Synthesis of Aromatic Polyesters by Interfacial Polycondensation Using Immiscible Binary Solvents

Hiroyuki NAKAMURA, Shohei IMANISHI, Kohei SANUI,
and Naoya OGATA

*Department of Chemistry, Sophia University, 7 Kioi-cho,
Chiyoda-ku, Tokyo, 102 Japan.*

ABSTRACT: Aromatic polyesters from bisphenols and terephthaloyl chloride have been synthesized by interfacial polycondensation using immiscible binary solvents such as adiponitrile (AN)–carbon tetrachloride (CCl_4) or ethylene glycol (EG)–CCl_4 systems. Yields and solution viscosities of the resulting polyesters increased with increasing concentration of monomers in binary solvents and a high-molecular-weight polyester was obtained from bisphenol A in a solvent system of AN–CCl_4. Partition coefficients of bisphenols in binary solvents had no influence on either yields or solution viscosities of the resulting polyesters. Copolyesters from bisphenol A and resorcinol have been synthesized by the same method.

KEY WORDS   Interfacial Polycondensation / Polyester / Copolyester / Bisphenol / Terephthaloyl Chloride / Partition Coefficient /

An Interfacial polycondensation reaction[1] takes place at the interface between a solution of a diacid chloride in a water-immiscible organic solvent and a water solution of, for example, a diamine containing an acid acceptor. This reaction is useful to prepare various condensation polymers under mild conditions. However, hydrolysis of the acid halide, which is always a possible side reaction, may compete with the acylation sufficiently in the reaction to prevent the formation of a high polymer. Moreover, when a monomer has somewhat lower solubility in water, the reaction must be carried out in a dilute solution, which leads to a poor yield of the resulting polymer with a low molecular weight.

In a previous paper[2] we reported that interfacial polycondensation using immiscible binary solvents is useful to prepare aromatic polyamides from *m*- or *p*-phenylenediamines, which are less-reactive with acid chloride and less-soluble in water than aliphatic diamines. The interfacial polycondensation using immiscible binary solvents has been extended to synthesize aromatic polyesters from bisphenols which are less-soluble in water. Copolyesters from different bisphenols were also prepared by the same method.

EXPERIMENTAL

Monomers and Solvents

Terephthaloyl chloride (TPC) was synthesized according to a conventional method and purified by vacuum distillation. bp 102°C [0.1 mmHg (13.3 Pa)]. Bis(4-hydroxyphenyl)-2,2-propane (bisphenol A) (BPA) and resorcinol (RN) were purified by distillation of commercially-available reagents. All solvents were purified by distillation.

Interfacial Polycondensation

Interfacial polycondensation of TPC with BPA or RN was carried out by using such immiscible binary solvents as adiponitrile (AN)–carbon tetrachloride (CCl_4), AN–dibutyl ether (Bu_2O), ethylene glycol (EG)–CCl_4, or EG–benzene (C_6H_6) systems. BPA or RN were dissolved in AN or EG at a desired concentration in the presence of twice the number of moles of triethylamine as an acid acceptor, while TPC was dissolved in CCl_4, Bu_2O, or C_6H_6. Two immiscible solutions were mixed with a vigorous stirring at room temperature for 5 min in a homoblender. The solutions were poured into excess acetone and the precipitated polymers were washed with water, ethanol, and acetone, followed by filtering and drying under vacuum. Copolyesters from

H. Nakamura, S. Imanishi, K. Sanui, and N. Ogata

BPA and RN with TPC were synthesized by the same method.

Solution viscosities of the resulting polymers were determined in a solvent made from *syn*-tetrachloroethane and phenol (50/50 in volume) at 30°C and thermal properties were measured by differential thermal analysis using a Rigakudenki thermoflex 8001. Copolyesters from BPA–RN with TPC were analyzed by NMR spectra, which were measured in trifluoroacetic acid solution using a Hitachi model R-22 spectrometer (90 MHz). Copolymer compositions were determined by measuring peak intensities of methyl protons of BPA units in the copolymers in comparison with total peak intensities of aromatic protons.

