Copolycondensation of IPA/TPA, BPA, and 4,4′-Dihydroxydipehnylsulfone and 4,4′-Dicarboxydiphenylsulfone

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ABSTRACT: Copolycondensations of IPA, TPA, bisphenol A (BPA), and several cimonomers were carried out to improve thermal properties, such as, the glass transition temperature (T_g) of the IPA/TPA (50/50)–BPA polyester. Among the comonomers examined, 4,4′-Dihydroxydiphenylsulfone (BPS) and 4,4′-Dicarboxydiphenylsulfone (DCDPS) having a strongly dipolar sulfonyl group in the chain were significantly effective. The favorable effect upon the T_gs was studied by varying the amounts of BPS and DCDPS incorporated into the copolymers. In the copolycondensation with BPS, two-stage copolycondensation of BPA first and then BPS, the reverse order of reaction, and their spontaneous addition were examined to investigate the effect of distribution of the BPS unit segments in the copolymer upon the T_gs of the resulted copolymers. The distribution was briefly studied from distribution of the IPA/TPA-BPA oligomers in the initial reaction using GPC. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 875–879, 2000

Key words: glass transition temperature; IPA/TPA(50/50)-BPA polyester; 4,4′-dihydroxydiphenylsulfone; 4,4′-dicarboxydiphenylsulfone; monomer sequence

INTRODUCTION

Interchain interaction between polymer chains has a significant effect upon the properties of polymers. The strong interaction between amide bonds in polyamides results in remarkably higher transition temperatures of polyamides. On the other hand, because the intermolecular interaction between carboxylate ester groups are not especially strong, the properties of polyesters are more sensitive to variations in structure than are those of strongly interacting polyamides.

To improve thermal properties of polyesters, such as the glass transition temperature (T_g) and polymer melting point, increase of aromatic charac-

ter of the polymers has been usually employed by copolymerizing with aromatic comonomers as in poly(ethylene terephthalate (PET)-*p*-hydroxybenzoic acid (PHB)[1] and PET-bisphenol A (BPA).[2] Alternatively, the insertion of a strongly dipolar sulfonyl group in the chain substantially increased the intermolecular forces, and hence, the polymer melting point, such as in aliphatic polyesters containing sulfonyl groups.[3,4] Therefore, it is easily expected that introduction of commercially available 4,4′-dihydroxydiphenylsulfone (BPS) would improve thermal properties of polyesters. The IPA/TPA(50/50)-BPA polyester is reported to be a prominent engineering plastics,[5] and the improvement of its thermal properties would give additional importance to the materials. However, neither the BPS polyesters with high molecular weight nor the BPS copolyesters have not been prepared by the conventional method, owing to the low reactivity of the

hydroxyl groups caused by the electron-withdrawing sulfonyl substituent.[6,7]

Recently, we have shown that high molecular weight copolyesters can be produced from ineffective aromatic diols with electron-withdrawing substituents such as carbonyl and sulfonyl groups by inducing initial oligomerization with selected monomers such as BPA followed by copolymerization.[8,9]

In this article we describe the results of copolycondensations of IPA/TPA(50/50), BPA, and BPS or 4,4′-dicarboxydiphenylsulfone (DCDPS) with TsCl/DMF/Py as the condensing agent. Factors such as the kind and content of comonomers and the mode of reaction with BPA and BPS were examined in terms of thermal properties of the resulted copolymers.

EXPERIMENTAL

All of the monomers were obtained from Tokyo Kasei Kogyo Co. Ltd., and used without further purification. Pyridine and DMF were purified by distillation over NaOH and CaH$_2$, respectively. Thermal properties of polymers were examined on a DSC analyser (Rigaku Thermoflex TG8110) at a heating rate of 10°C/min under a nitrogen atmosphere.

Two-Stage Copolycondensations of IPA/TPA, BPA, and 50 mol % of Several Diols

A mixture of TsCl (13 mmol) and DMF (10 mmol) in pyridine (5 mL), prepared and aged at room temperature for 30 min, was reacted with a pyridine (10 mL) solution of equal parts (2.5 mmol) of IPA and TPA at room temperature for 10 min and then at 80°C (bath temperature) for 10 min. To the resulting mixture BPA (2.5 mmol) in pyridine (10 mL) was added all at once, and the mixture was kept at 80°C for 30 min and then a pyridine (10 mL) solution of a diol comonomer (2.5 mmol) was added all at once. The whole mixtures were heated at 80°C for 2 h. In the copolycondensation of PHB, a pyridine (20 mL) solution of BPA (2.5 mmol) and PHB (2.5 mmol) was added dropwise over a period of 10 min and then heated for 2 h. The copolymers were isolated by diluting the reaction mixture with DMF or pyridine and pouring it into methanol.

