Novel High-Performance Materials from Starch. 1. Factors Influencing the Lyotropic Liquid Crystallinity of Some Starch Ethers

Wenyan Zhao,† Andrzej Kloczkowski, and James E. Mark*

Department of Chemistry and the Polymer Research Center, University of Cincinnati,
Cincinnati, Ohio 45221-0172

Burak Erman

School of Engineering and the Polymer Research Center, Bogazici University and the
TUBITAK Advanced Polymeric Materials Research Center, Bebek 80815, Istanbul, Turkey

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Starch ethers having side chains of various lengths, controlled and uniform degrees of substitution, and various amylose/amylopectin ratios were obtained by a one-step chemical modification of starch. Factors influencing the phase behavior of these starch ethers were carefully examined, and the ones having short side chains were found to exhibit lyotropic liquid crystallinity over wide ranges in degree of substitution and amylose/amylopectin ratio. The starch ethers having longer side chains failed to exhibit phase separation due to insufficient degrees of substitution. They generally possessed enhanced hydrophobicity relative to starch yet still had controllable numbers of free hydroxyl groups. The liquid crystallinity thus produced makes them ideal candidates for a novel processing technique designed specifically for permanently orienting main-chain, lyotropic, liquid-crystalline polymers.

Introduction

Biodegradable polymers have become of great interest, particularly over the past few years, owing to environmental concerns over the disposal of synthetic polymers.[1−11] The challenge in replacing conventional synthetic polymers is to design materials that exhibit structural and functional stability during processing, storage, and use, yet are susceptible to microbial and environmental degradation upon disposal, without any adverse environmental impacts.[3]

There are several ways of designing such biodegradable materials. The most obvious approach is modification of existing naturally occurring polymers, which are typically susceptible to biodegradation but usually do not have adequate physical properties. For example, many efforts have been made to increase the hydrophobicity of natural polymers without significantly reducing their inherent biodegradability.[12−15] The second approach involves blending synthetic polymers and biodegradable materials, with the former being viewed as improving the mechanical properties of the latter, or the latter improving the biodegradability of the former. For example, there have now been numerous studies using starch to modify otherwise nondegradable thermoplastics.[3,16−22] Another approach is to modify the basic structures of petroleum-based synthetic polymers, for

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* Corresponding author. E-mail: jemark@ucbeh.san.uc.edu, http://jemcom.crs.uc.edu/.

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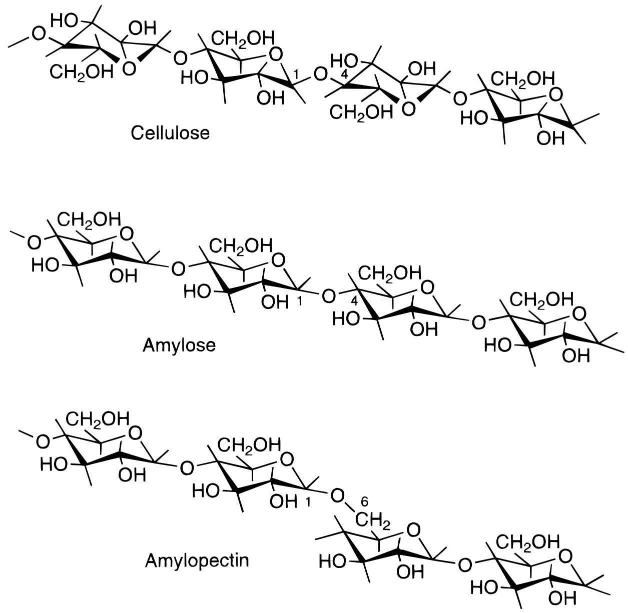


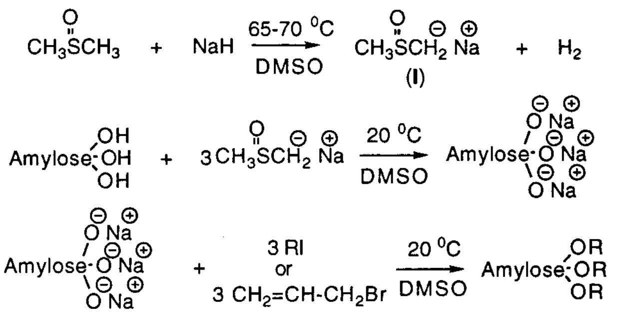
Figure 1. Structures of cellulose and starch (amylose, amylopectin).

example, by incorporating hydrolyzable linkages in both backbones and side groups.[22−24]

Although blending may be a relatively inexpensive method for generating biodegradable materials, the properties of the resulting composites are usually less than optimal.[3,22] Often, these so-called biodegradable blends show decreased mechanical properties, relative to those of the neat, typically hydrophobic synthetic polymers. The biodegradation rate seemingly increases, from removal of the dispersed phase (such as starch) from a blended film, but the synthetic polymer part still remains unattacked by water or enzymes. In addition, all these starch-blended films tend to absorb water, and this remains a drawback in many applications. Less hydrophobic petroleum-based polymers [such as polycaprolactone and poly(vinyl alcohol)] are also readily available from traditional plastics companies,[22] but these materials are generally significantly more expensive than commodity resins.

To balance performance, biodegradability, and cost (which often move in opposing directions in biodegradable material designing), recent efforts have focused more on chemical modification of existing natural polymers such as polysaccharides and proteins.[3] For example, numerous starch derivatives have now been synthesized, and site-selective modifications have been reported.[3,25,26] Starch is of particular interest since it occurs naturally as minute granules in the roots, seeds, and stems of many types of plants, including corn, wheat, rice, millet, barley, and potatoes. In fact, it constitutes the main carbohydrate reserve of plants. It consists of two polysaccharides, amylose and amylopectin, which can be separated on the basis of their differences in solubility.[27] Their structures are shown schematically in Figure 1. Amylose is mainly linear in structure, apart from the α linkage (axial C−O bond at carbon 1), and therefore resembles cellulose (the structure of which is also given in the figure). Amylopectin is highly branched through carbon 6 and is believed to consist of chains of 20−25 glucose units linked through carbons 1 and 4, as in amylose, but with the chains connected to each other through the 1, 6 linkage. There is usually 3 times as much amylopectin as amylose in natural starch, although much higher proportions of one or the other occur in certain plants.[3]

Scheme 1. Alkylation of Amylose Using Methylsulfinylmethylcarbanions



R is Me, Et, *n*-Pr, *n*-Bu, *n*-Pe, or *n*-He

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Because of its highly branched structure and permeability, starch is usually not used in the preparation of plastic objects or fibers, as is done with cellulose.[27] With regard to chemical modification, polysaccharides generally have a resistance to complete O-methylation, probably due to their three-dimensional structures, in which hydroxyl groups are highly restricted with intermolecular and intramolecular hydrogen bonds. The many known methods[28−32] for methylation of carbohydrates merely resulted in highly degraded products, since the reaction had to be repeated several times to complete the substitutions. In 1970, however, Husemann et al. developed a method[32] using methylsulfinylmethylcarbanions[33,34] to methylate polysaccharides. This had the great advantage of giving high degrees of substitution in one step, with little degradation. Following their model work, we prepared a series of starch ethers with various chain lengths, degrees of substitution, and amylose/amylopectin ratios to study their lyotropic liquid crystallinity and processability.[35] The reactions employed are shown in Scheme 1.

