

## ***In-Situ* Direct Polycondensation in Polymer Matrices I. *In-Situ* Direct Polycondensation in Polyarylate**

Naoya OGATA, Kohei SANUI, and Hiroharu ITAYA

*Department of Chemistry, Sophia University, 7-1 Kioi-cho,  
Chiyoda-ku, Tokyo 102, Japan*

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**ABSTRACT:** Direct polycondensation of *p*-aminobenzoic acid (ABA) or *p*-hydroxybenzoic acid (HBA) was carried out in solutions of polyarylate (copolyester from tere-/iso-phthalic acids (50/50) and bisphenol A) at 25°C in the presence of triphenylphosphine and hexachloroethane as an initiator for the direct polycondensation of these monomers. Solution casting after the direct polycondensation provided opaque films in which aromatic polyamide or polyester was finely dispersed within the matrix of polyarylate. Mechanical properties of these films indicated increase in modulus and tensile strength at elevated temperatures. *In-situ* direct polycondensation leads to the formation of new molecular composite materials.

**KEY WORDS** Direct Polycondensation / Triphenylphosphine / Polyarylate  
/ Molecular Composites / Aromatic Polyamide / Aromatic Polyester /

Direct polycondensation using triphenylphosphine (TPP) or triphenylphosphine dichloride (TPPCL<sub>2</sub>) is an effective method for the synthesis of either polyamides or polyesters under mild conditions and various types of condensation polymers have been obtained by this method.<sup>1-3)</sup> Direct polycondensation reactions can take place in inert polar solvents such as *N*-methylpyrrolidone (NMP) or methylene chloride in the presence of bases such as pyridine or triethylamine and the reactions are usually complete within half an hour at ambient temperature, with the precipitation of polymers.

When monomers are dissolved in these inert polar solvents in which various polymers are dissolved together with these monomers, and the direct polycondensation method is applied to the solutions, it is expected that an *in-situ* direct polycondensation of these monomers takes place in the polymer solutions into which condensation polymers may be finely dispersed, possibly on a molecular basis. Therefore, after the *in-situ* direct polycondensation, cast-

ing of polymer solutions would provide films of polymers containing finely-dispersed condensation polymers and molecular composite materials may be obtained.

Usually, the compatibilities of condensation polymers with other polymers are very poor so that blending of these two polymers is very difficult either in the melt state or in solvent casting. This concept of *in-situ* direct polycondensation in various polymers as matrices may be a novel approach to molecular composites containing condensation polymers, particularly condensation polymers which form liquid crystalline structures. The *in-situ* formation of condensation polymers in various matrix polymers may lead to improvement in the mechanical properties at elevated temperatures so that a self-reinforcement effect of the matrix polymer is attained.

This paper describes the *in-situ* direct polycondensation of *p*-aminobenzoic acid (ABA) or *p*-hydroxybenzoic acid (HBA) in polyarylate made from tere-iso-phthalic acids (50/50) and bisphenol A.

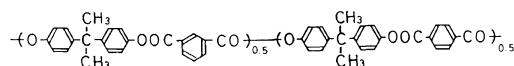
## EXPERIMENTAL

*Materials*

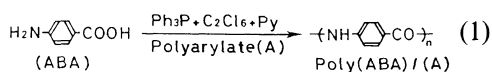
All reagents and monomers of special grade were used without further purification. Hexachloroethane and all solvents were purified by distillation before use.

The polyarylate used was a commercially available product of Amoco Co., with the name ARDEL polyarylate 100.

