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Synthesis and characterization of adamantane-containing poly(enaminonitriles)

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The first aliphatic bis(chlorovinylidene cyanide) monomer, 1,3-bis(1-chloro-2,2-dicyanovinyl)adamantane, has been synthesized and polymerized with appropriate diamines to give adamantane-containing aromatic-aliphatic and all aliphatic poly(enaminonitriles) (PEANs) via vinylic nucleophilic substitution polymerization. The PEANs showed excellent solubility in polar aprotic solvents and good thermal stability (10% weight loss in air > 320 °C), despite the aliphatic contents of the polymers. Solution inherent viscosities of 0.23–0.90 dL/g were obtained.

Three other new PEANs containing the adamantane-based cardo group were also synthesized via vinylic nucleophilic substitution polymerization from the adamanaine-containing cardo diamine 2,2-bis[4-(4-aminophenoxy)phenyl]adamantane. The cardo PEANs showed better solubility in common organic solvents than the corresponding cardo polyamides. They also showed good thermal stabilities (10% weight loss in air > 339 °C) comparable to those of the corresponding cardo polyamides.

1. Introduction

High molecular weight, processable poly(enaminonitriles) (PEANs), as analogs of polyamides, cure thermally by a molecular rearrangement without evolution of small molecules and are prepared by the polymerization of bis(chlorovinylidene cyanides) with diamines via vinylic nucleophilic substitution [1–5]. As Wallenfels reported [6], a carbon atom connected to a 2,2-dicyanomethylidene group is considered to be equivalent to a carbonyl group, which can activate the double bond to allow vinylic nucleophilic substitution.

Aromatic and aromatic-aliphatic PEANs are hydrolytically stable, have good to excellent thermal and mechanical properties, excellent solubility in polar aprotic solvents and good film forming properties [1–5]. PEANs can be cured thermally without elimination of volatile products to form insoluble, void-free films [1–5].

Adamantane (tricyclo[3.3.1.1^{3,7}]decane), a highly symmetrical and thermo-oxidatively stable, strain-free, fused chair cyclohexane structure can impart interesting properties such as increased glass transition temperature (T_g), enhanced solubility and thermo-oxidative stability. In addition this structural element in the backbone or as a pendent group decreases polymer chain mobility and inhibits polymer chain packing because of its rigidity and bulk [7–15]. These effects have been demonstrated by incorporating the adamantane-containing cardo (pendent loop) component, 2,2-bis[4-(4-aminophenoxy)phenyl]adamantane, into an aromatic polyamide (aramid) backbone [12–14].

To determine the effect of incorporating such units into PEANs, the first aliphatic bis(chlorovinylidene cyanide) monomer based on adamantane was successfully synthesized and polymerized with appropriate diamines [16–18]. The present work examines the influence of the adamantane and cardo moieties on the thermal and other properties of the PEANs.

2. Experimental section

2.1. Characterization

All melting points (mp) were measured using open or sealed capillary tubes (uncorrected) or by Differential Scanning Calorimetry (DSC) under nitrogen calibrated with indium and zinc standards.

Nuclear Magnetic Resonance (NMR) spectra were recorded on a Varian Unity 500 (500 MHz ^{1}H; 125 MHz ^{13}C) spectrometer. All ^{13}C NMR spectra were obtained using broadband decoupling. Peak assignments were based on comparisons with previously reported data for similar structures as well as with model compounds prepared in this work.

Fourier Transform Infrared (FT-IR) spectra were recorded on either a Bio-Rad FTS 3000MX MID-IR Excalibur spectrometer running Merlin software or a Perkin–Elmer Paragon 1000 spectrophotometer.

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DSC and Thermogravimetric Analysis (TGA) were carried out on Perkin–Elmer Series 7 instruments running Pyris™ software. DSC and TGA were carried out at heating rates of 10 °C/min and 20 °C/min under nitrogen or air, respectively. Glass transition temperatures (T_g) were calculated by the half C_p method using Perkin–Elmer Pyris™ software.

Size Exclusion Chromatography (SEC) was performed at room temperature using a Viscotek 22C HPLC pump connected with viscosity (Viscotek differential viscometer Model 100) and refractive index (Knauer differential refractometer) detectors in series running Viscotek UNICAL (v. 4.06) software. Two Jordi gel DVB mixed bed columns (Alltech) were used. Polystyrene standards were used and tetrahydrofuran was the eluent. Molecular weights were calculated with Viscotek UNICAL (v. 4.06) software.

Gas Chromatograph–Mass Spectrometer (GC–MS) data were obtained using a Shimadzu GCMS-QP5000 spectrometer. Ionization was done with electron-impact (EI) under ultra-high purity (UHP) helium as the carrier gas. The molecular ion is reported as M^+.

Solution viscosity measurements were carried out with a Cannon-Ubbelohde viscometer (# 75) in a constant temperature bath (25.00 °C or 30.00 °C). DMF was used as solvent. All solutions were filtered through Gelman Acrodisc CR PTFE 0.45 µm syringe filters.

Matrix-assisted laser desorption ionization time of flight mass spectra (MALDI-TOF MS) was recorded on a Micromass TOF-Spec-2E (Manchester, UK) instrument operating in linear and reflectron modes with detection of negatively charged ions and running MassLynx™ software. 2-(4-Hydroxyphenylazo)benzoic acid (HABA) was used as the matrix and tetrahyrofuran was used as the solvent.

Thermomechanical Analysis (TMA) was carried out on a Perkin–Elmer Series 7 instrument running Pyris™ software. The extension probe was used to measure glass transition temperatures of polymer films at a heating rate of 20 °C/min under helium. The applied force was set to the lowest possible value (~30 mN) to prevent the polymer film from breaking during measurement.

