

# Synthesis and Properties of Elastomeric Ionenes I. Polybutadiene Ionenes

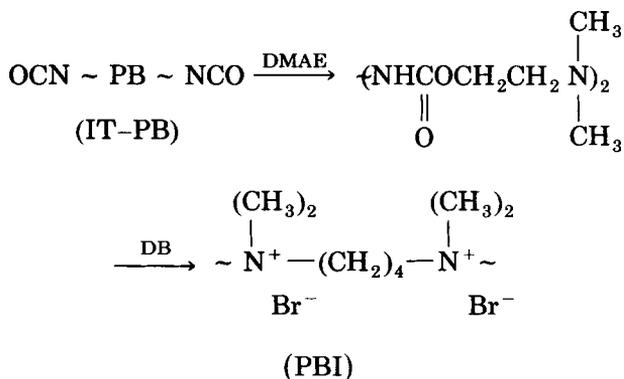
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## Synopsis

Polybutadiene ionene (PBI) carrying quaternary ammonium ions in the main chain was synthesized from dimethylamino-terminated polybutadiene and 1,4-dibromobutane. Dimethylamino-terminated polybutadiene was prepared by the reaction of isocyanate-terminated polybutadiene with 2-dimethylaminoethanol. The swelling property and the mechanical properties of PBI were compared with those of polybutadiene urethane (PBU), which was prepared by the reaction of hydroxy-terminated polybutadiene with a diisocyanate. The following points were found: (1) PBI shows almost the same solubility parameter  $\delta_p$  as that of PBU; (2) PBI attains a four time greater tensile strength at break than PBU at room temperature; (3) PBI shows a thermoplastic behavior.

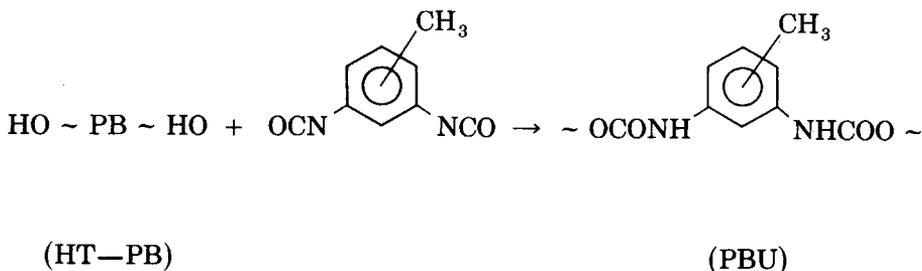
## INTRODUCTION

Since 1968, when Rembaum et al. published their first paper on ionenes,<sup>1</sup> extensive researches have been devoted to the application of ionene to the electrical and biomedical materials.<sup>2</sup> Elastomeric ionenes, elastomers carrying cationic charges, have a variety of potential applications.<sup>3-8</sup> The author synthesized a novel polybutadiene ionene (PBI) by the reaction of isocyanate-terminated polybutadiene (IT-PB) with 2-dimethylaminoethanol(DMAE) and 1,4-dibromobutane(DB);



and found that the film of this polymer attains 19.2 MPa in the tensile strength at break<sup>9</sup> which is much superior to that reported by Rembaum et al.<sup>10</sup> (1.73 MPa).

In the present article, we compared the swelling property and the mechanical properties of PBI with those of polybutadiene urethane (PBU) which was prepared by reacting hydroxy-terminated polybutadiene with 2,4-tolylene diisocyanate in order to clarify the effect of the ionene structure;



## EXPERIMENTAL

### Materials

Hydroxy-terminated polybutadiene (HT-PB) and isocyanate-terminated polybutadiene (IT-PB) were provided by Idemitsu Petrochemical Co. Ltd. Characteristic properties of HT-PB and IT-PB are given in Table I.<sup>11</sup> 2-Dimethylaminoethanol, 1,4-dibromobutane, tetrahydrofuran (THF), and methanol were purified by the usual procedures. Di-*n*-butyltindilaurate and 2,4-tolylene diisocyanate were used without further purification. It is noted that the functionality of HT-PB (= 2.2) is sufficient to form a crosslinked polymer by the reaction with a reagent whose functionality is 2.

