Preparation and Thermal Properties of New Poly(Enaryloxynitriles)

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Abstract: New poly(eryloxynitriles) with a variety of chemical structure in the main chain were prepared by interfacial polymerization of p-bis(1-chloro-2,2-dicyanovinyl) benzene (2) with disodium salts of diphenol derivatives containing sulfide, sulfone, azo, acetal, imide, ether and ester group. The resulting polymers possess inherent viscosities of 0.12~0.45 dL/g and Mw in the range 9000~12000. They are easily soluble in polar aprotic solvents. The polymers derived from diphenols with alkyl, acetal and ester units were even soluble in common organic solvents such as THF and acetone. Brittle and hard films can be cast from DMF solutions. These polymers show a large exotherm in differential scanning calorimetry and undergo a curing reaction around 350℃ to form insoluble materials. Almost all the poly (eryloxynitriles) retained a 10% weight loss being recorded between 350~450℃ in nitrogen and displayed 70~85% residual weight at 500℃.

요 旨 : 주체에 다양한 화학 구조를 가진 새로운 poly(eryloxynitriles)을 p-bis(1-chloro-2,2-dicyanovinyl)benzene (2)과 sulfide, sulfone, azo, acetal, imide, ether 그리고 ester 결합을 포함한 더 까다로운 유도체의 나트륨염과 계면조합에 의하여 합성하였다. 생성된 중합체는 고유 점도가 0.12~0.45 dL/g이었으며 중량 평균 분자량은 9000~12000이었다. 그룹 중합체는 극성 반응성 용매에 매우 잘 녹았으며 alkyl, acetal, ester 결합이 가진 diphenol로부터 합성된 중합체는 THF나 acetone에도 매우 잘 녹았다. 그러나 중합체의 DMF 용액으로 부터 용매 증발 후 단단하고 부서지지 않는막이 형성되었다. 중합체들은 350℃에서 열정화 반응이 진행되어 불용성 물질이 형성되었다. 거의 모든 중합체가 350~450℃ 사이에서 10% 중량 감량을 유지하였으며, 500℃에서 잔량은 70~85%로서 열안정성을 보여주었다.

1. Introduction

A wide variety of polymers having aromatic repeating units have been developed in recent years because of impetus arising from the needs of thermally stable polymers for high performance materials that will withstand extremes of temperature.[1] Among them, arylates, which are a family of aromatic polyesters based on aromatic diols and aromatic dicarboxylic acids, have been under inten-
sive industrial application as a results of excellent physical and thermal properties.[2, 3] Poly(enaminonitriles) derived from aromatic diamines were reported to form thermally stable polymers caused by a cyclization and/or intermolecular cross-linking reaction of dicyanovinyl group.[4-9]

The reactivity of 2,2’-dicyanovinyl chloride is comparable with that of carboxylic acid chloride, in accord with the principle that oxygen and dicyanomethylidene (=C(CN)₂) are analogous in chemical reactivity.[10] Recently, new class of poly (enaryloxynitriles),[11-16] which are thermally curable and stable, have been prepared by a vinylic nucleophilic substitution reaction. At this point, poly (enaryloxynitriles) can be considered analogous to polyester.

Earlier experiment in our laboratory showed that poly(enaryloxynitriles) could be produced by interfacial polymerization of p-bis(1-chloro-2,2-dicyanovinyl) benzene (2) and aromatic diols such as bisphenol A, dihydroxy benzenes[11] and dihydroxy naphthalenes.[12] The resulting polymers showed an excellent thermal stability without evolution of volatile byproduct after thermal curing.

When the various aromatic diols were employed, polymerizability of disodium salts of aromatic diols depend upon the pKa value of corresponding diols.[17] The nucleophilic phenoxide anion possessing pKa value of 10 has an appreciable reactivity to dicyanovinyl chloride to give enaryloxynitriles.[18] The aromatic diols possessing a variety of chemical structure such as ketone, sulfide, sulfone, azo, acetal, imide, ether and ester in the diphenols, have been used as a monomer for the preparation of thermally stable poly(enaryloxynitriles).