Two-Stage Copolycondensations of IPA/TPA, BPA, and Several mol % of BPS

A pyridine (15 mL) solution of equal parts (2.5 mmol) of IPA and TPA, TsCl (13 mmol), and DMF

(10 mmol), prepared as above, was reacted with a pyridine (10 mL) solution of BPA or BPS (3.5–0 mmol) at 80°C (bath temperature) for 30 min. To the resulting mixture BPS or BPA (1.5–5 mmol) in pyridine (10 mL) was added all at once, and the whole mixtures were heated at 80°C for 2 h. In the random copolycondensation, a pyridine (20 mL) solution of BPA and BPS was added over a period of 0–20 min, and then the resulting mixtures were heated at 80°C for 2 h. The copolymers were isolated by working up as above.

Copolycondensation of IPA/TPA, DCDPS, and BPA

A solution of TsCl (13 mmol) and DMF (10 mmol) in pyridine (10 mL) was reacted with a mixture of equal parts (1.25–2.5 mmol) of IPA and TPA and DCDPS (1.25–0 mmol) in pyridine (10 mL) as described above. To the mixture a pyridine (10 mL) solution of BPA (5 mmol) was added at 80°C over 10 min, and the whole mixture was kept at 80°C for 2 h. The copolymer was isolated by working up as above.

GPC Analyses of Polymers and the Distribution of Oligomers

A reaction mixture of IPA (2.5 mmol), TPA (2.5 mmol), TsCl (13 mmol), and DMF (10 mmol) in pyridine (15 mL), prepared as above was treated with a pyridine (10 mL) solution of BPA (1.5–3.5 mmol, 0.3–0.7 molar equivalent to IPA/TPA) at 80°C for 30 min. After removed from an oil bath, the mixture was reacted with methanol (10 mL) for 30 min to terminate the carboxyl end groups of oligomers, and evaporated under a reduced pressure. The residue was dissolved in chloroform and extracted with hydrochloric acid and water. The chloroform layer was dried over anhydrous sodium sulfate, and then subjected to the GPC analysis. GPC analysis of polymers and the oligomer distribution was determined using two polystyrene gels columns (8 × 300 mm) in series having exclusion limits of 4.0 × 10^5 and 2 × 10^4 and chloroform as the eluent at a flow rate of 1 mL/min. The BPA oligomers were assigned according to our previous article.[10]

RESULTS AND DISCUSSION

Two-stage copolycondensation of IPA/TPA, BPA, and 50 mol % of several aromatic diols were car-

Table I Two-Stage Copolycondensation of IPA/TPA (50/50), BPA, and Several Diols (50 mol %)[a]

Initial Reactn	Subsequent Reactn	η_{inh}[b] (dL/g)	M_w/M_n ($\times 10^{-4}/\times 10^{-4}$)	T_g (°C)
BPA	BPS	1.18	8.5/3.2	238
BPA/PHB	—	1.05	—	207
BPA	DHBP	1.21	9.5/3.4	200
BPA	DHDPTE	0.90	8.7/3.0	190
BPA	DHDPE	0.68	5.6/2.9	188

[a] BPA, 2,2′-(4-hydroxyphenyl)propane; PHB, 4-hydroxybenzoic acid; BPS, 4,4′-dihydroxydiphenylsulfone; DHBP, 4,4′-dihydroxybenzo-phenone; DHDPTE, 4,4′-dihydroxydiphenylthioether; DHDPE, 4,4′-dihydroxydiphenylether.
[b] Measured in phenol/*sym*-tetrachloroethane (60/40, by weight) at 30°C.

ried out at 80°C by initial oligomerization of BPA followed by copolycondensation with the diols according to the our previous paper (Table I).[8,9] Among the diols examined, only BPS with a sulfonyl group effected significant increase in T_g of the IPA/TPA-BPA polymer by ca. 35°C. Other diols with substituents such as, ether, thioether, and carbonyl groups rather lowered the T_g. These results indicated the strong effect of the interchain dipole–dipole interaction between sulfonyl groups upon thermal properties.

