

Rigid Rod Molecules as Liquid Crystal Thermosets. I. Rigid Rod Amides

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Synopsis

A series of rigid rod amide monomers based on 2,2'-disubstituted-4,4'-diaminobiphenyl were prepared and characterized by DSC and hot stage polarized light microscopy. The monomers were endcapped with maleimide, nadimide, and methylnadimide functionalities. With one exception, all of the materials could be thermally polymerized. Nematic liquid crystalline behavior was observed in three of the new materials which could be crosslinked in either the nematic or isotropic phase. Fast heating rates with hot stage polarized light microscopy were necessary to determine the melting and phase behavior before substantial crosslinking occurred during the heating process. One of the methylnadimide endcapped monomers also showed lyotropic liquid crystalline behavior.

INTRODUCTION

Liquid crystal polymers (LCP's) are recognized as having great potential for the development of new materials with exceptional physical and mechanical properties. In general, LCP's consist of polymer chains containing anisotropic structural units (mesogenic groups) that may be incorporated into the polymer backbone, as pendant groups, or both.¹⁻³ The mesogenic unit may be rodlike or disclike in nature. Fibers, films, and molded plastics processed from the liquid crystalline state have been shown to exhibit outstanding physical and mechanical properties.^{4,5} The objective of this research was the integration of liquid crystalline behavior into the field of thermoset polymers.

One possible version of the liquid crystal thermoset (LCT) concept involves synthesizing new monomers consisting of a rigid, rodlike central unit, a characteristic of conventional liquid crystals, capped at both ends with well known crosslinking moieties such as maleimide or epoxy. We were interested in preparing materials based on this concept and investigating the properties of these new materials. Known crosslinking groups were used as endcaps for the monomers to facilitate the transfer of potentially useful materials into composites manufacturing. The general concept of LCT's has been addressed⁶⁻¹¹ but not sufficiently developed to evaluate the full potential of these materials. Very few physical or mechanical properties were reported although it was stated that these materials showed very low shrinkage upon curing. In this paper, results are presented for a series of amide monomers synthesized based on the LCT concept. Preliminary results of this work have been presented elsewhere.^{12,13}

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EXPERIMENTAL

Characterization

Differential scanning calorimetry (DSC) was performed with a Perkin-Elmer DSC-2C at a heating rate of $20^{\circ}\text{C min}^{-1}$ under an argon atmosphere unless otherwise noted. DSC melting points were quoted as the extrapolated onset. Microscopy was performed with a Bausch and Lomb Micro-Zoom™ Microscope equipped with crossed polarizers and a Kofler hot stage controlled by a variable transformer. Infrared (IR) spectra were recorded using a Perkin-Elmer 283 Spectrophotometer with KBr pellets. Proton (^1H) nuclear magnetic resonance (NMR) spectra were recorded using a JEOL PMX60SI Spectrometer at 60 MHz. Chemical shifts are reported in parts per million downfield from tetramethylsilane. Elemental analyses were performed by Midwest Microlab, Indianapolis, IN.

Syntheses

N-(*p*-Carboxyphenyl)maleimide

Maleic anhydride (45.2 g, 0.46 mol) was dissolved in 300–400 mL acetone. To this was added, with rapid stirring, an equimolar amount of *p*-aminobenzoic acid (63.2 g). The reaction mixture solidified within a few seconds.¹⁴ Excess solvent was removed to yield the amic acid intermediate which was dried overnight at 65°C under vacuum.

The dried intermediate material was dissolved in 200 mL DMF and heated to 45°C . Acetic anhydride (66.5 g, 0.65 mol) and anhydrous sodium acetate (3.6 g, 0.044 mol) were then added with stirring. The reaction was allowed to proceed at 45°C for 2 h after which the mixture was poured into water¹⁵ that had been slightly acidified with HCl. The yellow product was collected by suction filtration, washed with water, and dried at 80°C under vacuum. Yield: 74.4 g (74.4%), mp $227\text{--}230^{\circ}\text{C}$ (lit.¹⁶ mp 234°C). The material was used without further purification, but could be recrystallized from acetone in good yield. IR, cm^{-1} : 3150 (m) (O—H), 1720 (s) (C=O). $^1\text{H-NMR}$ (DMF- d_7): δ 12.1 (s, 1H), 7.9 (dd, 4H, $J_1 = 26$ Hz, $J_2 = 8$ Hz), 7.2 (s, 2H).

ANAL. Calcd for $\text{C}_{11}\text{H}_7\text{NO}_4$: C, 60.54; H, 3.45; N, 6.57. Found: C, 60.80; H, 3.24; N, 6.45.

