

## Preparation of Polyesters Containing Enaryloxynitrile Moiety and Their Thermal Properties

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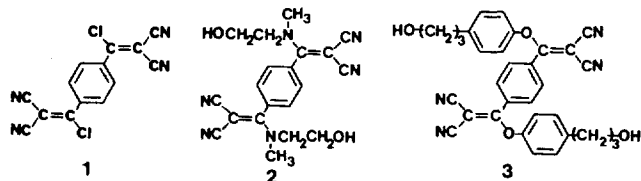
Received August 16, 1994

Polyesters containing enaryloxynitriles moiety have been newly prepared from *p*-bis[1-[4-(3-hydroxypropyl)phenoxy]-2,2-dicyanovinyl]benzene (**3**) and common diols with terephthaloyl chloride. The copolyesters have a good solubility in common organic solvents as well as polar aprotic solvents. They undergo a curing reaction at around 350 °C and show a 50-60% of residual weight at 500 °C. The enhanced thermal stabilities were due to the intramolecular cyclization or intermolecular cross-linking reaction of the dicyanovinyl group incorporated into polyester by copolymerization.

### Introduction

The development of new polymers that can be thermally cured to heat stable polymers has been the subject of considerable study in recent years. One of the promising method of synthesis of such polymer is an introduction of thermally curable function into polymer chain.<sup>1,2</sup> Dicyanovinyl group has been recently considered to be one of the functional groups undergoing a thermally induced crosslinking to a cured polymer.<sup>3-8</sup> The introduction of dicyanovinyl group as an enamionitriles or enaryloxynitriles moiety enhances the thermal stability through the curing in the case of polyurethanes<sup>9-10</sup> and polyesters.<sup>11</sup> These systems are of special interest since the enamionitriles or enaryloxynitriles groups were readily incorporated into polymer backbone by copolymerization.

Diol compounds containing enamionitriles or enaryloxynitriles units, *p*-bis[N-methyl-(N-hydroxyethyl)amino]-2,2-dicyanovinyl]benzene (**2**) and *p*-bis[1-[4-(3-hydroxypropyl)phenoxy]-2,2-dicyanovinyl]benzene (**3**) were readily prepared and they were polymerized to give polyurethanes and polyesters by condensation reaction.



In the present paper, we report a successful synthesis of new polyesters and copolyesters containing dicyanovinyl group as enaryloxynitriles units by reacting common diols and **3** with terephthaloyl chloride and their thermal properties.

### Experimental

Dicyanovinyl compound, *p*-bis(1-chloro-2,2-dicyanovinyl)benzene (**1**) was prepared by the method previously reported.<sup>3</sup> Ethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, 1,8-octanediol, hydroquinone and Bis-phenol A were purified by the conventional method. Terephthaloyl chloride

was purified by sublimation under reduced pressure. The polymerization solvent, THF, were purified by drying with calcium hydride and distillation over sodium metal.

NMR spectra were recorded on a Varian EM-360A spectrometer and FT-IR spectra were obtained from Midac spectrophotometer. The GPC data were obtained from Waters HPLC using three columns ( $\mu$ -Styragel 10<sup>2</sup>, 10<sup>3</sup> and 10<sup>4</sup> Å) in THF and calibrated with polystyrene standards.

Thermal analysis were performed with a Dupont 2100 and Mettler thermal analyzer. The elemental analyses were carried out by Yanaco MT-3 CHN-Analyzer.

**Preparation of *p*-Bis[1-[4-(3-hydroxypropyl)phenoxy]-2,2-dicyanovinyl]benzene (**3**).** 3-(4-Hydroxyphenyl)-1-propanol (1.00 g, 6.6 mmol) was dissolved in a solution of 0.30 g (7.5 mmol) of sodium hydroxide in 20 ml of water. The resulting solution was transferred to the jar of stainless steel blender and to it was added, in one portion, 1.00 g (3.3 mmol) of **1** in 20 ml of methylene chloride. The reaction mixture was stirred at full speed for 3 min and the solid product was filtered and recrystallized from isopropyl alcohol to give 1.20 g of yellow crystal.