The copolycondensation of IPA/TPA and BPA followed by BPS was studied by varying mol % of BPS to investigate how much of BPS can be effectively added (Table II). The T_g (200°C) of the IPA/TPA-BPA polymer determined in this study was a little higher than that (188°C) in the literature.[1] An increase in the BPS content increased the T_gs of the resulted copolymers, and raised it by 26 to 246°C at ca. 70 mol % BPS.

Table II Two-Stage Copolycondensation of IPA/TPA (50/50) of BPA First, and Then Several mol % of BPS

BPA (mol %)	BPS (mol %)	η_{inh}[a] (dL/g)	M_w/M_n ($\times 10^{-4}/\times 10^{-4}$)	T_g (°C)
30	70	1.10	10.5/3.0	244
50	50	1.18	10.5/3.5	237
70	30	1.37	13.0/4.0	220
100	0	0.94	—	200

[a] Measured in phenol/*sym*-tetrachloroethane (60/40, by weight) at 30°C.

Table III The Two-Stage Copolycondensation of IPA/TPA (50/50) of BPS First, and Then Several mol % of BPA

BPS (mol %)	BPA (mol %)	η_{inh}[a] (dL/g)	M_w/M_n ($\times 10^{-4}/\times 10^{-4}$)	T_g (°C)
0	100	0.94	—	200
30	70	1.10	10.0/3.6	222
50	50	0.96	8.4/3.7	230
70	30	0.56	7.6/2.1	235

[a] Measured in phenol/*sym*-tetrachloroethane (60/40, by weight) at 30°C.

It was expected that at a constant mol % of BPS wider distribution of BPS in the copolymer would enhance interchain interaction between the copolymer chains so that T_g would be higher than that blockly distributed copolymer. Therefore, when BPS could be suitably distributed, even a smaller amount of BPS would cause an effective increase in the T_g.

In two-stage copolycondensation as mentioned above the IPA/TPA-BPA oligomers were initially formed, and then BPS combined them to produce the copolymers. On the other hand, when BPS is added first and then BPA, BPA combines the IPA/TPA-BPS oligomers. Therefore, the order of reaction may produce the copolymer with different distribution of BPS from each other. Furthermore, randomly copolymerizied polymers may also have a different distribution of BPS from those prepared by two-stage copolycondensation.

Two-stage copolymerization of BPS followed by BPA was studied by varying mol % BPS, and the results are shown in Table III (see Fig. 1). The T_gs were also improved by the introduction of BPS, increasing with an increase of the BPS content. However, the effect was a little less favorable, especially at higher mol % of BPS than that observed in the copolymers prepared by initial reaction of BPA followed by BPS.

When BPA and BPS were randomly copolymerized by addition of a mixture of them, the increase in the T_gs was not as large, especially at a lower 30 mol % of BPS compared to that observed in the copolymers prepared by the stepwise reactions of BPA and BPS as mentioned above (Table IV). Dropwise addition of their mixture might affect a competitive reaction between BPA and BPS, which might change their sequences, and hence the T_g of the resulted copolymer, but no signifi-
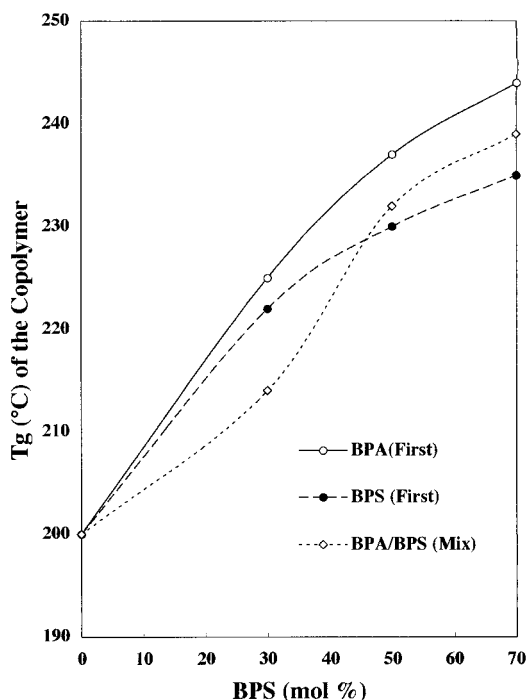
Figure 1 T_gs of the IPA/TPA(50/50)/BPA/BPS copolymers prepared by changing the order of reaction with BPA and BPS.

cant difference in the T_gs by the addition time was observed (Table V).

