Macromolecules 1993, *26*, 3504-3509

Aromatic–Aliphatic Polyenaminonitriles[1]

J. A. Moore,* Parag G. Mehta,[†] and Sang-Youl Kim[‡]

Department of Chemistry, Polymer Science & Engineering Program, Rensselaer Polytechnic Institute, Troy, New York 12180-3590

Received December 31, 1992; Revised Manuscript Received March 25, 1993

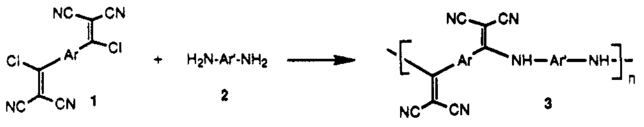
ABSTRACT: Bis-electrophilic aromatic monomers were polymerized with hexamethylenediamine to high molecular weight polyenaminonitriles. All the polymers, except that containing a sulfone group, were soluble in polar, aprotic solvents and possessed film-forming properties. The polymers and their model compounds were characterized by spectroscopic methods. Some of the polymers possessed varying degrees of crystallinity as shown by differential scanning calorimetry. Thermogravimetry also revealed a surprising amount of thermal stability for macromolecules containing aliphatic segments.

Introduction

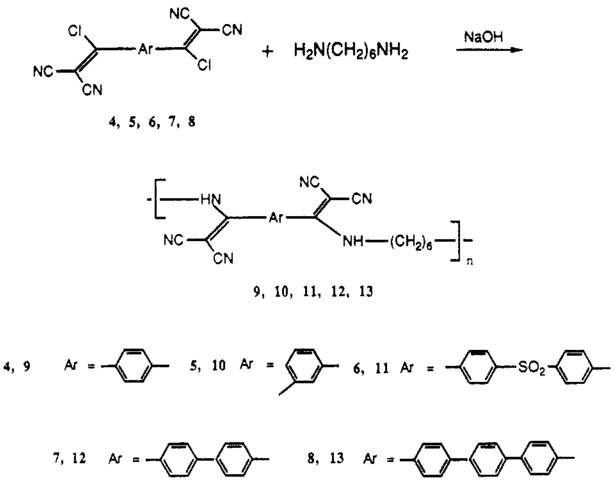
As a part of a program to prepare high molecular weight, processable polymers that cure thermally without evolution of small molecules, we have successfully exploited a vinylic nucleophilic substitution pathway to prepare novel polyenaminonitriles[2] 3 (Scheme I).

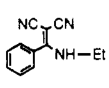
Normally, for an unactivated olefin, vinylic nucleophilic substitution is not a high-yield process and, therefore, is unsuitable for the synthesis of high molecular weight polymers by condensation polymerization. However, the success of the vinylic nucleophilic substitution reaction in the synthesis of polymers such as **3** rests upon the fact that bis(chlorovinylidene cyanides) such as **1** are sufficiently electrophilic because of the presence of $>C{=}C(CN)_2$ groups. This electrophilic activation of **1** by the dicyanomethylidene moieties toward a nucleophile can be rationalized on the basis of an analogy given by Wallenfels.[3] According to this analogy, a $>C{=}C(CN)_2$ group is considered electronically equivalent to a carbonyl group where oxygen is exerting an electron-withdrawing effect and serves to delocalize negative charge.

Scheme I

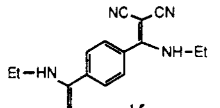


Scheme II





14



15

Results and Discussion

The ease of interfacial polymerization of dichloromethylidenepropanedinitrile with nucleophilic aliphatic diamines[4] led to the reactions of aromatic monomers[2] **4–8** with hexamethylenediamine (Scheme II). The polymerization process for monomers **4–8** was based on representative procedures for interfacial polymerization described by Morgan.[5] No attempts were made to optimize yield or molecular weight because the reaction worked very well yielding high molecular weight polymers. Appropriate model compounds (e.g., **14**, **15**) resembling the repeat unit of the polymers derived from aromatic monomers were synthesized (Scheme II). The spectral data of polymers **9–13** matched well with those of the corresponding model compounds (see, e.g., Figures 1 and 2). Polymers **9**, **10**, **12**, and **13** were soluble in polar, aprotic solvents such as DMF, NMP, DMAc, and DMSO while polymer **11** which contained in aromatic sulfone unit was completely insoluble in common organic solvents as well as in solvents such as hexafluoro-2-propanol, formic acid, and *m*-cresol which are known to dissolve polyamides. Intrinsic viscosities of polymers **9**, **10**, **12**, and **13** were measured in NMP or DMF at 25 °C, and the values obtained are given in Table I along with a summary of the thermal characterization data.

As can be seen from the data in Table I and Figures 3 and 4, polymers **9–13** possess surprisingly good thermal stability considering that they contain six methylene units in the polymer backbone. It may be recalled that the aliphatic C–H bond has a low dissociation energy compared to aromatic counterparts and hence the polymers having aliphatic units in the main chain do not usually have very high thermal stability. It is, therefore, remarkable to observe that the polymer with biphenyl units loses 50% of its weight at about 580 °C while the terphenyl analog reaches this benchmark at about 690 °C!

Polymers **9–13** exhibit interesting thermal behavior as evidenced by the calorimograms shown in Figures 5–9. Polymers **9**, **12**, and **13** show a broad exotherm at approximately 340 °C which does not reappear upon cooling and rescanning the sample. To understand the cause of this exotherm a sample of **9** was heated to 375 °C

[†] Current address: Materials Research Laboratory, 750 Main Street-5C, Polaroid Corporation, Cambridge, MA 02139.

