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# Synthesis and Optical Properties of Polystyrene-Polyarylate Block Copolymer

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**Abstract:**

*To create a new field of application for reactive polystyrene (PS), a new process was developed for the polymerization of a polystyrene-polyarylate block copolymer (PS-b-PAr). In the new process, carboxyl-terminated polystyrene reacts with bisphenol A to convert its terminal groups into aromatic hydroxyl groups of higher reactivity, and then solution condensation polymerizes it with bisphenol A, isophthaloyl dichloride and terephthaloyl dichloride to produce PS-b-PAr. When it contains 40 to 60 wt% PS, PS-b-PAr exhibits low birefringence and good transparency. It also features low melt viscosity, and therefore good moldability and high adhesion to metals like aluminum. These excellent properties make PS-b-PAr a suitable material for optical application.*

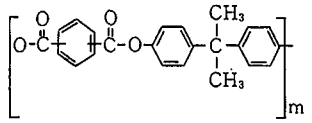
## 1. Introduction

In recent years, the polymer industry has paid great attention to the development of block and graft copolymers. Block and graft copolymers, in which different polymer segments are chemically bonded, can exert the synergetic effects of the polymer segments while exhibiting their intrinsic functions based on micro-domain separation structures. They can be utilized as functional materials, be added as compatibilizers to modify incompatible polymer blends, and be used as surface active agents to modify polymer surfaces[1-4].

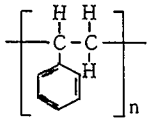
Nippon Steel has carried out the research and development of polystyrene and polyarylate block copolymer (PS-b-PAr) as a part of its effort to find new uses for reactive polystyrene (PS).

Polyarylate (PAr) is a polyester of bisphenol A with a 1:1 molar ratio mixture of terephthalic acid and isophthalic acid, as shown in **Fig. 1(a)**. It is a transparent resin with excellent heat resistance, mechanical strength, impact resistance, and ultraviolet stability[5]. However, PAr is poor in process ability because of its high melt viscosity. Moreover, because it has phenyl groups of high polariz ability in its backbone, it generates positive birefringence due to retained molecular orientation when it is injection molded[6].

Polystyrene (PS) is a transparent resin of high fluidity, has a phenyl group in the side chain as shown in **Fig. 1(b)**, and exhibits negative birefringence. So the birefringence and process ability would be much improved by blending PAr and PS[7], and the blend would be applicable to liquid crystal display electrode and optical disk (such as laser vision disk, compact disk and



(a) Molecular structure of PAr



(b) Molecular structure of PS

Fig. 1 Molecular structures of PAr and PS

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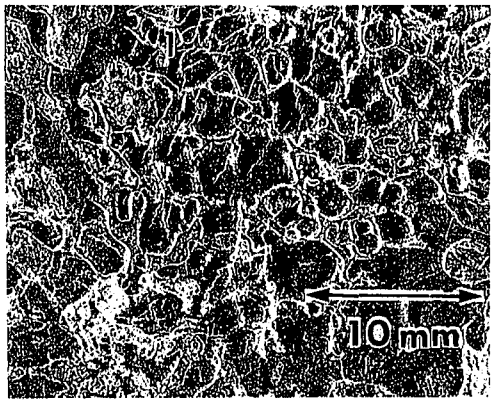



**Photo 1** Cast film of PS/PAr blend, 100 μm thick

magneto-optical disk) substrates[8,9]. However their limited compatibility makes it difficult to control micro domain structure less than wave length and electrode (see **Photo 1**). To obtain a transparent substrate, polystyrene and polyarylate molecules must be chemically bonded and the domain diameter must be reduced to less than the visible light wavelength.

This paper reports a novel PS-b-PAr polymerization process developed by Nippon Steel, and the properties of the PS-b-PAr block copolymer produced by the new process.

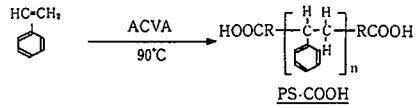
## 2. Experimental

### 2.1 Synthesis of polystyrene-polyarylate block copolymer (PS-b-PAr)

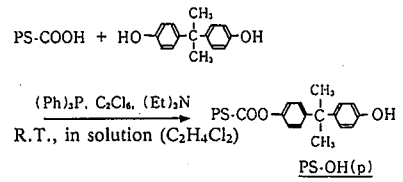
Polystyrene is an addition polymer, whereas polyarylate is a condensation polymer. The chemical bonding of these two polymers of different polymerization patterns is the primary theme of the present research.

