Novel High-Performance Materials from Starch. 2. Orientation and Mechanical Properties of Lightly Cross-Linked Starch−Ether Films

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Received August 11, 1997

Three types of reactants were used to introduce cross-links into the starch−ether polymers, specifically hexamethylene diisocyanate, a hydridosilane, and a silanol-terminated oligosiloxane. The resulting cross-linked starch−ether films in the dry state were extremely brittle (as they are in their un-cross-linked states), with glass transition temperatures between 30 and 40 °C. The desired chain orientations were therefore carried out in the swollen state, with an externally applied mechanical force, focusing on the diisocyanate-cured triethylamylose films. The solvents were removed from these materials while they were in the stretched state, either uniaxial or biaxial, and the improvements in the mechanical properties thus achieved were determined as a function of this stretch ratio. It was found that the tensile strengths, tensile moduli, and elongations at break increased monotonically and frequently dramatically with increase in orientation, as gauged by this ratio. In addition, two solvent-removal processes were investigated, drying in air and coagulation in a suitable nonsolvent. Films obtained from the coagulation processes showed smaller improvements in mechanical properties and rougher surfaces than those obtained by air-drying.

Introduction

Naturally occurring polysaccharides are, in general, not processable by conventional thermoplastic methods unless a plasticizer such as water is added.[1,2] This shortcoming is caused by the strong interactions present in these polysaccharide systems, specifically hydrogen bonding, which can cause thermal decomposition well below the polymer's melting point or softening temperature.[1,2] On the other hand, the rigidity of their backbones can give rise to lyotropic liquid-crystalline behavior in either unmodified or chemically modified forms.[1,3−6] Processing a polymer while in the liquid-crystalline state is very useful for generating high-performance materials, since the solidified products will retain much of their orientational order. This will usually endow these materials with greatly improved strength and toughness.[7,8]

In 1991, a novel orientation technique was proposed by Erman, Mark, and co-workers for the preparation of high-strength, high-modulus films and fibers from lyotropic main-chain liquid-crystalline polymers.[9−14] In contrast to conventional orientation techniques,[8] the procedures described would give controlled degrees of orientation among the anisotropic domains containing the liquid-crystalline chains, and these orderings would persist after the mechanical force that induced them was removed.[15−21] In brief, in this orientation tech-

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S0897-4756(97)00562-0 CCC: $15.00

nique, semirigid polymer chains were chemically cross-linked, typically in solution. Because of their rigid backbones, these polymer chains underwent isotropic-to-nematic phase transitions above certain concentrations, forming main-chain, lyotropic, liquid-crystalline polymer networks. The network structure thus introduced allowed the gels to be deformed by an external mechanical force in the swollen state (without excessive chain relaxation), uniaxially or biaxially, to induce the desired orientations. Subsequent removal of solvent in the cross-linked gels while in the deformed state would snap the chains into anisotropic domains that were *themselves* oriented in the stretching direction. This should produce highly oriented films with much-improved mechanical properties, i.e., high-performance materials. The results obtained on cellulose derivatives,[15−18] polyisocyanates,[19−21] and gelatin[22,23] confirmed the usefulness of this orientation technique.

The starch ethers prepared by the Husemann method[24,25] in the preceding paper have free hydroxyl groups on their backbones. They should therefore be easily chemically cross-linked into main-chain, lyotropic liquid-crystalline polymer networks suitable for this processing technique. They were therefore used in this second part of the three-part investigation, with several curing methods carefully investigated for the required generation of lightly cross-linked films. The resulting films were oriented, either uniaxially and biaxially in the swollen state, and dried under this deformation, and their mechanical properties then measured in simple elongation.

Experimental Details

Materials and Methods. The starch−ether polymers employed were those described in the preceding paper of this series.

Hexamethylene diisocyanate was purchased from Aldrich and distilled from CaH_2 before use, and triethylamine was purchased from Fisher and distilled from barium oxide before use. α,ω-Dihydrooligo(dimethylsiloxane) (MW = 400 g mol^{-1}, with hydride terminal groups), and silanol-terminated oligo(dimethylsiloxane) (MW = 400−750 g mol^{-1}) were purchased from United Chemicals, Inc. and used as received. The catalysts stannous octoate and dibutyltin dilaurate were purchased from Sigma and Aldrich, respectively, and also used as received.

Cross-Linking of Starch Ethers. Triethylamylose (from amylomaize VII) is used here to typify the cross-linking conditions, although conditions varied somewhat when a different starch source was used.

Diisocyanate Cross-Linking. Highly substituted triethylamylose (0.5 g, DS $\geq$ 1.95) was dissolved in 10 mL of dry toluene. An appropriate amount of hexamethylene diisocyanate was added via a syringe, followed by a catalytic amount of triethylamine. The mixture was stirred for about 3−4 h before being transferred into a round Teflon pan (2-in. diameter). The gelation was completed in the pan overnight at 40−50 °C, at which time almost all the solvent had evaporated. A brittle film was obtained after the remaining solvent was removed, and it did not dissolve in common organic solvents.

Hydridosilane Cross-Linking. In a drybox, 0.5 g of the highly substituted triethylamylose was dissolved in another 10 mL of dry toluene. The desired amount of α,ω-dihydrooligo(dimethylsiloxane) was added with a syringe, followed by 1 wt % dibutyltin dilaurate. The mixture was stirred overnight before being transferred into another Teflon pan. The gelation was completed in the pan overnight at 80 °C, and a brittle hard film was obtained after the solvent evaporated.

Silanol-Terminated Oligo(dimethylsiloxane) Cross-Linking. A toluene solution of the highly substituted triethylamylose was prepared as already described. The desired amount of silanol-terminated oligo(dimethylsiloxane) was added, followed by 1 wt % stannous octoate. The mixture was stirred overnight before being transferred into another Teflon pan. The gelation was completed overnight at 80 °C. Evaporation of the solvent yielded a hard, brittle film, which did not dissolve in common organic solvents.

