Synthesis of an Aliphatic Poly(enamino nitrile) Analogous to a Polyurea[1]

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ABSTRACT: The first example of an aliphatic poly(enamino nitrile) analogous to a polyurea prepared by interfacial condensation of (dichloromethylene)propanedinitrile and 1,6-diaminohexane is described and characterized.

Introduction

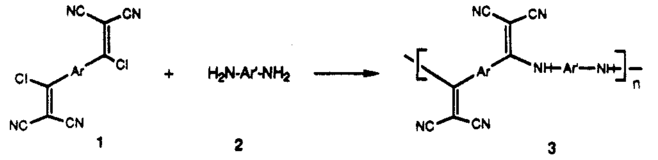
As a part of a program to prepare high molecular weight processable polymers that cure thermally without evolution of small molecules, we have successfully exploited a vinylic nucleophilic substitution pathway to prepare novel poly(enamino nitriles)[2] 3 (Scheme I). While studying the kinetics of the reactions of azide ion with (chlorophenylmethylene)propanedinitrile (4),[3] we became aware of the possibility that (azidophenylmethylene)propanedinitrile (5) can undergo a Curtius-like rearrangement[4] to form an intermediate ketenimine which could be trapped with aniline to form [bis(phenylamino)methylene]propanedinitrile (7) (Scheme II). In 1987 Shi and Wudl[5] carried out a similar reaction with 2,2′-[1,4-phenylenebis(chloromethylidyne)]bis(propanedinitrile) (8) and were able to trap the intermediate bisketenimine with aniline (Scheme III) to give 2,2′-[1,4-phenylenebis[imino(phenylamino)methylidyne]]bis(propanedinitrile) (10). Subsequently, Shi and Wudl[6] used this approach to prepare an aromatic polyurea analog 11 from the bisketenimine and *p*-phenylenediamine (Scheme IV).

Results and Discussion

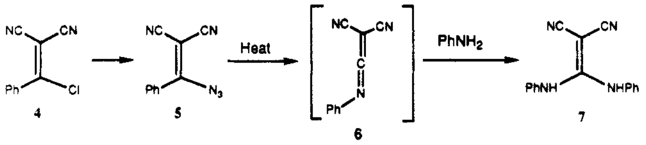
Our study of the properties of various poly(enamino nitriles)[2] led to the decision to use 4-aminophenyl ether (12) as a diamine in the hope of synthesizing polymer 13 (Scheme V). An attempt was made to isolate pure 2,2′-[1,4-phenylenebis(azidomethylidyne)]bis(propanedinitrile) (9) (Scheme III) so that we could maintain the precise stoichiometry necessary to attain high molecular weight in condensation polymerization. When solid 9 was collected on a fritted funnel, it exploded, shattering the glass frit and a beaker completely. At this point, considering the dangerous nature of this intermediate, it was thought prudent to abandon this approach to making polymers and to seek an alternative route to polymers of structure similar to 13. It was envisioned that (dichloromethylene)propanedinitrile (14), a phosgene analog, could be reacted with 4-aminophenyl ether to give polymer 15 (Scheme VI).

(Dichloromethylidene)propanedinitrile (14) was prepared (Scheme VII) according to a literature procedure.[7] Model compound 7 was obtained by reacting 14 with aniline 18 (Scheme VIII). However, reaction of 4-aminophenyl ether with 14 in an attempt to obtain polymer 15 (Scheme VI) produced either uncharacterizable solids or extremely fine suspensions of solid when the reaction mixture was poured into water. It is conceivable that once one of the chlorine atoms in 14 is replaced by reaction with an amine, the displacement of the second chlorine atom from the intermediate might be more difficult because of deactivation of the carbon atom bearing chlorine toward nucleophilic substitution by the already present enamine group. Such a difference in reactivity might make it difficult to obtain high molecular weight polymers from 14 and weakly nucleophilic aromatic diamines.

