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NOTES

New Method for the Preparation of Poly(enamino-enaryloxynitriles) by Interfacial Polymerization and Thermal Properties

Chil-Won LEE, Ne-Ri GEUM, and Myoung-Seon GONG†

Department of Chemistry, Dankook University,
Cheonan, Chungnam 330-714, Korea

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Many studies have utilized chemical modification to improve the processibility of thermally stable polymers. Among these works, introduction of thermally curable function such as dicyanovinyl group has been noted.[1–3] The first notable condensation polymerization of dicyanovinyl monomer, *p*-bis(1-chloro-2,2-dicyanovinyl)benzene (**2**) with aromatic diamines was reported by Moore and coworkers in 1986.[1] Some polymers obtained were polyenaminonitriles of high molecular weights and thermally curable, and showed good thermal stability.[1,4–8] Dicyanovinyl-containing copolymers were prepared using hydroxyl-,[9–11] amino-[12], and aldehyde-terminated[13] dicyanovinyl monomers. Polyenaryloxynitriles could be produced by interfacial polymerization of **2** and aromatic diols.[2,14–17]

Currently study on dicyanovinyl-containing polymers, we obtained poly(enamino-enaryloxynitriles) by copolymerization of **2** with aromatic diamine and diphenol.[18,19]

Certain aminophenol derivatives undergo interfacial polymerization with **2**. In this way we can simultaneously incorporate enamino- and enaryloxynitriles units into polymer backbone to afford new poly(enamino-enaryloxynitriles). This paper describes the preparation of poly(enamino-enaryloxynitriles) possessing enamino- and enaryloxynitriles units by reacting phenol- and aliphatic amine-containing monomers with **2** using interfacial polymerization, along with thermal properties including curability and thermal stability.

EXPERIMENTAL

Materials and Measurements

1-Chloro-1-phenyl-2,2-dicyanoethene (**1**) and *p*-bis(1-chloro-2,2-dicyanovinyl)benzene (**2**) were prepared as previously reported.[1] 4-(2-Aminoethyl)phenol (tyramine, 99%), norphenylephrine hydrochloride (α-aminomethyl-3-hydroxybenzyl alcohol hydrochloride) and L-tyrosin methyl ester (Aldrich Chem. Co.) were crystallized in 1,2-dichloroethane/benzene (1/1). 1,2-Dichloroethane was purified by distillation after drying over calcium hydride. Nitrobenzene was used without further purification. Solubility was estimated by dissolving 5 mg powdery polymer sample in 1 mL solvent after heating at 50℃. All melting points were determined on an Aldrich Mel-Temp II melting point apparatus using capillary tubes and are uncorrected. Fourier-transform infrared (FT-IR) spectra were obtained with a Midac Model M-1200 spectrophotometer, and ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Gemini 2000 spectrometer.

In all ^{1}H NMR experiments, chemical shifts were recorded in ppm from tetramethyl silane as internal standard. Elemental analysis conducted with a Yanaco MT-3 CHN-Analyzer. Gel-permeation chromatography (GPC) data were obtained with a Waters HPLC using three columns (μ-Stryragel 10^2, 10^3, and 10^4Å) in THF and calibrated with polystyrene standards at 20℃. Intrinsic viscosity of polymer solutions was measured in a Cannon–Ubbelode viscometer at 25℃ in DMF. Polymer solutions for the viscosity measurements were filtered through a sintered glass filter. Thermal analysis of polymers was carried out on a Dupont 2100 and a Mettler thermal analyzer at a heating rate of 10℃ min^{-1} under nitrogen. TGA thermograms were performed on a Perkin–Elmer System 7 analyzer interfaced with a Perkin–Elmer 7500 Computer.

N-(1-Phenyl-2,2-dicyanovinyl)-2-[p-(1-phenyl-2,2-dicyanovinyloxy)]phenylethyl amine (3)

In a stainless steel jar, was placed a solution of **1** (0.94 g, 5 mmol) dissolved in 1,2-dichloroethane (20 mL). A solution of 4-(2-aminoethyl)phenol (0.34 g, 2.5 mmol) and sodium hydroxide (0.24 g, 6 mmol) dissolved in water (20 mL) was added dropwise with vigorous stirring under nitrogen. The reaction mixture was moved to a round bottomed flask and maintained at 50℃ for 2 h with vigorous stirring. After the solvent was evaporated, the powdery product was washed with distilled water several times and recrystallized from acetonitrile to give pale yellow crystals, and dried under vacuum at 50℃ for 12 h.

