

Studies on the Formation of Novel Copolyesters Containing Naphthalene and Aralkyloxy Structures

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SYNOPSIS

Copolyesters containing naphthalene structure were synthesized from bis(hydroxyethyl)naphthalate (BHEN) and various aralkyloxy diols. The starting bis(4-(2-hydroxyethoxy)aryl) compounds were derived from a nucleophilic substitution of various bisphenols with ethylene carbonate in the presence of potassium iodide (KI). Copolyesters having intrinsic viscosities of 0.50 to 0.60 dL/g were obtained by melt polycondensation in the presence of metallic catalysts. The effects of reaction temperature and time on the formation of copolyesters were investigated in order to obtain an optimum condition for copolyester manufacturing. The optimal reaction temperature and time were found to be 290 to 310°C and 90 to 120 min, respectively. Most of these copolyesters have better solubilities than polyethylene naphthalate (PEN) in aprotic solvents such as *N*-methyl-2-pyrrolidone or *m*-cresol. The thermal properties of the copolyesters were investigated by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). Glass transition temperatures of these copolyesters were in the range of 90 to 141°C, and 10% weight loss values in nitrogen were all above 460°C. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Although the demand for polyethylene terephthalate (PET) is very large, better thermal and mechanical properties are desired for some applications. While polyimides are superior in these properties, their high price and processing problems remain to be overcome. The newly developed high-performance polyethylene naphthalate (PEN) seems to fill the gap between the two.

PEN, with a rigid naphthalene ring, should have superior physical and mechanical properties to the widely used PETs, as shown in Table I.¹ Due to its superior physical and mechanical properties, PEN has found many applications: Yamamoto et al.² reported PEN bottles with good gas barrier properties, transparency, and thermal resistance (up to 110°C). Teijin Ltd.³ has produced high-

quality fibers from PEN with flexibility, toughness, and resistance to heat and abrasion. An oriented multilayer polyester film for magnetic recording tape with good machine direction strength and heat resistance was reported by Tahoda et al.⁴ Since PEN film is particularly well suited for electronic and electrical applications,⁵ such as flexible printed circuits, class F insulation, wiring applications, tough membrane switches, and flexible heaters, ICI Americas⁶ has announced construction of a \$16 million plant to produce the new high-performance PEN film.

Because of the extraordinary effect on physical properties exhibited by the naphthalene ring structure, further studies into copolyesters containing naphthalene rings were attempted. In the studies, both the aryl ether linkage and the bulky pendant group were incorporated into the main chain of PEN, in hopes of increasing its solubility (this may have additional applications in paint, varnish, and structural adhesives) and processability without sacrificing its thermal property.

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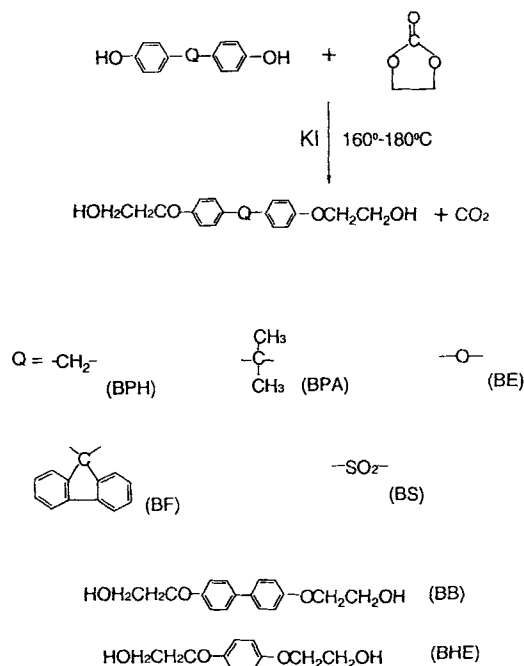
EXPERIMENTAL