These starch derivatives acquire enhanced hydrophobicity relative to starch, which enables them to maintain performance during processing, storage, and use. The

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existence of free hydroxyl groups on the starch−ether backbones (due to intentionally incomplete substitutions) allows these materials to interact with water and enzymes to initiate biodegradation upon disposal. In addition, they acquire lyotropic liquid crystallinity,[36] which allows them to be processed by a novel orientation technique designed specially for such main-chain lyotropic liquid-crystalline polymers.[37−50] In this first part of a three-part study, reaction conditions are investigated in depth to obtain controllable and uniform degrees of substitution; the phase behavior of these starch ethers is subsequently examined with regard to the degree of substitution, side chain length, amylose/amylopectin ratio, etc.

Experimental Details

General Methods and Materials. All syntheses were performed under nitrogen or argon atmosphere. Dimethyl sulfoxide was purchased from Aldrich and distilled over CaH_2 before use, and *n*-pentane was purchased from Fisher and distilled over NaH before use. All alkyl iodides and allyl bromide were purchased from Aldrich and distilled over $MgSO_4$ before use, and sodium hydride (as a 60% mineral oil suspension) was purchased from Aldrich and used as received. Pure amylose (essentially free of amylopectin, from potato starch) was purchased from Sigma and washed with methanol to remove any residual butanol before use. Two kinds of amylose were generously donated by the American Maize Co. and were used as received. They were of very high molecular weight (MW = 1 000 000 g mol^{-1}) and had known compositions ("Amylomaize VII": 70% amylose, and "Amylomaize V": 50% amylose) Four kinds of starch (from corn, rice, wheat, and potato, respectively) were purchased from Sigma, as was amylopectin; all were used as received.

^{1}H NMR spectra were recorded at 250 MHz on a Bruker AM-250 spectrometer, and ^{13}C NMR spectra were recorded at 60 MHz on the same instrument. Chemical shifts were reported in δ values with tetramethylsilane (TMS) as the internal standard. ^{1}H NMR data were tabulated by chemical shifts, multiplicity, and number of protons, and all ^{13}C NMR spectra were proton decoupled. The inverse HETCOR NMR spectra were recorded at 400 MHz on a Bruker AM-400 spectrometer, and infrared spectra were recorded on a Perkin-Elmer 1600 Series Fourier transform infrared spectrometer.

General Synthesis Procedures for Starch Ethers. Amylomaize VII was chosen as the starch source to typify the reaction conditions for this study. Reaction conditions varied somewhat in the case of different starch sources.

*Methylsulfinylmethylcarbanion (**I**).* **I** is prepared according to the procedure of Husemann.[32−34]

2,3,6-Trialkylamylose. A solution of 5 g of amylose in 250 mL of DMSO was mixed with **I** under argon. The mixture solidified to a greenish gray gel instantly but became liquid again after being stirred vigorously for 5−10 min. After continuous stirring for two additional hours, 1.5 times the stoichiometric amount of alkyl iodides (or allyl bromide) relative to starch was added at 20 °C over 2 h. The solution first became greenish and then turned dark yellow and, after complete addition of alkyl iodides, light yellow. The mixture was stirred continuously for two more hours before being poured into 0.5 L of iced water. The trialkylamylose separated out as pale yellow precipitates or light brown viscous gels (depending on the alkyl chain length). The crude products were washed several times with a sodium bisulfide solution to remove trace amounts of alkyl iodides. Purification was carried out by reprecipitating the trialkylamylose toluene solution from petroleum ether.

NMR data: *Trimethylamylose*: ^{1}H ($CDCl_3$) δ (ppm) 1.19−1.81 (m, 15H), 5.54 (s, 1H). ^{13}C ($CDCl_3$) δ (ppm) 58.89, 59.15, 60.06, 70.16, 70.71, 71.40, 82.11, 82.86, 96.75. *Triethylamylose*: ^{1}H ($CDCl_3$) δ (ppm) 1.15 (m, 9H), 1.31−1.89 (m, 12H), 5.62 (s, 1H). ^{13}C ($CDCl_3$) δ (ppm) 14.90, 15.36, 15.61, 66.50, 67.43, 67.81, 68.56, 69.99, 71.71, 80.08, 81.31, 95.97. *Tripropylamylose*: ^{1}H ($CDCl_3$) δ (ppm) 0.88 (s), 1.23 (s), 1.41−4.00 (m), 5.01 (s, br), 5.70 (s, br). *Tributylamylose*: ^{1}H ($CDCl_3$) δ (ppm) 0.88 (s), 1.22 (s), 1.32 (s), 1.20−4.20 (m), 5.07 (s, br), 5.79 (s, br). *Tripentylamylose*: ^{1}H ($CDCl_3$) δ (ppm) 0.87 (s), 1.29 (s), 1.57 (s), 1.20−4.10 (m), 5.0 (s, br), 5.69 (s, br). *Trihexylamylose*: ^{1}H ($CDCl_3$) δ (ppm) 0.86 (s), 1.26 (s), 1.56 (s), 1.20−4.10 (m), 5.0 (s, br), 5.66 (s, br). *Triallylamylose*: ^{1}H (DMSO) δ (ppm) 1.16−4.30 (m), 5.15−5.34 (m), 5.52−5.66 (m), 5.88 (t). *Tris(ethylallyl)amylose*: ^{1}H ($CDCl_3$) δ (ppm) 1.15 (t), 1.32−4.11 (m), 5.01−5.17 (m), 5.62 (s, br), 5.81 (s, br).

