Acyclic Polymeric Reissert Compounds: Chemically Reactive Polyamides. 2[1,2]

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ABSTRACT: Open-chain polymeric Reissert compounds, i.e., poly[α-(acylamino)nitrile]s **2**, can be prepared by condensation of bis(α-aminonitrile)s **1** with adipoyl chloride. When the bis(α-aminonitrile) possesses hindered internal secondary amine groups, e.g., **1b** and **1c**, no high molecular weight polymers could be obtained. From less hindered bis(α-aminonitrile)s amorphous polymeric Reissert compounds of intrinsic viscosity 0.15–0.24 dL·g^{-1} were synthesized. Their stability was found to exceed in most cases 350 °C in nitrogen (5% weight loss). By virtue of the Reissert moiety's acidic proton, chemical modification of such homo- and copolymers, e.g., by alkylation, provides a means of bulk and surface property control.

Introduction

The concept of condensing a bis(α-aminonitrile) with a diacid chloride has recently been developed in this laboratory. So formed polymeric Reissert compounds, i.e., poly[α-(acylamino)nitrile]s, open up a wide range of chemical modification possibilities, allowing transformation of the main chain and grafting.[2] For example, condensation of the Reissert anions with an alkyl halide results in the alkylation of the Reissert moieties (Scheme I).[3] This approach could allow alteration of surface or bulk properties of such homo- or copolymers.

Two routes have been considered for the preparation of these polymers, differentiated by the nature of the bis(α-aminonitrile) (Scheme II). Route (a) involves the preparation of polymeric Reissert compounds with the acidic Reissert proton (proton α to the cyano function) in the backbone. On the other hand, route (b) corresponds to the preparation of polymers which possess the functional acidic Reissert proton on side groups. To augment our prior approaches through route (a),[1,2] we report here the preparation of poly(Reissert compound)s according to route (b).

Results and Discussion

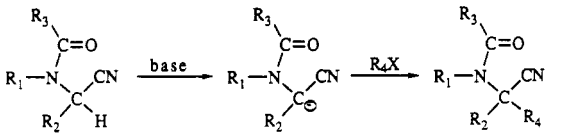
A. Acyclic Bis(α-aminonitrile)s. They were prepared by condensation of the bisulfite salt of the aldehyde with the amine, followed by the addition of sodium cyanide.[4] In spite of its entirely aliphatic nature, pure **1a** consists of transparent crystals.[5]

In order to obtain easily purifiable bis(α-aminonitrile)s, we introduced aromatic components into their structure. Thus, **1b** (Scheme II) was prepared in a manner similar to that of the above aminonitrile, with good yield. The bis(α-aminonitrile) **1c**, containing a longer spacer, although of similar hindrance to **1b**, was also prepared.

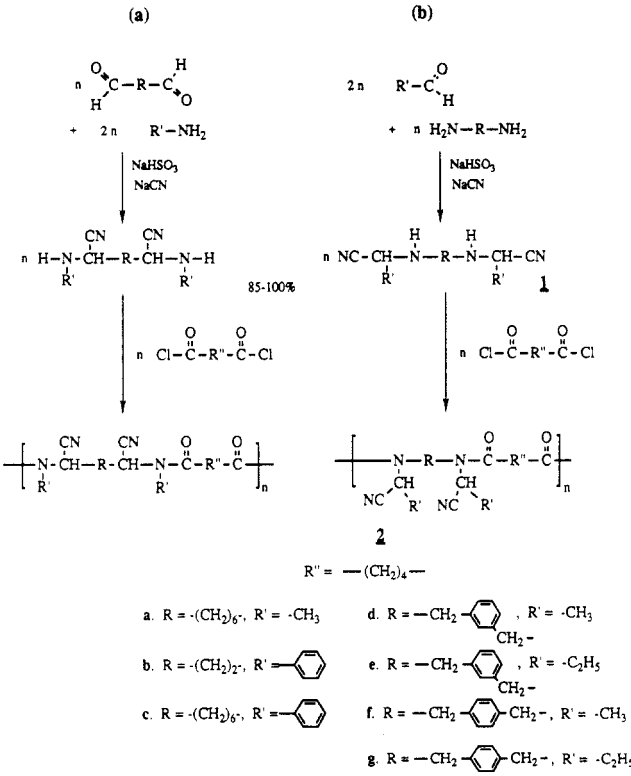
Monomers **1d–g**, in which the amino functions are not adjacent to a bulky phenyl group, were prepared, also in excellent yields.

