Articles

Preparation and Thermal Properties of Enaryloxynitriles End-Capped Polymer Precursors

Deog-Soo Kil† and Myoung-Seon Gong*

Department of Chemistry, Dankook University, Cheonan, Chungnam 330-714, Korea
†Department of Industrial Chemistry, Dankook University, Cheonan, Chungnam 330-714, Korea
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Various enaryloxynitriles-terminated reactive polymer precursors containing rigid aromatic units were prepared from various diamines and 1-(*p*-formylphenyl)-1-phenyl-2,2-dicyanoethene (**1**). Arylate end-capped model compounds linked with azomethine bond were also prepared by reacting *p*-formylphenyl benzoate with diamines to compare the curing ability. The oligomers were highly soluble in polar aprotic solvents such as *N*,*N*-dimethylformamide, dimethylsulfoxide and *N*-methyl-2-pyrrolidinone. They generally showed an exothermic curing process between 280-350 °C, attributable to the thermal crosslinking of the dicyanovinyl group in DSC analysis, and no weight loss at curing temperature. Upon heating the polymer precursors, heat-resistant and insoluble network polymers were obtained. Thermogravimetric analyses of the precursors containing rigid aromatic units showed thermal stability with a 77-92% residual weight at 500 °C under nitrogen.

Introduction

End-capped reactive oligomers have served as an attractive route to high performance and high temperature materials for a variety of applications. They provide processible materials with better solubility and wettability, and lower melting or softening temperature.[1] The end-capped reactive oligomers are mainly cured through an addition reaction, so no volatile by-products are evolved giving a voidless final matrix. These properties make end-capped reactive oligomers especially attractive for a matrix resin for composite materials and protective and insulating coatings for microelectronic applications.[2]

Dicyanovinyl group has been employed as one of the effective thermally curable functionalities.[3-12] The introduction of dicyanovinyl units into polymers enhanced the thermal stability as well as the solubility in common organic solvents.[3,4] An approach to the preparation of dicyanovinyl-terminated polymer precursors was first reported by Mikroyannidis.[13] The concept has been extended to the syntheses of reactive oligomers consisting of rigid rod or flexible units capped at both ends with curable enaminonitriles as dicyanovinyl group.[14,15]

In conjunction with a study of rigid rod polymer precursors as potential reinforcements for thermosetting matrices, new enaryloxynitriles-terminated reactive polymer precursors were synthesized and characterized, and their thermal properties were estimated.

Experimental Section

1-(*p*-Formylphenoxy)-1-phenyl-2,2-dicyanoethene (**1**) was prepared by the method previously reported.[6] The procedures of preparation of various diamine derivatives were modified from the method described in the literature.[14,16] *N*-Methyl-2-pyrrolidinone (NMP) was purified by vacuum distillation after removing water by azeotropic distillation with benzene. Copper(II) acetylacetonate (Aldrich Chem. Co. 97%) was used without purification. Toluene, methanol and ethanol were purified by conventional purification methods.

All melting points were determined on a melting point apparatus (Aldrich Mel-Temp II) using capillary tubes and uncorrected. The solubilities of polymer precursors were measured by dissolving 5 mg of a powdery sample in 1 mL of solvent. Fourier-transform infrared (FT-IR) spectra were obtained with a Midac Model M-1200 spectrophotometer and ^{1}H NMR spectra were recorded on a Varian Gemini-2000 spectrometer. Elemental analyses were performed using a Yanaco MT-3 CHN instrument. Gel fraction of the cured sample was measured by weighing the insoluble portion after filtering the NMP solution of the cured sample through a sintered glass filter. The catalytic curing reaction with 1 wt.% of copper(II) acetylacetonate was performed at 190-200 °C for 30 min. Differential scanning calorimetry measurements were performed on a Perkin-Elmer DSC 7 under nitrogen at a heating rate of 10 °C/min. Thermogravimetric analysis (TGA) measurements were carried out on a Shimadzu TGA 50 thermal analyzer at a heating rate of 10 °C/min under nitrogen.