**3:** Yield 86.7%; mp. 216 °C (uncorrected); FT-IR (KBr): 3500 (O-H), 3120-2990 (aromatic C-H), 2980-2865 (C-H), 2232 (C≡N), 1575 (C=C), 1250-1120 (C-O) cm<sup>-1</sup>; <sup>1</sup>H NMR (DMSO-d<sub>6</sub> + CDCl<sub>3</sub>):  $\delta$  7.7 (s, 4H, aromatic H's in **3**), 7.2 (m, 8H, 2-O-Ph-CH<sub>2</sub>-), 3.8 (br, 2H, 2-OH), 3.6 (t, 4H, 2-CH<sub>2</sub>-OH), 2.2 (t, 4H, 2-Ph-CH<sub>2</sub>-), 1.8 (m, 4H, 2-Ph-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH). Anal. Calcd for (C<sub>32</sub>H<sub>26</sub>N<sub>4</sub>O<sub>4</sub>): C, 72.45; H, 4.90; N, 10.57. Found: C, 72.08; H, 4.69; N, 10.24.

**Preparation of Model Compound, *p*-Bis[1-[4-(3-benzoyloxypropyl)phenoxy]-2,2-dicyanovinyl]benzene (**4**).** A mixture of **3** (2.00 g, 3.8 mmol) and triethylamine (1 g, 10 mmol) in 20 ml of THF was placed in a 100 ml of three-necked flask equipped with a dropping funnel, a condenser and a nitrogen inlet. After 1.06 g (7.6 mmol) of benzoyl chloride in 10 ml of freshly distilled THF was added to the reaction flask for 1 hr with a flush of nitrogen, the reaction mixture was stirred for 8 hr. The temperature was raised to 70 °C and maintained for an additional 24 hr. The pale yellow solution was evaporated and the solid product was washed with distilled water and recrystallized in isopropyl alcohol to give 2.25 g of the model compound **4**.

**4:** Yield 80.1%; mp. 150 °C (uncorrected); FT-IR (KBr): 3125-2985 (aromatic C-H), 2980-2860 (C-H), 2225 (C≡N), 1740 (C=O), 1575 (C=C), 1250-1110 (C-O)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (DMSO- $d_6$ + $\text{CDCl}_3$ ):  $\delta$  7.5 (s, 4H, -Ph-), 7.8-7.2 (m, 10H, 2 Ph-CO-), 6.9 (s, 8H, 2 -Ph-O-), 3.9 (m, 4H, 2 -CH $_2$ -O-), 2.3 (m, 4H, 2 -O-Ph-CH $_2$ -), 1.8 (m, 4H, 2-CH $_2$ CH $_2$ CH $_2$ -). Anal. Calcd for (C $_{46}$ H $_{34}$ N $_4$ O $_6$ ): C, 74.80; H, 4.60; N, 7.59. Found: C, 75.01; H, 4.51; N, 7.42.

**Representative Polymerization of 3 and Common diol With Terephthaloyl chloride.** Terephthaloyl chloride (0.80 g, 3.9 mmol) dissolved in 10 ml of THF was added dropwise to a solution of ethylene glycol and 3 (total amount; 3.9 mmol of the two component) in 20 ml of THF and 1.00 g of triethylamine. The reaction mixture was stirred vigorously at room temperature was raised to 70 °C, and maintained for an additional 24 hr.

When the reaction was complete, a viscosity increase was observed and the precipitation of triethyl ammonium chloride occurred. After the solid powder was filtered off, 300 ml of *n*-hexane was added. The polymer was isolated by filtration and washed with 0.1 N NaOH solution and distilled water. The polymers were purified by reprecipitation from THF solution into *n*-hexane.

The similar synthetic procedures were applied to the preparation of other polymers 5-16 with different content of 3.

**5:** Yield 91%; IR (KBr): 3120-2980 (aromatic C-H), 2975-2850 (C-H), 2234 (C≡N), 1752 (C=O), 1578 (C=C), 1320-1120 (C-O)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (DMSO- $d_6$ + $\text{CDCl}_3$ ):  $\delta$  7.8-7.4 (br, 8H, aromatic H's in 3 and terephthalate), 6.9 (br, 8H, 2 -O-Ph-), 4.0 (m, 4H, 2-CH $_2$ CH $_2$ CH $_2$ -O-), 2.3 (m, 4H, 2 -O-Ph-CH $_2$ CH $_2$ CH $_2$ -), 1.5 (m, 4H, 2 -CH $_2$ CH $_2$ CH $_2$ -).