Determination of Soluble Polymer Fractions and Extents of Equilibrium Swelling. *Soluble Fraction Measurements.* Representative samples from each of the amylose−ether films cross-linked as described above were accurately weighed after they were dried 1−2 days in vacuo. All of the samples were then swollen in toluene and extracted overnight in order to remove any unreacted materials. The networks were then slowly deswollen with petroleum ether and dried in air for 1−2 days, followed by in vacuo drying for an additional day, and then reweighed. Values of 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, expressed as the volume fraction of polymer v_{2m} in the swollen gel, was determined for each of the amylose−ether networks in toluene. Initial weights of extracted samples were accurately determined prior to swelling, and weights were remeasured periodically until they were constant with time. These weights, and specific volumes, were used to calculate values of v_{2m} under the assumption of simple additivity of volumes.

Cross-Polarized Optical Microscopy. Samples for optical characterization were examined between two cover glasses placed between cross polarizers. To observe 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 (DPTPHOT-PDL, Diagnostic Instrument, Inc.) equipped with an Olympus camera was used to study phase separations in the networks. The magnification of the lens used was 10× or 40×, and the camera lens had an additional magnification of 2.5×.

Determination of Glass Transition Temperatures. Differential scanning calorimetry (DSC) experiments were performed using a Thermal Science DL Series thermal analysis system equipped with liquid nitrogen cooling apparatus. All the DSC scans were carried out under a 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 the samples.

Orientation Procedures. Cross-linked amylose−ether films were swollen in chloroform or toluene overnight to the extent chosen. The swollen films were then uniaxially deformed to a desired extension by moving apart two clamps attached to their ends, or by simply stretching them by hand. The resulting extension ratio was defined as

$$\text{extension (\%)} = 100(L - L_0)/L_0 \qquad (1)$$

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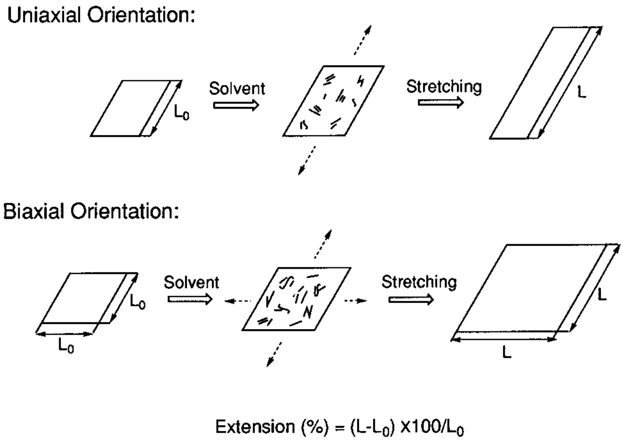


Figure 1. Schematic representation of the orientation procedure.

where *L* is the final length of stretched samples, and L_0 is its original length. The procedures are shown schematically in Figure 1.

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

In some cases, the solvent was removed from a deformed swollen gel by coagulation in petroleum ether. All types of films were stored in a desiccator.

Mechanical Property Measurements. The tensile strength and modulus of dried samples having dimensions of 50 × 5 × 0.5 mm^3 were measured using an Instron mechanical tester (Model 1122). The cross-head speed was 0.1 in./min with the initial gauge length of 0.7 in., and the force and deformation were recorded with an *x*−*y* recorder.

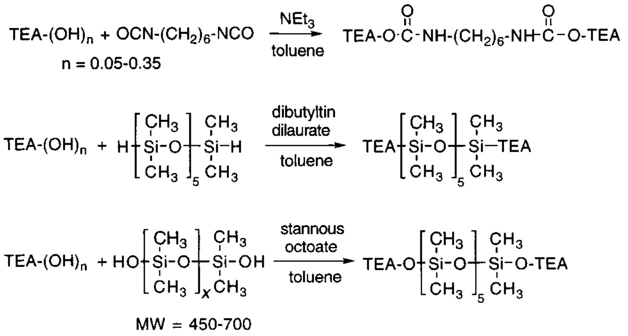
Birefringence Measurements. The birefringence of some of the oriented films was measured using a compensation method, with a Babinet-Soleil compensator (Karl Lambert Corp.). The light source was a He−Ne laser beam (Oriel Corp.) with a wavelength of 632.8 nm.

Scanning Electron Microscopy. Scanning electron microscopy (SEM) was used to characterize the film surfaces for uniaxially oriented samples prepared using the two methods for removing the solvent from the deformed swollen networks. Specimens were coated by gold, mounted on aluminum holders with silver cement, and then examined with a Model 90 Cambridge instrument.

Results and Discussion

Cross-Linking of Triethylamylose. Cross-linking was first attempted on highly substituted triethylamylose (TEA, prepared from amylomaize VII). Hexamethylene diisocyanate was chosen as the cross-linker because of its miscibility with toluene, and the flexibility of its methylene units (as shown in the first part of Scheme 1). The free hydroxyl groups on the D-glucose rings underwent addition reaction with the diisocyanate moiety. The appearance of the carbonyl (−C=O) vibrational stretching band at 1750 cm^{-1} of the carbamate linkage and the diminishing isocyanato (−C=N=O) stretching band at 2269 cm^{-1} confirmed the formation of the desired chemical cross links. The diisocyanate-cured films, however, were hard and brittle.

Scheme 1. Cross-Linking of Highly Substituted Starch Ethers. (Top) Hexamethylene Diisocyanate as Cross-Linker; (Middle) Hydridosilane as Cross-Linker; (Bottom) Silanol-Terminated Oligo(dimethylsiloxane) as Cross-Linker



Additional experiments employed the cross-linkers α,ω-hydridooligo(dimethylsiloxane) and silanol-terminated oligo(dimethylsiloxane). It was thought that by incorporating very flexible siloxane units, the glass transition temperatures of the materials could be reduced, thus yielding less brittle films suitable for the orientation procedures (as was observed with the polyisocyanates).[19−21] The condensations between the hydridosilane or silanol-terminated oligosiloxane and the remaining free hydroxyl on the triethylamylose backbones were carried out using dibutyltin dilaurate or stannous octoate as catalysts, respectively (Scheme 1). Although functional oligosiloxane cross-linked TEA films were softer in the dry state, they were very fragile and had higher soluble fractions. This probably was due to the poor reactivity of the hydroxyl groups on the D-glucose units with the Si−H or Si−OH terminals on the functional siloxanes. Condensation was incomplete and the cross-linking density was not high enough to achieve films with smaller soluble fractions.

