MW = 120 000) resulting from hydrosilation curing. It exhibited a Schlieren texture similar to the uncross-linked analog (Figure 8b). This supports the conclusion that, at low cross-link density, network structure does not affect mesophase formation in lyotropic systems.[23–27]

Conclusions

In this part of the two-part study, highly functional polyisocyanate copolymers were synthesized by organotitanium complex **I** ($TiCl_3(OCH_2CF_3)$). The molecular weights were found linearly related to the monomer/initiator ratio. NMR spectroscopic analysis reveals that the copolymer composition was close to the monomer feed. The reactivity ratios were calculated by using the copolymer composition data and the Fineman–Ross equation. The results indicated that the allyl isocyanate was more likely to cross-propagate with hexyl isocyanate than self-propagate. This characteristic helped in the production of cross-linked films with homogeneous cross-link density. Radical curing was carefully investigated, and a vinyl–vinyl addition plus a vinyl–hexyl abstraction mechanism was proposed. Since radical cured films were not suitable for phase behavior and

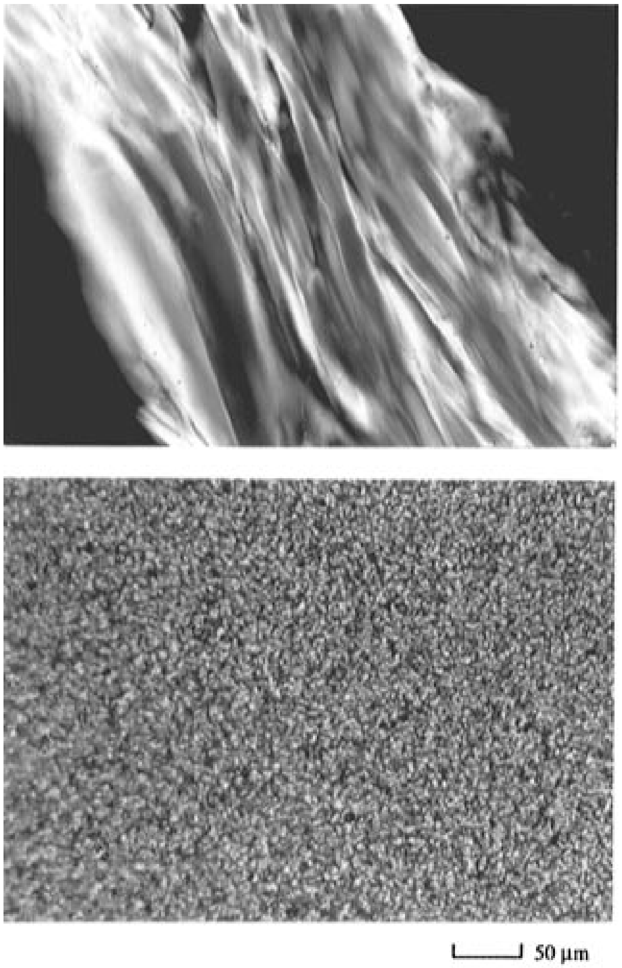


Figure 11. (a, top) Microphotograph of 40 wt % radical cross-linked PHAIC gel in chloroform; original magnification 350×. (b) Schlieren texture of 40 wt % hydrosilation cross-linked PHAIC gel anisotropic phase in chloroform; original magnification 350×.

orientation study due to the very rigid allyl–allyl linkage, hydrosilation curing was used to achieve lightly cross-linked films with flexible cross-links. Optimal reaction conditions were found for hydrosilation using $PtCl_2(SCH_2CH_3)_2$ as catalyst and a $SiH/CH{=}CH_2$ ratio of 20%. DSC measurements indicated the hydrosilation cross-linking led to a small reduction in glass transition temperature due to the presence of the very flexible oligo(dimethylsiloxane) linkages. The liquid-crystalline behavior of polyisocyanate copolymers and their networks was investigated as a function of molecular weight, allyl concentration, nature of the cross-linker, and cross-link density. It is demonstrated here that, at low cross-linking density, the network structure does not affect the mesophase transition in the lyotropic liquid-crystalline polymer networks.

The orientation of some of these materials and the investigation of their mechanical properties is described in the following paper.

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