**LIQUID CRYSTALLINE THERMOSETTING POLYIMIDES
FINAL REPORT
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ABSTRACT:

Phase separation of rodlike reinforcing polymers and flexible coil matrix polymers is a common problem in formulating molecular composites. One way to reduce phase separation might be to employ liquid crystalline thermosets as the matrix material. In this work, functionally terminated polyimide oligomers which exhibit lyotropic liquid crystalline behavior were successfully prepared. Materials based on 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl and 3,3',4,4'-biphenylenetetra-carboxylic dianhydride have been synthesized and characterized.

INTRODUCTION:

The ideal molecular composite system consists of single rigid rod molecules very finely dispersed in some sort of matrix polymer which can be either thermoplastic or thermosetting in nature. To date, all matrix materials employed have been flexible coil type polymers which exhibit isotropic behavior. This is in contrast to the reinforcing polymers which are rodlike and generally exhibit anisotropic behavior. In 1978 Flory¹ predicted that mixtures of rodlike polymers and flexible coil polymers would spontaneously phase separate and this is in fact observed experimentally.²⁻⁵ Such phase separation drastically reduces the strengthening potential of the reinforcing polymer and thus reducing phase separation in molecular composites has been the focus of much recent research. Flory's theoretical work assumed athermal solutions, concentrating solely on entropic contributions to the free energy of mixing. Thus a large portion of molecular composite research has focused on increasing enthalpic interactions between reinforcement and matrix materials.⁶⁻⁹ Work on improving the entropy of mixing has also been pursued to some extent.⁹⁻¹¹

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One way of modifying the entropy of mixing that is only beginning to be explored is the use of anisotropic matrix materials, liquid crystalline thermosets (LCTs) in particular. The 1978 theory of Abe and Flory¹² predicted the phase behavior of mixtures of rodlike molecules in a solvent, again in the absence of enthalpic interactions. The theory indicated that for mixtures of rodlike molecules with drastically different aspect ratios, multiphase behavior should be expected over a large portion of the ternary phase diagram. For mixtures of rodlike molecules in which the aspect ratios are closer together, the predicted miscibility gap is larger although multiphase regions should still exist. The theory is supported by recent work of Benicewicz and coworkers, who mixed short rod LCTs and a long rod reinforcing polymer.¹³ Though multiphase behavior was observed, substantial interpenetration of phases had occurred in the mixtures. It was felt that this interpenetration of phases could probably be attributed to enthalpic interactions not addressed by the theory.

If enthalpic interactions are taken into account along with the more favorable entropic effects of mixing longer rod thermosets with the reinforcing polymer, a fairly large miscibility gap should be realized, thus yielding a more ideal molecular composite system. This research has thus concentrated on the preparation of longer rod LCTs. These LCTs were functionalized polyimide oligomers based on polyimides which apparently exhibit lyotropic behavior as prepared. The oligomers were prepared from 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl and 3,3',4,4'-biphenylenetetracarboxylic dianhydride. Molecular weight control was achieved either through addition of excess diamine to yield amine-terminated oligomers or through the addition of a monofunctional endcapper, maleic anhydride, to afford maleimide-terminated oligomers. These oligomers were prepared using several different synthetic procedures and were evaluated for completeness of imidization, thermal stability, other thermal transitions of interest (e.g. T_g , T_m , LC transitions, etc.), lyotropic liquid crystalline behavior, and molecular weight. This report will discuss the synthesis and characterization of these polyimide oligomers.

EXPERIMENTAL:

Synthesis:

2,2'-Bis(trifluoromethyl)-4,4'-diaminobiphenyl was prepared according to the method of Rogers *et al.*¹⁴; 3,3',4,4'-biphenylenetetracarboxylic dianhydride was obtained from Occidental Chemical Company and used as received; maleic anhydride was obtained from Aldrich and used as received. *m*-Cresol, isoquinoline, 1-methyl-2-pyrrolidinone (NMP) and *o*-dichlorobenzene were distilled before use.