3: Yield 83%. Mp 158℃. IR (KBr) 3350 (N–H), 3080 (aromatic C–H), 1890 (aliphatic C–H), 2220 (s, C≡N), 1580 (C=C), 1260—1110 (C–O and C–N) cm^{-1}. ^{1}H NMR (DMSO-d_6+CDCl_3) δ 9.19 (s, 1H N-*H*), 7.82—7.51 (m, 10H, 2 *Ph*–), 7.23—6.82 (m, 4H, -*Ph*-O–), 3.24—3.61 (2 t, 2H, -CH_2-NH–), 2.44 (t, 2H, -*Ph*-CH_2–). ^{13}C NMR

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† To whom correspondence should be addressed (E-mail: msgong@anseo.dankook.ac.kr).

(DMSO-d_6) δ 29.2 (CH_2*C*H_2, NN–), 35.8 (–*C*H_2CH_2NN–), 71.9, 85.8 (=*C*(CN)2), 110.4, 111.7, 113.7, 116.7 (–*C*N), 128.1, 128.4, 129.4, 129.9, 133.4, 147.9, 152.3 (aromatic *C*'s), 169.8 (=*C*(NH–)–), 180.3 (=*C*(O–)–). *Anal* Calcd for $C_{28}H_{19}N_5O_1$ (441.27): C, 76.19%; H, 4.31%; N, 15.87%. Found: C, 75.98%; H, 4.24%; N, 15.89%.

Representative Interfacial Polymerization of 2 with 4-(2-aminoethyl)phenol

A solution of **2** (2.0 g, 6.6 mmol) in 1,2-dichloroethane (30 mL) was transferred to the stainless steel jar (150 mL) of a blender. A mixture of 4-(2-aminoethyl)phenol (0.92 g, 6.6 mmol), sodium hydroxide (0.62 g, 15.4 mmol) and tetra-*n*-butyl ammonium chloride (5 mol% of **2**) in 30 mL of water was added to the blender at full speed for 3 min. The polymer was collected by filtration and washed with distilled water. The crude polymer was dissolved in DMF and reprecipitated into methanol to produce a yellowish powdery polymer. Other polymers of norphenylephrine hydrochloride and L-tyrosin methyl ester were prepared by similar synthetic procedures.

4: Yield 87%. IR (KBr) 3350 (N–H), 3120 (aromatic C–H), 2980 (aliphatic C–H), 2224 (C≡N), 1582 (C=C), 1280—1100 (C–O and C–N) cm^{-1}. ^1H NMR (DMSO-d_6 +$CDCl_3$) δ 9.19 (br, 1H N–*H*), 7.82 (br, s, 4H –*Ph*–), 7.21—6.83 (m, 4H, –*Ph*–O–) 3.23—3.67 (br, 2H, –CH_2–NH–), 2.42 (br, 2H, –Ph–CH_2–). ^{13}C NMR (DMSO-d_6) δ 29.8 (–CH_2*C*H_2NN–), 36.1 (–*C*H_2CH_2NN–), 79.6, 85.4 (=*C*(CN)2), 111.4, 111.7, 112.7, 112.9 (–*C*N), 128.1, 129.4, 129.9, 147.9, 152.3 (aromatic *C*'s), 169.8 (=*C*(NH–)–), 180.3 (=*C*(O–)–). *Anal*. Calcd for $C_{22}H_{13}N_5O_1$ (364.38): C, 72.73%; H, 3.51%; N, 19.28%. Found: C, 72.44%; H, 3.61%; N, 18.85%.

