

Synthesis and characterization of aromatic–aliphatic poly(enaminonitriles)

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Abstract

Novel, high molecular weight aromatic–aliphatic poly(enaminonitriles) (PEANs) were prepared by the interfacial polymerization of 4 aromatic bis(chlorovinylidene cyanide) monomers with linear, aliphatic diamines containing 6, and 8–12 methylene units. Characterization was done with TGA, DSC, solution viscometry, GPC and spectroscopic methods. The PEANs displayed excellent solubility in polar aprotic solvents and showed good thermal stability (5% weight loss >325°C) considering the aliphatic content of the chains. The polymers appeared to be completely amorphous and showed no melting transitions by DSC. Molecular modeling studies suggested that steric interference caused by the 2,2-dicyanovinyl functionality may hinder the formation of crystalline regions. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(enaminonitriles); Interfacial polymerization; Amorphous polymers

1. Introduction

Poly(enaminonitriles) (PEANs) are a class of polymers prepared by the condensation polymerization of bis(chlorovinylidene cyanides) with diamines. The monomers were first prepared based upon a useful analogy reported by Wallenfels [1], which showed that a dicyano-substituted carbon atom has the same electron-withdrawing effect as an oxygen atom. The bis-electrophilic monomers readily react with diamines in a vinylic nucleophilic substitution pathway to form high molecular weight polymers. PEANs can be considered to be analogs of polyamides because the 2,2-dicyanovinyl group has been shown to be analogous to a carbonyl group.

Initial studies of PEANs primarily involved the reaction of aromatic bis(chlorovinylidene cyanides) with aromatic diamines [2–9]. The resulting polymers showed good thermal stability, high glass transition temperatures, and excellent solubility in polar, aprotic solvents such as NMP, DMF, DMAc and DMSO. The aromatic PEANs also showed the ability to undergo a thermal curing reaction without the evolution of small molecules [10].

The study of the influence of the 2,2-dicyanovinyl group on the structure-property relations in amide analogs has been continued with the preparation of aromatic-aliphatic

PEANs. The synthesis of aromatic-aliphatic PEANs by interfacial polymerization of aromatic bis(chlorovinylidene cyanides) with a series of linear, aliphatic diamines has been accomplished. Where possible, the effects of the dicyanovinylidene functionality on polymer properties were examined by comparison of the aromatic-aliphatic PEAN properties with those of the ‘parent’ polyamide. Also, the polymers prepared from the biphenyl and terphenyl monomers were examined for thermotropic and lyotropic properties.

2. Experimental

2.1. Solvents and reagents

All diamines except 1,11-diaminoundecane were purchased from Aldrich and were sublimed prior to polymerization. 1,11-Diaminoundecane was prepared by a four-step procedure from lauryl lactam and was sublimed just before use [11]. Methylene chloride was distilled from CaH₂. All other materials were used as received.

2.2. Monomer synthesis

The syntheses of the aromatic bis(chlorovinylidene cyanide) monomers (**1–4**) have been reported previously

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[2–4,7,8,10]. The monomers were recrystallized and dried over P₂O₅ before polymerization.

2.3. Model compound synthesis

2.3.1. 1,3-Bis(1-aminoethyl-2,2-dicyanovinyl) benzene (5)

A 50 ml three-neck round bottom flask equipped with a magnetic stirrer and reflux condenser was charged with a solution of 1,3-bis(1-chloro-2,2-dicyanovinyl)benzene (**1**) (0.3636 g, 0.0012 mol) dissolved in 10 ml of 1,2-dichloroethane. Hexylamine (0.65 ml, 0.50 g, 0.0049 mol) was added dropwise to the solution which was stirred at room temperature for 12 h. The reaction mixture was cooled and was washed with H₂O (1 × 10 ml) and brine (1 × 10 ml) in a separatory funnel. The organic layer was dried over MgSO₄ and concentrated to give a pale yellow oil which crystallized after standing for several hours. The crystals were collected and dried in a vacuum oven (~1 Torr) at 65°C (0.3027 g, 59%). Further purification was done by column chromatography on silica gel with a 30% ethyl acetate/hexane mixture as eluent, m.p. 124–126°C (DSC). FT-IR (KBr): 3274, 2931, 2858, 2214 (CN), 1578, 1458, 1425, 1361, 712 cm⁻¹. ¹H NMR (DMSO): ppm [9.21, 9.02] (t, 2H, NH), 7.71 (m, 4H, aromatic protons), 3.61 (q, 2H), 2.98 (m, 2H), 1.67 (m, 2H), 1.31 (m, 8H), 1.15 (s, 4H), [0.87, 0.78] (t, 6H, terminal CH₃). ¹³C NMR (DMSO): ppm [170.6, 168.1] (C=C(CN)₂), [135.0, 134.2, 132.4, 131.4, 131.2, 130.9, 129.7, 128.2] (aromatic carbon atoms), [117.9, 116.9, 115.8] (CN), [49.5, 47.7] (C=C(CN)₂), [45.8, 45.1, 30.9, 30.6, 29.4, 28.7, 25.7, 25.3, 22.1, 21.9, 14.0, 13.8] (aliphatic carbon atoms).