[‡] Current address: Lucky Chemical Co., Dae-Deog-Danji, Dae-Jeon 305-343, Chung-Nam, Korea.

0024-9297/93/2226-3504$04.00/0

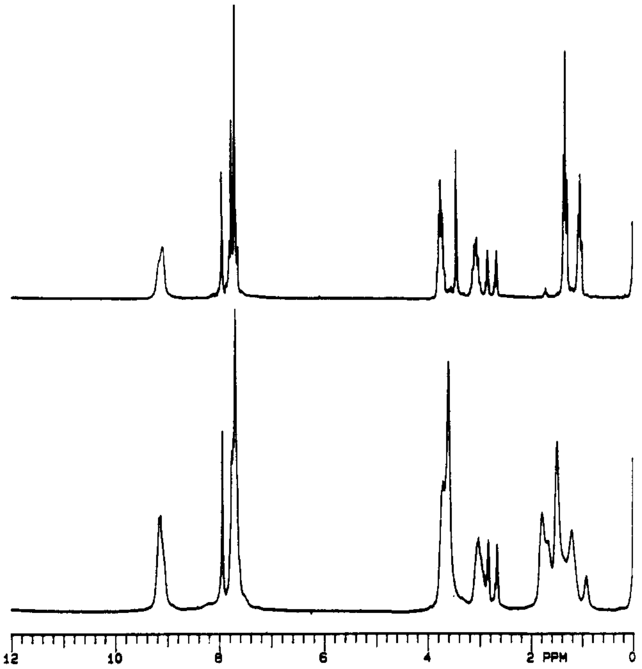


Figure 1. ^{1}H NMR spectra of model compound **15** (top) and polymer **9** (bottom).

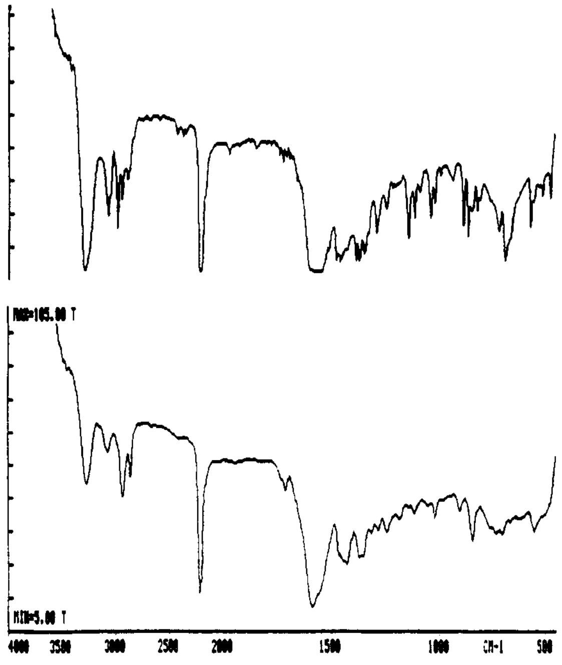


Figure 2. FTIR spectra of model compound **15** (top) and polymer **9** (bottom).

Table I. Characterization of Polymers 9–13

polymer	[η] (dL/g)	10% wt loss temp^a (°C)	50% wt. loss temp^a (°C)	T_g (°C)	T_m (°C)
9	1.25^b	314	514	155	
10	1.18^b	385	561	136	250
11		338	390	116^d	317
12	1.06^c	370	~580	190	
13	0.69^c	420	~690	214	

[a] In air; scanning rate = 10 °C/min. [b] Intrinsic viscosity was measured in NMP at 25 °C. [c] Intrinsic viscosity was measured in DMF at 25 °C. [d] Observed on rescan. See text for details.

in a nitrogen atmosphere in a DSC pan and cooled. The polymer was found to be insoluble in NMP and DMF. The IR spectrum of the "cured" material (Figure 10) indicated the presence of a broad peak at 3407 cm^{-1}. The bands at 3271 and 3071 cm^{-1} which were present in the IR spectrum of **9** (Figure 2) were absent. The band at 2210 cm^{-1} of the nitrile group had also diminished in intensity. An examination of the products formed when enaminonitriles derived from aromatic amines were heated through

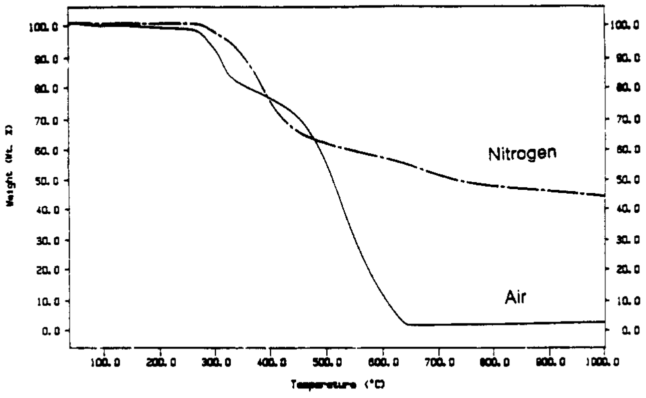


Figure 3. Thermogram of polymer **9** in air and in nitrogen.