Polyarylate (A):

*In-Situ Direct Polycondensation*

Typical examples of *in-situ* direct polycondensation were as follows: polyarylate (A) 5.75 g and ABA 2.745 g ( $2 \times 10^{-2}$  mol) were dissolved in a mixed solvent of 80 cm<sup>3</sup> methylene dichloride and 10 cm<sup>3</sup> pyridine, into which 6.3 g ( $2.4 \times 10^{-2}$  mol) of TPP were dis-

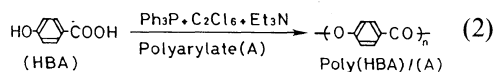


solved to make a clear solution. After complete dissolution, 7.1 g ( $3.0 \times 10^{-2}$  mol) of hexachloroethane were added to the solution with vigorous stirring. The reaction was carried out at 25°C for 24 h. After the addition of hexachloroethane, an exothermic reaction took place and the initial clear solution turned to a thick-milky suspension, owing to the formation of poly(ABA) in the solution of polyarylate. However, no macroscopic phase-separation occurred in the suspension even after standing for more than weeks and the resulting poly(ABA) was so well-dispersed in the solution that no precipitation of the coagulate took place.

The entire suspension was poured into excess methanol and the precipitated polymer was collected by filtration, followed by repeated washings with methanol so as to extract unreacted monomer and triphenylphosphine oxide (TPPO) formed by direct polyconden-

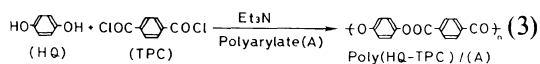
sation. The polymer was dried in vacuum.

The *in-situ* direct polycondensation of HBA in polyarylate solution was carried out as follows: 5.77 g of polyarylate and 2.762 g ( $2.0 \times 10^{-2}$  mol) of HBA were dissolved in 250 cm<sup>3</sup> of 1,1,2,2-tetrachloroethane, followed by complete dissolution of 5.508 g ( $2.1 \times 10^{-2}$  mol) of TPP. To the solution were added 5.681 g ( $2.4 \times 10^{-2}$  mol) of hexachloroethane and the solution was heated to 100°C for complete dissolution, followed by cooling down to 25°C.



A portion of 5.6 cm<sup>3</sup> ( $0.4 \times 10^{-2}$  mol) of triethylamine was added to the solution to initiate *in-situ* direct polycondensation. The obtained suspension of poly(ABA) was quite stable and no macroscopic phase-separation took place.

An *in-situ* polycondensation of terephthaloyl chloride (TPC) and hydroquinone (HQ) was carried out in methylene dichloride solution of A for comparison with *in-situ* direct polycondensation. A portion of 2 g of A was



dissolved in 15 cm<sup>3</sup> methylene dichloride, into which 0.63 cm<sup>3</sup> of triethylamine and 0.248 g ( $2.25 \times 10^{-3}$  mol) of HQ were dissolved. To the solution was added 0.457 g ( $2.25 \times 10^{-3}$  mol) of solid TPC all at once with vigorous stirring. The solution was continuously stirred for 24 h. Right after the addition of TPC, the solution turned to a milky suspension which was quite stable after standing for one week. The suspension was poured into excess methanol and the polymer was collected by filtration, followed by washing with methanol and drying in vacuum.

The content of the resulting poly(ABA), poly(HBA) or poly(hydroquinone terephthal-

ate) (HQ-TPC) in polyarylate was measured by weight increase after recovery of polyarylate.

#### Film Casting

A portion of 1.2 g of the recovered polymers was dissolved in 15 cm<sup>3</sup> of chloroform and the solution was cast onto a glass plate. Chloroform was evaporated at room temperature and films were obtained. The film containing poly(ABA) was slightly reddish and films containing poly(HBA) and poly(HQ-TPC) were white opaque.

#### Characterization of Polymers

Infrared spectra of the films were measured to confirm the formation of poly(ABA) in polyarylate. X-ray analyses of the films were carried out using a Rigakudenki RAD II-A. Thermal analyses of the films were carried out using a Seiko I DSC, TG/DTA 200 and viscoelastic properties of the films were measured at 1.0 Hz by a Seiko I DMS 100 at 1°C min<sup>-1</sup>.

