

The Preparation and Properties of Polyarylate Block Copolymers by Interfacial Polycondensation

TENG-YUAN TSENG, NING-JO CHU,* and YU-DER LEE,
*Department of Chemical Engineering, National Tsing Hua University,
Hsinchu, Taiwan 30043, Republic of China*

Synopsis

Block copolymers of bisphenol A isophthalate and sebacate were prepared by a two-step interfacial polycondensation. The copolymers had sebacate contents of 1 : 5 and 1 : 3 molar with block lengths (\overline{DP}) of 4, 9, and 19. Thermal analysis of the copolymers by DSC showed the T_m of PBI. The crystallizability of PBI chain segments in the block copolymers was confirmed by X-ray diffraction. The T_m of the copolymers was primarily influenced by the DP of the chain segments rather than the sebacate content. The T_g of the copolymers was mainly affected by the sebacate content rather than the \overline{DP} of chain segments. The independent T_g of sebacate in the copolymers was not detected by DSC, i.e., the two polymer chains were compatible without phase separation. Phase separation was only observed in the rheometric spectrum of a 1 : 1 blend of the two homopolymers. The sebacate, being compatible with the isophthalate, had a plasticizing effect upon the polyarylate, which resulted in an improvement in toughness of the copolymers.

INTRODUCTION

Polyarylates have good thermal stability and mechanical properties that are useful as heat-resistant engineering plastics. The homopolymers such as bisphenol A isophthalate and terephthalate are highly crystalline but brittle. Useful products are derived from amorphous copolymers.¹

Over the past decade, research on polyarylates has been directed toward improving their thermal properties by employing a rigid bisphenol moiety, e.g., naphthols,^{2,3} phenolphthalein,^{4,5} phenolfluorene,^{6,7} halogen-substituted bisphenols,^{8,9} etc. Soft chain segments have been incorporated into polyarylates for the purpose of improving their processability. These included alkyl siloxanes,^{10,11} polyoxyethylenes,^{12,13} polyoxypropylenes,¹³ and others.¹⁴⁻¹⁷

In a study of the reaction mechanism of polyarylate formation in interfacial polycondensation, Tsai and Lee¹⁸ have demonstrated the feasibility of producing block copolymers by a two-step reaction. This article describes the preparation of poly(bisphenol A isophthalate-*b*-sebacate) and the effect of \overline{DP} of chain segments and sebacate content on the thermal and mechanical properties of the block copolymers.

EXPERIMENTAL

Isophthaloyl chloride, supplied by Tokyo Chemical Industry (E.P. reagent) in 500-g bottles, was purified by distillation under reduced pressure, bp 110°C/

* To whom correspondence should be addressed.

0.5 mm Hg. Sebacyl chloride supplied by WAKO Chemical Co. in 25-g ampoules and bisphenol A from Hayashi Pure Chemical Ind. Ltd. (E.P. reagent) were used as received.

The following instruments were used in the experiments: UV spectrophotometer, Hitachi 320; differential scanning calorimeter, Perkin-Elmer DSC-2; infrared spectrophotometer, Perkin-Elmer 842; X-ray diffractometer, Rigaku Geigerflex; and rheometric dynamic spectrometer, Rheometrics RDS II.

Preparation of PBIS Block Copolymers

Poly(bisphenol A isophthalate-*b*-sebacate) (PBIS) was prepared from the acyl chloride-terminated prepolymers of poly(bisphenol A isophthalate) and poly(bisphenol A sebacate) by sequential interfacial polycondensation as follows:

An aqueous solution, 300 mL, containing 20.5 g of bisphenol A (0.09 mol), 8.4 g of sodium hydroxide (0.21 mol), and 1.0 g of triethylbenzylammonium chloride (TEBAC) was mixed by stirring (700 rpm) with a solution of 20.3 g isophthaloyl chloride (0.1 mol) in 200 mL of methylene dichloride at room temperature. After a reaction period of 7 min, the organic solution was separated from the aqueous phase.