B. Poly(Reissert compound)s. Condensation of **1a** with adipoyl chloride gave polymer **2a**, having an intrinsic viscosity of 0.18 dL·g^{-1} but a high polydispersity (7.9) (Tables I and II). This is also shown by a discrepancy in the elemental analysis results, and the presence of impurities was noted by ^{1}H NMR (cf. experimental results). Despite its entirely aliphatic structure, **2a** exhibits a good thermal stability (5% weight loss at 300 °C in nitrogen).

Scheme I



Scheme II



Condensation of **1b** with adipoyl chloride was carried out in DMAc/LiCl and $CHCl_3$/NEt_3 solvent systems. In both cases the mixture remained homogeneous and no viscosity increase was noted. GPC of polymer **2b** (Table I) shows that it is composed of low molecular weight species. The elemental analysis results match those of a polymer of DP_n of 12 and acidic end groups, i.e., M_n = 4950. Since the polymer did not show any viscous character in solution, we suspected the formation of cyclic species due to both the hindered position of the amino groups and the short flexible diamine spacer (R) of **1b**. We carried out the condensation for different concentrations of monomers.

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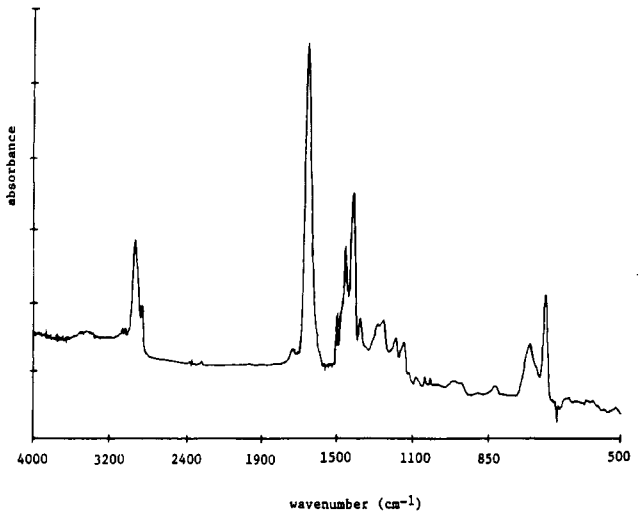

Figure 1. IR spectrum of **2c**.

Table I
Synthesis and GPC Values of Poly(Reissert compound)s

polymer	condensation solvent	yield (%)	GPC (THF, PS eq.) $M_n \times 10^3$	$M_w \times 10^3$	I_p
2a	$CHCl_3$	58	6.4	51.1	7.9
2b[a]	DMAc/LiCl	53	3.4	4.5	1.3
2c	DMAc/LiCl	67	1.5	3.3	2.2
2d	$CHCl_3$	68	4.0	6.4	1.6
2e	$CHCl_3$	67	10.2	22.2	2.15
2f[b]	DMAc	59	2.8	10.9	3.8
2g	$CHCl_3$	47	9.7	20.3	2.1

[a] After elution through a silica gel column. [b] GPC in $CHCl_3$.

Table II
Viscosity, Thermal Data, and Solubilities of Poly(Reissert compound)s

polymer	$[\eta]$ (dL·g^{-1}) (CH_2Cl_2, 25 °C)	T_g (°C)	TGA (5% wt loss in N_2)	solubility $CHCl_3$	THF	DMAc
2a	0.18	24	300	+	+	+
2c	0.09	45	312	+	+	+
2d	0.19	63	368	+	+, -	+
2e	0.24	59	364	+	+	+
2f	0.15	83	350	+	-	+
2g	0.21	64	374	+	+	+

If cyclics are formed, then their formation should be favored at low concentrations of reactants. Our results, however, indicate no difference whether a concentration in solids of 18 or 42% is used. Attempts to determine the molecular weight by mass spectrometry, which had been proven useful on some polyurethanes,[6] even using the FAB technique, were not successful with our condensates.

The best results with **1c** were obtained when the polycondensation was performed in a DMAc/5% LiCl solvent system. The polymer is also characterized by a low solution viscosity and the presence of few end groups as seen by spectral characterization (IR spectrum, Figure 1). GPC of **2c** (Figure 2) indicates a low molecular weight polymer (Table I) and clearly shows a multimodal distribution with a larger amount of low molecular weight constituents. We speculate that the presence of a very small amount of end groups for such an oligomer is also accounted for by the formation of cyclic oligomeric species. As in the case of **2b**, the FAB technique did not help in characterizing the material.

