

New Synthetic Method of Bisphenol A Polyarylate by Non-Halogen Method

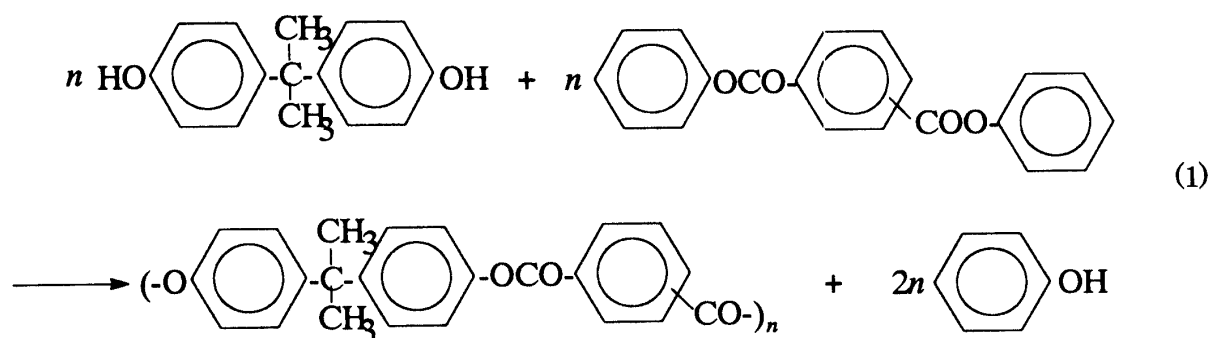
Junzo Masamoto¹ and Takashi Iwamoto²

Abstract: Solid-state polymerization of bisphenol A polyarylate was investigated. Bisphenol A polyarylate oligomers was crystallized and solid-state polymerization was done. Solid-state polymerization was found to give a high molecular weight polymer.

Introduction

On a commercial basis, bisphenol A polyarylate is produced by the intersurface condensation polymerization of the alkaline salt of bisphenol A and terephthaloyl/isophthaloyl chloride.

A typical method of the melt condensation polymerization is using bisphenol A and diphenyl terephthalate/isophthalate was also known (eq. 1)¹⁾.



We reported the synthesis of oligomeric polyarylate by the condensation polymerization of bisphenol A and diphenyl terephthalate/isophthalate²⁻⁵⁾. This reaction is controlled by the reaction equilibrium, and to eliminate the generated phenol from the polyarylate oligomer is very difficult because of the high viscosity of polyarylate oligomers¹⁾. From this view point, the solid-state condensation polymerization, which should be done under a flowing inert gas of N₂ to the polymerization zone and eliminating the generated phenol, is thought to be one of the best processes^{6, 7)}.

¹ Department of Management Science, Fukui University of Technology ² Asahi Kasei Corporation

For the semicrystalline polymer such as nylon 6, nylon 66, nylon 46, polyethylene terephthalate, solid-state condensation polymerization is well known. However, there is no concept for the amorphous bisphenol A polyarylate. It was reported that the random copolymer of bisphenol A polyarylate composed of terephthalic/isophthalic acids could not crystallize by contacting the solvent ^{8, 9)}, though the block copolymer of bisphenol A polyarylate composed of terephthalic acid - isophthalic acid can crystallize when in contact with solvent ⁸⁾.

We happened to find that the oligomers of bisphenol A polyarylate can crystallize under certain conditions, and then we tried the solid-state condensation polymerization.

Experimental

Synthesis of Bisphenol Polyarylate Oligomers

For the bisphenol A polyarylate oligomers by the condensation polymerization of bisphenol A and diphenyl terephthalate/isophthalate, polyarylate oligomers with various reduced viscosities were obtained according to the procedure in our previous report ⁵⁾. The reduced viscosity of the polymer was measured using the mixed solvent of *p*-chlorophenol/tetrachloroethane.

Crystallization of Bisphenol A Polyarylate Oligomers

The polyarylate oligomers by the condensation polymerization of bisphenol A and diphenyl terephthalate/isophthalate were pulverized and filtered under 355 μm , and then immersed in the solvent ⁶⁾.