In this report, we report the synthesis of new poly (enaryloxynitriles) incorporated various rigid or flexible diphenol derivatives and their thermal properties will be estimated.

2. Experimental

2.1. Chemicals and Instruments

1-Chloro-1-phenyl-2,2-dicyanoethene (1) and p-bis(1-chloro-2,2-dicyanovinyl)benzene (2) were prepared by the method previously reported by Moore and co-workers.[5] 4,4’-Biphenyl, 4,4’-sulphonyldiphenol, 4,4’-thiodiphenol, 4,4’-dihydroxybenzophenone, 2,2’-azidodiphenol and phenolphthalein (Aldrich Chem. Co.) were used after recrystallization from ethanol. 3,9-Di(p-hydroxyphenyl)-2,4, 8,10-tetraoxaspiro-[5,5]-undecone, bis[N-(4-hydroxyphenyl)] pyromellitic diimide, 1,2-bis(4-hydroxyphenoxy)ethane and 1,2-bis(4-hydroxybezoyloxy)ethane were prepared by the method previously reported. 1,2-Dichloroethane and dichloromethane were purified by conventional purification method. The solubility behaviors were tested by dissolving powdery polymer sample in excess solvent. Melting point was determined on a Aldrich Mel-Temp II melting points apparatus using capillary tubes and are uncorrected.

1H NMR spectra were recorded on a Varian EM-360A spectrometer. Fourier-transform infrared (FT-IR) spectra were taken on a Midac Model M-1200 spectrophotometer. Thermal analyses of polymers were carried out on a DuPont 2100 and a Mettler thermal analyzer. Gel-permeation chromatography (GPC) data were obtained with a Waters HPLC using three columns (10², 10³ and 10⁴ Å) in THF and calibrated with polystyrene standards. Inherent viscosities of polymer solution were measured in a Cannon-Ubbelohde viscometer at 25°C. The polymer solutions for the viscosity measurements were filtered through sintered glass filter. Elemental analyses were carried out with a Yanaco MT-3, CHN-analyzer.

2.2. Preparation of 1-Phenyl-1-[N-(4-Hydroxyphenyl)Phthalimido]-2,2-Dicyanoethene (3).

A solution of 2.39 g (10mmol) of N-(4-hydroxyphenyl)phthalimide and sodium hydroxide (0.48g, 12mmol) in 20mL of distilled water was transferred to the blender. A mixture of 1.89g (10mmol) of 1 in 20mL of 1,2-dichloroethane was poured, in one portion, into the blender. After the blender was stirred at full speed for 3min, organic layer was separated and the solvent was evaporat.
ed. The yellow solid product was filtered and recrystallized from acetonitrile and dried under vacuum. Similar procedures were applied to prepare other model compounds, p-bis(1-phenylazo-2,2'-dicyanovinyl)benzene (4) and 1,2-bis[4-(1-phenyl-2,2'-dicyanovinyl)oxy]phenoxoethane (5).

3: Yield 89%; mp 190°C; IR (KBr) 3120 (aromatic C-H), 2215 (C=O), 1750, 1735 (C=O), 1570 (C=C), 1320-1150 (C=O and C-N) cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 7.6 (m, 5 H, aromatic protons in 1), 7.6-7.2 (m, 5 H, phthalimide), 6.8-7.0 (m, 9 H, -O-Ph and -N-Ph-O-); Anal. Calcd for C\(_{30}\)H\(_{20}\)N\(_8\)
O\(_3\): C, 73.66; H, 3.32; N, 10.74. Found: C, 72.81; H, 3.91; N, 10.36.

4: Yield 86%; mp 238°C; IR (KBr) 3130-2985 (aromatic C-H), 2225 (C=O), 1580 (C=C), 1300-1120 (C-O) cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) 7.7 (s, 4 H, aromatic proton in 2), 7.1-6.8 (m, 10 H, 2 Ph-O-); \(^13\)C NMR (CDCl\(_3\)) 71.1 (\(=\)C(CN))\(_2\)), 111.5, 112.5 (-CN), 126.2, 127.3 128.2, 128.6, 129.6, 133.2 and 151.0 (aromatic C's) and 181.2 (\(=\)C-O-); Anal. Calcd for C\(_{30}\)H\(_{20}\)N\(_8\): C, 75.36; H, 3.38; N, 13.53. Found: C, 75.02; H, 3.31; N, 13.67.

