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Thermal Properties of Polyarylates Containing Dicyanovinyl Groups

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Introduction

Polyarylates are aromatic polyesters based on diphenols and aromatic dicarboxylic acids. As a result of their processibility, weatherability, high softening temperatures, and excellent physical and mechanical properties, polyarylates have been under intensive industrial development.[1]

The dicyanovinylidine group ($C{=}C(CN)_2$) can be considered structurally equivalent to the carbonyl group in reactions where the two functional groups have similar inductive and resonance effects.[2] Thus, poly(enaryloxynitrile)s can be considered analogous to polyesters.

Nadimide, acetylenic, biphenylenic, maleimide, and *N*-cyanourea are among the functional groups[3] most frequently employed for the preparation of thermally cross-linkable polymers. Although the curing mechanism has not been elucidated, the dicyanovinyl group should be one of the thermally curable functions. Recently, it was reported that poly(enaminonitrile)s[4–9] and poly(enaryloxynitrile)s[10,11] which contain the dicyanovinyl group are thermally curable and then show good thermal stabilities.

In the course of studying thermally curable polymers without the release of volatile byproducts, polyarylates which undergo heat curing are of a considerable interest. In this paper, we report a successful synthesis and thermal properties of novel polyarylates, which are thermally curable and stable, as a result of inserting the dicyanovinyl group in the main chain.

Experimental Section

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.[6] The disodium salt of Bisphenol A was prepared by reaction of Bisphenol A (Hayashi Pure Chemical Co.) with excess NaOH, followed by recrystallization from ethanol. Terephthaloyl chloride (Aldrich Chemical Co.) was purified by sublimation under vacuum. Benzoyl chloride was purified by distillation under reduced pressure. 1,2-Dichloroethane was purified by drying with calcium hydride and distillation.

The IR spectra were obtained with a Perkin-Elmer Model 1310 spectrophotometer, and ^{1}H NMR spectra were recorded on a Bruker Am-300 spectrometer. Elemental analyses were obtained with a Yanaco MT-3 CHN analyzer. Thermal analyses were performed with a Du Pont 2000 and Mettler thermal analyzer.

Representative Polymerization of Sodium Salts of Bisphenol A with 2 and Terephthaloyl Chloride. A solution of 0.5 g (1.8 mmol) of 2 and 0.37 g (1.8 mmol) of terephthaloyl chloride in 20 mL of 1,2-dichloroethane was transferred to a blender. The disodium salt of Bisphenol A (0.98 g, 3.6 mmol) in 20 mL of water was added quickly to the blender at full speed and maintained for 2 min. After the reaction, 100 mL of *n*-hexane was added to the reaction mixture, and the precipitate was filtered and washed with water. The resulting polymer was purified by Soxhlet extraction with boiling methanol for a day and dried under vacuum at 80 °C for 12 h.

Similar synthetic procedures were applied to the polyarylates with different contents of 2 in the main chain. The model compounds 2,2-bis[4-[(2,2-dicyano-1-phenylvinyl)oxy]phenyl]propane (3) and 2,2-bis[4-(benzoyloxy)phenyl]propane (4) were prepared similarly.

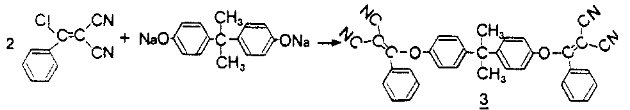
3. Yield: 91%. Mp: 196.6 °C (lit.[14] mp 196–197 °C). IR (KBr): 3060, 2980, 2220, 1570, 1220–1150 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.5 (m, 10 H, aromatic H's in 1), 7.2–6.6 (m, 8 H, aromatic H's in Bisphenol A), 1.4 (s, 6H, 2CH_3). ^{13}C NMR ($CDCl_3$): δ 30.5 ($-CH_3$), 42.3 ($-C-$), 71.9 ($=\underline{C}(CN)_2$), 110.5, 113.7 ($-CN$), 128.1, 128.4, 129.9, 129.4, 133.4, 147.9, 152.3 (aromatic C's), 180.3 ($=\underline{C}O-$).

4. Yield: 87%. Mp: 158 °C (uncorrected). IR (KBr): 3040, 2970, 1740, 1250–1100 cm^{-1}. ^{1}H NMR ($CDCl_3$): 7.6–7.2 (m, 4 H, aromatic H's in benzoate), 7.2–6.4 (m, 14 H, aromatic H's in Bisphenol A).