Estimation of Degree of Substitution. The degree of substitution (DS) for alkylation of amylose (starch) was estimated by integrating the proton NMR spectrum of the methine proton peaks on the C-4 carbon. The areas (*A*) of amylose C-4 proton (δ around 5.1 ppm) and trialkylamylose C-4 proton (δ around 5.6 ppm) were used to calculate the degree of substitution.

$$\mathrm{DS} = 3(A_{\text{trialkylamylose C−4 proton}})/(A_{\text{amylose C−4 proton}} + A_{\text{trialkylamylose C−4 proton}})$$

percent degree of substitution: %DS = 100(DS/3)

Cross-Polarized Optical Microscopy. Samples for optical studies were examined 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 phase separations of the starch ethers. The magnification of the lens used was 10× or 40×, and the camera lens has an additional magnification of 2.5×.

Determination of Glass Transition Temperatures of the Starch Ethers. 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.

Results and Discussion

Methylation of Amylose. Methylation was carried out using methylsulfinylmethylcarbanion as a base,

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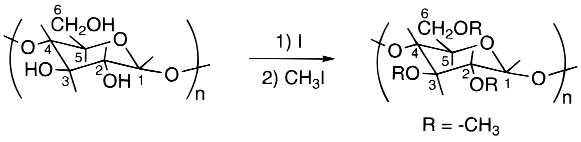
Table 1. Reaction Conditions vs Degree of Substitution for Methylation[a,b]

NaH:amylose ratio (mol)	time with CH_3I (h)	degree of substitution (%)
4.5:1	3	100
3:1	3	100
3:1	16	100

[a] The amylose source was amylomaize VII. [b] For the above reactions, the reaction time between methylsulfinylmethylcarbanion and amylose DMSO solution was held to 2 h; the addition of iodomethane was done at room temperature.



^{13}C NMR: in DMSO-d_6	^{13}C NMR: in $CDCl_3$
C-1: 100.24 ppm	C-1: 96.75 ppm
C-2: 72. 15 ppm	C-2: 71.40 ppm
C-3: 71.42 ppm	C-3: 82.11 ppm
C-4: 78.91 ppm	C-4: 82.86 ppm
C-5: 71.80 ppm	C-5: 70.71 ppm
C-6: 60.60 ppm	C-6: 70.10 ppm

Figure 2. ^{13}C NMR assignment of TMA.

with the carbanion being formed by the procedure of Corey and Chaykowsky.[33,34] It was found that this method could be easily applied, provided that care was exercised in the handling of the hydride. The washed pure sodium hydride had to be kept under anhydrous conditions to prevent explosions, and mild heating (60–70 °C) is recommended for accelerating the reaction between the sodium hydride and DMSO. In contrast to the report by Husemann,[32] a stoichiometric amount of NaH (NaH/amylose = 3) was enough to complete the methylation. Results are presented in Table 1.

The reaction time between amylose and the methylsufinylmethylcarbanion was held to about 2 h; this was long enough to complete the formation of the amylosetrialkoxy carbanion but short enough to prevent degradation of the amylose backbone.[32] Methylation was usually complete within 3 h after the addition of the iodomethane. Although the trimethylamylose (TMA) could be precipitated from the reaction mixture in iced water, it was water dispersible at room temperature. Solvent extraction was usually employed to obtain high yields. NMR spectroscopy confirmed the structure of TMA,[51,52] and the ^{13}C assignments are shown in Figure 2.

The most interesting feature of the ^{13}C NMR spectrum of TMA was that, after methylation, the chemical shift of the bridged carbon C-1 was shifted upfield (from 100.24 ppm of amylose to 96.75 ppm of TMA). From the ^1H NMR spectrum, it was found that the chemical shift of the methine hydrogen on C-1 shifted downfield after methylation (from 4.82 ppm in amylose to 5.54 ppm in TMA). This information was critical for identification of the triethylamylose (TEA) structure and, subsequently, estimation of its degree of substitution.

Table 2. Reaction Conditions vs Degree of Substitution for Ethylation[a,b]

NaH:amylose ratio (mol)	time with CH_3CH_2I (h)	degree of substitution (%)
4.5:1	3	50
4.5:1	5	66
4.5:1	10	76
4.5:1	15	87
4.5:1	18	95
3:1	18	65

[a] The amylose source was amylomaize VII. [b] For the above reactions, the reaction time between methylsulfinylmethylcarbanion and amylose DMSO solution was held to 2 h; the reaction temperature during addition of iodoethane was 20 ± 0.5 °C.

Completely substituted TMA was not suitable for the network preparation that was planned, because of the total absence of free hydroxyl groups. Furthermore, because of its solubility in water (or water dispersibility), it generally required elaborating the solvent extraction technique for isolation of the product, an unattractive feature for large-scale procedures. A search for new cross-linkable ethers of amylose (starch) having possible commercial interest prompted us to examine a number of other alkylation procedures.

Ethylation of Amylose. Ethylation was very different from methylation, in that complete ethylation was impossible to achieve using the same reaction conditions.[35] As is well-known, the alkylation is an S_N2 nucleophilic substitution and, because of the steric effect of iodoethane in the transition state, ethylation is much slower than methylation.[53] Reaction conditions must be carefully controlled to obtain highly substituted triethylamylose, as described in Table 2. A methylsulfinylmethylcarbanion-to-amylose ratio of 4.5 was necessary to catalyze the ethylation. A stoichiometric ratio (carbanion/amylose = 3/1) was insufficient, resulting in triethylamylose with lower degrees of substitution (usually DS ≤ 2.0). Higher degrees of substitution could be achieved, but that required very fine control of the addition rate of iodoethane and the reaction temperature. Very good temperature control was critical for obtaining optimal efficiencies and good correlation between degree of substitution and reaction time for the amylosetrialkoxy carbanion and iodoethane.

A large exotherm was observed as the rate of addition was increased, but temperature control could be achieved by external cooling and by adjusting the rate of addition of iodoethane. Lower temperatures (<18 °C) had to be avoided, to prevent solvent solidification, since the melting point of DMSO is 18.3 °C. Ethylation would have been much slower under the resulting heterogeneous conditions. For these reasons, a constant temperature of 20 ± 0.5 °C was chosen for the addition of iodoethane. Under these conditions, there is a good correlation between the degree of substitution and the reaction time for the amylosetrialkoxy carbanion and iodoethane, as documented in Table 2. This correlation was reproducible, providing the same starch source was used.