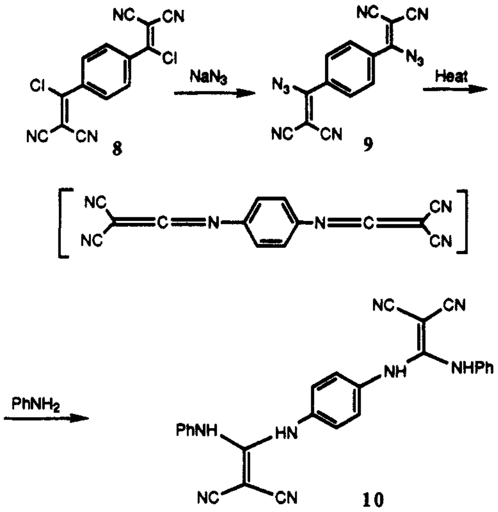
Scheme I



Scheme II



Scheme III



At this point, it was thought that it might be possible to prepare polymers by reacting 14 with more strongly nucleophilic diamines such as hexamethylenediamine. Indeed, when 14 was reacted with hexamethylenediamine by rapidly stirring immiscible solutions of the monomers together (interfacial polymerization),[8] high molecular weight polymer 19 was obtained (Scheme IX). Model compound 20, resembling the repeat unit of polymer 19, was synthesized by reacting ethylamine hydrochloride with 14 using sodium hydroxide as a base (Scheme X).

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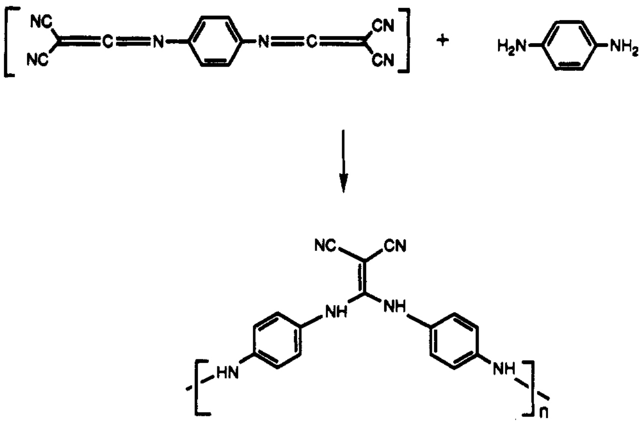
Scheme IV



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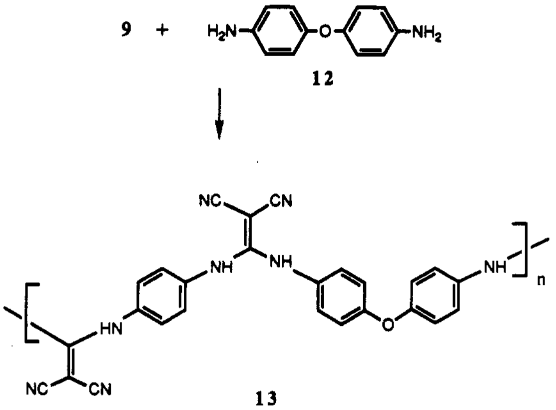
Scheme V



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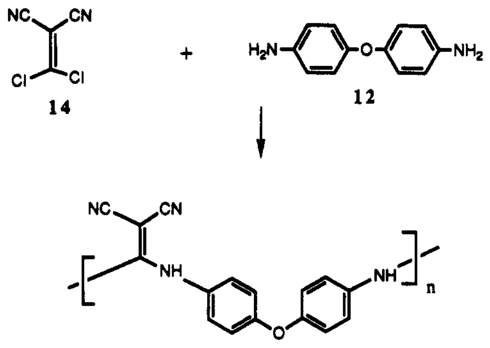
Scheme VI



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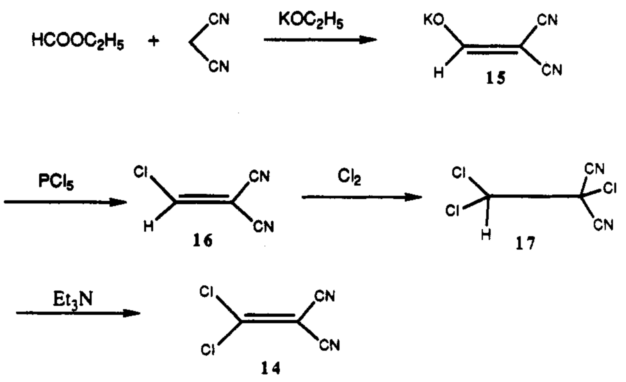
Scheme VII