Solid-State Polymerization

Using crystallized polyarylate oligomers with various reduced viscosities, polymerization was done using a glass tube apparatus immersed in Wood's metal bath. Polymerization was done using 2 g of polymer powder on the glass filter, and heated under N_2 flowing at 90 mL/min, and the condensation polymerization occurred.

Measurement

Reduced viscosity of the polymer was measured using the mixed solvent of *p*-chlorophenol/tetrachloroethane.

For the DSC (Differential Scanning Calorimeter) measurement a PERKIN-ELMER 7 Series was used. Thermal analysis was done by elevating the temperature at 20°C/min. The melting temperature was measured during the first scan, and glass transition temperature was measured during the second scan.

The molecular weight and molecular weight distribution were measured by gel permeation chromatography (GPC) using a Tohso GPC HLC 8020.

Results and Discussion

Fig. 1 shows the DSC chart of the polyarylate oligomers crystallized in toluene. The polyarylate oligomer showed a clear crystalline melting point around 207°C in the first scan, however, in the second scan, the DSC chart did not show any crystalline melting point.

Fig. 1 DSC example of the crystallized polyarylate oligomer.

Sample used: $\eta_{sp}/C = 0.16$, 0.5 g polymer, filtered under 355 μ m, 1.0 g toluene, immersed at 25°C, 1 h.

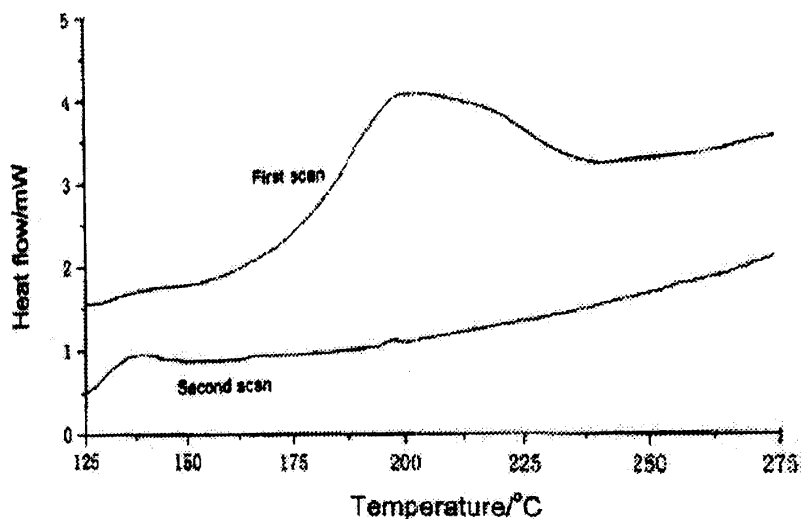
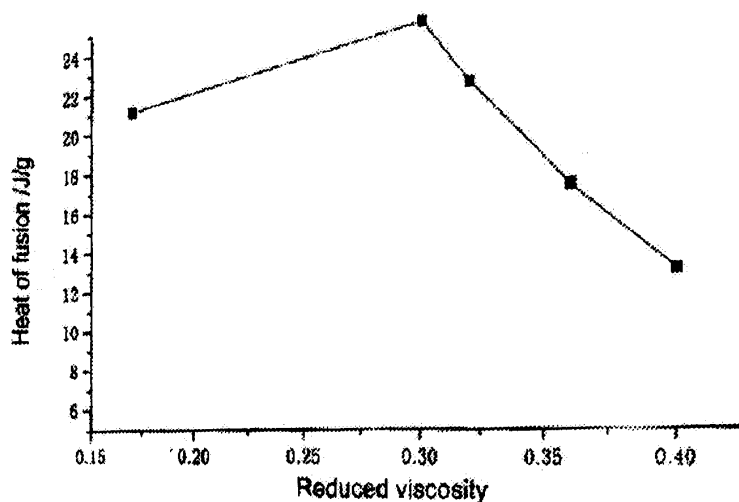


Fig. 2 shows the effect of the reduced viscosity of the crystallized polyarylate oligomers on the heat of fusion was checked.