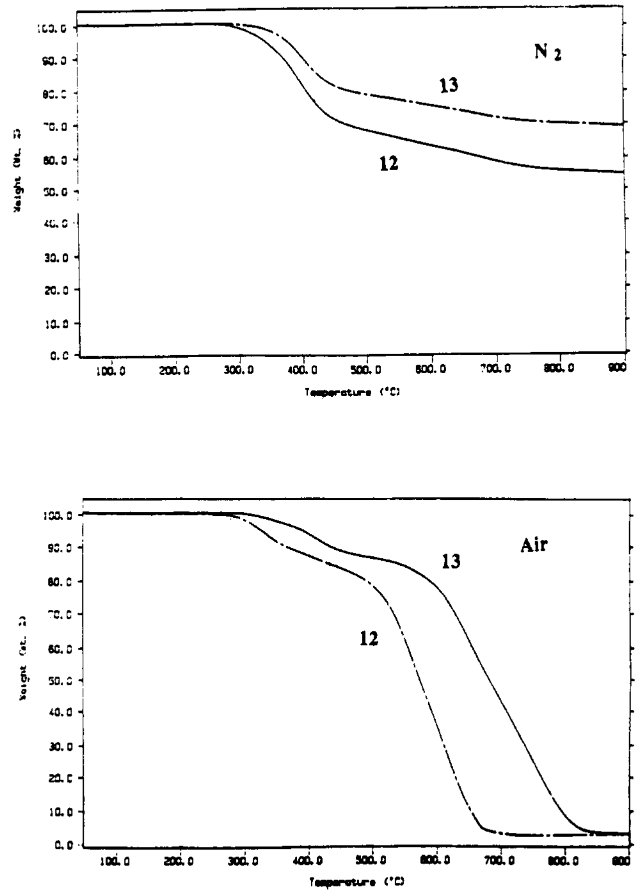


Figure 4. TGA curves of polymers **12** and **13** in nitrogen and in air.

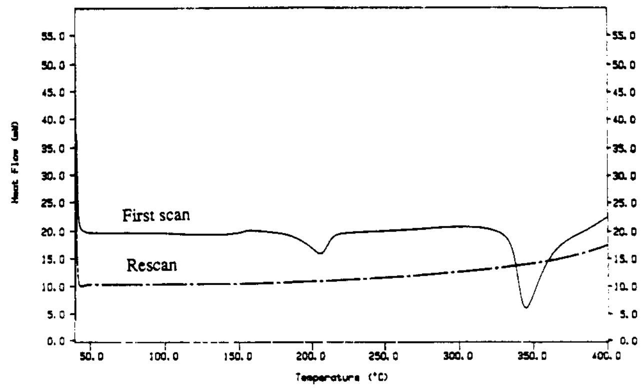


Figure 5. Differential scanning calorimogram of polymer **9**.

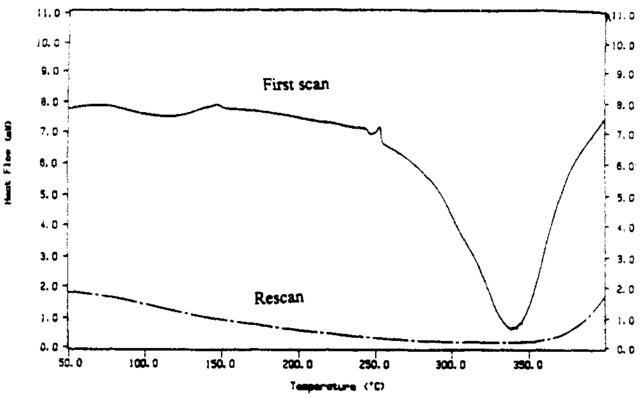


Figure 6. Differential scanning calorimogram of polymer 10.

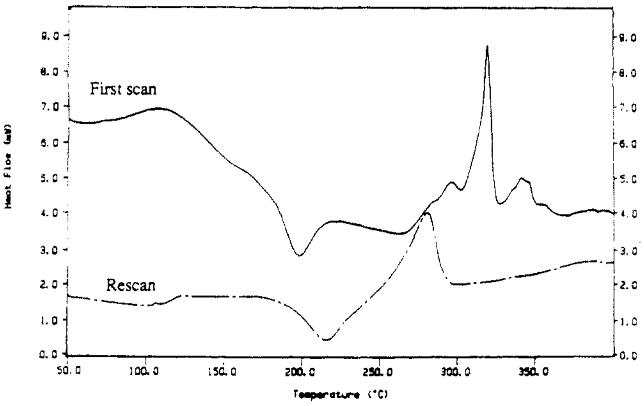


Figure 7. Differential scanning calorimogram of polymer 11.

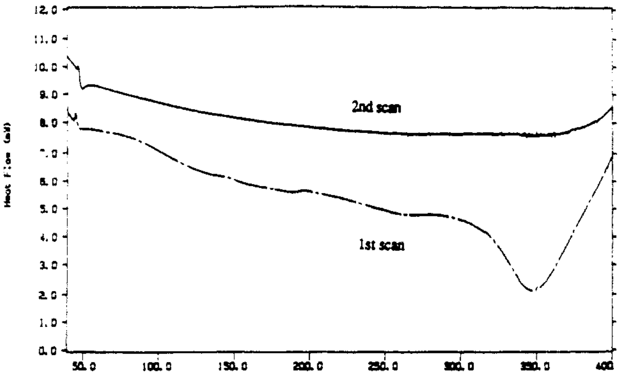


Figure 8. Differential scanning calorimogram of polymer 12.