### Synthesis of Dimethylamino-terminated Polybutadiene (AT-PB)

First, 100 g of isocyanate-terminated polybutadiene (IT-PB) was dissolved in 300 mL of THF under N<sub>2</sub> atmosphere and was allowed to react with 57.4 g of 2-dimethylaminoethanol (DMAE) ([DMAE]/[NCO] = 3) at room temperature in the presence of 0.047 mL of dibutyltindilaurate as a catalyst. The completion of the reaction was checked by the absence of infrared (IR) absorption of isocyanate at 2270 cm<sup>-1</sup>. The resulting polymer, AT-PB, was isolated by pouring the solution into methanol. The purity of AT-PB was

TABLE I  
Characterization of HT-PB and IT-PB

| Sample             | [OH]<br>mol/g           | Viscosity<br>poise | Microstructure (%) |              |       |
|--------------------|-------------------------|--------------------|--------------------|--------------|-------|
|                    |                         |                    | <i>cis</i>         | <i>trans</i> | Vinyl |
| HT-PB              | 8.1 × 10 <sup>-4b</sup> | 50 <sup>c</sup>    | 20                 | 60           | 20    |
| IT-PB <sup>a</sup> |                         | 71 <sup>d</sup>    | 20                 | 60           | 20    |

<sup>a</sup>IT-PB is derived from HT-PB.

<sup>b</sup>This amounts to the hydroxyl functionality of 2.2

<sup>c</sup>Measured at 30°C.

<sup>d</sup>Measured at 25°C.

confirmed by thin layer chromatography (TLC) using methanol as a developing solvent.

### Preparation of Polybutadiene Ionene (PBI) and Polybutadiene Urethane (PBU)

Dimethylamino-terminated polybutadiene (AT-PB), 5 g was dissolved in 50 mL of THF and made to react with 0.44 g of 1,4-dibromobutane ( $[\text{Br}]/[\text{N}(\text{CH}_3)_2] = 1.4$  (otherwise the amount of 1,4-dibromobutane is specified) for 10 min. The solution was cast under  $\text{N}_2$  stream, and heated at  $100^\circ\text{C}$  for 1 h to give a PBI film.

Next 5 g of hydroxy-terminated polybutadiene (HT-PB) was dissolved in 50 mL of THF and subjected to react with 0.44 g of 2,4-tolylene diisocyanate ( $[\text{NCO}]/[\text{OH}] = 1.2$ ) in the presence of 0.002 g of dibutyltindilaurate for 10 min. A PBU film was obtained in the same way as a PBI film.

Since the functionality of AT-PB is expected to be the same as that of HT-PB, PBI, as well as PBU, is a crosslinked polymer.

### Characterization

Molecular weights and molecular weight distributions were estimated by a Toyo Soda GPC HLC-802UR equipped with a low-angle light-scattering photometer LS-8. IR spectra and  $^1\text{H}$  nuclear magnetic resonance (NMR) spectra were measured by a Hitachi 215 grating infrared spectrophotometer and a Varian T-60A NMT spectrometer, respectively.

### Mechanical Properties

Tensile properties were determined on JIS #3 dumbbell-type specimens or ring-type specimens (11.6 mm inside diameter and 13.6 mm outside diameter) in  $\text{N}_2$  stream at an elongation speed of 10 mm/min using a TOM 200D-type tensile tester (Shinkoh Tsushin Co. Ltd.). A Rheovibron DDV-II (Toyo Baldwin Co. Ltd.) was used to measure dynamic mechanical properties at 110 Hz and temperature ranges from  $-100^\circ\text{C}$  to  $200^\circ\text{C}$ .

## RESULTS AND DISCUSSION

### Characterization of AT-PB

Figure 1 shows IR spectra of AT-PB together with those of HT-PB. The absorptions of AT-PB at  $3300$ ,  $1730$ ,  $1530$ , and  $1230\text{ cm}^{-1}$  which are not detected in HT-PB can be assigned as the structure of AT-PB, i.e.,  $-\text{NH}-$  stretching,  $-\text{C}=\text{O}$  stretching,  $-\text{NH}-$  bending, and  $-\text{CN}$  stretching, respectively. The NMR signals characteristic of AT-PB are shown in Figure 2 together with their assignments. Table II summarizes the molecular weights and the molecular weight distributions of AT-PB and HT-PB determined by GPC with light scattering. The larger molecular weight of AT-PB over that of HT-PB is due to not only the addition of dimethylaminoethanol but also to the effect of fractionation that made  $M_w/M_n$  smaller.