Raw Materials

According to the method reported in an earlier article,⁸ bis(hydroxyethyl)naphthalate (BHEN, mp 129–131°C) was synthesized from 2,6-dimethyl naphthalate (from Amoco) and ethylene glycol (from Ferak) and subsequently purified before using. Reagent grade aromatic bisphenols such as 2,2-bis(4-hydroxyphenyl)propane, bis(4-hydroxyphenyl)methane, 4,4'-bis(4-hydroxyphenyl)sulfone, 4,4'-dihydroxydiphenyl, 4,4'-dihydroxydiphenyl ether, and 1,4-bis(2-hydroxyethoxy)benzene (mp 105°C) were all from Tokyo Chemical Industry Co., Ltd. The 9,9-bis(4-hydroxyphenyl)fluorene (from Dow Chemical Co.) was used without further purification. *N,N*-Dimethylacetamide (DMAc), *N*-methyl-2-pyrrolidone (NMP), *N,N*-dimethylformamide (DMF), and pyridine were purified by distillation under reduced pressure over calcium hydride and stored over 4-Å molecular sieves. Zinc acetate, antimony trioxide, and potassium iodide were commercial products (guaranteed reagent grade) and were used without further purification.

Instrumentation

Elemental analyses were performed by the Heraeus CHN-O-Rapid elemental analyzer. Infrared (IR) spectra were recorded with an infrared spec-



Scheme 1

trophotometer (JASCO IR-810); Fourier transform infrared (FTIR) spectra were recorded with a Nicolet 5DX-B spectrophotometer. Mass spectra were recorded by the VG 70-250s Gas chromatography/Mass spectrometry (GC/MS). Intrinsic viscosities were obtained by using an Ubbelohde

Table I Syntheses of bis(4-(2-Hydroxyethoxy)Aryl) Compounds

Sample	Formula (Molecular Weight)	Yield (%)	Elemental Analysis (%)		
			Found (Calcd.)		
			C (%)	H (%)	O (%)
BHE	C ₁₀ H ₁₄ O ₄ (188)	a		a	
BB	C ₁₆ H ₁₈ O ₄ (274)	62	70.07 (70.07)	6.58 (6.57)	23.35 (23.36)
BE	C ₁₆ H ₁₈ O ₅ (290)	70	66.23 (66.20)	6.23 (6.21)	27.54 (27.59)
BS	C ₁₆ H ₁₈ O ₆ S (338)	67	56.81 (56.80)	5.30 (5.32)	28.6 (28.4)
BPA	C ₁₉ H ₂₄ O ₄ (316)	82	71.99 (72.12)	7.58 (7.59)	20.43 (20.29)
BPH	C ₁₇ H ₂₀ O ₄ (288)	80	70.85 (70.83)	6.98 (6.94)	22.17 (22.23)
BF	C ₂₉ H ₂₆ O ₄ (438)	63	79.48 (79.45)	6.05 (5.94)	14.47 (14.61)

^a 1,4-bis(2-Hydroxyethoxy)benzene (BHE) was a commercial product and was used without further purification.

Table II Characterization of bis(4-(2-Hydroxyethoxy)Aryl) Monomers

Sample Code	Melting Point (°C) (Unmodified)	Mass Spectrometry (m/e) (Relative Intensity %)	Infrared (cm ⁻¹)
BHE	105	^a	^a
BB	210–211 (281)	M ⁺ (274) 63.4 M–44 (230) 100 M–88 (186) 46.72 M–120 (154) 84.50	3450 (O—H) 3050 (Ar: C—H) 2900 (Alkyl: C—H) 1600 (Ar: C—C) 1245 (C—O—C) 1080 (C—OH)
BE	119–121 (164–167)	M ⁺ (290) 100 M–44 (246) 10.29 M–88 (202) 14.46	3500 (O—H) 3080 (Ar: C—H) 2950 (Alkyl: C—H) 1600 (Ar: C—C) 1247 (C—O—C) 1080 (C—OH)
BS	180–181 (245–247)	M ⁺ (339) 100 M–16 (323) 13.71 M–44 (295) 10.01 M–138 (201) 26.69	3450 (O—H) 3050 (Ar: C—H) 2900 (Alkyl: C—H) 1600 (Ar: C—C) 1240 (C—O—C) 1140 (SO ₂) 1070 (C—OH)
BPA	110–111 (158–159)	M ⁺ (316) 100 M–15 (301) 13.71 M–59 (257) 10.01 M–103 (213) 26.69 M–137 (179) 10.01 M–183 (133) 26.69	3450 (O—H) 3050 (Ar: C—H) 2900 (Alkyl: C—H) 1600 (Ar: C—C) 1245 (C—O—C) 1080 (C—OH)
BPH	109–110 (160–162)	M ⁺ (288) 100 M–45 (243) 13.51 M–89 (199) 22.09 M–137 (151) 93.47 M–181 (107) 78.5	3450 (O—H) 3050 (Ar: C—H) 2900 (Alkyl: C—H) 1600 (Ar: C—C) 1240 (C—O) 1080 (C—OH)
BF	126–128 (224–225)	M ⁺ (438) 100 M–45 (393) 18.02 M–61 (377) 6.49 M–88 (350) 9.57 M–137 (301) 18.57 M–181 (257) 37.58	3450 (O—H) 3050 (Ar: C—H) 2900 (Alkyl: C—H) 1600 (Ar: C—C) 1240 (C—O) 1080 (C—OH)