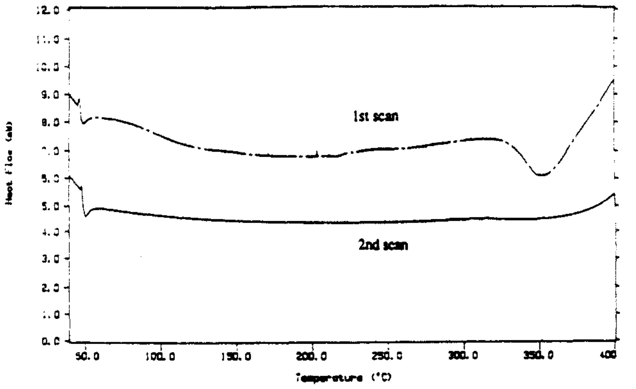


Figure 9. Differential scanning calorimogram of polymer 13.

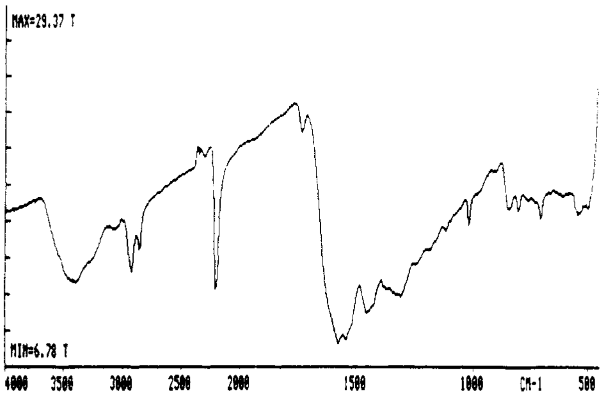
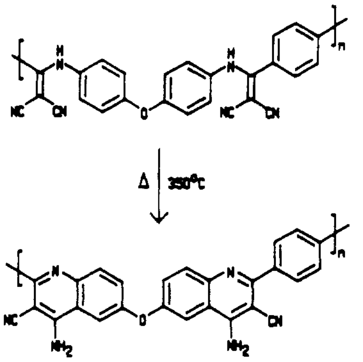


Figure 10. FTIR spectrum of the material obtained after heating polymer 9 to 375 °C.

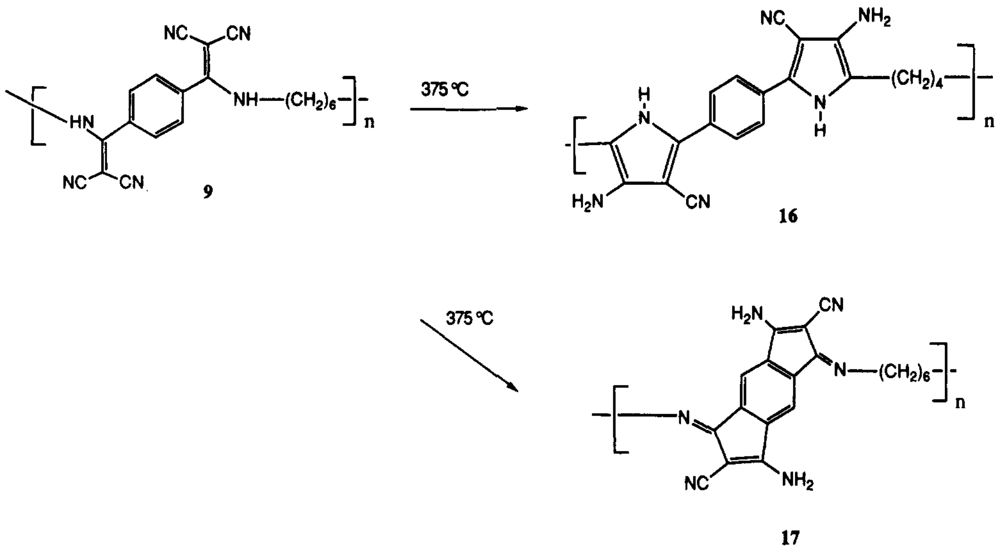
Scheme III



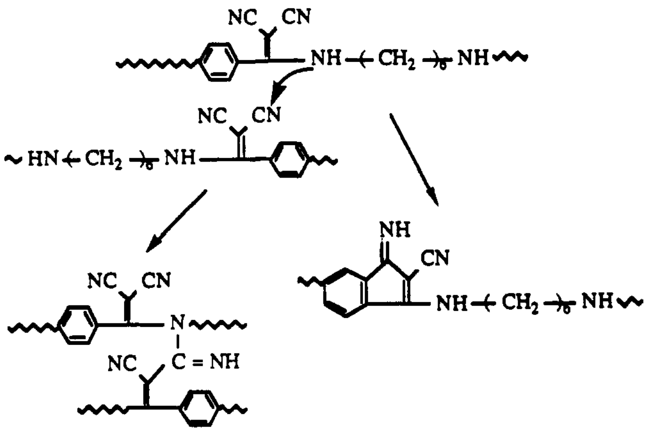
the exothermic transition at 350 °C indicated[2] that the formation of aminoquinolines, as shown in Scheme III, was (at least in part) responsible for this transition. Observation of a similar exotherm for enaminonitriles derived from an aliphatic amine requires that reaction pathways other than formation of aminoquinoline units must be operative. Among the products that might be formed which are consistent with the observed spectral changes are 16 and 17 (Scheme IV). Alternatively, the curing process may occur by an intermolecular path such as that shown in Scheme V. More experiments on model compounds are required to explicate the cause of this exotherm. Polymer 11 does not show such a transition. A rationale for the absence of this exotherm in the calorimogram for polymer 11 may be that this polymer has a higher degree of crystallinity (see discussion below) as a result of which the polymer chains may be less mobile, which in turn may require higher temperature to cause the reaction. Alternatively, the sulfone group may deactivate the aromatic ring by withdrawing electron density sufficiently to inhibit the cyclization process. This type of situation may preclude the formation of a product similar to 17 (Scheme IV) where the aromatic ring may participate in the cyclization process.[8]