5: Yield 88%. IR (KBr) 3400 (O–H), 3350 (N–H), 3122 (aromatic C–H), 2980 (aliphatic C–H), 2226 (C≡N), 1582 (C=C), 1280—1105 (C–O and C–N) cm^{-1}. ^1H NMR (DMSO-d_6+$CDCl_3$) δ 9.16 (br, 1H, N–*H*), 7.82 (br, s, 4H, –*Ph*–), 7.21—6.84 (m, 4H, –*Ph*–O–), 3.92 (br, 1H, –Ph–C*H*–OH), 3.64 (br, 1H, –Ph–CH–O*H*), 3.21—3.63 (br, 1 H, –CH_2–NH–). *Anal.* Calcd for $C_{22}H_{13}N_5O_2$ (379.29): C, 69.66%; H, 3.43%; N, 18.47%. Found: C, 69.64%; H, 3.29%; N, 18.29%.

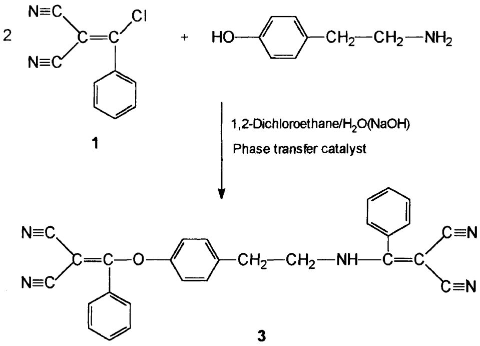
6: Yield 78%. IR (KBr), 3355 (N–H), 3110 (aromatic C–H), 2980 (aliphatic C–H), 2224 (C≡N), 1735 (C=O), 1580 (C=C), 1280—1100 (C–O and C–N) cm^{-1}. ^1H NMR (DMSO-d_6+$CDCl_3$) δ 9.18 (br, 1H N–*H*), 7.83 (br, s, 4H, –*Ph*–), 7.21—6.82 (m, 4H –*Ph*–O–), 3.91 (s, 3H –OCH_3), 3.22—3.64 (br, 1H, –*C*H–NH–), 2.46 (br, 2H –Ph–CH_2–). *Anal.* Calcd for $C_{23}H_{15}N_5O_3$(409.41): C, 67.48%; H, 3.68%; N, 17.12%. Found: C, 67.15%; H, 3.61%; N, 17.01%.

RESULTS AND DISCUSSION

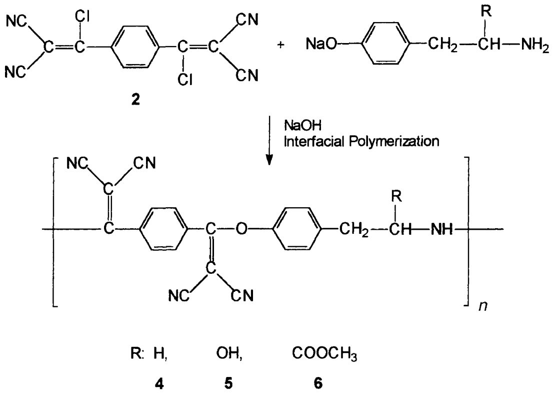
N-(1-Phenyl-2,2-dicyanovinyl)-2-[*p*-(1-phenyl-2,2-dicyanovinyloxy)]phenyl ethyl amine (**3**) was prepared by phase transfer reaction of 4-(2-aminoethyl)phenol with **1** in the presence of sodium hydroxide. The model reaction was based on a representative procedure for the interfacial technique, and proceeded rapidly in a two phase solvent system. The reaction was nearly complete within 3 min to form the model compound **3** at room temperature. After recrystallization, 83% yield of **3** was obtained. The model reaction demonstrated the feasibility of the polymerization and a confirmation of the structure of the resulting polymers because of resemblance of the repeating units of the polymer as shown in Scheme **1**.

Reactivity of phenoxide anions toward dicyanovinyl chloride was determined according to pK_a of the corresponding phenol derivative. pK_a of phenol and *p*-methylphenol were 10.00 and 10.26, respectively. The ability of the conjugate base of alkyl amine (RNH_2) was similar to that of the phenoxide anion (PhO^-).[20] Thus aminoalkyl-containing phenol derivatives can be monomers for the poly(enamino-enaryloxynitriles). Since the reactivities of alkyl amine and phenoxide to dicyanovinyl chloride are different because of different pK_a, it has possibility that compound **2** may be attacked by two phenoxides or two amines. At the present time, it is difficult, according to NMR and IR spectra, to determine whether the structures of polymers **4**, **5**, and **6**, obtained by both phenoxide and amine attack. The interfacial condensation polymerization of **2** with 4-(2-aminoethyl)phenol, norphenylephrine hydrochloride, and tyrosine methyl ester proceeded in the presence of a phase transfer agent in a two-phases solvent system as shown in Scheme 2.