N-(*p*-Carboxyphenyl)nadimide

cis-5-Norbornene-*endo*-2,3-dicarboxylic anhydride (19.14 g, 0.117 mol) was dissolved in 70 mL acetone with slight heating. An equimolar amount of *p*-aminobenzoic acid (16.05 g) was then slowly added with stirring. The mixture became white with a slight pink tinge. Heating was discontinued after 5 min and stirring was maintained for 20 min to insure complete reaction. The intermediate material was collected by suction filtration and dried overnight at 65°C under vacuum.

The cyclodehydration reaction was performed as described previously, using 1.5 mol acetic anhydride and 0.1 mol anhydrous sodium acetate for each mole of the open-chain acid to be cyclized. The white product was collected by suction filtration, washed with water, and dried at 80°C under vacuum. Yield: 18.54 g (62.3%), mp $225\text{--}228^{\circ}\text{C}$. The material was used without further purification,

but could be recrystallized from acetone in good yield. IR, cm^{-1} : 3000 (m) (O—H), 1715 (s) (acid C=O), 1685, 1695 (s) (imide C=O). $^1\text{H-NMR}$ (DMF- d_7): δ 12.05 (s, 1H), 7.75 (dd, 4H, $J_1 = 38$ Hz, $J_2 = 8$ Hz), 6.3 (s, 2H), 3.66 (d, 2H, $J = 1$ Hz), 3.3 (d, 2H, $J = 2$ Hz), 1.68 (s, 2H).

ANAL. Calcd for $\text{C}_{16}\text{H}_{13}\text{NO}_4$: C, 67.62; H, 4.60; N, 4.92. Found: C, 67.85; H, 4.63; N, 4.95.

N-(p-Carboxyphenyl)methylnadimide

Methyl-5-norbornene-2,3-dicarboxylic anhydride (18.48 g, 0.104 mol) was dissolved in 45 mL acetone. An equimolar amount of *p*-aminobenzoic acid (14.2 g) was then added with stirring. Stirring was continued for 20 min to insure complete reaction. The yellow intermediate material was collected by suction filtration and dried at 65°C under vacuum overnight.

The cyclodehydration reaction was performed as discussed previously to yield a white powder which was collected by suction filtration, washed with water, and dried at 80°C under vacuum. Yield: 13.91 g (45%), mp 205–210°C. The product was used without further purification, but could be recrystallized from acetone. IR, cm^{-1} : 3000 (m) (O—H), 1700 (s) (C=O). $^1\text{H-NMR}$ (DMF- d_7): δ 7.8 (dd, 4H, $J_1 = 28$ Hz, $J_2 = 10$ Hz), 5.9 (s, 1H), 3.2, 2.85 (2s, 4H), 1.85 (d, 3H, $J = 2$ Hz), 1.53 (d, 2H, $J = 2$ Hz).

ANAL. Calcd for $\text{C}_{17}\text{H}_{15}\text{NO}_4$: C, 67.89; H, 5.22; N, 4.55. Found: C, 68.68; H, 5.09; N, 4.71.

Preparation of Acid Chlorides

Acid chlorides were prepared according to the general method of Adams and Ulich.¹⁷ The procedure described is for preparing the acid chloride of *N*-(*p*-carboxyphenyl)maleimide, but can be transferred to the other imide acids without modification.

N-(*p*-Carboxyphenyl)maleimide (15 g, 0.07 mol) was suspended in approximately 80 mL benzene with stirring. To this was carefully added oxalyl chloride (21.83 g, 0.172 mol, 2.5 : 1 mol excess). Some gas was evolved upon addition of the oxalyl chloride. The mixture was then heated slowly to reflux and maintained at reflux for 2 h. The excess oxalyl chloride was removed by distillation. The reaction mixture was cooled and the yellow product collected by suction filtration. Hexane (or cyclohexane in the case of the methyl nadimide acid chloride) was added to the filtrate to recover any product remaining in solution. The combined product was washed with hexane and dried under vacuum at room temperature. Yield: 14.57 g (89.5%). All acid chlorides were used without further purification. This reaction can also be carried out in toluene, but the yield is greatly reduced.

p-Maleimidobenzoylchloride

Mp 170°C (DSC).

IR, cm^{-1} : 3120 (w) (olefin. C—H), 3080 (w) (arom. C—H), 1780 (s) (acyl chloride C=O), 1718 (s) (imide C=O). $^1\text{H-NMR}$ (CDCl_3): δ 7.9 (dd, 4H, $J_1 = 26$ Hz, $J_2 = 8$ Hz), 6.9 (s, 2H).