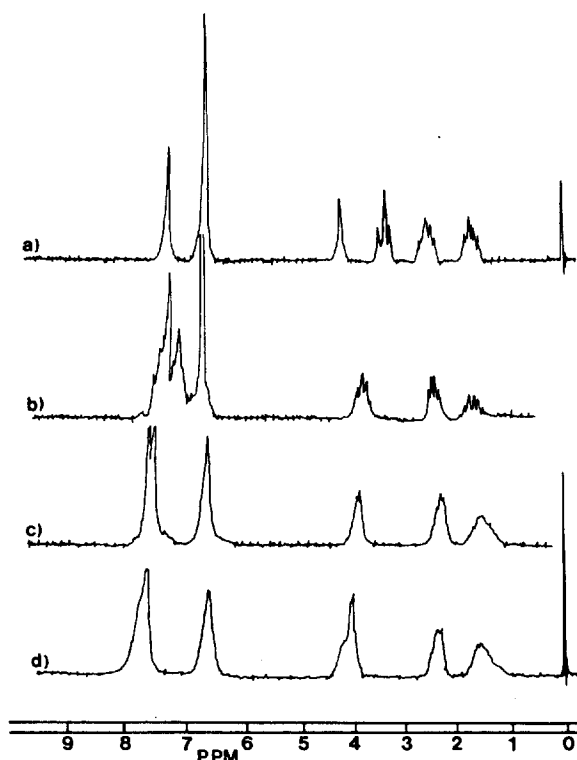
**8:** Yield 83%; IR (KBr): 3214-2975 (aromatic C-H), 2970-2845 (C-H), 2235 (C≡N), 1750 (C=O), 1575 (C=C), 1310-1130 (C-O)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (DMSO- $d_6$ + $\text{CDCl}_3$ ):  $\delta$  7.8-7.5 (br, m, 6H, aromatic H's in terephthalate and 1/2 3), 6.9 (br, m, 4H, 1/2 2 -Ph-O-), 4.2-4.0 (m, 4H, 1/2-OCH $_2$ CH $_2$ O-) and 1/2 2 -CH $_2$ CH $_2$ CH $_2$ -O-), 2.4 (m, 2H, 1/2 2 -PhCH $_2$ CH $_2$ CH $_2$ -), 1.8 (m, 2H, 1/2 2 -PhCH $_2$ CH $_2$ CH $_2$ -).

**12:** Yield 84%; IR (KBr): 3210-2985 (aromatic C-H), 2980-2830 (C-H), 2232 (C≡N), 1748 (C=O), 1580 (C=C), 1300-1110 (C-O)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (DMSO- $d_6$ + $\text{CDCl}_3$ ):  $\delta$  7.8-7.5 (br, m, 6H, aromatic H's in terephthalate and 1/2 3), 6.9 (br, m, 4H, 1/2 2 -Ph-O-), 4.2-4.0 (m, 4H, 1/2-OCH $_2$ CH $_2$ O-) and 1/2 2 -CH $_2$ CH $_2$ CH $_2$ -O-), 2.4 (m, 2H, 1/2 2 -PhCH $_2$ CH $_2$ CH $_2$ -), 1.8 (m, 4H, 1/2 2 -PhCH $_2$ CH $_2$ CH $_2$ - and 1/2 -OCH $_2$ CH $_2$ CH $_2$ CH $_2$ O-).

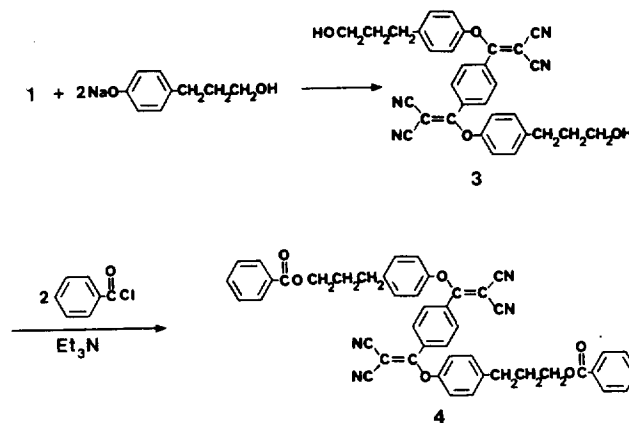
**15:** Yield 83%; IR (KBr): 3210-2850 (C-H), 2232 (C≡N), 1748 (C=O), 1578 (C=C), 1310-1120 (C-O)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (DMSO- $d_6$ + $\text{CDCl}_3$ ):  $\delta$  7.8-7.4 (br, 6H, aromatic H's in terephthalate and 1/2 3), 6.9 (br, 6H, 1/2 2 -Ph-O- and 1/2 -O-Ph-O-), 4.0 (m, 2H, 1/2 2 -PhCH $_2$ CH $_2$ CH $_2$ -O-), 2.4 (m, 2H, 1/2 2 -PhCH $_2$ CH $_2$ CH $_2$ -), 1.5 (m, 2H, 1/2 2 -PhCH $_2$ CH $_2$ CH $_2$ -).