The polymerization results are summarized in Table I along with viscosity and molecular weight data. The polymers obtained here were identified as poly(enamino-enaryloxynitriles) by comparing IR and NMR spectra with those of model compound **3**. In the IR spectra of the polymers, **4**—**6**, characteristic absorption bands of N–H, C≡N, C=C, and C–O were exhibited at 3420, 2220,



Scheme 1.



Scheme 2.

1580, and 1250—1120 cm^{-1}, respectively. Poly(enamino-enaryloxynitriles) **6** showed a strong ester absorption band at 1735 cm^{-1} in Figure 1e. In the ^{1}H NMR spectrum of polymer **4**, the presence of a broad signal at 9.19 ppm corresponding to N–H was noted and alkyl protons exhibited broad peaks at 3.23—3.62 and 2.42 ppm. Aromatic protons appeared at 7.2—6.8 ppm. In the NMR spectra of the model compound **3**, the phenyl proton in the fragment of **1** appeared at 7.82—7.51 ppm, whereas those of tyramine are present at 7.23—6.82 ppm. In the ^{13}C NMR spectrum, signals appeared at 29.2 ($-CH_2$ $-NH-$) and 35.8 ($-CH_2CH_2NH-$) ppm, and 169.8 ($=C(NH-)-$) and 180.3 ($=C(O-)-$). This observation is consistence with the presence of a set of enaminonitriles and enaryloxynitriles linkages. The representative FT-IR spectra of model compound **3** and poly(enamino-enaryloxynitriles) corresponded to assigned chemical structures as shown in a) and b) in Figure 1. Elemental analysis supported the formation of the model compound **3** and matched well with the calculated data.

Table I. Results of Model Reactions and Polymerization of **2** with Various Aromatic Phenol- and Aliphatic Amine-Containing Monomers

Polymers	Mp/℃^{a}	η_{inh}^{b}	$M_w \times 10^{-4c}$	MWD	Yield/%
3	158	—	—	—	83
4	—	0.57	0.97	2.1	87
4^{d}	—	0.69	1.25	1.8	91
5	—	0.45	0.92	2.6	88
6	—	0.59	1.02	2.4	78

[a] Mp was obtained by the capillary method. [b] Viscosity was measured using a Cannon-Ubbelode viscometer at a concentration 10 g dL^{-1} in DMF. [c] Weight average molecular weight was obtained by Gel-permeation chromatography using THF solution. [d] Interfacial polymerization was carried out using nitrobenzene as organic solvent.

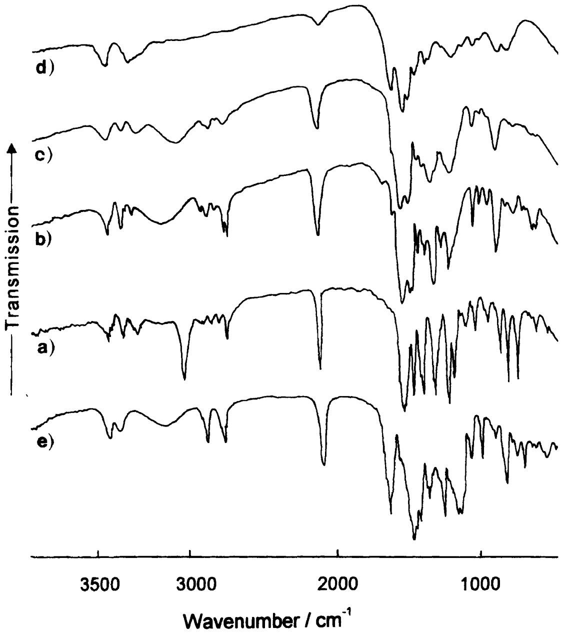


Figure 1. IR spectra of a) model compound **3**, b) polymer **4**, c) polymer **4** cured at 230℃ for 2 h, d) polymer **4** cured 300℃ for 2 h, and e) polymer **6**.

