Polymer Journal, Vol. 32, No. 3, pp 243—248 (2000)

Preparation and Thermal Properties of Dicyanovinyl End-Capped Reactive Oligomers Linked with Azomethine Bond

Deog-Soo KIL,* Seung-Jae CHOI,* 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*

(Received August 2, 1999)

ABSTRACT: New dicyanovinyl end-capped reactive oligomers **2**—**5** containing flexible alkyl units were prepared from the condensation reaction of diamines with 1-(*p*-formylphenyl)-1-phenyl-2,2-dicyanoethene (**1**) by forming an azomethine linkage. Two arylate oligomers **7** and **8** containing azomethine bond were also prepared and compared with oligomers **2**—**5**. All the oligomers were characterized by spectroscopies and elemental analysis. The reactive oligomers showed a good solubility in polar aprotic solvent such as *N, N*-dimethylformamide (DMF) and *N, N*-dimethylacetamide (DMAc), and they were partially soluble in common organic solvents such as tetrahydrofuran (THF) and acetone. Their thermal properties including melting temperature, curability and thermal stabilities were examined. These oligomers undergo a curing reaction around 280—340℃. Upon heating the oligomers, thermally stable and insoluble network polymers were obtained.

KEY WORDS End-Capped Reactive Oligomer / Thermal Stability / Enaryloxynitriles / Azomethine Group / Dicyanovinyl Group /

Introduction of reactive functional groups into oligomers, which undergo intramolecular cycloaddition or intermolecular crosslinking on heating, has important advantages over previously developed high molecular weight linear polymer system.[1,2] They provide processible materials with better solubility and wettability, lower melt or softening temperature. However, the cured products exhibit good mechanical strength and high thermal stability for composite materials, and protective and insulating coatings for microelectronic applications. As the resins are cured through an addition reaction, no volatile by-products are evolved giving a voidless final matrix.[2]

The dicyanovinyl group has been employed as one of the thermally curable functionalities.[3—5] It was widely known that the incorporation of dicyanovinyl units into a polymer backbone enhanced the thermal stability as well as the solubility in common organic solvents.[6—13] Dicyanovinyl end-capped reactive oligomers were first reported by Mikroyannidis.[14] In a previous article, enaminonitrile end-capped reactive oligomers were newly prepared and exhibited an excellent thermal stability through intermolecular addition reaction as a curing process. Particularly those based on aromatic rigid reactive oligomer are applicable to matrix resin for composite materials because of their thermal stability and high glass transition temperature. Unfortunately, they are too brittle for use alone and usually mixed with other resins to obtain sufficient strength and toughness. For these reasons, it was considered that substantial improvement in performance of oligomers could be achieved by use of suitable flexible backbone structure.

In the present article, we report the results of a study stimulated by the above work aimed at synthesizing and evaluating flexible alkyl-containing oligomers, which contained both a dicyanovinyl and an azomethine group as a functionality.

EXPERIMENTAL

1-(*p*-Formylphenoxy)-1-phenyl-2, 2-dicyanoethene (**1**) was prepared by the method previously reported.[14] Various diamine derivatives were prepared by the modified method described in the literature.[17] *N*-Methyl-2-pyrrolidinone (NMP) was purified by vacuum distillation after drying by azeotropic distillation with benzene.

All melting points were determined on a melting point apparatus (Aldrich Mel Temp-II) using capillary tubes and were uncorrected. The solubility of oligomers was estimated by dissolving 100 mg of powdery sample in 10 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 solution of the cured sample in NMP through sintered glass filter. The catalytic curing reaction with 1 wt% of copper(II) acetylacetonate was performed at 190—200℃ for 30 min. Differential scanning calorimetry measurements were performed on a Perkin-Elmer DSC-7 under nitrogen at a heating rate of 10℃ min^{-1}. Thermogravimetric analysis (TGA) measurements were carried out on a Shimadzu TGA-50 at a heating rate of 10℃ min^{-1} under nitrogen.