Dynamic Mechanical Analysis (DMA) was carried out on a Rheometric Scientific DMTA V using the single cantilever bending mode at 1 Hz with 0.01% strain. The T_g value is reported [21] as the maximum temperature in loss modulus (E″) or in loss tangent (tan δ).

2.2. Materials

N-methyl-2-pyrrolidone (NMP) was stirred over anhydrous barium oxide for 48 h and distilled under reduced pressure. 1,2-Dichloroethane (DCE) was distilled from calcium hydride under N_2. Tetrahydrofuran (THF) was distilled from sodium-benzophenone ketyl under N_2. Malononitrile was distilled under reduced pressure. Phosphorus oxychloride and thionyl chloride were fractionally distilled (1 atm) using a short Vigreux column. 1,4-Diazabicyclo[2.2.2]octane (DABCO), 4-(dimethylamino)pyridine and all diamines except 4.4′-ODA (sublimed, zone-refined, 99+%, Aldrich) were sublimed under reduced pressure just before polymerization. Aniline was distilled under reduced pressure from anhydrous K_2CO_3 and stored over KOH pellets. Triethylamine was distilled from anhydrous K_2CO_3 under nitrogen. 1-Adamantanecarbonyl chloride (95%), 1,3-adamantanedicarboxylic acid (98%), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 98%), benzyltriethylammonium chloride (BTAC, 98%), and chlorobenzene (99%) were purchased from Aldrich or Acros, and used as received.

2.3. Model compound synthesis

2.3.1. 1-Chloro-2,2-dicyanovinyl adamantane (**1**)

1-Chloro-2,2-dicyanovinyl adamantane (**1**) was synthesized by following previously reported procedures [1–3] (Scheme 1). 1-Adamantanecarbonyl chloride was condensed with malononitrile in the presence of DBU in THF, or KOH under phase transfer catalysis conditions (PTC = H_2O/DCE/BTAC) to give the corresponding DBU salt (63% yield), or the potassium salt (71% yield), respectively. The salts were converted to the desired model compound by heating them with excess phosphorus oxychloride at 70 °C for 12 h under nitrogen, mp 86–88 °C (FW for $C_{14}H_{15}N_2Cl$: 246.59). GC–MS (EI), m/e 246 (M^+), ^1H NMR ($CDCl_3$) (ppm) 2.11–1.67 (m, adamantane *H*). ^{13}C NMR ($CDCl_3$) (ppm) 182.7 (=*C*–Cl), [112.1, 111.4] (*C*N), 86.5 (=*C*(CN)$_2$), [45.3, 40.3, 38.1, 36.2, 35.6, 28.0] (adamantane *C*). FT-IR (KBr) 3355 br, 2919, 2855, 2230 (CN), 1548, 1451, 1346, 1216, 1106, 986, 889 cm^{-1}.

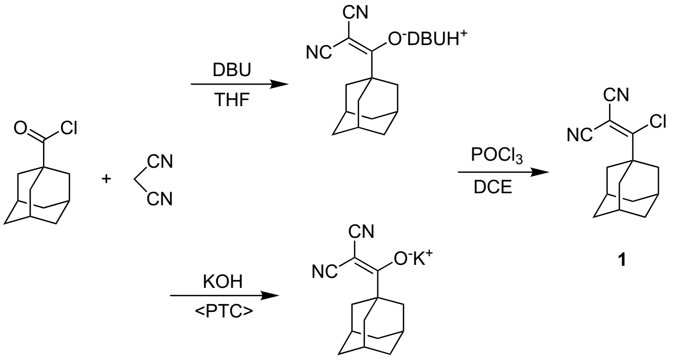
2.3.2. (Phenylamino)adamantylmethylenepropanedinitrile (**2**)

1-Chloro-2,2-dicyanovinyl adamantane (0.1 g, 0.41 mmol) was added to a dried 50 mL two-neck, round bottomed flask fitted with a magnetic stirring bar, an addition funnel with an argon inlet, and a reflux condenser. Dry ether (10 mL) was added to the flask, and triethylamine (2.5 mL, 17.9 mmol) was added to the reaction mixture. The reaction mixture became red, and freshly distilled aniline (0.24 mL, 2.58 mmol) was added via an addition funnel to form a white precipitate. The reaction mixture was stirred for an additional 24 h without an argon inlet. The reaction mixture was filtered, washed with 5% HCl followed by distilled water, and dried over P_2O_5 in vacuo (1–2 torr) for 24 h at 50 °C to give a light yellow solid (0.059 g, 48% yield), mp 234–236 °C (sealed tube), 236 °C (DSC). ^1H NMR (DMSO-d_6, 60 °C) (ppm) 9.01 (s, N*H*), 7.42–7.22 (m, arom. *H*), 2.19 (d, adamantane *H*), 1.76 (s, adamantane *H*). ^{13}C NMR (DMSO-d_6, 60 °C) (ppm) 177.9 (=*C*–NH), [138.1, 128.9, 127.8, 126.6] (arom. *C*), [118.7, 115.1] (*C*N), 49.7 (=*C*(CN)$_2$), [40.6, 38.1, 35.5, 27.8] (adamantane *C*). FT-IR (KBr) 3300 br (NH), 2912, 2855, 2204 (CN), 1510, 1451, 1267, 760 cm^{-1}.