5: Yield 92%; mp 227°C; IR (KBr) 3110-2865 (aromatic and aliphatic C-H), 2221 (C=O), 1580 (C=C), 1310-1150 (C-O) cm\(^{-1}\); \(^1\)H NMR (DMSO-d\(_6\)) \(\delta\) 7.5 (m, 10 H, 2 -Ph), 7.1-6.9 (2 d, 8 H, 2 -O-Ph-O-), 4.2 (s, 4 H, -CH\(_2\)CH\(_2\))-; Anal. Calcd for C\(_{30}\)H\(_{20}\)N\(_2\): C, 74.18; H, 4.00; N, 10.18. Found: C, 75.02; H, 3.82; N, 10.01

2. 3. Representative Polymerization of 2 with Disodium Salts of Aromatic Diols

Method 1: A solution of 1g (3.3mmol) of 2 in 20mL of 1,2-dichloroethane was transferred to the 100mL of stainless steel jar of blender. A mixture of disodium salts of 4,4'-biphenol (0.76g, 3.3mmol) and 4.5mg (0.17mmol) of tetra-n-butyl ammonium chloride in 20mL of water was added to the blender at full speed for 3min. The polymer was collected by filtration and washed with distilled water. The polymer was dried and reprecipitated from DMF into methanol. Similar procedures were applied to prepare other poly(aryloxyxynitriles) derived from other diols.

Method 2: A solution of 2 (1g, 3.3mmol) in 10mL of NMP was added to the mixture of disodium salts of 4,4'-biphenol (0.76g, 3.3mmol) in a solution of 10mL of NMP and 3mL of water under nitrogen with vigorous stirring. The temperature was raised to 60°C and maintained for 2hr. The yellow solution was allowed to cool and poured into a large amount of water to precipitate the polymer, which was reprecipitated from NMP into methanol. A greenish polymer was finally obtained in 87% yield.

6: Yield 87%; IR (KBr) 3120-2980 (C-H), 2218 (C=O), 1620 (C-H), 1576 (C=C), 1280-1180 (C-O) cm\(^{-1}\); \(^1\)H NMR (DMSO-d\(_6\)) \(\delta\) 7.5 (m, 4 H, aromatic protons in 2), 7.2-6.8 (m, 8 H, 2 -O-Ph-O-); Anal. Calcd for C\(_{30}\)H\(_{20}\)N\(_2\): C, 74.18; H, 4.00; N, 10.18. Found: C, 75.02; H, 3.82; N, 10.01.

7: Yield 98%; IR (KBr) 3140-2975 (C-H), 2218 (C=O), 1732 (C=O), 1600 (C-H), 1580 (C=C), 1300-1060 (C-O) cm\(^{-1}\); \(^1\)H NMR (DMSO-d\(_6\)) \(\delta\) 7.5 (s, 4 H, aromatic protons in 2), 7.8-7.1 (m, 4 H, -CO-Ph-O-), 7.2-6.8 (m, 8 H, 2 -O-Ph-O-); Anal. Calcd for C\(_{30}\)H\(_{20}\)N\(_2\): C, 75.00; H, 2.94; N, 10.29. Found: C, 75.22; H, 2.82; N, 10.01.

8: Yield 80%; IR (KBr) 3100-2970 (br, C-H), 2231 (C=N), 1736 (C=O), 1574 (C=C), 1310-1050 (C-O) cm\(^{-1}\); \(^1\)H NMR (DMSO-d\(_6\)) \(\delta\) 7.8-6.9 (m, 8 H, -Ph-CO-Ph-), 7.6 (s, 4 H, aromatic protons in 2).