It has been shown by Robello[6] that 1,4-bis[2,2-dicyano-1-[(4-phenoxyphenyl)amino]vinyl]benzene (18) does not undergo the exothermic process until the sample melts (see scanning calorimogram shown in Figure 11). Once the sample melts, sufficient intramolecular mobility is obtained so that a suitable conformation, which may be necessary for the exothermic process to occur, may be achieved. In line with the hypothesis presented here, the more organized crystal lattice of the low molecular weight compound in 18 prevents the molecular reorganization needed for the exothermic process (presumably cyclization) to occur. In the case of polymer 11, the temperature required to attain sufficient intramolecular mobility may be higher than the decomposition temperature of the polymer. Polymer 9 shows an additional exotherm at 210 °C (Figure 5). This transition may be indicative of transformation from an amorphous to a crystalline phase. However, no melting endotherm was noted below the exotherm near 350 °C. The polymer may melt higher than 350 °C or an insufficient amount of crystalline material

Scheme IV



Scheme V



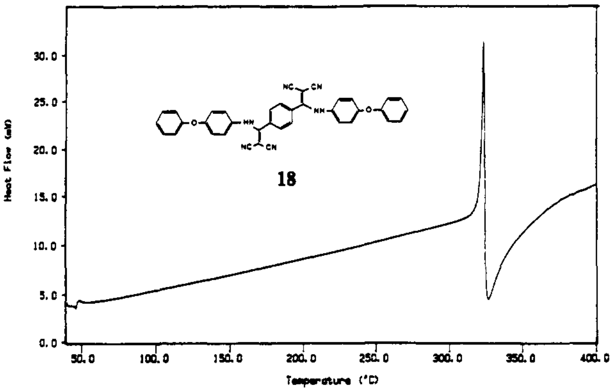


Figure 11. Differential scanning calorimogram of model compound 18.

formed during the measurement to exhibit a melting peak. It is likely that the polymer melt temperature is above 350 °C because, in our experience,[6] replacement of an amide group with an enaminonitrile group increases the melting temperature and it has been reported that poly(hexamethylene terephthalamide) melts at 371 °C.[7] Upon comparison of the structures of polymers 9 and 10 we notice that polymer 9 has 1,4-entrainment about the benzene ring which can lead to better packing of the chains. Consequently, we see a higher value of the glass transition temperature for 9 than for 10. Polymer 10 shows a glass transition as well as what may be a small melting endotherm slightly above 250 °C. Polymer 11 shows a crystallization exotherm and a melting transition in its calorimogram (Figure 7). When this polymer was melted in an open capillary tube, it melted at about 310–320 °C but became a dark brown viscous liquid upon further heating. When this polymer was melted in a test tube fibers could be formed by dipping a glass rod and withdrawing it from the melt. A sample of polymer 11 was heated in a DSC plan above its melting point and quickly quenched to room temperature. When this quenched sample of polymer 11 was rescanned (Figure 7, rescan), it showed a transition at 115 °C which appears to be a glass transition. More experiments are needed to understand the causes of the thermal transitions observed for polymer 9–13 in detail.

We observe once again that replacement of the amide function with the enaminonitrile group enhances the solubility with respect to the "parent" polyamide. Shashoua and Eareckson[7] have observed that "...polyterephthalamides from short chain aliphatic, primary diamines are among the most difficult polyamides to prepare and are quite intractable once obtained." Poly(hexamethyleneterephthalamide) is soluble in hot *m*-cresol and trifluoroacetic or sulfuric acids while polyenaminonitriles are readily soluble in most polar, aprotic solvents and some higher boiling ethers. We have attributed this improved solubility profile to the increased tendency toward *inter*molecular hydrogen bonding engendered by the poor hydrogen bond acceptor activity of the dicyanomethylidene group.[8] As a result, polymer–solvent interactions are favored and cause increased solubility in a wide variety of hydrogen bond acceptor solvents.

Conclusions

We have synthesized novel polyenaminonitriles employing a simple interfacial polymerization technique. These polymers, which are analogs of aromatic–aliphatic polyamides, have better solubilities in common organic solvents than the corresponding polyamides. Moreover, in keeping with the characteristic behavior of other polyenaminonitriles, they *cure without evolution of small molecules*. Experiments designed to clarify the processes operative during thermally initiated curing are currently underway.

Experimental Section

A. Instrumentation. Unless otherwise specified, all melting points were determined on a Thomas/Hoover melting point apparatus using open capillary tubes and are uncorrected. In some cases the melting points were also determined using differential scanning calorimetry.