#### Mechanical Properties

Tensile strength and modulus of the films were measured at 23°C, 100°C and 150°C using a Shimadzu Autograph IS-2000. The sample form was 10 × 50 mm with thickness of 0.11–0.14 mm and each 5 sample was measured in a 30 mm gauge at an elongation speed of 1.5 mm min<sup>-1</sup>.

## RESULTS AND DISCUSSION

Molecular composite materials which have improved mechanical properties due to a self-reinforcement mechanism have been proposed by Takayanagi's group as being producible by the *in-situ* polycondensation of diacid chloride/diamine in various polymer solutions.<sup>4,5)</sup>

On the other hand, *in-situ* direct polycondensation using TPP or TPPCl<sub>2</sub> is useful to initiate the polycondensation of bi-hetero functional monomers such as ABA or HBA which cannot be converted to acid chloride as monomers. Therefore, *in-situ* direct polycondensation in polymer matrices is a novel approach to make molecular composites containing poly(ABA) or poly(HBA).

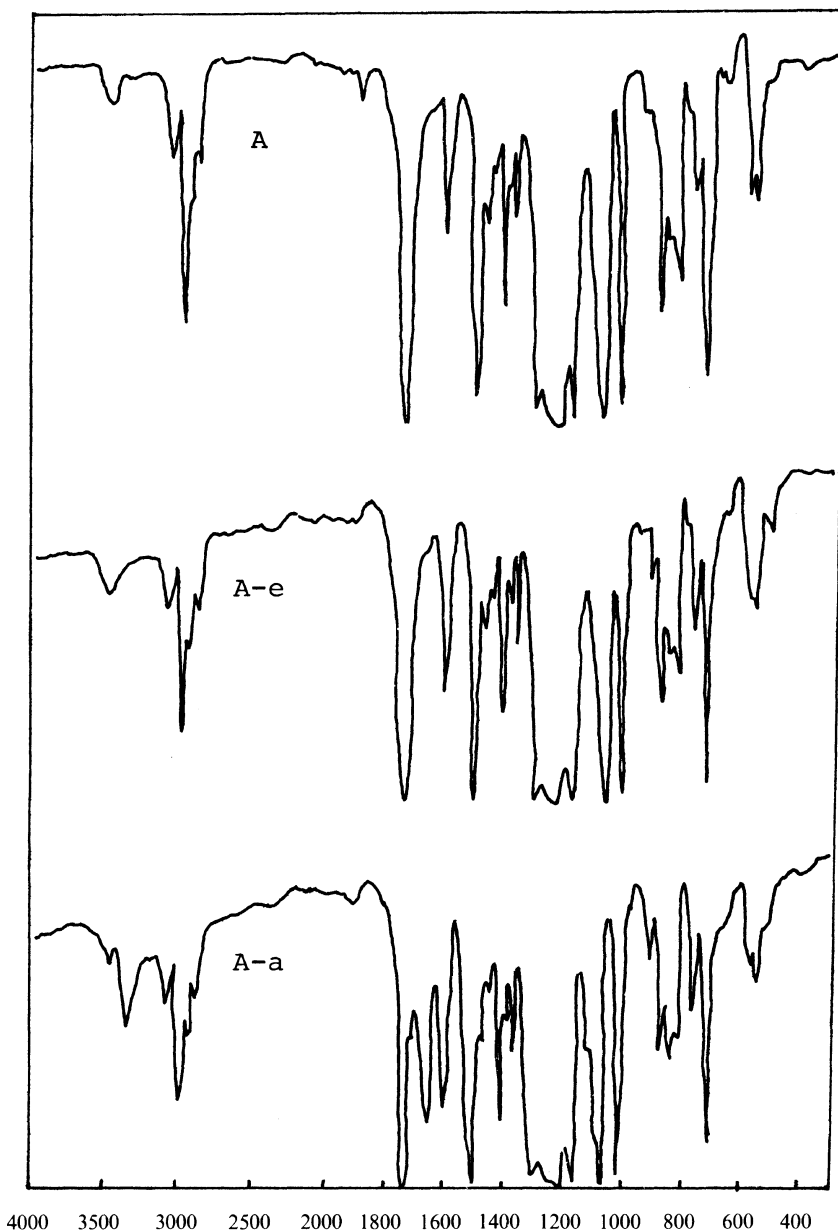
#### Characterization of Polymers

Table I summarizes the results of *in-situ* direct polycondensation and abbreviations of polymers. *In-situ* direct polycondensation of ABA reached almost 99% yields of poly(ABA), while that of HBA yielded a poor 65%. Extraction of the obtained films by chloroform did not result in a complete separation of poly(ABA) or poly(HBA) from polyarylate. The amount of poly(ABA) or poly(HBA) after extraction with chloroform was less than 5 wt% to polyarylate and was a large amount of poly(ABA) or poly(HBA) was considered to