Fig. 2 Effect of the reduced viscosity of the crystallized polyarylate oligomers on the melting point and glass transition point.

0.5 g polymer, filtered under 355 μ m, 1.0 g toluene, immersed at 25°C, 1 h.



With an increase in the polymer reduced viscosity, the heat of fusion decreased. This figure suggests that the increase in the molecular weight will make the polymer difficult to crystallize.

Fig. 3 shows the polarized microscopy of the crystallized polyarylate oligomer. Spherulites were clearly observed. These crystallized polyarylate oligomers are used for the solid-state polymerization.

Fig. 3 Polarized microscopy of the crystallized polyarylate oligomer. Dichloromethane solution of polyarylate oligomer having the reduced viscosity of 0.36 was cast on a glass plate, and on the cast film, a drop of toluene was dropped and observed after 10 min.

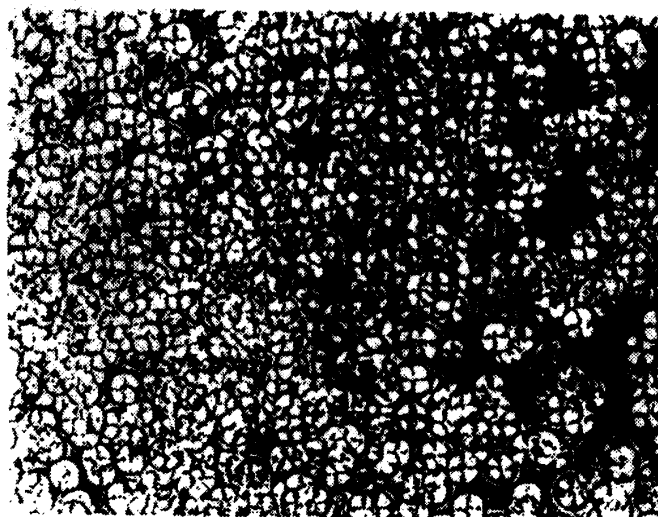


Fig. 4 shows the change in the melting temperature of polymer with polymerization bath temperature using the polymer with a reduced viscosity of 0.19. The melting point increased with an increase in the bath temperature.

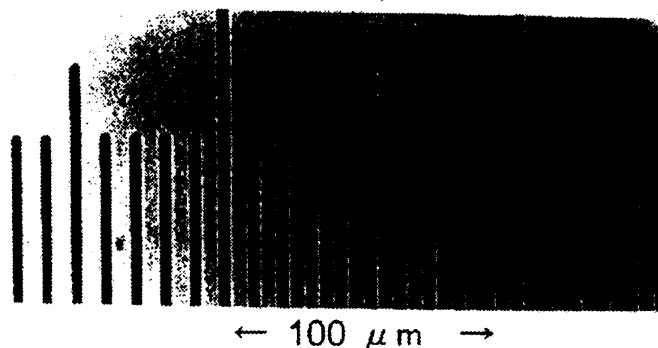


Fig. 4 Change in the melting point of the polymer during polymerization.

Initial polymer; Reduced viscosity is 0.19.