The three-step process illustrated in **Fig. 2** was developed for the polymerization of PS-b-PAr.

Step 1: Preparation of carboxyl terminated PS(PS-COOH)




Step 2: Conversion of the carboxyl groups of PS-COOH




Step 3: Synthesis of PS-b-PAr

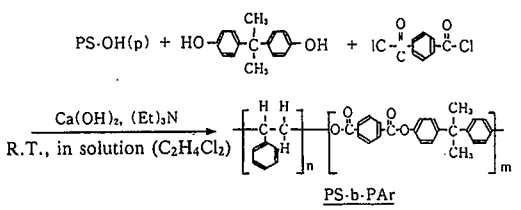



**Fig. 2** Synthetic route of PS-b-PAr

Step 1: Preparation of PS-COOH

Radical polymerization by the use of a chain transfer agent containing a carboxyl group is reported as a conventional process for the polymerization of carboxyl-terminated polystyrene (PS-COOH)[10-13]. The following problems are pointed out for the conventional process:

(1) The chain transfer reaction makes it difficult to produce high-molecular weight polymers.
(2) Since no functional groups are introduced at the initiating ends and chain transfer reaction stop ends, polystyrene without introduction of carboxyl groups is formed as a by-product[14,15].

An attempt was made to polymerize PS-COOH using a carboxyl group-containing initiator in order to inhibit the chain transfer reaction in the reaction system and to positively introduce functional groups at the initiating ends of polystyrene. The rate of polymerization by the process was calculated by a polymerization kinetic model. The initiator was continuously added to the reaction system to keep the initiator concentration constant. No chain transfer agents were used. The initiator used in the polymerization process is 4,4'-azobiscyanovaleric acid (ACVA).

Step 2: Conversion of PS-COOH terminal groups

Polyarylate is industrially produced by the solution polymerization or interfacial polycondensation of bisphenol A and a 1:1 molar ratio mixture of terephthaloyl dichloride and isophthaloyl dichloride. Since the carboxyl groups of PS-COOH are low in reactivity, the reactions involved do not sufficiently proceed when PS-COOH is directly added to the reaction system.

To counter this problem, PS-COOH was made to react with an excess amount of aromatic dihydroxy compound and convert the terminal carboxyl groups into aromatic dihydroxyl groups of higher reactivity. PS-COOH was then added to the polymerization system. The carboxyl groups and aromatic hydroxy groups are esterified by the most common method of heating and mixing at a temperature of 473K or higher[16]. The reaction system of **Fig. 2** was selected so that the esterification reaction may proceed under such mild conditions as to prevent the decomposition of PS-COOH.

Step 3: Synthesis of PS-b-PAr

The above-mentioned PS-OH(p) was added together with bisphenol A and a 1:1 molar ratio mixture of terephthaloyl dichloride and isophthaloyl dichloride to an organic solvent (1,2-dichloroethane), and PS-b-PAr was polymerized by the solution polycondensation process of **Fig. 2**[17]. The reaction solution was neutralized with an aqueous solution of acetic acid, rinsed to neutrality, and added to excess methanol to recover the polymer.

With this reaction system, the polymerization of PS-b-PAr from styrene monomer was continuously carried out from step 1 through step 3 without isolation and purification of the intermediate products PS-COOH and PS-OH(p).

### 2.2 Characterization

The molecular weight of the polymerization product by the reaction system was measured by gel permeation chromatography (GPC) (a Waters model) calibrated by monodispersed polystyrene. The number of the terminal carboxyl groups of PS-COOH introduced was determined by dissolving PS-COOH in tetrahydrofuran and performing neutralization titration with a NaOH aqueous solution. The conversion ratio of the terminal

groups of PS-COOH in step 2 was calculated by comparing the results of neutralization titration of PS-COOH before and after the reaction in step 2. The formation of PS-b-PAr was confirmed by $^1$H-NMR (nuclear magnetic resonance) after washing the polymer recovered in step 3 with cyclohexane and removing unreacted polystyrene components. The microstructure of PS-b-PAr was observed with a transmission electron microscope (made by JOEL). Its birefringence and melt viscosity were measured by a polarized microscope (made by Olympus Optical and using a white light source) and a capillograph (made by Toyo Seiki), respectively. An aluminum film of 200 nm thickness was evaporated onto the substrates using an ECR (electron cyclotron resonance) sputtering apparatus (made by Aftee).