^a 1,4-bis(2-Hydroxyethoxy)benzene (BHE) was a commercial product and was used without further purification.

capillary viscometer (Schott-AVS310). Melting points of bis(4-(2-hydroxyethoxy)aryl) compounds were determined by a polarizing microscope (Laboratory Devices MEL-TEMP. II). DSC data were obtained from 8- to 10-mg samples in a nitrogen atmosphere at a 20°C min⁻¹ heating rate using a DuPont 910 differential scanning calorimeter. Thermal gravimetric analysis (TGA) was employed with a DuPont 945 at a heating rate of 50°C min⁻¹ in a nitrogen atmosphere. The wide-angle X-ray measurements were performed at room temperature (ca. 25°C) with powdered specimens on a Rigaku Geiger Flex D-Max/IIIa X-ray diffractometer, using Ni-filtered CuK_α radiation (40 kV, 15 mA). The scanning rate was 2° min⁻¹.

Synthesis of bis(4-(2-Hydroxyethoxy)Aryl) Compounds

bis(4-(2-Hydroxyethoxy)aryl) compounds were prepared from corresponding phenols and ethylene carbonate by the modified method of Kem et al.,¹⁰ as indicated in Scheme 1. The general procedure for the preparation of bis(4-(2-hydroxyethoxy)aryl) monomers is as follows: The corresponding phenol (1 mol), ethylene carbonate (2.1 mol), and potassium iodide (2 g) were introduced into a 500-mL round-bottom glass flask equipped with a bubbler, a condenser, and a mechanical stirrer. The flask was flushed with nitrogen and heated to between 80 and 120°C. Agitation was commenced as soon as contents were melted. CO₂ evolution began immediately.

Table III Solubilities of Copolyesters^a

Solvent ^b	PEN	P _{BHE}	P _{BB}	P _{BE}	P _{BS}	P _{BPA}	P _{BPH}	P _{BF}
DMAC	—	—	—	—	—	—	—	—
DMF	—	—	—	—	—	—	—	—
DMSO	—	—	—	—	-h	—	—	—
NMP	—	++	-h	+h	++	+h	-h	++
<i>m</i> -Cresol	—	++	+h	+h	+h	++	-h	+h
Pyridine	—	—	—	—	—	—	—	-h
CHCl ₃	—	—	—	—	—	—	—	—
C ₂ H ₂ Cl ₄	-h	++	+h	++	+h	++	+h	++

^a (++) Soluble at room temperature; (+h) soluble on heating; (-h) partially soluble on heating; (—) insoluble.

^b DMAC: *N,N*-dimethylacetamide; DMF: *N,N*-dimethylformamide; DMSO: dimethyl sulfoxide; NMP: *N*-methyl-2-pyrrolidone.

The temperature was raised to between 150 and 180°C and maintained at that temperature until CO₂ evolution subsided. Upon cooling, an off-white crystalline solid was obtained. The solid was further purified by recrystallization from a mixture of toluene and ethanol, chloroform, or DMF several times. The purified bis(4-(2-hydroxyethoxy)aryl) monomers were identified by elemental analyses, mass spectra, IR spectra, and melting points, which are listed in Tables I and II.