2.3.2. 1,4-Bis(1-aminoethyl-2,2-dicyanovinyl) benzene (6)

A 50 ml three-neck round bottom flask equipped with a magnetic stirrer, a reflux condenser fitted with an argon inlet, and an addition funnel was charged with hexylamine (0.18 ml, 0.0013 mol) and triethylamine (0.20 ml, 0.0014 mol) dissolved in 5 ml of 1,2-dichloroethane. A solution of 1,4-bis(1-chloro-2,2-dicyanovinyl)benzene (**2**) (0.20 g, 0.0006 mol) in 10 ml of 1,2-dichloroethane was added dropwise through the addition funnel. The reaction was refluxed for 12 h. The reaction mixture was cooled to room temperature and was extracted with water and brine in a separatory funnel. The organic layer was dried over MgSO₄ and concentrated to give a brown solid which was purified by column chromatography on silica gel eluting with 40% ethyl acetate/hexane, m.p. 196–197°C (DSC). FT-IR (KBr): 3274, 2932, 2859, 2214 (CN), 1595, 1429, 1365 cm⁻¹. MS (CI): *m/z* 429 (M⁺, 20). ¹H NMR (DMSO): ppm 9.08 (s, 2H, NH), 7.67 (s, 4H, aromatic protons), 3.62 (t, 2H), 2.91 (t, ~2H), 1.69 (2H), 1.33 (s, 8H), 1.06, [0.89, 0.80] (t, 6H, terminal CH₃). ¹³C NMR (DMSO): ppm [170.7, 167.0] (C=C(CN)₂), [136.8, 133.4, 129.2, 128.9, 128.5, 128.1] (aromatic carbon atoms), [117.5, 116.7, 115.9, 115.1] (CN), [49.5, 47.1] (C=C(CN)₂), [45.6,

44.9, 30.7, 30.3, 29.2, 28.5, 25.5, 25.2, 21.8, 13.6] (aliphatic carbon atoms).

2.3.3. 4,4'-Bis(1-aminoethyl-2,2-dicyanovinyl) biphenyl (7)

A 50 ml three-neck round bottom flask equipped with a magnetic stirrer and a reflux condenser fitted with an argon inlet was charged with 4,4'-bis(1-chloro-2,2-dicyanovinyl) biphenyl (**3**) (0.2477 g, 0.0007 mol) and 25 ml of 1,2-dichloroethane. Hexylamine (0.45 ml, 0.34 g, 0.0034 mol) was added dropwise with a syringe to the stirred suspension. The reaction was heated to reflux with an oil bath, overnight. The reaction mixture was washed with 10% HCl (2 × 15 ml), H₂O (1 × 15 ml), and brine (1 × 15 ml). The organic layer was dried over MgSO₄ and concentrated to give a pale yellow solid which was purified by column chromatography on silica gel eluting with 40% EtOAc/hexane, (0.250 g, 75%), m.p. 177–178°C (DSC). FT-IR (KBr): 3275, 2929, 2858, 2212 (CN), 1580, 1440, 1350, 825 cm⁻¹. ¹H NMR (DMSO): ppm [9.18, 9.05] (s, 2H, NH), 7.93 (m, 4H, aromatic H), [7.66, 7.60] (d, 4H, central aromatic H), 3.61 (q, ~2H), 3.0 (br, ~2H), 1.69 (m, ~2H), 1.32 (m, ~5H), 1.07 (m, 4H), 0.88 (t), 0.76 (t). ¹³C NMR (DMSO): ppm [171.6, 167.9] (C=C(CN)₂), [141.8, 141.1, 134.0, 130.5, 129.7, 128.9, 127.4, 127.0] (aromatic carbon atoms), [118.1, 117.1, 115.6] (CN), [49.3, 46.9] (C=C(CN)₂), [45.6, 45.1, 30.9, 30.5, 29.3, 28.6, 25.7, 25.3, 22.0, 21.7, 13.9, 13.8] (aliphatic carbon atoms).

2.3.4. 4,4'-Bis(1-aminoethyl-2,2-dicyanovinyl) terphenyl (8)

A 50 ml three-neck round bottom flask fitted with a magnetic stirrer, reflux condenser, and argon inlet was charged with 4,4'-bis(1-chloro-2,2-dicyanovinyl)-*p*-terphenyl (**4**) (0.206 g, 0.0005 mol) and 25 ml of 1,2-dichloroethane. The suspension was heated to reflux with an oil bath. Hexylamine (0.28 g, 0.36 ml, 0.0027 mol) was added dropwise with a syringe. The reaction mixture was refluxed overnight. The reaction was cooled and the mixture was washed with 10% HCl (2 × 15 ml), H₂O (1 × 15 ml), and brine (1 × 15 ml). The organic layer was dried over MgSO₄ and was concentrated to give a yellow powder which was purified with column chromatography on silica gel eluting with a 40% EtOAc/hexane mixture, (0.2067 g, 78%), m.p. 193–194°C (visual). FT-IR (KBr): 3265, 2930, 2858, 2213 (CN), 1560, 1491, 1458, 819, 742 cm⁻¹. ¹H NMR (DMSO): ppm [9.12, 9.02] (s, 2H, NH), 7.88 (m, 8H, aromatic H), [7.64, 7.55] (d, 4H, central aromatic H), 3.60 (m, ~2H), 3.02 (q, ~2H), 1.68 (m, 2H), 1.37 (m), 1.30 (m), 1.15 (m), 1.07 (br), 0.88 (t), 0.76 (t). ¹³C NMR (DMSO): ppm 168.1 (C=C(CN)₂), [142.5, 138.6, 133.4, 129.9, 129.6, 128.8, 127.7, 127.1, 126.8] (aromatic carbon atoms), [118.2, 117.2, 117.0, 115.7] (CN), [49.3, 46.8] (C=C(CN)₂), [45.6, 45.2, 30.9, 30.5, 29.3, 28.7, 25.7, 25.3, 22.0, 21.8, 13.9, 13.8] (aliphatic carbon atoms).