## Results and Discussion

Diol monomer containing enaryloxynitriles unit, *p*-bis[1-[4-(3-hydroxypropyl)phenoxy]-2,2-dicyanovinyl] benzene (3) was prepared from the reaction of *p*-bis(1-chloro-2,2-dicyanovinyl)benzene (1) with sodium salt of 3-(4-hydroxyphenyl)-1-propanol in methylene chloride/water two phase solvent sys-



**Figure 1.** NMR spectra of a) 3, b) model compound 4, c) polyester 5 (3: EG=1:0) and d) 8 (3: EG=1:1).

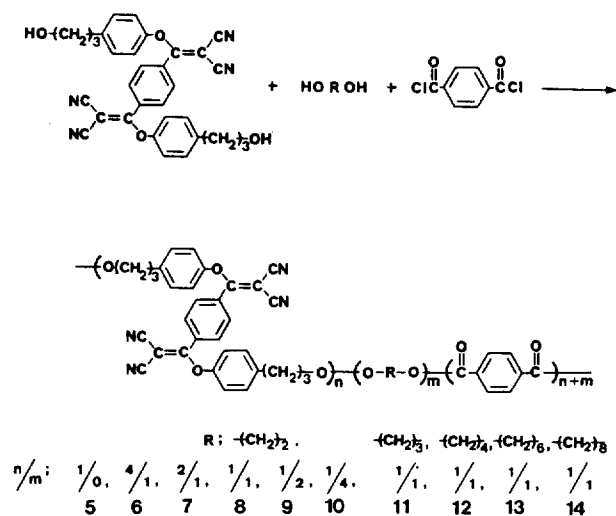


**Scheme 1.**

tem.

The reactivity of phenoxide anions toward dicyanovinyl chloride was determined according to the  $pK_a$  value of the corresponding phenol derivative. *p*-Methylphenol and phenol itself possess a  $pK_a$  value of 10.2 and 10.0, respectively. Anionic *p*-alkyl phenoxide can react rapidly with 1 by nucleophilic vinylic substitution due to electron donation of alkyl group at para-position. The reaction was almost complete within 3 min at room temperature. The product 3 was analyzed by the spectroscopies and identified to be enaryloxynitriles with terminal hydroxyl group (Figure 1(a)).

The model compound was prepared for demonstrating the feasibility of polymer formation and comparison with the polymers. *p*-Bis[1-[4-(3-benzoyloxypropyl)phenoxy]-2,2-dicyano-



Scheme 2.

Table 1. Results of Polymerization of 3 and various Diols with Terephthaloyl Chloride

Polymer	Diol*	3 : Diol	Conversion (%)	Mn	Mw
5	—	1 : 0	91	3700	9500
6	EG	4 : 1	71	3400	13500
7	EG	2 : 1	76	3200	11500
8	EG	1 : 1	83	3500	7000
9	EG	1 : 2	81	4300	9650
10	EG	1 : 4	69	4100	9500
11	PD	1 : 1	81	3500	9300
12	BD	1 : 1	84	4500	6400
13	HD	1 : 1	84	5300	15000
14	OD	1 : 1	79	3800	9500
15	HQ	1 : 1	83	4000	7600
16	BPA	1 : 1	72	7000	10000

\*EG, ethylene glycol; PD, 1,3-propanediol; BD, 1,4-butanediol; HD, 1,6-Hexanediol; OD, 1,8-octanediol; HQ, hydroquinone; BPA, bisphenol A.

vinyl] benzene (4) was obtained by reacting 3 with benzoyl chloride in the presence of triethylamine in 80% yield according to Scheme 1.