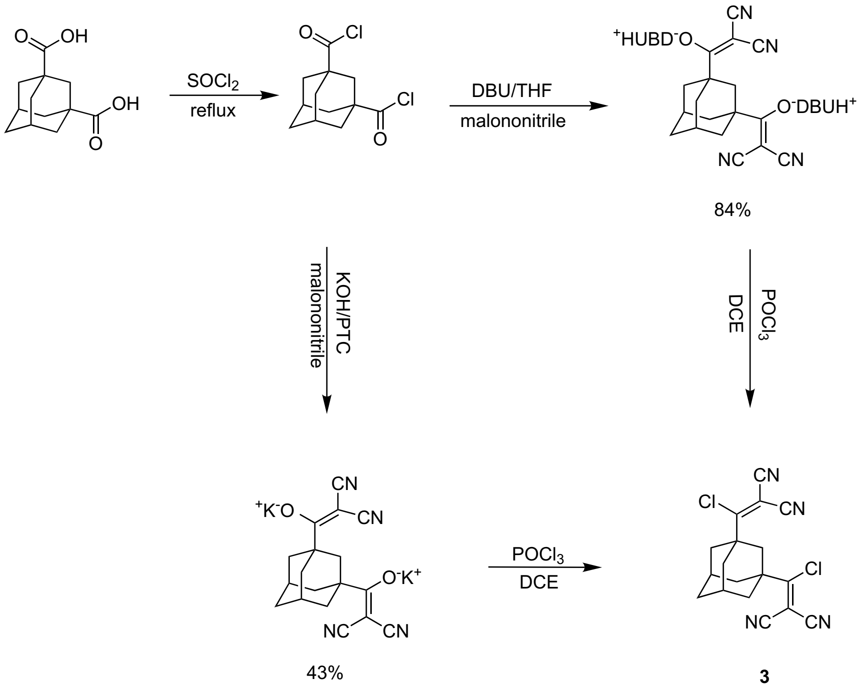
2.4. Monomer and model compound synthesis

2.4.1. 1,3-Bis(1-chloro-2,2-dicyanovinyl)adamantane (**3**)

1,3-Adamantanedicarboxylic acid was converted to the corresponding acyl chloride (mp 89–91 °C) by refluxing with thionyl chloride. The diacid chloride was converted to 1,3-bis(1-chloro-2,2-dicyanovinyl)adamantine according to previously reported procedures [1–3] (Scheme 2). Potassium salt (43% yield), DBU salt (84% yield), mp 152–154 °C. GC–MS (EI) of monomer (**3**) (FW for $C_{18}H_{14}N_4Cl_2$: 356.98), m/e 356 (M^+). ^1H NMR ($CDCl_3$) (ppm) 2.44–1.74 (m, adamantane *H*). ^{13}C NMR ($CDCl_3$) (ppm) 179.2 (=*C*–Cl), [111.5, 110.9] (*C*N), 87.9 (=*C*(CN)$_2$), [45.3, 42.2, 38.8, 33.8, 28.1] (adamantane *C*). FT-IR (KBr) 3409 br, 2922, 2863, 2229 (CN), 1556, 1452, 1349, 1208, 1009, 883 cm^{-1}.



Scheme 1. Synthesis of model compound **1**.



Scheme 2. Synthesis of the monomer **3**.

2.4.2. *1,3-Bis[2,2-dicyano-1-(phenylamino)vinyl]adamantane (**4**)*

1,3-Bis(1-chloro-2,2-dicyanovinyl)adamantane (0.1591 g, 0.45 mmol) was added to a dried 50 mL, two-neck, round bottomed flask fitted with a magnetic stirring bar, an addition funnel with an argon inlet, and a reflux condenser. Dry 1,2-dichloromethane (10 mL) was added to the flask, and triethylamine (2.5 mL, 17.9 mmol) was added to the reaction mixture. The reaction mixture turned red, and freshly distilled aniline (6 mL, 61.9 mmol) was added to the reaction mixture via the addition funnel. The homogeneous reaction mixture was stirred for an additional 24 h in air. The liquid reaction mixture was concentrated using a Rotavapor ($\sim$1–2 torr) at 60 °C. The reddish viscous residue was precipitated into ether. The light yellow solid was filtered, washed with 5% HCl followed by distilled water, and dried over P_2O_5 in vacuo for 24 h at 50 °C. The solid was re-dissolved in DMSO, reprecipitated in distilled water, washed with distilled water, and dried over P_2O_5 in vacuo (1–2 torr) for 48 h at 60 °C to give a yellow solid (0.1096 g, 51% yield), mp 290–292 °C (sealed tube). ^{1}H NMR (DMSO-d_6, 60 °C) (ppm) 9.36 (s, N*H*), 7.44–7.26 (m, arom. *H*), 2.4–1.71 (m, adamantane *H*). ^{13}C NMR (DMSO-d_6, 60 °C) (ppm) 176.4 (=*C*–NH), [137.7, 129.1, 128.3, 126.9] (arom. *C*), [118.6, 114.8] (*C*N), 64.9 (=*C*(CN)$_2$), [50.2, 41.5, 36.7, 33.5, 27.9] (adamantane *C*). FT-IR (KBr) 3424 br (NH), 2923, 2205 (CN), 1599, 1512, 1451, 761, 699 cm^{-1}.

2.4.3. *Monomers **5**–**8** (Scheme 4)*

2,2-Bis[4-(4-aminophenoxy)phenyl]adamantane (**5**) [11,13], 1,4-bis(1-chloro-2,2-dicyanovinyl) benzene (**6**) [1,2], 4,4′-bis(1-chloro-2,2-dicyanovinyl)biphenyl (**7**) [3], and 4,4′-bis(1-chloro-2,2-dicyanovinyl)-p-terphenyl (**8**) [3] were synthesized by following previously reported procedures. Monomer **6** and monomers **7**,**8** were recrystallized from chloroform and chlorobenzene, respectively, just before polymerization.

