Preparation of New Polyenaminonitriles Containing Cyclic and Methylene Units and Their Thermal Properties

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Abstract : Polyenaminonitriles containing cycloaliphatic and aliphatic units were prepared by interfacial or solution polymerization reaction of p-bis(1-chloro-2,2-dicyanovinyl)benzene (1) with 4-aminobenzyl-amine, 1-(2-aminoethyl)piperazine, 2-(aminomethyl)pyrrolidine and 4-(aminomethyl)piperidine. The chemical structure of the polymers was confirmed through a syntheses of the model compound. The resulting polymers possessed inherent viscosities of 0.29～0.62 dL/g and they were easily soluble in polar aprotic solvents and common organic solvents. Thermal properties of the polymers such as curability and stability were studied by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and infrared spectroscopy. The polymers exhibited a large exotherm in DSC analyses and underwent a curing reaction around 340-370°C to form insoluble materials. The polymers showed 70-80% residual weight at 600°C under nitrogen.

Introduction

Recently, thermally stable and curable polymers have been extensively studied in order to achieve a high-temperature polymeric materials with good thermal and mechanical properties which are useful for structural applications.[1,2] Recently, poly-enaminonitriles[3-13] and polyenaryloxynitriles[14-19] were prepared and studied as thermally stable polymers. Moreover, these polymers with dicy-anovinyl groups as enaminonitrile or enaryloxyni-trile units demonstrated a good solubility in common organic solvents.[20-23] Polyenaminonitriles are soluble in many organic solvents such as DMF, NMP, pyridine, glymes and THF. The good solubility of the polyenaminonitriles has been considered to be a result of weaker interchain hydrogen bonding interaction. The factors that may contribute to weaker hydrogen bonds in polyenaminonitriles is the presence of the rather bulky and polar enami-

nonitriles group in the backbone, which may steri-cally prevent strong hydrogen bonding and/or reduce crystallinity. It has been reported that poly(piperazinenaminonitriles) were prepared from p-bis(1-chloro-2,2-dicyanovinyl)benzene and pip-erazine.[9,12] While hydrogen-bonded interactions are suppressed with incorporation of the pipera-zine ring, the rigidity of the polymer backbone in poly(piperazinenaminonitriles) possibly remains relatively unchanged, therefore, solubility is not improved because there is no accompanying increase in the flexibility of the polymer backbone.

Some of the diamines possess cyclic and meth-ylene moieties in one molecule. The cyclic moiety is concerned with rigidity of polymer and the methylene unit can make polymer backbone flexi-ble through the bond rotation. Polyenaminonitriles derived from them could be endowed with both rigidity and flexibility of the polymer backbone. In this article, we explored a research to synthesize polyenaminonitriles containing both cyclic and methylene units by the interfacial or solution poly-

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merization reaction of *p*-bis(1-chloro-2,2-dicy-anovinyl)benzene with 4-aminobenzylamine, 1-(2-aminoethyl)piperazine, 2-(aminomethyl)pyrro-lidine and 4-(aminomethyl)piperidine and to examine their solubility and thermal properties.

Experimental

Chemicals and Instruments. 1-Chloro-1-phenyl-2,2-dicyanoethane and *p*-bis(1-chloro-2,2-dicyanovinyl)benzene **(1)** were synthesized according to the method previously reported.[6] 4-Aminobenzylamine, 1-(2-aminoethyl)piperazine, 2-(aminomethyl)pyrrolidine, 4-(aminomethyl)piperidine, and benzylamine hydrochloride (Aldrich Chemical Co.) were used without further purification. 1,4-Diazabicyclo[2,2,2]octane (DABCO) was sublimed under reduced pressure. 1,2-Dichloroethane was stirred over calcium hydride and fractionally distilled. *N*-methyl-2-pyrrolidinone (NMP) was stirred over anhydrous barium oxide for 48 h and distilled under reduced pressure.

