

# Solution Copolycondensation of Isophthalic Acid, Terephthalic Acid, 4,4'-Dihydroxydiphenylsulfone, and Bisphenols with a Tosyl Chloride/Dimethylformamide/Pyridine Condensing Agent

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**ABSTRACT:** The solution polycondensation of a mixture of various parts of isophthalic acid (IPA) and terephthalic acid (TPA) with 4,4'-dihydroxydiphenylsulfone (BPS) with tosyl chloride/dimethylformamide/pyridine as a condensing agent was studied. To elucidate how the reaction should be done to obtain copolymers of high molecular weights, we examined the two-stage copolycondensation with BPS and 2,2-bis(4-hydroxyphenyl)propanes (BPAs) by changing the content of IPA/TPA and the amount of BPS or BPA used in the initial reaction. Controlling the reaction at an earlier stage could facilitate the copolycondensation. The polyesters

of IPA/TPA and BPS of moderate inherent viscosity values up to 1.0 were obtained by the two-stage reaction with optimal amounts of BPS first and then additional BPS. Satisfactory results were also obtained by the dropwise addition of BPS over 10–20 min in the preparation of the IPA/TPA–BPS polymers containing less than 50 mol % TPA. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2607–2610, 2002

**Key words:** solution polycondensation; stepwise polycondensation; polyarylates; 4,4'-dihydroxydiphenyl sulfone; condensing agent

## INTRODUCTION

Although high-molecular-weight polyarylates of various bisphenols have been readily prepared by interfacial or melt polycondensation, little is known about high-molecular-weight polyarylates derived from sulfone-containing bisphenols such as 4,4'-dihydroxydiphenylsulfone (BPS).<sup>1–3</sup> This is assumed to be the case because the electron-withdrawing sulfonyl substituent lowers the nucleophilicity of the hydroxyl groups of BPS so that these bisphenols do not produce polyarylates of high molecular weight.<sup>1,2,4</sup>

Because of the intermolecular dipole–dipole associations of the sulfonyl groups in the polyester of isophthalic acid (IPA) and BPS, the polymer has a glass-transition temperature ( $T_g$ ; = 249°C)<sup>2</sup> higher than that (194°C)<sup>1</sup> of the commercially developed IPA/terephthalic acid (TPA) (50/50)–2,2-bis(4-hydroxyphenyl)propane (BPA) copolymer. If the IPA/TPA–BPS or IPA/TPA–BPA/BPS copolymer with a high molecular weight could be prepared, it would be a prominent material.

In connection with the improvement of the  $T_g$  of IPA/TPA (50/50)–BPA, we studied the copolycondensations of IPA/TPA (50/50), BPA, and several bis-

phenols with tosyl chloride (TsCl)/dimethylformamide (DMF)/pyridine (Py) as a condensing agent. We found that bisphenols with ineffective electron-withdrawing substituents, such as sulfonyl and carbonyl groups, did not disturb the copolycondensations to yield the copolymers with relatively high molecular weight.<sup>5,6</sup>

This led us to consider that the polycondensation with BPS could be facilitated if the reaction with BPS could be controlled as adequately as that with BPA and the bisphenols. Here, we studied in detail the solution polycondensations of various combinations of IPA and TPA with BPS with TsCl/DMF/Py as a condensing agent by examining the amounts of BPS in the initial reaction and the slow addition of BPS through the polycondensation. We also studied the copolycondensations of IPA/TPA, BPS, and several bisphenols to examine how the reaction should be controlled.

## EXPERIMENTAL

All of the monomers were obtained from Tokyo Kasei Kogyo Co. Ltd. (Tokyo, Japan) and were used without further purification. Py and DMF were purified by distillation over NaOH and CaH<sub>2</sub>, respectively.  $T_g$ 's were examined on a differential scanning calorimetry (DSC) analyzer (Rigaku Thermoflex TG8110; Tokyo, Japan) at a heating rate of 10°C/min under a nitrogen atmosphere.