In the IR spectrum, the model compound exhibited bands at 2231, 1758, 1583 and 1300-1120  $\text{cm}^{-1}$  assignable to  $\text{C}\equiv\text{N}$ ,  $\text{C}=\text{O}$ ,  $\text{C}=\text{C}$ , and  $\text{C}-\text{O}$ , respectively. In the NMR spectrum, the aromatic protons of fragment of 3 and benzoate appeared at 7.4-7.8 ppm, while the aromatic protons in phenoxy group appeared at 6.9 ppm. on the bases of these results, compound 4 was identified as the ester compound containing enaryloxynitriles moiety.

The polymerizations of terephthaloyl chloride with ethylene glycol and different amount of 3 were carried out. Polyesters and copolyesters were prepared with 3 and ethylene glycol in the following mole ratio: 0/1, 1/4, 1/2, 1/1, 2/1, 4/1 and 1/0. Copolyesters were also obtained from 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, 1,8-octanediol, hydro-

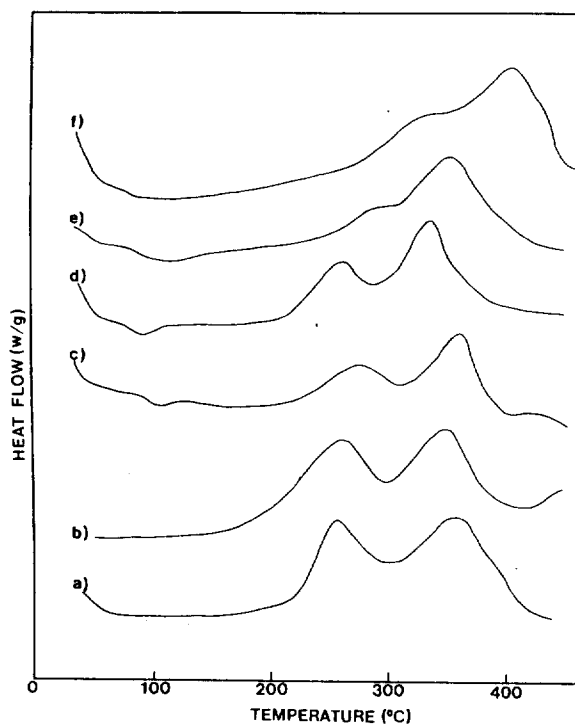


Figure 2. DSC Thermograms of polyesters, a) 5, b) 6, c) 7, d) 8, e) 9 and f) 10 obtained from 3 and ethylene glycol with terephthaloyl chloride at a heating rate of 10  $^{\circ}\text{C}/\text{min}$  in nitrogen.

quinone and Bisphenol A with terephthaloyl chloride as shown in the following Scheme 2.

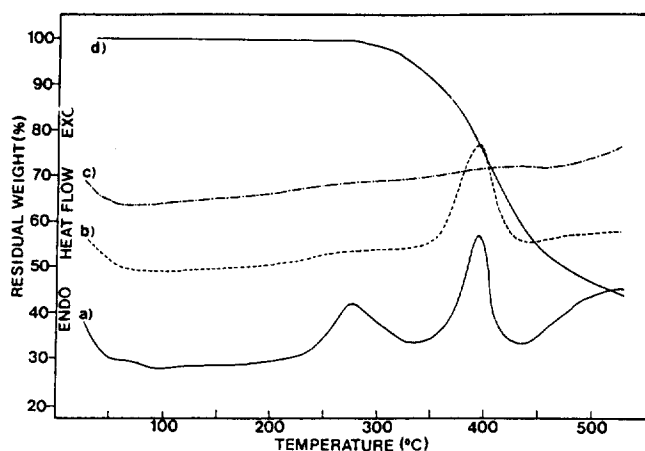
The polymerization results and conditions are summarized in Table 1. The solution polymerizations were carried out in THF solvent using triethylamine as the acid acceptor. When the homogeneous polymerization mixture was precipitated into *n*-hexane, the yellow powdery polymers were obtained in good yield. The spectral data of polymers 5-16 matched well with those of model compound. The comparison of NMR spectra of model compound 4 with polymers 5 and 8 is displayed in Figure 1(b), 1(c) and 1(d), respectively.