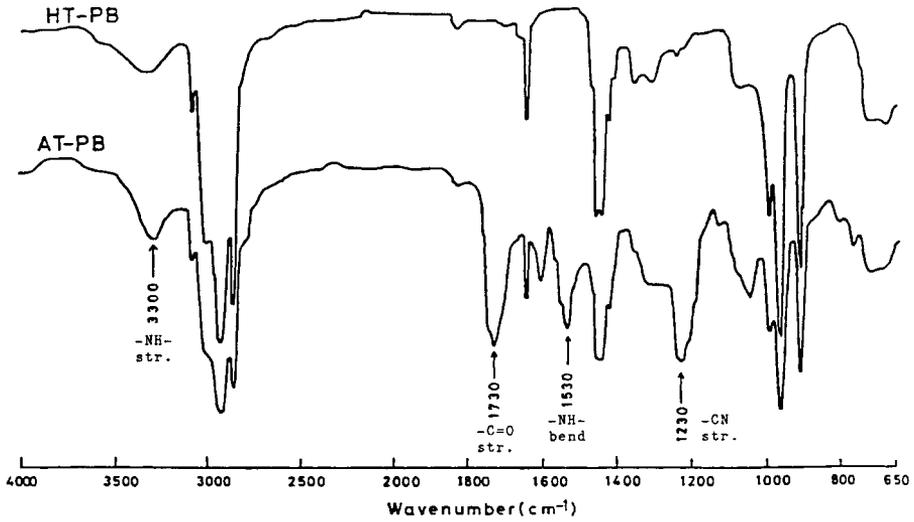
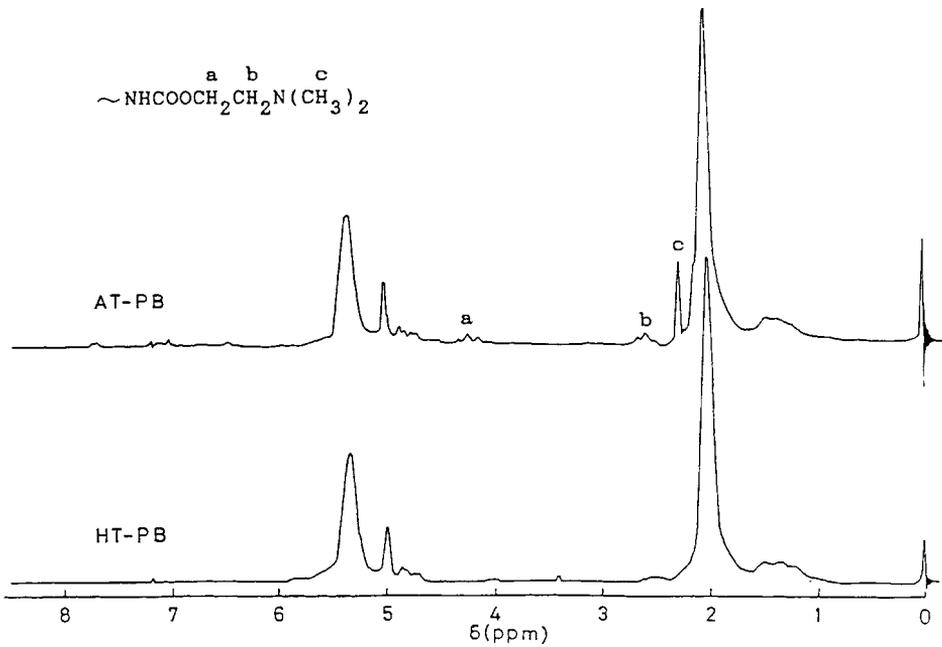


Fig. 1. IR spectra of AT-PB and HT-PB.