Representative reaction of 1 with aromatic diamines. In a round bottomed flask (100 mL) equipped with a nitrogen inlet, a dropping funnel and a Dean-Stark separator, was placed 2,2′-bis[(*p*-aminobenzoyloxy)phenyl]propane (4.86 g, 10 mmol) dissolved in NMP (20 mL) under nitrogen. To this solution was added 1-(*p*-formylphenoxy)-1-phenyl-2,2-dicyanoethene (6.03 g, 22 mmol) in NMP (30 mL) and toluene (20 mL) with stirring. After the reaction mixture was refluxed for 12 h, the yellow solution was poured into a large amount of anhydrous methanol to form precipitates. The crude product was purified by Soxhlet extraction with methanol and dried at 60 °C under vacuum for 10 h.

Other polymer precursors **3-6** containing enaryloxynitrile groups linked through azomethine bond were prepared by reacting formyl enaryloxynitriles **1** with corresponding diamines by using similar synthetic procedures.

2: Yield 88%. mp 193 °C (uncorrected). IR (KBr): 3120 (aromatic C-H), 2950-2845 (aliphatic C-H), 2210 (C≡N), 1735 (s, C=O), 1626 (CH=N), 1578 (C=C), 1320-1120 (s, C-O and C-N) cm^{-1}. ^{1}H NMR (DMSO-d_6 + CDCl$_3$): δ = 8.2 (s, 2H, 2 CH=N), 7.5 (m, 10H, 2 -Ph), 7.4-6.8 (m, 16H, 2 -O-Ph-CH=N-Ph-CO- and -Ph-(CH$_3$)$_2$-Ph-), 1.8 (s, 6H, -(CH$_3$)$_2$-). Anal. Calcd for $C_{63}H_{42}N_6O_6$(979.07): C, 71.99; H, 4.48; N, 9.33. Found : C, 71.67; H, 4.58; N, 9.25.

3: Yield 84%. mp 222 °C (uncorrected). IR (KBr): 3120 (aromatic C-H), 2210 (C≡N), 1732 (s, C=O), 1628 (CH=N), 1578 (C=C), 1320 (m, S=O), 1315-1120 (s, C-O and C-N), 1125 (C-S) cm^{-1}. ^{1}H NMR (DMSO-d_6 + CDCl$_3$): δ = 8.2 (s, 2H, 2 CH=N), 7.5 (m, 10H, 2 -Ph), 7.8-6.8 (m, 24H, 2 -O-Ph-CH=N-Ph-CO- and -Ph-SO$_2$-Ph-). Anal. Calcd for $C_{60}H_{36}N_6O_8S_2$(1033.10): C, 77.28; H, 4.32; N, 8.59. Found: C, 77.07; H, 4.28; N, 8.49.

4: Yield 82%. IR (KBr): 3320 (N-H), 3120 (C-H), 2212 (C≡N), 1732, 1678 (s, C=O), 1628 (CH=N), 1580 (C=C), 1320-1115 (s, C-O and C-N) cm^{-1}. ^{1}H NMR (DMSO-d_6 + CDCl$_3$): δ = 8.6 (br, 2H, NH), 8.2 (s, 2H, 2 CH=N), 7.5 (m, 10H, 2 -Ph), 7.8-6.7 (m, 24H, 2 -O-Ph-CH=NH-Ph-CO- and -NH-Ph-O-Ph-NH-). Anal. Calcd for $C_{60}H_{38}N_8O_5$ (951.02): C, 74.98; H, 5.10; N, 9.37. Found: C, 74.59; H, 5.06; N, 9.35.

5: Yield 88%. IR (KBr): 3120 (C-H), 2212 (C≡N), 1730, 1675 (s, C=O), 1628 (CH=N), 1582 (C=C), 1330-1160 (s, C-O and C-N) cm^{-1}. ^{1}H NMR (DMSO-d_6 + CDCl$_3$): δ = 8.2 (s, 2H, 2 CH=N), 7.5 (m, 10H, 2 -Ph), 7.8-6.7 (m, 20H, 2 -O-Ph-CH=N-Ph-CO-, 2 phenyl protons of phthalide and -Ph-O-Ph-). Anal. Calcd for $C_{62}H_{34}N_8O_7$(1003.00): C, 75.15; H, 5.1; N, 12.52. Found: C, 75.01; H, 5.16; N, 12.49.

