Preparation of Novel Tyrosine-Based Polymers and Thermal Properties

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Since the first notable condensation polymerization of dicyanovinyl monomer,[1] typically *p*-bis(1-chloro-2,2-dicyanovinyl)benzene (**2**), several kinds of dicyanovinyl-containing polymers using **2** were reported by many researchers.[2-11] Polyenaryloxynitriles could be produced by interfacial polymerization of **2** and aromatic diols.[12-17]

From the previous study on the dicyanovinyl-containing polymers, we obtained a series of poly(enamino-enaryloxynitriles)s by copolymerization of **2** with aromatic diamine and diphenol[18,19] or interfacial polymerization of **2** with aliphatic amine-containing phenol monomers.[20] In this way, we could simultaneously incorporate enaminonitriles and enaryloxynitriles or arylate and amide units into polymer backbone to produce new poly(enamino-enaryloxynitriles) or poly(arylate-amide).

The dicyanovinylidine group (C=C(CN)$_2$) can be considered structurally equivalent to the carbonyl group in reactions where the two functional groups have similar inductive and resonance effects.[21] Thus, polyenaminonitriles and polyenaryloxynitriles can be considered analogous to polyamides and polyarylates.

This work deals with the preparation of tyrosine-based poly(enamino-enaryloxynitriles) and poly(arylate-amide) by reacting tyrosine with **2** and terephthaloyl chloride using interfacial polymerization, and the decarboxylation reaction followed by curing reaction.

Model compounds *N*-(1-phenyl-2,2-dicyanovinyl)-*p*-(1-phenyl-2,2-dicyanovinyloxy)benzyl glycine (**5**) and *N*-

benzoyl-4-benzoyloxybenzyl glycine (**6**) were prepared by phase transfer reaction of tyrosine with 1-chloro-1-phenyl-2,2-dicyanoethene (**1**) and benzoyl chloride, respectively. The model reaction was based on a representative procedure for the interfacial technique using two phases solvent system. The reaction was nearly complete within 3 min to form the model compounds **5** and **6** at room temperature. After recrystallization, moderate yields of **5** and **6** were obtained after acidification as illustrated in Scheme 1.

In the ability as a conjugate base, alkyl amine (RNH$_2$) is similar to phenoxide.[22] Thus amino alkyl-containing phenol derivatives can be used as monomers for the poly(enamino-enaryloxynitriles) and poly(arylate-amide). The interfacial condensation polymerization of **2** and terephthaloyl chloride proceeded in the presence of a phase transfer agent in a two-phases solvent system as shown in Scheme 2 and 3.
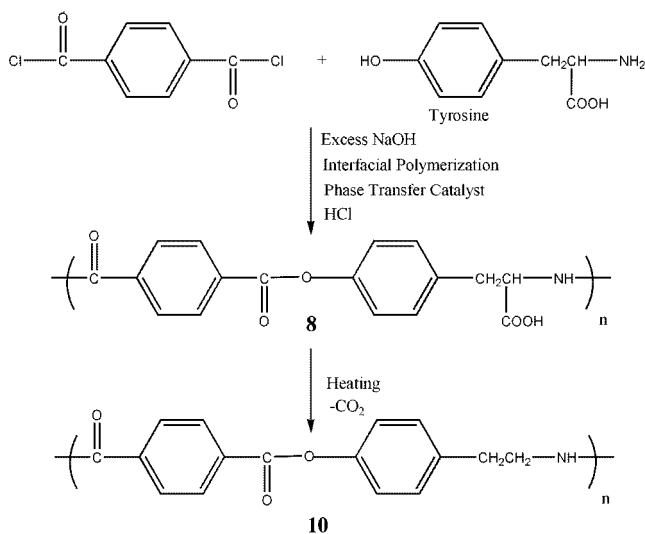
The polymerization results are summarized in Table 1. The polymers obtained here were identified as poly(enamino-enaryloxynitriles) **7** and poly(arylate-amide) **8** by comparing IR and NMR spectra with those of model compound **5**. In
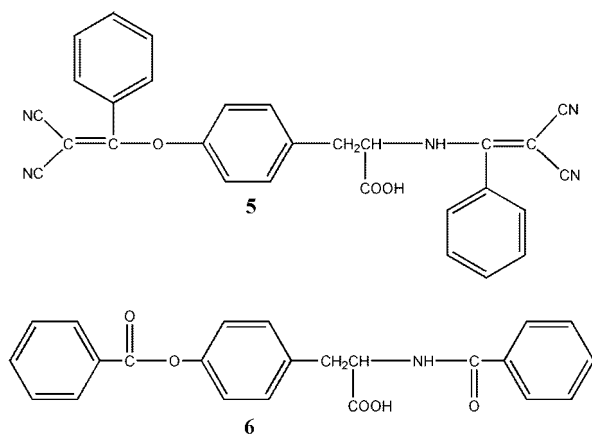
Scheme 1
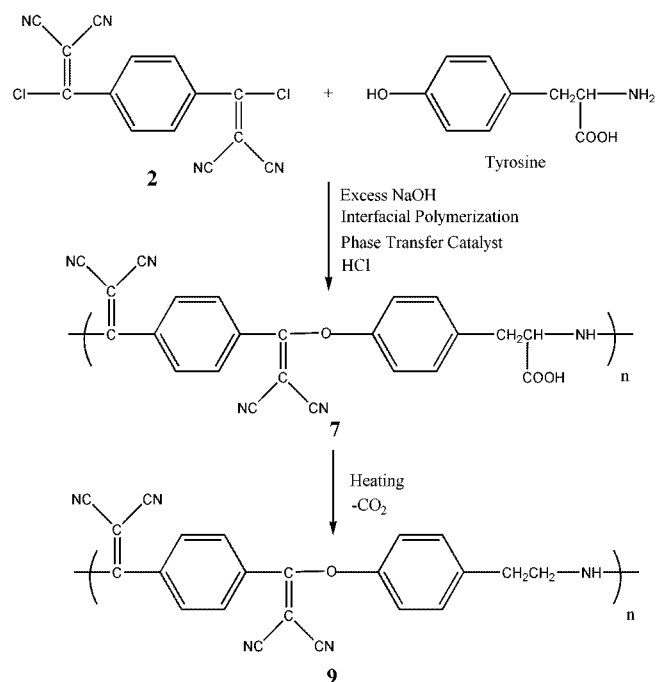
Scheme 2