The prepolymer of poly(bisphenol A sebacate) was prepared simultaneously by the same procedure from 5.13 g of bisphenol A (0.0225 mol) in 100 mL of water and 5.98 g of sebacyl chloride (0.025 mol) in 70 mL of methylene dichloride.

The two prepolymers in methylene dichloride solution were combined and reacted with 11.8 g of bisphenol A in 150 mL of water containing 4.86 g of sodium hydroxide and 0.5 g of TEBAC. The mixture was stirred 1 h at room temperature. The organic phase, after separation from the aqueous layer, was washed with water. The copolymer produced was precipitated from methanol, washed, then dried under reduced pressure.

A sample of prepolymer solution, 10 mL, was shaken with 20 mL of THF/H₂O (1 : 1) for 1 h for the hydrolysis of the terminal acyl chloride. The product was recovered by precipitation in methanol, and its molecular weight was determined by end-group analysis.

A weighted sample, about 1 g, was dissolved in 50 mL of a mixed solvent of DMF/THF (10 : 1). The solution was titrated with 0.1N alcoholic KOH with phenolphthalein as indicator. Blank test was carried out by the same procedure.

Characterization of PBIS Block Copolymers

Infrared spectra of poly(bisphenol A isophthalate), poly(bisphenol A sebacate), and their copolymers were recorded by a Perkin-Elmer 842 infrared spectrophotometer.

A sample of PBIS was extracted with THF overnight in a soxhlet extractor for the removal of any PBS homopolymer that was soluble in this solvent. The soluble fraction was characterized by infrared spectroscopy.

Inherent viscosity of the PBIS copolymers was measured in CH₂Cl₂ solution (0.5 g/dL) at 30°C with an Ubbelohde viscometer.

Morphology of PBI, PBS, and PBIS was examined by X-ray diffraction using a Rigaku Geigerflex X-ray diffractometer.

Thermal Properties of PBIS Block Copolymers

Transition temperatures of PBIS copolymers were recorded with a differential scanning calorimeter, Perkin-Elmer DSC-2. Thermal decomposition temperatures were recorded by TGA.

Mechanical Properties of PBIS Block Copolymers

The tensile strength of the PBIS copolymers was measured according to ASTM D-638 type IV from specimen prepared by compression molding. Dynamic mechanical properties were recorded by a rheometric dynamic spectrometer, Rheometrics RDS II.

RESULTS AND DISCUSSION

Preparation of PBIS Block Copolymers

Poly(bisphenol A isophthalate-*b*-sebacate) was prepared in two steps by interfacial polycondensation. In the first step, acyl chloride-terminated prepolymers of bisphenol A isophthalate and bisphenol A sebacate were prepared separately from bisphenol A in an alkaline aqueous solution and acyl chloride in CH_2Cl_2 solution, using TEBAC as a phase transfer agent. In the second step, the combined prepolymers dissolved in CH_2Cl_2 were further reacted with excess bisphenol A to yield the block copolymers. The synthetic scheme is shown in Figure 1.

The molar ratio of bisphenol A to acyl chloride used in the first step will determine the DP of chain segments in the subsequently formed block copoly-