Since the other two possible cross-linking procedures were eliminated due to their inefficiencies, diisocyanate curing was used for the remaining experiments. In particular, it was carefully studied to identify the cross-linking conditions that could lead to the formation of the most suitable films for orientation. It was found that usually a catalytic amount of triethylamine assisted the completion of the addition reaction (of the hydroxyl groups to the isocyanate moieties). If the starting polymer concentration was too low, the mixture could not be cross-linked even after being stirred for 2−3 days. Very high polymer concentrations were not desirable either, since this caused the formation of numerous air bubbles. The mole ratio of diisocyanate/polymer was carefully controlled to ensure low cross-linking density; 0.1 mol % diisocyanate usually gave form-retaining films suitable for orientation purposes.

The efficiencies of the cross-linking reactions varied very little with changes in degree of substitution or amylose/amylopectin ratio in the triethylamylose (triethylstarch). Tables 1 and 2 summarize these conditions and the results obtained. As can be seen from Table 1, the degree of substitution had little influence on the cross-linking conditions for TEA synthesized from amylomaize VII. Table 2, however, shows that with increase of the amylopectin amount in the starting material, more solvent was generally needed to dissolve the polymer at similar degrees of substitution. The only exception here was the TEA prepared from pure amylose; it required much more solvent to dissolve the

Table 1. Cross-Linking Conditions for Triethylamylose Having Different Degrees of Substitution[a]

amylose VII source DS	polym concn in toluene	diisocyanate (mL)	sol fraction (%)	comments
2.7	0.5 g/15 mL	60	N/A	too dilute to cross link
2.7	0.5 g/10 mL	60	10−12	suitable for orientation
2.7	0.5 g/8 mL	60	N/A	too viscous; numerous bubbles
2.7	0.5 g/10 mL	80	5−6	heavily cross-linked
2.25	0.5 g/10 mL	60	10−12	suitable for orientation
1.95	0.5 g/10 mL	60	10−12	suitable for orientation

[a] The curing temperature was 40−50 °C, and the curing time was about 2−3 days.

polymer. Part of the reason was the relatively low degree of substitution in this pure TEA. All of the specimens described in the following sections were diisocyanate cross-linked, and the soluble fractions were all removed before using them in the orientation procedures.

Glass Transition Temperatures. Figure 2 shows a typical DSC curve, specifically for a triethylamylose network cross-linked using the diisocyanate. As can be seen, this sample had a T_g of approximately 39.5 °C, which was essentially the same as that of the un-cross-linked sample.[25]

The hydridosilane cross-linked sample had a T_g of approximately 32.0 °C, which was slightly lower than that of the un-cross-linked sample, presumably because of the presence of the softer chain segments. The sample cross-linked with silanol-terminated oligosiloxane had a T_g at approximately 39.6 °C, which was somewhat higher than expected.

Phase Behaviors of the Starch−Ether Networks. As is well-known, networks consisting of liquid-crystalline polymers still possess the orientational degrees of freedom associated with liquid crystallinity so long as the cross-linking density is not excessively high.[26] The effect of network structure on liquid-crystalline phase behavior has been examined for several polymeric systems,[15−21,26−31] and all of the lightly cross-linked liquid-crystalline networks exhibited mesomorphic birefringence. The phase behavior of starch−ether networks was examined in a similar manner, for possible influences of the network structure on liquid-crystalline behavior.

The starch−ether films used for the orientation study had been cross-linked in dilute (3−5 wt/vol %) toluene solution. Their microphotographs (not presented) clearly showed mesomorphic birefringence, demonstrating that the network structure did not interfere with the formation of anisotropic domains. These results were obtained on both a cross-linked TEA (amylomaize VII) gel with a degree of substitution of 85%, and a cross-linked TES (corn) gel with a degree of substitution of 80%. It was confirmed that so long as the cross-linking density was relatively low, the cross-linked starch−ether gels exhibited liquid-crystalline behavior regardless of degree of substitution and amylose/amylopectin ratio.

The characteristic band textures found in liquid-crystalline solutions of cellulose derivatives[15−18] and polyisocyanates[19−21] were not observed for either the un-cross-linked or cross-linked starch ethers.

Orientation of Starch−Ether Thin Films. The orientation was first performed on triethylamylose gels prepared from amylomaize VII (70% amylose/30% amylopectin) with a degree of substitution of 90%. The TEA (amylomaize VII) gels can usually be swollen to 11−12 times their original volume in chloroform ($1/v_{2m} = 11-12$). This relatively high value of the maximum swelling ratio indicated low cross-link density, which would permit high chain extensibility. A polymer concentration at stretching of 0.2−0.25 was used for all these films. Within this swelling range, the specimens could be comfortably stretched to about 150% of their original lengths without breaking.

The TEA (amylomaize VII, 85% DS) gels in the shape of thin films were oriented as described in Figure 1. The extension ratio during drying defined in eq 1 will be used throughout the remainder of this report as a measure of the degree of orientation thus imposed. Figure 3 shows the microphotographs taken during the orientation process. In the first step, the extracted specimen was swollen in chloroform overnight, and the appearance of this swollen film before orientation is shown Figure 3a. The mesomorphic birefringence is clearly seen, suggesting the existence of liquid-crystalline domains, but these domains are obviously uncorrelated in direction. In the second step, the swollen specimen was deformed uniaxially to induce segmental orientation and the two ends were fixed at a desired length. The specimen was dried by subsequent removal of the solvent (chloroform) under ambient conditions, with the rate of solvent evaporation being controlled to prevent inhomogeneous shrinkage. After uniaxial stretching and drying under the deformed state, the specimen was highly birefringent under the cross-polarized microscope, suggesting a high degree of domain alignment. This is shown in Figure 3b.