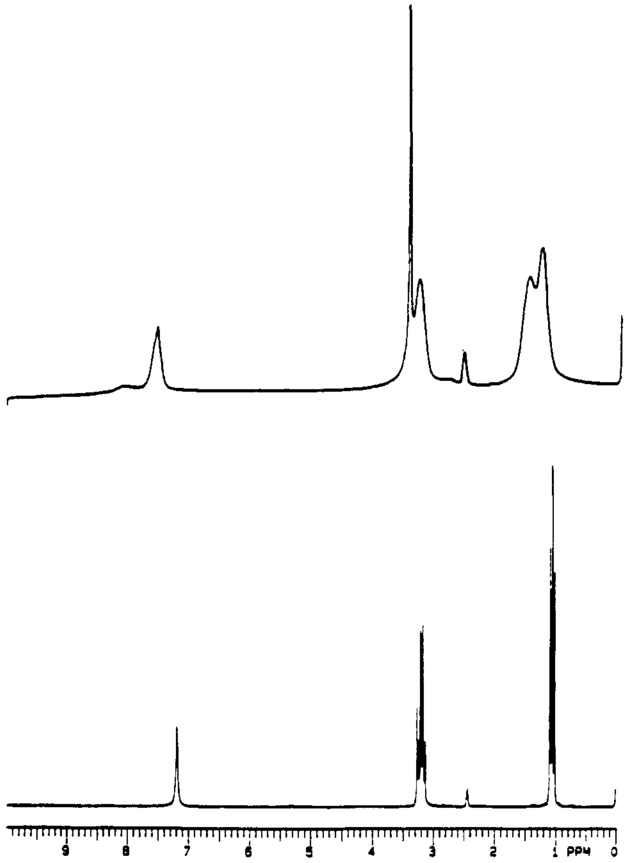
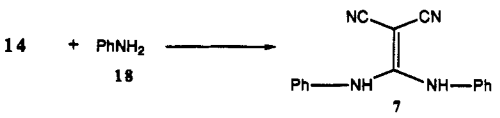
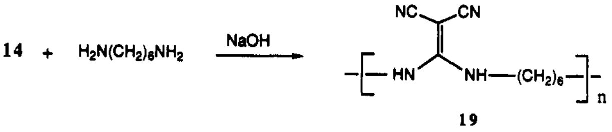


Figure 1. ^{1}H NMR spectra of polymer **19** (top) and model compound **20** (bottom) in DMSO-d_6.

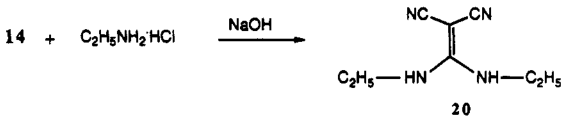
Scheme VIII



Scheme IX



Scheme X



The spectral data for polymer **19** matched very well with those obtained for model compound **20**. The proton and carbon NMR spectra of these materials are shown in Figures 1 and 2, respectively. Polymer **19** was soluble in polar aprotic solvents such as DMF, DMAc, NMP, and DMSO. Tough films of this polymer, which were somewhat resilient, could be cast from its solution in these solvents. When the films were cast by allowing the solvent to evaporate from the solution on a glass plate or an aluminum dish, a clear film (T_g = 66 °C) was obtained but when this transparent film was removed from the glass or aluminum surface, it became opaque and cloudy, indicating that crystallization may have been induced. Films of polymer **19** adhered very strongly to both glass and aluminum surfaces. No attempts were made to optimize yield or molecular weight because the reaction worked very well. The intrinsic viscosity of polymer **19** was measured in NMP at 25 °C and was found to be 1.08 dL/g, indicating that high molecular weight had been obtained. As can be seen from Figure 3, polymer **19** possesses surprisingly good thermal stability considering the fact that it contains six methylene units in the polymer