X-ray analysis of copolymers was carried out by using a Rigakudenki X-ray generator No. 4001B with Ni-filtered Cu-K_α radiation to investigate the crystalline character of the copolymers.

RESULTS AND DISCUSSION

Table I summarizes the results of the synthesis of polyester form BPA and TPC, while Table II indicates the polyester synthesis from RN and TPC in various binary solvent systrms. Results in Tables I and II suggest that the interfacial polycondensation using immiscible binary solvents was rather useful to prepare aromatic polyesters in terms of yields and solution viscosities of the polyesters, when compared with the interfacial polycondensation in aqueous system. Since the solubility of bisphenols in water is mostly limited up to 0.1 mol dm^{-3}, the interfacial polycondensation in aqueous system must be carried out in a dilute solution, which results in an unsatisfactory yield of the aromatic polyesters. Organic bases such as triethylamine are not so effective to yield a high-molecular-weight aromatic polyester in the interfacial polycondensation in an aqueous system, when they are used as an acid acceptor.[1] Nevertheless, triethylamine was found to be effective to prepare the aromatic polyesters.

Among the combination of binary solvents systems, the AN–CCl$_4$ system was superior to other solvents' systems in terms of the yields and solution viscosities of the resulting polyesters. In the interfacial polycondensation in aqueous system, a proper choice of a solvent system and reactant concentration is essential to allow sufficient diffusion of a monomer in aqueous phase into organic phase

Table I. Interfacial polycondensation of BPA with TPC in various solvent systems[a]

Solvent system	Monomer concn	Polymer	
		Yield	η_{sp}/c[b]
	mol dm^{-3}	%	
AN–CCl$_4$	0.1	77	0.40
	0.2	83	0.49
	0.3	90	0.55
	0.4	97	0.49
AN–Bu$_2$O	0.1	89	0.39
	0.2	96	0.43
	0.3	92	0.41
	0.4	82	0.39
EG–CCl$_4$	0.1	56	0.26
	0.2	76	0.33
	0.3	81	0.27
	0.4	87	0.30
EG–C$_6$H$_6$	0.1	64	0.25
	0.2	80	0.29
	0.3	86	0.31
	0.4	88	0.32
H$_2$O–CCl$_4$	0.1	75	0.21

[a] Acid acceptor, triethylamine; temp, room temp; time, 5 min.
[b] 0.01 g cm^{-3} in phenol–tetrachloroethane (1 : 1) at 30°C.

Table II. Interfacial polycondensation of RN with TPC in various solvent systems[a]

Solvent system	Monomer concn	Polymer	
		Yield	η_{sp}/c[b]
	mol dm^{-3}	%	
AN–CCl$_4$	0.2	99	0.23
	0.3	92	0.23
AN–Bu$_2$O	0.2	98	0.22
	0.3	88	0.23
EG–CCl$_4$	0.2	78	0.16
	0.3	80	0.19
EG–C$_6$H$_6$	0.2	74	0.16
	0.3	82	0.17
H$_2$O–CCl$_4$	0.2	83	0.15
	0.3	79	0.13

[a] Acid acceptor, triethylamine; temp. room temp; time: 5 min.
[b] 0.01 g cm^{-3} in phenol–tetrachloroethane (1 : 1) at 30°C.

and to ensure enough mobility of the growing chain to permit a high molecular weight to be reached.[1] Therefore, the partition coefficient of bisphenols between two immiscible solvents was determined. Table III summarizes partition coefficients K of BPA or RN in binary solvents at room temperature, these were measured by mixing one solution containing BPA or RN with other solvents in a homoblender for 5 min. The transferred amount of BPA or RN was determined by UV spectrum of the solutions.

Comparing results in Table I or II with Table III, no systematic corelationship between the partition coefficient of bisphenols and the polycondensation reaction was observed in terms of yields and solution viscosities of resulting polyesters, although the partition coefficient of bisphenols greatly changed in each binary solvents' system. Therefore, the diffusion of bisphenols from one solution to the other may not have a significant influence on the interfacial polycondensation.

