

Synthesis and Characterization of New Aromatic Polyesters Containing Biphenyl Side Groups

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ABSTRACT: Aromatic polyesters containing biphenyl side groups were synthesized by phase-transfer catalyzed interfacial polycondensation of 1-(4-biphenyl)-1,1-bis(4-hydroxyphenyl) ethane (BBHPE) with terephthaloyl chloride (TPC), isophthaloyl chloride (IPC), and a mixture of TPC/IPC (50 : 50 mol ratio). Copolyesters were synthesized by utilizing different molar proportions of BBHPE and 4,4'-isopropylidenediphenol (BPA) with IPC and TPC. The inherent viscosities of polyesters were in the range 0.44–1.26 dL/g. All the polyesters were soluble in organic solvents such as dichloromethane, chloroform, tetrahydrofuran, *meta*-cresol, pyridine, *N,N*-dimethylformamide, *N,N*-dimethylacetamide, and 1-methyl-

2-pyrrolidinone. Tough, transparent, and flexible films could be cast from chloroform solutions of these polyesters. WAXD measurements indicated that all the polyesters and copolyesters were amorphous in nature. Glass transition temperature of polyesters were in the range 198–256°C, while the initial degradation temperature of polyesters were in the range 444–481°C. Copolyesters derived from BBHPE exhibited improved solubility and higher glass transition temperatures compared to the corresponding polyesters based on BPA. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 3105–3110, 2007

Key words: aromatic polyesters; biphenyl side groups

INTRODUCTION

Aromatic polyesters exhibit good thermal stability, solvent resistance, and good mechanical properties and are, therefore, applied widely in the aviation, automobile, and electronic industries.^{1–3} However, most polyarylates encounter processing difficulties because of their high glass transition or melting temperatures coupled with insolubility in common organic solvents. Copolymerization and utilization of unsymmetrically substituted monomers are the two most commonly used synthetic approaches in obtaining compositions whose transition temperatures lie in a manageable temperature range either for processing or for characterization.^{4,5} In other methods for improving solubility of aromatic polyesters, several approaches have been taken: introduction of kinks of flexible units in the main chain^{6–8} or replacement of the conventional monomers with ones containing bulky pendant groups.^{9–16} The latter approach is of particular interest and has been exploited in the past. Depending upon the bulkiness and position of the substituent, the resulting polyarylates, in some cases, are amorphous with improved solubility in organic solvents.

In this study, we report synthesis of new polyesters containing biphenyl side groups from terephthaloyl chloride (TPC)/isophthaloyl chloride (IPC) and 1-(4-biphenyl)-1,1-bis(4-hydroxyphenyl) ethane (BBHPE). Copolyesters were also synthesized by utilizing different molar proportions of BBHPE and 4,4'-isopropylidenediphenol (BPA) with TPC and IPC. The properties of copolyesters such as solubility and thermal properties were investigated. The effect of incorporation of biphenyl side groups on the properties of aromatic polyesters is discussed.

EXPERIMENTAL

Materials

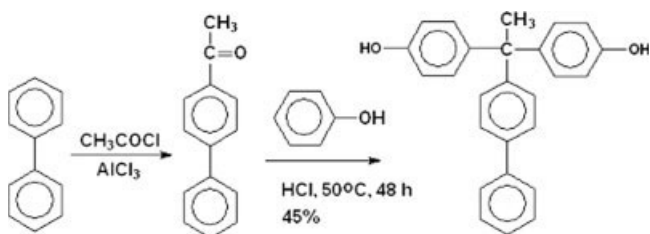
Biphenyl and aluminum chloride were obtained from Merck, India. 4,4'-Isopropylidenediphenol (BPA) and benzyltriethylammonium chloride (BTEAC) were purchased from M/s Sigma-Aldrich, India. 4-Acetyl-biphenyl was prepared according to the reported procedure.¹⁷ TPC and IPC were prepared by standard methods¹⁸ and purified by distillation under reduced pressure. The solvents were purified according to standard procedures.¹⁹

Synthesis of monomer

Synthesis of 1-(4-biphenyl)-1,1-bis(4-hydroxyphenyl) ethane (BBHPE): into a 500-mL three-necked round-

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Scheme 1 Synthesis of 1-(4-biphenyl)-1,1-bis(4-hydroxyphenyl) ethane (BBHPE).