## 3. Results and Discussions

### 3.1 Synthesis of PS-b-PAr

3.1.1 Preparation of PS-COOH

**Fig. 3** shows the relationship between the initiator concentration and the molecular weight (Mn) of PS-COOH. In the reaction system, the molecular weight of PS-COOH can be controlled over the range of 3,000 to 80,000 by adjusting the initiator concentration. Incidentally, such a high molecular weight of 20,000 and above was difficult to accomplish by any conventional technique. The experimental results generally agreed with the molecular weight values calculated by the polymerization kinetic model, and verified the validity of the model. The molecular weight dispersion (Mw/Mn where Mw is the weight-average molecular weight of PS-COOH) was controlled to less than 3 at each molecular weight by adding the initiator continuously to the reaction system so as to keep the concentration constant. The reaction yield of PS-COOH was higher than 80% at a reaction time of 6 h.

**Fig. 4** shows the relationship between molecular weight and the number of introduced terminal carboxyl groups of PS-COOH. At each molecular weight, the number of the carboxyl groups of PS-COOH was more than 1.0, and at least one carboxyl group was introduced to every PS-COOH molecular. Particularly when the molecular weight was higher than 20,000, the number of carboxyl groups introduced was about 2, and they were introduced into the ends of almost all polystyrene molecules.

3.1.2 Conversion of terminal groups of PS-COOH

When PS-COOH was made to react with ten equivalents of bisphenol A in step 2, the number of carboxyl groups of PS-COOH was reduced to less than 95% of that before the reaction. This indicates that more than 95% of the PS-COOH carboxyl groups could be converted into aromatic hydroxyl groups.

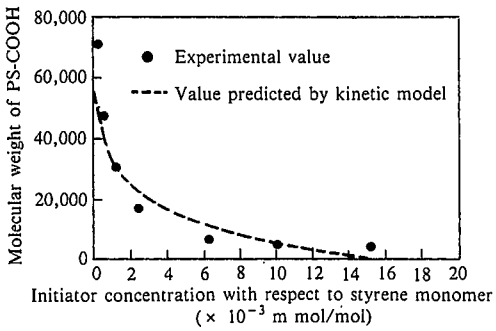



**Fig. 3** Relationship between the initiator concentration and molecular weight of PS-COOH

3.1.3 Synthesis of PS-b-PAr

Typical $^1$H-NMR spectra of PS-b-PAr polymerized by this reaction system are shown in **Fig. 5**. Peaks resulting from both the polystyrene and polyarylate chains are observed, and the formation of PS-b-PAr is confirmed.

**Table 1** lists the molecular weight of PS-b-PAr, composition ratio of PS-b-PAr as calculated from the $^1$H-NMR spectra, and the copolymerization ratio of polystyrene. The first two digits in the four-digit designation of each sample correspond to the molecular weight (Mn) of PS-OH(p) used in step 3, and the last two digits correspond to the polystyrene composition ratio of PS-b-PAr. With each sample, the molecular weights (Mn and Mw) of PS-b-PAr formed in step 3 were greater than those of the starting material PS-OH(p), and there was formed PS-b-PAr with polyarylate chains introduced into polystyrene chain ends. In the reaction system, PS-b-PAr was successfully polymerized with a