Preparation of Copolyesters

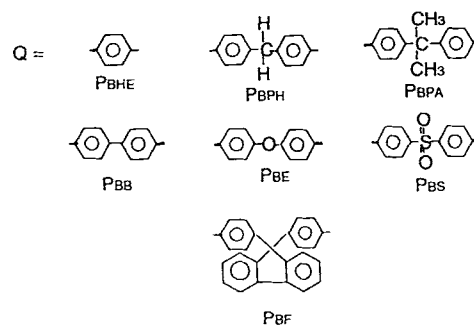
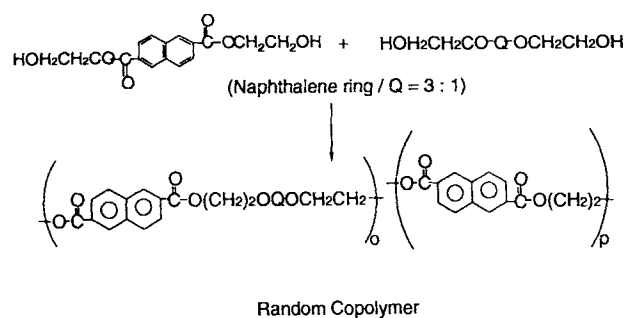
The synthesized monomers (hydroxyethoxy and BHEN) were mixed in a mole ratio of 1 : 3 for the copolymerization reaction. Besides the esterification of hydroxyethoxy monomer with BHEN, the polycondensation of BHEN itself could occur at the same time and a copolymer would be generated. The reaction equations and products are indicated in Scheme 2. A mixture of BHEN (0.3 mol), bis(4-(2-hydroxyethoxy)aryl) monomers (0.1 mol), zinc acetate (20×10^{-5} mol/BHEN mol), and antimony trioxide (20×10^{-5} mol/BHEN mol) was introduced into a 250-mL three-neck flask fitted with a reflux condenser, a gas inlet, a gas outlet tube, and a mechanical stirrer. The reaction mixture was heated to between 240 and 245°C and maintained at that temperature for 90 min under dry nitrogen. The temperature was raised to 270°C, and stirring was continued for 30 min. The pressure of the reaction system was gradually reduced, first to between 180 and 200 mm Hg over the course of 10 min. In the course of another 10 min, the pressure was further reduced to between 1 and 3 mm Hg and the reaction temperature was raised to 290°C. The polymerization proceeded isothermally at $290 \pm 5^\circ\text{C}$ for the required period of time with simultaneous removal of ethylene glycol and other volatiles by distillation.

Finally, the pressure was returned to normal atmospheric pressure using nitrogen to prevent degradation by oxidation; light amber colored, amorphous copolymers were obtained.

Other copolyesters were synthesized according to the foregoing procedure with slight modifications in the temperature of the polycondensation step.

Solubility Test

Polymer (1 to 2% by weight) was added to a solvent to be tested in a test tube, and the tube was left to stand at ambient temperature for 24 h to observe

**Scheme 2**

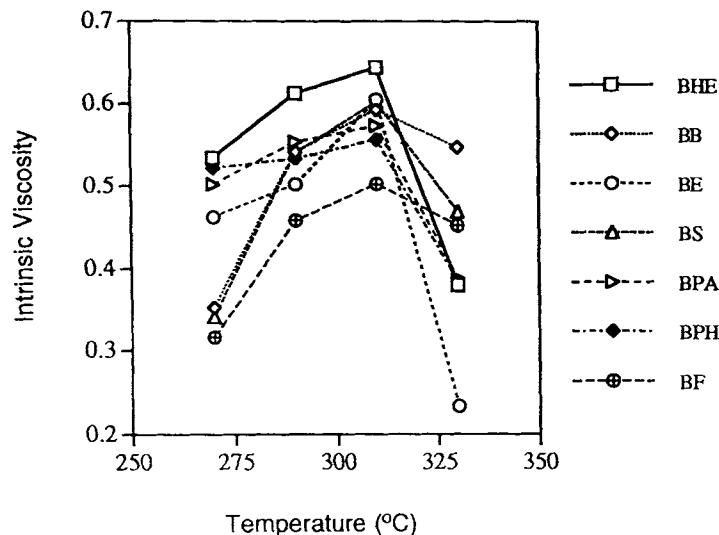


Figure 1 Effect of temperature on the polycondensation of copolyester: (□) P_{BHE} ; (◇) P_{BB} ; (○) P_{BE} ; (△) P_{BS} ; (▽) P_{BPA} ; (◆) P_{BPH} ; (⊕) P_{BF} .

whether the polymer dissolved. Then any test tube in which some polymer seemed to be left undissolved was heated to 75°C for 5 min and cooled. We defined that the polymer was soluble on heating when no polymer precipitated after the tube was cooled.