When we attempted the condensation of bis(α-aminonitrile)s **1d–g** by adding adipoyl chloride to the mixture of bis(α-aminonitrile) and triethylamine, the extent of the reaction was very low (50% in the case of **1d**, as determined by ^1H NMR spectroscopy). However, by adding the bis(α-aminonitrile) to adipoyl chloride and then immediately adding triethylamine, a complete conversion was obtained (as seen by ^1H NMR spectroscopy). We thus used this addition sequence for the synthesis of polymers **2d–g**. Like the previous polymers, **2d–g** are amorphous, but with higher values of T_g (Table II) due to the aromatic bis(α-aminonitrile) contribution. Also, their thermal stability is greater than that of the previous polymers (Table II). The elemental analyses on the polymers are in agreement with structures with $10 < DP_n < 15$ and acidic end groups. The nonhindered position of the amino functions in monomers **1d–g** as opposed to **1b** and **1c** thus enabled us to obtain higher molecular weight open-chain polymeric Reissert compounds. It is interesting to note the obtention of higher molecular weight polymers (as indicated by $[\eta]$ and GPC, Tables I and II) when propionaldehyde was used for the preparation of the bis(α-aminonitrile) (R′ = C_2H_5, **2e** and **2g**). A more electron-donating substituent (R′) on the aminonitrile may attenuate somewhat the loss of nucleophilicity of the amine due to the nitrile functionality, enhancing its reactivity. The weakness of the aminonitrile's reactivity is indeed consistent with the determination by elemental analysis of acidic end groups. A more convincing argument in favor of the latter is the possible shielding effect of ethyl substituents (R′ = C_2H_5), limiting the extent of side reactions occurring at the aminonitrile function. Indeed in the case of the aliphatic, nonhindered bis(aminonitrile) **1a**, a huge polydispersity (7.9) had been obtained. With a more hindered system, i.e., the xylylenediamine-based monomers, higher molecular weights could be attained, which turned out even better with a larger substituent on the amine (R′ = C_2H_5, **2e** and **2g**). Since we may not expect a much greater nucleophilicity when R′ = C_2H_5 than when R′ = CH_3, the protecting effect of these groups appears to be a more tangible explanation for the rise in molecular weight observed.

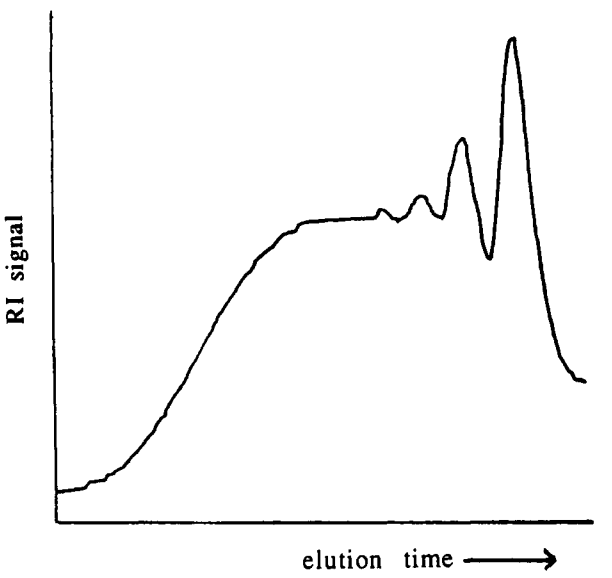

Figure 2. GPC trace (RI detection) of **2c**.

Conclusion

Aliphatic bis(α-aminonitrile)s **1** upon condensation with adipoyl chloride give completely aliphatic open-chain polymeric Reissert compounds **2**. Bis(α-aminonitrile)s such as **1b** and **1c** having amino functionalities hindered by bulky neighboring substituents and located in the center of the molecule are believed to form oligocyclic species. From bis(α-aminonitrile)s derived from xylylenediamines

(1d-g), higher molecular weight polymers were obtained when the aminonitrile group was slightly more hindered. An explanation is given in terms of protection of the aminonitrile group, preventing side reactions to a larger extent.

Experimental Section

All melting points were determined on a Haake-Buchler melting point apparatus and are corrected. ^{1}H NMR spectra were recorded on a Bruker 270-MHz instrument using TMS as the reference. FTIR (KBr) spectra were recorded on a Nicolet MX-1. Elemental analyses were performed by Atlantic Microlab (Norcross, GA). DSC experiments were performed with a 10 °C/min heating rate on a Perkin-Elmer 7700 thermal analysis system. Thermogravimetric analysis was carried out at 10 °C/min on a Du Pont 951 TGA coupled to a Du Pont Instruments thermal analyst 2100. Viscosity measurements were performed at 25 °C in CH_2Cl_2 using an Ubbelohde type viscometer. GPC analyses were run on a Waters 490 equipped with RI and UV (254-nm) detectors, using THF as the solvent and polystyrene standards.