Solubilities were estimated by dissolving 5 mg of polymer powder in 1 mL of solvent upon heating to 80 °C. ^{1}H NMR spectra were recorded on a Bruker AM-300 spectrometer operating at 300 MHz. In all ^{1}H NMR experiments, the chemical shifts are recorded in ppm from tetramethylsilane as internal standard. FT-IR spectra were taken on a Midac 2000 spectrophotometer. Differential scanning calorimetry of polymers were carried out on a Perkin-Elmer system 7 analyzer at a heating rate of 10 °C/min under nitrogen. The samples for DSC were encapsulated in an aluminum pan, and the blank aluminum pan was used as the reference. TGA thermograms were performed on Shimadzu TGA-50 analyzer at a heating rate of 10 °C/min under nitrogen. Inherent viscosities of polymer solutions were measured with a Cannon-Ubbelohde viscometer at 25 °C in DMSO. The gel fraction was obtained by weighing the insoluble portion after filtering the NMP solution of the sample cured at 310 °C for 30 min.

Preparation of Model Compound (2). Solutions of benzylamine hydrochloride (0.244 g, 1.7 mmol) in water (10 mL) and sodium hydroxide (0.167 g, 4.2 mmol) in water (10 mL) were poured

into the solution of **1** (0.5 g, 1.7 mmol) in 1,2-dichloroethane (20 mL) in the blender jar and then stirred at full speed for 3 min. The reaction mixture was evaporated and washed with water several times. The solid product was filtered and recrystallized from ethylacetate. The white crystalline product was dried at 80 °C under vacuum for 12 h. A similar procedure was applied to prepare model compound **3** using 1-chloro-1-phenyl-2,2-dicyanoethene and 2-(aminomethyl)pyrrolidine.

2 : Yield 92%. FT-IR (KBr) 3450 (N-H), 3258 (aromatic C-H), 2210 (C≡N), 1572 (C=C), 1210-1110 (C-N) cm^{-1}. ^{1}H NMR (DMSO-d_6) δ 9.7 (m, 2H, 2 -CH$_2$-*NH*-), 7.9-7.4 (s, 4H, -*Ph*-), 7.5-6.9 (s, 10H, 2 *Ph*-CH$_2$-), 4.2 (m, 4H, 2 -*CH$_2$*-NH-).

3 : Yield 88%. FT-IR (KBr) 3430 (N-H), 3270 (aromatic C-H), 2930 (aliphatic C-H), 2210 (C≡N), 1580 (C=C), 1210-1115 (C-N) cm^{-1}. ^{1}H NMR (DMSO-d_6) δ 9.2 (m, ^{1}H, -CH$_2$-*NH*-), 7.6 (m, 10H, 2 *Ph*-), 3.1-2.4 (m, 5H, -*CH$_2$*-N-CH(CH$_2$NH-)-CH$_2$CH$_2$-), 1.9-1.6 (m, 4H, -CH$_2$N-CH(CH$_2$NH-)-*CH$_2$CH$_2$*-).

Polymerization of 1 with 4-Aminobenzyl-amine. In a three necked round bottomed flask equipped with a dropping funnel, a reflux condenser and a nitrogen inlet, a solution of 4-aminobenzylamine (0.48 g, 4 mmol) and DABCO (0.54 g, 4.8 mmol) in dry NMP (10 mL) was placed. After the solution was purged with nitrogen, a solution of 2 (1.20 g, 4 mmol) in NMP (10 mL) was added dropwise at 20 °C for 30 min. The stirred mixture was heated to 60 °C for 6 h. The reaction mixture was cooled and was added to water to give a yellow precipitate which was filtered and washed well with methanol. The product was dried under vacuum at 80 °C for 12 h.

P1 : Yield 77%. FT-IR (KBr) 3454 (N-H), 3261 (aromatic C-H), 2928 (C-H), 2214 (C≡N), 1582 (C=C) cm^{-1}. ^{1}H NMR (DMSO-d_6) δ11.1-10.9 (1H, -*NH*-Ph-), 9.9-9.7 (1H, -CH$_2$-*NH*-), 7.9-7.6 (4H, -*Ph*-), 7.5-6.8 (4H, -NH-*Ph*-CH$_2$-), 2.1 (2H, -*CH$_2$*-NH-).