Mechanical Properties of the Uniaxially Oriented Triethylamylose. As already mentioned, the triethylamylose films and their diisocyanate cross-linked networks were brittle in the dry state and mechanically useless. Very unexpectedly, however, the orientation made the TEA films (amylomaize VII, 90% DS) much tougher. As can be seen from Figure 4, the tensile strengths and moduli increased monotonically and frequently dramatically with increase of extension ratio during drying. A 3.5-fold increase in tensile strength, and a 30% increase in tensile modulus (relative to the cross-linked unoriented films) were observed at a drying extension ratio of 135%. These profound improvements in mechanical properties are better illustrated by the stress−strain curves in Figure 5. A 20-fold increase in elongation at break and a 100-fold increase in toughness were obtained from the oriented films with this extension ratio of only 135%. These dramatic improvements in mechanical properties demonstrated the utility of the novel orientation technique employed. Furthermore, in the practical sense, mechanically useless triethylamylose films were trans-

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Table 2. Cross-Linking Conditions for Triethylstarch (Triethylamylose) with Various Amylose/Amylopectin Ratios[a]

amylose source	polym concn in toluene	diisocyanate (mL)	sol fraction (%)	comments
amylomaize V, DS = 2.4	0.5 g/12 mL	60	7−8	suitable for orientation
amylose (pure), DS = 2.1	0.5 g/18 mL	60	7−8	suitable for orientation
corn starch, DS = 2.4	0.5 g/15 mL	60	5−6	suitable for orientation
wheat starch, DS = 2.4	0.5 g/15 mL	60	9−10	possibly suitable for orientation
rice starch, DS = 2.4	0.5 g/15 mL	60	6−7	possibly suitable for orientation
potato starch, DS = 2.4	0.5 g/15 mL	60	8−9	too brittle
amylopectin, DS = 2.4	0.5 g/18 mL	60	10−12	not suitable for orientation

[a] The curing temperature was 40−50 °C, and the curing time was about 2−3 days.

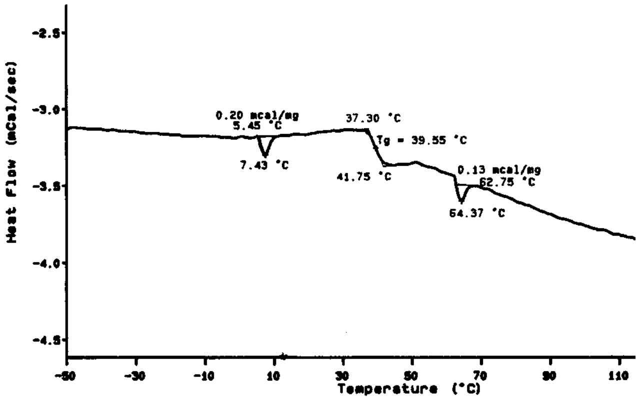

Figure 2. DSC curve of an diisocyanate cross-linked TEA network.

formed into tough plastics with useful ranges of tensile strengths (12.6−25.1 MPa), moduli (373−478 MPa), and elongations at break (15−120%). These mechanical property values are comparable to those of medium-to-high density polyethylene. This success in improving the properties of these starch derivatives (reduced brittleness, dramatically increased toughness, and increased hydrophobicity), the low cost of starch, and the biodegradability of its backbone certainly provide new directions for preparing high-performance biodegradable materials.

Another interesting feature observed was the existence of yield points in the stress−strain curves of the oriented TEA (amylomaize VII, 90% DS) films. It has been well established that the yield stress varies with the degree of crystallinity of a polymer.[32−34] As can be seen from Figure 5, increase in extension ratio during drying makes the yield point more distinct and increases the yield stress. For a TEA (amylomaize VII) specimen with the extension ratio during drying of 65%, the material failure occurred just beyond the yield point, but this post-yield brittle failure might be due to insufficient orientation. For a TEA specimen with extension ratio during drying of 100%, a plateau developed after the yield point (at approximately 22.43 MPa). Finally, a TEA specimen with extension ratio during drying of 135% had a stress−strain curve with a sharper yield point (at approximately 22.35 MPa), followed by extensive elongation at an almost constant stress. This indicates a higher level of ordering, from the higher stretching ratio. As already mentioned, the tensile strength (defined as the stress at break) increased with increased orientation. The increase in tensile strength was certainly important, but for engineering applications, a material is rarely stressed so greatly that it breaks instantaneously. For this reason, the toughness of the polymer is frequently a more useful parameter. It is measured as the area under the stress−strain curve, which represents the energy required to break a material. For these TEA (amylomaize VII, 90% DS) films, as indicated by the stress−strain curves in Figure 5, the toughness was also found to increase monotonically with increase in extension ratio during drying.

The only disadvantage of the uniaxially oriented TEA (amylomaize VII, 90% DS) samples was the following: although the mechanical properties had been greatly improved in the direction parallel to the orientation, they showed no improvements, or even showed *decreases*, in the perpendicular direction. Figure 5 demonstrates this effect. For a TEA (amylomaize VII, 90% DS) with an extension ratio during drying of 70%, the perpendicular direction showed decreased tensile strength and tensile modulus, and more brittleness (decreased elongation at break), relative to those of the cross-linked but unoriented sample. This behavior was typical for uniaxially oriented samples.

Mechanical Properties of Some Biaxially Oriented Samples. Equibiaxial orientation was subsequently introduced in an attempt to prepare materials with good mechanical properties in all directions within the plane of the film. As can be seen from Figures 6 and 7, the results of biaxial extension are similar to those for uniaxial orientation; both tensile strengths and moduli again increased monotonically with increase in extension ratio during drying (ranging from 30 to 70%). A 4-fold increase in tensile strength, a 40% increase in modulus, and an approximately 15-fold increase in toughness were observed *in all directions* for films with a biaxial extension ratio during drying of 70%. The only distinctive difference between the uniaxial and biaxial orientations was the values of extension ratio during drying. An extension ratio of 135% could easily be achieved for uniaxial orientation without breaking the sample in the swollen state, compared to a maximum 70% extension ratio for biaxial orientation. All these biaxially oriented specimens broke before or at the yield points, which was attributed to the relatively low stretching ratios (below 100%). Even with these relatively low biaxial stretching ratios, however, useful ranges of tensile strengths (19.46−30.64 MPa), moduli (357−510 MPa), and elongations at break (11.7−15.5%) were obtained for these films.