At high degrees of substitution, triethylamylose (from amylomaize VII) displayed excellent solubility in organic solvents (such as chloroform, toluene, etc.), similar to

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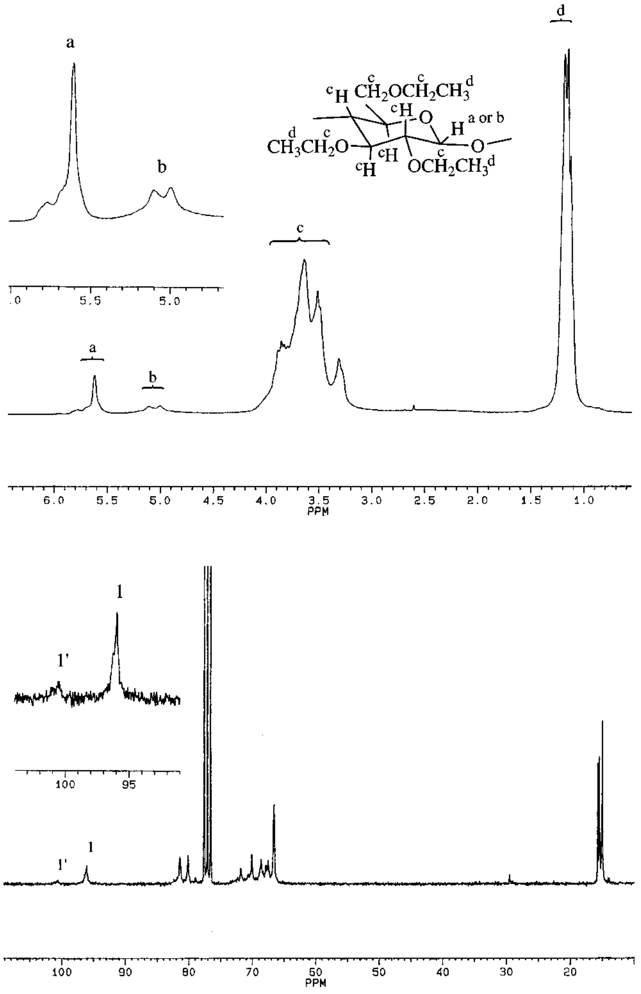

Figure 3. ^{1}H (top) and ^{13}C (bottom) NMR spectra of a partially substituted TEA.

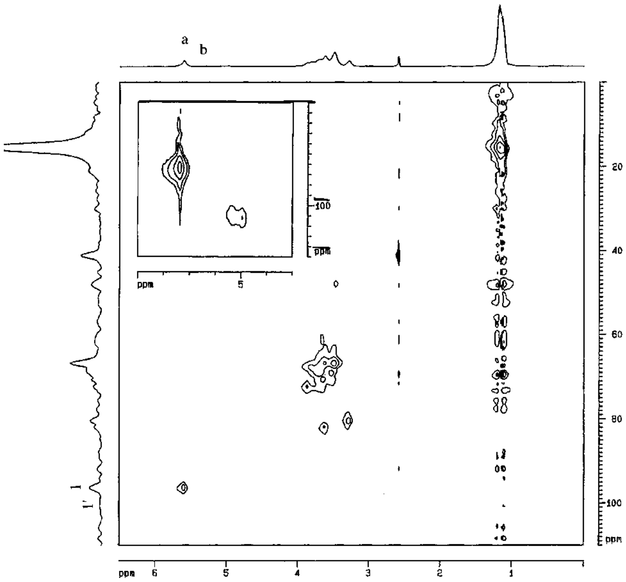

Figure 4. Inverse HETCOR NMR spectrum of a partially substituted TEA.

that of completely substituted trimethylamylose. At low degrees of substitution (<1.5), its solubility in organic solvents decreased, but it remained soluble in DMSO and slightly soluble in water. For degrees of substitution ranging from 1.8 to 2.85, the triethylamylose could be readily separated from the reaction mixture in iced water, in moderate-to-high yields. Usually the lower the degree of substitution, the higher the water dispersibility. Since the product was isolated by collecting the precipitated material from the water, lower degrees of substitution also resulted in lower yields. Usually, chloroform extraction was needed to obtain lower-substituted triethylamylose in high yield. All the amylose triethyl ethers were washed several times with a sodium bisulfide solution to remove trace amounts of iodoethane.

Estimation of Degree of Substitution of the Starch Ethers. The degrees of substitution of TEA samples described above were determined using ^{1}H NMR spectroscopy, and Figure 3 shows the ^{1}H NMR spectrum of the partially substituted triethylamylose. At early stages in the synthesis, the assignment of peaks *a* (5.62 ppm) and *b* (5.0−5.11 ppm) in the spectrum caused confusion. At first, one of the *a* and *b* peaks was considered as free hydroxyl groups from the incomplete substitution of the TEA. Adding D_2O to the TEA DMSO solution did not reduce or diminish the peak areas, which ruled out the possibility of free hydroxyl protons. The anomeric configuration of the methine proton on C-1 was subsequently proposed, but it seemed to contradict the observation of only one peak of the methine proton in the completely substituted TMA ^{1}H NMR spectrum (Figure 3).

Inverse heteronuclear chemical shift correlation (HETCOR) was employed to identify the nature of those two peaks (*a* and *b*). The HETCOR spectrum correlates the peaks of a ^{1}H spectrum with the peaks of a ^{13}C spectrum and thus shows the specific proton attachment to each ^{13}C. The standard HETCOR approach detects the ^{1}H and ^{13}C correlations, but due to the low sensitivity and long relaxation time of ^{13}C, the experiments normally take a long time. This problem is circumvented in the inverse HETCOR in which the C−H correlation is detected via the proton spectrum. In a typical representation, the ^{1}H spectrum is presented on the horizontal axis and the ^{13}C broad-band-decoupled spectrum is presented on the vertical axis. The ^{1}H−^{13}C correlation is shown by a cross-peak contour at the intersection of a horizontal line drawn from a proton peak or multiplet and a vertical line drawn from a ^{13}C peak. From Figure 4, it can be seen that the *a*, *b* peaks in the ^{1}H NMR spectrum are correlated to the 1 and 1′ peaks on the ^{13}C NMR spectrum, suggesting they were all methine protons.

Combined with the information obtained from the completely substituted TMA ^{1}H NMR spectrum, it was not difficult to conclude that the *a* proton peak was the methine proton on C-4 due to the substitution on the backbone, and the *b* peak was the methine proton on C-4 due to incomplete substitution. The degree of the substitution (as percent DS) was estimated by integrating the areas under peaks *a* and *b*.