Reaction in *m*-cresol/isoquinoline

To a solution of 4.5 mmol 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl in 15 mL *m*-cresol with 2% (v/v) isoquinoline was added a mixture of 4.5 mmol 3,3',4,4'-biphenylenetetracarboxylic dianhydride and 2.7 mmol maleic anhydride. This solution was stirred at room temperature in an inert atmosphere for approximately 4 hours. The mixture was then heated to ~200°C and maintained at that temperature for 4 hours. The resulting product was precipitated into a mixture of ethanol and ice using a high speed blender and isolated by suction filtration. The polymer was then dried at 130°C under vacuum.

Reaction in NMP/pyridine/acetic anhydride

To a solution of 5.85 mmol 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl in 15 mL NMP was added 4.5 mmol 3,3',4,4'-biphenylenetetracarboxylic dianhydride. This mixture was stirred overnight in an inert atmosphere at room temperature to yield the amine-terminated polyamic acid.

To the solution of polyamic acid in NMP was added 2.7 mmol maleic anhydride. The mixture was stirred for 4 hours after which 17.55 mmol pyridine and 17.55 mmol acetic anhydride (3:1 mol excess of each component) were added. Stirring was continued in an inert atmosphere at room temperature until gelation occurred in the sample. The gel was allowed to stand at room temperature overnight before the product was precipitated into a mixture of ethanol and ice using a high speed blender. Collection of the product by suction filtration afforded the product which was then dried at 90°C under vacuum.

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Reaction in NMP/*m*-cresol

To a solution of 4.5 mmol 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl in 13.5 mL distilled NMP was added 2.7 mmol maleic anhydride. After stirring for 45 min, 4.5 mmol 3,3',4,4'-biphenylenetetracarboxylic dianhydride was added. This solution was stirred overnight at room temperature. 1.5 mL *m*-cresol was added to the reaction mixture which was then heated to 150°C for 4.5 hours. The product was precipitated into ethanol/ice using a high speed blender, collected by suction filtration and dried at 95°C under vacuum.

Reaction in NMP/*o*-dichlorobenzene

To a solution of 4.5 mmol 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl in 13.5 mL distilled NMP was added 2.7 mmol maleic anhydride. After stirring for 30 min, 4.5 mmol 3,3',4,4'-biphenylenetetracarboxylic dianhydride was added. This solution was stirred for 4 hours at room temperature. 1.5 mL *o*-dichlorobenzene (*o*-DCB) was then added to reaction mixture, the flask fitted with a Dean Stark apparatus filled with *o*-DCB and heated to 165°C for 24 hours. The product was precipitated into ethanol/ice using a high speed blender, collected by suction filtration and washed with acetone overnight.

Copolyimide synthesis

A solution of 2.25 mmol 2,5-diaminotoluene sulfate in 8 mL distilled NMP was placed in a round bottom flask and 4.5 mmol triethylamine added to free the diamine for reaction. A solution of 2.25 mmol 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl in 7 mL NMP was then added followed by 4.5 mmol 3,3',4,4'-biphenylenetetracarboxylic dianhydride. This solution was stirred at room temperature for 3 hours.

Triethylamine (1.9 mL) and acetic anhydride (1.27 mL) were then added to induce imidization. The reaction mixture was heated at 65°C overnight. After cooling for 4.5 hours, the product was precipitated in methanol/ice using a high speed blender, collected by suction filtration, extracted with methanol overnight, and dried at 130°C under vacuum.

Characterization:

Infrared spectra were collected using a Mattson Cygnus 100 FTIR Spectrometer at a resolution of 4 cm⁻¹. Samples were in the form of films cast onto KBr windows unless stated otherwise.

Differential scanning calorimetry (DSC) was performed using a Perkin-Elmer DSC-7 under nitrogen atmosphere. Heating rates used were 20°C/min for isolated samples and 10°C/min for gels. The quench rate was 200°C/min when a quench was employed.

Thermogravimetric analysis (TGA) was performed using a Perkin-Elmer TGA-7 at a heating rate of 10°C/min in both flowing nitrogen and static air atmospheres. Decomposition temperatures are reported as the onsets of major decomposition, char yields are reported at 800°C.