9: Yield 93%; IR (KBr) 3061-2980 (C-H), 2231 (C=N), 1570 (C=C), 1331-1012 (C=S and C-O) cm\(^{-1}\); \(^1\)H NMR (DMSO-d\(_6\)) \(\delta\) 7.6 (s, 4 H, aromatic protons in 2), 7.3-6.9 (m, 8 H, 2 -Ph-S-Ph-); Anal. Calcd for C\(_{30}\)H\(_{20}\)N\(_2\): C, 75.73; H, 2.91; N, 13.59. Found: C, 75.03; H, 2.84; N, 13.11.

11: Yield 97%; IR (KBr) 3075-2985 (C-H), 2225 (C=N), 1652 (N=N), 1570 (C=C), 1290-1020 (C

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-O and C-N) cm⁻¹; 'H NMR (DMSO-d₆)  δ 7.6 (s, 4 H, aromatic protons in 2), 7.4-6.9 (m, 8 H, 2 -Ph-
N=N-Ph-).

12: Yield 98%; IR (KBr) 3145-2975 (C-H), 2220
(C=N), 1612 (C-H), 1580 (C=C), 1310-1120 (C-
O) cm⁻¹; 'H NMR (DMSO-d₆+CDCl₃) δ 7.6 (s, 4 H, aromatic protons in 2), 7.2-6.9 (m, 8 H, 2 -O-
Ph-), 5.8 (s, 2 H, 2 -Ph-CH), 3.9 (s, 8 H, 4 -CH₂-
O-); Anal. Calcd for C₂₃H₂₃N₂O₆: C, 69.47; H, 3.86;
N, 9.82. Found: C, 68.86; H, 3.82; N, 9.62.

13: Yield 51%; IR (KBr) 3140 (C-H), 2223 (C=
N), 1765, 1742 (C=O), 1580 (C=C), 1310-1110
(C-O) cm⁻¹; 'H NMR (DMSO-d₆+CDCl₃) δ 8.0 (s,
2 H, aromatic protons in pyromellitic diimide), 7.6
(s, 4 H, aromatic protons in 2), 7.2-6.8 (m, 8 H,
2 -O-Ph-N-), 5.8 (s, 2 H, 2 -Ph-CH), 3.9 (s, 8 H,
4 -CH₂-O-); Anal. Calcd for C₂₇H₂₇N₂O₆: C, 69.00;
H, 2.23; N, 13.42. Found: C, 68.86; H, 3.82; N, 9.62.

14: Yield 90%; IR (KBr) 3120-2910 (C-H), 2218
(C=N), 1575 (C=C), 1360-1145 (C-O) cm⁻¹; 'H
NMR (DMSO-d₆+CDCl₃) δ 7.5 (br, 4 H, aromatic
protons in 2), 7.1-6.9 (br, 8 H, 2 -O-Ph-O-), 3.8
(br, 4 H, -CH₂CH₂-); Anal. Calcd for C₂₇H₂₇N₂O₆:
C, 72.58; H, 3.22; N, 11.29. Found: C, 71.98; H, 3.
16; N, 11.15.

3. Results and Discussion

The reactivity of phenoxide anions to dicy-
anovinyl chloride was dependent upon the pKa
value of the corresponding phenol derivatives. The
larger the value of the pKa, the greater is the ten-
dency of the phenoxide anion to react with the
dicyanovinyl compounds. p-Methoxy- or p-methyl
phenoxide anion is highly effective for the
nucleophilic vinylic substitution reaction because of
electron donating substituent, thereby enhancing
the ability of phenoxide anion to serve as a good
nucleophile. But the electron withdrawing substi-
tuents such as ester, ketone and sulfone group deacti-
vated reactivity of phenoxide anion, therefore the
diphenols, of which one of the hydroxyl group once
reacted with dicyanovinyl chloride, react more slow-
ly than that of phenol itself to other dicyanovinyl
chloride.[17, 18]

