Synthesis of New Aromatic Polyenaminonitriles with Improved Processability and Thermal Stability[1]

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ABSTRACT: Four new polyenaminonitriles, soluble in common organic solvents, are synthesized by condensation of bis(chlorovinyledene cyanide) monomers with two different aromatic diamines. Thermal stability of these heat-resistant polymers is discussed in terms of their structure–property relationships. Curing of polyenaminonitriles, which cure without evolution of small molecules, was studied by differential scanning calorimetry (DSC) and infrared spectroscopy.

Introduction

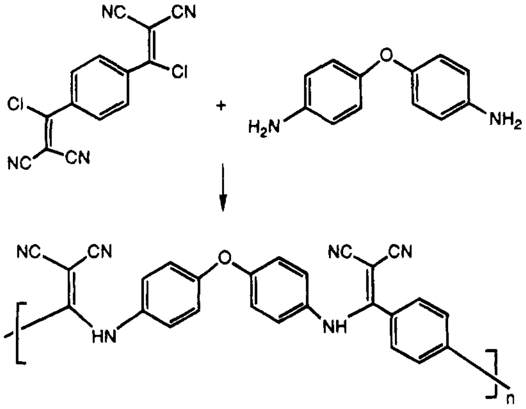
As a part of the program to synthesize polymers that cure without evolution of small molecules, we have synthesized novel aromatic polyenaminonitriles,[2] aromatic–aliphatic polyenaminonitriles,[3] and polypyrazoles.[4]

Polyenaminonitriles are synthesized, in general, by condensing bis(chlorovinylidene cyanide) monomers with the appropriate diamine (Scheme 1). Until recently, most of the aromatic polyenaminonitriles synthesized in our laboratory employed 4-aminophenyl ether as a diamine. The resultant polyenaminonitriles possessed good to excellent thermal stability and had sufficient solubility in the common organic solvents to allow solution processing. Our preliminary studies[2,5] on the dielectric properties of these polymers indicate the possibility of using them as polymeric dielectrics. Also, some of the polyenaminonitriles form miscible blends with some electron-rich polymers.[6] We decided to employ new diamines and study the effect of the resultant structure on the aforementioned, as well as other, properties.

Results and Discussion

We first employed bis[4-(*p*-aminophenoxy)phenyl]propane (**1**) and condensed it with **5** to give polyenaminonitrile **2** (Scheme 2). This polymer possessed moderately high molecular weight as judged from the intrinsic viscosity value which was found to be 1.45 dL/g when measured in *N,N*-dimethylacetamide at 25 °C. The polymer was soluble in polar, aprotic solvents such as DMF, DMAc, DMSO, NMP, and acetone. The differential scanning calorimogram of **2** showed a glass transition at 145 °C and an exotherm at 340–350 °C which did not reappear when the sample was cooled and rescanned. This observation indicates that the polymer has undergone irreversible "curing" (please see the discussion on curing of polyenaminonitriles **7–9**, Scheme 4, and Figure 5 for a representative DSC of the polyenaminonitriles). Thermogravimetric analysis of polymer **2** (Figure 1) indicates that it has only moderately good thermal stability. Comparison of the thermograms in air and nitrogen shows that this polymer experiences initial weight loss at ~400 °C in air.

Scheme 1. Synthesis of Polyenaminonitrile



The most likely reason for the decreased thermal stability of polyenaminonitrile **2** in air as compared to that in a nitrogen atmosphere as well as the overall decreased thermal stability of **2** as compared to other polyenaminonitriles, **7–9**, is the presence of isopropylidene groups in the polymer backbone. The isopropylidene moiety possesses bonds of low dissociation energy and hence represents "weak" links in the polymer chains.

At this point it was decided to choose a diamine that could substantially improve the thermal stability of the resulting polymer. Hergenrother's success in using 1,3-bis(4-aminophenoxy-4′-benzoyl)benzene (**3**) as a monomer which confers both toughness and solvent resistance on a series of polyimides which he studied[7] prompted us to try this diamine in our system. Diamine **3** was condensed with biselectrophilic monomers **4–6** (Scheme 3) to give polyenaminonitriles **7–9**. 1,3-Bis-[4-[(2,2-dicyano-1-phenylvinyl)amino]phenoxy-4′-benzoyl]-benzene (**11**), a model compound resembling the repeat unit of the polymers **7–9**, was also synthesized from diamine **3** and (chlorophenylmethylidene)propanedinitrile (**10**) (Scheme 3). Spectral data of the polymers matched very well with those of model compound **11**. Figures 2 and 3 show the proton and carbon NMR spectra of model compound **11** and polyenaminonitrile **8**. All three polymers possessed moderate to high molecular weight as indicated by the intrinsic viscosity values. The characterization data of all three polymers are summarized in Table 1. All three polymers exhibited good to excellent thermal stability in both air and nitrogen (Figure 4). In air, the temperatures at which all three polymers lose 50% of their weight are above 500 °C. In nitrogen, polymers **7** and **8** have comparable stability,