The solubility of polymers containing dicyanovinyl group was investigated. In the case of polymer **4**, solubility in THF and acetone was variable according to isolation of synthesized polymers from the reaction mixture. Sample **4** isolated by reprecipitation from DMF solution into a methanol after synthesis was insoluble in THF and acetone at room temperature. However film of **4** cast from DMF was readily soluble in THF and acetone. This may be caused by partial crystallinity. Apparently, crystalline samples have poorer solubility than amorphous materials. This was further explained by the shoulder in DSC thermogram in Figure 2c. But, at present, more work is required to clarify the cause of this behavior.

Table II presents the solubility of poly(enamino-enaryloxynitriles). Most polymers exhibited solubility in acetone, chloroform, THF, and 1,2-dimethoxyethane, and fairly good solubility in polar aprotic solvents such as *N*-methyl pyrrolidone, *N*,*N*-dimethylformamide, dimethylsulfoxide and *N*,*N*-dimethylacetamide. Alkyl-containing poly(enamino-enaryloxynitriles) displayed better solubility than previously reported rigid aromatic polyenaminonitriles[1] and polyenaryloxynitriles.[2,10]

Interfacial polymerization gave the polymers of a moderate molecular weight judging from the data of viscosity

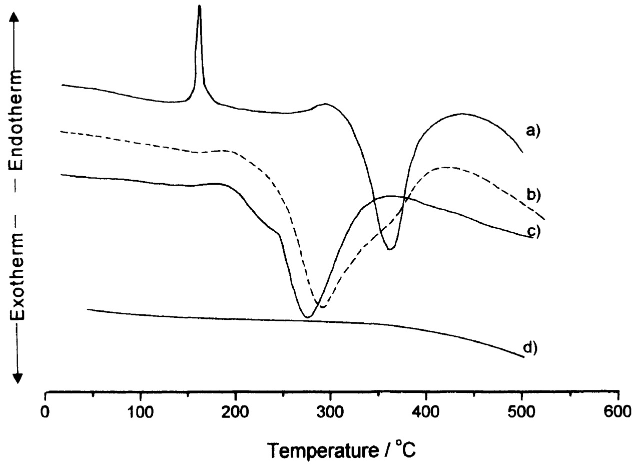


Figure 2. DSC thermograms of a) model compound **3**, b) polymer **6**, c) polymer **4**, and d) polymer **4** (2nd scan).

Table II. Solubility of various Poly(enamino-enaryloxynitriles) η_{inh}^{a}

Solvent / Polymers	DMF	NMP	*m*-Cresol	EtOH	Acetone	THF	η_{inh}^{a}	Hexane	MeCN
4	++	++	++	−	+	+	−	−−	+
5	++	++	++	+	+	+	−	−−	++
6	++	++	++	−	+	+	$+_{\text{inh}}$	−−	+

[a] Viscosity was measured using a Cannon-Ubbelode viscometer at a concentration 10 g dL^{-1} in DMF. ++, Soluble at room temperature; +, soluble at 50—60℃; −, slightly soluble; −−, insoluble; DMF, *N*,*N*-dimethylformamide; NMP, *N*-methyl pyrrolidone; MeCN, acetonitrile.

Table III. Thermal Properties of Model Compound and Various Poly(enamini-enaryloxynitriles)

Polymers	T_{exo} [a]	T_{endo} [b]	T_{idt} [c]	$T_{10\%}$ [d]	Gel Fraction	Residual Weight/%		
	℃				%	400℃	500℃	500℃ [e]
3	360	158	300	375	—	83.2	40.3	—
4	276	—	372	497	93	94.3	89.4	92.3
4 [f]	283	—	365	—	95	93.7	—	—
5	290	—	367	407	92	92.1	82.2	89.7
6	281	—	358	375	95	90.7	76.4	80.1

[a] T_{exo}: temperature of exotherm, [b] T_{endo}: temperature of endotherm, [c] T_{idt}: initial decomposition temperature, [d] $T_{10\%}$: temperature determined at a weight loss of 10%. [e] Residual weight of cured Polymers at 300℃ for 30 min. [f] Interfacial polymerization was found using nitrobenzene as the organic layer.