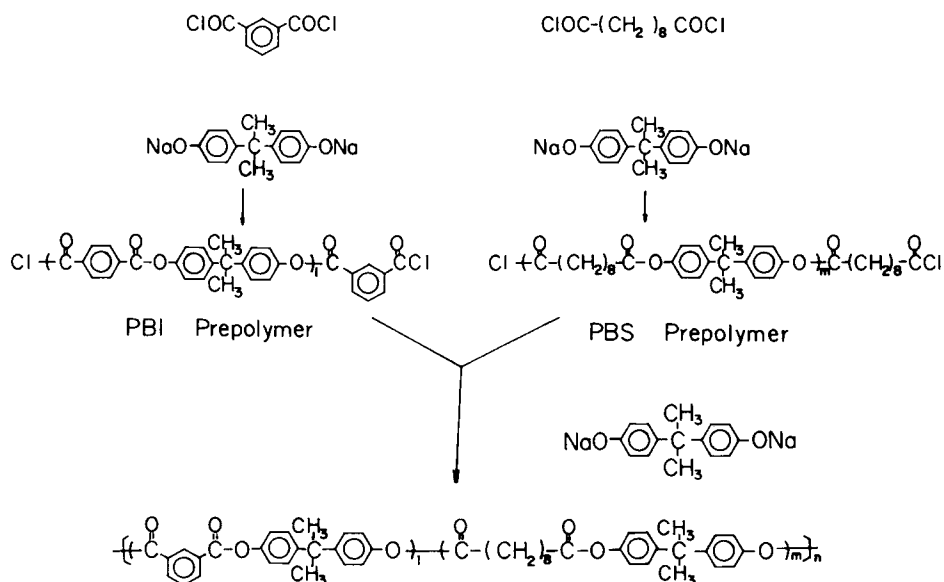


Fig. 1. The synthetic scheme of block copolymer preparation via two-step interfacial polycondensation.

TABLE I
Molecular Weight and Inherent Viscosity of PBI and PBS Prepolymers

Prepolymer	PBI			PBS		
Molar ratio ^a	0.8	0.9	0.95	0.8	0.9	0.95
\overline{M}_n found	1600	3140	6040	1450	2780	5440
\overline{DP} found	4.0	8.3	16.4	3.2	6.5	13.4
\overline{DP} cal'd	4	9	19	4	9	19
η_{inh} (dL/g) ^b	0.20	0.32	0.44	0.18	0.28	0.39

^a Denotes the molar ratio of bisphenol A to acyl chloride.

^b Measured in CH₂Cl₂ solution (0.5 g/dL) at 30°C.

mers. As given in the experimental section, the block copolymer was prepared from prepolymers with a calculated \overline{DP} of 9 and a molar ratio of 4 between the isophthalate and sebacate. This copolymer was designated as PBIS 409. Various copolymers were prepared by changing the relative amount of reactants.

Characterization of Prepolymers

The aqueous layers separated from prepolymer preparations were analyzed for bisphenolate content by UV spectroscopy.¹⁹ The concentrations found were in the range of 10⁻³ to 10⁻⁴ mol/L. Thus the conversion of bisphenol A reached a minimum of 99.6%.

The molecular weight of the prepolymers was determined by end-group analysis of the carboxyl derived from hydrolyzed acyl chloride terminals. The results are given in Table I. In the case of PBI, the average molecular weight of the prepolymers found was in close agreement with the calculated values. However, the experimental values were lower in the case of PBS, possibly due to partial hydrolysis of the ester linkages under the experimental conditions.

Characterization of PBIS Block Copolymers

PBIS 409, which contained 20.5% of sebacate by weight, was extracted with THF for the removal of any sebacate homopolymer that is soluble in this solvent. The weight loss after extraction was 3.0%. The soluble fraction showed absorption peaks of both the isophthalate and sebacate in the infrared spectrum. It appeared to be a fraction of low molecular weight copolymers. In the absence of sebacate homopolymer in any appreciable quantity, the formation of block copolymers was established by the present synthetic route.

The inherent viscosity of the copolymers produced is given in Table II.

TABLE II
Inherent Viscosity of PBIS Block Copolymers

PBIS sample	404	409	419	204	209	219	109
η_{inh} (dL/g) ^a	1.67	1.97	2.05	1.42	1.54	1.65	1.32

^a Measured in CH₂Cl₂ solution (0.5 g/dL) at 30°C.