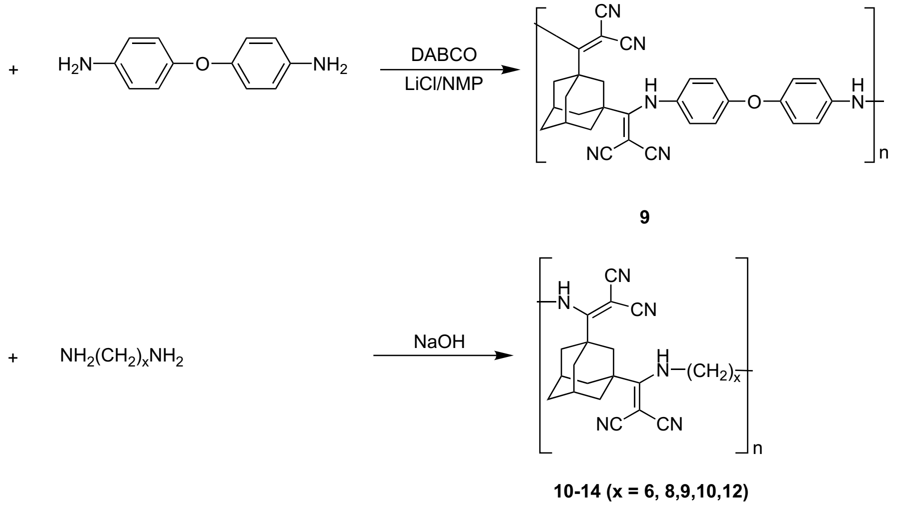
2.5. *Polymer synthesis*

The aromatic–aliphatic (**9**) and aliphatic (**10**–**14**) PEANs were synthesized from bis(chlorodicyanovinyl) monomer (**3**) with 4,4′-diaminodiphenyl ether (ODA) and aliphatic diamines containing 6,8,9,10, and 12 methylene units by solution polycondensation (PEANs **9**,**10A**) [1–3] and interfacial (PEANs **10B**–**14**) [5,19,20] polymerization, respectively, by following the procedures cited above (Scheme 3). The spectral data for PEANs **9**–**14** are given below.

The cardo PEANs **15**–**17** were also synthesized similarly by solution polycondensation (Scheme 4) [1–3]. A representative procedure for synthesis of polymer **15** follows. 2,2-Bis[4-(4-aminophenoxy)phenyl]adamantane (0.275 g, 0.546 mmol) and DABCO (0.061 g, 0.546 mmol) were added to a dry 50 mL two-necked round bottomed flask fitted with a magnetic stirring bar, and addition funnel with an argon inlet, and a reflux condenser connected to a mineral oil bubbler. Dry NMP (5 mL) was added to the flask, and 1,4-bis(1-chloro-2,2-dicyanovinyl)benzene (0.1633 g, 0.546 mmol) in 5 mL of dry NMP was added, dropwise, to the solution via the addition funnel at room temperature. The reaction mixture turned brown, was heated to 70 °C in an oil bath for 12 h and cooled to room temperature. The mixture was stirred for an additional 12 h at room temperature, and added, dropwise, to vigorously stirred distilled water. The polymer was filtered, washed with distilled water, and dried in vacuo for 48 h at 80 °C. The tan polymer was re-dissolved in DMF and added, dropwise, to 300 mL of distilled water. The precipitated polymer was washed with methanol followed by distilled water, and dried over P_2O_5 in vacuo (1–2 torr) for 48 h at 95 °C to give a solid. The spectral data for cardo PEANs **15**–**17** are given below.

2.5.1. *Poly[oxy-1,4-phenyleneimino-(2,2-dicyanoethene-1,1-diyl)-1,3-adamantyl-(2,2-dicyanoethene-1,1-diyl)imino-1,4-phenylene] (**9**)*

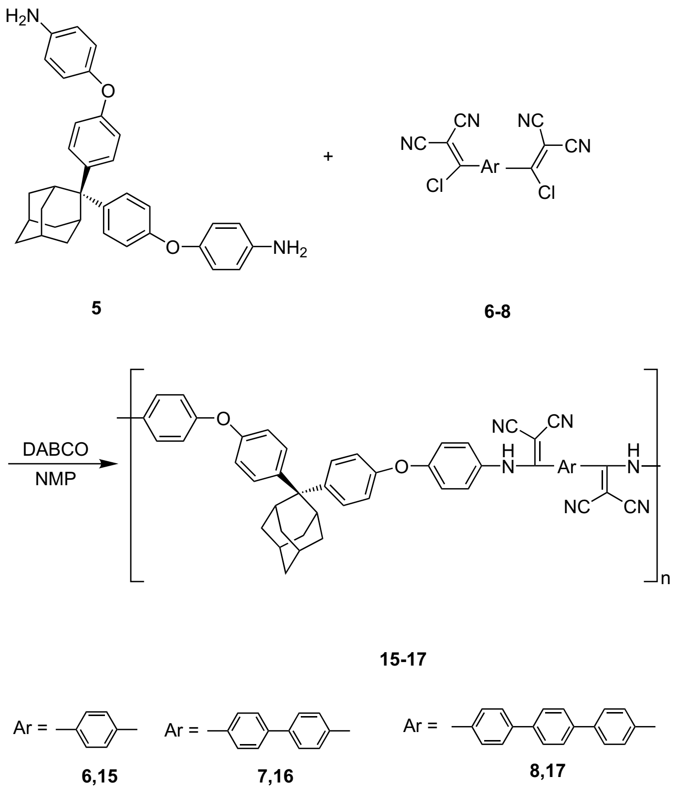
75% yield, T_g (2nd heating DSC) 199 °C. ^{1}H NMR (DMSO-d_6) (ppm) 9.3 (s, N*H*), 7.3 (d, ODA *H*), 7.0 (d, ODA *H*), 2.4 (s), 2.3 (s), 2.0 (s), 1.7 (s). ^{13}C NMR (DMSO-d_6) (ppm) 176.9 (=*C*–NH), 156.5 (*C*–O of ODA), 133.1 (*C*–N– of ODA), [129.2, 119.1] (CH of ODA), [118.6, 115.0] (*C*N), 49.9 (=*C*(CN)$_2$), 41.4, 39.0, 36.5, 27.8; FT-IR (KBr) 3419 br (NH), 2923, 2207 (CN), 1499, 1242, 831 cm^{-1}.