ANAL. Calcd for $\text{C}_{11}\text{H}_6\text{ClNO}_3$: C, 56.03; H, 2.60; N, 5.89; Cl, 14.79. Found: C, 56.07; H, 2.57; N, 5.94; Cl, 15.04.

p-Nadimidobenzoylchloride

Mp 148°C (DSC).

IR, cm^{-1} : 3120 (w) (olefin. C-H), 3100 (w) (arom. C-H), 1775 (s) (acyl chloride C=O), 1715 (s) (imide C=O). $^1\text{H-NMR}$ (CDCl_3): δ 7.8 (dd, 4H, $J_1 = 38$ Hz, $J_2 = 8$ Hz), 6.3 (s, 2H), 3.5 (s, 4H), 1.8 (dd, 2H, $J_1 = 4$ Hz, $J_2 = 8$ Hz).

ANAL. Calcd for $\text{C}_{16}\text{H}_{12}\text{ClNO}_3$: C, 63.41; H, 3.92; N, 4.61; Cl, 11.94. Found: C, 63.69; H, 4.01; N, 4.64; Cl, 11.75.

p-(Methylnadimido)benzoylchloride

Mp 150°C (DSC).

IR, cm^{-1} : 3120 (w) (olefin. C-H), 2980 (w) (aliph. C-H), 1785 (s) (acyl chloride C=O), 1715, 1710 (s) (imide C=O). $^1\text{H-NMR}$ (CDCl_3): δ 7.9 (dd, 4H, $J_1 = 32$ Hz, $J_2 = 8$ Hz), 5.9 (s, 2H), 3.4, 3.2, 2.9 (s, 4H), 1.9 (d, 3H, $J = 2$ Hz), 1.4 (s, 2H).

ANAL. Calcd for $\text{C}_{17}\text{H}_{14}\text{ClNO}_3$: C, 63.96; H, 4.36; N, 4.36; Cl, 11.75. Found: C, 64.67; H, 4.47; N, 4.44; Cl, 11.22.

2,2'-Bis(trifluoromethyl)-4,4'-Dinitrobiphenyl

Into a 1000 mL three-neck flask equipped with a condenser and overhead mechanical stirrer was placed a solution of 2-bromo-5-nitrobenzotrifluoride (200 g, 0.741 mol) in 350 mL DMF. To this was added, with stirring, purified copper powder (189 g, 2.97 mol, 4 : 1 mol excess). The mixture was stirred at reflux for 6 h and allowed to cool slowly to room temperature. The mixture was then filtered to remove copper residue and poured into water to precipitate the product. The product was collected by suction filtration and dried for 3 days at 65°C under vacuum. The product was recrystallized from ethanol/water and dried at 65°C under vacuum. Yield: 82.57 g (58.6%), mp 139°C (DSC) (lit.¹⁸ mp 134°C). IR, cm^{-1} : 3110 (w) (arom. C-H), 900-800 (w) (C-H oop). $^1\text{H-NMR}$ (CDCl_3): δ 8.6 (d, $J = 2$ Hz), 8.45 (dd, $J_1 = 9$ Hz, $J_2 = 2$ Hz), 7.5 (d, $J = 9$ Hz).

ANAL. Calcd for $\text{C}_{14}\text{H}_6\text{F}_6\text{N}_2\text{O}_4$: C, 44.76; H, 1.46; N, 7.40; F, 28.76. Found: C, 44.93; H, 1.62; N, 7.49; F, 28.86.

2,2'-Bis(trifluoromethyl)-4,4'-Diaminobiphenyl

2,2'-Bis(trifluoromethyl)-4,4'-dinitrobiphenyl (17.11 g, 0.045 mol) was placed into a round bottom flask with 140 mL hot 95% ethanol. To this was added, with stirring, stannous chloride dihydrate (72 g, 0.32 mol, 7 : 1 mol excess). Concentrated HCl (108 mL) was then added carefully. Some evolution of gas was noted upon addition of HCl. The mixture was refluxed for 18 h. Ethanol was removed by rotary evaporation and water was added to the remaining mixture which was basified with 20% aqueous NaOH. The product was collected by suction filtration and dried overnight at 65°C under vacuum. Recrystallization from chloroform/hexane yielded tan crystals (11.834 g, 82.1%), mp 182°C (DSC) (lit.¹⁸ mp 181-182°C). IR, cm^{-1} : 3100 (w) (arom. C-H), 900-800 (w) (C-H oop). $^1\text{H-NMR}$ (CDCl_3): δ 6.6-7.3 (m, 6H), 3.8 (s, 4H).