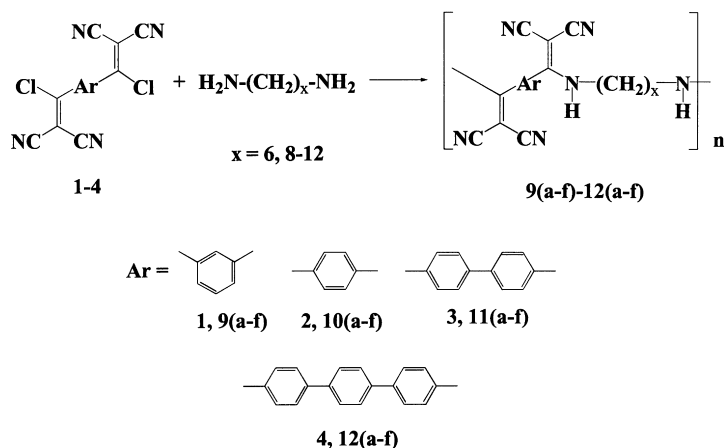


Fig. 1. Synthetic scheme of aromatic-aliphatic poly(enaminonitriles) (9–12).

2.4. Polymer synthesis

All polymers (**9a–12f**) were prepared by interfacial polycondensation. A typical procedure is as follows: A 100 ml test tube fitted with a Vibro-Mixer™ was charged with NaOH (0.0834 g, 0.0021 mol), 1,12-diaminododecane (0.2084 g, 0.0010 mol), sodium lauryl sulfate (10.7 mg), and 10 ml of H₂O. A solution of 1,4-bis(1-chloro-2,2-dicyanovinyl)benzene (**2**) (0.3124 g, 0.0010 mol) in 10 ml of CH₂Cl₂ was prepared in a sample vial. The Vibro-Mixer™ was set to maximum speed and the monomer solution was added in one portion. Mixing was continued for 30 min. The polymer was collected by filtration, air-dried overnight, and precipitated into vigorously stirred H₂O from a 2% (mg/ml) solution in DMF. The white, fibrous precipitate (**10f**) was collected, washed with H₂O, and dried in vacuo (0.5 Torr) for 48 h at 60°C (0.36 g, 82%).

2.5. Characterization

All visual melting points were determined on a Thomas/Hoover capillary melting point apparatus and should be considered uncorrected. In some cases melting points were determined using differential scanning calorimetry (DSC).

Thermogravimetric analysis (TGA) and DSC analyses were carried out on Perkin–Elmer 7 Series instruments running Pyris™ software. TGA analyses were done under N₂ or air at a heating rate of 20°C/min. DSC analyses were done under N₂ at a heating rate of 10°C/min.

¹H and ¹³C NMR spectra were recorded either on Varian Inova 300 MHz or Varian Unity 500 MHz instruments. All NMR shifts are reported as parts per million (ppm) and are referenced to residual protons in the deuterated solvent resonances. The reference peaks used for ¹H and ¹³C in ppm are, respectively, DMSO (2.49, 39.6), chloroform (7.24, 77.0), and acetone (2.04, 204.1). ¹H NMR data are reported as follows: chemical shift in ppm (multiplicity, integration, assignment); ¹³C NMR data are given in ppm. Multiplicities

are abbreviated as singlet (s), doublet (d), triplet (t), multiplet (m), quartet (q), and broad (br). ¹³C NMR spectra were collected using broadband decoupling.

FT-IR spectra were recorded on a Perkin–Elmer Paragon 1000 spectrophotometer. The absorption bands are reported in reciprocal centimeters (cm⁻¹) and are classified as strong (s), weak (w), or broad (br).

Intrinsic viscosities were determined with a Cannon–Ubbelohde viscometer in 0.01 M LiNO₃ in DMF at 25.00°C. The polymer solutions were filtered through a .45 μm filter (ACRODISC CR, Gelman Sciences).

Gel permeation chromatography (GPC) was done with a Viscotek model 200 instrument using refractive index and viscosity detectors. Two 10 μm linear, mixed-bed Jordi Associates columns were used with DMF containing 0.01 M LiNO₃. Column temperature was maintained at 60°C. A universal calibration curve was constructed using narrow molecular weight poly(ethylene oxide) standards purchased from Scientific Polymer Products (Sp²) and a flow rate of 1.0 ml/min.

3. Results and discussion

Interfacial polycondensation, such as described by Morgan [12], was utilized to react four aromatic bis(chlorovinylidene cyanide) monomers with a series of linear aliphatic diamines as illustrated in Fig. 1. In general, high molecular weight polymers were obtained using methylene chloride as the organic solvent, and solution concentrations of 0.1 M. Monomers **3** and **4** were not completely soluble in methylene chloride, so the monomers were added to the stirred diamines as suspensions. The polymerization process was not optimized because the conditions mentioned above resulted in high molecular weight polymers. The use of approximately 5% (based on monomer mass) of sodium lauryl sulfate increased the obtainable molecular weights of polymers prepared from monomers **1** and **2** because of

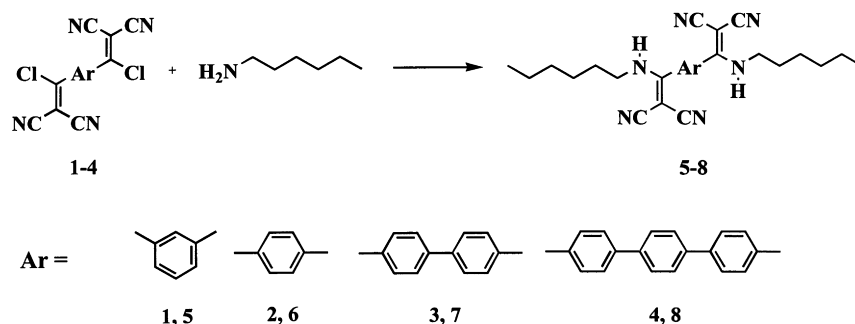


Fig. 2. Synthetic scheme of model compounds (5–8).

improved mixing which eliminated the formation of gelled material.