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TABLE I  
Polycondensation of IPA/TPA and BPS

IPA/TPA (mol %/mol %)	$\eta_{inh}^a$ (dL/g)	$T_g^b$ (°C)
100/0	0.61 <sup>c</sup>	234
80/20	0.76	240
70/30	0.85	247
50/50	0.94	246
30/70	0.68 <sup>c</sup>	255

<sup>a</sup> Measured at 0.5 wt % concentration in phenol/1,1,2,2-tetrachloroethane (6/4, by weight) at 30°C.

<sup>b</sup> Determined by DSC.

<sup>c</sup> Measured at 0.5 wt % concentration in *p*-chlorophenol at 50°C.

### Polycondensation of IPA, TPA, and BPS

In accordance with our previous work,<sup>5-7</sup> a mixture of TsCl (13 mmol) and DMF (10 mmol) in Py (5 mL), prepared and aged at room temperature for 30 min, was reacted with a Py (10 mL) solution of IPA (5–1.5 mmol) and TPA (0–3.5 mmol) at room temperature for 10 min and then at 80°C (bath temperature) for 10 min. To the resulting mixture of BPS (5 mmol) in Py (10 mL) was added dropwise over a period of 0–20 min at 80°C (Tables I and II). Similarly, the reaction was conducted by the addition of BPS in Py, first all at once (2.5–4.5 mmol BPS; 10 mL of Py) and after 30 min (0.5–2.5 mmol BPS; 10 mL of Py; Table III). The whole mixtures were kept at 80°C for an additional 2 h. We isolated the copolymers by diluting the reaction mixture with Py and pouring it into methanol.

### Two-stage copolycondensations of IPA, TPA, BPS, and BPAs

To the reaction mixture of IPA (1.5–5 mmol), TPA (0–3.5 mmol), TsCl (13 mmol), and DMF (10 mmol) in Py (15 mL), prepared and aged as mentioned previously, BPA (2.5–4.5 mmol) in Py (10 mL) was added all at once, and the mixture was kept at 80°C for 30 min. Then, a Py (10 mL) solution of BPS (0.5–2.5

TABLE II  
Polycondensation of IPA/TPA and BPS by the Dropwise Addition of BPS

IPA/TPA (mol %/mol %)	$\eta_{inh}^a$ addition period (min)		
	0	10	20
100/0	0.61 <sup>b</sup>	0.75 <sup>b</sup>	0.80 <sup>b</sup>
80/20	0.76	0.98	0.95
70/30	0.85	0.92	0.93
50/50	0.94	0.90	0.93
30/70	0.68 <sup>b</sup>	0.46 <sup>b</sup>	

<sup>a</sup> Measured at a 0.5 wt % concentration in phenol/1,1,2,2-tetrachloroethane (6/4 by weight) at 30°C.

<sup>b</sup> Measured at a 0.5 wt % concentration in *p*-chlorophenol at 50°C.

TABLE III  
Two-Stage Copolycondensation of IPA/TPA and BPS with Various Amounts of BPS Initially Used

BPS used in the initial reaction (mol %)	$\eta_{inh}$ IPA/TPA (mol %/mol %)			
	100/0 <sup>a</sup>	70/30 <sup>b</sup>	50/50 <sup>b</sup>	30/70 <sup>a</sup>
100	0.61	0.85	0.94	0.68
90	0.75	0.84	0.77	
80	0.82		0.64	0.40
70	0.70	0.88	0.69	0.35
60	0.64	0.71	0.98	
50	0.51	0.58	1.01	0.35

<sup>a</sup> Measured at a 0.5 wt % concentration in *p*-chlorophenol at 50°C.

<sup>b</sup> Measured at a 0.5 wt % concentration in phenol/1,1,2,2-tetrachloroethane (6/4 by weight) at 30°C.

mmol) was added all at once. The whole solution was kept at 80°C for 2 h. The copolymers were isolated by the method mentioned previously. Similarly, the copolycondensations were carried out by the reverse order of addition of BPS first and then BPA, as well as simultaneous addition of their mixture. The results are shown in Tables IV–VI.