Table I. *In-situ* direct polycondensation in polyarylate

Polyarylate (g)	Monomer		Composite			Abbreviation
	Kind	Amount	Recovered amount	Conversion	Content	
		g			g	
5.76	ABA	2.745	8.16	99	29	A-a
2.75	ABA	0.549	2.66	58	2	A-2
5.77	HBA	2.762	7.32	65	21	A-e
2.00	HQ/TPC	0.248/0.457	2.39	100	17	H-17
3.00	HQ/TPC	0.248/0.457	3.26	86	8	H-8
4.5	HQ/TPC	0.248/0.457	4.60	48	3	H-3

<sup>a</sup> wt% of poly(ABA), poly(HBA), or poly(HQ-TPC) in polyarylate.



**Figure 1.** Infrared spectra of the films. A, polyarylate; A-e, polyarylate containing 21 wt% of poly(HBA); A-a, polyarylate containing 29 wt% of poly(ABA).

be grafted at the end of polyarylate through end terminal groups because infrared spectra of the extracted films were identical to those of original films were identical to those of original films shown in Figure 1.

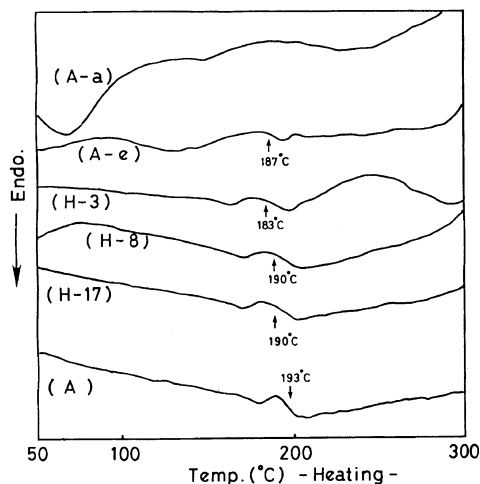
Figure 1 indicates infrared spectra of the films which suggest the existence of poly(ABA) or poly(HBA) since absorptions owing to amide linkages appeared at 3300 and 1650  $\text{cm}^{-1}$  in the case of poly(ABA). This

confirms the formation of poly(ABA) or poly(HBA) in polyarylate.

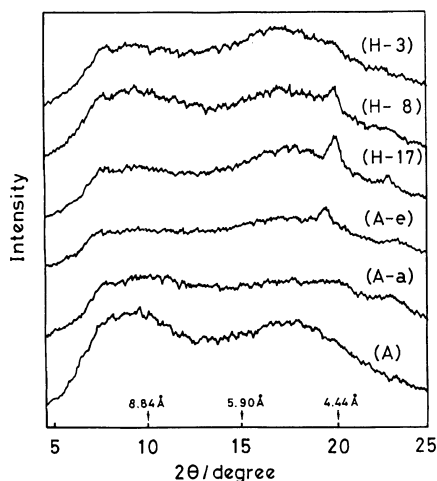
Optimum concentrations of monomers for direct polycondensation are usually in the range of 0.2 and 0.5 mol<sup>-1</sup> and more detailed experiments may be necessary to obtain high

yields of poly(HBA) in polyarylate.