The results of Tables III–V obtained by three procedures of copolycondensation were summarized in Figure 1 for comparison. In a wide range of the BPS content, the copolymers, especially with 50–70 mol % BPS, obtained by the initial reaction with BPA showed higher T_gs than those by the initial reaction of BPS and random reaction as well. We tried to study the results in terms of the distribution of the BPS oligomers in the copolymer using GPC. Because the IPA/TPA-BPS oligomers were insolu-

Table IV   Random Copolycondensation of IPA/ TPA (50/50) of BPS and Several mol % of BPA

BPS/BPA (mol %/mol %)	η_{inh}[a] (dL/g)	M_w/M_n ($\times 10^{-4}/\times 10^{-4}$)	T_g (°C)
0/100	0.94	—	200
30/70	1.10	10.0/3.6	222
50/50	0.96	8.4/3.7	230
70/30	0.56	7.6/2.1	235

[a] Measured in phenol/*sym*-tetrachloroethane (60/40, by weight) at 30°C.

Table V   Random Copolycondensation of IPA/ TPA (50/50) by Dropwise Addition of a Mixture of BPS and BPA

BPS/BPA (mol %/mol %)	Addition (min)	η_{inh}[a] (dL/g)	M_w/M_n ($\times 10^{-4}/\times 10^{-4}$)	T_g (°C)
50/50	0	0.96	9.5/3.9	238
	10	1.05	8.5/3.2	232
	20	1.14	11.0/3.4	233
30/70	0	0.92	8.6/3.4	239
	10	1.03	9.5/3.6	241

[a] Measured in phenol/*sym*-tetrachloroethane (60/40, by weight) at 30°C.

ble in usual organic solvents suitable for GPC, the distribution was examined, though indirectly, from the distribution of the IPA/TPA-BPA oligomers shown in Table VI, assuming that distribution of the IPA/TPA-BPS oligomers is similar to that of the IPA/TPA-BPA oligomers. Initial origomerization of 70 mol % BPS would probably yield large amounts of the oligomers having more than two IPA/TPA-BPS segment units (ca. 85 wt % for the IPA/TPA-BPA oligomers, $n \geq 2$ in the third column in the table), and the following copolycondensation by 30 mol % BPA would produce the copolymer with the longer IPA/TPA-BPS segment units. On the other hand, initial reaction with 30 mol % BPA produced only about 25 wt % of the IPA/TPA-BPA oligomer ($n = 0$ in the first column) capable of affording longer IPA/TPA-BPS segment units so that the following copolycondensation by 70 mol % BPS would afford the copolymer of smaller amounts of longer IPA/

Table VI   Distribution of (IPA/TPA-BPA)$_n$-IPA/ TPA Oligomers Formed at the First Stage of Polycondensation

Product Components	wt % Components for Various r[a]		
	$r = 0.3$	$r = 0.5$	$r = 0.7$
$n = 0$ IPA/TPA ester	25.24	6.95	1.74
$n = 1$	41.47	31.03	13.34
$n = 2$	20.53	27.07	15.30
$n = 3$	8.88	15.16	15.67
$n = 4$	3.85	9.65	11.67
$n \geq 5$	0.03	10.14	42.28

[a] Molar ratios of BPA to IPA/TPA at the first stage of reaction.

TPA-BPS segment units. This would also be the case for the copolymer with 50 mol % of BPS. Initial reaction of 50 mol % BPA resulted in ca. 7 wt % of the oligomer capable of affording longer IPA/TPA-BPS segment units, while that of 50 mol % BPS might produce the oligomers having more than two IPA/TPA-BPS segment units (ca. 62 wt % for the IPA/TPA-BPA oligomers, $n \geq 2$ in the second column in the table). From these results, it is likely that a higher T_g of the IPA/TPA-BPA/BPS copolymer can be obtained when BPS is widely distributed in the IPA/TPA-BPA/BPS copolymer.