*Representative Reaction of **1** with Triethyleneglycol Bis(p-aminobenzoate)*

In a 100 mL round bottomed flask equipped with a nitrogen inlet, a condenser and a Dean-Stark separator, triethyleneglycol bis (*p*-aminobenzoate) (4.0 g, 10 mmol) was dissolved in *N*-methyl-2-pyrrolidinone (20 mL) and toluene (10 mL) under nitrogen. To this solution was added a 2.2 equivalent weight of 1-(*p*-formylphenoxy)-1-

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

phenyl-2, 2-dicyanoethene (5.83 g, 22 mmol) in NMP (10 mL) with stirring. After the reaction mixture was refluxed for 24 h, the resulting yellow solution was precipitated into a large amount of anhydrous methanol. The yellowish powdery product was filtered and dried at 60 ℃ under vacuum for 10 h.

Other oligomers **3**—**6** containing dicyanovinyl group and Schiff bases were prepared by reacting different content of formyl enaryloxynitriles **1** and diamines by using similar synthetic procedures.

2: Yield 83%. mp 165℃(uncorrected).

IR (KBr): 3125 (C–H), 2850 (aliphatic C–H), 2210 (C≡N), 1732 (C=O), 1624 (CH=N), 1579 (C=C), 1320—1120 (C–O and C–N) cm^{-1}.

^1H NMR (dimethyl sulfoxide (DMSO)-d_6+$CDCl_3$): δ =8.3 (s, 2H, 2CH=N), 7.5 (m, 10H, 2-*Ph*), 7.8—7.0 (m, 16H, 2-O-*Ph*-CH=N-*Ph*-CO-), 4.4—3.8 (m, 12H, -O-($CH_2CH_2O)_3$-).

Anal. Calcd for $C_{54}H_{40}N_6O_8$: C, 77.28%; H, 4.32%; N, 8.59%. Found: C, 77.01%; H, 4.28%; N, 8.61%.

3: Yield 77%. mp 172℃(uncorrected).

IR (KBr): 3125 (C–H), 2850 (aliphatic C–H), 2210 (C≡N), 1736 (C=O), 1624 (CH=N), 1580 (C=C), 1320—1115 (C–O and C–N) cm^{-1}.

^1H NMR (DMSO-d_6+$CDCl_3$): δ=8.3 (s, 2H, 2CH=N), 7.5 (m, 10H, 2-*Ph*), 7.8—7.0 (m, 16H, 2-O-*Ph*-CH=N-*Ph*-CO-), 4.4—3.8 (t, 4H, 2-O-CH_2-), 1.5 (m, 12H, -$(CH_2)_6$-).

Anal. Calcd for $C_{56}H_{44}N_6O_6$: C, 75.07%; H, 4.03%; N, 11.79%. Found: C, 74.91%; H, 3.99%; N, 11.71%.

4: Yield 72%. mp 175℃(uncorrected).

IR (KBr): 3315, 3265 (N–H), 3120, 2850 (aliphatic C–H), 2210 (C≡N), 1734, 1672 (C=O), 1624 (CH=N), 1580 (C=C), 1320—1122 (C–O and C–N) cm^{-1}.

^1H NMR (DMSO-d_6+$CDCl_3$): δ=9.1 (m, 2H, amide N-*H*), 8.3 (s, 2H, 2CH=N), 7.5 (m, 10H, 2-*Ph*), 7.8—7.0 (m, 16H, 2-O-*Ph*-CH=N-*Ph*-COO-), 2,4 (br, 4H, 2NH-CH_2-), 1.9 (m, 12H, -$(CH_2)_6$-).

Anal. Calcd for $C_{56}H_{46}N_8O_4$: C, 74.39%; H, 3.42%; N, 12.60%. Found: C, 74.31%; H, 3.36%; N, 12.49%.

5: Yield 86%.

IR (KBr): 3120, 2850 (aliphatic C–H), 2210 (C≡N), 1736 (C=O), 1623 (CH=N), 1580 (C=C), 1320—1110 (C–O and C–N) cm^{-1}.