## RESULTS AND DISCUSSION

Table I shows the results of the copolycondensations of several combinations of IPA and TPA with BPS at 80°C by the addition of BPS in one portion. Copolymers with moderate inherent viscosity ( $\eta_{inh}$ ) values were obtained, and the values increased with higher TPA contents up to 50 mol %. The reaction of a higher content (70 mol %) of stiffer TPA gave a less satisfactory result. The effect of the TPA contents on the viscosity of the resultant polymers was also observed in the interfacial polycondensation of terephthaloyl and isophthaloyl chlorides with BPA, where nearly equal parts of the chlorides yielded the most favorable results.<sup>1</sup> The IPA/TPA–BPS copolymer examined exhibited only one  $T_g$  at about 230–250°C. The  $T_g$  of the

TABLE IV  
Copolycondensation of IPA, BPA, and BPS by Stepwise Reaction with BPA and BPS

Initial reaction		Subsequent reaction		Initial reaction		Subsequent reaction	
BPA (mol %)	BPS (mol %)	$\eta_{inh}^a$ (dL/g)	BPS (mol %)	BPA (mol %)	$\eta_{inh}^a$ (dL/g)	BPA (mol %)	$\eta_{inh}^a$ (dL/g)
70	30	1.10	30	70	0.90		
50	50	0.95	50	50	0.92		
30	70	0.87	70	30	0.83		
0	100	0.61 <sup>b</sup>	100	0	0.61 <sup>a</sup>		

<sup>a</sup> Measured at a 0.5 wt % concentration in phenol/1,1,2,2-tetrachloroethane (6/4 by weight) at 30°C.

<sup>b</sup> Measured at a 0.5 wt % concentration in *p*-chlorophenol at 50°C.

**TABLE V**  
Copolycondensation of IPA/TPA (50/50), BPA, and BPS  
by Variation of the Addition Order of BPA and BPS

BPA/BPS (mol %/mol %)	$\eta_{inh}^a$		
	BPA and then BPS	BPS and then BPA	Mixture of BPA and BPS
50/50	1.17	1.06	0.96
40/60	1.10	0.92	0.80
30/70	1.00	0.67	0.69
20/80	—	0.64	0.46
10/90	0.96	0.70	0.47
0/100	0.94 <sup>b</sup>	0.94 <sup>b</sup>	0.94 <sup>b</sup>

<sup>a</sup> Measured at a 0.5 wt % concentration in phenol/1,1,2,2-tetrachloroethane (6/4 by weight) at 30°C.

<sup>b</sup> Measured at a 0.5 wt % concentration in *p*-chlorophenol at 50°C.

IPA–BPS polymer (234°C) prepared in this study was a little different from reported values; it was lower than 249°C<sup>2</sup> but higher than 189°C.<sup>3</sup> Although a higher  $\eta_{inh}$  value for the IPA/BPS polymer was obtained compared to those<sup>2,3</sup> by the conventional interfacial polycondensation (about 0.4), the result was not satisfactorily high enough.

To obtain further information about which stage, earlier or later, of the polycondensation with BPS should be done to produce copolymers of higher molecular weight, we examined the two-stage copolycondensation of IPA, BPS, and various molar percentages of BPA (Table IV). The reaction was carried out by the addition of BPA or BPS and, after 30 min, BPS or BPA. The  $\eta_{inh}$  values of the copolymers were improved by copolymerization with BPA, increased with molar percentages of BPA in the copolymers, and were not affected by the order of the addition of BPS and BPA. This was a little different from the copolycondensation with IPA/TPA (50/50) as shown later.

The favorable introduction BPA, as in the reaction of IPA and BPS, was not always observed in the reaction of a mixture of equal parts of IPA and TPA with BPS. Table V shows the results of the copolycondensations of IPA/TPA (50/50), BPA, and several molar percentages of BPS at 80°C by variation of the addition order of BPA and BPS and by the addition of the two all at once. When BPA was first reacted followed by BPS, the resultant copolymer showed high  $\eta_{inh}$ , increasing with an increase in the BPA contents, as observed previously in the reaction of IPA, BPS, and BPA. However, the reverse order of reaction, with BPS first and then BPA, and their simultaneous addition resulted in less satisfactory results. Particularly for the reactions of 70–90 mol % BPS, the introduction of BPA rather retarded the copolycondensation, yielding copolymers of considerably lower  $\eta_{inh}$  values than that of the IPA/TPA–BPS polymer.