Determination of the Glass Transition Temperature of Triethylamylose. Glass transition temperatures T_g were determined using the differential scanning calorimetry results. Figure 5 presents the DSC curve for the highly substituted TEA (amylomaize VII, 90% DS), and shows the T_g at approximately 40 °C. Compared to the T_g of starch (approximately 230 °C), the substitutions onto the starch are seen to dramati-

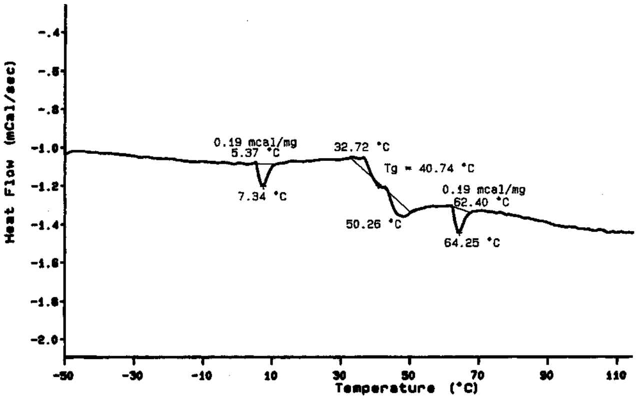

Figure 5. DSC curve for a highly substituted TEA film.

Table 3. Dissolution Time in DMSO for Starches from Different Sources[a]

amylose source	dissolution time in DMSO
amylomaize VII	2−3 days
amylomaize V	3−4 days
pure amylose	overnight
corn starch	5 days
wheat starch	5 days
rice starch	5−7 days
potato starch	5−7 days
amylopectin	more than a week

[a] The concentration was 5 g of polymer in 250 mL of DMSO.

Table 4. Reaction Conditions vs Degree of Substitution for Ethylation Using Starches from Different Sources[a,b]

amylose source	time with CH_3CH_2I (h)	degree of substitution (%)
amylomaize VII	18	~95
pure amylose	18	~65
amylomaize V	18	~80
corn starch	18	~80
wheat starch	18	~80
rice starch	18	~80
potato starch	18	~70
amylopectin	18	~80

[a] The amylose source was amylomaize VII. [b] For the above reactions, the reaction time between methylsulfinylmethylcarbanion and amylose DMSO solution was held to 2 h; the reaction temperature during addition of iodoethane was 20 ± 0.5 °C.

Table 5. Reaction Conditions vs Degree of Substitution for Other Alkylations[a,b]

R in RI or RBr	time with RI (h)	degree of substitution (%)
$-(CH_2)_2CH_3$	10	~10
$-(CH_2)_3CH_3$	10	~20
$-(CH_2)_4CH_3$	18	~20
$-(CH_2)_5CH_3$	18	~20
$-CH_2-CH=CH_2$	18	~100

[a] The amylose source was amylomaize VII. [b] For the above reactions, the reaction time between methylsulfinylmethylcarbanion and amylose DMSO solution was held to 2 h; the reaction temperature during the addition of RI was 20 ± 0.5 °C.

cally reduce its T_g, because of an increase in free volume and reduced hydrogen bonding.[54]

Ethylation of Starch Having Various Amylose/Amylopectin Ratios. The correlation between the reaction time and the degree of substitution did not hold exactly when a different amylose source was used. First, an increase in the amylopectin ratio in the starting material usually increased the time required for the starch to dissolve in DMSO. Table 3 summarizes the dissolution times generally required for starch with various amylose/amylopectin ratios.

It generally took about 3−5 days to dissolve all the amylose (or starch) used for this study in DMSO. The only exception was pure amylose, which usually dissolved in DMSO instantly. The complete dissolution of starch in DMSO was essential since it directly affected uniformity in degree of substitution, and homogeneity of the final products. As can be seen from Table 3, the larger the amount of amylopectin in the starting material, the longer it took for the starting material to dissolve in DMSO. This was understandable, given the highly branched nature of amylopectin.

For ethylation, the same reaction conditions generally gave a lower degree of substitution in the case of a starch source having a higher amylopectin content, as demonstrated in Table 4. This was also due to the fact that amylopectin is highly branched in comparison to amylose, and nucleophilic addition by alkyl iodides would therefore be more difficult upon increase of amylopectin content. Potato starch had a more dramatic decrease in its degree of substitution. Its DMSO solution exhibited an unusually high viscosity relative to the other starch−DMSO solutions at the same concentration (5 g polymer/250 mL DMSO). Higher dilutions were necessary to achieve higher degrees of substitution in potato starch ether. For pure amylose, the degree of substitution was also low, and its DMSO solutions also exhibited unusually high viscosities. Fine control of the reaction temperature and addition rate of iodoethane were still critical for achieving higher degrees of substitution, regardless of the amylose source.

Other Alkylations of Starch. Etherification with longer alkyl chains also was attempted using the Husemann method.[35] These long-chain amylose ethers no longer separated from the reaction mixture in iced water as precipitates, but as viscous gels. ^1H NMR spectra indicated a very low degree of substitution (as summarized in Table 5), which was definitely due to the poor nucleophilicity of the longer-chain alkyl iodides.[53] Tripropylamylose (TPrA), tributylamylose (TBuA), tripentylamylose (TPeA), and trihexylamylose (THA) displayed good solubility in chloroform and toluene. Understandably, the longer alkyl chains facilitated the solubility of these amylose ethers in organic solvents, presumably through both their hydrophobic characters and increased entropies of mixing.

Films could be cast from chloroform solutions of the longer-chain amylose ethers. The tripropyl-, tributyl-, and tripentylamylose films were still very brittle, similar to those cast from trimethyl- and triethylamylose, but the trihexylamylose one exhibited at least some toughness.

In addition, triallylamylose was synthesized using the same Husemann method. Usually, complete substitution was obtained due to the high reactivity of allyl bromide. Triallylamylose was slightly soluble in DMSO but not soluble in toluene, chloroform, or dimethylformamide, in contrast to an earlier report.[55] Since some hydrosilation cross-linking of these materials was

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(54) Huber, A. E.; Stayton, P. S.; Viney, C.; Kaplan, D. L. *Macromolecules* **1994**, *27,* 951.

(55) Lee, K. S.; Gilbert, R. D. *Carbohydr. Res.* **1981**, *88,* 162.