Model compounds **5–8** were prepared from the reaction of monomers **1–4** with hexylamine (Fig. 2). The ^1H NMR, ^{13}C NMR, and FT-IR spectra of the model compounds were obtained and compared with the corresponding polymers. The ^1H NMR (Fig. 3) and FT-IR (Fig. 4) spectra show good agreement between model compound **7** and polymer **11e** in each figure. This type of agreement was observed with all model compounds (**5–8**) and polymers (**9a–12f**). The ^1H NMR spectrum of compound **7** collected in DMSO at 25°C is somewhat complex because of the presence of

rotational isomers, which are evident from the splitting of the enamine proton peak at 9.1 ppm. The isomers result from a rotational barrier around the C–N bond of the enammonitrile functionality which has been studied previously using dynamic NMR spectroscopy [13,14]. The ^1H NMR spectrum of polymer **11e** was collected in DMSO at 50°C and does not show the splitting of the enamine proton peak because there is enough energy at this temperature to overcome the rotational barrier. At lower temperatures the splitting of the enamine proton peak is observed in the ^1H NMR spectra of the polymer.

Polymers **9a–12f** all showed excellent solubility in polar aprotic solvents such as DMF, DMAc, DMSO, and NMP. Lower molecular weight fractions were also soluble in CH_2Cl_2 , 1,2-dichloroethane, and acetone. The polymers

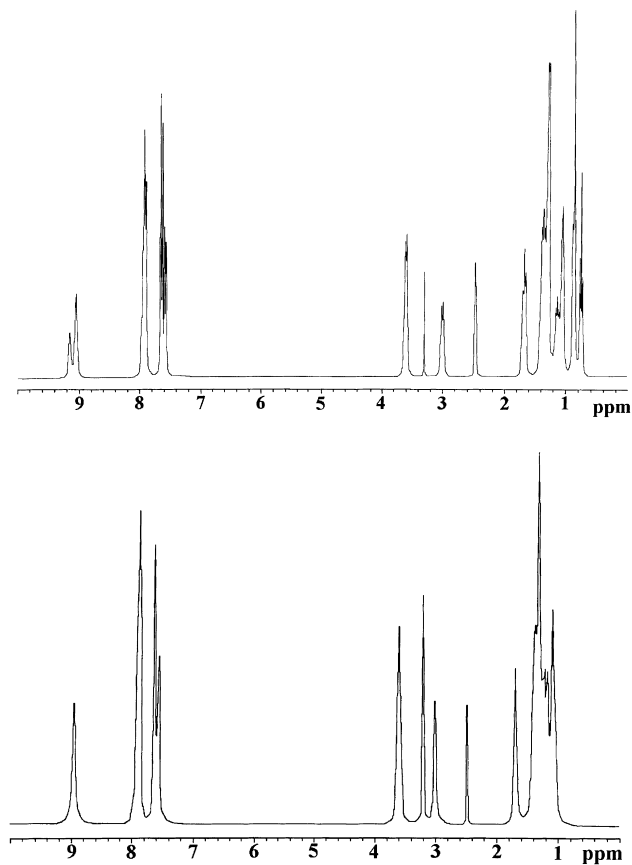
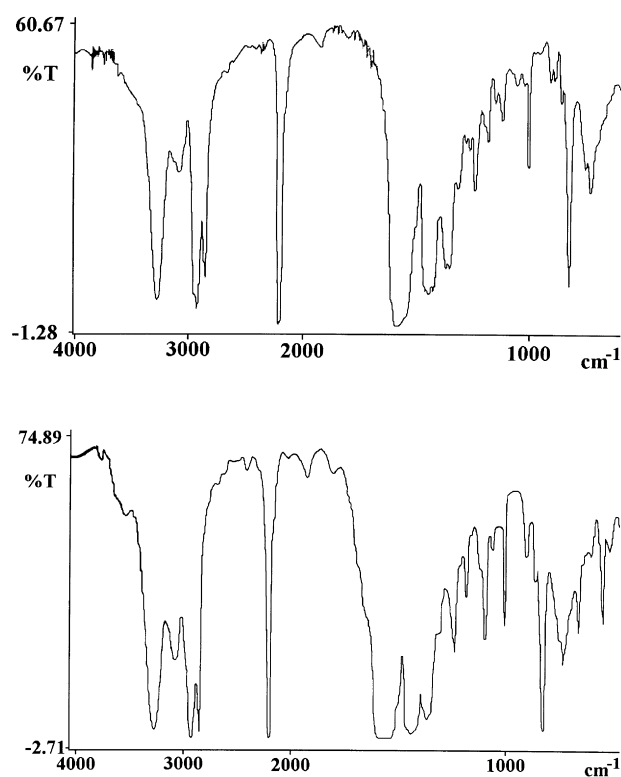
Fig. 3. ^1H NMR spectra of model compound **7** (top) and polymer **11e** (bottom) in DMSO.Fig. 4. FT-IR spectra of model compound **7** (top) and polymer **11e** (bottom).

Table 1
Solution viscometry and GPC results for polymers **9a–12f**

Polymer	Monomer	<i>x</i>	$[\eta]^a$ (dl/g)	M_n	M_w
9a	1	6	0.9	57 760	175 200
9b	1	8	0.8	18 860	107 600
9c	1	9	1.1	31 020	93 740
9d	1	10	0.9	34 300	96 070
9e	1	11	2.6	126 200	449 200
9f	1	12	2.0	70 140	248 300
10a	2	6	0.9	19 940	110 500
10b	2	8	3.1	–	–
10c	2	9	1.0	31 020	88 820
10d	2	10	0.8	27 260	81 350
10e	2	11	1.4	59 190	169 300
10f	2	12	1.8	67 400	259 300
11a	3	6	1.2	7844	86 570
11b	3	8	1.0	25 570	100 300
11c	3	9	1.7	43 570	249 900
11d	3	10	0.8	23 230	63 540
11e	3	11	1.8	57 610	213 300
11f	3	12	1.3	11 480	114 500
12a	4	6	0.3	9405	29 290
12b	4	8	0.6	17 680	51 140
12c	4	9	0.5	6324	43 460
12d	4	10	0.7	18 290	58 260
12e	4	11	1.6	40 010	187 200
12f	4	12	1.9	89 160	251 300

^a 25.0°C in solutions of DMF containing 0.01 M LiNO₃.