bottomed flask equipped with a magnetic stirring bar, a gas inlet, and an air condenser were charged 4-acetylbiphenyl (50 g, 0.25 mol), phenol (169 g, 1.80 mol),

and 3-mercaptopropionic acid (2.73 g, 0.02 mol). The reaction mixture was heated at 50°C with stirring and dry HCl gas was bubbled for 48 h. The reaction mixture was dissolved in ethyl acetate and washed with aqueous sodium bicarbonate solution to remove HCl . Excess phenol was removed by distillation under reduced pressure and the crude product was purified by column chromatography using petroleum ether-ethyl acetate (90:10, v/v) as an eluent followed by recrystallization from chlorobenzene. Yield = 41.18 g (45%); M.P. = 184°C (Lit.²⁰ M.P. $184\text{--}185^\circ\text{C}$); IR (KBr): 3380 cm^{-1} (OH).

Elem. anal. Calcd for $\text{C}_{26}\text{H}_{22}\text{O}_2$: C, 85.24%; H, 6.0%. Found: C, 85.51%; H, 5.86%.

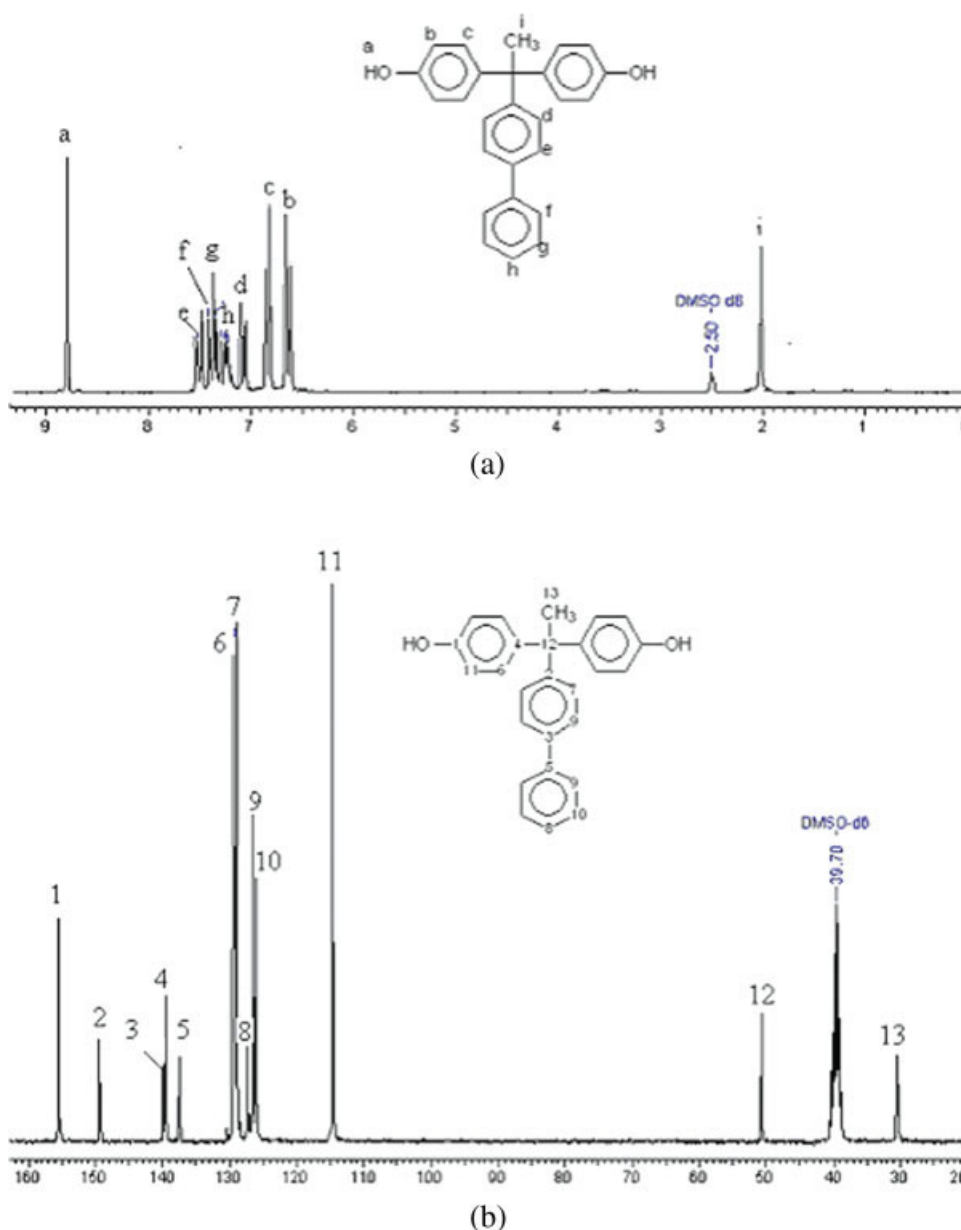
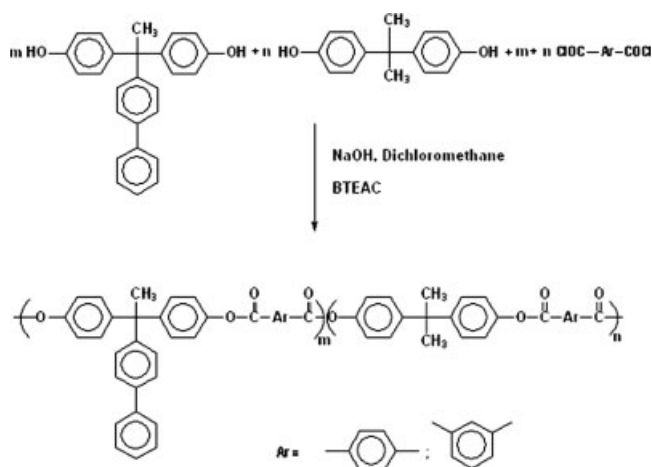