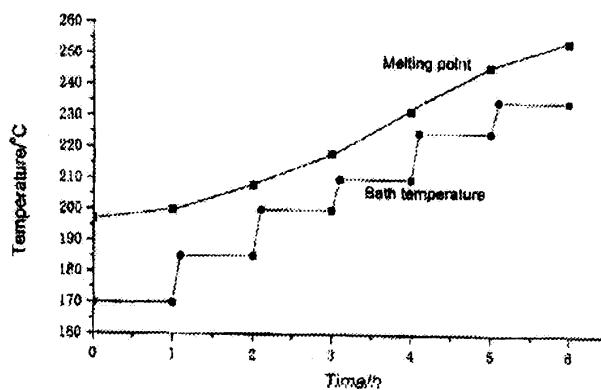
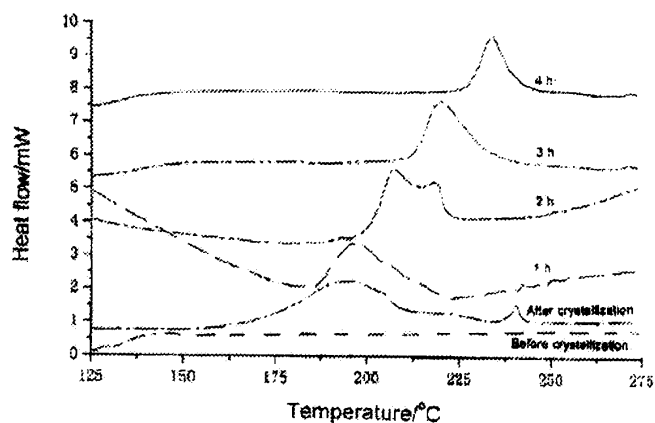


Fig. 5 Change in the DSC with the polymerization.

Initial polymer; Reduced viscosity is 0.19.



In Fig. 5 the change of the DSC chart

with polymerization time is also shown. These changes clearly show the increase in the melting temperature with the polymerization time. Based on these changes, it was understood that the polymerization temperature can be elevated with by raising the melting point.

Fig. 6 shows the change in GPC chart with polymerization time, when the polymerization temperature increased with the increase in the melting point of the polymer. With the polymerization time, the molecular weight increased.

Fig. 6 Change in the GPC during the solid-state condensation polymerization.

Polymerization conditions: 8 g polymer, 300 mL N₂ flow; initial polymer; reduced viscosity is 0.34 and -OH mol% is 52.

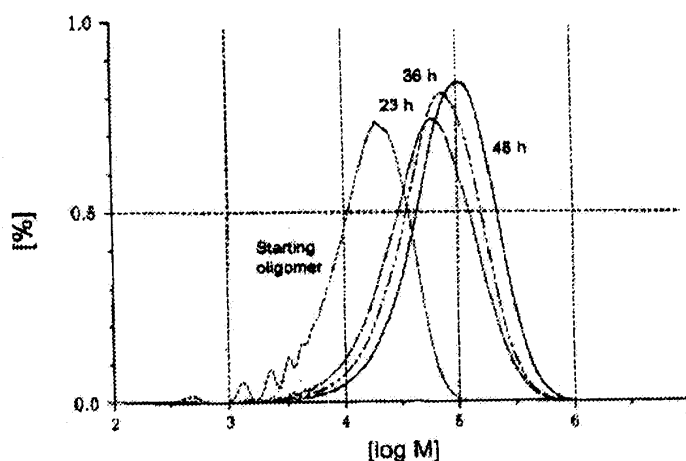
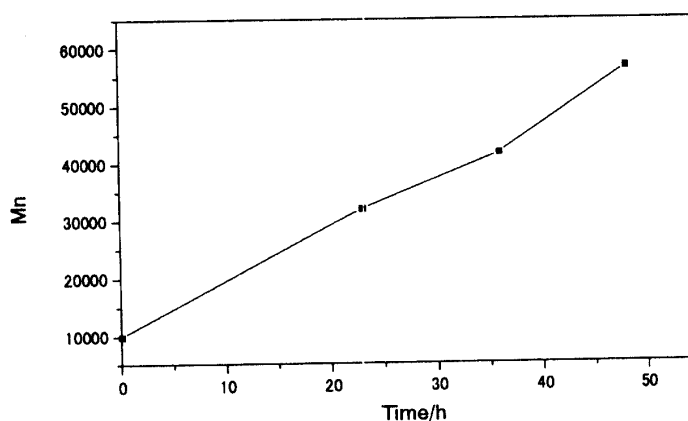


Fig. 7 Effect of the polymerization time on the number average molecular weight.

Polymerization conditions: 8 g polymer, 300 mL N₂ flow; initial polymer; reduced viscosity is 0.34 and -OH mol % is 52.