Preparation of a Bis(α-aminonitrile). General Procedure. *N,N'*-Bis(α-cyanopropyl)-*p*-xylylenediamine (1g). A mixture of water (250 mL), propionaldehyde (8.7 g, 150 mmol), and sodium metabisulfite (14.76 g, 78 mmol) in a 500-mL erlenmeyer was stirred for 2 h. *p*-Xylylenediamine (10.10 g, 74 mmol) was added, and the mixture was stirred for 2 h. Sodium cyanide (7.2 g, 148 mmol) was then added, and the stirring was continued overnight. The mixture was taken up with dichloromethane (150 mL). The organic layer was further washed with water (100 mL) and dried over anhydrous sodium sulfate, filtered, and evaporated (rotary evaporator) at room temperature. The resulting solid was recrystallized from xylenes/hexanes or toluene/hexanes and then from ethyl acetate to afford light yellow crystals (17.4 g, 87%). Mp: 92.1–95.4 °C. IR (neat): 3326, 3302 (NH), 2970, 2938, 2879 (CH), 2230 (weak, CN), 1490, 1463, 1138, 865 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.35 (s, 4 H, ArH), 4.05, 3.82 (2d, 4 H, $ArCH_2$), 3.42 (m, 2 H, CHCN), 1.82 (qn, 4 H, CH_2CH_3), 1.55 (s, 2 H, NH), 1.10 (t, 6 H, CH_3). Anal. Calcd for $C_{16}H_{22}N_4$: C, 71.07; H, 8.20. Found: C, 71.05; H, 8.18.

***N,N'*-Bis(α-cyanoethyl)-1,6-hexanediamine (1a)** was prepared following the procedure for **1g**. The dichloromethane extract was partly evaporated at room temperature. A colorless solid formed slowly; this was filtered and washed with hexanes/dichloromethane to give pure, colorless crystals (17%). Mp: 53.7–54.9 °C (lit.[5] mp 54 °C). IR (KBr): 3316 (NH), 2987, 2924, 2846, 2815 (CH), 2225 (CN), 1473, 1144, 825, 794 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.61 (q, 2 H, CH), 2.92–2.80 + 2.68–2.53 (m, 4 H, CH_2NH), 1.6–1.45 (2s, br at base, 10 H, CH_2CH_2NH + CH_3), 1.45–1.35 (m, 4 H, central CH_2), 1.2–1.08 (br s, 2 H, NH).

***N,N'*-Bis(α-cyanobenzyl)-1,2-ethanediamine (1b).** The procedure was similar to that for **1g**, starting from benzaldehyde and ethanediamine. The solid obtained was recrystallized from ethyl acetate/hexane to give light yellow crystals. Yield: 85%. Mp: 118–120 °C (lit.[7] mp 121–122 °C).

***N,N'*-Bis(α-cyanobenzyl)-1,6-hexanediamine (1c).** The procedure was similar to that for **1g**. Yield: 91%. Mp: 65–66 °C (from ethyl acetate/hexane) (lit.[5] mp 68 °C). IR: 3316 (NH), 3000–2850 (aliphatic and aromatic CH), 2230 (CN), 1484, 1450, 1115, 753, 698 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.5 (d, 4 H, ArH), 7.4 (m, 6 H, ArH), 4.8 (s, 2 H, CHCN), 2.7–2.9 (m, 4 H, CH_2N), 1.55 (d, 4 H, CH_2), 1.35 (d, 4 H, CH_2).

***N,N'*-Bis-(α-cyanoethyl)-*m*-xylylenediamine (1d).** The procedure was similar to that for the preparation of **1g**, using *m*-xylylenediamine and acetaldehyde. Evaporation of the organic phase was performed at room temperature using a rotary evaporator and then under high vacuum at 35 °C; this last operation required several days. A viscous, very light yellow liquid was obtained (92% yield). Purification was performed by chromatography over neutral alumina (solvent dichloromethane). IR: 3326, 3306 (NH), 2988, 2939, 2848 (aromatic and aliphatic CH), 2225 (CN), 1612, 1452, 1143 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.40–7.25 (m, 4 H, ArH), 4.08, 3.85 (2 doublets due to the diastereotopic effect, 4 H, CH_2NH), 3.75–3.55 (m, 2 H, CHCN), 1.50 (d, 8 H, CH_3 + NH). ^{13}C NMR ($CDCl_3$): δ 138.50 (CN), 128.26, 127.64 (ArCH), 126.85 (2 ArCH, α to CCH_2), 120.28 ($ArCCH_2$), 50.89 (CH_2), 44.14 ppm (CH), 19.10 (CH_3). Anal. Calcd for $C_{14}H_{18}N_4$: C, 69.39; H, 7.49. Found: C, 69.12: H, 7.44.