Infrared (IR) and Fourier transform infrared (FTIR) spectra were recorded on a Perkin-Elmer Model 298 spectrophotometer and a Perkin-Elmer Model 1800 Fourier transform infrared spectrometer, respectively. The positions of the absorption bands are reported in cm^{-1}. The bands are denoted by s (strong), w (weak) or br (broad). NMR spectra were recorded on a Varian Model XL-200 spectrometer operating at 200 MHz for ^1H and 50.3 MHz for ^{13}C spectra. Some ^{13}C spectra were also obtained on an IBM Model WP/SY 100 spectrometer operating at 25.1 MHz. In all ^1H NMR experiments the chemical shifts are recorded in parts per million from tetramethylsilane as an internal standard when $CDCl_3$ was used as a solvent and from hexamethyldisiloxane in the case of all other solvents. The data are reported as follows: shift (multiplicity, coupling constant, integration). Abbreviations used to report multiplicity are s (singlet), d (doublet), t (triplet), q (quartet), d of d (doublet of doublets), m (complex multiplet), br (broad). In all ^{13}C NMR spectra the chemical shifts are reported in ppm. The solvent peaks (in the case of DMSO-d_6 a peak at 39.5 ppm and in the case of $CDCl_3$ a peak at 77.0 ppm) were used as reference. All ^{13}C NMR spectra were obtained using broad-band decoupling. Mass spectra were obtained on a Hewlett-Packard Model 5987 integrated gas chromatograph–mass spectrometer. All sample introductions were made via the direct insertion probe (DIP). Ionization was done by 70 eV electron impact (EI) or methane or isobutane chemical ionization (CI). 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). When polymers **9**, **10**, **12**, and **13** were dissolved in polar aprotic solvents some microgel could be seen in the solution which could not be filtered. The presence of microgel in the polymer solutions also made the precise determination of the concentration of the polymers in the solutions difficult. Hence, the solutions for viscosity measurements were prepared as follows. The polymer samples were dissolved in NMP or DMF, and the suspensions were centrifuged at approximately 2400 rpm for about 30 min in a Precision Universal Centrifuge. The supernatant solution was decanted, and films of the polymers were cast by evaporation of the solvent. The films were dried at 80–90 °C *in vacuo*. The polymer films thus obtained were weighed and dissolved for the viscosity measurements.

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., P.O. Box 51610, Knoxville, TN 37950-1610. It has been observed that this class of polymers tends to form thermally stable chars at high temperatures which result in elemental analyses which are low in carbon values. Hence, only the model compounds for each class of polymers were submitted for elemental analysis. The results were found to be in accord with the proposed structures.

B. Solvents and Reagents. 1,6-Hexanediamine (Aldrich) was purified by sublimation just prior to polymerization. The sublimed material was quickly transferred to a preweighed container in a drybox.

C. Syntheses. Poly[imino(dicyanoethenylidene)-1,4-phenylene(dicyanoethenylidene)iminohexamethylene] (9). A solution of 1,6-hexanediamine (0.5824 g, 5.026 mmol) and sodium hydroxide (0.4317 g, 10.7 mmol) in distilled water (15 mL) was stirred vigorously in a blender jar and to it was added, in one portion, a solution of 1,4-bis(1-chloro-2,2-dicyanovinyl)benzene[2] (**4**) (1.5017 g, 5.026 mmol) in methylene chloride (10–12 mL). Before the monomers were mixed the solution in the blender was stirred at a moderately high speed, and after the dichloride was added the mixture was stirred at the maximum speed obtainable. The fibrous polymer precipitated almost instantaneously, and the reaction mixture was stirred for 2–3 min. The polymer was removed from the jar and rinsed with large amounts of distilled water. The stringy fragments were replaced in the jar with about 30 mL of water and blended to a fine powder which was filtered and dried *in vacuo* ($p < 1$ Torr) at 60–70 °C for 36 h (1.2915 g, 75.27%). The intrinsic viscosity was found to be 1.25 dL/g when measured in NMP at 25 °C. FTIR (KBr): 3271, 3071, 2936, 2862, 2213, 1703 *w*, 1580, 1424, 1362, 1312, 1279, 1240, 1187, 1116, 1051, 1020, 903, 841, 727, 699, 549 cm^{-1}. ^1H NMR (DMF-d_7): 0.8–3.8 (broad multiple peaks, aliphatic methylene protons), 7.5–7.8 (m, aromatic protons), 9.2 δ (broad singlet with some fine splitting, enamine protons). ^{13}C NMR (DMSO-d_6): (25.28, 25.55) [$CH_2CH_2CH_2NH$], (28.42, 29.13) [CH_2CH_2NH], 44.91, 45.45, 47.12, 47.44, 49.41, 49.54, (115.23, 116.48, 116.81, 117.53, 117.71) [$=C(CN)_2$], 128.22, 128.99), (133.07, 133.36), (136.38, 136.75) [arom *C*], (167.08, 170.80) [$=C$-NH].