Table 2
Thermal characterization of polymers **9a–12f**

Polymer	Monomer	<i>x</i>	T_g (°C) ^a	TGA ^b (N ₂)	TGA ^b (air)
9a	1	6	140	403	412
9b	1	8	121	400	398
9c	1	9	120	357	362
9d	1	10	113	358	397
9e	1	11	106	376	349
9f	1	12	100	344	340
10a	2	6	156	385	350
10b	2	8	138	344	324
10c	2	9	127	344	318
10d	2	10	123	338	338
10e	2	11	113	390	368
10f	2	12	108	332	312
11a	3	6	187	385	356
11b	3	8	173	323	325
11c	3	9	163	375	315
11d	3	10	153	387	294
11e	3	11	145	390	346
11f	3	12	143	345	315
12a	4	6	213	350	345
12b	4	8	190	397	255
12c	4	9	185	375	350
12d	4	10	172	380	260
12e	4	11	165	405	337
12f	4	12	163	400	346

^a DSC, second scan, 10°C/min.

^b 5% weight loss, 20°C/min.

having intrinsic viscosities ≥ 0.8 dl/g formed fingernail-creasable films when cast from DMF.

Solution viscometry and GPC results are listed in Table 1. In general the aromatic–aliphatic PEANs were prepared having high molecular weights. The GPC calculations show the polymers to have broad polydispersities ($M_w/M_n > 2$), which are typical for condensation polymers. An interesting observation was made during the GPC analysis of polymers **9e**, **9f**, **10f**, and **12f** (Table 1). These polymers were partly excluded on the GPC column set. The calculated molecular weights are based upon how the instrument extrapolates the data, and can not be considered completely accurate. The information we can gather from these samples are that some fractions contained chains with molecular weights $>10^6$ which is rather unusual for condensation polymers.

The aromatic–aliphatic PEANs show excellent thermal stability considering the aliphatic content of the polymers with 5% decomposition temperatures under N₂ ranging from 321°C for polymer **9b** to 405°C for polymer **12e** (Table 2). The increase of aromatic character that occurs when comparing polymers from series **9–12** appears to have little effect on the thermal stability as shown by the TGA traces of polymers **9e**, **10e**, **11e** and **12e** (Fig. 5). The good thermal stabilities of all polymers (**9–12**) are probably a result of the inter- and intramolecular hydrogen bonding that is known to exist between the enamine proton and the nitrile group. The 5% weight loss temperatures under air are generally lower than the corresponding values measured under N₂ indicating that oxidative degradation has occurred. The exceptions occur with polymers **9a–9d**, **9f** and **11b** for which the 5% weight loss values in air are slightly higher than the values under N₂ presumably due to a slightly different decomposition pathway (Fig. 6).

The glass transition temperatures for polymers **9a–12f** range from 102 to 215°C (Fig. 7). As expected, the T_g values decrease with increasing numbers of methylene units along a monomer series because of increasing chain flexibility. Also, the glass transition temperatures increase with increased aromatic character of the polymers because of chain stiffening. The DSC traces of all the aromatic–aliphatic PEANs show no thermal transitions other than T_g up to temperatures just below the initial decomposition point except for polymer **9b**, which contains a broad exotherm starting at 180°C. The exotherm was not observed when the sample was cooled and rescanned (Fig. 8). The observed T_g was reproducible when the sample was heated to only 175°C (Fig. 9). The exotherm could be an indication of crystallization, or some form of curing. The aromatic PEANs are known to undergo an exothermic cyclization around 350°C to form aminoquinoline units [10]. It is interesting to note that the samples of polymer **9b** used to generate the DSC traces shown in Figs. 8 and 9 were no longer soluble in DMF at the completion of the analysis. The loss of solubility indicates that some form of crosslinking had occurred at the elevated temperatures.

It was initially thought that monomers **3** and **4** could

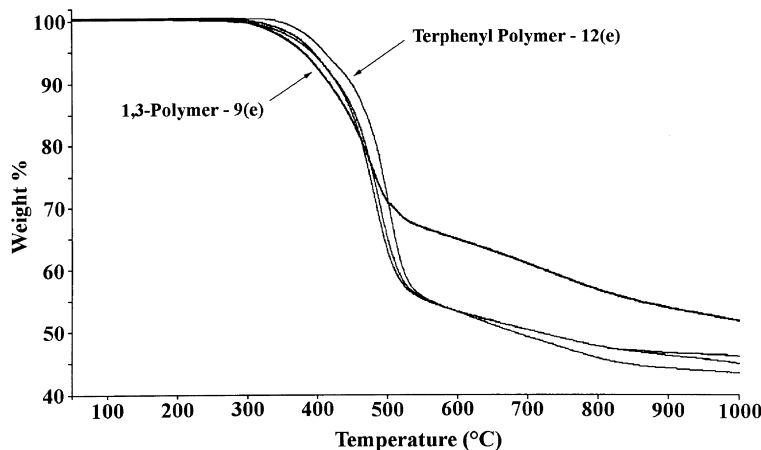


Fig. 5. TGA thermograms of polymers prepared from 1,11-diaminoundecane in N_2 .

generate liquid crystalline (LC) systems when polymerized with flexible spacers such as the linear aliphatic diamines. DSC and optical microscopy were used to analyze polymers **11a–12f** and model compounds **7** and **8** for thermotropic behavior. The DSC scans of model compounds **7** and **8** displayed in Fig. 10 show only a melting transition and no evidence of thermotropic behavior. The DSC scans of the polymers only show a glass transition as can be seen in the traces of polymers **11e** and **12e** in Fig. 11. Optical microscopy using a hot stage also failed to show any evidence of thermotropic behavior for polymers **11a–12f**. It is presumed that the crosslinking that occurs when the polymers are heated above T_g could be preventing the formation of a thermotropic phase. Studies have been started to examine the polymers for lyotropic characteristics. Unfortunately, the initial results have yet to show any evidence of lyotropic phases.