ANAL. Calcd for $C_{14}H_{10}F_6N_2$: C, 52.32; H, 3.30; N, 8.54; F, 35.70. Found: C, 52.51; H, 3.15; N, 8.75; F, 35.59.

Amide Monomer Syntheses

The general procedure for monomer synthesis is as follows: 1 mol of the diamine was dissolved in chloroform with 2 equiv. of triethylamine added as a scavenger for HCl. Four equivalents of triethylamine were added if the diamine dihydrochloride was used. This solution was chilled in an ice bath and 2 mol of the acid chloride were carefully added with stirring. In some cases a reaction exotherm was apparent. Stirring was continued for 30 min to insure complete reaction. The product was collected by suction filtration, recrystallized from an appropriate solvent, and dried at 80°C under vacuum. All monomers synthesized for this work are shown in Figure 1.

2,2'-Dimethylbiphenyl Bismaleimide Amide (**1a**)

The compound was recrystallized from nitrobenzene.

IR, cm^{-1} : 3400 (w) (N-H), 3100 (w) (arom. C-H), 1730, 1720 (s) (imide C=O), 1670, 1505 (s) (amide C=O). 1H -NMR (DMF- d_7): δ 10.3 (s, 2H), 7.9 (dd, 8H, $J_1 = 28$ Hz, $J_2 = 8$ Hz), 7.9 (t, 6H, $J = 6$ Hz), 7.2 (s, 4H), 2.1 (s, 6H).

ANAL. Calcd for $C_{36}H_{26}N_4O_6$: C, 70.71; H, 4.18; N, 9.16. Found: C, 70.81; H, 4.29; N, 9.18.

2,2'-Dimethylbiphenyl Bisnadimide Amide (**2a**)

The compound was recrystallized from DMF/ CH_3CN .

IR, cm^{-1} : 3395 (m) (N-H), 3290 (m) (arom. C-H), 3000 (w) (aliph. C-H), 1700 (s) (imide C=O), 1670, 1505 (s) (amide C=O). 1H -NMR (DMF-

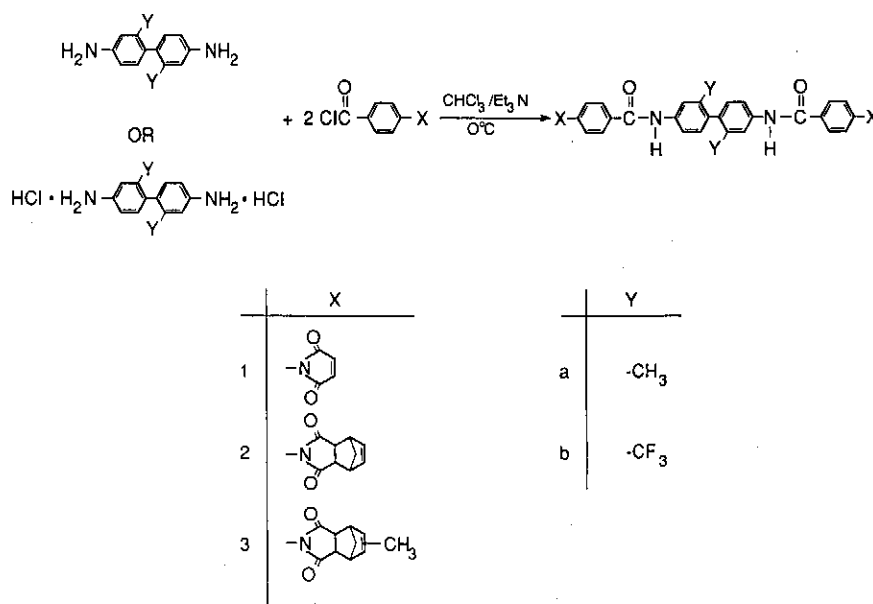


Fig. 1. Reaction scheme for the synthesis of rigid rod amide monomers.

d_7): δ 10.3 (s, 2H), 7.0–8.2 (m, 14H), 6.3 (s, 4H), 3.4–3.7 (m, 8H), 2.1 (s, 6H), 1.7 (s, 4H).

ANAL. Calcd for $C_{46}H_{44}N_4O_6$: C, 74.12; H, 5.39; N, 7.65. Found: C, 74.38; H, 5.16; N, 7.54.

2,2'-Dimethylbiphenyl Bis(methylnadimide) Amide (3a)

The compound was recrystallized from DMF/ H_2O .

IR, cm^{-1} : 3390 (m) (N–H), 2960 (m) (arom., aliph. C–H). 1H -NMR (DMF- d_7): δ 10.4 (s, 2H), 7.85 (dd, 8H, $J_1 = 32$ Hz, $J_2 = 8$ Hz), 7.9 (t, 6H, $J = 6$ Hz), 5.9 (s, 2H), 3.0–3.4 (m, 8H), 2.13 (s, 6H), 1.9 (d, 6H, $J = 1$ Hz), 1.6 (s, 4H).