Scheme 3

**Table 1.** Results of Model Reactions and Polymerization of 2 with Tyrosine

Model compounds and Polymers	Mp. °C[a]	η_{inh}[b]	M_w[c]	MWD	Yield. %
5	259(dec.)	–	485	–	72
6	263(dec.)	–	389	–	84
7	–	0.51	9520	2.6	88
8	–	0.67	12900	2.2	92
9[d]	–	0.57	9700	2.1	87

[a]Mp was obtained by the capillary method. [b]Viscosity was measured using a Ubbelode viscometer at a concentration 1 g/dL in DMF. [c]Weight average molecular weight was obtained by gel-permeation chromatography using THF solution. [d]Polymer 9 was prepared from 2 and tyramine.

the IR spectra of the polymer 7. absorption bands at 3420. 2220, 1735, 1580 and 1250-1120 cm^{-1} are corresponding to N-H. CN, C=O. C=C and C-O, respectively (Figure 1d). Poly(arlyate-amide) **8** also showed a strong carboxyl, ester and amide absorption bands at 1735-1685 cm^{-1}.

In the ^{1}H NMR spectrum of polymer 7, proton resonances for the carboxylic acid and N-H are found at 10.20 and 9.12 ppm. respectively. The alkyl protons of the tyrosine moiety are found at 4.56 and 2.47 ppm, while aromatic protons appeared at 7.20-6.81 ppm. In the case of the model compound 5, the phenyl protons of 1 appeared at 7.82-7.52 ppm. whereas those of tyrosine are present at 7.20-6.81 ppm. The spectral data of model compound 5 and 6 are consistent with the spectral data of corresponding polymers 7 and 8, respectively. Elemental analysis also supported the formation of the model compounds, and polymers 7 and 8 matched well with the calculated data.