8. IR (KBr): 3040, 2960, 2210, 1730, 1590, 1270–1100 cm^{-1}. ^{1}H NMR (DMSO): δ 8.0 (s, 4 H, aromatic H's in terephthalate units), 7.7 (s, 4 H, aromatic H's in fragment of 2), 6.4–7.0 (m, 8 H, aromatic H's in Bisphenol A), 1.4 (s, 6 H, 2CH_3). Anal. Calcd for $(C_{26}H_{18}N_2O_3)_n$: C, 87.15; H, 5.02; N, 7.82. Found: C, 86.76; H, 4.93; N, 7.50.

Results and Discussion

Polyarylates prepared from disodium salts of Bisphenol A with terephthaloyl chloride were previously reported by Conix[12] and Temin.[13] 2,2-Bis[4-[(2,2-dicyano-1-phenylvinyl)oxy]phenyl]propane (3)[10,14] and 2,2-bis[4-(benzoyloxy)phenyl]propane (4), chosen as model compounds, were also synthesized by interfacial techniques.



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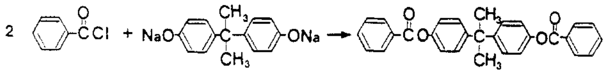

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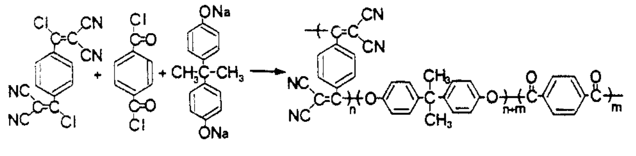
In previous work,[10,11] it was demonstrated that interfacial polymerization of an aryl oxide dianion with monomer 2 containing dicyanovinyl groups proceeded in good yield and provided a convenient method for the preparation of poly(enaryloxynitriles).



m/n = 1/0, 0/1, 4/1, 2/1, 1/1, 1/2, 1/4

5 6 7 8 9 10 11

The polymerization of different contents of 2 and terephthalate units was attempted to obtain a controlled amount of enaryloxynitrile units in the main chain of aromatic polyesters.

The conditions and results of copolymerization are summarized in Table I.

The copolymerizability of disodium salts of Bisphenol A with 2 and terephthaloyl chloride was determined by comparing the formation of model compounds under similar synthetic conditions. Dicyanovinyl chlorides are reactive with aliphatic amines and phenoxide anions as are aromatic acid halides.

The chemical structure of the copolymer was characterized by spectroscopy. In the IR spectrum of polymer 8 the characteristic bands at 2210, 1730, 1590, and 1250–1100 cm^{-1} attributable to $C{\equiv}N$, $C{=}O$, $C{=}C$, and C–O, respectively, appeared. The ^{1}H NMR spectrum shows the aromatic protons of a fragment of 2 at 7.6 ppm as a

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Table I. Results and Conditions of Polymerization of Terephthaloyl Chloride and *p*-Bis(1-chloro-2,2-dicyanovinyl)benzene with the Disodium Salt of Bisphenol A at 20 °C

polymer	TC[a]/2	time (min)	yield (%)	η_{inh}[b]	M_n[c]	M_w[c]
5	1/0	2	94	-	-	-
6	0/1		95	0.29	4900	16 800
7	4/1		93	-	-	-
8	2/1		92	-	3600	10 800
9	1/1		92	0.18	4700	12 100
10	1/2		94	0.14	4320	10 500
11	1/4		92	0.25	3880	12 400

[a] TC = terephthaloyl chloride. [b] Measured in dimethyl sulfoxide at 1 g/dL at 25 °C. [c] Apparent molecular weights were obtained with a Waters HPLC using three columns (μ-Styragel: 10^2, 10^3, and 10^4 Å) in THF. Polystyrene standards were used for calibration.

singlet, whereas those of the terephthalate appeared at 7.8 ppm. The integration ratios of aromatic protons in 2 and terephthalate units were almost the same. This result was also confirmed by elemental analysis. The ratio of two monomer units in the copolymers was variable according to the monomer ratio in the feed.

In the IR spectrum, the polymer with a higher content of 2 units in the main chain showed a stronger nitrile band at 2210 cm^{-1} and a weaker carbonyl band at 1730 cm^{-1}.

The polyarylate composed only of terephthalate units is insoluble in methylene chloride, chloroform, DMAc, and DMF and shows good resistance to aliphatic hydrocarbons, oils, fats, and alcohols. As the amount of 2 increased, the solubility in polar aprotic solvents such as DMF, DMSO, and NMP increased. Polyarylates containing enaryloxynitrile moieties 8, 9, and 10 are even soluble in acetonitrile and swellable in THF.