Thermomechanical analysis (TMA) was performed on a Perkin-Elmer TMA-7 using the expansion probe and dilatometer accessory. Sample sizes were 50 mg or larger, the static force was 1 mN and the heating rate was 10°C/min. Glass transition temperatures are reported as the onset of large displacement of the probe.

Oligomer molecular weight distributions were obtained using a Waters 150C Gel Permeation Chromatograph with NMP as the mobile phase. Injector, column and pump temperatures were 30°C, and the flow rate was 0.5 mL/min. Polystyrene calibration standards were employed and a universal calibration curve constructed using values for intrinsic viscosity determined from dilute solution viscosity measurements performed on 0.5%(w/v) solutions of polymer in NMP at 30.0°C using a Cannon Micro viscometer.

Optical microscopy was performed using a Nikon Labophot microscope equipped with crossed polarizers, a Kofler hot stage, and a camera assembly. Samples were prepared by pressing either hot polymer solutions or gels between glass slides.

RESULTS AND DISCUSSION:

Oligomers:

The work of Harris' group has indicated that several polyimides prepared from 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl and various dianhydrides show potential liquid crystalline phases in solution as prepared.¹⁵ Several of these high molecular weight polymers were prepared in our laboratory and a likely candidate chosen for the preparation of functionalized oligomers for use in molecular composites. The oligomer chosen for further study was based on 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl (PFMB) and 3,3',4,4'-biphenylene-tetracarboxylic dianhydride (BPDA). Molecular weight was

controlled by addition of excess diamine to the reaction or by the addition of a monofunctional endcapper, in this case maleic anhydride, to the system. The reaction stoichiometry required to achieve the desired molecular weight (~2000) was calculated using the following expression:

$$X_n = \frac{N_A(1 + N_B)/2}{N_B(1 - N_A/N_B)/2}$$

where X_n is the number of monomer units (not repeat units) in the polymer, N_A is the number of functional groups of type A and N_B is the number of functional groups of type B. Extent of reaction is assumed to be equal to 1 and $N_A/N_B < 1$. The general reaction is shown in Scheme 1.

Scheme 1. Preparation of polyimide oligomers

Maleimide-terminated oligomers were prepared using four different synthetic procedures. Additionally, amine-terminated materials were prepared using the *m*-cresol/isoquinoline and NMP/pyridine/acetic anhydride procedures. These materials were characterized for completeness of imidization, thermal stability and any other thermal transitions of interest (e.g. T_g , T_m , LC transitions, etc.). Once a promising material was identified, it was analyzed for liquid crystalline behavior and then for molecular weight.

Completeness of imidization was evaluated using infrared spectroscopy, in particular, the relative magnitudes of imide characteristic bands and amic acid characteristic bands. Bands characteristic of imide structures include: asymmetric C=O stretch $\sim 1780\text{ cm}^{-1}$, symmetric C=O stretch $\sim 1725\text{ cm}^{-1}$, C-N

stretch at $\sim 1370\text{ cm}^{-1}$, and an imide ring bending mode $\sim 735\text{ cm}^{-1}$. Bands characteristic of amic acid structures include O-H stretch absorbances in the range $2500\text{--}3500\text{ cm}^{-1}$, N-H stretch $\sim 3328\text{ cm}^{-1}$, amide C=O stretch (amide I) $\sim 1685\text{ cm}^{-1}$, and N-H bending (amide II) $\sim 1620\text{ cm}^{-1}$. Other useful bands include the olefin C-H stretch, characteristic of the maleimide endgroup, $\sim 3100\text{ cm}^{-1}$, and the aromatic ring C=C stretching mode $\sim 1491\text{ cm}^{-1}$.