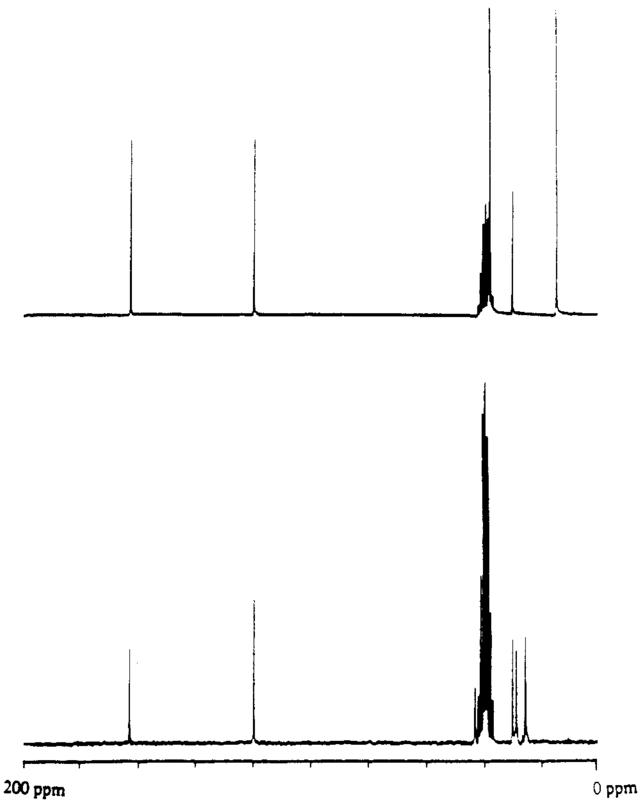


Figure 2. 50.3-MHz ^{13}C NMR spectra of model compound **20** (top) and polymer **19** (bottom) in DMSO-d_6.

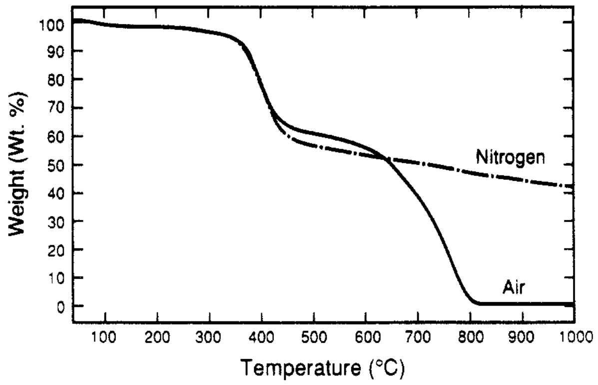


Figure 3. Thermogram for polymer **19** in air and in nitrogen.

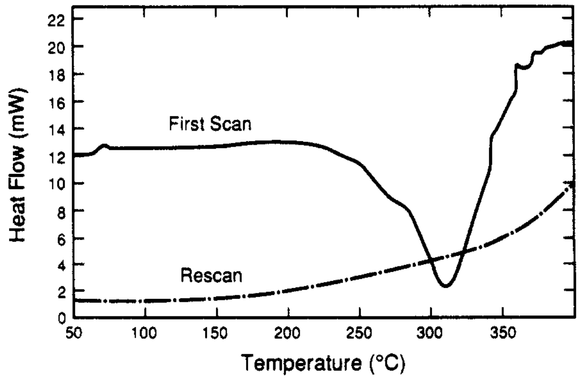


Figure 4. Differential scanning calorimogram of polymer **19**.