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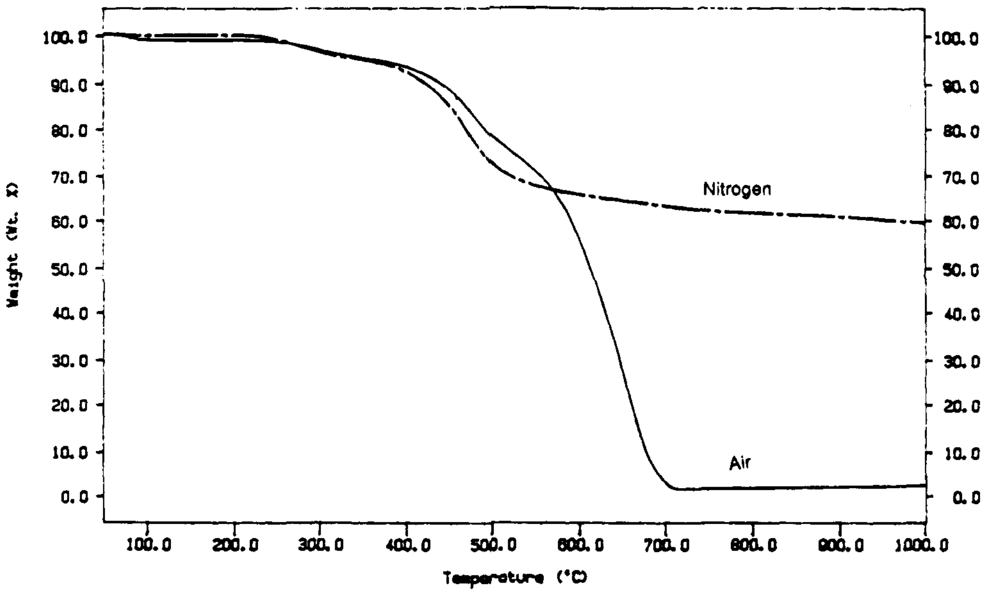
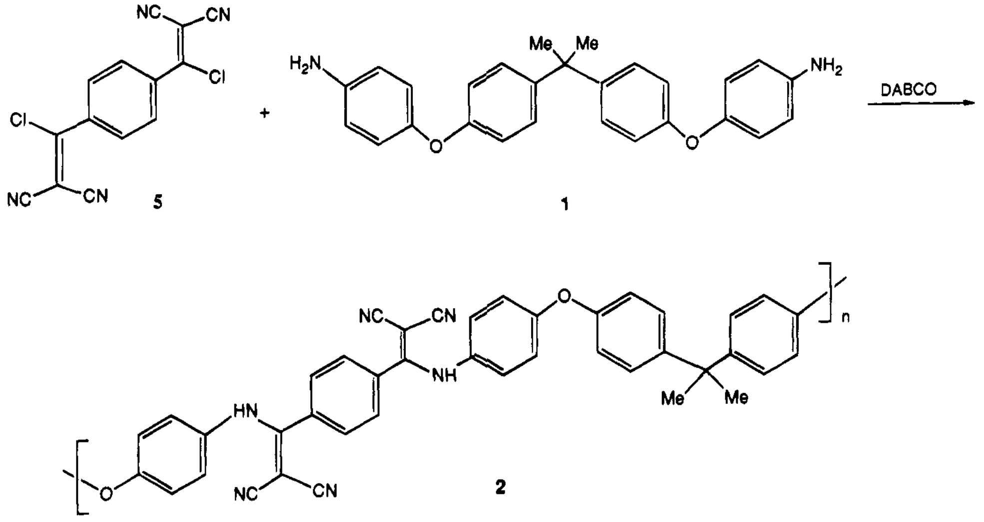
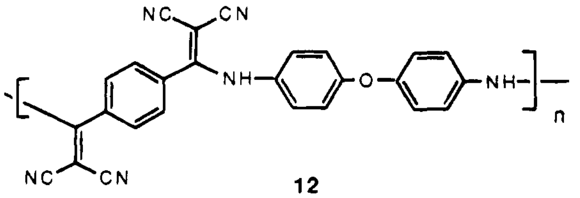


Figure 1. Thermogram for polyenaminonitrile **2** in air and nitrogen.

Scheme 2. Synthesis of Polymer 2



but in air polymer **7** is found to be superior to polymer **8**. A rationale for this observation does not readily spring to mind. The presence of sulfone groups in polymer **9** is probably responsible for its decreased thermal stability because chain cleavage would release sulfur dioxide, a stable gaseous product. Hence, the cleavage reaction may be a thermodynamically favored process. The differential scanning calorimograms of all three polymers also showed clearly defined glass transition temperatures (e.g., see Figure 5 for the calorimogram of polymer **9**). Polymer **12**, derived from 1,4-bis(1-chloro-2,2-dicyanovinyl)benzene (**5**) and 4-aminophenyl ether, showed a glass transition at 260 °C.[5]