6: Yield 86%. IR (KBr): 3120 (C-H), 2213 (C≡N), 1730, 1678 (s, C=O), 1618 (CH=N), 1580 (C=C), 1335-1152 (s, C-O and C-N) cm^{-1}. ^{1}H NMR (DMSO-d_6 + CDCl$_3$): δ = 8.2 (s, 2H, 2 CH=N), 7.8 (s, 2H, phenyl protons of trimellitimide, 7.5 (m, 10H, 2 -Ph), 7.4-6.8 (m, 16H, 2 -O-Ph-CH=N-Ph-). Anal. Calcd for $C_{56}H_{30}N_9O_6$ (924.91): C, 72.88; H, 4.33; N, 7.85. Found: C, 72.47; H, 438; N, 7.79.

***N,N′*-Oxydi-1,4-phenylenebis[4-(p-benzoyloxyphenylmethylimino)benzamide] (7).** In a 100 mL round bottomed flask equipped with a nitrogen inlet, a dropping funnel and a Dean-Stark separator was placed *N,N′*-oxydi-1,4-phenylenebis(4-aminobenzamide) (4.38 g, 10.00 mmol) dissolved in NMP (20 mL) under nitrogen. To this solution were added a *p*-formylphenyl benzoate (4.98 g, 22.00 mmol) in NMP (20 mL) and toluene (20 mL) with stirring. The reaction mixture was refluxed for 14 h and was precipitated into a large amount of methanol, and the resulting powder was filtered. The solid product was washed with ethanol several times and dried at 60 °C under vacuum for 10 h.

The other compound containing azomethine and arylate *N,N′*-oxydi-1,4-phenylenebis[4-(*p*-benzoyloxyphenylmethylimino)phthalide] (**8**) was prepared by reacting *N,N′*-oxydi-1,4-phenylenebis(4-aminophthalide) and *p*-formylphenylbenzoate by the method described above.

7: Yield 84%. mp 251 °C (uncorrected). IR (KBr): 3322 (N-H), 3120 (C-H), 1735, 1676 (s, C=O), 1626 (CH=N), 1325-1110 (s, C-O and C-N) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ = 8.6 (br, 2H, NH), 8.2 (s, 2H, 2 CH=N), 7.8-6.8 (m, 34H, 2 Ph-COO-Ph-CH=N-Ph-CO- and -NH-Ph-O-Ph-NH-). Anal. Calcd for $C_{54}H_{38}N_4O_7$(854.92): C, 74.82; H, 4.71; N, 6.23. Found: C, 74.61; H, 4.67; N, 6.19.

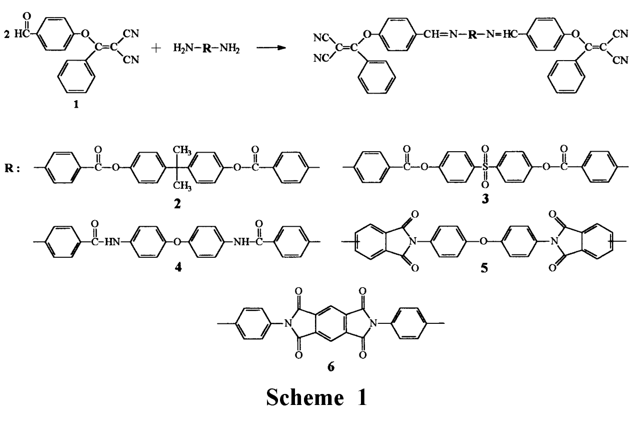
8: Yield 87%. mp 302 °C (uncorrected). IR (KBr): 3120 (C-H), 1735, 1678 (s, C=O), 1626 (CH=N), 1335-1155 (s, C-O and C-N) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ = 8.2 (s, 2H, 2 CH=N), 7.8-6.7 (m, 32H, 2 Ph-COO-Ph-CH=N-, 2 phenyl protons of phthalide and -N-Ph-O-Ph-N-). Anal. Calcd for $C_{56}H_{34}N_4O_9$(906.91): C, 76.57; H, 5.47; N, 6.62. Found: C, 76.37; H, 5.51; N, 6.60.