The two-stage copolycondensations of IPA/TPA (50/50), BPS, and several bisphenols (BPAs) through

the initial reaction of BPAs and then BPS were examined (Table VI). The copolycondensation was significantly affected by BPAs and was promoted in the following order: BPA  $\approx$  2,2-bis(3-methyl-4-hydroxyphenyl)propane (DM-BPA) > 2,2-bis(3,5-dimethyl-4-hydroxyphenyl)propane (TM-BPA) > 2,2-bis(3,5-dichloro-4-hydroxyphenyl)propane (TC-BPA). The order was quite similar to that previously observed in the two-stage copolycondensation of BPAs and then 4,4'-dihydroxydiphenyl ketone and could be explained by the effect of the distribution of oligomers formed from BPAs at the initial stage.<sup>5</sup>

These results in the copolycondensations of BPS and BPAs indicated that the copolycondensation of BPS and BPAs could be facilitated when the initial stage of the reaction of BPA could be favorably controlled for the subsequent reaction with BPS. This led us to consider that the without introduction of BPA, the polycondensation of IPA, TPA, and BPS could also be promoted to give IPA/TPA–BPS polymers with more satisfactorily higher  $\eta_{inh}$  values than those shown in Table I if the reaction at an earlier stage could be favorably arranged.

To estimate how the initial reaction should be led to obtain better results, we added BPS in two portions by varying the initial amounts of BPS in the polycondensations of IPA/TPA and BPS (Table III); the results are depicted in Figure 1. Compared to the results obtained by the addition in one portion, higher  $\eta_{inh}$  values were obtained at the optimal amounts of BPS, which depended on the IPA/TPA contents. About 80, 70, and 50 mol % BPS were better used in the reactions of IPA, IPA/TPA (70/30), and IPA/TPA (50/50), respectively. However, the reaction of IPA/TPA (30/70) was followed by further precipitation by the addition of BPS in two portions, yielding a poor result. In the initial reaction of IPATPA (50/50) and 70–90 mol % BPS, a rapid precipitation also took place in 5 min, and the whole reaction did not proceed homogeneously, which may have been due to the unsatisfactory results. Although the reactions with IPA and IPA/TPA (70/30) proceeded homogeneously throughout the polycondensation, the initial addition of 50–60 mol % BPS gave unfavorable results compared with those obtained by the addition of BPS all at once. Because a

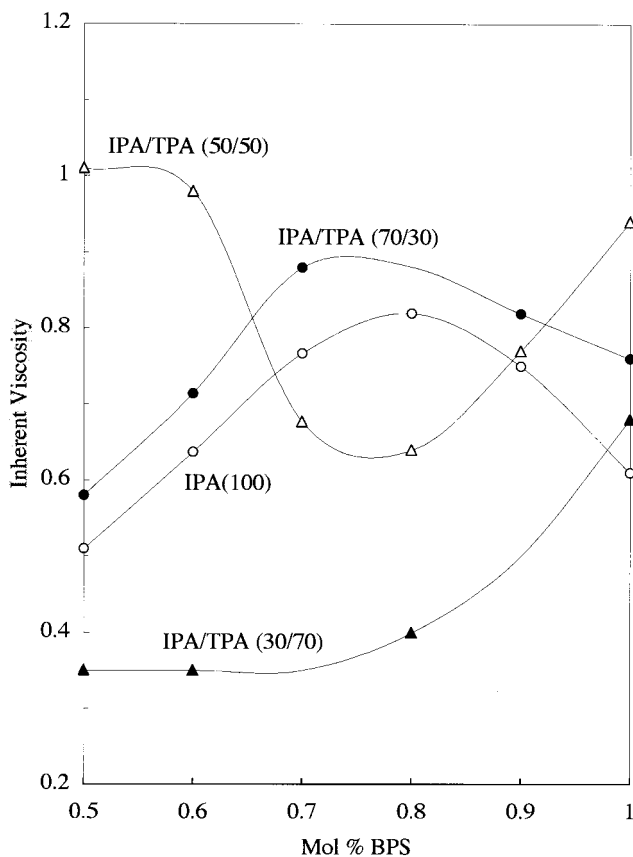
**TABLE VI**  
Two-Stage Copolycondensations of IPA/TPA (50/50)  
and BPAs (50 mol %) Followed by BPS