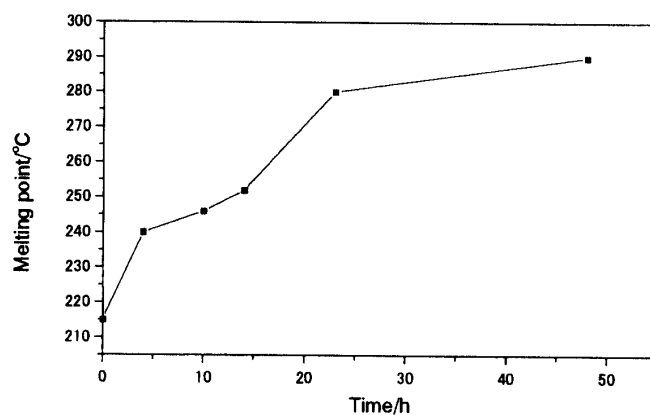
In Fig. 7 the relation between polymerization time and number average molecular weight is shown. A good linearity was observed between polymerization time and number average molecular weight. This means that condensation polymerization proceed with second order. That is to say, the condensation reaction between -OH of bisphenol A unit and phenyl ester of aromatic carboxylic acid. Linearity means the phenol, which was generated in the solid polymerization system under the N₂ gas flow, might be quickly eliminated from the

reaction zone. Thus, the phenol generated in the condensation reaction may do not effect on the polymerization. These phenomena is a great difference between the melt polymerization, in which it was said there exist the diffusion problem of the generated phenol ¹⁾, and the solid-state polymerization under N₂ gas flow.

In Fig. 8, effect of the polymerization time on the melting point of the polymer obtained is shown. The polymer obtained here showed the melting point over 280 °C, and these values are much higher than the value reported by Eguiazabal et al. ⁹⁾. Eguiazabal et al. ⁹⁾ reported that the commercially available bisphenol A polyarylate could be crystallized when the polymer was dissolved in σ -dichlorobenzene and the solvent was vaporized gradually. In these case, the melting point of the polymer is 250 °C, and this value can be increased to 260 °C under heat treatment, which was the highest value for the bisphenol A polyarylate from terephthalic/isophthalic acids ever reported. However, our polymer, obtained in the solid-state polymerization showed the value of the melting point of 290 °C, which is 30 °C higher than the value reported by Eguiazabal et al. ⁹⁾ and this value was increased to 301 °C by further prolonged polymerization time (polymerization time of 71 hrs).

Fig. 8 Effect of the polymerization time on the melting point of the obtained polymer.

Polymerization conditions: 8 g polymer, 300 mL N₂ flow; initial polymer: reduced viscosity is 0.34 and -OH mol % is 52.



In Table 1, molecular weight and molecular weight distribution of obtained polyarylates are shown. The molecular weight distribution of $M_w/M_n = 2$ is shown. This means that the molecular weight distribution show the most probable distribution, which is said to be valid for the condensation polymerization.

In Table 2, comparison of the obtained polymer with commercially available polymer is shown. The polymer obtained in the solid-state polymerization showed the value of the molecular weight twice that of the commercially available polymer.

Table 1 Molecular weight and molecular weight distribution of obtained polyarylates

Polymerization	Mn	Mw	Mw/Mn
Starting oligomer	10,000	21,000	2.1
23 hrs	32,000	78,100	2.4
36 hrs	41,700	90,800	2.2
48 hrs	56,700	119,000	2.1

Polymerization conditions: 8 g polymer, 300 mL N₂ flow; initial polymer: reduced viscosity is 0.34 and -OH mol % is 52.