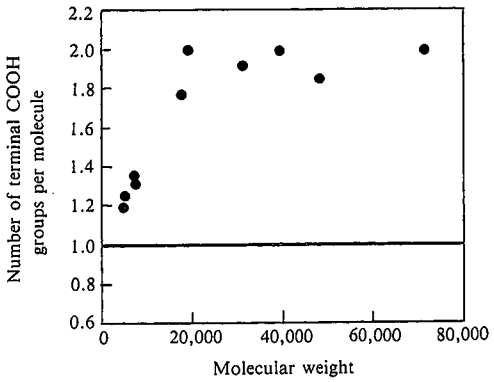



**Fig. 4** Number of introduced functional groups of PS-COOH

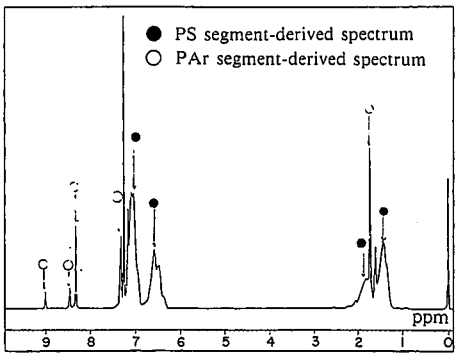



**Fig. 5** $^1$H-NMR spectra of PS-b-PAr

**Table 1** Molecular weights and compositions of PS-b-PAr and reactive ratios of PS in (step 3)

| Sample | PS-OH(p) | | | PS-b-PAr | | | |
|---|---|---|---|---|---|---|---|
| | Mn | Mw | wt% | Mn | Mw | Composition (PS/PAr) | Reactive ratio of PS* |
| run0950 | 9000 | 15000 | 50 | 24000 | 81000 | 59/41 | 85% |
| run3725 | 37000 | 100000 | 25 | 38000 | 113000 | 30/70 | 85% |
| run3740 | | | 35 | 39000 | 140000 | 40/70 | 83% |
| run3763 | | | 60 | 70000 | 216000 | 62/38 | 85% |
| run7759 | 77000 | 180000 | 55 | 87000 | 275000 | 59/41 | 88% |

*PS reactive ratio = {1 − $Y_1$ × (conversion in step 3)/PS-OH(p) wt%} × 100
$Y_1$ = wt% of the exclusions by cyclohexane in the product of (step 3)

polystyrene copolymerization ratio of more than 80%, even when the charge and molecular weight (Mn) of the starting material PS-OH(p) were changed from 25 to 60 wt% and from 9,000 to 77,000, respectively.

### 3.2. Properties of PS-b-PAr

3.2.1 Phase structure and transparency of PS-b-PAr

Transmission electron micrographs of PS-b-PAr (63 and 59 wt% PS) stained by osmium tetroxide are given in **Photo 2**. In PS-b-PAr (63 and 59 wt% PS), domains of PAr (stained) are formed in the matrix of PS (not stained). Even when polystyrenes with molecular weights of 37,000 and 77,000 are used, the domain diameter is about 100 nm and is smaller than the visible light wavelength of 400 to 700 nm.

The light transmission of a 1.2-mm thick plate of PS-b-PAr in the semiconductor laser wavelength region of 600 to 800 nm was more than 85%.

3.2.2 Birefringence

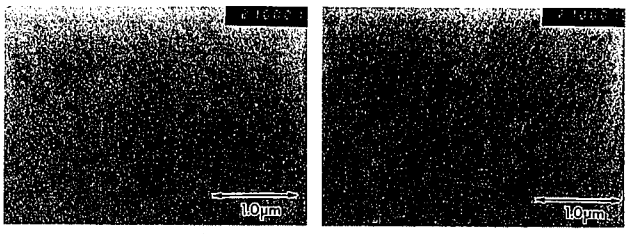
A 100-$\mu$m thick cast film of PS-b-PAr was drawn by 10 to 50% at 488K (glass transition temperature of PAr + 15K), and its birefringence was measured. The birefringence of PS-b-PAr containing only 30 wt% PS was approximately the same as that of PAr, whereas the birefringence of PS-b-PAr containing 40 to 60 wt% PS was less than 1/100 of that of PAr even under 50% drawing (see **Fig. 6** and **Photo 3**).

3.2.3 Melt viscosity

The melt viscosity values of PS-b-PAr and PAr are given in **Fig. 7**. The melt viscosity of PS-b-PAr (63 wt% PS) was normalized from that of run 3736 by the equation of **Fig. 7**[18], in order to insure the same molecular weight as that of commercial polyarylate (tradenamed U-100 and made by Unitika). The melt viscosity of PS-b-PAr containing 63 wt% PS was less than 1/1000 of that of PAr. PAr is high in melt viscosity and is difficult to mold at temperatures lower than 573K. When molded, PAr undergoes thermal decomposition, which makes it difficult to obtain transparent molded products. PS-b-PAr is low in melt viscosity and can be molded into transparent products at a temperature lower than 573K.