As an alternative monomer, we examined commercially easily available 4,4′-dicarboxydiphenyl-sulfone (DCDPS). Introduction of DCDPS into the IPA/TPA-BPA polyester was expected to have a more favorable effect upon the T_g of the resulted copolyester, because the DCDPS-BPA polyester has a higher T_g (267°C)[7] than that (194°C)[6] of the IPA/TPA-BPA polymer. In addition, as observed in the thermotropic liquid crystalline copolyesters,[11] incorporation of a dicarboxyl component into the IPA/TPA-BPA polyester was expected to have stronger influence upon the thermal properties than that of the dihydroxy components.

The copolycondensation of equal parts of IPA and TPA, BPA, and DCDPS was studied in the range of up to 50 mol % DCDPS (Table VII). Expectedly, introduction of a wide range of mol % DCDPS into the IPA/TPA-BPA polymer was more effective than random incorporation of BPS (Fig. 2). The favorable effect was more significant at the lower contents, and addition of 10 mol % DCDPS was as effective as that of 30 mol % BPS.

In conclusion, although higher TPA contents in the IPA/TPA-BPA polymer raised the T_g from 194°C by 50 mol % up to 203°C by 80 mol %,[6] more significant improvement of the T_g was achieved by introducing sufonyl containing monomers such as BPS and DCDPS, even in a smaller amount.
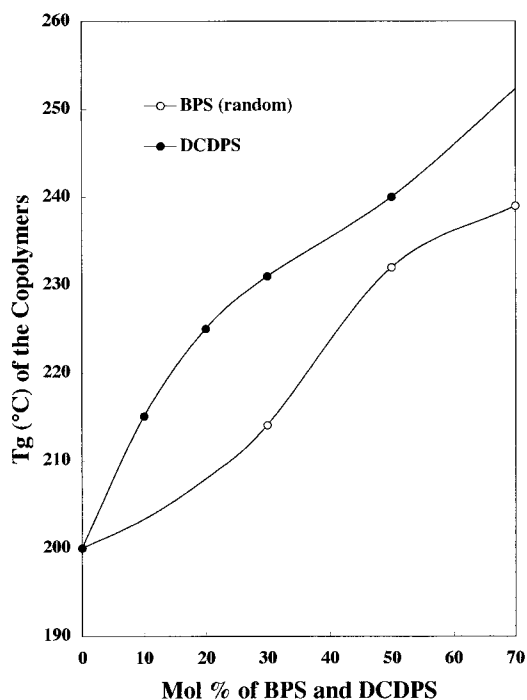

Figure 2 T_gs of the IPA/TPA/BPA/BPS and IPA/TPA/DCDPE/BPA copolymers.

Table VII Copolycondensation of Equal Parts of IPA and TPA, DCDPS, and BPA

DCDPS (mol %)	η_{inh}[a] (dL/g)	M_w/M_n ($\times 10^{-4}/\times 10^{-4}$)	T_g (°C)
0	1.16	11.1/41	200
10	1.09	10.6/2.8	215
20	1.13	11.1/3.6	225
30	1.05	10.0/3.1	231
50	0.91	9.0/3.3	240

[a] Measured in phenol/sym-tetrachloroethane (60/40, by weight) at 30°C.

REFERENCES

1. Jackson, W. J., Jr.; Kuhfuss, H. K. J Polym Sci Polym Chem Ed 1976, 14, 2043.
2. Hamb, F. L. J Polym Sci Polym Chem Ed 1972, 10, 3217.
3. Horn, C. F. Makromol Chem 1959, 10, 3217.
4. Huffman, K. R.; Casey, D. J. J Polym Sci Polym Chem Ed 1985, 23, 2043.
5. Union Carbide Engineering Polymers, Technical Brochure F-47141B, Union Carbide Corp., New York, Aug. 1984.
6. Eareckson, W. J Polym Sci 1959, 40, 399.
7. Manami, H.; Nakazawa, M.; Oishi, Y.; Kakimoto, M.; Imai, Y. J Polym Sci, Part A: Polym Chem 1990, 28, 465.
8. Higashi, F.; Hayashi, R.; Mitani, K. Polym Prepr Jpn 1997, 46, 256.
9. Higashi, F.; Ong, C.-H.; Okada, Y. J Polym Sci, Part A: Polym Chem 1999, 37, 3625.
10. Higashi, F.; Ong, C.-H.; Kim, J.-H. J Polym Sci, Part A Polym Chem 1999, 37, 2371.
11. Higashi, F.; Ong, C.-H.; Kim, J.-H. J Polym Sci, Part A Polym Chem 1999, 37, 621.