To put the advantages of equibiaxial orientation into context, both tensile strength and modulus were plotted against the extension ratio during drying by the two orientation methods. As can be seen from Figures 8 and

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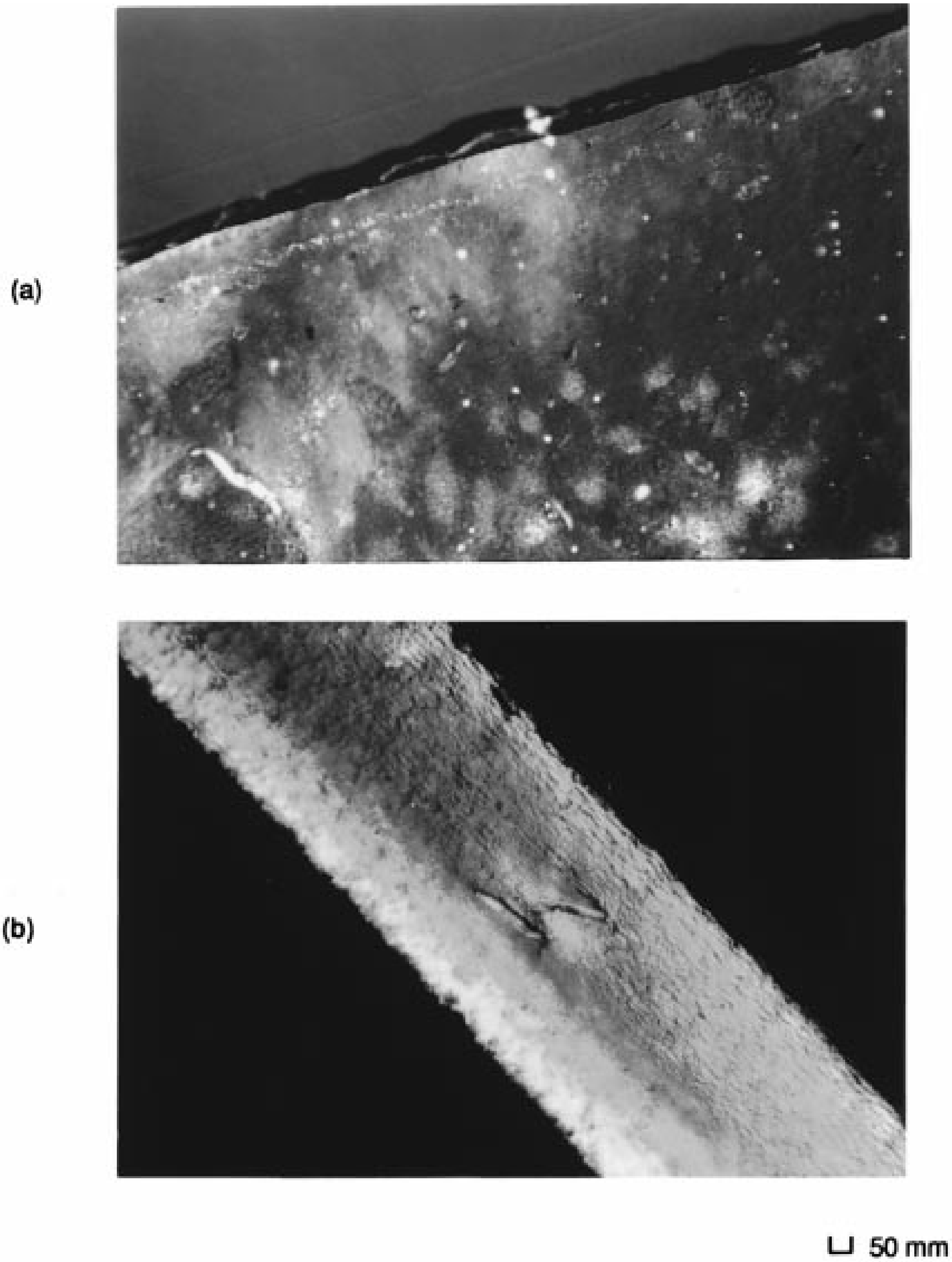

Figure 3. (a) Piece of swollen TEA (amylomaize VII, 85% DS) film in chloroform before orientation; magnification: 350×. (b) Piece of dried TEA (amylomaize VII, 85% DS) film after orientation; magnification: 350×.

9, uniaxial orientation gave films with substantial improvements in the parallel direction and this improvement increased with increase in extension ratio during drying. There were no increases, and possibly even decreases, however, in the perpendicular directions, for either tensile strength or modulus. In contrast, it can be seen that biaxial orientation yielded more striking changes. At a similar extension ratio, the improvements in mechanical properties were almost twice as large, relative to the improvements obtained on the uniaxial oriented samples in the orientation direction. This was probably due to the fact that after biaxial orientation, not only different layers had chains and domains aligned into a given direction, but also their directions were presumably different in different layers. Given these observations, biaxial orientation would be more interesting commercially since even relatively small stretching ratios during drying were sufficient to produced much-improved properties in all directions within the plane of the film.

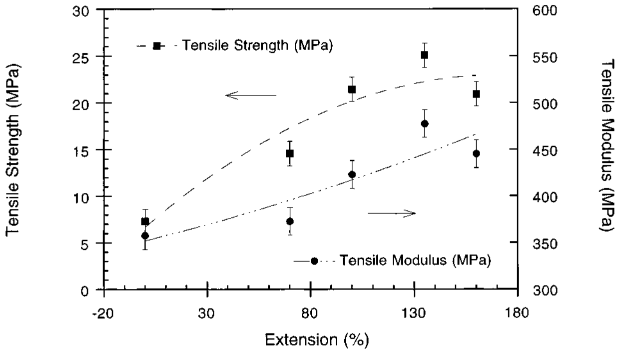

Figure 4. Tensile strength (■) and modulus (●) as a function of extension ratio during drying for uniaxially oriented films prepared from TEA (amylomaize VII) (90% DS, air-dried).