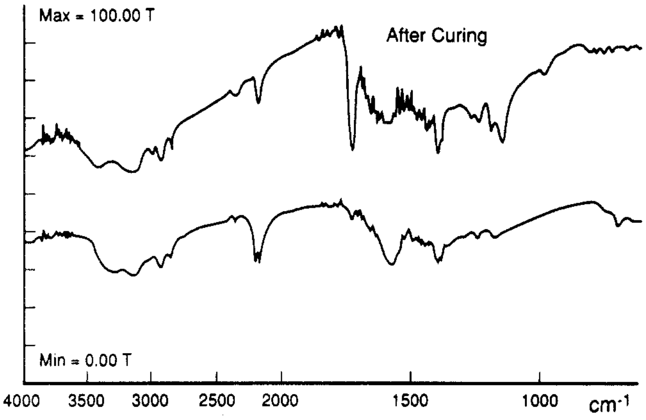


Figure 5. Infrared spectra of polymer **19** before and after curing.

backbone. Significant weight loss does not become evident until about 350 °C (10% weight loss at 380 °C; 50% weight loss at 645 °C; heating rate = 10 °C/min in air). Polymer **19** shows interesting thermal behavior as evidenced by its calorimogram (Figure 4). Polymer **19** shows an exotherm which is not in evidence on rescanning the sample but it appears at relatively lower temperature (310 °C) as compared to other poly(enamino nitriles). An examination of the products produced when enamino nitriles derived from aromatic amines were heated through the exothermic transition at 350 °C showed[2] that the formation of aminoquinolines was (at least in part) responsible for this transition. Observation of a similar exotherm for enamino nitriles derived from an aliphatic backbone requires that reaction pathways other than formation of aminoquinoline units must be operative. After the exotherm had occurred, the previously soluble sample was completely insoluble in THF, DMF, or triglyme. Examination of the IR spectra of a sample of the polymer before and after it had been heated through the exothermic transition (Figure 5) reveals that the nitrile absorption at 2186 cm^{-1} (doublet) has decreased significantly and an absorption in the carbonyl region at 1730 cm^{-1} has appeared. The absorptions in the region around 2800–3500 cm^{-1} are essentially unchanged, indicating that the insolubilization process involves condensation of the nitrile groups in an, as yet, unclarified fashion. More experiments on the model compounds are required to understand this process and are in progress. No indication of crystalline melting was apparent. However, the polymer may melt higher than 310 °C or an insufficient amount of crystalline material may have been formed during the measurement to exhibit a melting peak. It is likely that the polymer melt temperature is above 310 °C because, in our experience,[2] replacement of an amide group with an enamino nitrile group increases the melting temperature and it has been reported that poly(hexamethylene urea) melts at 295 °C.[9]

Conclusions

We have synthesized the first completely aliphatic poly(enamino nitrile) employing a simple interfacial polymerization technique which appears to have wide applicability. The use of this compound in the synthesis of a wide variety of new polymers is currently underway. This polymer, which is an analog of an aliphatic polyurea, possesses better solubility in common organic solvents than analogous polyamides or polyureas, which are, typically, only soluble in solvents such as *m*-cresol or sulfuric acid. The all-aliphatic poly(enamino nitrile) exhibits unusually good thermal stability and undergoes an, as yet, unidentified cross-linking process without evolution of volatile byproducts.

Experimental Section

(A) Instruments and Techniques. 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 ^{1}H and 50.3 MHz for ^{13}C spectra. In all ^{1}H NMR experiments the chemical shifts are recorded in parts per million (ppm) 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, percent 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 polymer **19** was 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 polymer solution difficult. Hence, for the viscosity measurements the solutions of the polymer were prepared as follows. The polymer sample was dissolved in NMP, and the solution was centrifuged at approximately 2400 rpm for about 30 min in a precision universal centrifuge. The supernatant solution was decanted and films of the polymer 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 in NMP 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.

(B) Solvents and Reagents. 4-Aminophenyl ether (Aldrich Gold Label, zone refined) was used. 1,6-Hexanediamine (hexamethylenediamine) (Aldrich) was purified by sublimation just prior to polymerization. The sublimed material was quickly transferred to a preweighed container in a drybox. Aniline was dried by distillation over KOH pellets. Ethyl formate was stirred overnight with anhydrous potassium carbonate (J. T. Baker) and distilled over P_2O_5.