Intrinsic Viscosity Determination

Intrinsic viscosity of the polymer was measured using an Ubbelohde viscometer. The advantage of using this viscometer is that the measurement is independent of the amount of solution in the viscometer, and viscosity can easily be calculated by the Ram Mohan Rao equation.¹³ The polymer sample (0.06 g) was accurately weighed (± 0.001 g) and dissolved in 25 mL of symmetric tetrachloroethane phenol (2 : 3 w/w). The solution was maintained at 120°C for 20 to 25 min to achieve a complete solution of the polymer in the solvent. The solution was then cooled to room temperature and filtered through a 0.45- μ m disposable membrane filter (cellulose acetate). Using the viscometer at 30°C, the intrinsic viscosity was calculated from the relative viscosity by means of the Ram Mohan Rao equation.

Determination of the Moisture Absorption of Copolyesters

Samples were dried under vacuum at 120°C until moisture had been expelled. Then the samples were put inside a dry box for cooling. After being weighed, the samples were placed in boiling water (100°C) for 72 h and then weighed again. The moisture ab-

sorption was calculated as percent weight gain = $(W/W_0 - 1) \times 100$, where W = weight of copolymer sample after standing in 100°C water for 72 h, and W_0 = weight of copolymer sample after dried under vacuum at 120°C.

RESULTS AND DISCUSSION

Monomer Synthesis

The synthetic procedure described by Kem¹⁰ was used to prepare the bis(4-(2-hydroxyethoxy)aryl) monomers. The following was observed during the experiments:

1. Faster reaction rates were observed at higher temperature; however, the decomposition of reactants and products was also likely to occur at higher temperature. The preferred operating temperature for most phenols was from 160 to about 180°C.
2. The time for substantial completion of reaction varied depending on the particular reactant. Gas chromatography or liquid chromatography was used to follow the reaction and to determine the end of the process. However, the subsidence of carbon dioxide evolution was a convenient indicator for the completion of reactions. In general, about 6 to 7 h is adequate; however, for bisphenol with fluorene, the reaction rate was much slower due to the steric hindrance gen-

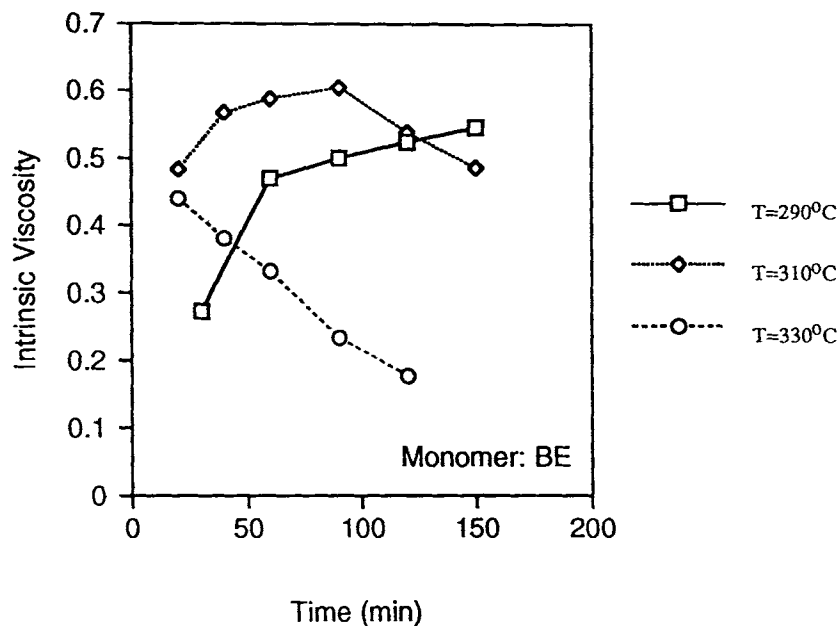


Figure 2 Time-intrinsic curve for the polycondensation of BHEN with BE: (□) 290°C; (◇) 310°C; (○) 330°C.

erated by the bulky fluorene structure, and it took 20 h to complete.