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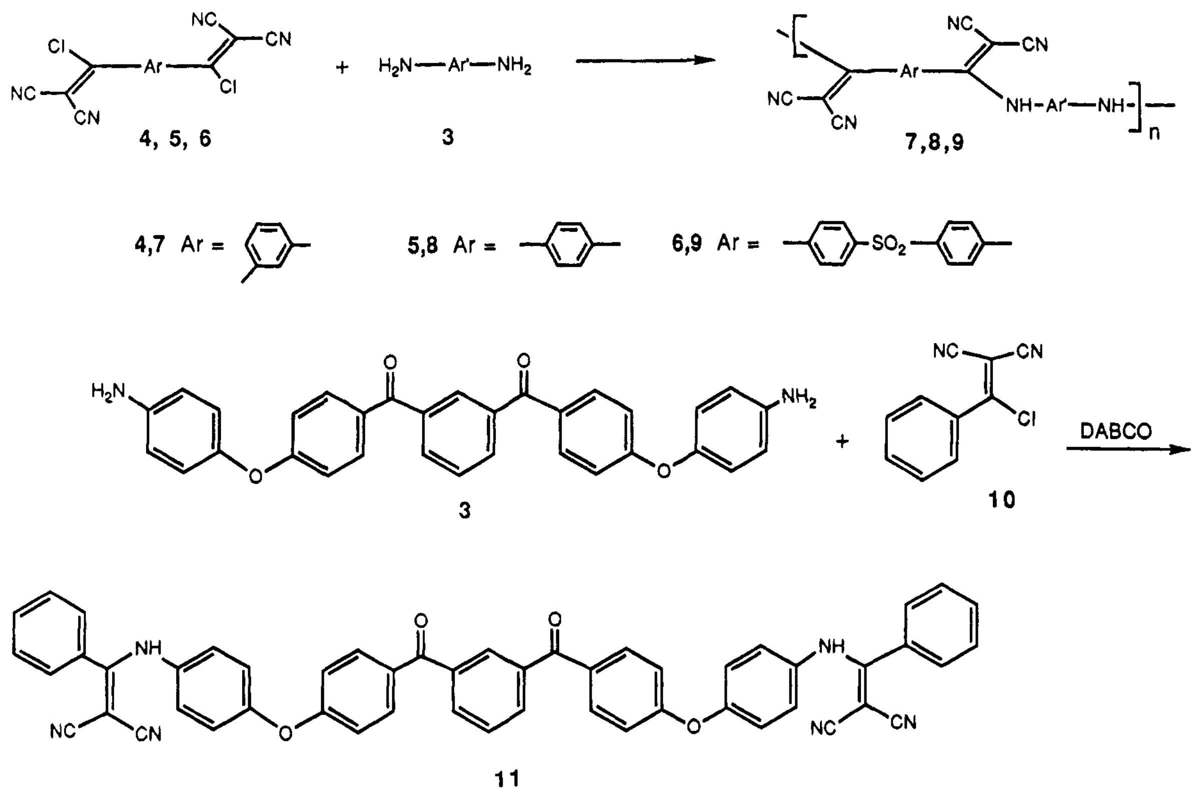
Comparing this value with the glass transition temperature of polymer **8** indicates the influence of the diamine portion of the repeat unit on the glass transition temperature. The data in Table 1 bear out structure–property relationships among polymers **7**–**9**. The diamine comonomer is common to all three polymers. Therefore, the structural units derived from the three different electrophilic monomers largely affect the properties of the resultant polymers. 1,4-Phenylene units in the backbone of polymer **8** lend rigidity to this polymer, and therefore it has the highest glass transition temperature (T_g). The presence of sulfone groups in polymer **9** makes the polymer chain more flexible as compared to other polymers and thus lowers the glass transition temperature when the powdered sample was used. The higher T_g of **9** in the case of the film sample may be explained by considering the possibility of a more ordered arrangement of the polymer chains taking

Table 1. Characterization of Polymers

polymer	$[\eta]^a$	50% wt loss temp (air) (°C)	residual wt % at 1000 °C (N_2)	T_g (°C)
7	0.60	569	73	164.3 (film)
8	1.99	531	70	240.4 (powder)
9	2.15	525	62	184.21 (powder), 237.35 (film)

[a] Measured in *N*,*N*-dimethylacetamide at 25 °C.