Synthesis of model compounds were attempted
before preparation of polymers to demonstrate the
feasibility of the polymer formation and to obtain a
model enaryloxyanilines for comparison with the
polymers. Three different model compounds, 1-
phenyl-1-[N-(4-hydroxyphenyl)phthalimido]-2,2-
dicyanoethene (3), p-bis(1-phenoxy-2,2-dicyano-
vinyl)benzene (4) and 1,2-bis[4-(1-phenyl-2,2-
dicyanoxyloxy) phenoxy]ethane(5) were pre-
pared in high conversion by reacting the corre-
sponding aryloxy anions with 1-chloro-1-phenyl-
2,2-dicyanoethene (1) or p-bis(1-chloro-2,2-dicya-
novinyl)benzene (2) under two phase solvent
system as shown in Scheme 1. The polymerization

of 2 with disodium salts of various diphenol derivatives were carried out interfacial polymerization techniques based on representative procedures by using phase transfer catalyst described in the literature.[19] The various rigid aromatic diols such as 4,4'-biphenol, phenolphthalein, 4,4'-sulfonyl diphenol, 4,4'-thiodiphenol, 4,4'-dihydroxybenzophenone, 2,2'-azodiphenol and bis[N-(4-hydroxyphenyl)] pyromellitic diimide were selected and their disodium salts were readily polymerized with 2 to give the corresponding poly (enarylxylnitriles) 6-11 and 13 in high conversion. 3,9-Di-p-hydroxyphenyl-2,4,8,10-tetraoxaspiro-[5,5]-undecane, 1,2-bis(4-hydroxyphenoxo) ethane and 1,2-bis(4-hydroxybenzoyloxy)ethane were also effective for the polymerization with 2. Equimolar quantity of monomer 2 in 1,2-dichloethane and disodium salts of aromatic diol in water were polymerized at room temperature in the presence of tetra-n-butylammonium chloride as a phase transfer agent. The stirred mixture turned to yellow cake within 3 min. Another method of polymerization was adopted for the polymerization of 4,4'-biphenol with 2. The homogeneous solution polymerization proceeded in NMP at 60°C. The conditions and results of polymerizations were summarized in Table 1. When the polymer 7 and 14 were compared with model compounds resembling the repeating unit of polymer, the spectral data of polymers corresponded to the model compounds and consistent with their assigned chemical structure. In NMR spectra of polymers 6 and 12 and model compound 4, the phenyl protons in fragment of 2 appeared at 7.6 ppm,

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Diolsa</th>
<th>Time(min)</th>
<th>Temp.(°C)</th>
<th>Yield(%)</th>
<th>η·cm⁻¹</th>
<th>Mw¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>BP</td>
<td>3</td>
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<td>60</td>
<td>92</td>
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</tr>
<tr>
<td>7</td>
<td>PP</td>
<td>3</td>
<td>25</td>
<td>98</td>
<td>0.13</td>
<td>9600</td>
</tr>
<tr>
<td>8</td>
<td>DBP</td>
<td>3</td>
<td>25</td>
<td>80</td>
<td>0.14</td>
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<tr>
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<td>TDP</td>
<td>3</td>
<td>25</td>
<td>93</td>
<td>0.26</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>SDP</td>
<td>3</td>
<td>25</td>
<td>83</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td>11d</td>
<td>ADP</td>
<td>3</td>
<td>25</td>
<td>97</td>
<td>0.38</td>
<td>11200</td>
</tr>
<tr>
<td>12</td>
<td>DTU</td>
<td>3</td>
<td>25</td>
<td>98</td>
<td>0.12</td>
<td>10200</td>
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<tr>
<td>13</td>
<td>BHP</td>
<td>3</td>
<td>25</td>
<td>51</td>
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<td>BHE</td>
<td>3</td>
<td>25</td>
<td>90</td>
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<tr>
<td>15</td>
<td>BHBE</td>
<td>3</td>
<td>25</td>
<td>91</td>
<td>0.12</td>
<td>10500</td>
</tr>
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a : BP, 4,4'-diphenol; PP, phenolphthalein; DBP, 4,4'-dihydroxy benzophenone; TDP, 4,4'-thiodiphenol; SDP, 4,4'-sulfonyl diphenol; ADP, 2,2'-azodiphenol; DTU, 3,9-di(p-hydroxyphenyl)-2,4,8,10-tetraoxaspiro-[5,5]-undecane; BHP, bis[N-(4-hydroxy phenyl)] pyromellitic diimide; BHE, bis-1,2-(4-hydroxyphenoxo)ethane; BHBE, bis-1,2-(4-hydroxybenzoyloxy)ethane.

b : Viscosities were measured in DMF solution in 1 g/dL at 25°C.

c : Molecular weights were measured from the soluble portion in THF.

d : 2,2'-Azodiphenol contained ortho-positioned aromatic diol was used.