The infrared spectra of maleimide-endcapped materials prepared by the four synthetic methods are shown in Figure 1. Spectrum (a) corresponds to the reaction in *m*-cresol/isoquinoline, (b) to the reaction in NMP/pyridine/acetic anhydride, (c) to the reaction in NMP/*m*-cresol and (d) to the reaction using NMP/*o*-dichlorobenzene. Characteristic imide bands are noted on spectrum (a), characteristic amic acid bands are noted on spectrum (b). From these spectra, it is clear that imidization is most efficient for the reaction taking place in *m*-cresol containing 2%(v/v) isoquinoline. There is little evidence of amic acid remaining in the system. Only a small absorbance at 1620 cm^{-1} can be attributed to amic acid. The next most effective reaction appears to be the standard two-step procedure, that in NMP/pyridine/acetic anhydride. It is apparent, however, that a substantial amount of amic acid still remains. Heating of the reaction mixture had no major effect on the extent of imidization. Amic acid bands that are evident include a broad absorbance between 2700 and 3500 cm^{-1} and a band at 1678 cm^{-1} . Reactions in NMP/*m*-cresol and NMP/*o*-dichlorobenzene were not as effective in producing fully imidized material. There is excess dianhydride remaining in the system in both cases, as evident from the anhydride C=O stretch band appearing at 1853 cm^{-1} (indicated in spectrum (c)). The presence of excess dianhydride is most likely due to the stoichiometry employed in these reactions. However, extraction with acetone removes very little of this excess dianhydride from the product and adversely affects the thermal stability as indicated in Table 1. Broad absorbances from $2700\text{--}3500\text{ cm}^{-1}$ and other characteristic amic acid bands (1680 cm^{-1} , 1620 cm^{-1}) are also present in relatively large amounts as compared to the imide characteristic bands. It appears that a substantial amount of acidic solvent must be present for the reaction to proceed. The diamine used in these experiments is a relatively weak nucleophile due to the presence of the electron-withdrawing trifluoromethyl groups. Thus, the imidization step is more difficult and may possibly be encouraged by protonation of the -OH in the amic acid to yield a better leaving group in the

cyclization. Although the mechanism of the one-step synthesis is not yet known, the acidic nature of the *m*-cresol is expected to play a major role.

Thermogravimetric analysis provides additional data to support the conclusion that imidization is not complete for reactions in NMP/pyridine/acetic anhydride, NMP/*m*-cresol, and NMP/*o*-dichlorobenzene. All TGA thermograms of products from these three reactions show a weight loss $\sim 180^\circ\text{C}$ which corresponds to loss of the water of imidization. This weight loss is not observed for the oligomers obtained from the *m*-cresol/isoquinoline system. Information regarding thermal stability can also be obtained from the TGA traces. Table 1 summarizes the results of TGA experiments performed on the maleimide-encapped oligomers synthesized by each of the four methods described earlier. Results obtained for an analogous high molecular weight polymer are included for the purpose of comparison.

The infrared spectra of amine-terminated oligomers are shown in Figure 2. Spectra labelled (a)-(c) are from materials prepared in *m*-cresol/isoquinoline, spectrum (d) is from material prepared in NMP/pyridine/acetic anhydride. Imide characteristic bands are noted on spectrum (a), amic acid characteristic bands are noted on spectra (c) and (d). The spectra indicate that for the reaction in *m*-cresol/isoquinoline, imidization is quite efficient, the band at 1620 cm^{-1} being very small relative to imide C=O stretch bands at 1780 cm^{-1} and 1726 cm^{-1} . This was not the case, however, for the material prepared in NMP/pyridine/acetic anhydride. As in the case of the maleimide-terminated oligomer, there is significant amic acid remaining in the sample.

Thermogravimetric analysis again supports the conclusion that the imidization proceeds better in *m*-cresol than in other reaction systems. TGA results for amine-terminated oligomers are summarized in Table 2.

Optical microscopy was then employed to evaluate all oligomer/solvent systems for lyotropic liquid crystalline behavior. Only oligomers prepared in *m*-cresol/isoquinoline exhibited birefringence. The amine-terminated oligomer gels exhibited what appears to be a typical nematic texture in some regions of the gel. An example is shown in Figure 3. Heating of the gel led to flow in the system as well as to clearing of birefringence to yield an isotropic solution. DSC analysis of these gels showed a broad endothermic transition in the range 60°C to 120°C corresponding to the trends observed using optical microscopy. Annealing of the gels at 90°C for two hours led to sharpening of this broad endotherm, revealing two overlapping transitions, likely to be a gel-sol

transition and a liquid crystalline to isotropic transition. Similar behavior was reported in the literature for the analogous high molecular weight polymer.^{15b} It was also stated in the literature that it was impossible to separate the gel-sol and liquid crystalline to isotropic transitions.