TABLE III
Transition Temperatures of PBI, PBS, and PBIS

Sample	T_g ($^{\circ}\text{C}$)	T_m ($^{\circ}\text{C}$)	Calculated $\overline{\text{DP}}$ of blocks	PBI/PBS mole ratio
PBI	180	285		
PBS	18	—		
PBIS 419	158	285	19	4
PBIS 409	155	282	9	4
PBIS 404	150	265	4	4
PBIS 219	127	280	19	2
PBIS 209	125	275	9	2
PBIS 204	120	260	4	2
PBIS 109	85	240	9	1

Thermal Properties of PBIS Block Copolymers

The transition temperatures of poly(bisphenol A isophthalate), PBI, poly(bisphenol A sebacate), PBS, and their block copolymers were recorded by a differential scanning calorimeter. The results are given in Table III.

PBI is a crystalline polymer with a T_m of 285°C and a T_g of 180°C , whereas PBS is amorphous with a T_g of 18°C . All the copolymers prepared were opaque in appearance. They showed the transition temperature T_m of PBI, which was depressed to various degree in the presence of sebacate. Thus, the chain segments of PBI in the copolymers were crystallizable, even at a DP of segments as low as 4. The partial crystallinity of the copolymer was confirmed by X-ray diffraction (Fig. 2).

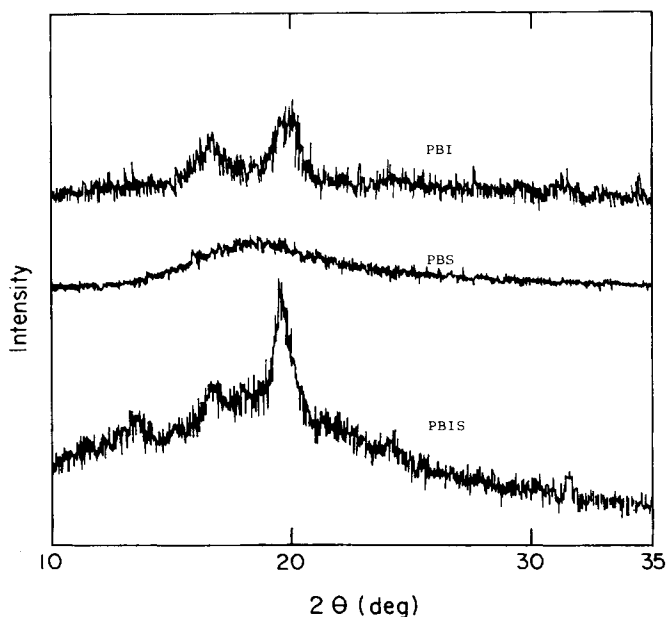


Fig. 2. The X-ray diffractograms of PBI, PBS, and PBIS.

From the results shown in Table III, the T_m of the copolymers was influenced primarily by the \overline{DP} of the chain segments rather than the sebacate content. At a \overline{DP} of 19, PBI segments can be crystallized without contamination. On the other hand, the T_g of the copolymers was mainly affected by the sebacate content rather than the \overline{DP} of the chain segments. The T_g of PBS was not detected by the differential scanning calorimetry in any case. This indicates good compatibility between the isophthalate and sebacate blocks.

In order to investigate the extent of their mutual compatibility, PBI was blended with PBS in 1 : 1 and 2 : 1 by weight (PBI and PBS are very close in molecular weight; weight ratio does not vary much from mole ratio), and their thermomechanical property was recorded by a rheometric dynamic spectrometer. The results shown in Figure 3 indicated clearly the occurrence of phase separation in blend 1 but not in blend 2. This confirmed the compatibility between PBI and PBS chain segments in the block copolymers up to a sebacate content of at least 33%. Various authors have reported good compatibility of polyarylates with other constituents such as alkyl siloxanes,¹¹ arylene sulphonoxides,²⁰ polyoxyethylenes,¹² and polyoxypropylenes.¹³

The decomposition temperature of PBIS block copolymers was determined by thermogravimetric analysis (TGA), and the results are given in Table IV. Insertion of sebacate blocks into the polymer chains lowers the decomposition temperature of the polyarylate. This adverse effect of sebacate on the thermal stability of PBI can be minimized by increasing the DP of chain segments at moderate levels of sebacate content.