3. Because of the high melting point (211°C) of 4,4'-biphenol, DMF was used as solvent and the reaction was carried out in the solution state.

A series of hydroxyethoxy monomers were synthesized under the most preferable conditions determined, and the results are summarized in Tables I and II. The yields of products were relatively low because of the several recrystallizations required to achieve the high purity. A polarized microscope was used to determine the melting

point of bis(4-(2-hydroxyethoxy)aryl) monomers. The sharp melting points indicated the high purity of the monomers synthesized. Another phenomenon was that the melting points of bis(4-(2-hydroxyethoxy)aryl) monomers were lower than that of the unmodified bisphenol because of their extended oxyethylene chains ($\text{CH}_2\text{CH}_2-\text{O}$) (Table II).

The results of elemental analyses of these monomers (Table I) were in good agreement with the assigned structures. Electron impact-induced fragmentation patterns of these monomers at 30 eV have been obtained. The common features observed in the mass spectra and the infrared spectra of bis(4-

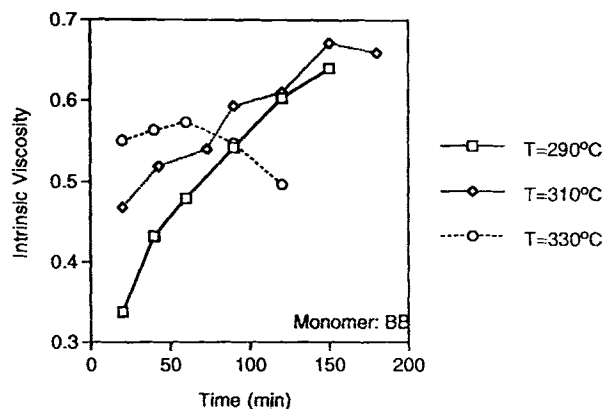


Figure 3 Time-intrinsic curve for the polycondensation of BHEN with BB: (□) 290°C; (◇) 310°C; (○) 330°C.

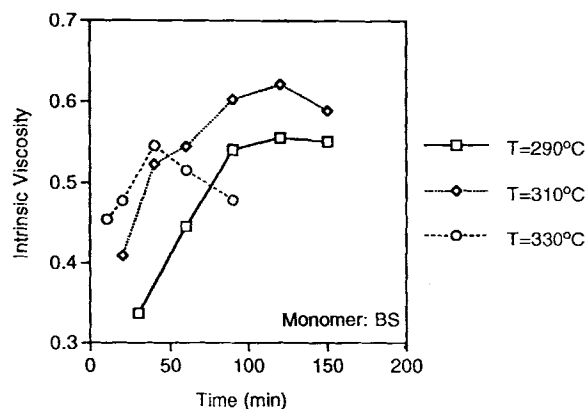


Figure 4 Time-intrinsic curve for the polycondensation of BHEN with BS: (□) 290°C; (◇) 310°C; (○) 330°C.

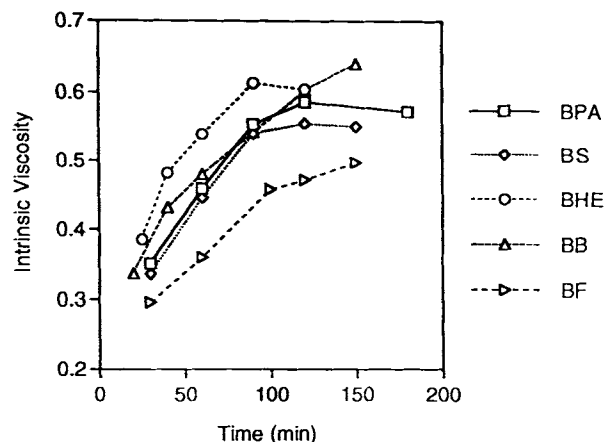


Figure 5 Effect of various structures of reactants on the polycondensation of copolyester: (□) P_{BPA} ; (◇) P_{BS} ; (○) P_{BE} ; (△) P_{BB} ; (▽) P_{BPA} .

(2-hydroxyethoxy) aryl) monomers are shown in Table II. From these results, it can be concluded that the products were of high purity.