***N,N'*-Bis-(α-cyanopropyl)-*m*-xylylenediamine (1e).** The procedure was similar to that above using propionaldehyde instead of acetaldehyde. Yield: 85%. Purification of the compound was performed by chromatography over a neutral alumina column (solvent dichloromethane) (yield 72% of pale yellow oil after this operation). IR: 3329, 3320 (NH), 3030, 2972, 2937 (aromatic and aliphatic CH), 2223 (CN), 1608, 1461, 1158, 1136 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.35 (s, 1 H, ArH), 7.30 (m, 3 H, ArH), 4.08, 3.85 (2d, 4 H, CH_2NH), 3.45 (t, 2 H, CHCN), 1.80 (m, 4 H, CH_2CH), 1.55 (s, 2 H, NH), 1.10 (t, 6 H, CH_3). Anal. Calcd for $C_{16}H_{22}N_4$: C, 71.07; H, 8.20. Found: C, 71.06; H, 8.21.

***N,N'*-Bis-(α-cyanoethyl)-*p*-xylylenediamine (1f).** The procedure was similar to that of **1g** using *p*-xylylenediamine and acetaldehyde. A yellow solid was obtained. Yield: 99%. Recrystallization from ethanol yielded very light yellow plates. Mp: 88.5–91.0 °C. IR: 3304 (NH), 2987, 2820 (aromatic and aliphatic CH), 2226 (CN), 1492, 1456, 1142, 1075, 834 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.32 (d, 4 H, ArH), 4.05, 3.83 (2d, 4 H, CH_2), 3.60 (m, 2 H, CHCN), 1.60 (s, 2 H, NH), 1.50 (d, 6 H, CH_3). Anal. Calcd for $C_{14}H_{18}N_4$: C, 69.39; H, 7.49. Found: C, 69.32; H, 7.46.

Condensation of a Bis(α-aminonitrile) with a Diacid Chloride. Poly[*N,N'*-bis(α-cyanopropyl)-*m*-xylylenediyladipamide] (2e). The condensation of *N,N'*-bis(α-cyanopropyl)-*m*-xylylenediamine (**1e**) with adipoyl chloride is given as a standard procedure. A three-neck, 250-mL flask equipped with an argon inlet, an addition funnel, and a mechanical stirrer was flame-dried under argon. After cooling 0.8622 g (4.73 mmol) of adipoyl chloride in 2 mL of chloroform was introduced. In the addition funnel 1.279 g (4.73 mmol) of diamine was introduced in 8 mL of chloroform. On top of it was placed 1.4 mL (10 mmol) of triethylamine. The content of the addition funnel was introduced over 2 min into the reaction flask under rapid stirring. An exothermicity was noted as triethylamine entered the reaction flask. The reaction was allowed stir for 4 h or more. The mixture was poured into 150 mL of methanol, the solid dissolved in 20 mL of dichloromethane, and poured into 200 mL of absolute ethanol. The white gum obtained was dried under vacuum at 65 °C for 20 h, becoming a fluffy white solid (1.2 g, 67%). IR (film): 3057, 2976, 2937, 2879 (aliphatic and aromatic CH), 2242 (CN), 1655 (CO), 1462, 1408, 1192 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.38 (br s, 1 H, ArH), 7.20 (br s, 2 H, ArH), 7.12 (s, 1 H, ArH), 5.33 (br s, 2 H, CHCN), 4.65 (q, 4 H, CH_2N), 2.29 (br s, 4 H, CH_2CO), 1.77 (br s, 4 H, CH_2), 1.60 (s, 4 H, CH_2), 1.00 (t, 6 H, CH_3). Anal. Calcd for DP_n = 10 and acidic end groups (M_n = 3950): C, 68.69; H, 7.41; N, 14.18. Found: C, 68.87; H, 7.38; N, 13.94.