Scheme 3. Synthesis of Polymers 7–9 and Model Compound 11



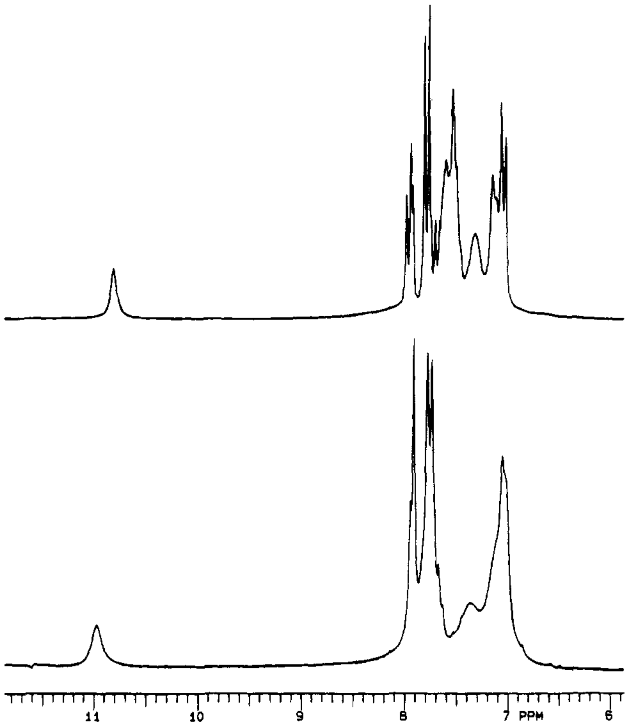


Figure 2. ^{1}H NMR spectra of model compound **11** (top) and polyenaminonitrile **8** (bottom).

place during the casting of the film. In the case of polymer **7**, the presence of 1,3-substitution patterns in both comonomers further tends to decrease the ordered arrangement of polymer chains. Consequently polymer **7** shows the lowest glass transition temperature of the three polymers studied here.

Differential scannng calorimetry of these polymers (Figure 5) also showed a somewhat broad exotherm around 350 °C. This exotherm was absent when samples were cooled and rescanned. This phenomenon is believed to indicate the occurrence of a thermally induced cyclization reaction which leads to further reactions which render the polymers insoluble in polar aprotic solvents in which they were soluble before "curing".[2a] For example, it was shown that enamino-

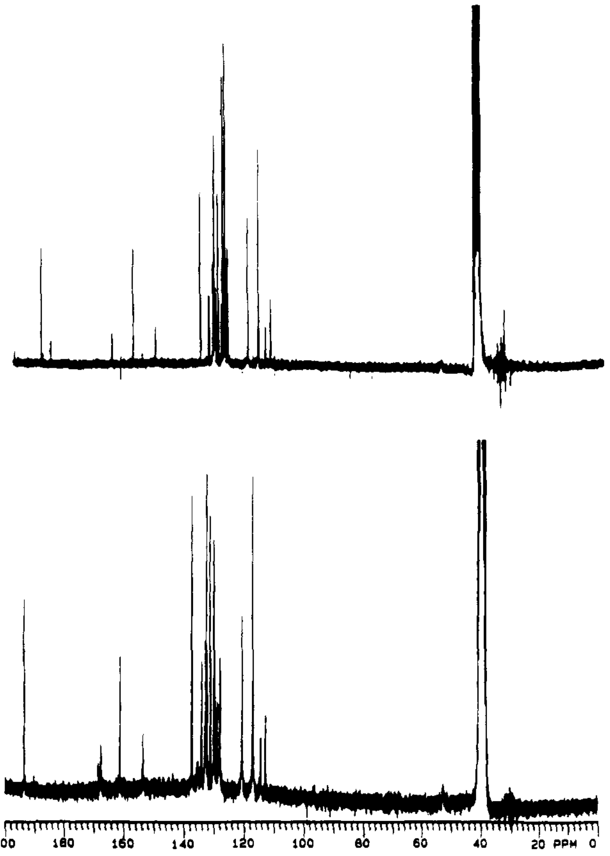


Figure 3. ^{13}C NMR spectra of model compound **11** (top) and polyenaminonitrile **8** (bottom).