Scheme 3. Synthesis of adamantane-containing PEANs **9–14**.

2.5.2. *Poly[imino-(2,2-dicyanoethene-1,1-diyl)-1,3-adamantyl-(2,2-dicyanoethene-1,1-diyl)iminohexamethylene] (**10A**,**10B**)*

Solution and interfacial polymerization were done to synthesize polymer **10A** (52% yield) and **10B** (78% yield), respectively. A 100 mL test tube fitted with a Vibro-Mixer™ was used in interfacial polymerization. T_g (2nd heating DSC) 169 °C. ^{1}H NMR (DMSO-d$_6$) (ppm) 7.7 (s, N*H*), 3.5 (s), 2.4–1.8 (m), 1.6 (s), 1.2 (s). ^{13}C NMR (DMSO-d$_6$) (ppm) [175.9, 175.8] (=*C*–NH), [119.0, 118.1] (*C*N), 45.2 (=*C*(CN)$_2$), 41.7, 36.6, 33.6, 27.9, 25.2, 24.9. FT-IR (KBr) 3364 br (NH), 2924, 2861, 2205 (CN), 1527, 1456, 1369, 1268, 673, 560 cm^{-1}.



Scheme 4. Synthesis of adamantane-containing cardo PEANs **15–17**.

2.5.3. *Poly[imino-(2,2-dicyanoethene-1,1-diyl)-1,3-adamantyl-(2,2-dicyanoethene-1,1-diyl)iminooctamethylene] (**11**)*

76% yield, T_g (2nd heating DSC) 142 °C. ^{1}H NMR (DMSO-d$_6$) (ppm) 7.7 (s, N*H*), 3.5 (s), 2.2–1.8 (m), 1.6 (s), 1.2 (s). ^{13}C NMR (DMSO-d$_6$) (ppm) 175.7 (=*C*–NH), [118.9, 118.1] (*C*N), [45.1, 44.9] (=*C*(CN)$_2$), 40.0, 36.6, 33.6, 28.5, 28.4, 27.9, 25.4. FT-IR (Film) 3351 br (NH), 2925, 2858, 2205 (CN), 1555, 1455, 1370, 1270, 1225, 1116, 972, 814, 668, 560 cm^{-1}.

2.5.4. *Poly[imino-(2,2-dicyanoethene-1,1-diyl)-1,3-adamantyl-(2,2-dicyanoethene-1,1-diyl)iminononamethylene] (**12**)*

75% yield, T_g (2nd heating DSC) 136 °C. ^{1}H NMR (DMSO-d$_6$) (ppm) 7.7 (s, N*H*), 3.5 (s), 2.2–1.8 (m), 1.5 (s), 1.2 (s). ^{13}C NMR (DMSO-d$_6$) (ppm) [175.7, 164.0] (=*C*–NH), [118.9, 118.0] (*C*N), [45.1, 44.9] (=*C*(CN)$_2$), 40.0, 36.6, 28.4, 27.9, 25.5. FT-IR (Film) 3351 br (NH), 2925, 2857, 2205 (CN), 1553, 1455, 1369, 1270, 1220, 1161, 1116, 972, 923, 815, 682 cm^{-1}.

2.5.5. *Poly[imino-(2,2-dicyanoethene-1,1-diyl)-1,3-adamantyl-(2,2-dicyanoethene-1,1-diyl)iminodecamethylene] (**13**)*

78% yield, T_g (2nd heating DSC) 124 °C. ^{1}H NMR (DMSO-d$_6$) (ppm) 7.7 (s, N*H*), 3.5 (s), 2.2–1.8 (m), 1.5 (s), 1.2 (s). ^{13}C NMR (DMSO-d$_6$) (ppm) 175.7 (=*C*–NH), [118.9, 118.0] (*C*N), 45.2 (=*C*(CN)$_2$), 40.0, 36.6, 28.7, 28.5, 27.9, 25.5. FT-IR (Film) 3352 br (NH), 2925, 2857, 2206 (CN), 1555, 1454, 1370, 1271, 816, 682, 560 cm^{-1}.