^1H NMR (DMSO-d_6+$CDCl_3$): δ=8.3 (s, 2H, 2CH=N), 7.5 (m, 10H, 2-*Ph*), 7.8—7.0 (m, 24H, 2-O-*Ph*-CH=N-*Ph*-COO-*Ph*-), 5.4 (s, 2H, 2 benzyl acetal H), 4.0 (m, 8H, $C(CH_2O-)_4$).

Anal. Calcd for $C_{65}H_{46}N_6O_{10}$: C, 71.32%; H, 3.44%; N, 14.33%. Found C, 71.19%; H, 3.42%; N, 14.26%.

6: Yield 88%. mp 196℃(uncorrected).

130℃. IR (KBr): 3120 (C–H), 2950—2845 (aliphatic C–H), 2210 (C≡N), 1735 (C=O), 1624 (CH=N), 1578 (C=C), 1320—1120 (C–O and C–N) cm^{-1}.

^1H NMR (DMSO-d_6+$CDCl_3$): δ=8.2 (s, 2H, 2CH=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 $C_{63}H_{42}N_6O_6$: C, 71.99%; H, 4.48%; N, 9.33. Found: C, 71.67%; H 4.58%; N 9.25%.

N,N′-Octamethylene bis[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′*-octamethylene bis(*p*-aminobenzoamide) (3.82 g, 10 mmol) dissolved in NMP (20 mL) under nitrogen. To this solution were added a 2.2 equivalent weight of **1** (4.97 g, 22 mmol) in NMP (10 mL) and toluene (10 mL) with stirring. The reaction mixture was refluxed and maintained for 24 h. After the reaction mixture was cooled, the resulting solution was precipitated into a large amount of methanol. The white powdery product was filtered, and washed with methanol several times. The product was recrystallized from NMP and dried at 60℃ under vacuum for 10 h.

Other oligomer containing azomethine and arylate groups 2, 2′-bis[4-[4-(*p*-benzoyloxyphenylmethyl)iminobenzoyloxy]phenyl]propane (**8**) was prepared by reacting 2, 2′-bis[(4-aminobenzoyloxy)phenyl]propane and *p*-formylphenylbenzoate by the similar procedures described above.

7: Yield. 79%. mp 230℃ (uncorrected).

IR (KBr): 3315, 3265 (N–H), 3120, 2850 (aliphatic C–H), 1736, 1672 (C=O), 1624 (CH=N), 1320—1120 (C–O and C–N) cm^{-1}.

^1H NMR (DMSO-d_6+$CDCl_3$): δ=9.1 (m, 2H, amide N*H*), 8.3 (s, 2H, 2CH=N), 7.8—7.0 (m, 26H, 2*Ph*-COO-*Ph*-CH=N-*Ph*-CO-), 2,4 (br, 4 H, 2-NH-CH_2-), 1.9 (m, 12H, -$(CH_2)_6$-).

Anal. Calcd for $C_{54}H_{46}N_4O_6$: C, 74.16%; H, 3.78%; N, 6.18%. Found: C, 74.02%; H, 3.67%; N, 6.19%.

8: Yield 90%. mp 277℃(uncorrected).

IR (KBr): 3120 (C–H), 2950—2845 (aliphatic C–H), 1735 (C=O), 1624 (CH=N), 1320—1120 (C–O and C–N) cm^{-1}.

^1H NMR (DMSO-d_6+$CDCl_3$): δ=8.2 (s, 2H, 2CH=N), 7.5 (m, 10H, 2-*Ph*), 7.4—6.8 (m, 34 H, 2 *Ph*-COO-*Ph*-CH=N-*Ph*-CO- and -*Ph*-$(CH_3)_2$-*Ph*-), 1.8 (s, 6H, -$(CH_3)_2$-).

Anal. Calcd for $C_{56}H_{42}N_4O_8$: C, 75.86%; H, 4.48%; N, 6.56%. Found: C, 75.51%; H, 4.37%; N, 6.29%.