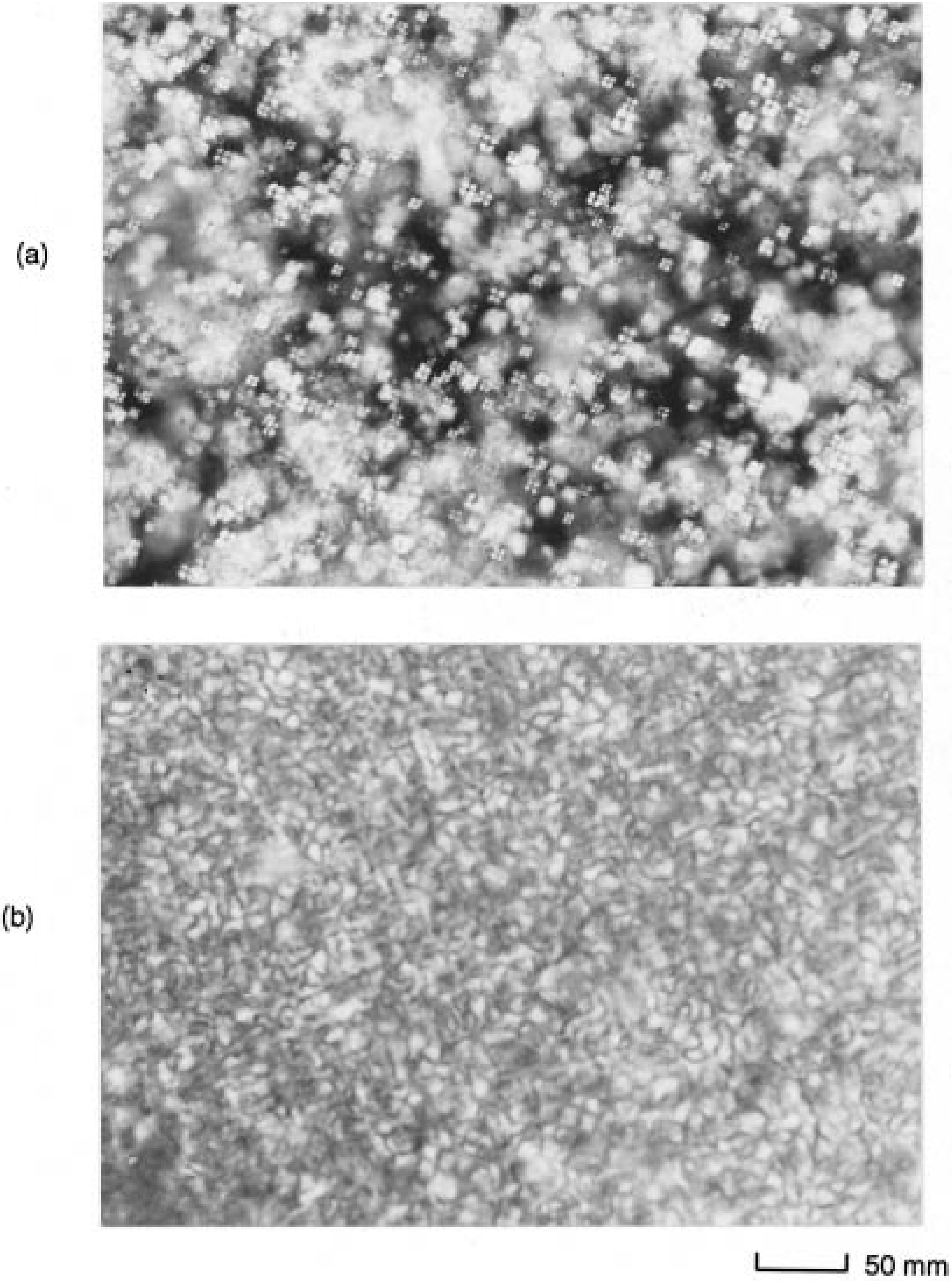

Figure 6. (a) Microphotograph of 40 wt % TEA (amylomaize VII, 55% DS) in toluene; magnification: 350×. (b) Microphotograph of 40 wt % TEA (amylomaize VII, 95% DS) in toluene; magnification: 350×.

planned, some triethylamylose having a small percentage of allyl side chains to facilitate this was also synthesized. This was done by premixing a small amount of the allyl bromide into the iodoethane. The properties of tris(ethylallyl)amylose were similar to those of triethylamylose; for example, this polymer also displayed high solubilities in toluene and chloroform.

Liquid-Crystalline Behavior of the Starch Ethers. The mesophase birefringence of TMA and TEA was first observed by Zugenmaier.[36] In this section, the corresponding liquid-crystalline behavior of the present starch ethers was studied in depth with regard to the effects of degree of substitution, amylose/amylopectin ratio, side-chain length, and types of solvents employed.

The trimethylamylose used in the phase-behavior study was completely substituted. For a 30 wt % TMA chloroform solution, only anisotropic spherulites dispersed in an isotropic background were observed. With increase in concentration, the anisotropic phase became predominant, and the mesomorphic structure started to be discernible when the concentration exceeded 40 wt % for TMS chloroform solution. Concentration played a very important role in the formation of the liquid-crystalline phase for these starch ethers, as in