Figure 1 (a) ^1H NMR (top) and (b) ^{13}C NMR (bottom) spectra ($\text{DMSO-}d_6$) of BBHPE. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]



Scheme 2 Synthesis of aromatic polyesters containing biphenyl side groups.

Preparation of polyesters

Polymerizations were carried out in a 100-mL three-necked flask equipped with a mechanical stirrer. In a typical polymerization reaction, BBHPE (1.83 g, 5 mmol) was dissolved in 10 mL of 10 mmol solution of sodium hydroxide. The mixture was stirred for 1 h at 10°C. Next, BTEAC (30 mg) was added to the reaction mixture and the stirring was continued. After 30 min, solution of IPC (1.015 g, 5 mmol) in 20 mL of dichloromethane was added to the reaction mixture and the mixture was stirred vigorously (2000 rpm) for 1 h. The reaction mixture was poured into hot water; the precipitated polymer was filtered and washed several times with water. The polymer was dissolved in chloroform and reprecipitated into methanol. The polymer was filtered, washed with methanol, and dried under reduced pressure at 80°C for 24 h. The yield of polyester was almost quantitative.

Similar procedure was followed for the synthesis of other polyesters and copolyesters.

Characterization

Inherent viscosity (η_{inh}) of polyester was measured using Ubbelohde viscometer in chloroform at a concentration of 0.5 g/dL at $(30 \pm 0.1)^\circ\text{C}$. Infrared spectra were recorded as KBr pellets on a PerkinElmer FTIR spectrophotometer. ^1H and ^{13}C NMR spectra of the monomer and polyesters were obtained using Bruker 200 MHz NMR spectrometer. Molecular weights of polyesters and copolyesters were measured on a GPC in chloroform (Gel Permeation Chromatography, ThermoFinnigan, using the following conditions: column – polystyrene-divinylbenzene [10^5 – 50^5 Å], detector-RI) at room temperature. Polystyrene was used as the reference standard. Glass transition temperature (T_g) of the polyesters was determined on DSC-7 (PerkinElmer) at a scanning rate $20^\circ\text{C}/\text{min}$ under nitrogen. The initial decomposition temperature (IDT) was determined from TG curves of polyesters recorded on TGA-7 (PerkinElmer) at a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen.

RESULTS AND DISCUSSION

Scheme 1 depicts route for the synthesis of BBHPE. 4-Acetylbiphenyl was synthesized by monoacylation of biphenyl, a commercially available chemical, using acetyl chloride as an acylating agent and AlCl_3 as the catalyst. BBHPE was obtained by the reaction of 4-acetylbiphenyl with phenol in the presence of dry HCl gas and 3-mercaptopropionic acid as the catalyst system. BBHPE was characterized by IR and NMR spectroscopy. Figure 1(a,b) shows ^1H - and ^{13}C NMR spectra of BBHPE, respectively, along with the assignments. The purity of BBHPE was determined by HPLC and was found to be 99.9%.