One goal of the project was to examine the effect of the 2,2-dicyanovinyl group on polymer properties through comparison with the analogous polyamides. The corre-

sponding isophthalamides (**6, 8–12I**) and terephthalamides (**6, 8–12T**) are known polymers [15–18]. Unfortunately very little information was found in the literature for the corresponding biphenyl and terphenyl containing polyamides. The isophthalamides and terephthalamides containing 10, 11 and 12 methylene units were prepared in our lab for direct comparisons. Efforts are currently under way to prepare the corresponding biphenyl and terphenyl polyamides.

The polyamides analogous to polymers **9a–9f** and **10a–10f** are generally insoluble in polar aprotic solvents. It was necessary to use aggressive, acidic solvents such as sulfuric acid or trifluoroacetic acid to dissolve the polyamides that were prepared in our lab. The thermal properties of the analogous isophthalamides (**6, 8–12I**) and terephthalamides (**6, 8–12T**) are listed in Table 3. The polyamides show greater thermal stability compared to the PEAN analogs which is most likely because of stronger hydrogen bonding observed with the amide functionality. The isophthalamides were generally amorphous, and the observed glass transition

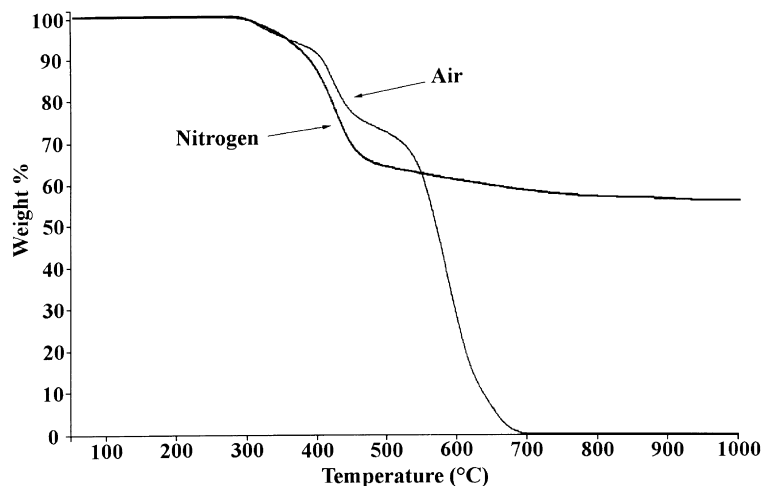


Fig. 6. TGA thermograms of polymer **9c** in air and nitrogen.

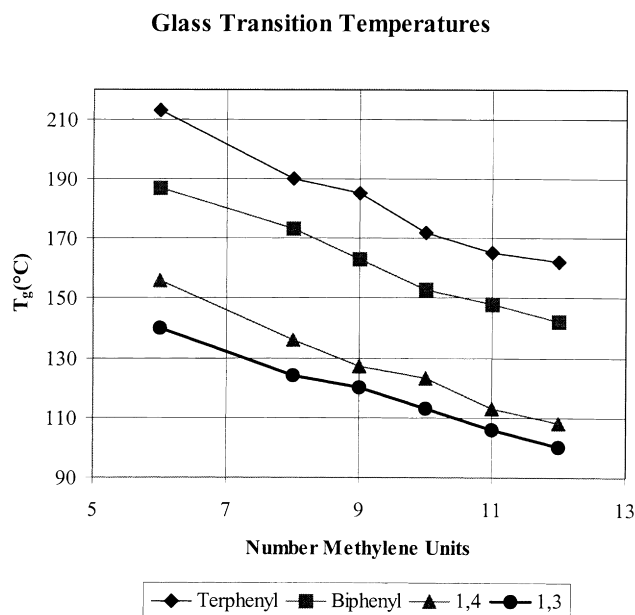


Fig. 7. T_g (°C) comparison among reported aromatic–aliphatic PEANs.

temperatures were lower than the PEAN analogs (**9a–9f**). Crystallinity can be induced in the isophthalamides [15], therefore melting points are reported. The terephthalamides were highly crystalline. DSC analysis of the terephthalamides showed only a broad, reproducible T_m .

One of the major differences between the aromatic–aliphatic PEANs and the polyamides was the lack of crystallinity in the PEANs. To date, the reported aromatic–aliphatic PEANs have shown no unequivocal evidence of crystallinity. The PEAN films were completely amorphous, and no melting points have been observed by DSC. It is important to note, that as seen with polymer **9b**, all the aromatic–aliphatic PEANs crosslink when heated above

T_g . The crosslinking will prevent the observation of a T_m . Low temperature methods to induce crystallinity have been attempted but have yet to show evidence of crystallite formation.