Results and Discussion

1-(*p*-Formylphenoxy)-1-phenyl-2,2-dicyanoethene (**1**) was prepared from 1-chloro-1-phenyl-2,2-dicyanoethene and sodium salt of hydroxybenzaldehyde *via* vinylic nucleophilic substitution reaction in 73% yield.[6]

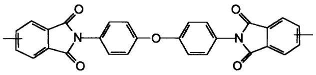
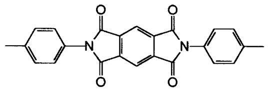
Prior to the present work, *p*-bis[1-[4-[(phenylimino)methyl]-phenoxy]-2,2-dicyanovinyl]benzene and *p*-bis[4-[(2,2-dicyanovinyloxy)]benzal]imino]phenylether have been previously reported.[6] However, the syntheses of reactive polymer precursors containing both an azomethine group and enaryloxynitrile functionality shown in Scheme 1 have not been reported.

The reaction of **1** with aromatic diamines such as 2,2′-bis[(*p*-aminobenzoyloxy)phenyl]propane, 4,4′-bis(*p*-aminobenzoyloxy)phenylsulfone, *N,N′*-oxydi-1,4-phenylenebis(*p*-aminobenzamide), *N,N′*-oxydi-1,4-phenylenebis(4-aminophthalide) and bis(*p*-aminophenyl)pyromellitic diimide was conducted in NMP solution to give the reactive polymer precursors **2-6**. The results of the condensation reaction are summarized in Table 1. The reaction of 2.2 molar quantity of **1** with aromatic diamines at 110 °C was rapid and led to 77-90% yields of enaryloxynitriles-terminated reactive polymer prcursors.



Scheme 1

Table 1. Reasults and Conditions of Preparation of Enaminonitriles-Terminated Reactive Polymer Precursors[a]

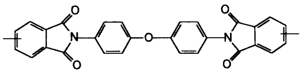
Pre-cursors	Chemical Structure $(NC)_2C=C(Ph)OPh-CH=N-X-N=CH-PhO(Ph)C=C(CN)_2$	Yield in %	m.p. in °C
2	$-Ph-COOPh-C(CH_3)_2-PhOCOPh-$	83	193
3	$-Ph-COOPh-SO_2-PhOCOPh-$	88	222
4	-Ph-CONH-Ph-O-Ph-NH-Ph-	77	–
5		72	–
6		86	–

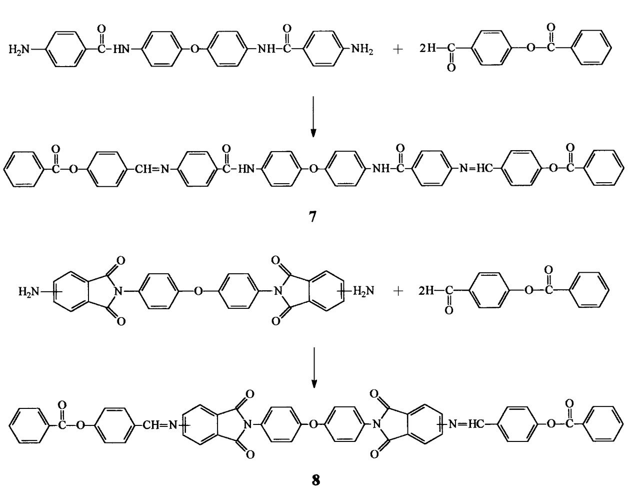
[a]Reaction temperature, 110 °C; time, 10 hr; solvent, NMP.

Wallenfels reported that $C=C(CN)_2$ group was considered structurally equivalent to a C=O group in reactions where oxygen is exerting an electron withdrawing effect. According to this analogy, 1-phenyl-2,2-dicyanovinyl group corresponds to benzoyl group. Two model compounds, *N*,*N*′-oxydi-1,4-phenylenebis[4-(*p*-benzoyloxyphenylmethylimino)benzamide] and *N*,*N*′-oxydi-1,4-phenylenebis[4-(*p*-benzoyl-oxyphenylmethylimino)phthalide] containing azomethine groups were prepared by reacting *N*,*N*′-oxydi-1,4-phenylenebis(*p*-aminobenzamide) and *N*,*N*′-oxydi-1,4-phenylene-bis(4-aminophthalide) with *p*-formylphenyl benzoate as illustrated in Table 2 and Scheme 2.