ANAL. Calcd for $C_{44}H_{42}N_4O_6$: C, 73.41; H, 5.64; N, 7.28. Found: C, 74.79; H, 5.49; N, 7.27.

2,2'-Bis(trifluoromethyl)biphenyl Bismaleimide Amide (1b)

The compound was recrystallized from DMF/ CH_3CN .

IR, cm^{-1} : 3400 (m) (N–H), 3100 (w) (arom. C–H), 1720 (s) (imide C=O), 1675, 1510 (s) (amide C=O). 1H NMR (DMF- d_7): δ 10.8 (s, 2H), 7.6–8.9 (m, 14H), 7.2 (s, 2H).

ANAL. Calcd for $C_{36}H_{20}F_6N_4O_6$: C, 59.93; H, 2.93; N, 8.03; F, 16.02. Found: C, 60.17; H, 2.81; N, 7.80; F, 15.86.

2,2'-Bis(trifluoromethyl)biphenyl Bisnadimide Amide (2b)

The compound was recrystallized from DMF/ H_2O .

IR, cm^{-1} : 3400 (m) (N–H), 3100 (w) (arom. C–H), 1720 (s) (imide C=O), 1675, 1510 (s) (amide C=O). 1H NMR (DMF- d_7): δ 10.8 (s, 2H), 7.3–8.5 (m, 14H), 6.4 (s, 2H), 3.3–3.9 (m, 8H), 1.8 (s, 4H).

ANAL. Calcd for $C_{46}H_{32}F_6N_4O_6$: C, 63.50; H, 3.88; N, 6.75; F, 13.04. Found: C, 64.94; H, 3.79; N, 6.59; F, 13.40.

2,2'-Bis(trifluoromethyl)biphenyl Bis(methylnadimide) Amide (3b)

The compound was recrystallized from MeOH/ H_2O .

IR, cm^{-1} : 3380 (m) (N–H), 3120 (w) (arom. C–H), 2980 (w) (aliph. C–H), 1715 (s) (C=O). 1H -NMR (acetone- d_6): δ 10.0 (s, 2H), 7.4–8.5 (m, 14H), 5.9 (s, 2H), 3.0–3.4 (m, 8H), 1.9 (s, 6H), 1.6 (s, 4H).

ANAL. Calcd for $C_{46}H_{36}F_6N_4O_6$: C, 64.29; H, 4.24; N, 6.38; F, 12.88. Found: C, 65.60; H, 4.13; N, 6.38; F, 12.97.

RESULTS AND DISCUSSION

Synthesis

The molecules synthesized for this study were designed according to the liquid crystal thermoset (LCT) concept described briefly in the Introduction section of this paper. In general, they consist of rigid rodlike molecules with two reactive terminal groups. The building blocks for the molecules were selected such that good solubility and/or relatively low melting points could be achieved in the final thermoset monomer. In addition, suitable endgroups were chosen so that the cured thermoset material would have high temperature stability. Furthermore, the monomer should have an axial (length to diameter) ratio

conductive to liquid crystalline behavior, whether that behavior is lyotropic or thermotropic in nature. The axial ratios of the monomers reported here are approximately 5–6. The predicted critical value of the axial ratio for phase separation in an undiluted system of hard rods is 6.4.¹⁹ However, both hard and soft interactions may contribute to the stabilization of the nematic phase of undiluted thermotropic materials and thus molecules with axial ratios less than 6.4 may exhibit liquid crystalline behavior.²⁰

The central structural unit of the molecules investigated in this study was based upon 2,2'-disubstituted-4,4'-diaminobiphenyl. It was reported by Gaudiana et al.²¹ that substituents in the 2- and 2' positions of a biphenyl moiety increased the solubilities and in some instances decreased the glass transition temperatures of aromatic polyamides relative to the unsubstituted analogues. This behavior was attributed to the noncoplanarity of the adjacent phenyl rings introduced by steric interactions between the substituents in the ortho positions on the rings. This noncoplanar conformation also inhibits hydrogen bonding between amide molecules and should lead to the desired increase in solubility and lower melting points.