Poly[imino(dicyanoethenylidene)-1,3-phenylene(dicyanoethenylidene)iminohexamethylene] (10). Synthesized from 1,3-bis(1-chloro-2,2-dicyanovinyl)benzene[2] (**5**) and 1,6-hexanediamine by the procedure described above in 70.48% yield. The intrinsic viscosity was found to be 1.18 when measured in NMP at 25 °C. FTIR (KBr): 3269, 3084, 2932, 2213 *s*, 1576, 1455, 1348, 1241, 1177, 1152, 999, 909, 808, 708, 551 cm-11. ^{H} NMR (DMSO-d_6): 0.7–3.6 (broad multiple peaks, 12H, aliphatic methylene protons), 7.5–7.8 (m, 4H, aromatic protons), 9.15 (broad single with some fine splitting, 2H, enamine protons). ^{13}C NMR (DMSO-d_6): (25.23, 25.58) [$CH_2CH_2CH_2NH$], (28.45, 29.18) [CH_2CH_2NH], 44.96, 45.56, 46.95, 47.56, 49.50, 49.65, (115.23, 115.40, 116.64, 116.79, 117.84) [$=C(CN)_2$], (127.22, 128.08, 128.78, 129.12, 129.53, 129.91, 130.07, 130.82, 131.11, 131.21, 131.52, 131.64, 132.10, 133.96, 134.82) [arom *C*], (166.87, 166.98, 170.48) [$=$CNH].

Poly[imino(dicyanoethenylidene)-1,4-phenylenesulfonyl-1,4-phenylene(dicyanoethenylidene)iminohexamethylene] (11). Synthesized from 4,4′-bis(1-chloro-2,2-dicyanovinyl)diphenyl sulfone[2] (**4**) and 1,6-hexanediamine in 80% yield by the procedure described above. The polymer was found to be insoluble in almost all common organic solvents as well as solvents such as hexafluoropropanol and formic acid. Mp: (by DSC) 317.24 °C. FTIR (KBr): 3333, 2931, 2856, 2200, 1657, 1642, 1563, 1547, 1536, 1486, 1399, 1162, 1145, 1105, 1015, 857, 741, 616 cm^{-1}.

Poly[imino(2,2-dicyanoethenylidene)-4,4′-biphenylene(2,2-dicyanoethenylidene)iminohexamethylene] (12). Synthesized from 4,4′-bis(1-chloro-2,2-dicyanovinyl)biphenyl[1b] (**7**) and 1,6-hexanediamine in 77% yield by the procedure described above. A tough, slightly yellow film was cast from DMF solution. The product was soluble in NMP, DMSO, DMAc, and DMF. The intrinsic viscosity of the polymer was 1.06 dL/g in DMF at 25.0 °C. IR (thin film): 3278 (NH), 3076 (arom. CH), [2934, 2860] ($-CH_2-$), 2212 s (CN), 1666, 1580, 1502, 1442, 1350, 1240, 1182, 1006, 826, 734 cm^{-1}. ^1H NMR (DMSO-d_6): δ 9.05 (br s, 2H, N*H*), 7.88-7.61 (8H, arom. C*H*), 3.61–0.88 (br m, 12H, aliphatic CH_2) ppm. ^{13}C NMR (DMSO-d_6): [171.5, 167.8.0] ($=$*C*NH), [141.7, 133.8] (arom *C*), [129.6, 128.8, 127.0] (arom *C*H), [116.9, 115.2] (*C*N), [49.3, 46.9] ($=C(CN)_2$), [45.6, 44.9] (CH_2NH), [29.1, 28.5] (CH_2CH_2NH), 25.6 ($CH_2CH_2CH_2NH$).

Poly[imino(2,2-dicyanoethenylidene)-4,4″-terphenylene-(2,2-dicyanoethenylidene)iminohexamethylene] (13). Synthesized from 4,4′-bis(1-chloro-2,2-dicyanovinyl)-*p*-terphenyl[1b] and 1,6-hexanediamine in 81% yield by the procedure described above. The product was soluble in NMP, DMSO, DMAc, and DMF. The intrinsic viscosity of the polymer was 0.69 dL/g in DMF at 25.0 °C. IR (thin film): 3278 (NH), 3068 (arom. CH), [2934, 2860] ($-CH_2-$), 2192 s (CN), 1666, 1608, 1580, 1492, 1442, 1370, 1004, 820 cm^{-1}. ^1H NMR (DMSO-d_6): δ 9.03 (br s, 2H, N*H*), 7.91–7.52 (12H, arom. C*H*), 3.60–0.86 (br m, 12H, aliphatic CH_2) ppm. ^{13}C NMR (DMSO-d_6): [171.8, 168.0.0] ($=$*C*NH), [142.4, 138.5, 133.3] (arom *C*), [129.6, 127.6, 126.7] (arom *C*H), [118.2, 117.2] (*C*N), [49.5, 46.8] ($=C(CN)_2$), [45.6, 45.0] (CH_2NH), [29.1, 28.5] (CH_2CH_2NH), [25.7, 25.4] ($CH_2CH_2CH_2NH$).