As an azomethine bond was easily formed during the condensation reaction of an amine and an aldehyde function, enaryloxynitriles could be incorporated to the rigid aromatic main chain through an azomethine linkage.

Table 2. Reasults and Conditions of Preparation of Azomethine-Terminated Model compounds

Pre-cursors	Chemical Structure PhCOOPh-CH=N-X-N=CH-PhOCOPh	Yield in%	m.p. in °C
7	-Ph-CONH-Ph-O-Ph-NH-Ph-	79	251
8		90	302



Scheme 2

The chemical structures of polymer precursors were characterized by spectroscopic techniques such as FT-IR, ^1H NMR and elemental analysis. The analytical results obtained are consistent with the proposed structure, although the elemental analyses tend to be somewhat low in carbon. This is a common problem with many thermally resistant polymers.[16] In the Infrared spectra, all the precursors showed characteristic absorption bands around 2210, 1628 and 1580 cm^{-1} corresponding to C≡N, N=CH and C=C linkage, respectively. In the case of oligomers **2**, **4** and **5** bearing arylate, aramide and imide-amide moieties, the characteristic C=O absorption bands were exhibited at 1735, 1678-1732 and 1675-1730 cm^{-1}, respectively. In the ^1H NMR spectrum of oligomer **2**, the aromatic protons in fragment of phenyl proton of **1** and in benzoyl moiety appeared at 7.5 and 7.5-6.8 ppm as a multiplet, respectively. On the other hand, the N=CH proton appeared between 8.5-8.2 ppm as a singlet peak. The chemical structures of **7** and **8** containing azomethine and arylate groups, were also identified by IR and ^1H NMR spectra, giving characteristic absorption peaks of C=O and N=CH at 1735-1676 and 1626 cm^{-1}, respectively.

The purification of polymer precursors was conducted first by successive extractions of the crude product using hot ethanol, followed by precipitation from NMP solution to methanol. The solubilities of the oligomers were tested in various solvents such as DMF, DMAc, NMP, acetonitrile, THF, acetone and ethanol. A series of polymer precursors were soluble in common organic solvents including THF and pyridine as well as typical polar aprotic solvents such as DMF and NMP. Introduction of the rather bulky and polarizable dicyanovinyl groups into rigid aromatic backbones seems to result in the good solubility of these oligomers. On the other hand, they displayed virtually no solubilities in ethanol. The solubilities of **7** and **8** derived from *p*-formylphenylbenzoate were somewhat different from those of **4** and **5**, and this may be attributed to the arylate instead of the enaryloxynitriles. They exhibited poor solubility even in NMP.

The DSC data of enaryloxynitriles- and arylate-terminated oligomers were summarized in Table 3. The precursors **2** and **3** displayed an endothermic peak at 196 and 225 °C, respectively, attributed to the melting temperature, which was consistent with the melting point determined by a capillary tube method. The exothermic peak is presumably derived from the cross-linking reaction of dicyanovinyl group and spans the range of 280-400 °C showing the maximum intensity around 340 °C as shown in the Figure 1. The onset of the curing exothermic transition and the maximum temperature of the exotherm follow the similar trend regardless of the chemical structures of the oligomers.