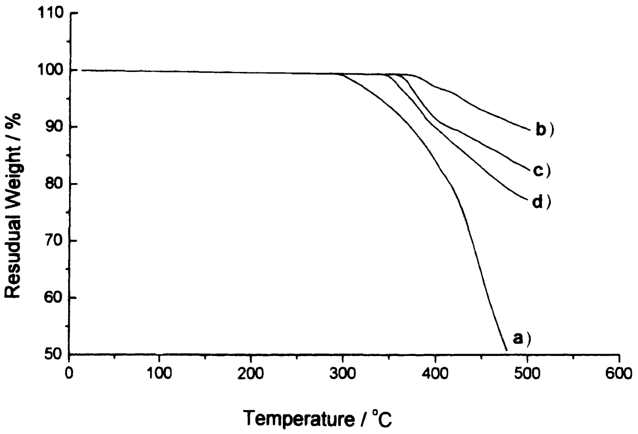


Figure 3. TGA traces of a) model compound **3**, b) polymer **4**, c) polymer **5** and d) polymer **6**.

and GPC. The polymers obtained from interfacial polymerization possessed inherent viscosity of 0.45—0.69 dL g^{-1}. Average molecular weight was 8400—12500.

These polymers exhibit interesting thermal behavior as evidence from Figure 2 and the data in Table III. Typical DSC traces of the polymers **4, 5**, and **6** involved large exotherm around 275—290℃ at a heating rate of 10℃ min^{-1} as shown in Figure 2. The exotherm does not reappear upon cooling and rescanning the sample as shown in d) in Figure 2. When the polymers were heated at 300℃ in nitrogen atmosphere, the cured polymers became completely insoluble in solvents such as NMP and DMF even at an elevated temperature. The IR spectrum of the cured material indicated that the nitrile band at 2220 cm^{-1} decreased in intensity and peaks at 1550—1640 cm^{-1} broadened as shown in Figures 1b–1d. These phenomena could be associated with changes of double bond, as well as nitrile groups to C=N and other C=C caused by the curing reaction. According to experiments on the poly(enaminonitriles) reported by Moore and coworkers, the curing reactions are assumed to proceed by intramolecular cyclization or cross-linking of the dicyanovinyl group during heating at the temperature of the maximum exotherm.[1,8,21] The cured poly(enamino-enaryloxynitriles) should have complex network structures, Chemical pathways of curing reaction proceeded *via* the similar mechanism described above, but further work in search for dicyanovinyl group as a new curable function is required.

No melting endotherm was noted below the exotherm near 290℃. The polymer may melt at a higher temperature than the curing temperature. A glass transition temperature (150—155℃) was detected in DSC thermogram for most polymers. The polymers contain more flexible backbones, and this may partly result in a glass transition temperature that is lower than the curing temperature. Polymer **6** derived from tyrosine ester showed similar thermal behavior as seen in Figure 2b. At the temperature of the exotherm, detectable weight loss of the polymer was not observed (Figure 3d). This indicates that poly(enamino-enaryloxynitriles) was cure thermally without release of volatile byproducts. The polymers began to lose weight at 358—372℃ in nitrogen. Thermal stability data are listed in Table III and TGA traces in Figure 3. Polymers **4, 5**, and **6** sustained a 10% weight loss at 497, 407, and 375℃ at a heating rate of 10℃ min^{-1}, and gave residual weight varying from 76.4 to 89.4% at 500℃ in nitrogen. Compared to the data in Table III, polymer **4** showed improved thermal stability over the alkyl substituted poly(enamino-enaryloxynitriles) **5** and **6**.

In conclusion, poly(enamino-enaryloxynitriles)s bearing enaminonitriles and enaryloxynitriles were newly prepared by interfacial polymerization from aminialkyl-containing phenol derivatives and **2**. They showed enhanced solubility in common organic solvents. Polymers containing enamino-enaryloxynitriles units generally displayed crosslinking exotherms around 300℃ and good thermal stability.

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