The lack of crystallinity could be a result of the reduced hydrogen bonding observed with the enamionitrile group as compared to the amide group. Another possibility for the lack of crystallinity is the structural difference between the 2,2-dicyano group and the carbonyl group. Comparisons of the X-ray structures of benzamide and the enamionitrile analog (**13**) show that the increased bulkiness of the 2,2-dicyanovinyl group results in this functionality being rotated farther out of the plane of the phenyl ring as compared to the amide (Fig. 12). Molecular modeling studies were carried out on short polyamide and PEAN segments using CAChe Mopac™. The results suggested that the increased rotation of the 2,2-dicyanovinyl group, when extended along a polymer chain, resulted in increased steric bulkiness along the chain relative to what is seen with the analogous polyamide (Fig. 13). The increased steric bulkiness along the PEAN chain could be hindering its ability to form crystalline regions.

4. Conclusions

Several novel, high molecular weight aromatic–aliphatic poly(enamionitriles) were prepared by the interfacial polymerization of aromatic bis(chlorovinylidene cyanides) with linear aliphatic diamines. These PEANs showed excellent thermal stability by TGA analysis. The PEANs showed excellent solubility in polar, aprotic solvents, unlike the parent polyamides which were only soluble in aggressive, acidic solvents. The PEANs formed strong, flexible films and appeared to be completely amorphous. Molecular modeling studies and X-ray structures of small compounds suggest that the dicyanovinylidene functionality could be