Polymer 7 exhibited solubility in acetone, chloroform, THF, and 1.2-dimethoxyethane, and fairly good solubility in polar aprotic solvents such as NMP. DMF. DMSO and DMAc. But the polymer **8** was soluble only in polar aprotic solvents. Interestingly, polymer 7 dissolved in aqueous alkaline solution. The polymers 7 and 8 obtained from interfacial
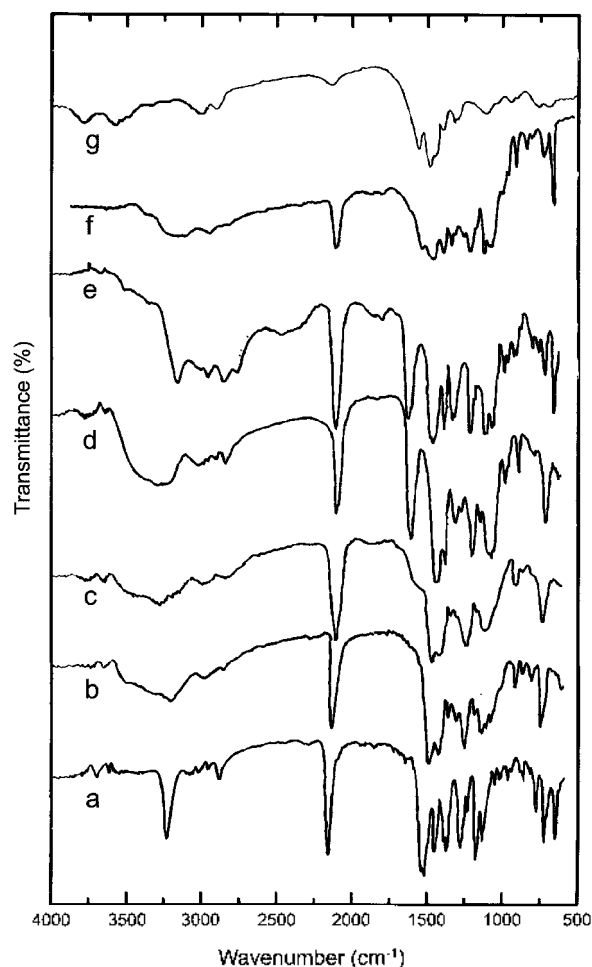
Figure 1. IR spectra of (a) **3**. (b) **9**. (c) polymer 7 cured at 265 °C, (d) polymer 7, (e) model compound **5**, (f) model compound **5** cured at 265 °C and (g) polymer 7 cured 300 °C.

polymerization possessed inherent viscosity of 0.51 and 0.67 dL/g. Weight average molecular weights were 9250 and 12500 g/mol, respectively, as determined by gel permeation chromatography.

These polymers exhibited interesting thermal behavior as evidenced from Figure 2 and the data in Table II. Typical DSC traces of the model compounds 5, 6, and polymers 7 and 8 involved large endotherm around 260 °C.

The model compound 5 melted at 259 °C. followed by decomposition. The decomposition products were carbon dioxide and N-(1-Phenyl-2.2-dicyanovinyl)-p-(1-phenyl-2.2-dicyanovinyloxy)phenylethyl amine.[20] which was verified by HPLC. Decarboxylation reaction was also confirmed using IR spectrum (Figure 1e and 1g). The other model compound 6 underwent decarboxylation under the same condition to give 2-(p-benzoyloxyphenyl)ethylbenzamide.

The first endothermic peak on the DSC curve of polymer 7 corresponds to decarboxylation. CO_2 is evolved and the weight loss is ~18% calculated according to TGA traces (Figure 2d). The chemical structure of resulting decomposition product is poly(enamino-enaryloxynitriles) **9**, which is obtainable from 2 and tyramine (Figure 1b and 1c) as
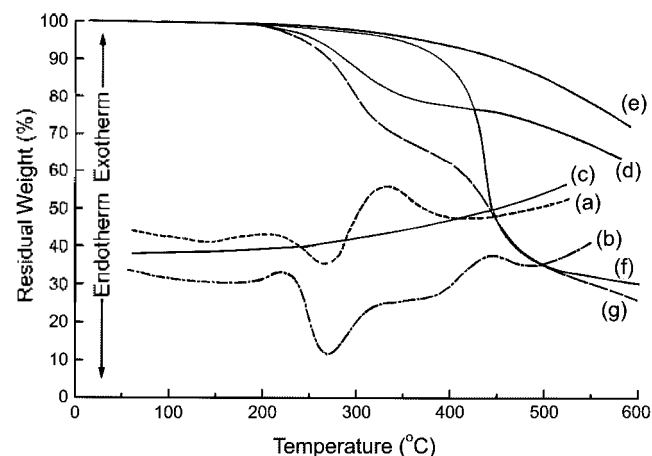
Notes

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Figure 2. DSC thermograms of (a) polymer **7**. (b) **8**, (c) **7** (2nd scan) and TGA traces of (d) polymer **7**, (e) polymer **9**, (f) **10** and (g) polymer **8**.