Representative Interfacial Polymerization of 1 with Diamine. A solution of 1-(2-aminoethyl)piperazine (0.214 g, 1.7 mmol) and sodium hydroxide (0.167 g, 4.2 mmol) in water (20 mL) was prepared with stirring at room temperature. The resulting solution was poured into the solu-

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tion of **1** (0.5 g, 1.7 mmol) in 1,2-dichloroethane (20 mL) in the blender jar and then stirred at full speed for 3 min. The reaction mixture was filtered and washed with water. The polymer was dried at 80 °C under vacuum for 12 h. A similar procedure was applied to prepare other polyenaminonitriles using 2-(aminomethyl)pyrrolidine, 4-(aminomethyl)piperidine.

P2 : Yield 89%. FT-IR (KBr) 3430 (N-H), 3263 (aromatic C-H), 3000-2870 (aliphatic C-H), 2208 (C≡N), 1580 (C=C), 1210-1110 (C-N) cm^{-1}. ^{1}H NMR (DMSO-d_6) δ 8.9 (m, 1H, -CH_2-CH_2-NH-), 7.6 (s, 4H, -Ph-), 3.2-2.6 (m, 8H, piperazine -N-CH_2-CH_2-N- and -N-CH_2-CH_2-NH-).

P3 : Yield 91%. FT-IR (KBr) 3435 (N-H), 3278 (aromatic C-H), 2937 (aliphatic C-H), 2212 (C≡N), 1577 (C=C), 1210-1115 (C-N) cm^{-1}. ^{1}H NMR (DMSO-d_6) δ 9.3 (m, 1H, -CH_2-NH-), 7.6 (s, 4H, -Ph-), 3.1-2.4 (m, 5H, -CH_2-N-CH(CH_2NH-)-CH_2CH_2-), 1.9-1.6 (m, 4H, -CH_2N-CH(CH_2NH-)-CH_2CH_2-).

P4 : Yield 93%. FT-IR (KBr) 3432 (N-H), 3263 (aromatic C-H), 2925 (aliphatic C-H), 2208 (C≡N), 1575 (C=C), 1205-1115 (C-N) cm^{-1}. ^{1}H NMR (DMSO-d_6) δ 9.3 (m, 1H, -CH_2-NH-), 7.7 (s, 4H, -Ph-), 3.1 (br, 6H, -CH_2-CH_2-N-CH_2-CH_2- and -CH_2-NH-), 1.9-1.7 (br, 5H, -CH_2-CH_2-CH(-) -CH_2-CH_2-).

Results and Discussion

Preparation of Model Compound. The model compound, 1,4-p-bis[2,2-dicyano-1-(benzylamino)vinyl]benzene (**2**) and 2-[N-(1-phenyl-2,2-dicyanovinyl)aminomethyl]-1-(1-phenyl-2,2-dicyanovinyl)pyrrolidine was prepared by the interfacial reaction of p-bis(1-chloro-2,2-dicyanovinyl) benzene (**1**) with benzylamine hydrochloride and 2-aminomethyl)pyrrolidine, respectively, as shown in Scheme I and used for the conditions of polymer formation and the identification of chemical structure of polymers.

Preparation of Various Polyenaminonitriles. The polymerization reactions of **1** with aromatic- or cycloaliphatic- and aliphatic-containing diamines such as 4-aminobenzylamine, 1-(2-aminoethyl) piperazine, 2-(aminomethyl)pyrrolidine, and 4-(aminomethyl)piperidine were conducted in solu-