In contrast, maleimide-terminated oligomer gels showed a texture which appears spherulitic in nature. This is shown in Figure 4. Upon heating, flow and clearing behavior similar to that of the amine-terminated oligomer gels was observed. DSC thermograms were also similar. However, on cooling, rather than returning to the spherulitic-type texture of the as-prepared sample, a nematic texture developed.

Several different concentrations of amine-terminated oligomer in *m*-cresol were evaluated by optical polarized light microscopy. Concentrations ranged from 2.5% (w/v) to the reaction mixture concentration of 21.4% (w/v). All solutions appeared biphasic as prepared with birefringent areas gradually disappearing upon heating for concentrations up to 7.5%. For concentrations of 10% (w/v) and higher, birefringence never completely disappeared up to the maximum temperature of 150°C. The cooling behavior was also interesting. Solutions of low concentration (2.5%, 5% and 7.5%) remained isotropic after cooling. The 10% solution seems to be a boundary sample, showing birefringence in some areas of the sample after cooling although the majority of the sample remained isotropic. In the samples of concentration greater than 10% (w/v), the entire sample became biphasic or totally birefringent during cooling.

DSC thermograms of the isolated oligomers were virtually featureless over the range 50-400°C. In some samples a feature was noted ~200°C which looked like a glass transition (T_g) and some of the maleimide-terminated oligomer showed an exothermic event ~260°C which may be due to thermally induced reaction of the maleimide double bonds. Thermomechanical analysis (TMA) was used to more accurately determine oligomer T_g s. All glass transitions occurred in the range 180°C to 225°C.

The oligomer materials which were identified earlier as potentially liquid crystalline materials were then evaluated for molecular weight using a combination of size exclusion chromatography and dilute solution viscosity measurements. Dilute solution viscosity measurements were performed for the purpose of constructing and using a universal calibration curve. The use of the universal calibration curve is required since the oligomers are rodlike in nature

as opposed to the polystyrene standards which are coil-like. Intrinsic viscosities were estimated as the average of the inherent and reduced viscosities determined from a solution of 0.5%(w/v) polymer in NMP at 30.0°C. The intrinsic viscosities obtained in this manner are only estimates since there are many possible sources of error. However, for determining an approximate molecular weight of the oligomers prepared for this research, these estimates should be sufficient to construct and use a universal calibration curve.

Representative chromatograms for amine-terminated and maleimide-terminated oligomers are shown in Figures 5 and 6, respectively. The universal calibration curve is shown in Figure 7. The amine-terminated oligomers showed multimodal distributions with the lowest molecular weight fraction dominating the composition. The molecular weight distributions may not really be multimodal, however. Since the endgroups of these materials are polar in nature, there is a possibility that material could be adsorbing onto the columns in the chromatograph causing the appearance of multimodal distributions. This possibility will be investigated by endcapping these oligomers with a nonreactive group and then repeating the experiment. In contrast to the amine-terminated oligomers, the maleimide-terminated oligomers exhibited single mode distributions, but the molecular weights appear to be quite a bit higher than expected based on the stoichiometric calculations performed earlier. There are two possible reasons for this: (1) Michael addition reactions (chain extension) between free amine groups and maleimide groups and (2) crosslinking of maleimide groups during synthesis. Crosslinking during synthesis might be expected since the reaction temperature of 200°C is very close to the crosslinking temperature for maleimide groups in commercially available materials. It was possible to dissolve a small amount of the material in deuterated N,N-dimethylformamide for proton nuclear magnetic resonance spectroscopy. The presence of maleimide groups was noted from the olefin proton resonance $\sim\delta 7$, but there were also some resonances in the region $\delta 2-4$ which could be due to aliphatic protons resulting after reaction of maleimide double bonds.