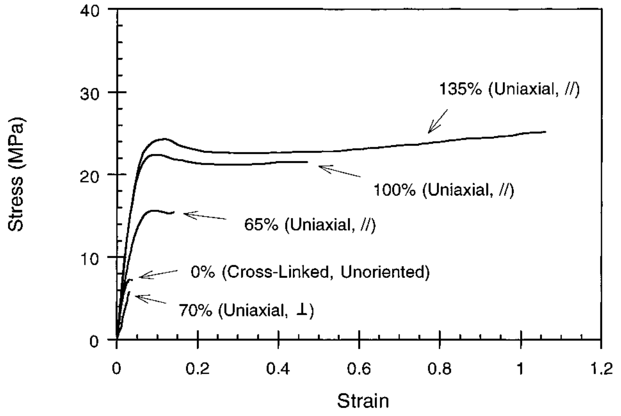

Figure 5. Stress–strain behavior of uniaxially oriented films prepared from TEA (amylomaize VII, 90% DS, air-dried).

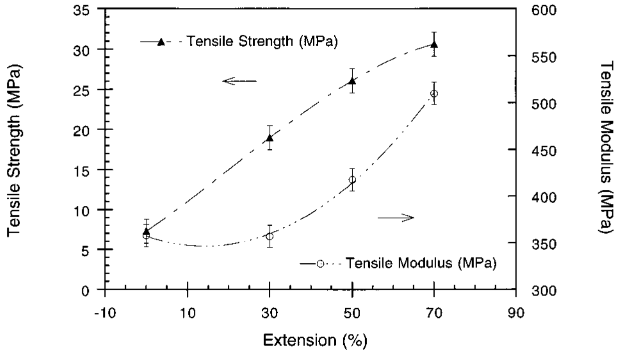

Figure 6. Tensile strength (▲) and modulus (○) as a function of extension ratio during drying for biaxially oriented films prepared from TEA (amylomaize VII), 90% DS, air-dried).

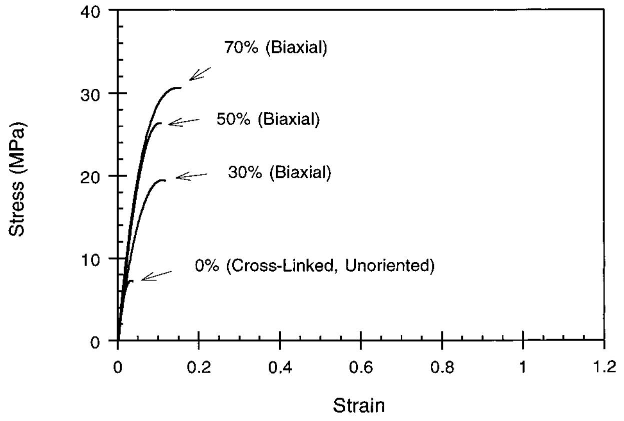

Figure 7. Stress–strain behavior of biaxially oriented films prepared from TEA (amylomaize VII, 90% DS, air-dried).

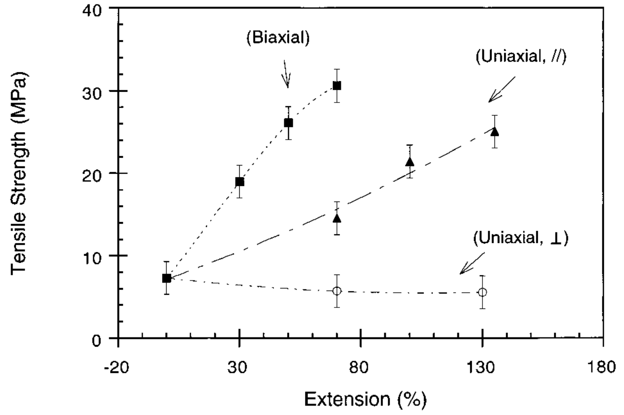

Figure 8. Tensile strength as a function of extension ratio during drying for uniaxial and biaxial orientation for films of TEA (amylomaize VII, 90% DS, air-dried).

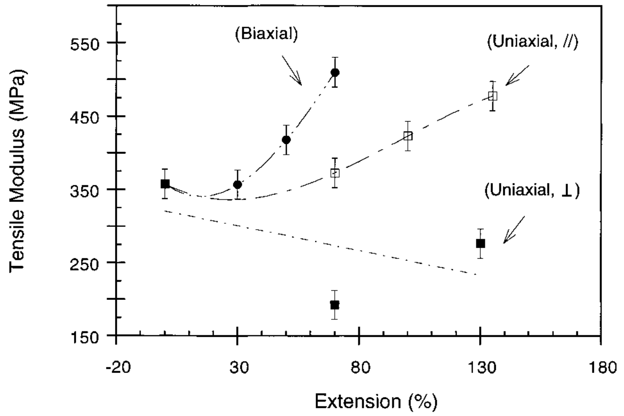

Figure 9. Tensile modulus as a function of extension ratio during drying for uniaxial and biaxial orientation for films of TEA (amylomaize VII, 90% DS, air-dried).

Birefringence of the Oriented Triethylamylose Films. Since for all these TEA (amylomaize VII) films, the mechanical properties increased with increase of the extension ratio during drying, it was interesting to study the correlation between the degree of orientation and the extension ratio during drying. Measurements of birefringence, a classical method for characterizing orientation,[35] was used for this purpose. The larger the birefringence, the higher the degree of orientation.