Table 2. Thermal Properties of Tyrosine-Based Model Compound, Poly(enamino-enaryloxynitriles) and Poly(arlyate-amide)

Polymers	$T_{exo}{}^a$	$T_{endo}{}^b$	$T_{id}{}^c$	$T_{10\%}{}^d$	Gel Fraction	Residual Weight %		
	°C				%	400 °C	500 °C	500 °C[e]
5	315	259	–	–	–	83.2	40.3	–
6	–	263	–	–	–	94.3	89.4	–
7	329	267	215	291	89	78.6	73.4	89.1
8	–	274	211	275	12	63.8	36.7	–
9	279	–	274	469	92	95.6	87.1	91.4

$^a T_{exo}$: Temperature of exotherm. $^b T_{endo}$: temperature of endotherm. $^c T_{id}$: initial decomposition temperature. $^d T_{10\%}$: temperature measured at a weight loss of 10%. ^{e}Residual weight of polymers cured at 300 °C for 30 min.

illustrated in Scheme 3. In the case of polymer 7, endothermic peak was followed by exothermic peak. After the decarboxylation reaction of polymer 7, the resulting polymer was cured thermally without splitting off volatile byproducts as shown in Figure 2(d). The decarboxylation reaction was confirmed again using polymer 8 as shown in Scheme 4. The same thermal behavior was observed.

The exothermic peak did not reappear upon cooling and rescanning the sample as shown in Figure 2c. When the polymers were heated at 300 °C 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 carbonyl band of carboxylic acid and nitrile band at 3380 and 2220 cm^{-1} apparently decreased in intensity and peaks at 1560-1640 cm^{-1} were broadened (Figure 1g). These phenomena could be associated with changes of vinyl group, as well as nitrile groups to C=N caused by the curing reaction. The decarboxylation reaction assumed to proceed at a temperature of endotherm and followed by intramolecular cyclization or cross-linking of the dicyanovinyl group during heating at a temperature of the maximum exotherm.[1-11] The cured poly(enamino-enaryloxynitriles) should have complex network structures.

Although the polymers possess an alkyl moiety, no melting endotherm was observed in DSC thermograms because of hydrogen bond between carboxylic acid groups. Polymer 8 derived from terephthaloyl chloride showed similar thermal behavior. The polymers began to lose weight at 251 °C in nitrogen. Thermal stability data are summarized in Table 2 and TGA traces in Figure 2. Polymers 7 and 8 sustained a 10% weight loss at 291 and 275 °C at a heating rate of 10 °C min^{-1}. and gave residual weight varying from 75.1 and 37.6% at 500 °C in nitrogen. Comparing with the poly(arylate-amide) 8. poly(enamino-aryloxynitriles) 7 showed improved thermal stability.

In conclusion, novel tyrosine-based poly(enamino-enaryloxynitriles) and poly(arylate-amide) were newly prepared by

interfacial polymerization of tyrosine with 2 or terephthaloyl chloride. They showed an enhanced solubility in common organic solvents. Polymer 7 underwent thermal decarboxylation reaction followed by thermal curing reaction.

Experimental Section

Materials and Measurements. 1-Chloro-1-phenyl-2,2-dicyanoethene (1). *p*-bis(1-chloro-2,2-dicyanovinyl) benzene (2) and *N*-(1-Phenyl-2,2-dicyanovinyl)-2-[*p*-(1-phenyl-2,2-dicyano vinyloxy)]phenylethyl amine (3) were prepared as previously reported.[1,12,20]

Fourier-transform infrared (FT-IR) spectra were obtained with a Midas Model M-1200 spectrophotometer. and ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Gemini 2000 spectrometer. 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-Stryagel 10^2, 10^3 and 10^4 Å) in THF and calibrated with polystyrene standards at 20 °C. Inherent viscosity of polymer solutions was measured in an Ubbelode viscometer at 25 °C in DMF. Thermal analysis of polymers was carried out on a Dupont 2100 and a Mettler thermal analyzer at a heating rate of 10 °C/min under nitrogen. TGA thermograms were performed on a Perkin-Elmer System 7 analyzer.

N-(1-Phenyl-2,2-dicyanovinyl)-*p*-(1-phenyl-2,2-dicyanovinyloxy)tyrosine (5). In a stainless steel jar, was placed a solution of 1 (0.94 g, 5 mmol) in 1.2-dichloroethane (20 mL). A solution of tyrosine (0.45 g, 2.5 mmol) and sodium hydroxide (0.36 g, 9 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 °C for 2 h with vigorous stirring. After 1,2-dichloroethane was evaporated, the reaction mixture was neutralized with 0.1 N HCl. The precipitated powdery product was washed with distilled water several times and recrystallized from acetonitrile to give white crystals, and dried under vacuum at 50 °C for 12 h. Other model compound 6 was prepared from benzoyl chloride by similar procedures as described above.