The homo-polyester composed only of ethylene glycol units is insoluble in common organic solvent. However, the copolyesters incorporated with 3 were soluble in common organic solvents such as THF and acetone as well as in polar aprotic solvents such as DMF, DMSO, DMAc and NMP. Polymers 15 and 16 containing aromatic units were less soluble in such solvents. As the amount of 3 increased, the solubility in organic solvent increased. When the films were cast by allowing the solvent to evaporate from solution on a glass plate, a clear and brittle film was obtained. The polymers were found to possess Mn in the range of 3500-7000 and Mw in the range of 8000-15000 from the results of GPC data.

Polymers show interesting differential scanning calorimograms as illustrated in Figure 2. Most copolyesters do not show a clear endothermic peak attributable to melting of polymer. The calorimogram of polymers show a trace of glass transition temperature changing with the length of alkylene chain diols. Especially, copolymers show two consecutive

**Table 2.** Thermal Properties of Polyesters Obtained from 3 and Various Diols with Terephthaloyl Chloride

Polymer	Diol	3 : Diol	$T_g$	1st	2nd	10%	Residual	
				Exo	Exo		Wt. Loss	Weight (%)
							400 °C	500 °C
5	EG	1 : 0	—	250	355	355	80	59
6	EG	4 : 1	—	260	344	350	78	57
7	EG	2 : 1	83	275	361	375	84	63
8	EG	1 : 1	63	263	334	355	76	52
9	EG	1 : 2	73	268	345	350	74	48
10	EG	1 : 4	70	318	391	370	74	45
11	PD	1 : 1	58	269	345	346	75	53
12	BD	1 : 1	76	271	385	357	73	47
13	HD	1 : 1	60	276	379	370	74	46
14	OD	1 : 1	50	270	369	375	76	53
15	HQ	1 : 1	—	270	368	396	85	67
16	BPA	1 : 1	110	277	386	400	88	55

**Figure 3.** DSC Thermograms of polyester a) 12 (1st scan), b) 12 (heated up to 270 °C, 2nd scan), c) 12 (heated up to 360 °C, 2nd scan), and d) TGA trace of polyester 12.

exotherms. The 1st exothermic peak exists at around 250 °C and the 2nd exotherm falls between 330 °C and 390 °C. As a typical DSC thermogram, the copolymer 5 obtained from 1 equiv. of 3 and ethylene glycol with terephthaloyl chloride shows 1st exotherm at 263 °C and 2nd exotherm at 334 °C as shown in Figure 2(d). As the content of 3 units in the copolymer was increased, the area of the 1st exotherm increased gradually. The 1st exothermic peak appears at relatively higher temperature in the case of polymers of long chain diols and aromatic diols.

When the polymer 12 was heated to its 1st exothermic temperature at 270 °C, the peak does not reappear upon cooling and rescanning the sample as shown in Figure 3(b). In the IR spectrum, the noticeable change of bands was not observed. However 2-3% weight loss was observed in the TGA trace in Figure 3(d). At this point, we have been yet unable to assign a particular pathway for the chemical process.

When the polymers were heated at a beginning tempera-

ture to its 2nd exothermic temperature and rescanned in DSC thermogram, they do not reappear as shown in Figure 3(c). After these polymers have been heated beyond the temperature of the 2nd exotherm, they were no longer soluble in the solvent of the untreated polymer, indicating that insolubility is associated with the exotherm.

The IR spectrum of the polymer 12 cured at its 2nd exothermic temperature of 350 °C showed the presence of a broad peak at 3400  $\text{cm}^{-1}$  and 1580  $\text{cm}^{-1}$ , and reduction of a band at 2235  $\text{cm}^{-1}$  assignable to nitrile group. This observation may be due to the change of nitrile group to other functions such as C=N and N-H caused by intra- or intermolecular addition or crosslinking of dicyanovinyl group.<sup>4,12</sup>

These polymers showed thermal degradation onset of 310 °C. thermogravimetric analysis showed a 10% loss in weight at around 360 °C which is the beginning temperature of its 2nd exotherm temperature as exhibited in Figure 3. The homo-polyester itself shows thermal stability exhibiting a 20 % residual weight up to a temperature of 500 °C. The polymers having aliphatic units in the main chain do not usually show high thermal stability due to a low dissociation energy of aliphatic C-H bond compared with aromatic one. However, the copolyesters retained almost 50-60% of their mass at 500 °C in nitrogen. The polymer with higher content of enaryloxynitriles units in polymer chain showed greater thermal stability than those with higher content of ethylene glycol. Consequently, the enhanced stability can be attributed to the presence of dicyanovinyl group in the polymer chain.