Scheme I

Scheme II
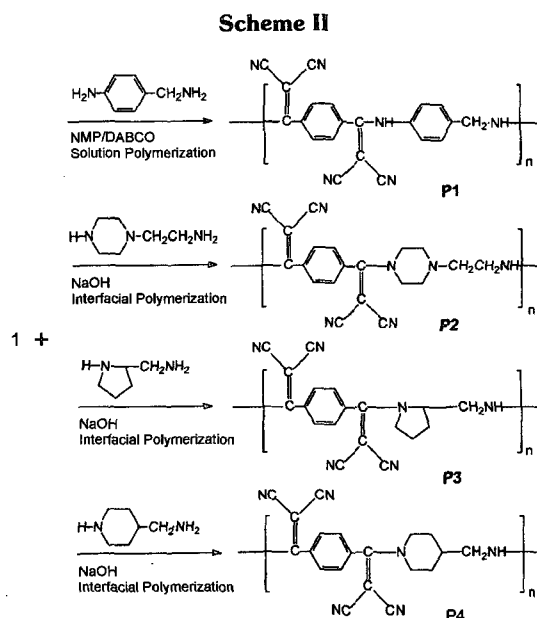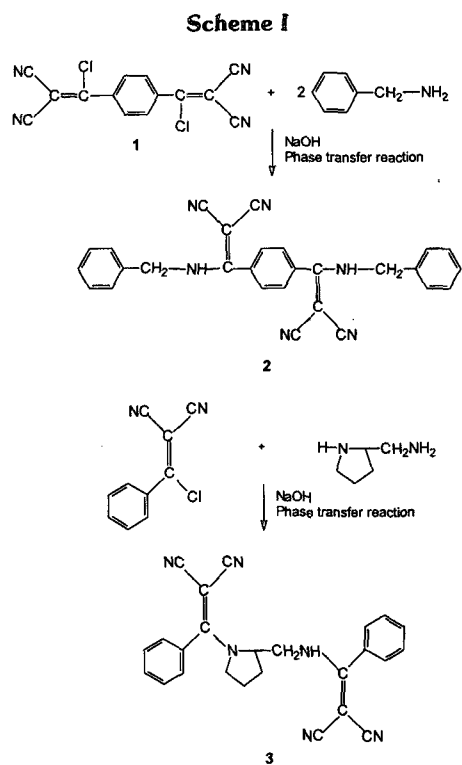
tion or interfacial polymerization to give the polymers **P1-P4**. The polymerization of **1** with 4-aminobenzylamine was carried out by solution

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Table I. Results of Polymerization of 1 with Various Diamines

Model Compound & Polymer	Monomer[a]	η_{inh}[b] (dL/g)	Yield (%)	Gel Fraction[c] (%)
2	BA	-	92	-
3	AP	-	88	-
P1	ABA	0.62	77	95
P2	AEP	0.41	89	99
P3	AP	0.29	91	95
P4	AMP	0.47	93	97

[a]ABA, 4-aminobenzylamine; AEP, 1-(2-aminoethyl)piperazine; AP, 2-(aminomethyl)pyrrolidine; AMP, 4-(aminomethyl) piperidine; BA, benzylamine.

[b]Inherent viscosities were measured in DMSO in 1 g/dL at 25 °C.

[c]The gel fraction was obtained by weighing the insoluble portions after filtering the NMP solution of the cured sample at 310 for 30 min.

polymerization technique in NMP and polymers **P2**, **P3** and **P4** were prepared by the interfacial reaction using two phases solvent system as illustrated in Scheme II. The results of the polymerization reaction are summarized in Table I. The reaction of **1** with various diamines was rapid and led to 77-93% yields of the corresponding polyenaminonitriles.

Polymer Characterization. The chemical structures of polymers were characterized by common spectroscopic techniques such as FT-IR and ^{1}H NMR. The polymer obtained was compared by their IR and NMR spectra with those of model compounds **2** and **3**. The spectral results were in good agreement with the structures of each polymer. In the FT-IR spectra, all four polymers showed characteristic absorption bands around 3450, 2210 and 1580 cm^{-1} corresponding to N-H, C≡N and C=C bond, respectively. The representative FT-IR spectra of model compound **2** and **3**, and polymers also matched to their assigned chemical structures. Figure 1 showed the ^{1}H NMR spectra of model compound **2**, **3** and polymer **P2**.