3.2.4 Adhesion to aluminum film

A 2000-nm thick aluminum film was vapor deposited on PS-b-PAr, commercial polycarbonate (PC) (tradenamed Panwrite AD9000TG and made by Teijin Kasei), and commercial amorphous polyolefin (APO) (tradenamed Zeonex and made by Nippon Zeon) (see **Table 2**). **Table 3** lists the cross-cut test results of the vapor-deposited aluminum films. PS-b-PAr had better adhesion to the aluminum film than the commercial optical resins.




Run 3763 $\bar{r}$ : 99 nm

Run 7759 $\bar{r}$ : 121 nm

**Photo 2** Micro domain structure of PS-b-PAr

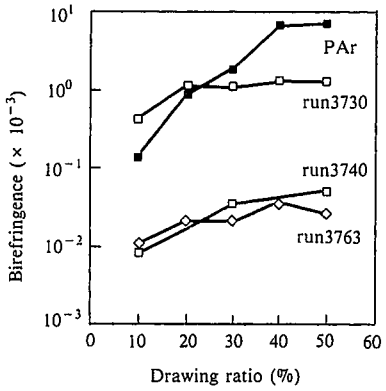



**Fig. 6** Birefringence of drawn films of PAr and PS-b-PAr

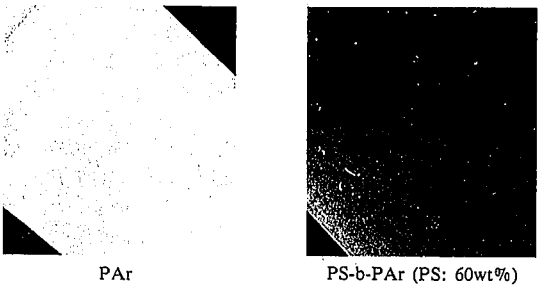



**Photo 3** Birefringence comparison of PAr and PS-b-PAr (50% drawn film inserted between cross Nicol polarizing plates)

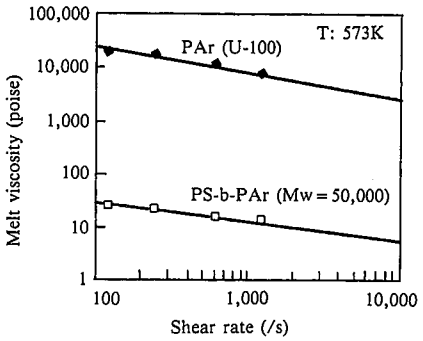



**Fig. 7** Melt viscosities of PAr and PS-b-PAr normalized at Mw = 50,000
$\mu$ 50,000 = $\mu$ Mw × (50,000/Mw)$^{3.4}$

**Table 2** Vapor deposition conditions

| | |
|---|---|
| Argon partial pressure | 1.5 × $10^{-5}$ Pa |
| Substrate temperature | 298K |
| Vapor deposition speed | 10 nm/min |

**Table 3** Cross-cut test results of aluminum films

| PS-b-PAr | PC | APO |
|---|---|---|
| 100/100 | 10/100 | 10/100 |

## 4. Conclusions

A novel synthesis route of PS-b-Par using styrene macromer is proposed. The new process can continuously synthesize PS-b-PAr from styrene monomer without isolating the intermediate products PS-COOH and PS-OH(p) and can achieve a high PS copolymerization ratio of over 80%, even when the charge and molecular weight of the polystyrene (PS-OH(p)) are changed from 25 to 60 wt% and from 9,000 to 77,000, respectively.

The birefringence of a 50% stretched sheet of PS-b-PAr is less than 1/100 of that of PAr when the PS content is 40 to 63 wt%. The melt viscosity of PS-b-PAr is less than 1/1000 of that of PAr when the PS content is 63 wt%. PS-b-PAr has better adhesion to aluminum films than other optical resins.

PS-b-PAr is a resin that features excellent transparency, low birefringence, low melt viscosity and superior adhesion, and is a promising material in optical applications.

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