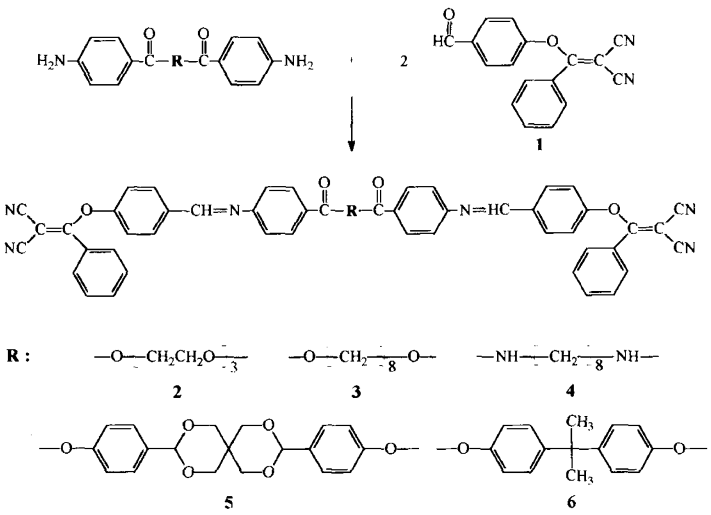
RESULTS AND DISCUSSION

Various diamine derivatives were prepared by reacting aliphatic diols and diamine with *p*-nitrobenzoyl chloride, followed by catalytic hydrogenation with 10% Pd/C.[17] 1-(*p*-Formylphenoxy)-1-phenyl-2, 2-dicyanoethene (**1**) was synthesized by the vinylic nucleophilic substitution reaction of 1-chloro-1-phenyl-2, 2-dicyanoethene with sodium salt of hydroxybenzaldehyde in the presence of benzyl triethyl ammonium chloride as a phase transfer catalyst.

In the previous paper ,1-[4[(phenylimino) methyl]-phenoxy-1-phenyl-2, 2-dicyanoethene, *p*-bis[1-[4-[(phenylimino) methyl] phenoxy-2, 2-dicyanovinyl] benzene, *p*-bis[4-[(2, 2-dicyanovinyloxy] benzal] imino] phenylether and various polyenaryloxynitriles containing an azomethine group have also been reported.[12]

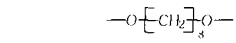
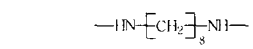
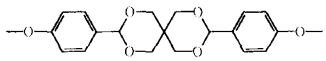
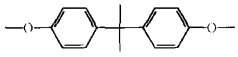
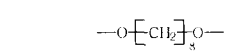
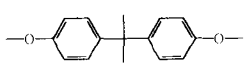
General reaction scheme and five new structurally different dicyanovinyl- and azomethine-containing ester, amide and acetal compounds are outlined in Scheme 1.

The condensation reaction of **1** with diamines such as triethyleneglycol bis (*p*-aminobenzoate), octanediol bis (*p*-aminobenzoate), *N,N′*-octamethylenebis(*p*-aminobenzamide), 3,9-di-4-[(*p*-aminobenzoyloxy) phenyl]-2,4,8,10-



Scheme 1.

Table I. Results of preparation of dicyanovinyl end-capped reactive oligomers[a]

Oligomers	Chemical Structure $(NC)_2C=C(Ph)OPhCH=N-Ph-CO-X-COPh-N=CHPhO(Ph)C=C(CN)_2$	Yield %	Mp ℃
2		88	165
3		82	172
4		88	175
5		86	—
6		84	222
7[b]		84	230
8[b]		87	277

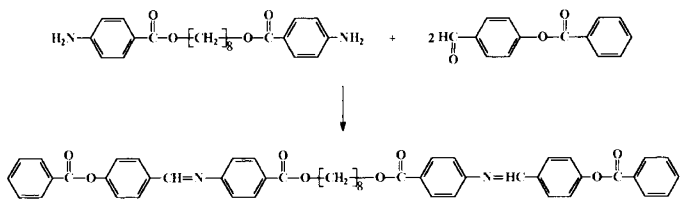
[a] Reaction temperature, 110℃ ; time, 12 h ; solvent, NMP. [b] Arylate end-capped reactive oligomers.

tetraoxaspiro-[5,5]-undecane, 2,2′-bis[(*p*-aminobenzoyloxy)phenyl]propane were carried out in NMP solution to give the oligomers **2**—**6** in the presence of 1, 4-diazabicyclo[2. 2. 2]octane (DABCO) as an acid acceptor. The reaction of excess **1** with diamines led to moderate yield of dicyanovinyl end-capped reactive oligomers. The results of the condensation reaction and melting points are summarized in Table I.