The polymers have inherent viscosities of 0.14–0.29 with M_n in the range of 3600–3800 and M_w in the range of 11 000–17 000. These materials are not of high molecular weight as shown by the GPC data. They form brittle films from DMF solution. In the case of interfacial polymerization of terephthaloyl chloride with Bisphenol A, excess diacid chloride (1.04–1.7 equiv) and a phase-transfer agent are necessary to obtain high molecular weight polymer.[15-17] In this experiment, equimolar ratios of the two monomers and no phase-transfer agent were used to obtain a controlled content of 2 and terephthalate units in the polymer backbone. The polymers seemed to contain a large amount of low molecular weight material as shown by dispersity in the GPC traces. After Soxhlet extraction in boiling methanol, the GPC curve is sharpened.

In the DSC thermograms shown in Figure 1, polyarylate 5 prepared by interfacial techniques shows a large endotherm at 390 °C corresponding to melting of the homopolymer, whereas poly(enaryloxynitrile) shows two consecutive exotherms at 245 and 380 °C, which are attributed to changes in chemical structure. As the content of 2 units in the polymer increased, the area of the exotherm at 250 °C increased gradually and the endotherm between 320 and 380 °C broadened.

The copolymer 8 obtained from 1 equiv of 2 and 2 equiv of terephthaloyl chloride shows both the exothermic and endothermic peaks at 250 and 320 °C, respectively.

As shown in Figure 2, at the temperature of the first exotherm, no loss of weight is observed. This result indicates that the polyarylate containing dicyanovinyl groups cured thermally without release of volatile byproducts. The exothermic peak was completely absent when the samples heated to 420 °C were cooled and rescanned. The polymers were no longer soluble in a solvent for the untreated polymers. The second exotherm was observed in the range of temperature between 320 and 400 °C in most of the polyarylates. This observation may be attributable to further thermal transformation of residual cyano groups. The thermal decomposition of these polymers may begin at 380 °C. Thermogravimetric analysis indicates a 5% loss in weight below 400 °C. It was, therefore, decided that we would perform thermal curing of these polymers at 250 °C. A sample of polymer 9 heated around 250 °C displayed a gradual change in its IR spectra as it was heated.

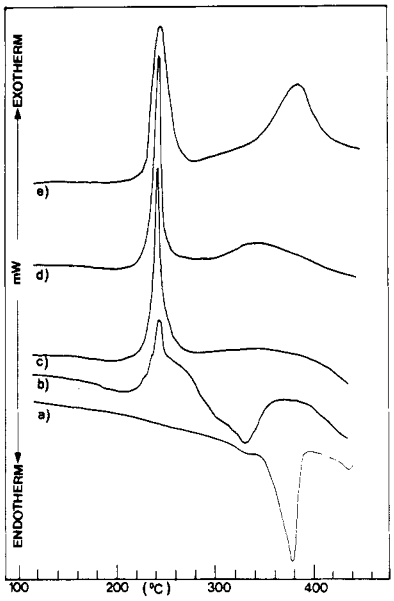

Figure 1. DSC thermograms of polymers obtained from terephthaloyl chloride and *p*-bis(1-chloro-2,2-dicyanovinyl)benzene: (a) 1/0, (b) 2/1, (c) 1/1, (d) 1/2, (e) 0/1 with the disodium salt of Bisphenol A.

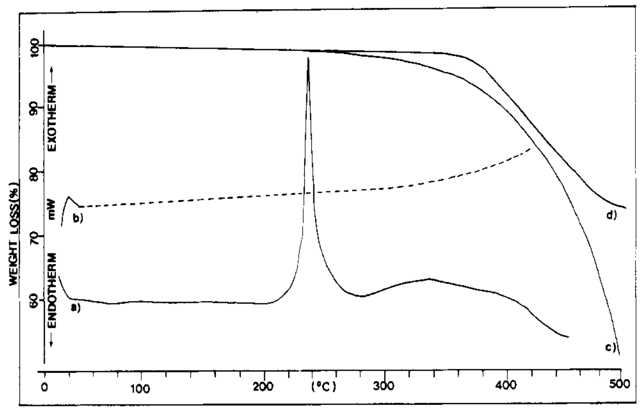

Figure 2. DSC thermograms, (a) 1st scanning and (b) 2nd scanning, and TGA traces, (c) in N$_2$ and (d) in air of polyarylate obtained from an equimolar ratio of terephthaloyl chloride and *p*-bis(1-chloro-2,2-dicyanovinyl)benzene with the disodium salt of Bisphenol A.