Synthesis of Copolyesters

The polycondensation of aromatic diester with aliphatic diol, using zinc acetate and antimony trioxide as catalysts and developed by the authors,⁹ is a convenient method for the preparation of copolyesters on a laboratory scale. The same technique was applied here to prepare the oxyethylene chain containing copolyesters from BHEN and various structurally different bis(4-(2-hydroxyethoxy) aryl) monomers, as indicated in Scheme 2.

The dependencies of polycondensation rates on the reaction temperature in the region between 275 and 330°C have been investigated. Figure 1 shows plots of the intrinsic viscosities of these copolymers at various reaction temperatures after 90 min of reaction. The results indicated an increase in intrinsic viscosity with an increase in reaction temperature at the beginning; however, when reaction temperatures exceeded 310°C, drastic decreases in viscosities were observed. This may be explained as follows: The increase in temperature at the beginning of reaction helps it overcome the obstacle of activation energy easily and results in an increase in the reaction rate. However, in the high-temperature region, the degradation reaction is more dominant than the propagation reaction and leads to the decay of viscosity (i.e., the reduction in polymerization degree). It was also observed that the high reaction temperatures always ended in the formation of deeply colored products.

Figures 2, 3, and 4 show plots of the intrinsic viscosities of copolymers versus time at various reaction temperatures using BE, BB, or BS as a diol monomer. The results also indicate that the higher the reaction temperature, the faster the degradation of the produced polymers. This phenomenon illustrates once more that the degradation reaction is influenced by the temperature change much more so than the propagation reaction. Another interesting phenomenon is observed from these figures: The heat resistance characteristics of the resultant copolyesters depend greatly on the structure of the hydroxyethoxy compounds introduced. The copolymers with biphenyl or sulfone groups (P_{BB} and P_{BS}) degrade slower than the P_{BE} copolymer with the ether chain in the backbone at high reaction temperatures.

Figure 5 shows the plots of the intrinsic viscosities of copolymers versus time at 290°C. The reaction rates were slower for BF, which may be attributed to the steric hindrance of the bulky fluorene structure. Consequently, the viscosity of P_{BF} was lower under the same reaction condition.

It may be concluded that the polycondensation temperature should not exceed 310°C, and each hydroxyethoxy diol has its own optimum operation temperature. For the mole ratio of hydroxyethoxy compound, BHEN = 1 : 3, the optimum operation temperature is between 290 and 300°C. The following section compares the resultant copolyesters under a fixed reaction condition of 290°C and 90 min with a fixed catalyst concentration of 20×10^{-5} mol/BHEN mol.

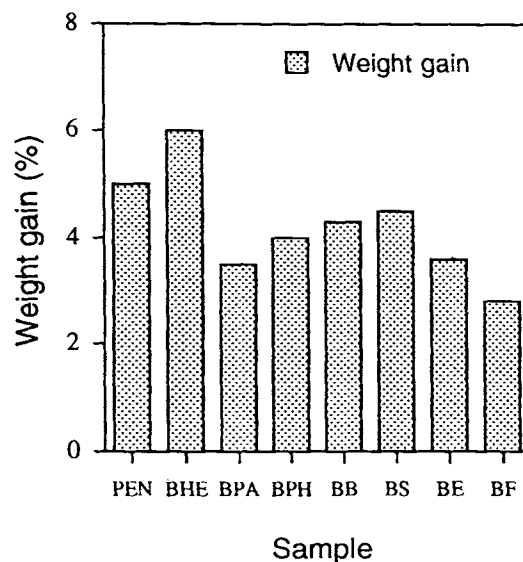


Figure 6 Moisture absorption for various copolyesters.

Table IV Thermal Properties of Copolyesters

Polymer	T_g (°C) ^a	T_m (°C)	Decomposition Temperature ^b in N ₂ (°C)		Residue at 600°C (wt %) ^c
			$T_{10\%}$		
PEN	116.0	261	468		22.1
P_{BHE}	94.7	—	466		20.6
P_{BB}	120.3	—	474		35.7
P_{BE}	98.7	—	460		21.1
P_{BS}	122.3	—	466		29.6
P_{BPA}	110.5	—	468		26.7
P_{BPH}	90.1	—	464		28.6
P_{BF}	140.9	—	475		36.7

^a Determined by DSC at a heating rate of 20°C/min.