Homo- and copolyesters were synthesized by phase transfer-catalyzed interfacial polycondensation technique (Scheme 2). A series of polyesters and copoly-

TABLE I
Synthesis and Characterization of Aromatic Polyesters Containing Biphenyl Side-Groups

Entry	Polymer	Composition of bisphenols (mol %)		Diacid chloride	η_{inh} (dL/g ^a)	M_n^b	M_w^b
		BBHPE	BPA				
1	A	100	0	TPC	0.56	25,800	57,000
2	AI	75	25	TPC	0.49	19,150	38,550
3	AII	50	50	TPC	0.7	37,750	64,750
4	AIII	25	75	TPC	1.26	66,600	1,60,200
5	B	100	0	IPC	0.45	13,650	29,950
6	BI	75	25	IPC	0.47	21,100	44,550
7	BII	50	50	IPC	0.48	31,700	60,150
8	BIII	25	75	IPC	0.7	52,500	98,350
9	C	100	0	IPC/TPC 50/50	0.44	20,700	37,650

^a Inherent viscosity measured in chloroform at a concentration of 0.5 g/dL at $(30 \pm 0.1)^\circ\text{C}$.

^b Measured by GPC in chloroform; polystyrene was used as a reference standard.

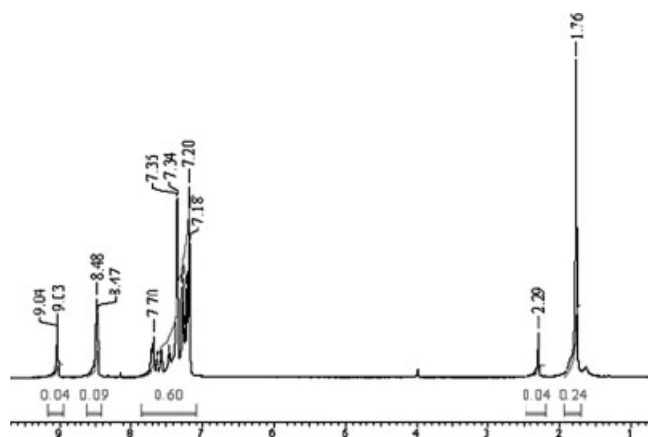


Figure 2 ^1H NMR (CDCl_3) spectrum of copolyester from a mixture of BBHPE (25%) and BPA (75%) with IPC.

lyesters were synthesized from combinations of BBHPE, BPA, IPC, and TPC in dichloromethane—aqueous sodium hydroxide system using BTEAC as a phase transfer catalyst (Table I). The inherent viscosities of polyesters were in the range 0.44–1.26 dL/g indicating the formation of medium to reasonably high molecular weight polymers. This is also reflected in the results of measurement of molecular weights of the polyesters by GPC (Table I).

IR and NMR spectra confirmed the formation of polyesters. IR spectra of the polyesters exhibited absorption band for ester carbonyl in the range 1730–1740 cm^{-1} . The compositions of copolyesters were determined by ^1H NMR spectroscopy. In the NMR spectra of the copolyesters (Fig. 2), there are two different characteristic singlet peaks in the aliphatic region: 2.30 and 1.77 ppm, which were assigned to the protons of methyl group bonded to a quaternary carbon bearing the biphenyl side group of BBHPE and the methyl group protons of isopropylidene linkage of BPA, respectively. The relative intensity ratios of the peaks were used to determine the amount of BBHPE and BPA present in copolyesters. There was a reasonably good agreement between the observed

TABLE II
Copolyester Composition Determined from ^1H NMR Spectra

Copolyester	Observed BBHPE (mol %)	Feed BBHPE (mol %)
AI	72.3	75
AII	48.9	50
AIII	25	25
BI	70.9	75
BII	48.3	50
BIII	25	25

incorporation of BBHPE and the amount taken for polymerization (Table II).

Solubility data of copolyesters in several organic solvents at 3% (w/v) are presented in Table III. Copolyesters dissolved readily in solvents such as dichloromethane, chloroform, tetrahydrofuran, *meta*-cresol, pyridine, *N,N*-dimethylformamide, *N,N*-dimethylacetamide, and 1-methyl-2-pyrrolidinone at room temperature. In contrast, polyesters based on BPA with TPC and IPC showed less solubility in common organic solvents.⁹ This result indicates that the incorporation of biphenyl side groups into the polyester backbone enhanced the solubility of polyesters and copolyesters. This is because of the disturbance in the dense chain packing of the polymer by the biphenyl side groups, which, in turn, facilitates the penetration of solvent molecules resulting in improved solubility.