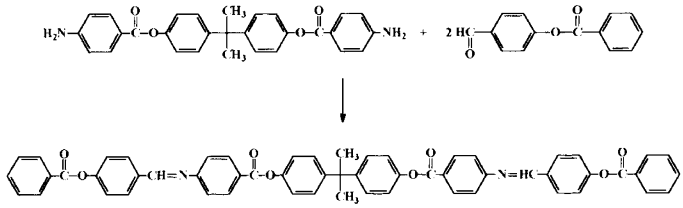
Model arylate compounds, 2,2′-bis[4-[4-(*p*-benzoyloxyphenylmethyl)iminobenzoyloxy]phenyl] propane and *N,N′*-octamethylenebis[4-[4-(*p*-benzoyloxyphenylmethy)-limino]benzamide] containing azomethine groups were obtained by reacting *N,N′*-octamethylenebis(*p*-aminobenzamide) and 2, 2′-bis[(4-aminobenzoyloxy)phenyl]-propane with *p*-formylphenylbenzoate as illustrated in Scheme 2.

Characterizations of the synthesized oligomers were performed by spectroscopic techniques such as FT-IR and ^{1}H NMR, and elemental analysis. The experimental results are in good agreement with the chemical structure obtained on the synthetic route. The IR spectrum of a representative oligomers showed characteristic absorption bands around 2210, 1735 and 1624 cm^{-1} corresponding to C≡N, C=O and CH=N linkage, respectively, as shown in Figure 1. In the cases of oligomers **2**, **4**, and **5** incorporating ester, amide and acetal-ester moieties, the characteristic absorption bands were exhibited at 1732, 1672—1736, and 1735 cm^{-1}, corresponding to C=O. In the ^{1}H NMR spectrum of oligomer **2**, the aromatic protons in fragment of **1** and in benzoyl moiety appeared at 7.5 and 7.8—6.8 ppm as a multiplet, respectively.

The elemental 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.[18] The oligomers were purified by successive washing with boiling methanol or ethanol, and reprecipitation because of difficulties in recrystallization. The solubility of the oligomers was tested in various solvents such as *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), NMP, acetonitrile, tetrahy-



7



8

Scheme 2.

Table II. Thermal properties of dicyanovinyl end-capped reactive oligomers

Oligomer	T_{exo} [a]	T_{endo} [b]	T_{idt} [c]	$T_{10\%}$ [d]	Gel fraction	Residual weight in %		
	in℃				in %	400℃	500℃	500℃[e]
2	314	167	325	375	94	81	61	70
3	320	170	323	382	96	87	55	64
4	307	175	330	380	93	80	58	64
5	312	—	345	389	95	88	70	79
6	338	196	360	424	98	93	77	84
7	324	252	313	390	75	87	42	—
8	418	277	323	409	77	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 oligomers.

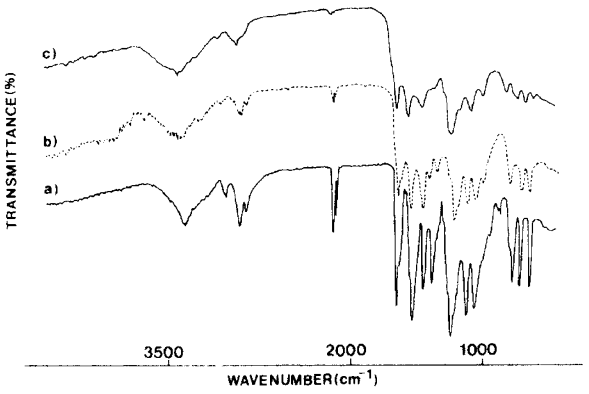


Figure 1. IR spectra of a) **4**, b) **4** cured at 330℃ for 30 min and c) **4** cured with Cu catalyst at 190℃ for 30 min.