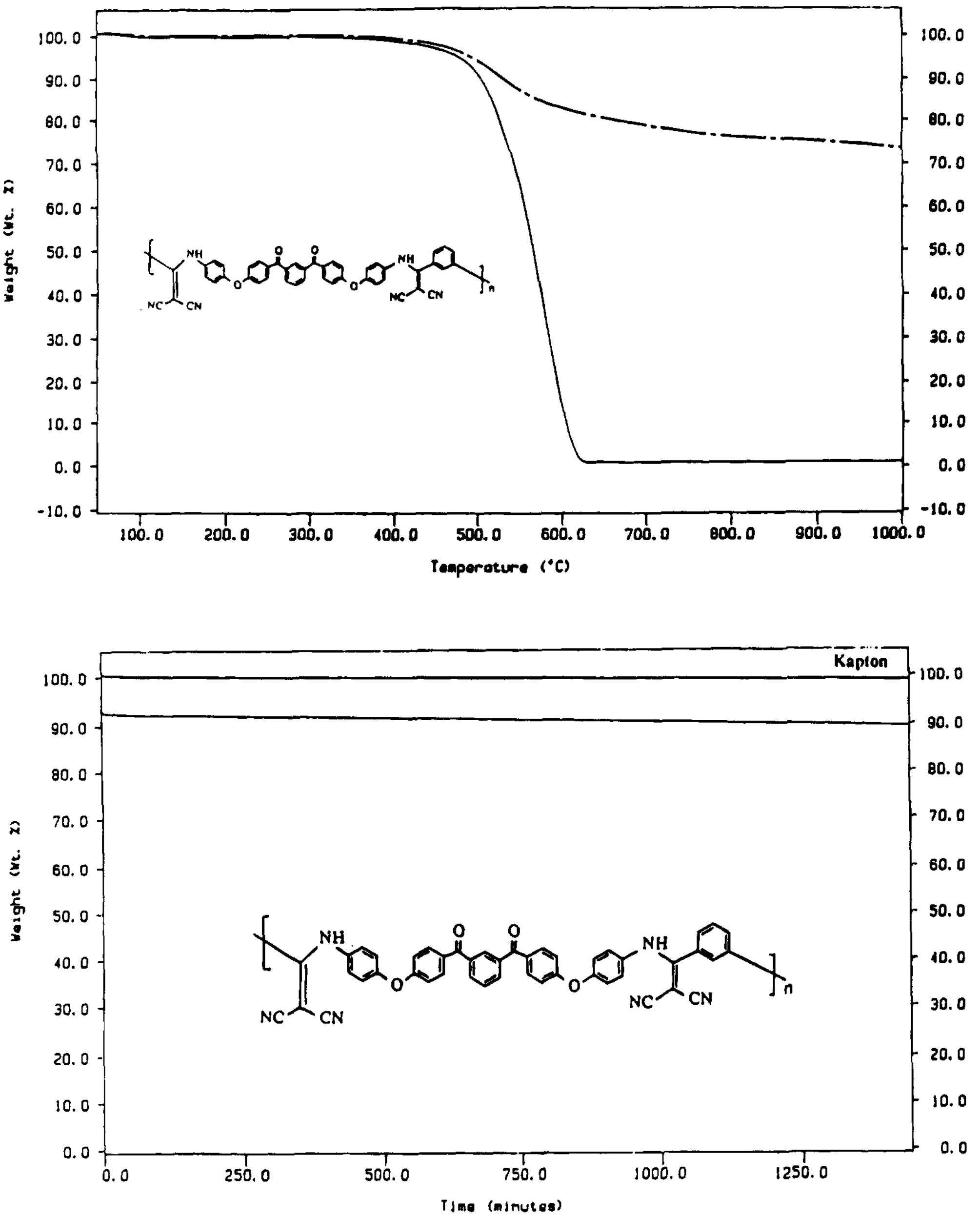
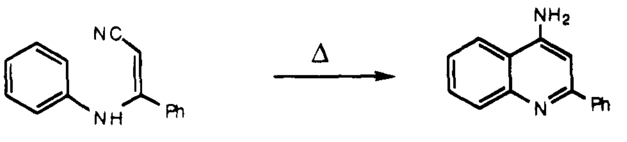


Figure 4. Thermogram for polyenaminonitrile **7** in air and in nitrogen (top) and isothermal aging of polyenaminonitrile **7** and Kapton at 300 °C.

nitrile **13** could be cyclized thermally to aminoquinoline **14**.



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The curing reaction of the polymers was monitored using FTIR spectroscopy. IR spectra of the polymers, heated at 400 °C in an argon atmosphere, were recorded periodically and compared with those of uncured materials. Intensities of the enamine N–H stretching mode in uncured polymer at 3252 cm^{-1} and the nitrile band at 2211 cm^{-1} diminished. At the same time, new bands at 3854, 3465, and 3371 cm^{-1} for primary amino groups appeared (Figure 6). These characteristic changes in the IR spectra are consistent with intramolecular cyclization of an enaminonitrile moiety to a 4-aminoquinoline unit, as shown for polyenaminonitrile **8** in Scheme 4.

Conclusions

Four new high molecular weight aromatic polyenaminonitriles were synthesized, further exhibiting the utility of the vinylic nucleophilic substitution reaction. The polymers derived from diamine **3** exhibited improved thermal stability. Introduction of a flexible diamine comonomer resulted in a lower glass transition temperature. We have also studied the dielectric properties of these and other polyenaminonitriles which will be reported separately.

Experimental Section

Fourier transform infrared (FTIR) spectra were recorded on a Perkin-Elmer Model 1800 Fourier transform infrared spectrometer. NMR spectra were recorded in deuterated dimethyl sulfoxide on a Varian Model XL-200 spectrometer operating at 200 MHz for ^{1}H and 50.3 MHz for ^{13}C spectra. Hexamethyldisiloxane was used as a reference for the proton NMR spectra.