^b Temperature at which 10% weight loss was recorded by means of thermogravimetry at a heating rate of 50°C/min.

^c Residual weight (%) at 600°C in nitrogen.

Properties of Copolyesters

A series of copolyesters containing naphthalene were synthesized by reacting BHEN with bis(4-(2-hydroxyethoxy)aryl) monomers at a mole ratios of 3 : 1 under the most preferable condition, determined according to the aforementioned data. The structure of the resultant copolymers was confirmed by IR spectra: Two strong aromatic absorptions appeared at 1600 and 1500 cm⁻¹ due to the naphthalene and benzene ring; prominent absorptions due to the ester carbonyl group (CO) at 1700 cm⁻¹ and the ether group (C—O—C) at 1230 ± 10 cm⁻¹ were also present. The strong and broad absorption at 3450 cm⁻¹ for the starting hydroxyethoxy compounds weakened as the reactions proceeded. These results support the formation of high-molecular-weight copolyesters.

The solubilities of copolymers were determined using powdery specimens in various solvents at ambient, and the results are summarized in Table III. The PEN homopolymer had the poorest solubility, which dissolved only partially in symmetric tetrachloroethane on heating; while the solubilities of copolyesters improved dramatically as expected in suitable solvents, such as NMP, *m*-cresol, and tetrachloroethane. Copolymer containing aryl sulfone was soluble even in dimethyl sulfoxide (DMSO). Their enhanced solubilities are attributed mainly to the lack of crystallinity of copolyesters and partly to the incorporation of bulky fluorene groups or aryl ether units along the copolyester backbone. Another explanation for the better solubility may be the increase in the molecular polarity of copolyester (i.e., P_{BS}).

The X-ray diffraction patterns of the copolymers indicated that all these copolyesters are amorphous. Three factors may influence this phenomenon:

1. There is a substantial difference in angle between the two inter-ring linkages.¹² This could make it more difficult for the repeating unit to fit into a crystal lattice (e.g., P_{BS} , P_{BPA} , and P_{BB}).
2. The mobility of the polymer chain must be one of the important factors governing the crystallinity of copolyester.¹² A bulky rigid group in the copolyester chain could make it more difficult for this molecule to adopt a configuration that would fit into a lattice structure (e.g., P_{BF} and P_{BB}).
3. Upon cooling of the block copolymers, the ester segment may crystallize faster than the ether segment¹³; the ether segments which are located in the amorphous region are restricted in their motion and hence reduce the crystallinity of copolymer.

The disk samples [3 mm (*T*) × 20 mm (*D*)] were fabricated from copolyesters and placed into 100°C boiling water for 72 h. The weight gains from this moisture absorption test are shown in Figure 6. As observed from Figure 6, P_{BHE} , with a single benzene ring, is the highest among all these copolyesters, while P_{BF} is the lowest.

The thermal behavior of copolyesters was evaluated by DSC and TGA, and results are summarized in Table IV. All copolymers show similar patterns of decomposition with no significant weight loss below 600°C in nitrogen, and their 10% decomposition temperatures were in the range of 460 to 475°C in nitrogen. The glass transition temperatures (T_g) of copolyesters ranged between 90 and 141°C, depending on the structure of the starting bis(4-(2-hydrox-

ethoxy)aryl) monomer, and increased with increasing rigidity, symmetry, and polarity of the monomers; for example, P_{BB} with rigid and symmetric biphenyl and P_{BS} with sulfone groups for intermolecular force had higher T_g than others, while P_{BF} with the bulky, rigid fluorene structure had the highest T_g of 141°C.

CONCLUSION

A series of novel copolyesters have been successfully prepared by introducing various hydroxyethoxy diols into PEN structure:

1. Each diol has its own optimum copolymerization temperature, and for the mole ratio of diol, BHEN = 1 : 3, the optimum temperature is 290 to 300°C.
2. The addition of aryl ether linkage or bulky fluorene structure into the polyester chain increased the solubility of PEN greatly, which may extend the applications of this type of polymer.
3. The glass transition temperatures of copolyesters from various hydroxyethoxy monomers and BHEN ranged from 90 to 141°C. Since the glass transition temperature is related to the use temperature and mechanical property of the polymer, it can be tailored to fit specific applications.

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