Poly[*N,N'*-bis(α-cyanoethyl)-1,6-hexanediyladipamide] (2a). IR: 3400, 3150 (w), 2930, 1650 (CO), 1430, 1080 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.42 (br s, 2 H, CHCN), 3.36 (br s, 4 H, CH_2N), 2.38 (br s, 4 H, CH_2CO), 1.70 (br s, 8 H, CH_2), 1.52 (d, 6 H, CH_3), 1.41 (br s, 4 H, CH_2). Impurities are also seen at 4.9 ppm. Anal. Calcd for $C_{18}H_{28}N_4O_2$: C, 65.03; H, 8.49; N, 16.85. Found: C, 59.65; H, 7.73; N, 13.43.

Poly[*N,N'*-bis(α-cyanobenzyl)-1,2-ethanediyladipamide] (2b). The condensation product of **1b** and adipoyl chloride was chromatographed on silica gel using first dichloromethane as the solvent. A first fraction (13%) was eluted. The IR spectrum of this part was similar to that of the starting material. By elution with methanol/chloroform (30:70), a second fraction, **2b** (75%), could be isolated. ^{1}H NMR ($CDCl_3$): δ 7.4 (br s, 10 H, ArH), 7.0 (br s, 2 H, CHCN), 3.7–3.3 + 3.15–2.8 (br s, 4 H, CH_2N), 2.7–2.25 + 2.1 (br s, 4 H, CH_2O), 1.7 (br s, 4 H, CH_2). Impurities are also seen at 6.25 and 6.0 ppm. Anal. Calcd for DP_n = 12 and acidic end groups (M_n = 4950): C, 71.31; H, 6.07; N, 13.58. Found: C, 71.16; H, 6.15; N, 13.74.

Poly[*N,N'*-bis(α-cyanobenzyl)-1,6-hexanediyladipamide] (2c). ^{1}H NMR ($CDCl_3$): δ 7.41 (br s, 10 H, ArH), 7.01 (s, 2 H, CH), 3.3–3.0 (br s, 4 H, CH_2N), 2.44 (br s, 4 H, CH_2O), 1.78 (br s, 4 H, CH_2), 1.60 (br s, 2 H), 1.20 (br s, 2 H, CH_2), 1.08 (br s, 4 H, CH_2). Impurities are detected at 6.05 ppm. Anal. Calcd for DP = 4 and acidic end groups (M_n = 2000): C, 73.65; H, 7.07; N, 12.27. Found: C, 71.43; H, 7.22; N, 11.89.

Poly[*N,N'*-bis(α-cyanoethyl)-*m*-xylylenediyladipamide] (2d). ^{1}H NMR ($CDCl_3$): δ 7.39 (br s, 1 H, ArH), 7.18 (d,

2 H, ArH), 7.11 (s, 1 H, ArH), 5.47 (br s, 2 H, CHCN), 4.67 (q, 4 H, CH_2N), 2.29 (br s, 4 H, CH_2CO), 1.58 (br s, 4 H, CH_2), 1.44 (d, 6 H, CH_3). Anal. Calcd for DP_n = 11 and acidic end groups (M_n = 4000): C, 67.48; H, 6.87; N, 15.32. Found: C, 67.27; H, 6.89; N, 15.59.

Poly[*N,N'*-bis(α-cyanoethyl)-*p*-xylylenediyladipamide] (2f). ^1H NMR ($CDCl_3$): δ 7.25 (d, 4 H, ArH), 5.50 (br s, 2 H, CHCN), 4.65 (q, 4 H, CH_2N), 2.29 (br s, 4 H, CH_2CO), 1.60 (br s, 4 H, CH_2), 1.44 (d, 6 H, CH_3). Anal. Calcd for DP_n = 10 and acidic end groups (M_n = 3670): C, 67.41; H, 6.87; N, 15.26. Found: C, 67.59; H, 6.88; N, 15.71.

Poly[*N,N'*-bis(α-cyanopropyl)-*p*-xylylenediyladipamide] (2g). ^1H NMR ($CDCl_3$): δ 7.25 (d, 4 H, ArH), 5.33 (br s, 2 H, CHCN), 4.64 (q, 4 H, CH_2N), 2.29 (br s, 4 H, CH_2CO), 1.74 (m, 4 H, CH_2), 1.59 (br s, 4 H, CH_2), 1.01 (t, 6 H, CH_3). Anal. Calcd for DP_n = 15 and acidic end groups (M_n = 5850): C, 68.94; H, 7.40; N, 14.36. Found: C, 68.99; H, 7.46; N, 14.23.

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References and Notes

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