2.5.6. *Poly[imino-(2,2-dicyanoethene-1,1-diyl)-1,3-adamantyl-(2,2-dicyanoethene-1,1-diyl)iminododecamethylene] (**14**)*

60% yield, T_g (2nd heating DSC) 114 °C. ^{1}H NMR (DMSO-d$_6$) (ppm) 7.7 (s, N*H*), 3.5 (s), 2.2–1.8 (m), 1.5 (s), 1.2 (s). ^{13}C NMR (DMSO-d$_6$) (ppm) 175.7 (=*C*–NH), [118.9, 118.0] (*C*N), 45.2 (=*C*(CN)$_2$), 40.0, 36.6, 28.9, 28.8, 28.6, 28.4, 27.9, 25.5. FT-IR (Film) 3353 br (NH), 2924, 2855, 2188 (CN), 1514, 1455, 1369, 1271, 1187, 1058, 972, 847, 720, 682, 560 cm^{-1}.

2.5.7. *Poly[oxy-1,4-phenylene-2,2′-adamantyl-1,4-phenyleneoxy-1,4-phenyleneimino-(2,2-dicyanoethene-1,1-diyl)-1,4-phenylene-(2,2-dicyanoethene-1,1-diyl)imino-1,4-phenylene] (**15**)*

75% yield, T_g was not observed by DSC (heating up to 250 °C). M_w was 15,200 by SEC. ^{1}H NMR (DMSO-d$_6$, 60 °C) (ppm) 10.7 (s, N*H*), 7.73–6.74 (br m, arom. C*H*), [6.62, 6.25] (d, arom. C*H* of amine end group), 3.01(s, adamantane C*H*), 2.48–1.67 (br m, adamantane C*H*). ^{13}C NMR (DMSO-d$_6$, 60 °C) (ppm) 167.8 (=*C*–NH), [154.9, 153.6, 143.2, 141.6, 133.1, 130.1, 127.2, 127.1, 126.8, 126.4, 119.1, 117.7] (arom.

C), [117.0, 114.3] (*C*N), 52.1 (=*C*(CN)$_2$), [49.3, 32.7, 31.1, 26.7] (adamantane *C*). FT-IR (KBr) 3359 br (NH), 3041 (arom. C–H), 2214 (CN), 1567, 1499, 1235, 1171, 845 cm^{-1}.

2.5.8. Poly[oxy-1,4-phenylene-2,2′-adamantyl-1,4-phenyleneoxy-1,4-phenyleneimino-(2,2-dicyanoethene-1,1-diyl)-4,4′-biphenylene-(2,2-dicyanoethene-1,1-diyl)imino-1,4-phenylene] (**16**)

79% yield, T_g was not observed by DSC (heating up to 290 °C). T_g (TMA: 30 mN of applied force, 20 °C/min) 341 °C. The maximum in loss tangent (tan δ) by DMA was 349 °C. M_w was 69,500 by SEC after removing low molecular weight fractions by extraction with acetone. ^{1}H NMR (DMSO-d$_6$, 60 °C) (ppm) 10.7 (s, N*H*), 7.91–6.84 (m, arom. C*H*), [6.64, 6.63] (br. d, arom. C*H* of amine end group), 3.12 (s, adamantane C*H*), 1.91–1.52 (br m, adamantane C*H*). ^{13}C NMR (DMSO-d$_6$, 60 °C) (ppm) 168.7 (=*C*–NH), [154.9, 153.6, 143.2, 141.6, 133.1, 127.2, 127.1, 126.8, 124.9, 119.99, 119.12] (arom. *C*), [117.7, 114.3] (*C*N), 52.1 (w, =*C*(CN)$_2$), [49.3, 38.5, 32.7, 31.1, 26.7] (adamantane *C*). FT-IR (KBr) 3448 br (NH), 3039 (arom. C–H), 2908, 2854, 2213 (CN), 1566, 1498, 1234, 1171, 829 cm^{-1}.

2.5.9. Poly[oxy-1,4-phenylene-2,2′-adamantyl-1,4-phenyleneoxy-1,4-phenyleneimino-(2,2-dicyanoethene-1,1-diyl)-4.4″-terphenylene-(2,2-dicyanoethene-1,1-diyl)imino-1,4-phenylene] (**17**)

90% yield, T_g was not observed by DSC (heating up to 290 °C). M_w (PDI = 3.0) was 15,800 by SEC after removing low molecular weight fractions by extraction with acetone. ^{1}H NMR (DMSO-d$_6$, 60 °C) (ppm) 10.7 (s, N*H*), 7.89–6.72 (br m, arom. C*H*), 6.62 (br s, arom. C*H* of amine end group), 3.18 (br s, adamantane C*H*), 1.88–1.63 (br m, adamantane C*H*). ^{13}C NMR (DMSO-d$_6$, 60 °C) (ppm) 168.1 (=*C*–NH), [154.9, 153.8, 143.1, 142.3, 138.3, 133.3, 130.0, 129.8, 127.3, 127.1, 126.4, 119.2] (arom. *C*), [117.6, 114.4] (*C*N), 53.2 (w, =*C*(CN)$_2$), [49.3, 37.2, 32.6, 31.0, 26.6] (adamantane *C*). FT-IR (KBr) 3439 br (NH), 3038 (arom. C–H), 2909, 2213 (CN), 1604, 1566, 1499, 1235, 1172, 823 cm^{-1}.

3. Results and discussion

3.1. Synthesis of model compounds, monomers and polymers

The novel aliphatic bis(chlorovinylidene cyanide) monomer **3** was prepared from 1,3-adamantanedicarboxylic acid via two different synthetic routes [1–3] as shown in Scheme 2. In the preparation of monomer **3**, the % yield for the potassium salt (43% yield) was almost a half of the DBU salt (84% yield) because hydrolysis of the acid chloride under phase transfer conditions caused significant losses [3]. Because adamantane-containing products are easily sublimed at much lower temperature than their melting points, care must be taken not to evaporate products during the removal of residual solvents and phosphorus oxychloride, as well, while drying the product. The structures of monomer **3** (FW for $C_{18}H_{14}N_4Cl_2$: 356.98) and model compound **1** (FW for $C_{14}H_{15}N_2Cl$: 246.59) were confirmed by GC–MS (EI) which showed single peaks at molecular ion of 356 (M$^+$) and 246 (M$^+$), respectively.