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while the phenyl protons of fragment of diphenol or phenol are shown at 6.8-7.2 ppm as shown in Figure 1. In case of model compound 4, the presence of a peak at 180.5 ppm of $^{13}C$ NMR attributable to enaryloxy linkage indicate that the polynaryloxyranitiles was prepared. Infrared spectra of the model compound 4 and polymer 6 showed absorption bands at 3120, and 2218cm$^{-1}$ assignable to C-H and C=O, as well as two characteristic bands of C=C and C-O at 1575 and 1310 ~ 1150cm$^{-1}$, respectively.

Poly(ernaryloxyxynitiles) were soluble in polar, aprotic solvents such as DMF, NMP, DMAC and DMSO. Polymers 7, 12, 14 and 15 were even soluble in THF and polymer 8 and 11 were soluble in acetonitrile and acetone. Anyhow they showed better solubility due to the existence of flexible alkyl or alkanoid ring along the polymer main chain. The polymers derived from diphensols, which contained ketone, sulfide,azo and sulfone group, showed more solubility in polar amide-type solvents such as DMF and NMP than those of dihydroxy benzene and dihydroxy napththalene formerly synthesized.[11, 12]

Inherent viscosities of polymers obtained from DMF solution was between 0.12 and 0.42 dL/g. The $M_w$ and $M_n$ were in the range 3500 ~ 7200 and 9000 ~ 12000. These are not high molecular weight judging from the viscosities and GPC data. Brittle and hard films were cast from the polymer solution in DMF after evaporation of solvent. To find suitable conditions for preparation of poly(ernaryloxyxynitiles) having high molecular weights, further study on the effects of monomer concentration, organic medium and ratio of two monomers are needed in detail. The polymer obtained from solution polymerization in NMP exhibited higher molecular weight than that of interfacial polymerization.

All the poly(ernaryloxyxynitiles) in this work were characterized by DSC measurements with a heating rate of 10°C/min. Most polymers show a noticeable glass transition temperature in differential scanning calorimetry. On the contrary, they do not exhibit the endothermic temperature attributable to the melting of polymer. Poly(ernaryloxyxynitiles) with rigid aromatic moiety retain a more rigid backbone, and this effect may partially result in a high melting temperature. Thus the resulting polymers had no melting endotherm, but showed an exothermic peak near 350°C. In the case of most polymers, the temperature required to obtain sufficient intermolecular mobility may be higher than the curing temperature of the polymer. But the polymers 14 and 15 showed endotherm at 314°C and 322°C,
Table 2. Thermal Properties of Poly(ennaryloxylnitriles) Obtained from 2 and Various Aromatic Diols

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Diols</th>
<th>Tg (°C)</th>
<th>Endo (°C)</th>
<th>Exo (°C)</th>
<th>10% Wt. Loss</th>
<th>Residual Weight (%)</th>
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<tr>
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<td>350</td>
<td>395</td>
<td>89.1</td>
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</tr>
<tr>
<td>8</td>
<td>DBP</td>
<td>312</td>
<td>220, 340</td>
<td>402</td>
<td>90.5</td>
<td>77.2</td>
</tr>
<tr>
<td>9</td>
<td>DMP</td>
<td>210</td>
<td>245, 335</td>
<td>450</td>
<td>92.5</td>
<td>81.9</td>
</tr>
<tr>
<td>10</td>
<td>SDP</td>
<td>239</td>
<td>340</td>
<td>435</td>
<td>93.6</td>
<td>87.9</td>
</tr>
<tr>
<td>11</td>
<td>ADP</td>
<td></td>
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<td>85.2</td>
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</tr>
<tr>
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<td>DTU</td>
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<td>340</td>
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<td>68.4</td>
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<td>240, 340</td>
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<td>314</td>
<td>355</td>
<td>393</td>
<td>89.0</td>
<td>81.0</td>
</tr>
<tr>
<td>15</td>
<td>BHBE</td>
<td>230</td>
<td>322</td>
<td>361</td>
<td>85.1</td>
<td>70.1</td>
</tr>
</tbody>
</table>