(C) Syntheses. [Bis(phenylamino)methylene]propanedinitrile (7). Method A. To a solution of aniline (3.4503 g, 37.04 mmol) in dry methylene chloride (15 mL), stirred and cooled to 0 °C, was added a solution of **14** (1.0866 g, 7.409 mmol) in dry methylene chloride (~5 mL) under nitrogen. The reaction mixture was stirred and allowed to warm to room temperature over a period of 1 h. The reaction mixture was heated at reflux overnight and then cooled to room temperature, and the thick precipitate which had formed was filtered. The precipitate was stirred in warm water (40–45 °C) for about 30 min and filtered. The colorless solid thus obtained was washed with methanol (15 mL) and dried (1.3401 g, 69.5%), mp 271 °C (by DSC) (lit.[4] mp 263 °C). IR (KBr): 3238 (s, NH), 3060, 3040, 2218 w, 2192 s, 1610, 1585, 1500, 1435, 1372, 1250, 750 s, 705, 692 cm^{-1}. MS (CI/positive ion): 261 (M$^+$ + 1, 100), 216 (60), 204. ^{1}H NMR (DMSO-d_6): δ 6.96 (t, J = 6.6 Hz, 1 H), 7.04 (d of d, J = 0.92, 7.41 Hz, 2 H), 7.19 (t, J = 7.93 Hz, 2 H), 9.94 (s, 2 H). ^{13}C NMR (power-gated decoupling) (DMSO-d_6): δ 40.23 [=*C*(CN)$_2$], 117.26 [=C(*C*N)$_2$], (121.21, 124.33, 129.04, 133.56) [aromatic *C*], 159.41 [=*C*(NH)].

Method B.[5,6] To a solution of (chlorophenylmethylene)propanedinitrile (**4**)[2a] (0.100 g, 0.53 mmol) in dry acetone (5 mL) was added a solution of sodium azide (0.0646 g, 0.93 mmol) in water (1.5 mL) at 0 °C with stirring. The reaction mixture was stirred at 0 °C for 1 h and then poured into 15 mL of water. (*Caution*: From this point onward until the intermediate ketenimine is quenched with an amine, all the operations should be carried out behind a protective shield.) The light yellow solid was filtered very quickly and dissolved on the frit (while it was still somewhat wet) in 1,2-dimethoxyethane (~10 mL). If precipitate sticks on the side of the funnel, use a porcelain spatula or one coated with Teflon to remove it. The solution was dried over anhydrous magnesium sulfate at 0 °C for 2 h. The solution was filtered, and aniline (0.0816 g, 0.877 mmol) was added. The reaction mixture was heated at 60–70 °C for 90–100 min, the solvent was removed with a rotary evaporator, and the residue (0.082 g, 59.94%) was characterized as the desired product by proton NMR and IR, and which compared very well with those reported by Shi and Wudl.[6]

(Hydroxymethylene)propanedinitrile Potassium Salt (15).[7] A 2-L, three-necked, round-bottomed flask was fitted with a mechanical stirrer and a reflux condenser. Freshly cut potassium metal (71.4 g, 1.82 mol) was carefully cleaned and weighed in petroleum ether and was quickly transferred to the reaction flask. Absolute ethyl alcohol (200 mL) was immediately added, followed by four more portions of 200 mL each over a period of 1 h. After all the potassium had dissolved in the ethanol and while the reaction contents were still warm, malononitrile (115.6 g, 1.749 mol) and ethyl formate (262.93 g, 3.549 mol) in absolute ethanol (200 mL) were added to the reaction flask successively. A light yellow solid started precipitating soon after the addition of malononitrile and ethyl formate to the reaction flask. The reaction mixture was stirred at room temperature for 30 min followed by stirring at reflux for 2 h. The reaction mixture was cooled to room temperature and the solid was filtered, washed with diethyl ether (4 × 500 mL), and dried overnight in vacuo (P ~ 0.5–1 Torr) over phosphorus pentoxide using a liquid nitrogen trap in the vacuum line (216.55 g, 93.67%).