Molecular weight values obtained using the universal calibration curve are summarized in Table 3. Many of the calculated values for molecular weight obtained using the universal calibration are not reasonable. These values are well into the millions, unrealistic for condensation polymers under even the most ideal circumstances. However, for the lowest molecular weight fraction of

the amine-terminated oligomers, the molecular weight values are indeed reasonable, ranging from 2300 to 3000. From these numbers, shown in boldface in Table 3, it can be seen that oligomers were successfully prepared within the desired molecular weight range. But there is still no accurate measure of maleimide-terminated oligomer molecular weight. It is apparent that in order to obtain accurate values for molecular weight, a technique must be employed in which the results are independent of polymer chain conformation.

The materials evaluated above appear to meet the criteria mentioned in the introductory section of this report. That is, functionally terminated oligomers of molecular weight ~2000 were prepared and exhibit lyotropic siquid crystalline behavior. However, it is important to note that lyotropic behavior is only observed in the *as-prepared* gels or in dilutions of the original reaction mixture. Once the oligomers are isolated, they are very difficult to redissolve. In an effort to increase solubility, a copolyimide was considered.

Copolyimide:

The work of Schmidt's group¹⁶ indicated that copolyamides containing 2,5-diaminotoluene in addition to 2,2'-disubstituted diaminobiphenyls were much more soluble than their counterparts without the diaminotoluene. It was also noted that for the copolyamides, the range of lyotropic liquid crystalline behavior was much wider than found for the homopolymers.

Since the polyimide oligomers discussed earlier are only slightly soluble after isolation from the reaction solution and the solvent used for preparation (*m*-cresol) may not be suitable for the desired reinforcing phases, copolymerization was investigated as a means of enhancing solubility of polyimide oligomers.

A high molecular weight copolyimide based on 25 mol% 2,5-diaminotoluene, 25 mol% 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl and 50 mol% 3,3',4,4'-biphenylenetetracarboxylic dianhydride was prepared using a standard two-step procedure. The infrared spectrum of this polyimide, shown in Figure 8, indicates fairly complete imidization based on the relative intensities of imide characteristic bands (1775 cm^{-1} , 1724 cm^{-1} , 1364 cm^{-1}) and amic acid bands (1618 cm^{-1}). This is in contrast to the homopolyimide

case described earlier in which the two-step synthesis afforded poorly imidized product.

Thermogravimetric analysis indicated excellent thermal stability in nitrogen with a char yield of 57.7% at 800°C and virtually no weight loss before major decomposition at 571°C. Nearly identical behavior was observed when the polymer was heated in static air. The decomposition onset is lower for the copolyimide in comparison with the homopolyimide, probably due to the methyl group on the diaminotoluene. However, the char yield is significantly higher than in the homopolyimide case. Additionally, the as prepared gel showed some birefringent areas when observed with optical polarized light microscopy. A specific texture could not be determined as features were very small.

Unfortunately, the copolyimide is virtually insoluble once isolated from the reaction mixture. It is possible that solubility might be enhanced by changing the ratio of the diamines in the copolymer. Schmidt's polyamides showed optimum solubility at ratios of diaminotoluene:diaminobiphenyl greater than or equal to 3:2. The ratio employed for this study was 1:1. Oligomers should also be expected to show higher solubility with respect to the high polymer. However, no further copolyimide work was pursued at this time.

WORK IN PROGRESS:

Now that polyimide oligomers which exhibit lyotropic liquid crystalline behavior have been prepared, preliminary studies on network formation utilizing these materials have begun. The amine-terminated oligomer in *m*-cresol is being used for these studies. A variety of bismaleimides can be employed in the curing studies, ranging from commercially available materials such as Ciba-Geigy's Matrimid 5292A (I),

to more extended bismaleimides such as that based on Bisphenol-A (II)

to a short rigid bismaleimide (III) prepared by our group.

Compound III was chosen for the preliminary network studies with amine-terminated polyimide oligomers. This bismaleimide is highly soluble, but doesn't appear to show lyotropic behavior. However, this material does show a very brief period of thermotropic liquid crystalline behavior and should not cause a loss of liquid crystalline behavior during the course of the reaction.