Copolycondensation of BPA and RN with TPC was carried out by the interfacial polycondensation

Table III. Partition coefficients K of BPA or RN in binary solvent systems at room temperature

Solvent system	Partition coefficient	
	K_{BPA}	K_{RN}
AN–CCl$_4$	3100	1700
AN–Bu$_2$O	10	8
EG–CCl$_4$	1800	1700
EG–C$_6$H$_6$	2200	17

Table IV. Interfacial copolycondensation of BPA and RN with TPC in AN–CCl$_4$ system[a]

Molar ratio BPA/RN	Copolymer properties				
	Yield/ %	η_{sp}/c	BPA/ %	RN/ %	T_m/ °C
100/ 0	90	0.55	100	0	306
80/ 20	91	0.68	83	17	238
60/ 40	85	0.59	65	35	190
50/ 50	75	0.70	45	55	182
40/ 60	78	0.77	38	62	228
20/ 80	89	0.41	—	—	228
0/100	92	0.23	0	100	278

[a] Monomer concn, 0.3 mol dm^{-3}; acid acceptor, triethylamine; temp, room temp; time, 5 min.
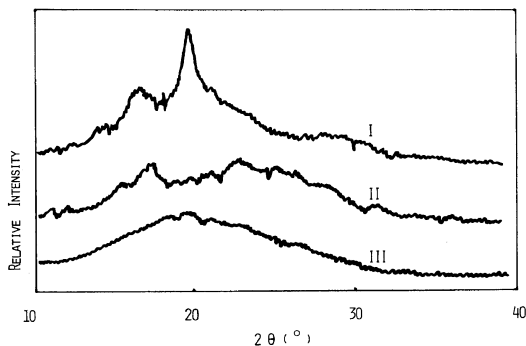

Figure 1. X-ray diffraction of polyesters: I, polyester from BPA and TPC; II, polyester from RN and TPC; III, copolyester from BPA/RN (50/50) and TPC.

Table V. Solubility test of aromatic polyester and copolyesters in various solvents

Composition BPA/RN	Solubility test						
	DMF	DMAC	Dioxane	THF	DCE[a]	TCE[b]	CF$_3$COOH
100/ 0	—	—	—	—	—	+	—
80/ 20	—	—	—	—	—	+	—
60/ 40	—	+	+	+	+	+	+
50/ 50	+	+	+	+	+	+	+
40/ 60	+	+	+	+	+	+	+
20/ 80	—	—	—	—	—	+	+
0/100	—	—	—	—	—	—	—

[a] 1, 2-Dichloroethane.
[b] *syn*-Tetrachloroethane.

using the AN–CCl$_4$ system; results are summarized in Table IV. Compositons of resulting copolyseters were almost the same as those of monomer feed ratios. On the other hand, yields of the copolyesters reached a minimum at the 50/50 feed ratio of BPA and RN, while solution viscosities showed a maximum in the range of 50/50—40/60 feed ratios of the two monomers. This phenomenon may be ascribed to the reason that the solvent affinity of the growing polymer chains may permit the sufficient swelling and increase the mobility of the polymer chains to reach a high molecular weight, because yields of the copolyesters were poor, presumably owing to the dissolution of a low-molecular-weight polymer in the range of 50/50—40/60 feed ratios of the two monomers. The high affinity of the copolyesters to solvents was also confirmed by the solubility test of the copolyesters in various organic solvents, as shown in Table V. The copolyester obtained from 50/50 feed ratio of BAP and RN was quite soluble in many organic solvents including dioxane or tetrahydrofuran (THF). The copolyester obtained from 50/50 feed ratio of BPA/RN had an amorphous structure with a low melting point (180°C), while the homopolyesters derived from BPA or RN were crystalline, as was observed in the X-ray diffraction patterns shown in Figure 1.

In summary, it was found that the interfacial polycondensation using immiscible binary solvent systems was useful to prepare aromatic polyesters with a high molecular weight, in comparison with the interfacial polycondensation in aqueous system.

REFERENCES

1. P. W. Morgan, "Condensation Polymers by Interfacial and Solution Methods," Interscience, New York, N.Y., 1965.
2. N. Ogata, K. Sanui, and T. Onozaki, *Kobunshi Ronbunshu*, **35**, 551 (1978).