Thermal properties of the polymers were investigated by TGA and DSC analyses which showed DSC thermograms in Figure 2. Polyarylate exhibited a transition temperature at 193°C owing to the glass transition temperature ( $T_g$ ), which shifted toward a somewhat lower temperature for the A-e and H series.<sup>6</sup> It was confirmed from the results of dynamic mechanical measurements that the transition temperature in each DSC curve corresponds to the  $T_g$ s polyarylate containing poly(HBA) or poly(HQ-TPC).



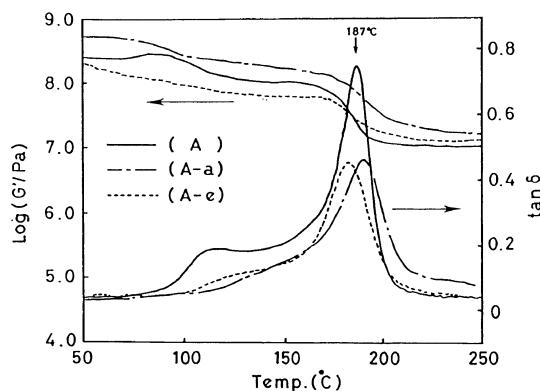
**Figure 2.** DSC thermograms of the films. A, polyarylate; A-a, polyarylate containing 29 wt% of poly(ABA); A-e, polyarylate containing 21 wt% of poly(HBA); H-3, 8, and 17, polyarylate containing 3, 8, and 17 wt% of poly(HQ-TPC).



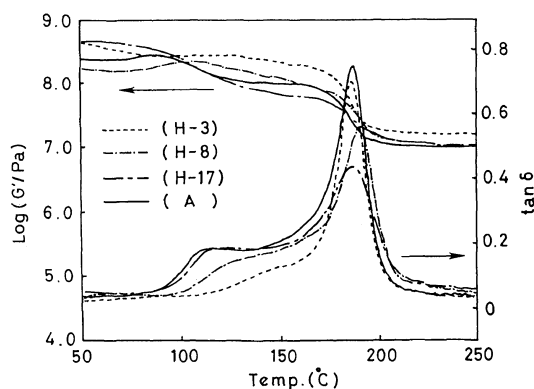
**Figure 3.** X-Ray diffraction patterns of the films. A, polyarylate; A-a, polyarylate containing 29 wt% of poly(ABA); A-e, polyarylate containing 21 wt% of poly(HBA); H-3, 8, and 17, polyarylate containing 3, 8, and 17 wt% of poly(HQ-TPC).

Figure 3 shows the X-ray diffraction patterns of the films A, A-a, A-e or H series. It is seen in Figure 3 that polyarylate A shows broad peaks at 8.84 and 4.6 Å, while no peak appears for A-a. The existence of rigid poly(ABA) may thus prevent the crystallization of polyarylate. The A-e or H series showed a small peak at  $2\theta = 19^\circ$  possibly due to crystalline aromatic polyesters.

Viscoelastic properties of the polymers were measured as the storage modulus ( $G'$ ) and the loss tangent ( $\tan \delta$ ) of the polymers. Figure 4 shows  $G'$  and  $\tan \delta$  of each A, A-a, and A-e as functions of temperature, whereas Figure 5 indicates those of H series. It is seen in Figure 4 that polyarylate A shows a main relaxation owing to  $T_g$  at 187°C with an auxiliary peak at



**Figure 4.** Temperature dependences of  $G'$  and  $\tan \delta$  measured at 1 Hz. A, polyarylate; A-a, polyarylate containing 29 wt% of poly(ABA); A-e, polyarylate containing 21 wt% of poly(HBA).