Table 2 Comparison of the obtained polyarylate with the commercial polymer

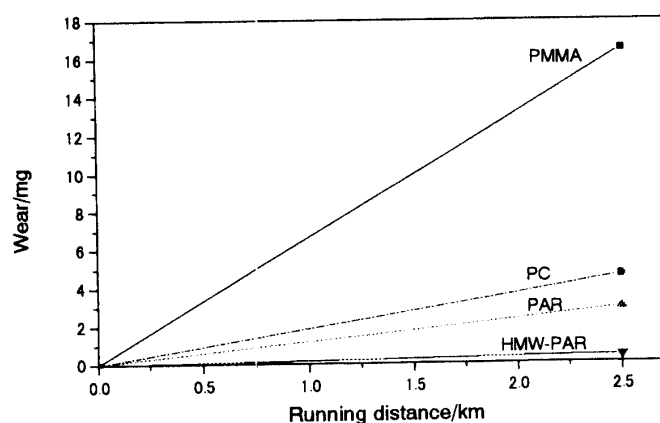
	Mn	Mw	Mw/Mn
This experiment	56,700	119,000	2.1
U-100*	26,100	61,000	2.3
Durel**	25,600	58,400	2.3

* Commercial polyarylate from Unitika (trade name: U Polymer)

** Commercial polyarylate from Hoechst-Celanese

Fig. 9 Wear properties of high molecular weight polyarylate.

PMMA: Asahi Chemical polymethyl methacrylate 80N, PC: Teijin Chemical polycarbonate L1250, PAR: Unitika polyarylate U-100, HMW-PAR: Polyarylate with number average molecular weight of 56,700 (twice that of U-100)



Color of the polyarylate obtained in the solid-state polymerization was checked and compared with the commercially available polyarylate (U-100). The level of the color index of U-100 is about 10, while the level of that of high molecular weight polyarylate obtained by the solid-state polymerization showed the level of 4.5. This means that the color of the polymer obtained in the solid-state polymerization is superior to U-100.

In Figure 9 the wear properties of high molecular weight polyarylate was shown compared with other amorphous polymer. High molecular weight polyarylate obtained in this experiment showed excellent wear properties.

Conclusions

As a conclusions, solid-state polymerization of bisphenol A polyarylate oligomers can give high molecular weight polymer, and give excellent color with excellent wear properties.

References

- 1) B. D. Dean, M. Matzner, J. M. Tibbet, "*Polyarylate*", in "*Comprehensive Polymer Science*", Pergaman, New York, 1989, Vol. 5, Chapter 18, pp. 317-329.
- 2) T. Iwamoto, T. Kinoshita and J. Masamoto, *Sen'i Gakkaishi*, **54**, 429-434 (1998).
- 3) T. Iwamoto, T. Kinoshita and J. Masamoto, *Kobunshi Ronbunshu*, **56**, 31-40 (1999).
- 4) T. Iwamoto, T. Kinoshita and J. Masamoto, *Sen'i Gakkaishi*, **55**, 234-239 (1999); T. Iwamoto, T. Kinoshita, K. Takaya and J. Masamoto, *Rep. Prog. Polym. Phys. Jpn.*, **42**, 499-500 (1999).
- 5) T. Iwamoto, T. Kinoshita and J. Masamoto, *Nippon Kagaku Kaishi*, **1999**, 51-57.
- 6) T. Iwamoto, T. Kinoshita and J. Masamoto, *Nippon Kagaku Kaishi*, **1999**, 131-136; T. Iwamoto, T. Kinoshita, K. Takaya and J. Masamoto *Rep. Prog. Polym. Phys. Jpn.*, **42**, 189-190 (1999).
- 7) T. Iwamoto, T. Kinoshita and J. Masamoto, *Nippon Kagaku Kaishi*, **1999**, 185-192; T. Iwamoto, T. Kinoshita, K. Takaya and J. Masamoto, *International Conference on Advanced Fiber MaTerial*, Ueda, October 3-5, pp. 293-294 (1999); T. Iwamoto, T. Kinoshita, K. Takaya and J. Masamoto, *Rep. Prog. Polym. Phys. Jpn.*, **42**, 497-498 (1999).
- 8) Y. -D. Lee and H. -B Tsai, *Makromol. Chem.*, **190**, 1413 (1989).
- 9) J. I. Eguizabal, J. J. D. Val, M. Cortazar and J. J. Iruin, *Eur. Polym. J.* **27**, 965 (1991).

(Received November 15, 2001)