1-Chloro-2,2-dicyanovinyl adamantane **1** was reacted with aniline in dry ether and triethylamine as an acid acceptor to prepare model compound **2**. In addition, 1,3-bis[2,2-dicyano-1-(phenylamino)vinyl]adamantine, as model compound **4**, was successfully prepared from 1,3-bis(1-chloro-2,2-dicyanovinyl)adamantane **3** and aniline. The structures of these model compounds were confirmed by ^{1}H NMR, ^{13}C NMR, and FT-IR spectra. The preparation of these materials was conducted under conditions different from the polymerization process and neither was optimized.

With a series of linear aliphatic diamines as shown in Scheme 3, the interfacial polymerization method was chosen to obtain higher molecular weight polymers **10B**–**14** because it can overcome stoichiometric imbalance and the presence of impurities better than solution polymerization [5,19,20].

3.2. Polymer characterization

All PEANs **9**–**17** showed excellent solubility in polar aprotic solvents such as DMF, DMSO, DMAc, and NMP, and polymers containing cardo group **15**,**16**,**17** were also soluble in glyme, diglyme, and THF as shown in Table 1. When the solubility of cardo PEANs **15**,**16** is compared with those of the corresponding cardo polyamides **18** (η_{inh} = 0.82 dL/g) and **19** (η_{inh} = 0.90 dL/g), it is apparent that cardo PEANs have better solubility in the tested solvents than the corresponding cardo polyamides [14] presumably because of the structural difference between the 2,2-dicyanomethylidene and the carbonyl groups. That is, the presence of the rather bulky

Table 1
Solubility[a] behavior of PEANs **9**–**17** and polyamides **18**,**19**.

Polymer code	Solvents[b]						
	DMF	DMSO	DMAc	NMP	Glyme	Diglyme	THF
9	++	++	++	++	−−	−−	−−
10	++	++	++	++	−−	−−	−−
11	++	++	++	++	+−	+−	+−
12	++	++	++	++	+−	+−	+−
13	++	++	++	++	+−*	+−*	+−
14	++	++	++	++	+−*	+−*	++
15	++	++	++	++	++*	++	++
16	++	++	++	++	++*	++*	++
17	++	++	++	++	++*	++*	++
18[c]	+h	s	++	++			−−
19[c]	−−	−−	+h	++			−−

[a] Solubility: ++, soluble at room temperature; *, reversible phase separation upon heating; +−, partially soluble; +h, soluble on heating; −−, insoluble even on heating; s, swelling.

[b] DMF: *N*,*N*-dimethylformamide; DMSO: dimethyl sulfoxide; DMAc: *N*,*N*-dimethylacetamide; Glyme: 1,2-dimethoxyethane; Diglyme: diethylene glycol dimethyl ether.

[c] Data for polymers **18**,**19** from Ref. [14];

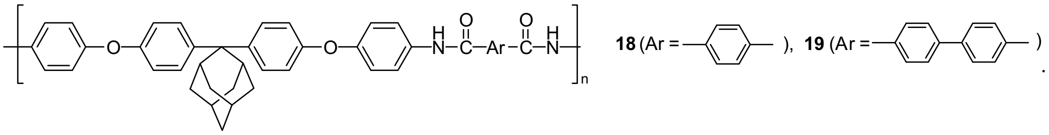


Table 2
Inherent viscosities and film quality of PEANs **9**–**14**.

Polymer code	η_{inh}[a] (dL/g)	Film quality[b]
9	0.32	Brittle
10A	0.23	Brittle[c]
10B	0.60	Brittle[d]
11	0.79	Flexible
12	0.82	Flexible
13	0.67	Flexible
14	0.90	Flexible

[a] Measured in DMF containing 0.16 g/dL at 25.00 °C (**9**–**10A**) and 0.40 g/dL at 30.00 °C (**10B**–**14**).
[b] Films were cast from DMF.
[c] Solution polycondensation.
[d] Interfacial polycondensation.

and polarizable dicyanovinylidene group inhibits chain packing and reduces hydrogen bonding interactions in the PEANs. PEANs **13**–**17** in glyme became cloudy upon heating and clear upon cooling to room temperature (reversible phase separation), which indicates lower critical solution temperature (LCST) behavior. It has been reported that PEANs showed LCST behavior in polyether solvents (glymes) [22].

As shown in Table 2, the aliphatic PEANs **11**–**14** had inherent viscosities in the range of 0.67–0.90 dL/g and formed fingernail-creasable films when cast from DMF. SEC traces of cardo PEANs **15**–**17** showed low molecular weight tailing (Table 3). The low molecular weight fractions of cardo PEANs **16** and **17** were removed by extraction with acetone. However, cardo PEAN **15** is soluble in acetone. Even if cardo PEANs **16** and **17** showed increased M_n and M_w after extraction, the polydispersity index (PDI) of cardo PEANs was still high because the low molecular weight fractions were not completely removed. The low molecular weight fractions of cardo PEANs **16** and **17** were studied by MALDI-TOF MS and showed molecular ions which correspond to the molecular weights of cyclic dimer (FW: 804), tetramer (FW: 1608), and hexamer (FW: 2412) for cardo PEAN **16** and dimer (FW: 881) and tetramer (FW: 1762) for cardo PEAN **17**, respectively [23]. Based on the MALDI MS spectra collected by varying operational conditions, higher molecular weight ions than tetramer or hexamer could not be reproducibly observed.