The functional role of dicyanovinyl and azomethine for curability was estimated by comparing reactive polymer precursors **4** and **5** with model compounds **7** and **8** without enaryloxynitriles group. Conjugated azomethine moiety was reported to be cured thermally, but required high curing temperature greater than 390 °C.[6] Since polymer precursors possess enaryloxynitrile and azomethine group, each of which

Table 3. Thermal Properties of Eenaryloxynitriles-Terminated Polymer Precursors and Arylate-Terminated Compounds

Oligomers	T_{exo}[a]	T_{endo}[b]	T_{idt}[c]	$T_{10\%}$[d]	Gel fraction	Residual Weight (%)		
	(°C)				(%)	400 °C	500 °C	500 °C[e]
2	338	196	360	424	98	93	77	84
3	340	225	372	450	97	94	86	90
4	312	–	365	433	97	93	84	89
5	349	–	374	476	98	95	89	92
6	351	–	389	524	96	97	92	94
6[f]	–	–	401	550	–	99	94	–
7[g]	390	252	375	450	92	98	80	–
8[g]	402	305	351	405	87	90	74	–

[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 polymer precursors at 330 °C for 30 min.. [f] Data were obtained from polymer precursor **6** cured at 330 °C for 30 min. [g] Gel fraction was obtained by heating the samples at 390 °C for 10 min.

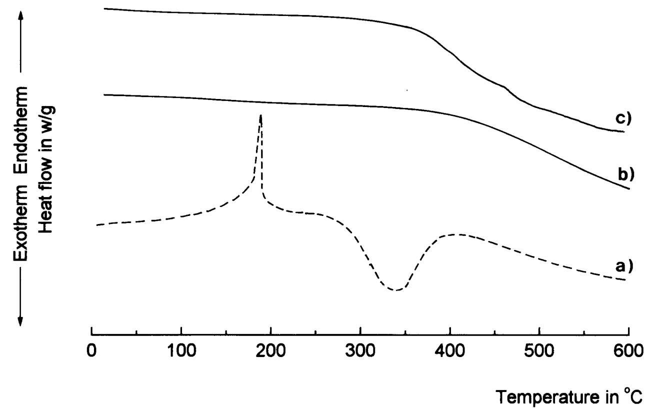


Figure 1. DSC thermograms of a) polymer precursor **2**, b) **2** (2nd scanning) and c) **7** at a heating rate of 10 °C/min in nitrogen.

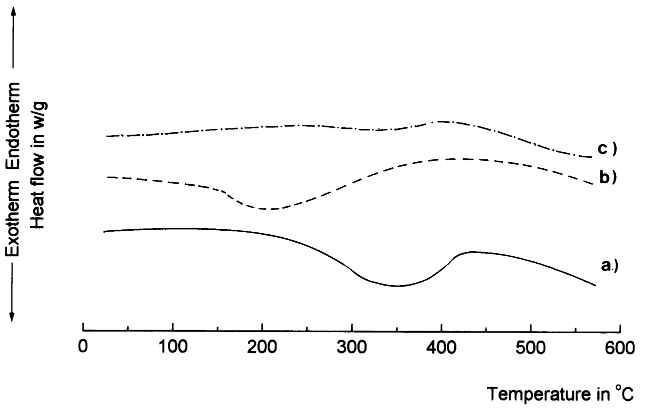


Figure 2. DSC thermograms of a) polymer precursor **6**, b) **6** with copper catalyst and c) **6** with copper catalyst (2nd scanning) at a heating rate of 10 °C/min in nitrogen.

may be curable by different mechanism, it was thought that precursors could perhaps be made to react independently with either enaryloxynitrile groups or azomethine group on other molecules. In the cases of model compounds **7** and **8**, any significant curing exothermic peak was not observed below 400 °C, however gradual exothermic reaction might proceed over 400 °C. It was considered that the exotherm occurred by decomposition and concurrent cross-linking. In this case, the thermal curing process of azomethine group was difficult to elucidate with the results of TGA and DSC analysis at the present time. The second run, when the first heating was stopped at 320 °C, measured at the same heating rate for sample **2** showed no exothermic peaks as shown in Figure 1(b). This result may indicate that further cross-linking of dicyanovinyl group did not occur up to 350 °C. All the cured samples did not redissolve completely in DMF and NMP, which are good solvents for the oligomers. The cured oligomers showed gel fractions ranging from 87 to 98%.