The addition of an excess of this monomer, compound III, to a nematic *m*-cresol solution of the amine-terminated oligomer at 150°C results in an immediate color change from golden yellow to bright red, the red color indicating that the Michael addition of diamine to bismaleimide is indeed taking place. The solution remains nematic. Subsequent heating at 200°C to react the remaining maleimide groups and removal of solvent resulted in a brittle brown film, the edges of which appear to retain a nematic texture.

The film produced in this way is very weak, indicating that perhaps crosslinking of residual maleimide groups had not occurred. The solvent, *m*-cresol, would be expected to quench any free radicals in the system, thus inhibiting the radical polymerization of maleimide groups. However, anionic initiation of polymerization may still be possible. The amic acid structures formed during the Michael addition reaction are known to act as built-in anionic catalysts,¹⁷ but do not seem to have much effect here. Therefore an additional catalyst might be required. Suitable ionic catalysts might include tertiary amines or quaternary ammonium compounds, alkali metal alcoholates or hydroxides.¹⁸ A different solvent, perhaps an amide solvent, should also be considered.

CONCLUSIONS:

Functionally terminated polyimide oligomers which exhibit lyotropic behavior have been successfully prepared using a one-pot procedure in *m*-cresol. The molecular weights of these materials range from 2000 to 3000 and polarized light microscopy points toward a lyotropic critical concentration between 12% and 15% solids in *m*-cresol. The thermal stability of these materials is excellent, onsets of decomposition are ~580°C and char yields at 800°C are near 50% in both nitrogen and static air atmospheres. Work in progress at this time is focusing on the preparation of networks from amine-terminated oligomers and various bismaleimides.

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Figure 1. Infrared spectra of maleimide-terminated oligomers

	Decomposition Onset (°C)		Char Yield at 800°C (%)	
	N ₂	air	N ₂	air
<i>m</i> -cresol	594	582	48.3	55.2
NMP/pyr/Ac ₂ O	581	589	47.1	49.0
NMP/ <i>m</i> -cresol	596	598	48.4	48.6
NMP/ <i>o</i> -DCB	586	584	39.9	27.6
high polymer	603	605	41.9	29.4

Table 1. TGA Summary: Maleimide-terminated oligomers

Figure 2. Infrared spectra of amine-terminated oligomers

	Decomposition Onset (°C)		Char Yield at 800°C (%)	
	N ₂	air	N ₂	air
<i>m</i> -cresol-1	602	586	54.5	50.2
<i>m</i> -cresol-2	611	614	44.7	45.1
<i>m</i> -cresol-3	600	608	41.0	41.1
<i>m</i> -cresol-4	609	616	46.8	48.3
NMP/pyr/Ac ₂ O	581	589	47.1	49.0
high polymer	603	605	41.9	29.4

Table 2. TGA Summary: Amine-terminated oligomers

Figure 3. Polarized light micrograph of amine-terminated oligomer gel

Figure 4. Polarized light micrograph of maleimide-terminated oligomer gel

Figure 5. Size exclusion chromatogram: amine-terminated oligomer

Figure 6. Size exclusion chromatogram: maleimide-terminated oligomer

Figure 7. Universal calibration curve: Polystyrene standards in NMP, 30.0°C

sample	v_r (mL)	(η) (mL/g)	$\log(\eta)M$	M
amine 87	26.75	21.9	8.107	5.84M
	37.38		4.807	2928
amine 121	26.81	18.6	8.088	6.58M
	37.57		4.748	3009
amine 137	19.32	20.0	10.413	1.29B
	26.75		8.107	6.40M
	37.82		4.670	2339
amine 153	19.19	20.4	10.454	1.39B
	26.75		8.107	6.27M
	37.57		4.748	2744
maleimide 91	28.00	45.8	7.719	1.14M
maleimide 117	19.56	48.8	10.339	447M
	27.56		7.855	1.47M

Table 3. Oligomer molecular weights determined using universal calibration

Figure 8. Infrared spectrum of copolyimide

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