5: Yield 72%. mp 259 °C (dec.). IR (KBr. cm^{-1}) 3380

(OH), 3320 (N-H), 3080 (aromatic C-H), 2890 (aliphatic C-H), 2220 (s, C≡N), 1730 (C=O), 1580 (C=C), 1260-1110 (C-O and C-N). ^{1}H NMR (DMSO-d_6+CDCl$_3$) δ 10.81 (s, br. 1 H, CO*OH*), 9.19 (s, br. 1H N-*H*), 7.81-7.52 (m, 10H, 2 *Ph*-), 7.20-6.81 (m, 4H, -*Ph*-O-), 4.56 (br, 1H, -C*H*(COOH)-NH-), 2.47 (t, 2H, -Ph-C*H$_2$*-). ^{13}C NMR (DMSO-d_6) δ 35.8 (-C*H$_2$*-CH$_2$NN-), 54.3 (CH$_2$*C*H(COO-)-), 71.8, 86.1 (=*C*(CN)$_2$), 110.2, 111.4, 114.2, 116.2 (-*C*N), 128.2, 128.6, 129.3, 130.6, 133.3, 148.7, 152.4 (aromatic C's), 170.1 (=*C*(NH-)-), 176.7 (*C*O), 180.5 (=*C*(O-)-). *Anal.* Calcd for C$_{29}$H$_{19}$N$_5$O$_3$ (485.32): C, 71.75%; H, 3.92%; N, 14.43%. Found: C, 71.57%; H, 3.86%; N, 14.39%.

6: Yield 84%, mp 263 °C (dec.). IR (KBr, cm^{-1}) 3385 (OH), 3320 (N-H), 3060 (aromatic C-H), 2890 (aliphatic C-H), 1735, 1730 (s, C=O), 1680 (C=O), 1250-1100 (C-O and C-N). ^{1}H NMR (DMSO-d_6+CDCl$_3$) δ 10.8 (s, br. 1H, -O*H*), 9.26 (s, 1H, N-*H*), 7.82-7.21 (m, 10H, 2 *Ph*-), 7.22-6.81 (m, 4H, -*Ph*-O-), 4.54 (s, br, 1H, -C*H*(COO-)NH-), 2.47 (t, 2H, -Ph-C*H$_2$*-). *Anal.* Calcd for C$_{23}$H$_{19}$N$_1$O$_5$ (389.35): C, 70.95%; H, 4.84%; N, 3.60%. Found: C, 70.76%; H, 4.69%; N, 3.57%.

Interfacial Polymerization of 2 with Tyrosine. 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 tyrosine (1.19 g, 6.6 mmol), sodium hydroxide (0.89 g, 23.1 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 **7**. Other polymer of terephthaloyl chloride, **8**, was prepared by similar synthetic procedures.

7: Yield 88%. IR (KBr, cm^{-1}), 3385 (COOH), 3315 (N-H), 3050 (aromatic C-H), 2980 (aliphatic C-H), 2220 (C≡N), 1735 (s, C=O), 1580 (C=C), 1235-1100 (C-O and C-N). ^{1}H NMR (DMSO-d_6+CDCl$_3$) δ 10.20 (s, 1H, -O*H*), 9.12 (br, 1H, N-*H*), 7.82 (br, s, 4H, -*Ph*-), 7.20-6.81 (m, 4H -*Ph*-O-), 4.16 (br, 1H, -C*H*(COO-)-NH-), 2.43 (br, 2H -Ph-C*H$_2$*-). *Anal.* Calcd for C$_{23}$H$_{13}$N$_5$O$_3$ (365.25): C, 75.62%; H, 3.56%; N, 7.67%. Found: C, 75.72%; H, 3.63%; N, 7.58%.

8: Yield 92%. IR (KBr, cm^{-1}), 3380 (s, br, OH), 3325 (br,

N-H), 3050 (aromatic C-H), 2980 (aliphatic C-H), 1735 (s, C=O), 1680 (s, amide C=O), 1250-1100 (C-O and C-N). ^{1}H NMR (DMSO-d_6+CDCl$_3$) δ 10.41 (br, 1H, OH), 9.18 (br, 1 H N-*H*), 7.83 (s, 4 H, -*Ph*-), 7.21-6.82 (m, 4 H -*Ph*-O-), 4.13 (br, 1H, -C*H*(COO-)-NH-), 2.46 (br, 2H -Ph-C*H$_2$*-). *Anal.* Calcd for C$_{17}$H$_{13}$NO$_5$(301.22): C, 67.77%; H, 4.32%; N, 4.65%. Found: C, 67.72%; H, 4.23%; N, 4.58%.

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