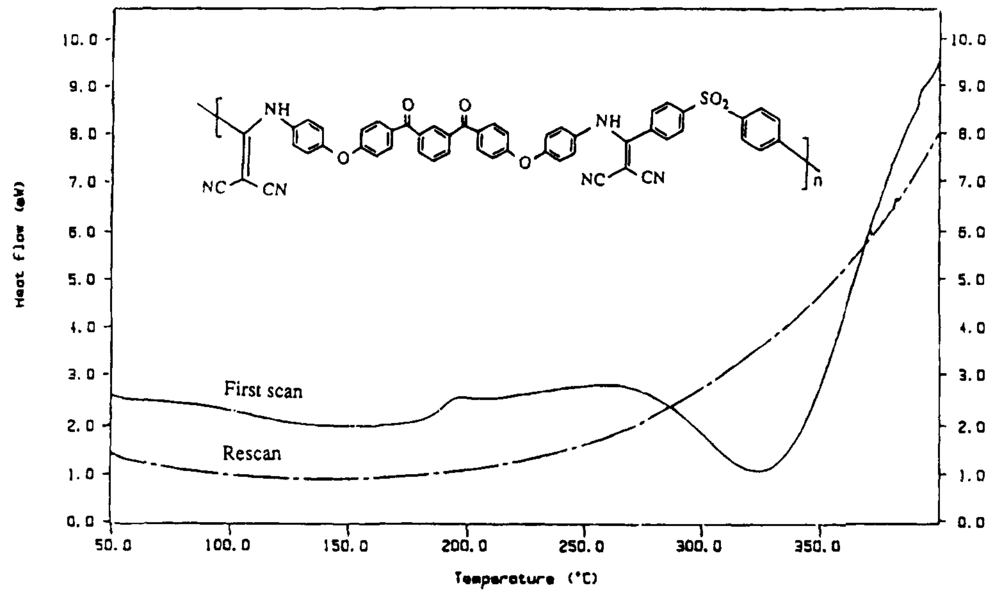


Figure 5. Differential scanning calorimogram of polyenaminonitrile **9**.

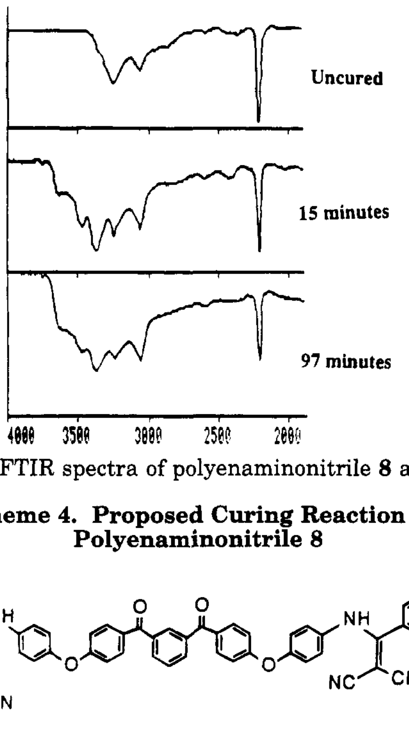
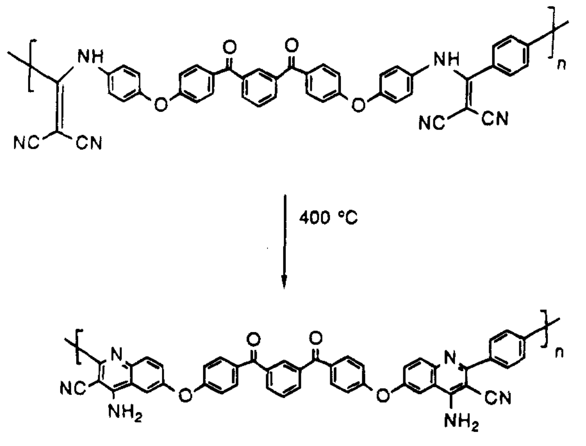


Figure 6. FTIR spectra of polyenaminonitrile **8** at 400 °C.

Scheme 4. Proposed Curing Reaction of Polyenaminonitrile 8



The solvent peak in DMSO-d_6 at 39.5 ppm was used as a reference peak in the ^{13}C NMR spectra. The fast atom bombardment (FAB) mass spectrum was obtained on a VG 70E mass spectrometer using 2-nitrobenzyl alcohol. The molecular ion is represented as M$^+$. The peaks corresponding to various fragments are reported as *m/e* (assignment, % relative intensity).

Intrinsic viscosities of the polymer solutions were measured in a Cannon–Ubbelohde viscometer at 25 °C. The polymer solutions for the viscosity measurements were filtered through a 0.45 μm filter (ACRODISC CR, Gelman Sciences).

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed on Perkin-Elmer System 7 analyzers interfaced with a Perkin-Elmer 7500 computer. The samples for DSC were encapsulated in an aluminum pan, and an empty aluminum pan was used as a reference. Unless otherwise noted, heating rates were 10 °C/min for DSC and TGA.

Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. The materials described in this paper are highly thermally stable materials. Therefore, many times the carbon content in these molecules, obtained by elemental analysis, is slightly lower than the theoretical value because of incomplete combustion of the material.

Monomers **4**–**6** were synthesized by a previously reported procedure.[2a] Diamine **3** was prepared by Hergenrother's procedure.[7] 2,2-Bis[4-(*p*-aminophenoxy)phenyl]propane (**1**) was obtained from Hypertech Inc., Delanson, NY. It was found to be quite pure by proton NMR and was used as received.

Syntheses. All four polymers (**2** and **7**–**9**) were synthesized by a similar procedure. A representative procedure for the synthesis of **8** is described below. The spectral data for other polymers are also given below.