The endgroups used in this study are expected to provide high temperature stability after crosslinking. The maleimide endgroup is found in many commercially available materials marketed for their high temperature properties. These commercial bismaleimide resins exhibit good high temperature stability and good hot-wet performance, but are quite brittle due to their very high crosslink density.²² The nadimide endgroup is found in the NASA-developed PMR-15 resin, currently one of the most promising high temperature resin systems. The methyl substituted nadimide endgroup was investigated for comparison with the nadimide endgroup. The cure chemistry is expected to be similar, but the methyl substituent on the double bond may lead to further improvements in processability such as slower reaction kinetics. Several other endgroups, e.g., cyanate ester, phenylacetylene, and benzocyclobutene, may also offer high thermal stability, but are not discussed in this paper.

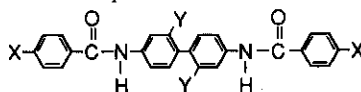
The monomers were synthesized using a Schotten-Baumann type reaction between one equivalent of the 2,2'-disubstituted-4,4'-diaminobiphenyl and 2 equiv. of the acid chloride endcap in the presence of triethylamine. The reaction scheme is shown in Figure 1 and the detailed procedures are described in the Experimental section of this paper.

Thermal Behavior

The thermal behavior of these compounds was investigated using a capillary melting apparatus, hot stage polarized light microscopy and differential scanning calorimetry. Only one of the monomers, **3b**, displayed melting behavior at slow heating rates. At fast heating rates, **1a**, **2a**, and **3a** were also observed to melt. The DSC thermal behavior of the monomers can be related to the curing reactions of the endgroups. These thermal data are presented in Table I.

The DSC curve of **1a**, shown in Figure 2, exhibited a sharp endotherm at 342°C, followed immediately by an exotherm at 345°C. When heated in a capillary melting point apparatus this sample did not melt up to 350°C, although it was observed to darken at about 340°C. However, if the capillary apparatus was preheated to 350°C prior to inserting the sample, the sample melted, flowed,

TABLE I
Thermal Properties of Amide Monomers



Monomer	X	Y	DSC transitions ^a
1a		-CH ₃	342, endo; 345, exo
2a		-CH ₃	292, 333, endo; 350, exo
3a		-CH ₃	290, 304, endo; 350, exo
1b		-CF ₃	no transitions
2b		-CF ₃	265, 324, endo; 350, exo
3b		-CF ₃	284, 288 ^b

^a Endotherms and exotherms reported as peak temperatures.

^b Transition temperatures determined by polarized light microscopy. The first transition represents $k \rightarrow n$, the second represents $n \rightarrow i$.

and polymerized (solidified). Crosslinking occurred almost instantly after melting into the isotropic phase. Liquid crystalline phases were not observed for **1a**. As in the case of the capillary observation, melting behavior was not observed by optical microscopy upon slow heating of the sample. It appears that the melting behavior is only evident when the heating rate is sufficiently fast to preclude extensive crosslinking of the sample during the heating process. Crosslinking of bismaleimides is known to occur at approximately 240°C.²³ Therefore, with bismaleimides that melt at temperatures higher than the known crosslinking temperature range, slow heating will allow crosslinking to occur in these reactive systems before reaching the melting point of the pure compound. Visual observation of the melting point in these reactive systems thus depends on the extent of reaction during the heating process.

The DSC curve of **2a**, shown in Figure 3, exhibited two broad endotherms at 292°C and 333°C, followed by an exotherm that was attributed to an addition polymerization reaction. The two broad endotherms are commonly seen in the DSC curves of nadimide endcapped materials and are attributed to the curing of the nadimide group. The first step in the curing of nadimide materials is the formation of cyclopentadiene through a reverse Diels-Alder reaction to yield cyclopentadiene and a maleimide. The reactions of the *endo*- and *exo*- nadimide