Tough, transparent, and flexible films could be cast from chloroform solutions of these copolyesters.

Wide angle X-ray diffraction (WAXD) patterns of the copolyesters showed an amorphous halo over 2 θ range of 2°–40°. The introduction of biphenyl side groups into polymer backbone hinders the chain packing resulting in amorphous nature of these polyesters, which is also reflected in their enhanced solubility.

The effect of polymer structure on thermal properties of copolyesters was studied by TGA and DSC. The IDT of polyesters are given in Table IV and were

TABLE III
Solubility of Aromatic Polyesters Containing Biphenyl Side Groups^a

Polyester	DCM	CHCl_3	THF	<i>m</i> -Cresol	Pyridine	DMF	DMAc	NMP	DMSO
A	++	++	++	++	++	++	++	++	-+
AI	++	++	++	++	++	++	++	++	-+
AII	++	++	++	++	++	++	++	++	-+
AIII	++	++	++	++	++	++	++	++	-+
B	++	++	++	++	++	++	++	++	-+
BI	++	++	++	++	++	++	++	++	-+
BII	++	++	++	++	++	++	++	++	-+
BIII	++	++	++	++	++	++	++	++	-+
C	++	++	++	++	++	++	++	++	-+

DCM, dichloromethane; CHCl_3 , chloroform; THF, tetrahydrofuran; DMF, *N,N*-dimethylformamide; DMAc, *N,N*-dimethylacetamide; MP, 1-methyl-2-pyrrolidinone; DMSO, dimethyl sulfoxide.

^a Solubility: ++ = soluble at room temperature; -+ = partially soluble on heating at 70°C.

TABLE IV
Thermal Properties of Aromatic Polyesters Containing Biphenyl Side Groups

Sr. No.	Polymer	T_g (°C) ^a	T_g (°C) ^b	T_g (°C) ^c	IDT (°C) ^d
1	A	256	—	—	481
2	AI	249	247	245	476
3	AII	244	237	235	473
4	AIII	228	227	226	467
5	B	232	—	—	478
6	BI	219	221	219	470
7	BII	214	211	208	456
8	BIII	201	199	196	444
9	C	238	—	—	478

^a Measured on DSC at a heating rate of 20°C/min.

^b Calculated by using simple mixing rule.

^c Calculated by using Fox equation.

^d Measured on TGA at a heating rate of 10°C/min under nitrogen.

in the range 444–481°C under nitrogen atmosphere (Fig. 3). DSC thermograms of BBHPE-based polyesters with TPC and IPC obtained from second heating run

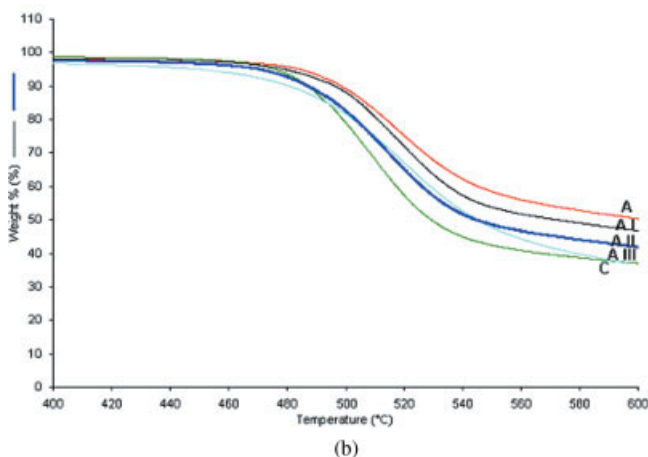
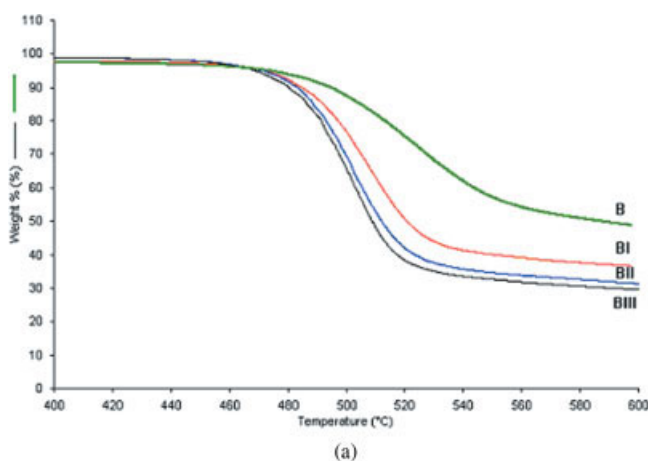