3-(Ethylamino)-3-phenyl-2-cyanopropenenitrile (14). A 25-mL round-bottomed flask, equipped with a magnetic stirring bar and a reflux condenser, was charged with ethylamine hydrochloride (0.3114 g, 3.81 mmol). To this mixture was added an aqueous solution of sodium hydroxide (0.3052 g, 7.632 mmol in 5 mL of water). The reaction flask was cooled to 0 °C in an ice bath. To this cold, stirred solution was added a solution of chlorophenylmethylidenepropanedinitrile[2a] (0.6 g, 3.18 mmol) in dry methylene chloride (4.5 mL). The reaction mixture was stirred at 0 °C for 2 h followed by stirring at room temperature overnight. The methylene chloride layer was separated, washed with water and brine, dried over anhydrous magnesium sulfate, and concentrated *in vacuo* to give an almost pure (by proton NMR) colorless solid (0.2836 g, 45.22%). An analytical sample was obtained by crystalliniation from benzene/hexanes, mp 120–121 °C. Anal. Calcd for $C_{12}H_{11}N_3$: C, 73.07; H, 5.62; N, 21.30. Found: C, 73.32; H, 5.63; N, 21.50. IR (KBr): 3270 *s*, 3153, 2991, 2209 *s*, 1593 *s*, 1446, 1426, 1384, 1335, 1281, 1241, 1185, 1148, 1106, 1073, 1041 *w*, 1029, 803, 769 *s*, 708 *s*, 696, 614 cm^{-1}. MS (CI/pos ion): 198 ($M^+ + 1$, 100). ^{1}H NMR (DMF-d_7): 1.03 (t, $J = 7.14$ Hz, 3H, methyl protons), 1.30 (t, $J = 7.14$ Hz, 3H, methyl protons), 3.05 (q, $J = 7.23$ Hz, 2H, methylene protons), 3.72 (q, $J = 7.26$ Hz, 2H, methylene protons), 7.46–7.55 (m, aromatic protons), 8.90 (s, broad, enamine hydrogen). ^{1}H NMR (DMSO-d_6) (power gated decoupling): (14.31, 15.24) [CH_3], (40.01, 40.71) [CH_2], (46.08, 49.08) [$=C(CN)_2$], (115.55, 116.72, 117.04, 117.94) [$=C(CN)_2$], (127.62, 128.52, 128.66, 128.94, 130.62, 130.88, 131.52, 134.11) [arom *C*], (168.20, 171.80) [$=CNH$].

1,4-Bis[(2,2-dicyano-1-ethylvinyl)amino]benzene (15). A 50-mL, round-bottomed flask equipped with a magnetic stirring bar and a reflux condenser was charged with ethylamine hydrochloride (0.6542 g, 8.02 mmol) in water (10 mL). To this solution was added an aqueous solution of sodium hydroxide (0.6017 g, 15.04 mmol in 10 mL of water). The reaction flash was cooled to 0 °C in an ice bath. To this cold and stirred solution was added a solution of 4 (1.0 g, 3.34 mmol) in dry methylene chloride (10–12 mL). The reaction mixture was stirred at 0 °C for 2 h followed by stirring at room temperature overnight. The solid that precipitated was separated, washed with water and methanol, and dried (0.8656 g, 81.9%). The proton NMR spectrum of the solid confirmed the structure and indicated that the crude product was quite pure. An analytical sample was obtained by crystallization from THF/hexanes, mp 290–292 °C. FTIR (KBr): 3284, 2206, 1559, 1509, 1475, 1456, 1384, 1367, 1343, 1326, 1289, 1143, 885, 861, 713, 684 cm^{-1}. MS (CI/ pos ion.): 317 $M^+ + 1$, 10.4), 219 (7.8), 97.0 (13.9), 92 (13.2), 85 (77.8), 81 (100). ^{1}H NMR (DMF-d_7): 1.02 [t, $J = 6.98$ Hz, 3H, methyl protons], 1.31 [t, $J = 6.98$ Hz, 3H, methyl protons], 3.06 [p, $J = 6.7$ Hz, 2H, methylene protons], 3.74 [p, $J = 6.0$ Hz, 2H, methylene protons], (7.64, 7.70, 7.76, 7.80) [aromatic protons], 9.08–9.16 [broad multiplet with fine splitting, 2H, enamine protons]. ^{13}C NMR (DMSO-d_6): (14.30, 15.17) [CH_3CH_2], (40.15, 40.80) [$-CH_2-CH_3$], 47.04, 47.25, 49.33, (115.37, 116.56, 116.90, 117.82) [$=C-(CN)_2$], (128.11, 128.50), (129.08, 129.42), (133.08, 133.45), (136.31, 136.79) [arom *C*], (167.01, 170.68) [$=CNH$].

Acknowledgment. We thank Dr. Herbert Schwartz and Mr. Savely Goldin for assistance in obtaining NMR and mass spectra data, respectively. Mr. Craig Thompson conducted the interfacial polymerization which yielded polymer **13**. This work was supported, in part, by a grant from the Office of Naval Research.

References and Notes

(1) Preliminary accounts of portions of this work have appeared: (a) Moore, J. A.; Mehta, P. G. *Polym. Mater. Sci. Eng.* **1990**, *63*, 351. (b) Moore, J. A.; Kim, S.-Y. *Polym. Prep.* **1991**, *32*, 403.

(2) (a) Moore, J. A.; Robello, D. R. *Macromolecules* **1989**, *22*, 1084. (b) Moore, J. A.; Mehta, P. G. *Polym. Mater. Sci. Eng.* **1989**, *60*, 74.

(3) (a) Wallenfels, K. *Chemia* **1966**, *20*, 303. (b) Wallenfels, K.; Friedrich, K.; Rieser, J.; Ertel, W.; Thieme, K. *Angew Chem., Int. Ed. Engl.* **1976**, *15*, 261.

(4) Moore, J. A.; Mehta, P. G. *Macromolecules* **1993**, *26*, 916.

(5) Morgan, P. W. *Condensation Polymers by Interfacial and Solution Methods*; Wiley-Interscience: New York, 1965.

(6) Robello, D. R. Ph.D Dissertation, Rensselaer Polytechnic Institute, Troy, NY, 1986.

(7) Shashoua, V. E.; Eareckson, W. M. *J. Polym. Sci.* **1959**, *40*, 343.

(8) Moore, J. A.; Kim, J.-H. *Macromolecules* **1992**, *25*, 1427.