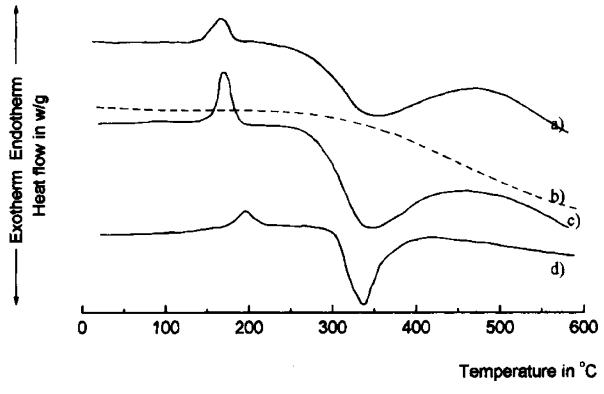


Figure 2. DSC thermograms of a) **2**, b) 2nd scanning of **2**, c) **4** and d) **6** at a heating rate of 10℃ min^{-1} in nitrogen.

drofuran (THF), acetone and ethanol. Incorporation of the rather polar dicyanovinyl groups into rigid aromatic backbones seems to result in a good solubility. A series of oligomers could be dissolved in THF and pyridine as well as DMF and NMP while they displayed virtually no solubilities in ethanol. The solubilities of oligomers **2**—**5** derived from alkyl-containing diamines were found to be better than aromatic derivative **6**, which may be mainly attributed to the flexibility of the chemical structure. They were even soluble in boiling THF and acetone.

The DSC data of dicyanovinyl end-capped oligomers were summarized in Table II. The DSC thermograms for the purified oligomers are presented in Figure 2. The endothermic transitions of oligomers **2**, **3**, and **4** appeared around 170℃ as a small peak, which was similar to the melting transitions obtained with a capillary method. DSC analysis also exhibited a broad and large exothermic transition starting near 290℃ and reaching the maximum intensity around 350℃ as shown in the Figures 2 and 3a. In the cases of alkyl-containing precursors **2**—**5**, the exotherms are presumably due to the crosslinking reaction of the dicyanovinyl group as well

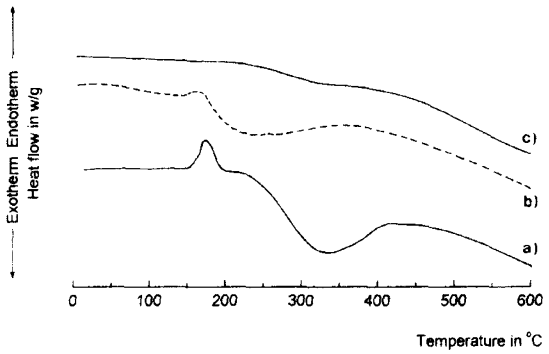


Figure 3. DSC thermograms of oligomers a) **3**, b) **3** cured with Cu catalyst at 190℃ and c) 2nd scanning of **3** cured with Cu catalyst in nitrogen.

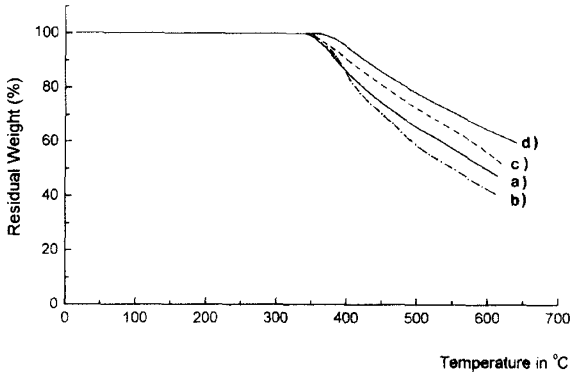


Figure 4. TGA thermogram of a) **2**, b) **4**, c) **5** and d) **6** at a heating rate of 10℃ min^{-1} under nitrogen.