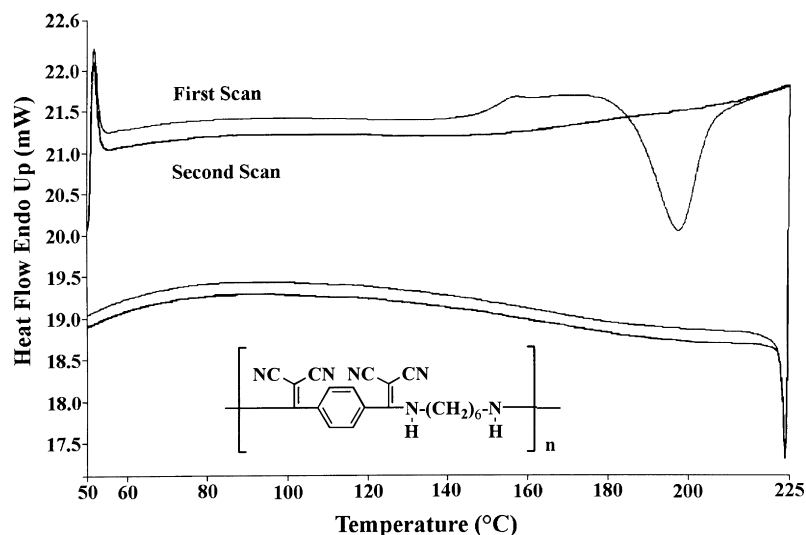
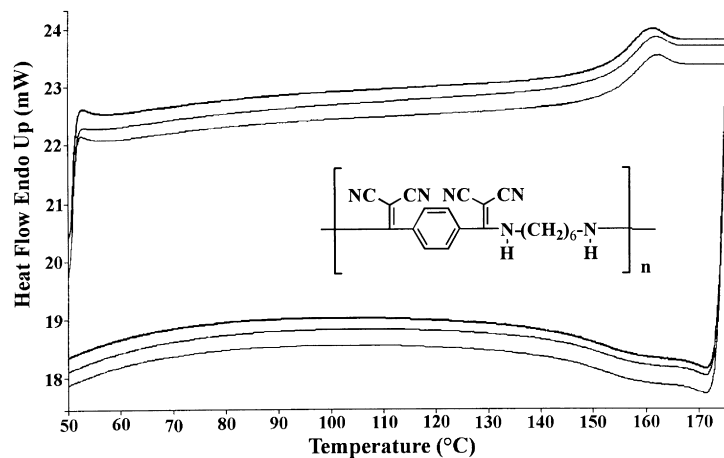
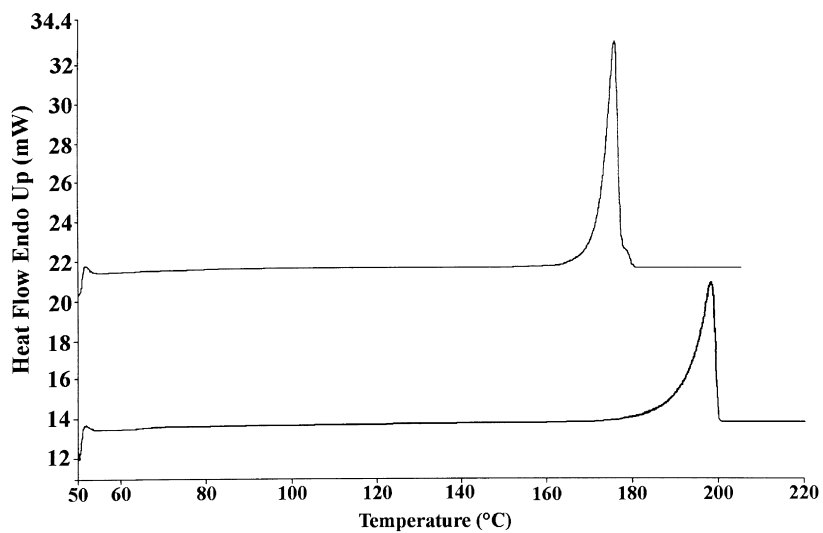
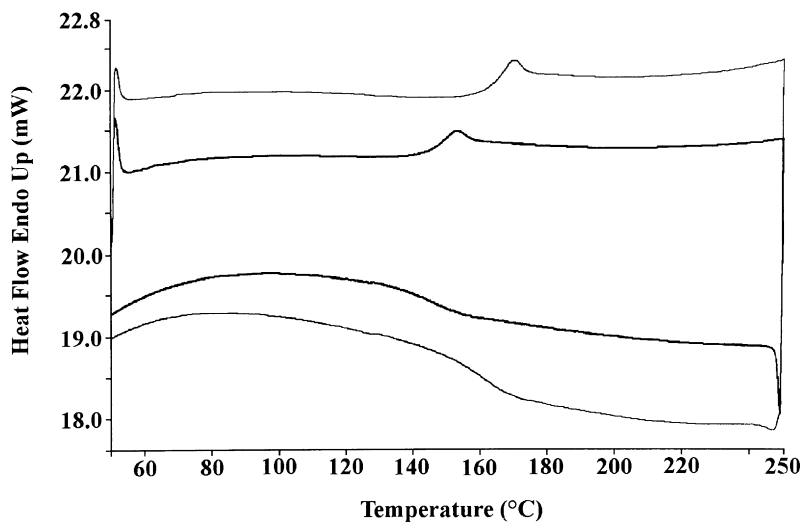
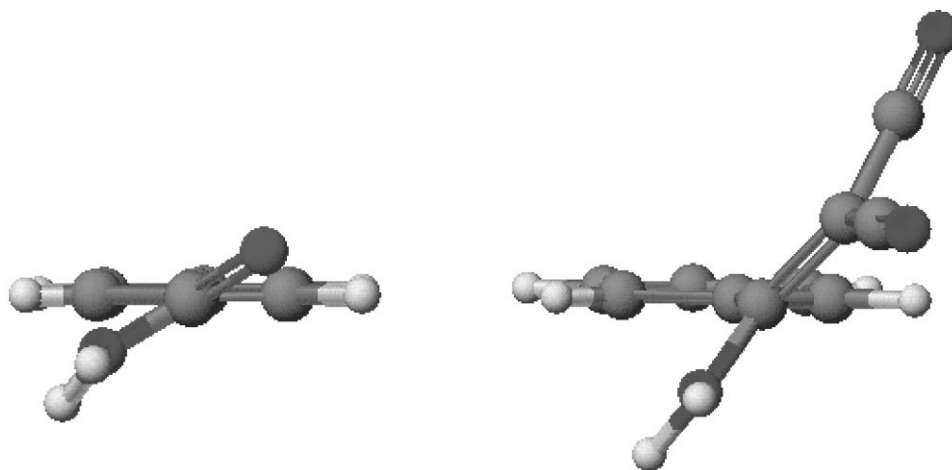
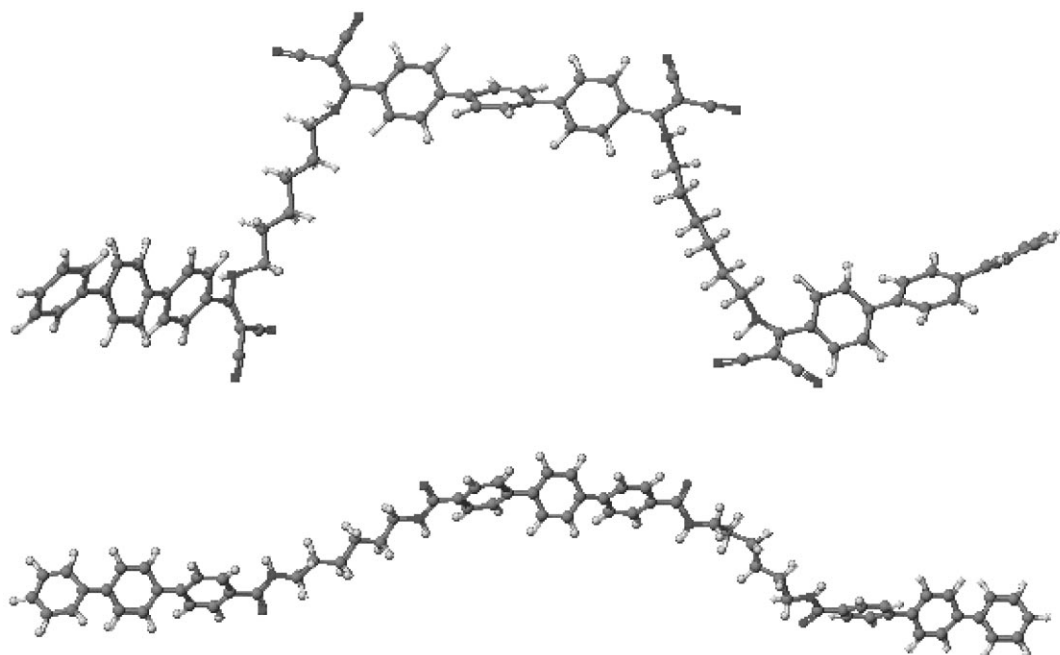


Fig. 8. Differential scanning calorimogram of polymer **9b** up to 175°C.

Fig. 9. Differential scanning calorimogram of polymer **9b** up to 225°C.Fig. 10. Differential scanning calorimogram of model compounds **7** (top) and **8** (bottom).Fig. 11. Differential scanning calorimogram of polymers **11e** and **12e**.

Fig. 12. X-ray structures of benzamide and compound **13**.Fig. 13. Molecular modeling structures of short segments of polymer **10a** (top) and polyamide **6T** (bottom).Table 3
Thermal properties of aromatic–aliphatic iso (I) and tere (T) phthalamides

Polymer	T_g (°C)	T_m (°C)	TGA (N ₂)
6I	125 [16]	170–230 [17]	390 [18]
8I	106 [16]	150–200 [17]	–
9I	103 [16]	–	–
10I	–	166–194 [17]	430
11I	95	160–200	410
12I	88	160–192	433
6T	–	371 [17]	410
8T	–	322–333 [17]	–
9T	–	309 [17]	–
10T	–	316 [17]	425
11T	–	280	423
12T	120	290	430

preventing the formation of crystalline regions through steric interference.

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