(Chloromethylene)propanedinitrile (16). To a slurry of the potassium salt of (hydroxymethylene)propanedinitrile (160 g, 1.21 mol) in dry methylene chloride (900 mL) was added phosphorus pentachloride (249 g, 1.21 mol) in one portion. The reaction mixture was stirred, under nitrogen, at reflux for 6 h and then cooled to room temperature, and the precipitated solid was filtered. The solid was washed with dry methylene chloride (10 × 100 mL), and the washings were combined with the filtrate obtained earlier. Methylene chloride was removed under reduced pressured (no heating, ~12 Torr), and the residue in the flask was distilled at ~70 °C (10 Torr) to give a colorless liquid (118.28 g, 85.68%) (lit[7]. 73 °C/10 mm). IR (thin film): 3122, 3062 s, 2240 s, 1565, 1420 w, 1390 w, 1281, 1160, 900 s, 871 s, 810 w, 746. MS (EI): 114.0 (M$^+$ + 2, 31.49), 113.0 (M$^+$ + 1, 5.81), 112.0 (M$^+$, 100), 85.05 (M − HCN, 14.6), 77 (M − Cl, 79.8), 76 (M − HCl, 22.22), 51 (60.9). ^{1}H NMR (CDCl$_3$): δ 7.83 (s, vinylic hydrogen). ^{13}C NMR (CDCl$_3$): δ 93.46 [=*C*(CN)$_2$], (108.91, 110.10) [=C(*C*N)$_2$], 154.70 [=*C*Cl]. ^{13}C NMR (CDCl$_3$) (power-gated nondecoupled spectrum): δ 93.21 [=*C*(CN)$_2$, J = 7.02 Hz], (108.70, 109.87) [=C(*C*N)$_2$, J = 11.6, 5.4 Hz], 154.51 [=*C*Cl, J = 203.37 Hz].

2-Chloro-2-(dichloromethyl)propanedinitrile (17).[7] A solution of **16** (68.2185 g, 600 mmol) in dry methylene chloride (100 mL) was cooled to 0 °C, and chlorine gas was bubbled through the solution for 2 h. Benzyltriethylammonium chloride (0.38 g, 1.15 mmol) was added to the reaction mixture, and a vigorous reaction took place and the solution almost boiled with evolution of gas. The color of the reaction mixture changed from yellow to colorless. Chlorine gas was bubbled through the reaction mixture overnight. The reaction flask was surrounded with an ice bath, and methylene chloride was removed in vacuo (10 Torr). The residue was fractionally distilled (hot water was circulated through the condenser) under reduced pressure to yield a colorless liquid which crystallized upon standing (92.8261 g, 84.46%). Mp

45 °C (lit.[7] mp 46–47 °C), bp ~75 °C/10 mm (lit.[7] bp 76–76.5 °C/10 mm). IR ($CDCl_3$): 2984, 2255, 1212, 1082, 817, 810 cm^{-1}.

(Dichloromethylene)propanedinitrile (14).[7] A solution of 2-chloro-2-(dichloromethyl)propanedinitrile (17) (65.6674 g, 0.3578 mol) in dry diethyl ether (400 mL) was placed in a 1-L round-bottomed flask equipped with a mechanical stirrer, a reflux condenser connected to a mineral oil bubbler, and an addition funnel bearing a nitrogen inlet. The flask was cooled to 0 °C in an ice bath, and the solution was stirred under nitrogen. A solution of dry triethylamine (36.2118 g, 0.3578 mol) in dry diethyl ether was added over a period of 20–30 min. When addition had been completed, the mixture was stirred for 30 min and then filtered. The filtrate was cooled in a round-bottomed flask in an ice bath, and ether was removed in vacuo using a vacuum pump employing a liquid nitrogen trap in the vacuum line. The brown solid left in the flask was sublimed three times to give colorless crystalline material (26.1313 g, 49.4%), which was stored under argon. Mp 59–60 °C (lit.[7] mp 61.5–62 °C). This monomer was freshly sublimed prior to use in polymerization. IR ($CDCl_3$): 2927 s, 2855, 2240, 1545 s, 1225 w, 1075, 973 s, 950, 905 br, 845, 813, 628 cm^{-1}. MS (EI): 148 ($M^+ + 2$, 21.6), 146 (M^+, 35), 111 (M – Cl, 17.5), 87.5 (30), 85.0 (M – ClCN, 100), 76 (M – Cl_2, 43.5). ^{13}C NMR ($CDCl_3$): δ 91.74 [$=C(CN)_2$], 109.37 [$=C(CN)_2$], 157.49 [$=C(Cl)_2$].