as to a partial degradation, which was confirmed from their TGA thermograms. The initial and the maximum temperatures of the exotherms follow the similar trend regardless of the chemical structures of the backbone of oligomers. When the heated samples were cooled and rescanned in DSC analysis, the exothermic peaks were completely absent. Note that the cured samples exhibited only large exotherm above 400℃ assigned to their thermal degradation (Figure 1b). The increase in the areas of the exothermic peaks of precursors **2**—**5** compared with **6** may be due to partial alkyl chain scission as well as the curing of the dicyanovinyl groups.

The curing of dicyanovinyl group requires high temperature between 280—350℃ and without a catalyst, curing reaction did not proceed below 200℃. When the curing reaction was carried out with copper (II) acetylacetonate as a catalyst, the curing reaction undergoes at relatively low temperature 190℃ to give a crosslinked polymer as shown in DSC curve in Figures 1b. It was widely known that copper, zinc and cobalt catalysts were adopted for the curing of nitriles to intermolecular and other cyclization product.[19] The shallow exotherm in second scanning indicated that most of dicyanovinyl group underwent a curing reaction as shown in Figure 3c. It was also found that a weak nitriles absorption peak in the IR spectra was still present after 30 min reaction with copper catalyst at 190℃ in Figure 1c, therefore the residue was further cured at around 350℃ as shown in Figure 3c. But the nitrile peak at 2200 cm^{-1} decreased over the course of the reaction concomitant with crosslinking. After 1 h the nitrile absorption had totally vanished.

The TGA analyses of these precursors showed no loss in weight around 280—350℃ as shown in Figures 4 and 5. The solubilities of the cured samples at 330℃ for 30 min reduced apparently in the solvents such as DMF and NMP, which are good solvents for the uncured oligomers. This solubility decrease of the cured samples after heating seems to be due to crosslinking of dicyanovinyl group. The oligomers showed a gel fraction ranging 65—93%.

IR spectroscopy was used to follow the thermal curing of a sample on KBr salt plate. Figure 1b shows the IR spectral changes after the curing of oligomer **4**. The intensity of the nitrile band around 2210 cm^{-1} decreased apparently and peaks between 1500—1600 cm^{-1} broad-

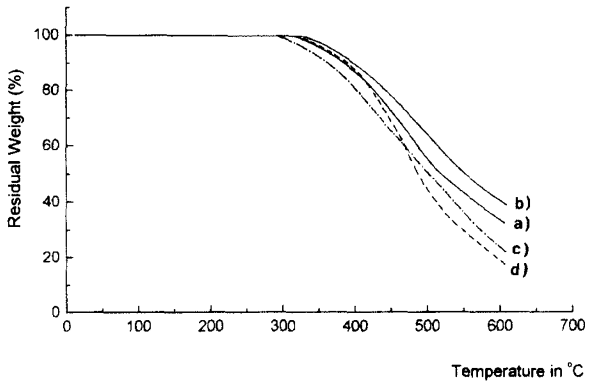


Figure 5. TGA thermograms of oligomers a) **3**, b) **3** cured at 330 ℃for 30 min, c) **3** in air and d) **7**.

ened. Similar IR spectrum of the cured sample with copper catalyst indicates that the copper catalyzed curing reaction proceeded at low temperature. The changes in IR spectra are consistent with the intermolecular crosslinking of most cyano groups and vinyl groups proposed previously. Dicyanovinyl compounds will form intermolecular and intramolecular addition compounds with polar nitrile groups and the electron deficient double bond upon heating. This mechanism is facilitated by the active hydrogen-containing function such as aromatic amines and phenols to form imine intermediates. The role of copper catalyst is primarily coordination, gathering cyano groups in proximity to form a ring.[3—5, 14]