Figure 10 shows tensile strength and birefringence as functions of extension during drying for amylose ether films prepared from amylomaize VII with a degree of substitution of 85% and dried under ambient conditions. As can readily be seen, tensile strengths increased with increase in extension ratio from 0 to 135%, as did the birefringence. Obviously, the increase in extension during drying usually increased the alignments of the chains and the anisotropic domains, resulting in the observed increases in birefringence and mechanical properties.

Influence of the Solvent-Removal Method on Mechanical Properties. In the above orientation procedure, the solvent was removed from the oriented TEA (amylomaize VII) films by allowing it to evaporate

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[35] White, J. L.; Cakmak, M. In *Encyclopedia of Polymer Science and Engineering*; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Kroschwitz, J. I., Eds.; John Wiley & Sons: New York, 1987; Vol. 10, p 614.

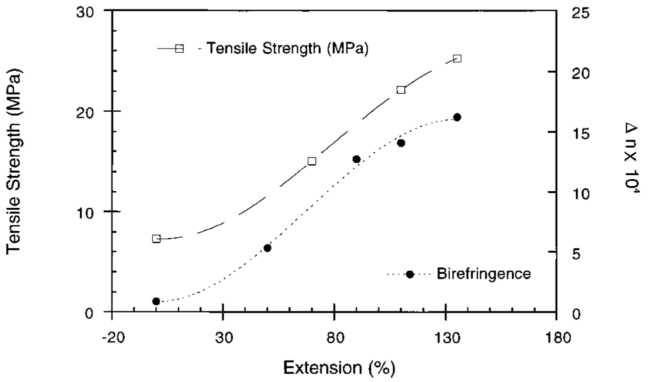

Figure 10. Tensile strength (□) and birefringence (●) as functions of extension during drying for uniaxially oriented TEA (amylomaize VII, 85% DS, air-dried).

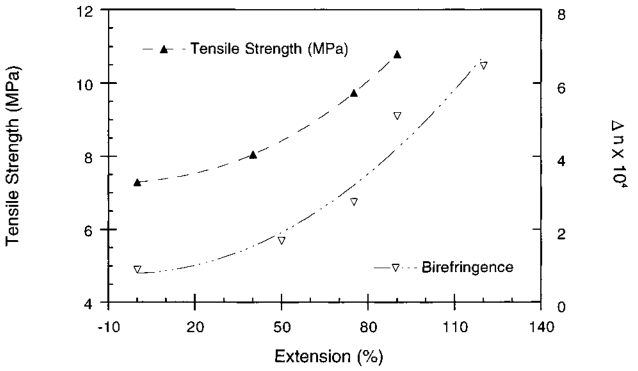

Figure 11. Tensile strength (▲) and birefringence (▽) as functions of extension during drying for uniaxially oriented TEA (amylomaize VII, 85% DS, coagulation for removal of solvent).

under ambient conditions. The rate of the evaporation had to be kept low to prevent inhomogeneous shrinkage in the direction perpendicular to the stretching. Usually several days were required to obtain a dried film without cracking, and this would be too long for large-scale production.

A different approach was investigated for removing the solvent more rapidly, namely, coagulation. Coagulation processes are widely used in industry to obtain films and fibers from polymer solutions,[36] for example, by "wet spinning". Film formation by coagulation depends on the differential solubility of polymers in a blend of solvents and nonsolvents and on the solubility changes resulting from concentration changes of any added materials. For example, consider solvents *A* and *B* as a good solvent and a poor solvent (or nonsolvent), respectively, for polymer Y. A polymer solution of Y is prepared in *A* and extruded into a bath of solvent mixture of *A* and *B*. The concentration difference causes diffusion of *A* into the bath and *B* into the polymer solution. As the concentration of *B* increases and that of *A* decreases, the polymer becomes less and less soluble and eventually deswells, yielding the desired unswollen film. Changes of pH or the use of supersaturated solutions may also be sufficient to reverse the solubility or to change the chemical nature of a polymer in solution, transforming it into an insoluble, stable film.

The first step in adapting this approach to the orientation procedures involved the selection of the poor solvent or nonsolvent. Since the TEA films were swollen in chloroform, a nonsolvent with good miscibility with chloroform was required. Petroleum ether was chosen because of its poor solvent power for triethylamylose, low cost, low boiling point, ready availability, and good miscibility with the swelling solvent chloroform.

The second step involved selecting the appropriate apparatus for performing the coagulation process. Since the key feature of the orientation technique required drying the stretched films at constant length (or at constant force) to preserve the long-range ordering, the deformed specimens had to be kept at constant length during the entire coagulation process. In this experiment, the TEA (amylomaize VII, 85% DS) films were deformed in a manner similar to the previous cases and fixed at two ends on a Teflon sheet. They were then submerged into a large tray containing petroleum ether and were observed to become more and more cloudy from the polymer precipitations. After about 30 min, the specimens were taken from the coagulation bath to allow the small amount of petroleum ether to evaporate. These samples were usually cloudier than those finished by the air-dry process.

Mechanical properties were also measured for the samples finished by the coagulation process. As shown in Figure 11, the tensile strength increased monotonically with increase in extension ratio during drying, as did the birefringence. Although the mechanical properties of both the air-dried samples and the coagulation-finished samples increased monotonically with increase in extension ratio during drying, the tensile strengths for the coagulated samples were considerably lower than those obtained by air-drying. The differences are presumably due to decreases in orientation, as characterized by differences in birefringence. This is consistent with the observation that the films obtained from coagulation had lower birefringence. This might be due to the presence of microprecipitations during the coagulation process which interfered with the desired long-range ordering.

It should be stressed, however, that for these coagulation specimens, only low ranges of stretching ratios were achieved (from 40 to 90%). Samples could be deformed to higher stretching ratios but broke upon being submerged in the petroleum ether. The rapid change in the nature of solvents presumably caused uneven stresses in these highly deformed samples, with premature cracking. Although the coagulation process yielded less than optimal improvements in mechanical properties in this case, these samples still exhibited moderate ranges of tensile strengths (7.3−10.9 MPa), which were comparable to those of low-density polyethylene. It may be possible to achieve better properties by exerting closer control over the immersion technique, diffusion time, and most importantly the ratio of the solvent to coagulants.