BPA	$\eta_{inh}^a$ (dL/g)
BPA	1.18
DM-BPA	1.16
TM-BPA	0.94
TC-BPA	0.73

<sup>a</sup> Measured at a 0.5 wt % concentration in phenol/1,1,2,2-tetrachloroethane (6/4 by weight) at 30°C.

mixture of IPA and TPA activated by TsCl/DMF/Py formed the associates whose structures were affected by the IPA/TPA content,<sup>8</sup> it is likely that the initial reaction of the optimal amounts of BPS with the associates led the reaction to produce a narrow distribution of the preformed IPA/TPA oligomers.

It would be easier to modify the reaction of the associates of the activated IPA and TPA with BPS by the dropwise addition of BPS instead of the carefully optimized addition in two portions as mentioned previously. The slow addition would lead BPS to a reaction with an apparent excess of the activated IPA and TPA so that the distribution of the resulting oligomers could be controlled by the period. The dropwise addition of BPS in the polycondensation of various parts of a mixture of TPA and IPA gave satisfactory results nearly comparable to those in Table III (see Table II). The addition over a period of 10–20 min facilitated the reactions with less than 50 mol % TPA. However, for the reaction of 50 mol % TPA, any substantial improvement in  $\eta_{inh}$  by the addition was not observed. The reaction of 70 mol % TPA was accompanied by precipitation with the slow addition and was rather retarded.



**Figure 1** Effect of the amount of BPS initially reacted in the two-stage polycondensation of IPA, TPA, and BPS.

**TABLE VII**  
Copolycondensation of IPA/TPA (50/50), BPA, and BPS by the Addition of a Mixture of BPA and BPS over 10 min

BPA/BPS (mol %/mol %)	$\eta_{inh}$ of the copolymers <sup>a</sup> (dL/g)
50/50	1.05
40/60	1.03
30/70	1.01
20/80	0.95
10/90	0.95
0/100	0.94 <sup>b</sup>

<sup>a</sup> Measured at a 0.5 wt % concentration in phenol/1,1,2,2-tetrachloroethane (6/4 by weight) at 30°C.

<sup>b</sup> Measured at a 0.5 wt % concentration in *p*-chlorophenol at 50°C.

Furthermore, the promoted reaction by the slow addition was more clearly observed in the copolycondensation of IPA/TPA (50/50), BPA, and 60–90 mol % BPS (Table VII). The copolycondensation with BPS and then BPA and their mixtures did not give copolymers with high  $\eta_{inh}$  values (see the second and third columns in Table V), but the addition of their mixtures over 10 min significantly improved  $\eta_{inh}$ , with values as high as those obtained by the initial reaction of BPA and then BPS (see the first column in Table V).

## CONCLUSIONS

In conclusion, the IPA/TPA–BPS copolymers of high  $\eta_{inh}$  values could be prepared by the polycondensation of IPA, TPA (0–50 mol %), and BPS with TsCl/DMF/Py as a condensing agent at 80°C by the two-stage reaction of the addition of BPS in two portions or by its dropwise addition throughout the polycondensation. When several physical properties of the IPA/TPA–BPS and the IPA/TPA–BPA/BPS copolymers other than thermal ones are investigated, they could be shown to be injection-molding plastics comparable to or more prominent than commercial polymers such as the IPA/TPA–BPA polymer and polysulfone.

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