Poly[imino(dicyanoethenylidene)iminohexamethylene] (19). A solution of hexamethylenediamine (2.3684 g, 20.41 mmol) and sodium hydroxide (1.796 g, 44.9 mmol) in distilled water (40 mL) was stirred vigorously in a blender jar and to it was added, in one portion, a solution of (dichloromethylidene)propanedinitrile (3.0 g, 20.41 mmol) in 1,2-dichloroethane (20 mL). Before the monomers were mixed, the solution in the blender was stirred at a moderately high speed and after the monomers were mixed, the blender was turned to its top speed (the speed of the blender was controlled with a Variac). The fibrous polymer precipitated almost instantaneously, and the reaction mixture was stirred for about 2–3 min. The polymer was removed from the blender jar and washed with plenty of distilled water. The polymer was placed back in the blender along with some water (50–60 mL), the blender was turned on at full speed, and the polymer was chopped into small pieces. The polymer was filtered and dried in vacuo at 60–70 °C using a vacuum pump for 36 h (3.1 g, 80.10%). The intrinsic viscosity was found to be 1.08 dL/g when measured in NMP at 25 °C. FTIR (KBr): 3320, 2925, 2857, 2201 s, 2170, 1573, 1494, 1453, 1344, 1246, 1178, 700, 550 cm^{-1}. ^1H NMR (DMSO-d_6): δ 1.24 (br s, 4 H), 1.43 (br s, 4 H), 3.15 br s, 4 H), 7.21 (s, 4 H, enamine protons). ^{13}C NMR (DMSO-d_6): δ 25.70, 28.86, 30.22, 43.15 [$=C(CN)_2$], 119.50 [$=C(CN)_2$], 162.90 [$=CNH$].

[Bis(ethylamino)methylene]propanedinitrile (20). A 50-mL round-bottomed flask equipped with a magnetic stirring bar and a reflux condenser was charged with ethylamine hydrochloride (1.4643 g, 17.95 mmol) in water (15 mL). To this solution was added an aqueous solution of sodium hydroxide (1.4367 g, 35.91 mmol in 15 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 (dichloromethylene)propanedinitrile (14) (1.200 g, 8.16 mmol) in dry methylene chloride (10–15 mL). The reaction mixture was stirred at 0 °C for 2 h followed by stirring at room temperature overnight. The solid was filtered, washed with water, and dried. More of this solid was obtained by evaporating the washed (H_2O) and dried ($MgSO_4$) methylene chloride filtrate in vacuo. The total yield was 0.7672 g, 57.33%. An analytical sample was obtained by crystallization from benzene/hexanes, mp 130 °C. Anal. Calcd for $C_8H_{12}N_4$: C, 58.51; H, 7.36; N, 34.12. Found: C, 58.84; H, 7.53; N, 34.58. FTIR (KBr): 3289 s, 3150, 3124, 3048, 3977, 2936, 2202 s, 2170 s, 1588, 1469, 1449, 1421, 1383 s, 1336 s, 1293, 1249, 1195, 1155, 1143, 1115, 799, 697, 640, 600, 580 cm^{-1}. MS (CI/positive ion): 166 ($M^+ + 2$, 10), 165 ($M^+ + 1$). ^1H NMR (DMSO-d_6): δ 1.09 (t, J = 7.11 Hz, 3 H), 3.22 (m, 2 H), 7.14 (t, J = 5.23 Hz, 2 H). ^{13}C NMR (DMSO-d_6): δ 14.72 (CH_3), 30.18 [$=C(CN)_2$], 37.01 (CH_2), 119.52 [$=C(CN)_2$], 162.58 ($=CNH$).

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