Solubility. Introduction of the rather bulky and polarizable dicyanovinyl groups into rigid aromatic backbones seems to result in good solubility of these polymers. They were easily soluble in polar aprotic solvents such as DMSO, DMF, and NMP. The solubility of the polymers was tested in various solvents such as DMSO, DMF, DMAc, NMP, acetonitrile, THF, acetone and ethanol. The poly(piperazineaminonitriles) were insoluble in
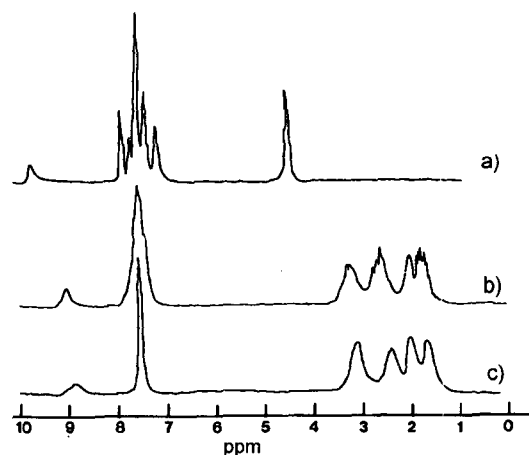

Figure 1. ^{1}H NMR spectra of a) model compound **2**, b) **3** and c) polymer **P2**.

chloroform, THF, acetone, DMF, dioxane, and pyridine but showed limited solubility in NMP, DMAc and DMSO. The poor solubility is in contrast to polyenaminonitriles derived here from diamines containing both cycloaliphatic and methylene units, which are easily soluble in NMP, DMSO, DMAc and DMF.[12] They contains cyclo-alkyl, flexible alkyl and NH site, which permit both intermolecular hydrogen bond and interaction with proton-accepting solvents. Thus the polymers were soluble even in common organic solvents such as THF, 1,2-dimethoxyethane and pyridine. With the incorporation of only cycloaliphatic rings such as piperazine in polyenaminonitrile, hydrogen bonding is no longer available and

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the reduced solubility of these polymers may be attributted to the absence of hydrogen-bonded interaction with polar aprotic solvents.

Moderate molecular weight polymers were obtained in the synthesis of **P1**, **P2**, **P3** and **P4**, as estimated by the inherent viscosities. The polyenaminonitriles **P1** was obtained with relatively high molecular weight even though the polymer is expected to show lower solubility than the other polymers **P2-P4**. The cyclic diamine such as piperazine is likely to increase the steric hindrance during polycondensation of piperazine with enaminonitriles. The results, therefore, suggest that chain rigidity is also a reason for the reduced molecular weights of poly(piperazinoenaminonitriles), along with the low solubility of the polymers. The steric hindrance was relieved for the polymers **P1-P4** because of the aliphatic units in the diamine molecule. Therefore, an improvement in solubility was observed.

Thermal Properties. DSC and TGA data of polymers summarized in Table II. Differential scanning calorimetry of these polymers showed somewhat broad exotherm around 340-470°C Polyenaminonitriles generally show an exothermic curing process between 300 and 370°C, which has been proposed to be linked to inter- and intrachain cyclization processes. This exotherm was absent when polymers were cooled and rescanned. This phenomenon is believed to indicate the occurrence of a thermally induced cross-linking reaction which renders the polymers insoluble in polar aprotic solvents in which they were soluble before curing. The gel fraction data were included in Table I.

The curing reaction of polymers was monitored using FT-IR spectroscopy. IR spectra of polymers,

heated at 310°C in nitrogen atmosphere, were recorded periodically and compared with those of uncured materials. Intensities of the enamine N-H stretching band in uncured polymer at 3530 cm^{-1} and the nitrile band at 2208 cm^{-1} decreased dramatically as shown in Figure 2.

All the polymers exhibited good thermal stability though the polyenaminonitriles possessed aliphatic units. Polymer **P2** possesses the most flexible polymer backbone of the four polymers and hence it has glass transition temperature 261 °C. The thermal analyses including DSC data were summarized in Table II.