The curing of dicyanovinyl group requires a high temperature between 280-350 °C and without a catalyst, curing reaction did not proceed below 200 (Figure 2(a)). When the curing reaction was carried out with copper(II) acetylacetonate as a catalyst, the curing reaction undergoes at a relatively low temperature 190 °C to give cross-linked polymer as shown in the DSC curve of Figure 2(b) and 2(c). It was widely known that copper, zinc and cobalt catalysts accelerated the curing of nitriles to intermolecular and other cyclization product.[17] A weak nitriles absorption peak was found in the IR spectra after 30 min reaction with a copper catalyst at 190 °C and the residue was further cured around 350 °C as shown in Figure 2(c). The the nitrile peak at 2200 cm^{-1} decreased over the course of the reaction concomitant with cross-linking. After 1 h the cyano absorption peak had totally vanished.

IR spectroscopy was used to follow the thermal curing of a sample on KBr salt plate. The IR spectra showed a spectral change after the curing of oligomers. The presence of C=N linkages formed during the curing reaction was established, a strong absorption was observed in 1450-1650 cm^{-1}. At the same time, the intensity of the nitrile band around 2210 cm^{-1} decreased apparently. The changes in the IR spectra are consistent with the intermolecular cross-linking of dicyanovinyl groups proposed previously.[5,8,13] It was well established by a variety of techniques that dicyanovinyl group was cured to form cross-linked networks. In the case of polyenaminonitriles, the dicyanovinyl group was consumed in intramolecular cyclization.[5] The thermal stability of polymers containing enaryloxynitriles group is probably enhanced through intermolecular cross-linking process.[10,13]

The thermal stability data are listed in Table 3. The TGA thermograms shown in Figure 3 are characterized by a shallow weight loss followed by a gentle degradation peak. The

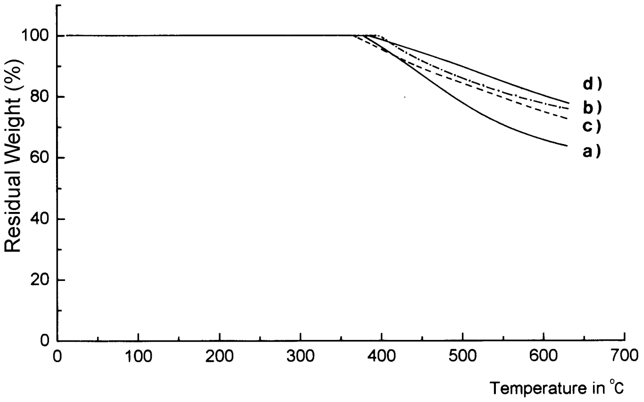


Figure 3. TGA thermograms of polymer precursors a) **2**, b) **3**, c) **4** and d) **5** at a heating rate of 10 °C/min under nitrogen.

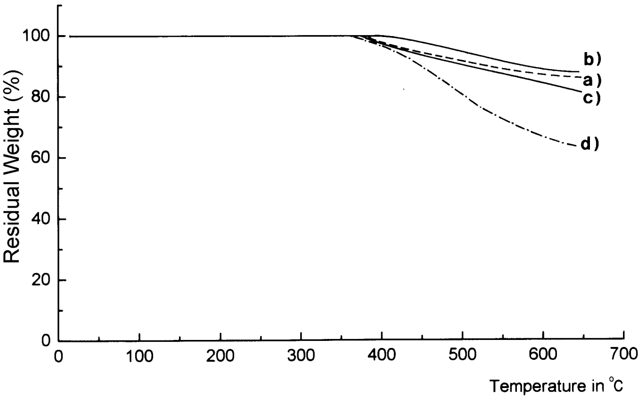


Figure 4. TGA thermograms of a) polymer precursor **6** cured at 330 °C, b) **6**, c) **6** cured at 190 °C with copper catalyst and d) **7** at a heating rate of 10 °C/min under nitrogen.

polymer precursors were stable up to 350 °C under nitrogen as determined by thermogravimetric analysis. The process of degradation starts around 380 °C with slight weight loss above 400 °C for all the samples irrespective of the chemical structure of polymer precursors. The lowest initial decomposition temperature (IDT) and the residual weight were exhibited by polymer precursor **2**.