The thermal stability data are listed in Table II and the TGA traces are exhibited in Figures 4 and 5. The initial decomposition temperature (IDT) and the % residue at 500℃ for oligomer **3** were 323℃ and 55%, respectively. The polymers with flexible alkyl units gave a residual weight varying from 55% to 70% at 500℃ at a heating rate of 10℃ min^{-1} in nitrogen and sustained a 10% weight loss around 380℃. Char yields of these thermally treated dicyanovinyl-containing precursors depended on their backbone structures. The precursor **6**, which contained aromatic units, has been found to be the most thermally stable and showed about 77% residual weight at 500℃. On the other hand, the flexible alkyl-containing oligomers do not show high stability because of low dissociation energy of alkyl moiety. As can be seen from the data in Table II, it is notable that the maxi-

mum residual weight of 55—70% was obtained in alkyl-containing diamine based precursors **2**—**5**. The initial temperature of weight loss has been found to be in the range of 320 to 345℃. The thermal stabilities of reactive oligomers are in the order of **5**>**4**>**2**>**3**, when comparing the initial weight loss, initial degradation temperature and % residue. When the thermal properties of cured polymers at 330℃ for 30 min were compared with those of the uncured precursors, the thermal stabilities of the cured samples were improved for all the polymers in Figure 5b.

Note that the cured resin of this investigation displayed lower thermal stabilities than rigid aromatic one and analogous polymers obtained from dicyanovinyl containing polyenaminonitriles and enaryloxynitriles. However, alkyl containing dicyanovinyl end-capped reactive oligomers still exhibit high thermal stability for the oligomeric structure.

Acknowledgments. This work was supported by Dankook University, Research Fund, 1998.

REFERENCES

1. G. Allen and J. C. Bevington, "Comprehensive Polymer Science", Vol. 5, Pegamon Press, Oxford, 1989, p 499.
2. H. J. Spinelli and F. W. Harris, "Reactive Oligomers", ACS Sym. Ser. 282, Am. Chem. Soc., Washington, D.C., 1985.
3. D. R. Robello and J. A. Moore, *Macromolecules*, **22**, 1084 (1989).
4. H. S. Moon, S. T. Kim, and M. S. Gong, *Makromol. Chem. Rapid Commun.*, **12**, 591 (1991).
5. P. G. Mehta and J. A. Moore, *Macromolecules*, **26**, 916 (1993).
6. P. G. Mehta, S. Y. Kim, and J. A. Moore, *Macromolecules*, **26**, 3504 (1993).
7. H. S. Moon, J. S. Kim, C. B. Kim, and M. S. Gong, *Polym. J.*, **25**, 193 (1993).
8. Y. S. Kim, B. G. Kim, and M. S. Gong, *Polym. J.*, **26**, 1910 (1994).
9. H. G. Cho, B. G. Kim, S. H. Choi, and M. S. Gong, *Macromolecules*, **26**, 6654 (1993).
10. J. C. Shin, T. M. Kim, and M. S. Gong, *Macromolecules*, **28**, 2212 (1995).
11. J. H. Ha, C. Kim, and M. S. Gong, *Polym. J.*, **27**, 536 (1995).
12. S. G. Kim, S. J. Lee, and M. S. Gong, *Macromolecules*, **28**, 5638 (1995).
13. J. H. Ha, S. J. Lee, and M. S. Gong, *Macromol. Chem. Phys.*, **196**, 4001 (1995).
14. J. A. Mikroyannidis, *J. Polym. Sci., Part A : Polym. Chem.*, **31**, 1771 (1993).
15. W. S. Park, D. S. Gil, and M. S. Gong, *Bull. Korean Chem. Soc.*, **19**, 291 (1998).
16. W. S. Park and M. S. Gong, *Macromol. Chem. Phys.*, **199**, 433 (1998).
17. H. Li, K. Y. Hsu, and T. C. Chang, *J. Polym. Sci., Part A : Polym. Chem.*, **29**, 1447 (1991).
18. V. V. Korshak and A. L. Rusanov, *J. Macro. Sci.-Revs. Macro. Chem.*, **C 21**, 275 (1982).
19. J. K. Stille, N. G. Nelb, and S. O. Norris, *Macromolecules*, **9**, 516 (1976).