Poly[oxy-1,4-phenylenecarbonyl-1,3-phenylenecarbonyl-1,4-phenyleneoxy-1,4-phenyleneimino(dicyanoethenylidene)-1,4-phenylene(dicyanoethenylidene)imino-1,4-phenylene] (8). A dry, 100-mL, three-necked, round-bottomed flask was fitted with a mechanical stirrer, an addition funnel with an argon inlet, and a reflux condenser connected to a mineral oil bubbler. The assembly was charged with 1,3-bis(4-aminophenoxy-4′-benzoyl)benzene (**3**) (1.5 g, 2.99 mmol), freshly sublimed DABCO (0.3365 g, 2.99 mmol), and dry *N*-methyl-2-pyrrolidone (NMP) (10 mL). To this solution, stirred under argon and cooled to 0 °C, was added, dropwise, a solution of 1,4-bis(1-chloro-2,2-dicyanovinyl)benzene (2.000 g, 6.68 mmol) (**5**) in dry NMP (10 mL). The color of the reaction mixture changed to dark brown and then to light yellow (ca. 2 min). The viscosity of the reaction mixture started increasing rapidly, and in about 30–40 min it became almost a thick paste. At this stage the reaction mixture was diluted with an additional 10 mL of NMP and stirred at room temperature for 12 h followed by stirring at 60–70 °C for an additional 12 h. The reaction mixture was cooled to room temperature and poured into vigorously stirred water to precipitate the polymer which was filtered and reprecipitated from NMP solution into water. The polymer was filtered and dried at 70–80 °C *in vacuo* ($P < 1$ Torr) for 36 h (2.0858 g, 95.75%).

FTIR (film): 3252, 3067, 2217 (s), 1660, 1595, 1570 (b), 1505–1495 (d), 1420, 1317, 1308, 1240, 1165, 1018, 920, 880, 850, 750, 710, 615 cm^{-1}. λ_{max} (ϵ) (NMP): 344.4 (17767), 295.6

(51222.6), 261.1 (25786). ^{1}H NMR (DMSO-d_6): δ 6.9–8.0 (m, 24H), 10.96 (s, br, 2H). ^{13}C NMR (DMSO-d_6): 52.62 [=*C*(CN)$_2$], 114.30, 116.84 [=C(*C*N)$_2$], 117.00, 120.54, 127.92, 128.87, 129.74, 129.91, 131.08, 132.29, 132.84, 134.15, 135.36, 137.37, 153.55, 161.09 [aromatic *C*], 167.52 [=*C*NH], 193.56 [>*C*=O]. (Note: A peak at 135.36 ppm is slightly broadened (probably corresponding to a quarternary carbon atom having a very long relaxation time. It can be observed clearly only upon increasing the line broadening parameter significantly).

Poly[oxy-1,4-phenyleneimino(dicyanoethenylidene)-1,4-phenylene(dicyanoethenylidene)imino-1,4-phenyleneoxy-1,4-phenyleneisopropylidene-1,4-phenylene] (2). FTIR (film): 3448, 3038, 2969, 2870, 2217 (s), 1599, 1567, 1499, 1420, 1364, 1286, 1236, 1171, 1104, 1082, 1014, 949, 877, 850, 835, 756, 720, 656, 610 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 1.5 (s, 6H, methyl), 6.4–7.85 (m, 20H), 10.85 (s, br, 2H). ^{13}C NMR (DMSO-d_6): δ 8.40 [*C*(Me)$_2$], 30.58 [*C*H$_3$], 51.29 [=*C*(CN)$_2$], 112.02, 114.34 [nitrile carbons], 117.78, 119.13, 127.68, 127.99, 129.77, 132.88, 145.29, 154.45, 155.27, 155.54 [aromatic *C*], 167.23 [=*C*NH].

Poly[oxy-1,4-phenylenecarbonyl-1,3-phenylenecarbonyl-1,4-phenyleneoxy-1,4-phenyleneimino(dicyanoethenylidene)-1,3-phenylene(dicyanoethenylidene)imino-1,4-phenylene] (7). FTIR (film): 3251, 3065, 2960, 2893, 2217 (s), 1658, 1594, 1565, 1498, 1447, 1417, 1362, 1307, 1238, 1202, 1164, 1126, 1107, 1014, 999, 987, 918, 877, 846, 821, 775, 748, 708 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 6.8–8.1 (m, 24H), 11.0 (s, br, 2H, N*H*). ^{13}C NMR (DMSO-d_6): δ 53.46 [=*C*(CN)$_2$], 114.04, 116.27 [=C(*C*N)$_2$], 117.0, 120.16, 127.47, 128.58, 128.99, 129.53, 130.19, 131.16, 131.99, 132.15, 132.26, 132.50, 133.96, 137.35, 153.36, 160.76 [aromatic *C*], 167.19 [=*C*NH], 193.34 [>*C*=O]. Note: Peaks at 132.15 and 132.26 ppm are found buried between two intense peaks at 131.99 and 132.50 ppm when the FID is Fourier transformed using a normal value of line broadening (1 Hz). These peaks can be clearly seen when FID is Fourier transformed using no line broadening as this improves the resolution of the spectrum.