The polymer precursors with rigid aromatic units gave a residual weight varying from 77% to 92% at 500 °C at a heating rate of 10 °C/min in nitrogen and sustained a 10% weight loss around 424-524 °C. Anaerobic char yields of these thermally treated enaryloxynitriles containing reactive polymer precursors depended on their backbone structures. The precursor **6**, which contains imide units, has been found to be the most thermally stable as compared to other precursors and about 92% residual weight has been observed at 500 °C. The thermal stabilities of reactive polymer precursors are in the order of **6** > **5** > **4** > **2** by comparing the initial degradation temperature and % residual weight at 500 °C.

When the thermal properties of cured polymer precursors at 330 °C for 30 min were compared with those of the uncured ones, they were improved for all the polymers in Figure 4(a) and Table 2. The copper catalyzed cured polymer was also compared as shown in Figure 4(d). But they showed slightly lower thermal stabilities than those of cured one without a catalyst.

The thermal stabilities of reactive polymer precursors are lower than those of the corresponding polymers, which were ranging between 450 and 650 °C, previously reported.[6] Despite the low molecular weights of polymer precursors, the thermal stabilities of enaryloxynitriles end-capped reactive polymer precursors are good with a 10% weight loss ranging between 424 and 524 °C in nitrogen (Table 3). They still exhibit higher thermal stability than previous enaminonitriles-terminated polymer precursors due to the presence of azomethine function.[14,15]

In conclusion, polymer precursors containing enaryloxynitrile units linked with azomethine linkage were generally displayed crossliking exotherms around 340 °C and no weight loss at curing temperature. Thermogravimetric analyses of the precursors containing rigid aromatic units showed thermal stability with a 77-92% residual weight at 500 °C under nitrogen. But there was no clear evidence of a role of azomethine linkage in thermal curing reaction from the results of TGA and DSC analysis at the present time and the curing reaction of azomethine likage remained to be pursued further.

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References

1. Allen, G.; Bevington, J. C. *Comprehensive Polymer Science*; Pegamon Press: Oxford, 1989; vol. 5, pp 499-532.
2. Spinelli, H. J.; Harris, F. W.; *Reactive Oligomers*; ACS Sym. Ser. 282, Am. Chem. Soc., Washington, DC, 1985.
3. Kim, Y. S.; Kim, B.G.; Gong, M. S. *Polym. J.* **1994**, *26*, 1910.
4. Cho, H. G.; Kim, B. G.; Choi, S. H.; Gong, M. S. *Macromolecules* **1993**, *26*, 6654.
5. Robello, D. R.; Moore, J. A. *Macromolecules* **1989**, *22*, 1084.
6. Kim, S. G.; Lee, S. J.; Gong, M. S. *Macromolecules* **1995**, *28*, 5638.
7. Mehta, P. G.; Moore, J. A. *Macromolecules* **1993**, *26*, 916.
8. Mehta, P. G.; Kim, S. Y.; Moore, J. A. *Macromolecules* **1993**, *26*, 3504.
9. Moon, H. S.; Kim, J. S.; Kim, C. B.; Gong, M. S. *Polym. J.* **1993**, *25*, 193.
10. Shin, J. C.; Kim, T. M.; Gong, M. S. *Macromolecules* **1995**, *28*, 2212.
11. Ha, J. H.; Kim, C.; Gong, M. S. *Polym. J.* **1995**, *27*, 536.
12. Ha, J. H.; Lee, S. J.; Gong, M. S. *Macromol. Chem. Phys.* **1995**, *196*, 4001.
13. Mikroyannidis, J. A. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 1771.
14. Park, W. S.; Gong, M. S. *Macromol. Chem. Phys.* **1998**, *199*, 433.
15. Park, W. S.; Gil, D. S.; Gong, M. S. *Bull. Korean Chem. Soc.* **1998**, *19*, 291.
16. Li, H.; Hsu, K. Y.; Chang, T. C. *J. Polym. Sci., Part A: Polym. Chem.* **1991**, *29*, 1447.
17. Korshak, V. V.; Rusanov, A. L. *J. Macro. Sci. -Revs. Macro. Chem.* **1982**, *C21(2)*, 275.
18. Stille, J. K.; Nelb, N. G.; Norris, S. O. *Macromolecules* **1976**, *9*, 516.