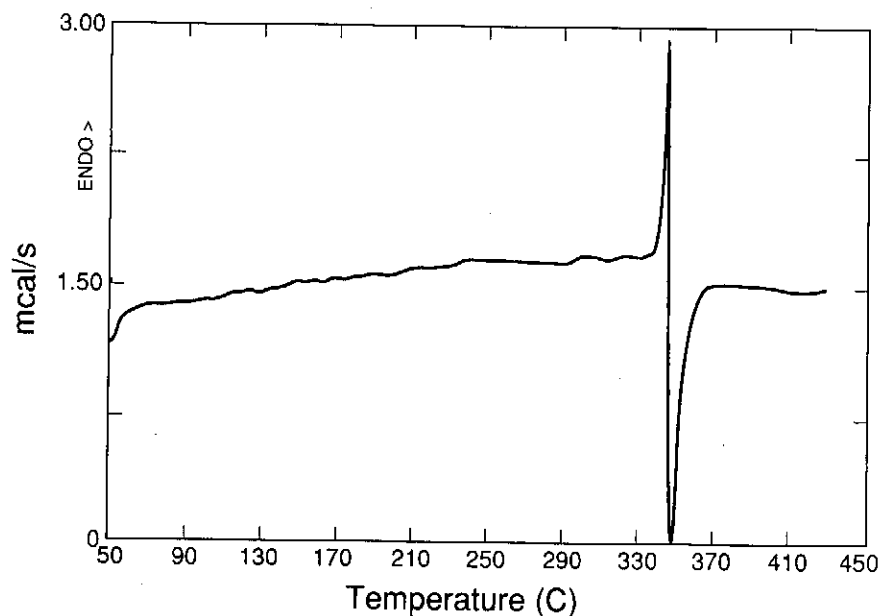


Fig. 2. DSC trace of monomer **1a**.

isomers are represented by two broad endotherms on the DSC trace. There has been some discussion regarding the subsequent steps of the curing mechanism, as several mechanisms are theoretically possible. These mechanisms have been discussed by Wong et al.²⁴ and by Hay et al.²⁵ for the curing of *N*-phenylmaleimide. Microscope observation of **2a** on a preheated hot stage at 350°C showed melting of the sample into a nematic liquid crystalline phase. The sample crosslinked in the nematic phase after a short period of time (10–20 s). At 360 and 370°C the sample melted and crosslinked in the isotropic phase. Although the exact transition temperatures could not be determined due to the reactive nature of the material, the existence of a nematic phase was verified and the nematic structure was preserved upon crosslinking.

The general nature of the DSC curve of **3a** was very similar to that of **2a**. The endotherms and exotherm were not as clearly defined as those of **2a**, probably due to the presence of additional structural isomers associated with the methyl substituents on the endgroups. Like **2a** discussed above, **3a** melted into a nematic liquid crystalline phase when placed on a preheated microscope hot stage at 340°C. Crosslinking occurred at this temperature with retention of the nematic texture. At temperatures of 350°C and higher, melting and crosslinking in the isotropic phase was observed.

Compound **1b** behaved quite differently than the other compounds studied in this investigation. The DSC trace did not exhibit any endotherms or exotherms up to 400°C. Compound **1b** was also analyzed by polarized light microscopy. Crystals of the material remained visually unchanged upon heating to 400°C. To further confirm that a reaction did not take place at these temperatures, a sample of **1b** was heated in argon at 350°C for 5 min. The NMR

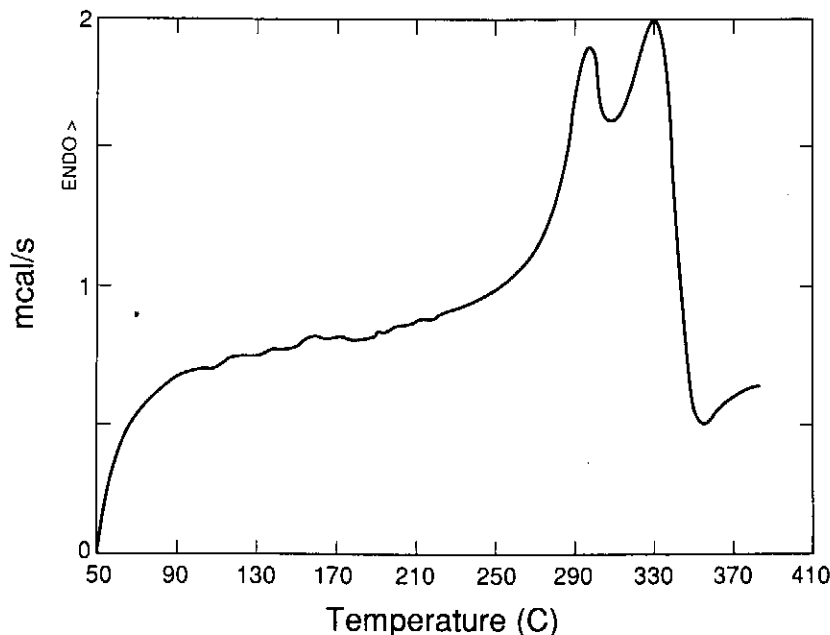


Fig. 3. DSC trace of monomer **2a**.

spectrum of the sample heated at 350°C was identical to the NMR spectrum of the original sample indicating that the sample did not readily crosslink at these temperatures.

Two endotherms appeared on the DSC curve of **2b**, characteristic of the reverse Diels–Alder reactions of the nadimide group. The first endotherm appeared at 275°C and the second endotherm appeared at 310°C. This was followed immediately by an exotherm that was attributed to addition polymerization reactions. This behavior was similar to that of **2a** as discussed previously. Melting was not observed by hot stage polarized light microscopy up to 370°C at slow or fast heating rates.