Figure 3 TG curves of aromatic polyesters containing biphenyl side groups. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

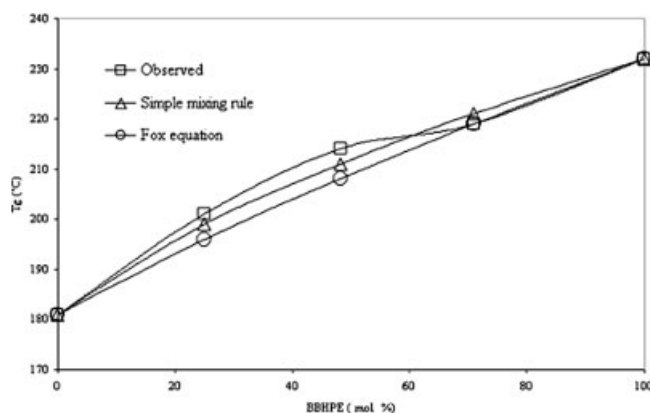


Figure 4 Glass transition temperature as a function of concentration of BBHPE in copolyesters derived from a mixture of BBHPE and BPA with IPC.

showed T_g at 256 and 232°C, respectively. The T_g value for copolyester from BBHPE with IPC/TPC (50:50 mol %) was observed at 238°C. It was observed that T_g values obtained for BBHPE-based polyesters with IPC, TPC, and IPC/TPC were higher than those of the corresponding polyesters based on bisphenol-A.²¹ This behavior is attributed to the presence of biphenyl side groups in BBHPE-based polyesters, which hinder free rotation of polymer chain and leads to higher T_g values. In the copolyesters synthesized utilizing different molar proportions of BBHPE and BPA with IPC and TPC, the T_g and IDT values tend to increase as the molar proportion of BBHPE was increased.

There are several approaches to predict the expected T_g in random copolymer or miscible blend as a function of concentration of the comonomers. For the prediction of T_g of copolyesters, BPA/IPC and BPA/TPC polyesters were synthesized and T_g values determined were found to be 181 and 210°C, respectively.

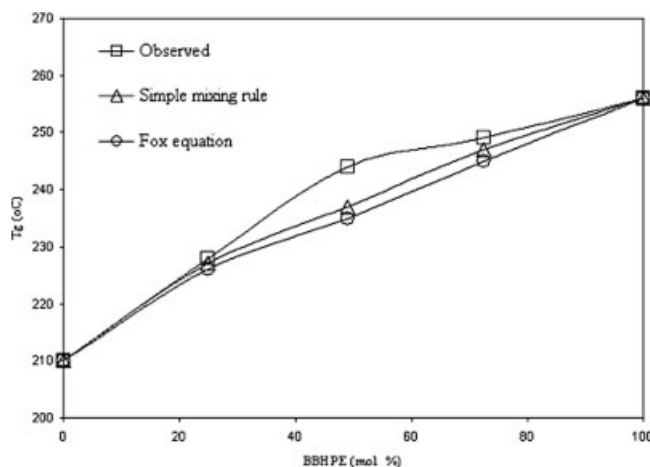


Figure 5 Glass transition temperature as a function of concentration of BBHPE in copolyesters derived from a mixture of BBHPE and BPA with TPC.

The observed T_g values of copolyesters compared well with the T_g values predicted using Fox equation²² and a simple mixing rule²³ (Table IV, Figs. 4 and 5).

CONCLUSIONS

The incorporation of biphenyl side groups derived from BBHPE into aromatic polyesters resulted in improved solubility and increased T_g and thermal stability compared to the corresponding polyesters derived from BPA. In the copolyesters synthesized utilizing different molar proportions of BBHPE and BPA with IPC and TPC, the T_g and IDT values tend to increase as the molar proportion of BBHPE was increased. Tough, transparent, and flexible films could be cast from chloroform solution of these polyesters. Therefore, polyesters-containing biphenyl side groups may be considered as promising processable aromatic high performance polymers.

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