**Figure 5.** Temperature dependences of  $G'$  and  $\tan \delta$  measured at 1 Hz. A, polyarylate; H-3, 8, and 17, polyarylate containing 3, 8, and 17 wt% of poly(HQ-TPC).

110°C.<sup>6</sup> The main relaxation of A-a and A-e did not significantly change, while no auxiliary peak appeared at around 110°C for A-a and A-e. The existence of rigid rod-like poly(ABA) or poly(HBA) within the matrix of A may prevent movement of the main chains of polyarylate so that the auxiliary peak at 110°C owing to side chain movements of isopropane units of bisphenol A moiety may disappear.

The H series which contains poly(HQ-TPC) in polyarylate exhibited an auxiliary peak at 110°C, as shown in Figure 5. The auxiliary peak of H series shifted toward higher temperature as the content on poly(HQ-TPC) decreased in polyarylate.

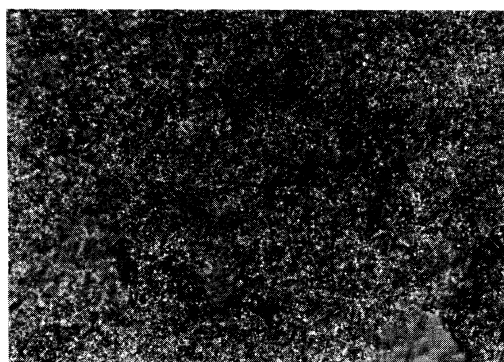
Increasing content of poly(HQ-TPC) may cause phase separation from polyarylate matrix so that an auxiliary peak of A appear again.

Figure 6 shows cross-sections of the films of A-a and A-e, observed under a cross-polarized microscope. As shown in Figure 6, poly(ABA) in polyarylate had an aggregated form, like chains, while poly(HBA) was well-dispersed in polyarylate in a fine particle form with a diameter of about 0.01 mm. Since polyamides form strong hydrogen-bonding among chains, the aggregation tendency of poly(ABA) may



( A-a )

0.3mm



( A-e )

**Figure 6.** Cross-polarized microscopic pictures of cross-sections of the films. A-a, polyarylate containing 29 wt% of poly(ABA); A-e, polyarylate containing 21 wt% of poly(HBA).

be stronger than that of poly(HBA) in polyarylate. Moreover, the affinity of poly(HBA) to polyarylate may be better than poly(ABA) since they belong to the same family of polyesters.

#### *Mechanical Properties of the Films*

Table II summarizes the mechanical properties of A, A-a, and A-e films at 23°C, 100°C, and 150°C, for tensile strength and modulus. Tensile strength dropped at 23°C from 41 MPa to 30–33 MPa in the presence of rigid poly(ABA) or poly(HBA), while the modulus

**Table II.** Mechanical properties of films at various temperatures

Sample	Temp.	Tensile strength	Tensile modulus
	°C	MPa	MPa
A	23	41	1800
	100	20	980
	150	7.3	270
A-e	23	33	2100
	100	21	1300
	150	6.0	400
A-a	23	30	2100
	100	20	1300
	150	13	1100

A, polyarylate; A-e, polyarylate containing 21 wt% of poly(HBA); A-a, polyarylate containing 29 wt% of poly(ABA).

of the films increased from 1800 MPa to 2100 MPa, a 17% increase. The tensile strength of polyarylate A decreased remarkably with increasing temperature up to 150°C from 41 MPa to 7.3 MPa, while A-a which contained poly(ABA), maintained the high tensile strength at 150°C, presumably owing to the

self-reinforcement effect of the rigid rod-like polymers well dispersed within the matrix polymer A. In particular, the modulus of A-a and A-e was in the range of 400 and 1100 MPa at 150°C. These results show that the mechanical properties of polyarylate were greatly improved in the presence of poly(ABA) or poly(HBA) within polyarylate A. *In-situ* direct polycondensation is an unique method to improve the mechanical and thermal properties of various conventional polymers and further research on this point is being conducted.

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