In the IR spectra, bands of uncured polymer at 2210, 1580, and 1320 cm^{-1} corresponding to nitrile and C=C bonds were reduced, while the absorption bands at 1620–1550 cm^{-1} were broadened as shown in Figure 3.

These observations may be due to the change of nitrile groups to other functions such as C=N or C=C caused by the curing reactions.

All the polymers show excellent thermal stabilities despite their low molecular weights. The results of TGA are listed in Table II.

The homopolyarylate itself shows good thermal stability, exhibiting 73% weight loss at 500 °C, because of its aromatic repeating units. The polymers with dicyanovinyl groups suffered a 10% weight loss up to a temperature of 450 °C in nitrogen and 400 °C in air at a heating rate of

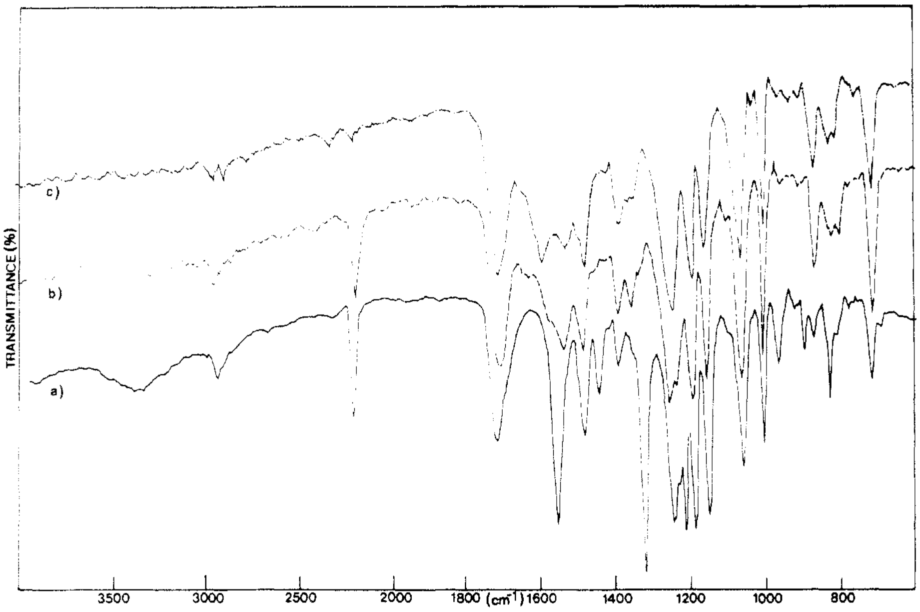

Figure 3. Superimposed IR spectra of polymer with a 1–2 molar ratio of *p*-bis(1-chloro-2,2-dicyanovinyl)benzene and terephthaloyl chloride with the disodium salt of Bisphenol A after (a) 0, (b) 0.5, and (c) 2 h at 250 °C under nitrogen.

Table II. Thermal Properties of Polyarylates Obtained from Terephthaloyl Chloride and *p*-Bis(1-chloro-2,2-dicyanovinyl)benzene (2) with the Disodium Salt of Bisphenol A

polymer	TC/2	temp (°C) exo	temp (°C) endo	10% wt loss (°C)	residual wt (%) 400 °C	residual wt (%) 500 °C
5	1/0		380	437	96	73
6	0/1	245, 380		491	94	89
7	4/1	240	365	461	92	89
8	2/1	240	335	469	96	85
9	1/1	240		428	93	84
10	1/2	240		443	95	87
11	1/4	240		445	94	85

10 °C/min. The polymers retained almost 85% of their mass at 500 °C in nitrogen.

No loss of weight in their TGA curves at the temperature of the exothermic transition indicates that the structure of the polymer changed without decomposition or release of volatile byproducts.

It is reported that, among several possible curing reactions, poly(enaminonitriles) undergo intramolecular cyclization to amino–cyano quinoline units as well as cross-linking.[4–6] Polypyrazoles[7] were prepared by cyclization of the presumed intermediate poly(enhydrazinonitriles).

In the case of polyarylates containing dicyanovinyl groups, the curing reaction is assumed to proceed by intermolecular and intramolecular addition of dicyanovinyl groups, but we have been as yet unable to assign a particular pathway for the chemical curing process.

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