PEANs **9**–**14** showed good thermal stability by TGA considering the lower viscosities (**9**) and the aliphatic contents of the polymers (Table 4). The 10% weight loss temperatures under air and nitrogen ranged from 320 to 400 °C and from 360 to 506 °C, respectively. In addition, the 50% weight loss temperatures under air and nitrogen ranged from 401 to 535 °C and from 446 to 956 °C. There was no apparent relationship between numbers of methylene units and thermal stability in aliphatic PEANs **10B**–**14**. All cardo PEANs **15**–**17** showed good thermal stabilities with 10% and 50% weight loss in air occurring from 339 to 427 °C and from 479 to 567 °C by TGA, respectively. The 10% weight loss of cardo PEANs **15**,**16** in nitrogen ranged from 436 to 466 °C, which is comparable to that of the corresponding cardo polyamides **18**,**19**. The char wt.% of cardo PEANs **15**–**17** and corresponding aramids **18**,**19** at 800 °C in nitrogen were over 50%.

Table 3
SEC results and film quality of cardo PEANs **15**–**17**[a].

Polymer code	M_w ($\times 10^{-4}$)	PDI	M_w[b] ($\times 10^{-4}$)	PDI[b]	Film quality[c]
15	1.52	21.1	–	–	Brittle
16	0.63	15.5	6.95	15.6	Flexible
17	1.04	12.2	1.58	3.0	Brittle

[a] Measured by SEC with polystyrene standards.
[b] After removing low molecular weight fractions from each polymer by extraction with acetone.
[c] Films were cast from DMF.

Table 4
Thermal properties of PEANs **9**–**17** and polyamides **18**,**19**.

Polymer code	T_g (°C)[a]	10% wt. loss[b] (°C)		50% wt. loss[b] (°C)		Char yield[c] (%)
		Air	N_2	Air	N_2	
9	199	363	506	521	956	76
10B	169	343	376	415	497	34
11	142	400	360	535	450	26
12	136	320	362	500	446	23
13	124	400	370	498	450	24
14	114	364	393	451	446	18
15	–	427	466	567	–	64
16	341[d]	421	448	540	–	63
17	–	339	436	479	–	54
18[f]	264	472	462	–	–	51
19[f]	308[e]	516	515	–	–	59

[a] DSC, second scan, 10 °C/min (**9**–**17**) and 20 °C/min (**18**,**19**[f]).
[b] TGA, 20 °C/min.
[c] Residual wt.% when heated to 800 °C in nitrogen, TGA, 20 °C/min.
[d] TMA, 30 mN, 20 °C/min (the maximum in loss tangent (tan δ) by DMA was 349 °C).
[e] Softening temperature measured by TMA (penetration method) with a load of 5 g at 10 °C/min.
[f] From Ref. [14].

The DSC of aliphatic PEANs **10B**–**14** showed that the glass transition temperature (T_g) values for the polymers ranged from 114 to 169 °C. The T_g values decreased as the number of methylene units increases in the monomers because of increasing polymer chain flexibility, which was also observed in aromatic–aliphatic PEANs [5]. PEANs **9**–**14** did not exhibit any thermal transitions between T_g and the onset of exothermic reaction. Therefore, PEANs **9**–**14** were probably amorphous polymers. As reported [2], curing could cause an exotherm, which started around 275–284 °C and ended in the range of 320–353 °C for PEANs **9**–**14**. This curing makes the polymers insoluble in solvents in which they were previously soluble. This exothermic transition was not observed upon cooling and subsequent heating (2nd heating) indicating that the curing process was complete. The DSC of cardo PEANs **15**–**17** did not show T_g values possibly due to the incorporation of the cardo group, but showed a broad exothermic transition. This exothermic transition started at around 260 °C for cardo PEAN **15** and 300 °C for cardo PEANs **16**,**17**, and reached maximum intensity around 360 °C. This exothermic transition was not observed when the samples were rescanned. The cardo PEANs **15**–**17** became insoluble in solvents in which they were previously soluble before curing, as observed in previous reports [2]. In the case of cardo PEAN **16**, the glass transition temperature could be measured by TMA and DMA, respectively because the film quality of cardo PEAN **16** was sufficiently flexible, as shown in Table 3. The high T_g value (341 °C) of cardo PEAN **16** by TMA may be the result of a stiffer backbone caused by partial curing as well as the incorporation of the cardo group. The curing processes may obscure the T_g for cardo PEANs **15**–**17** by DSC. The maximum in loss tangent (tan δ) for cardo PEAN **16** by DMA was 349 °C, which is similar to the T_g value (341 °C) measured by TMA.

4. Conclusions

The first aliphatic bis(chlorovinylidene cyanide) monomer has been synthesized and polymerized with appropriate diamines to give adamantane-containing aromatic–aliphatic and aliphatic PEANs via vinylic nucleophilic substitution polymerization. The PEANs showed excellent solubility in polar aprotic solvents and good thermal stability, considering the aliphatic contents of the polymers.

Three new adamantane-containing cardo PEANs were also synthesized via vinylic nucleophilic substitution polymerization. The cardo PEANs showed better solubilities in common organic solvents than the corresponding cardo polyamides because the presence of rather bulky and polarizable dicyanovinylidene group in place of the oxygen atom in the amide group inhibits chain packing and reduces hydrogen bonding interactions in the PEANs. The cardo PEANs showed good thermal stabilities, comparable to those of the corresponding cardo polyamides.

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