The thermal stabilities of polymers containing enaminonitrile groups is probably enhanced through intramolecular cyclization and intermolecular cross-linking processes. The temperatures at which all four polymers lose 30% of their weight are above 600°C as shown in Figure 3. The lower thermal stabilities of polyenaminonitriles **P2-P4** relative to polymer **P1** may be due to
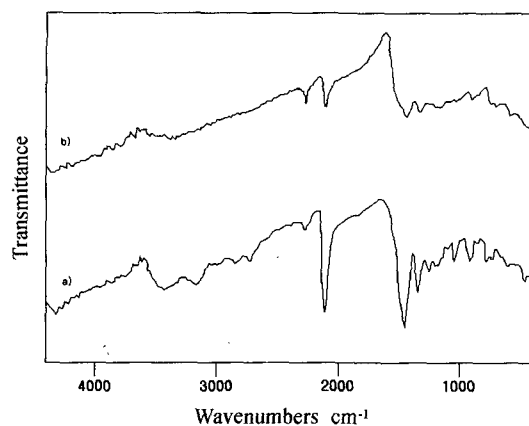

Figure 2. FT-IR spectra of polymer **P1** a) before curing and b) after curing at 310°C for 30 min.

Table II. Thermal Properties of Polyenaminonitriles

Polymer	Monomer	$T_g{}^a$	$T_{exo}{}^b$	$T_{10\%}{}^c$	Residual Weight (%)		
					400°C	600°C	600°C^d
2	BA	-	343	395	67.9	-	-
P1	ABA	-	341	452	93.5	79.2	85.5
P2	AEP	261	340-368	385	86.1	70.9	79.2
P3	AP	-	342-367	457	95.1	79.2	83.2
P4	AMP	-	345-363	415	93.3	71.1	76.7

^aT_g ; Glass transition temperature. $^bT_{exo}$; Temperature of exotherm.
$^cT_{10\%}$; Temperature of 10% weight loss. ^{d}Residual weight of cured samples at 310 °C for 30 min.

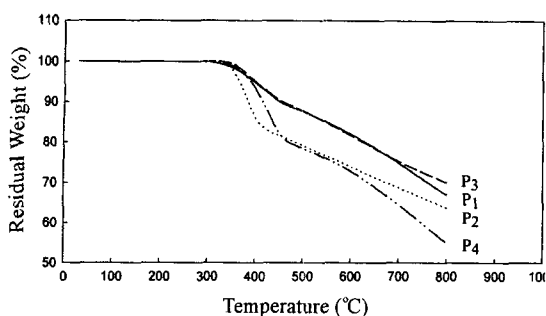Korea Polym. J., Vol. 8, No. 5, 2000

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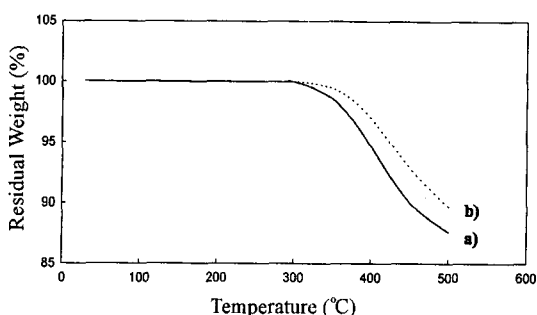**Figure 3.** TGA traces of polymers at a heating rate 10°C/min in nitrogen.

Figure 4. TGA traces of polymer **P1** a) as prepared and b) after heating at 310 °C for 30 min in nitrogen.

the incomplete curing of the enaminonitrile group because of the lack of NH groups that can added to the cyano group. When the thermal properties of the polymers cured at 310°C for 30 min were compared with those of the uncured polymers, the thermal stabilities including residual weight were improved for all the polymers as shown in Figure 4. The cured resin retains almost 76-85% of its mass at 600°C in nitrogen.

Conclusions

p-Bis(1-chloro-2,2-dicyanovinyl)benzene **(1)** was polymerized with various cyclic- and methylene-containing diamines to form new polyenaminonitriles. The polymers showed good solubility in NMP, DMSO, DMAc, THF and 1,2-dimethoxy-ethane. Upon curing the polymers at a temperature of exotherm, heat resistant and insoluble polymers were obtained by cross-linking reaction. The TGA traces exhibited thermal stability with 71-79% residual weight at 600°C in nitrogen.

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