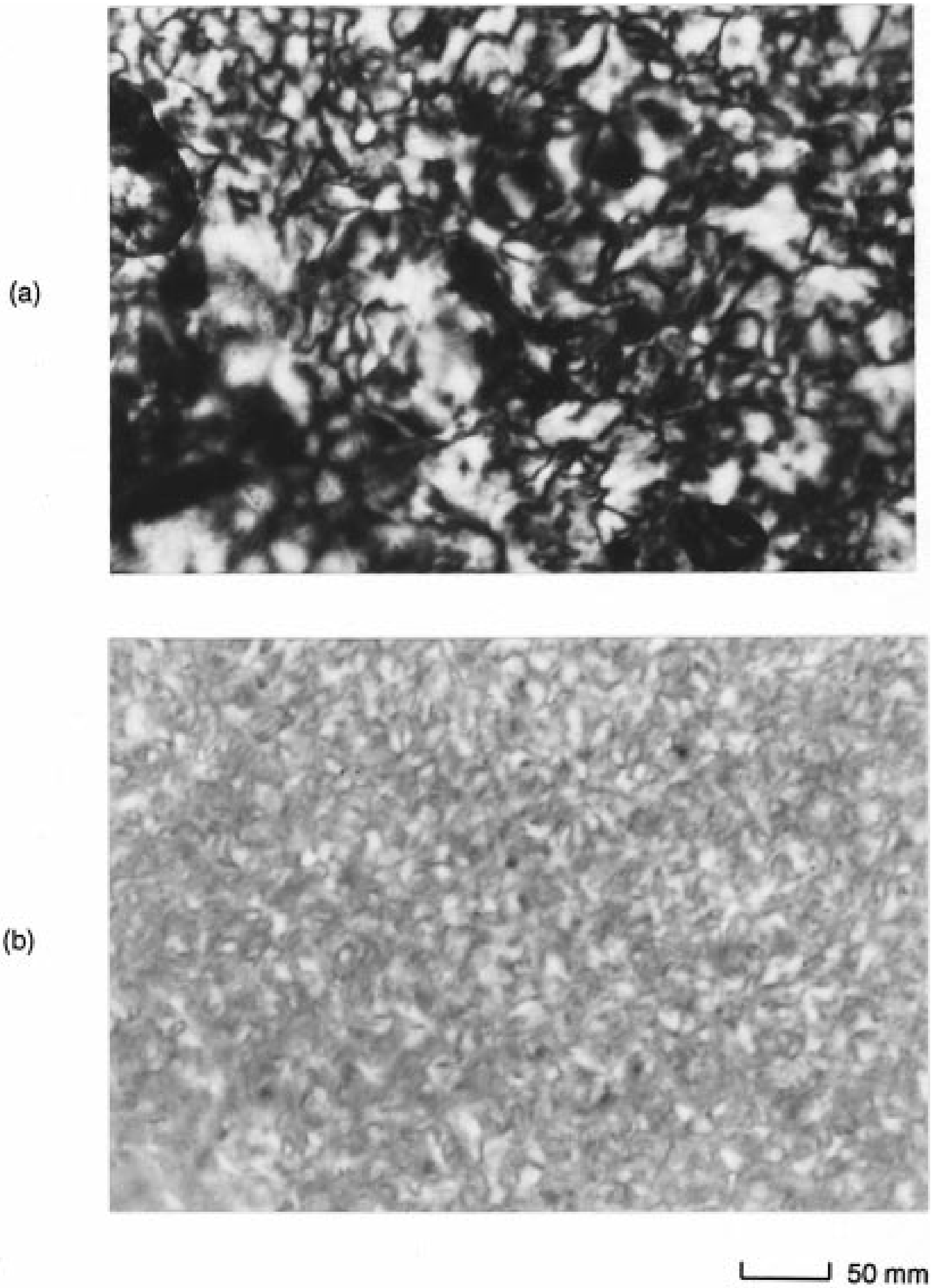

Figure 7. (a) Microphotograph of 40 wt % TEA (amylomaize V, 80% DS) in toluene; magnification: 350×. (b) Microphotograph of 40 wt % TEA (pure, 70% DS) in toluene; magnification: 350×.

many other lyotropic systems. As is well-known, lyotropic liquid-crystalline polymers exhibit phase separation above a certain critical concentration v_2*.[56] Below this concentration, the solution is isotropic, but at this concentration and above, an anisotropic phase appears.

For the triethylamylose with a low degree of substitution (DS = 55%), only anisotropic spherulites of the TEA (amylomaize VII) in the isotropic phase were observed at a concentration of 30 wt %. Increasing the concentration (40 wt % TEA) did increase the number of spherulites in the mixture (shown in Figure 6a). Complete formation of the anisotropic phase was not observed, however, for the TEA with a degree of substitution of 55%, presumably because of the low degree of substitution. Degree of substitution regulated the liquid-crystalline behavior of starch ethers in two ways: solubility and intermolecular repulsion. With

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(56) Ciferri, A. *Liquid Crystallinity in Polymers*; VCH Publishers: New York, 1991.

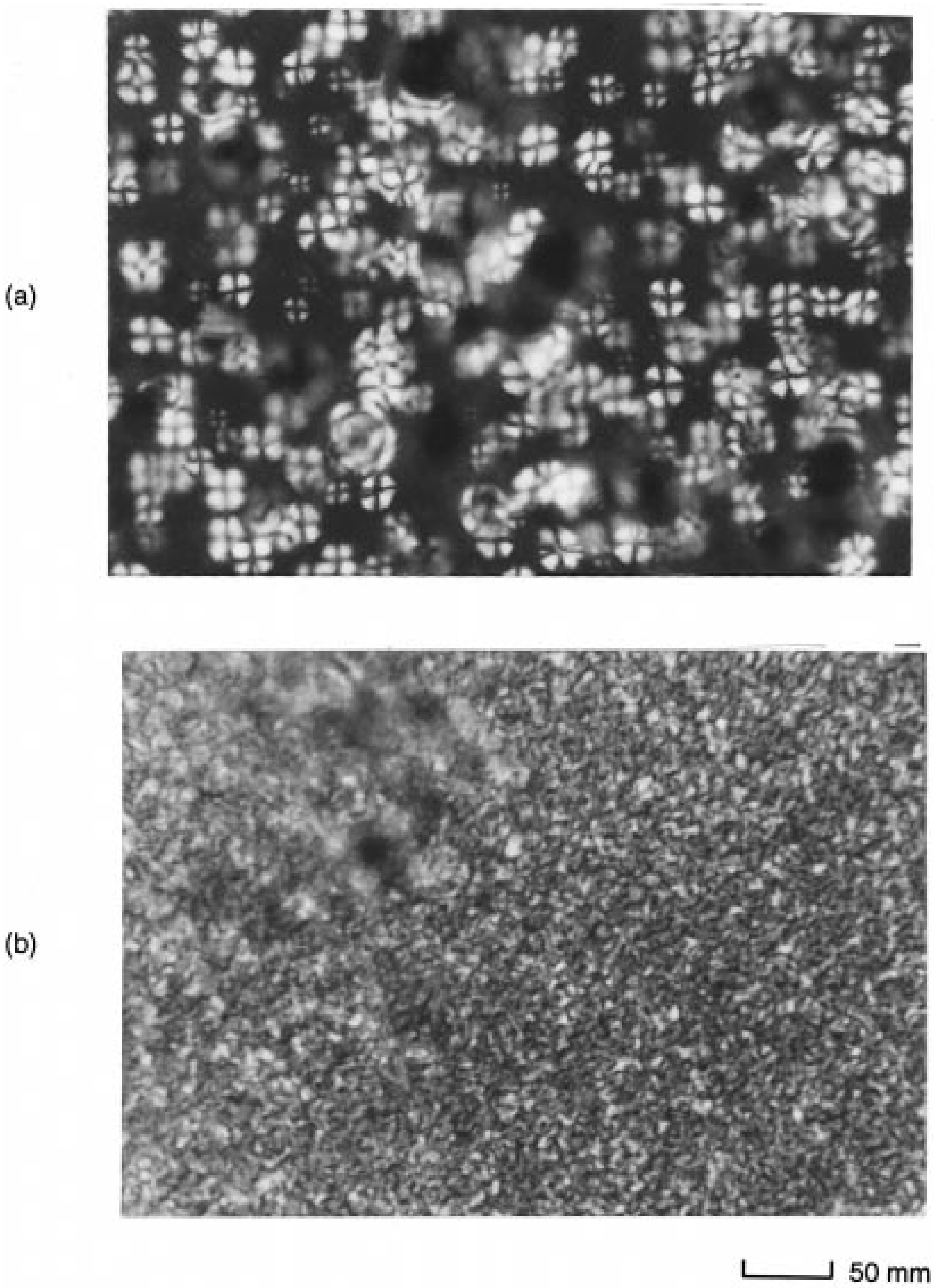

Figure 8. (a) Microphotograph of 40 wt % TES (corn, 55% DS) in toluene; magnification: 350×. (b) Microphotograph of 40 wt % TES (corn, 80% DS) in toluene; magnification: 350×.