The differences between those two drying processes could be further illustrated by some results obtained by scanning electron microscopy (SEM). Figure 12 shows the surfaces of the samples obtained by the two solvent-

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(36) Park, H. C.; Mount, E. M. In *Encyclopedia of Polymer Science and Engineering*; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Kroschwitz, J. I., Eds.; John Wiley & Sons: New York, 1987; Vol. 10, p 103.

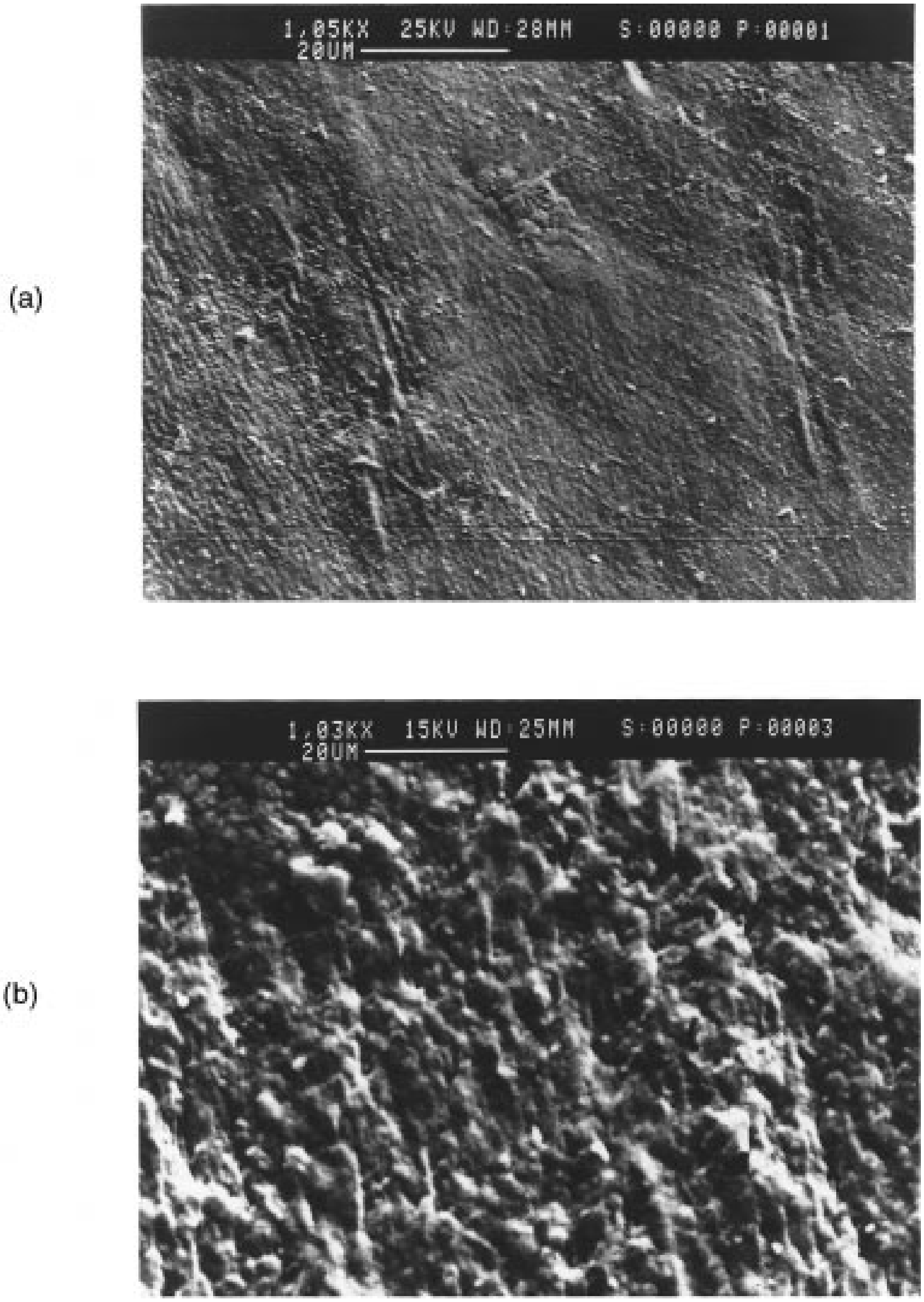

Figure 12. SEM microphotographs of uniaxially oriented TEA (amylomaize VII, 85% DS) finished by (a) air-drying; (b) coagulation process.

removal methods. The surface of the film air-dried under ambient condition was relative smooth, but the one obtained by coagulation clearly showed a rougher surface. The particles observed were probably microprecipitates, an observation that is consistent with results obtained on other commercial polymers finished by the coagulation process.[36]

Conclusions

In this second part of the three-part investigation, several types of cross-linking reactions were studied, all leading to starch−ether films that had glass transition temperatures above room temperature and were very brittle in the dry state. The diisocyanate curing method was used to obtain lightly cross-linked TEA films suitable for orientation and mechanical property measurements. It was demonstrated that the network structure imposed did not interfere with mesophase formation at low cross-linking densities. Diisocyanate cross-linked triethylamylose (TEA) films were therefore uniaxially oriented by a mechanical force applied in the swollen state, with the solvent removed by drying in the deformed state. There were dramatic improvements in mechanical properties, especially toughness. Biaxial orientation was shown to have the advantages of giving almost 2-fold improvements relative to uniaxial orientation, with improvements in all directions in the plane of the film. It was also found that removal of the solvent by coagulation instead of air-drying usually resulted in smaller improvements and rougher film surfaces. In all cases, the improvements in mechanical properties increased monotonically with increase in extension ratio during drying, due to increases in orientation of the chains and the anisotropic domains in which they reside.

Acknowledgment. The authors gratefully acknowledge the financial support provided by the National Science Foundation through Grant DMR-9422223 (Polymers Program, Division of Materials Research). W.Z. also thanks the University of Cincinnati Chemistry Department for a fellowship.

CM970562Q