On the bases of these results, the chemical structure of polymers was changed during heating up to 350 °C in its maximum. However, the decomposition of polymer seemed to occur simultaneously during the cross-linking *via* dicyanovinyl group.

## Conclusion

Diol monomer containing enaryloxynitriles units, *p*-bis[1-[4-(3-hydroxypropyl)phenoxy]-2,2-dicyanovinyl]benzene (3) was prepared from *p*-bis(1-chloro-2,2-dicyanovinyl)benzene (1) and sodium salt of 3-(4-hydroxyphenyl)-1-propanol.

Polyesters with dicyanovinyl group were newly prepared from **3** and common diols with terephthaloyl chloride. They showed an enhanced solubility in polar aprotic and common organic solvents.

The polymers showed two consecutive exotherms in DSC thermograms attributable to the chemical change of dicyanovinyl group along with decomposition.

They undergo a curing reaction at around 350 °C, and show a 50-60% of residual weight at 500 °C indicating that the thermal stabilities were enhanced.

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## MO Calculation for the Dissociative Adsorption of Oxygen Molecule on Ni44(111) Model Surface

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*Received August 17, 1994*

The interaction of oxygen molecule with Ni44(111) model surface to which the molecule approaches is studied by calculating the relevant DOS and COOP with the tight-binding EHT method. It is found that the dissociative adsorption of oxygen takes place as a result of electron transfer from the Ni  $d\pi$  orbital to the antibonding  $1\pi_g$  orbital of the oxygen molecule. This finding is noteworthy to contrast with the case of Ni(100) surface in which the electron transfer takes place from the Ni  $d\delta$  orbital of the nickel surface.

### Introduction

It is widely accepted that oxygen is dissociatively adsorbed on nickel metal surface via molecular precursor state. Shyegan *et al.*<sup>1</sup> studied the work function of Ni(111) surface at 5.5 K with varying degrees of oxygen coverage, and reported the existence of molecular oxygen which might be the precursor species to the dissociatively adsorbed oxygen. The life-time of this molecular precursor is so short that it can hardly be detected. Ahn *et al.*<sup>2</sup> showed an evidence of the molecular precursor state by calculating the activation energy of the dissociative adsorption of oxygen molecule on a polycrystalline nickel surface by means of the X-ray photoelectron spectroscopy. Beckerle *et al.*,<sup>3</sup> on the other hand, reported that they were unable to find an evidence of the molecular state precursor at 8 K from EELS and work function measurements.

The experimental studies with LEED,<sup>4,5</sup> AES,<sup>6-8</sup> XPS<sup>9,10</sup> and many other surface analyzing techniques show that the

dissociatively adsorbed oxygen atoms on the nickel surfaces form  $p(2 \times 2)$  structure initially. This structure changes to  $c(2 \times 2)$  structure followed by NiO formation with increasing oxygen adsorption.<sup>4,6,11,12</sup> Ahn *et al.*<sup>13</sup> observed that the dissociatively adsorbed oxygen atoms on polycrystalline nickel surface show several different degrees of oxidation from the XPS measurements at the temperature ranges from 300 K through 500 K. Marcus *et al.*<sup>14</sup> investigated the  $p(2 \times 2)$  oxygen layer on a Ni(111) plane with LEED spectroscopy and concluded that the oxygen atoms occupy the three-fold centre of the nickel surface with the Ni-O distance of 19.4 nm.

Hoffmann *et al.*<sup>15-17</sup> introduced the Hückel type tight-binding method in the MO calculation of the dissociative adsorption of diatomic molecules on metal surfaces. In case of CO on Ni(100) and Ni(111) surface,<sup>16,17</sup> they found that the overlap population between the two atoms of carbon monoxide decreases by filling the CO  $2\pi$  orbital with the  $d\pi$  electrons of Ni surface to result in the dissociation of the CO molecule. In a previous paper of authors,<sup>18</sup> the MO calcu-