respectively, due to the existence of moderately flexible alkyl unit. The DSC measurements of the poly(ennaryloxylnitriles) 6, 7, 11, 14 and 15 display a broad exotherm starting 290°C and reaching maximum intensity near 350°C. Anyway, this exothermic peak was completely absent, when the sample was cooled and rescanned. When the polymers were heated around 340°C, the polymers were no longer soluble in the solvents such as DMF and NMP. On the other hand, two consecutive exotherms appeared in the case of polymers 8 and 9. When the sample of polymer 8 was annealed, the first exothermic peak at 220°C disappeared as shown in Figure 2(c). No changes of absorption bands were detected upon comparison with the untreated polymers in its IR spectrum. Therefore this may be due to the phase change attributable to the crystallization. Similar behavior was also found in the case of polymer 13 containing more rigid aromatic imide unit. When a sample of polymer 6 was heated around 340°C, its IR spectrum changed gradually as it was heated. The nitrile band at 2220cm⁻¹ decreased apparently and also peak at 1580~1600cm⁻¹ broadened. At the same time, a new band around 3400cm⁻¹ in its IR spectrum was consistent with an imine function generated by the cyclization reaction.[4, 5, 6, 8] It was reported that among several possible curing reaction, intramolecular cyclization reaction was partly considered as well as the intermolecular cross-linking of dicyanovinyl group. In case of poly(ennaryloxylnitriles), the chemical pathways of curing of dicyanovinyl group have not been clearly elucidated. According to the experiments on the poly(ennaminonitriles) reported by Moore and Coworkers, it might happen that intramolecular cyclization or cross-linking of the dicyanovinyl group occurred during heating at the temperature of its exotherm.[5, 8] More experiments on model compounds are required to explicate curing mechanism. The insolvibility of the cured polymers after heating may be due to the stiffness of the rearranged chain or cross-linking of dicyanovinyl group.

The thermal stability of the poly(ennaryloxylnitriles) was characterized by means of thermogravimetical analysis conducted at a heating rate of 10°C/min in nitrogen. Figure 3 and Table II show TGA curve and thermal data of polymer 6~15. From the values compiled in Table III for the thermal stability, it can be concluded that the thermal stability does not depend directly on the structure of diphenol derivatives. Table II also shows the residual weight of poly(ennaryloxylnitriles) at 500°C under nitrogen. As it could be expected, the lowest values correspond to the polymers containing alkyl unit in the case of polymer 12. But the TGA data displayed 70~85%
residual weight at 500°C and revealed a good thermal stability for polymers 14 and 15 containing aliphatic segments. The thermal decomposition of most polymers may began at 350°C. Thermogravimetric analysis indicates a 10% loss in weight between 350 and 450°C.

4. Conclusions

Poly(enaryloxynitriles) with various chemical structure were synthesized from difunctional dicyanovinyl chloride p-bis(1-chloro-2,2-dicyanovinyl)benzene (2) and disodium salts of diphenol derivatives by interfacial polymerization. The polymers with alkyl or unsymmetrical ester units were soluble in common organic solvents such as THF and acetone as well as polar aprotic solvents such as DMF, DMSO, DMAC and NMP. They show a large exotherm in DSC scan and undergo a curing reaction around 350°C to form insoluble material. Moreover, thermally curable and stable polymers were formed to give 70~85% residual weight at 500°C in nitrogen. Extention to the synthesis of poly (enaryloxynitriles) by solution polymerization to enhance the molecular weight are needed and now in progress.

References