increase in degree of substitution, the hydrophobicity of the starch derivatives usually increased significantly, which would allow the polymers to surpass their critical concentrations v_2* to exhibit phase separation. Also, with increase in degree of substitution, the interactions between polymer chains decreased due to the reduction in hydrogen bonding from free hydroxyl groups. Since the formation of liquid-crystalline phases occurs largely as a result of intermolecular repulsion,[57] a higher degree of substitution would presumably be needed before the TEA would self-assemble into ordered domains.

At higher degrees of substitution, phase separation was more obvious. In the case of triethylamylose having DS = 95%, strongly anisotropic phases were present in both chloroform and toluene. Figure 6 is the micropho-

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(57) Flory, P. J. *Proc. R. Soc. London* **1956**, *234A*, 71.

tograph for 40 wt % TEA (amylomaize VII, 95% DS) in toluene. The brilliant birefringence indicated the desired lyotropic liquid crystallinity for this starch ether having a high degree of substitution.

Microphotographs were also obtained for TEA (amylomaize VII) with degrees of substitution of 90, 85, 75, and 65% (not shown), and all four TEA−toluene solutions exhibited brilliant mesomorphic birefringence. It can be concluded that above a certain degree of substitution [about 60% DS for TEA (amylomaize VII)], the materials exhibit mesomorphic birefringence in the vicinity of certain concentrations (around 40 wt % for all the triethylamylose studied).

In addition to investigating the effect of degree of substitution, the liquid-crystalline behavior was studied with regard to the amylose/amylopectin ratio in the starting material. This is important since the linear amylose was believed to be responsible for the formation of liquid-crystalline phases. It was observed that triethylamylose synthesized from pure amylose gave phase separations that were similar to those of the triethylamylose prepared from amylomaize VII (70% amylose and 30% amylopectin, MW = 1 000 000). This is shown in Figure 7. A brilliant anisotropic phase was observed in toluene solution for TEA (pure) having a degree of substitution of 70%. For TEA made from amylomaize V (50% amylose and 50% amylopectin; 80% DS), a Schlieren texture of the anisotropic phase was also observed.

Four types of starch triethyl ethers were synthesized from corn, rice, wheat, and potato starch (all approximately 30% amylose and 70% amylopectin). Mesomorphic birefringence was observed for all of these starch ethers with a degree of substitution above 55%. This is illustrated in Figure 8a, which is a microphotograph of the 40 wt % TES (corn, 55% DS) in toluene. As can readily be seen, a significant number of anisotropic spherulites were dispersed in the isotropic media, similar to what was found for the solution of TEA (amylomaize VII, 55% DS). With increase in degree of substitution, the anisotropic phase completely formed, due to the enhanced solubility and reduction in hydrogen bonding. This is shown in Figure 8b, which is for TES from corn, but at 80% DS. Obviously, a relatively high degree of substitution was needed for the starch−ether chains to self-assemble, regardless of the amylose/amylopectin ratios.

Microphotographs of the 40 wt % TES (wheat, 80% DS), 40 wt % TES (rice, 80% DS), and 40 wt % (potato, 80% DS), toluene solutions (not shown) all exhibited brilliant birefringence, as in the case of triethylamylose (from amylomaize VII). Only triethylamylopectin (80% DS) failed to exhibit mesomorphic birefringence. This suggested that the existence of a certain amount of linear amylose was essential for the formation of the mesomorphic birefringence.

TPrA, TBuA, TPeA, and THA were also studied in this way (microphotographs not shown). As mentioned earlier, all of these longer-chain amylose ethers displayed excellent solubility in chloroform, and their 40 wt % chloroform solutions were very viscous and dark brownish. Unfortunately, however, none of the samples exhibited any liquid-crystalline behavior, probably due to insufficient substitution. The existence of a large number of free hydroxyl groups in the backbones probably enhanced the intermolecular interactions and thus interfered with the formation of a mesophase.

As mentioned earlier, triallylamylose was not soluble in toluene, chloroform, or other organic solvents. This greatly limited the study of its liquid-crystalline behavior, since high-concentration solutions were impossible to prepare.

Of the materials prepared, those that were most promising with regard to ability to form mesophases were further investigated, in the following paper, with regard to orientation techniques for improving mechanical properties.

Conclusions

In this first part of the three-part study, starch triethyl ethers with controlled and reproducible degrees of substitution and various amylose/amylopectin ratios were prepared in high yields, using the Husemann method. The syntheses were quite convenient, and the aqueous product-isolation procedures employed would facilitate large-scale production. The liquid-crystalline behaviors of these polymers were investigated with regard to degree of substitution, amylose/amylopectin ratio, solvent type, and side-chain length. It was found that above a certain degree of substitution (>60% DS), the starch triethyl ethers exhibited brilliant birefringence over wide ranges of amylose/amylopectin ratios. The corresponding triethyl ether of the amylopectin failed to exhibit liquid-crystalline phases due to the absence of linear amylose chains. Longer-chain amylose ethers ($n = 3-6$ C atoms) were also prepared, but they failed to exhibit phase separation due to insufficient degrees of substitution. The highly substituted triethylamylose had a glass transition temperature of approximately 40 °C, dramatically below that of starch itself (230 °C).

The enhanced hydrophobicity of these starch ethers will enable them to maintain performance during processing, storage, and use. In addition, they should still exhibit substantial biodegradability because of the existence of free hydroxyl groups. Finally, the acquired lyotropic liquid crystallinity over a wide range of degree of substitution and amylose/amylopectin ratio will allow them to be processed by some novel orientation techniques, as described in the second part of this investigation.

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