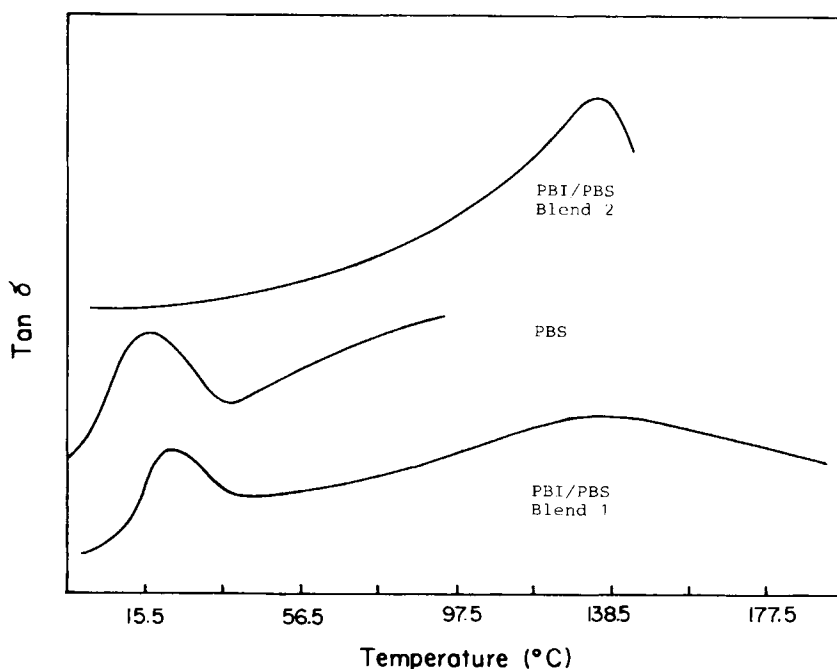


Fig. 3. The $\tan \delta$ of PBS and PBI/PBS Blends: blend 1, PBI/PBS in 1 : 1 by weight; blend 2, PBI/PBS in 2 : 1 by weight.

TABLE IV
Decomposition Temperatures of PBI, PBS, and PBIS Block Copolymers

Sample	Decomposition temperature ^a (°C)
PBI	467
PBS	390
PBI 419	444
PBI 409	443
PBI 404	439
PBI 219	429
PBI 209	421
PBI 204	404

^a Temperature at which a 10% weight loss was recorded by TGA at a heating rate of 20°C/min under nitrogen.

The Mechanical Properties of PBIS

The mechanical properties of PBIS were tested according to ASTM D638 from specimen prepared by compression molding. The results are given in Table V. PBI is highly crystalline but somewhat brittle. The sebacate, being compatible with the isophthalate, had a plasticizing effect to PBI and resulted in copolymers with improved toughness. At lower sebacate content, longer segment blocks appeared to be more effective in toughness improvement, but reversed results were obtained at higher sebacate content.

CONCLUSIONS

Block copolymers of bisphenol A isophthalate and sebacate were prepared by sequential interfacial polycondensation. The PBI and PBS blocks were found to be compatible up to a sebacate content of at least 33%.

The PBI chain segments in the block copolymers were crystallizable. Their T_m was influenced primarily by the DP of chain segments rather than the

TABLE V
Mechanical Properties of PBI, PBS, and PBIS Block Copolymers

Sample	Tensile strength (kg/cm ²)	Elongation (%)	Tensile modulus (kg/cm ²)
PBI	385	1.8	21,000
PBS	45	21.5	209
PBIS 419	468	2.7	17,000
PBIS 409	453	2.5	18,000
PBIS 404	455	2.4	19,000
PBIS 219	327	3.9	8,000
PBIS 209	371	3.5	11,000
PBIS 204	381	3.5	11,000

sebacate content. On the other hand, T_g of the copolymers was affected by sebacate content rather than the DP of chain segments.

The sebacate, being compatible with the isophthalate, had a plasticizing effect to PBI and resulted in copolymers with improved toughness.

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