Poly[oxy-1,4-phenylenecarbonyl-1,3-phenylenecarbonyl-1,4-phenyleneoxy-1,4-phenyleneimino(dicyanoethenylidene)-1,4-phenylenesulfonyl-1,4-phenylene(dicyanoethenylidene)imino-1,4-phenylene] (9). FTIR (film): 3240, 3064, 2955, 2893, 2216 (s), 1665 (with a shoulder at 1685), 1594, 1577, 1557, 1498, 1457, 1420, 1399, 1320, 1307, 1287, 1238, 1202, 1163, 1104, 1072 (w), 1015, 999, 987, 933, 918, 876, 880, 846, 771, 746, 708, 656 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 7.0–8.4 (m, 28H), 10.91 (s, br, 2H, enamine N*H*). ^{13}C NMR (DMSO-d_6): δ 52.77 [=*C*(CN)$_2$], 113.63, 116.55 [=C(*C*N)$_2$], 116.99, 120.44, 127.76, 127.95, 128.72, 129.67, 130.81, 131.12, 132.13, 132.63, 133.61, 137.36, 137.72, 142.92, 153.83, 160.99 [aromatic *C*], 166.55 [=*C*NH], 193.45 [>*C*=O].

1,3-Bis[4-[(2,2-dicyano-1-phenylvinyl)amino]phenoxy-4′-benzoyl]benzene (11). A dry, 50-mL, three-necked flask, equipped with a magnetic stirring bar, a reflux condenser attached to a mineral oil bubbler, and a nitrogen inlet, was charged with 1,3-bis(4-aminophenoxy-4′-benzoyl)benzene (**3**) (0.3350 g, 0.669 mmol), DABCO (0.0751 g, 0.669 mmol), and dry NMP (15 mL). To the stirred and cooled (0 °C) flask contents was added, in one portion, a solution of (chlorophenylmethylidene)propanedinitrile[2a] (0.2525 g, 1.339 mmol.) in dry NMP (~2–3 mL). The reaction mixture was stirred at room temperature for 6 h, followed by stirring at 70 °C for 12 h. The reaction mixture was cooled and poured into an ice–water mixture (50 mL). A yellow solid was obtained which was filtered and dried (0.4361 g, 80.93%). It was further purified by column chromatography (silica gel, EtOAc/petroleum ether).

Anal. Calcd for $C_{52}H_{32}N_6O_4$: C, 77.64; H, 4.01; N, 10.45. Found: C, 76.25; H, 4.04; N, 10.12. MS: 805 (M$^+$ + 1, 100), 739 (M − 65, 22). FTIR (KBr): 3441, 3250, 3060 (w), 2925 (w), 2852 (w), 2215 (s), 1655 (s), 1594 (s), 1559, 1520, 1498 (s), 1455, 1418, 1307, 1238 (s), 1202, 1163, 1110, 1014, 999, 918, 877, 846, 750, 704, 650, 615 cm^{-1}. λ_{max} (ϵ) (NMP): 346.9 (32102), 296.1 (49170), 258.1 (44874). ^{1}H NMR (DMSO-d_6): δ 7.0–8.0 (m, 30H), 10.80 (s, br, 2H). ^{13}C NMR (DMSO-d_6): δ 52.1 [=*C*(CN)$_2$], 114.59, 117.33 [=C(*C*N)$_2$], 116.96, 120.71, 127.82, 128.66, 129.02, 129.48, 130.12, 131.10, 131.99, 132.41, 132.94, 134.50, 137.38, 153.45, 161.29 [aromatic *C*], 168.64 [=*C*NH], 193.66 [>*C*=O].

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References and Notes

(1) A preliminary account of this work was presented at the Spring 1989 meeting of the American Chemical Society held in Dallas, TX. Moore, J. A.; Mehta, P. G. *Polym. Mater. Sci. Eng.* **1989**, *60*, 74.

(2) (a) Moore, J. A.; Robello, D. R. *Macromolecules* **1989**, *22*, 1084. (b) Kim, S. Y. Ph.D. Dissertation, Rensselaer Polytechnic Institute, Troy, NY, 1989.

(3) (a) Moore, J. A.; Mehta, P. G. *Polym. Mater. Sci. Eng.* **1990**, *63*, 351. (b) Moore, J. A.; Mehta, P. G. *Macromolecules* **1993**, *26*, 916.

(4) Moore, J. A.; Mehta, P. G. *Macromolecules* **1988**, *59*, 835.

(5) Moore, J. A.; Robello, D. R.; Mehta, P. G. Proceedings of the 3rd International SAMPE Electronics Materials and Process Conference, Los Angeles, CA, June 20–22, 1989.

(6) (a) Moore, J. A.; Kim, J.-H. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1990**, *31* (2), 696. (b) Moore, J. A.; Kim, J.-H. *Polym. Mater. Sci. Eng.* **1989**, *61*, 679.

(7) Hergenrother, P. M.; Wakelyn, N. T.; Havens, S. J. *J. Polym. Sci., Polym. Chem. Ed.* **1987**, *25*, 1093.

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