Hot stage polarized light microscopy of **3b** revealed the presence of a nematic phase in the 284–288°C temperature range. DSC investigations of this compound were inconclusive. However, when **3b** was heated on the hot stage into this temperature range it was clearly observed to melt into the nematic phase that was preserved upon supercooling below the original crystal to nematic transition temperature. The fluid nematic phase was observed and remained fluid for approximately ten minutes before crosslinking occurred in the nematic phase.

Solubility

The solubilities of the monomers based on the 2,2'-dimethylbiphenyl unit (**1a**, **2a**, **3a**), were moderate to high in aprotic solvents. The solubilities ranged from 15% (w/w) for **1a** in DMF and DMAc to 40% (w/w) for **3a** in DMAc containing 4% (w/v) LiCl. Lyotropic liquid crystalline behavior was not ob-

served in any of these solutions. The solubility data for all the compounds synthesized in this study are given in Table II.

Compounds **1b** and **2b**, based on the 2,2'-bis(trifluoromethyl)biphenyl unit, were less soluble than the 2,2'-dimethylbiphenyl analogues. The solubility of **1b** was less than 10% (w/w) in DMF and DMAc compared to greater than 15% (w/w) for **1a** in these solvents. Rogers et al.¹⁸ reported that the presence of the 2,2'-bis(trifluoromethyl)biphenyl unit was necessary but not sufficient for observing enhanced solubility in wholly aromatic polyamides. This may explain the lack of solubility enhancement for these two 2,2'-bis(trifluoromethyl)biphenyl based monomers. However, it was surprising that the 2,2'-dimethylbiphenyl based monomers (**1a**, **2a**) had greater solubilities than the 2,2'-bis(trifluoromethyl)biphenyl analogues (**1b**, **2b**).

Compound **3b** showed much greater solubilities than any of the other monomers discussed previously. Concentrated solutions of this monomer were made as high as 33% (w/w) in acetone. In addition, a solution of 50% (w/w) in DMAc/LiCl was made and examined on the microscope between crossed polarizers. Upon slow evaporation of the solvent on a microscope slide, the initial isotropic solution was transformed into a lyotropic nematic liquid crystalline solution before any precipitation occurred. Although the liquid crystalline behavior of these monomeric amides is rather limited, it is interesting to note that Rogers et al.¹⁸ were unable to observe any lyotropic behavior in their series of 2,2'-bis(trifluoromethyl)biphenyl based polyamides, even in solutions with concentrations up to 45% (w/v).

SUMMARY AND CONCLUSIONS

A series of rigid rod thermoset amides have been prepared by combining rigid central units with conventional crosslinking functionalities. All of the monomers except **1b** could be thermally polymerized. Three of the monomers (**2a**, **3a**, **3b**) in this series were observed to form nematic thermotropic liquid crystalline phases and **3b** also showed evidence of forming a nematic lyotropic liquid crystalline phase. The liquid crystalline nature of these materials was rather limited, but demonstrated the concept of a LCT amide monomer. Crosslinking could be performed in both the nematic and isotropic phases. When crosslinking was conducted in the nematic phase, the nematic texture was preserved in the final solid crosslinked material.

Due to the reactive nature of the monomers, crosslinking may occur during heating at temperatures below the melting point of the pure monomer. This would seem to be a general characteristic of any thermoset material that has a melting point higher than the crosslinking temperature. Fast heating rates with hot stage polarized light microscopy were used to determine the approximate melting points and phase behavior of these materials before substantial reaction occurred that would change the structure of the original monomer.

Lower melting points in similar systems might be achieved by changing the chemical structure of the rigid rodlike portion of the molecule or through lower melting eutectic mixtures of the materials synthesized in this study. The reasonably high solubilities of these monomers should also permit opportunities

TABLE II
Room Temperature Solubilities of Amide Monomers

Monomer	X	Y	Solubility range ^a (% w/w)				
			DMF	DMAc	NMP	DMAc/ LiCl ^b	Acetone
1a		-CH ₃	15-20	15-20	20-30	30-40	—
2a		-CH ₃	15-20	20-30	25-30	30-40	—
3a		-CH ₃	20-25	15-20	20-30	> 40	—
1b		-CF ₃	< 5	< 5	5-10	20-25	—
2b		-CF ₃	15-20	25	15-20	30	—
3b		-CF ₃	25-30	20-25	40-50	> 50	33

^a Maximum solubility lies within the range of values given here.

^b DMAc/LiCl solution contained 4% (w/v) LiCl.

for additional experiments and modifications to improve the processability and liquid crystalline nature of these types of materials.

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