Fig. 2.  $^1\text{H}$  NMR spectra of AT-PB and HT-PB.

### Swelling Behavior

Table III summarizes the degrees of swelling  $Q$  and the sol fractions of PBI and PBU in various solvents. It is possible to estimate the solubility parameter  $\delta_p$  of PBI and PBU using the results in Table III with the equation of the degree of swelling  $Q$ ,<sup>12</sup>

$$Q = Q_m \exp[-KV_s(\delta_s - \delta_p)^2] \quad (3)$$

TABLE II  
Molecular weight of AT-PB and HT-PB

| Polymer | Mn   | Mw     | Mw/Mn |
|---------|------|--------|-------|
| HT-PB   | 4600 | 6800   | 1.5   |
| AT-PB   | 8000 | 10,100 | 1.3   |

where  $Q_m$  is the maximum degree of swelling given in Table III (2.5 for PBI and 5.1 for PBU),  $K$  is a constant which depends on the kind of the polymer,  $V_s$  and  $\delta_s$  are the molar volume and the solubility parameter of the solvent, respectively.<sup>13</sup> Rewriting Eq. (3) in the form

$$[1/V_s \ln(Q_m/Q)]^{1/2} = K^{1/2}(\delta_s - \delta_p), \quad (4)$$

one can find a linear relationship between  $\delta_s$  and the quantity of the left-hand side of Eq. (4) as shown in Figure 3. In this figure,  $\delta_p$  values for PBI and PBU were estimated to be 8.5 and 8.6, respectively. These values are almost the same as those of polybutadiene ( $\delta_p = 8.1 - 8.6$ )<sup>14</sup> and HT-PB crosslinked by diisocyanate ( $\delta_p = 8.4$ ).<sup>15</sup> These results indicate that the ionene structure does not have any measurable effect on the solvent interactions. This might be because the volume fraction of the polar group (cation in the main chain of PBI) is much smaller than that of polybutadiene part.

### Mechanical Properties

The effects of the ionene structure on mechanical properties can be seen clearly in Figures 4 and 5. In Figure 4, the tensile strength at break ( $T_B$ ) and the elongation at break ( $E_B$ ) are plotted against temperature. PBI attains a 4 times larger  $T_B$  (4.2 MPa) than PBU at room temperature. Figure 5 shows the

TABLE III  
Degree of Swelling and Sol Fraction

| Solvent                 | $V_s^a$<br>(cm <sup>3</sup> /mol) | $\delta_s$<br>(cal/cm <sup>3</sup> ) <sup>1/2</sup> | PBI                         |            | PBU                         |            |
|-------------------------|-----------------------------------|-----------------------------------------------------|-----------------------------|------------|-----------------------------|------------|
|                         |                                   |                                                     | $Q$<br>(cm <sup>3</sup> /g) | Sol<br>(%) | $Q$<br>(cm <sup>3</sup> /g) | Sol<br>(%) |
| Diethyl ether           | 103.7                             | 7.4                                                 | 1.6                         | 4          | 2.6                         | 18         |
| Diisobutyl ketone       | 176.1                             | 7.8                                                 | 1.5                         | 2          | 4.4                         | 19         |
| Isobutyl acetate        | 133.3                             | 8.3                                                 | 1.6                         | 4          | 4.2                         | 18         |
| Methyl isobutyl ketone  | 133.6                             | 8.4                                                 | 1.5                         | 4          | 4.6                         | 17         |
| <i>n</i> -Butyl acetate | 124.9                             | 8.5                                                 | 2.5                         | 6          | 4.8                         | 16         |
| Methyl methacrylate     | 105.9                             | 8.8                                                 | 2.1                         | 4          | 5.1                         | 18         |
| Methyl acrylate         | 90.3                              | 8.9                                                 | 0.9                         | 3          | 1.9                         | 15         |
| Ethyl acetate           | 98.5                              | 9.1                                                 | 1.0                         | 3          | 2.2                         | 17         |
| Methyl ethyl ketone     | 90.2                              | 9.3                                                 | 1.2                         | 7          | 2.4                         | 17         |
| Methyl acetate          | 80.0                              | 9.6                                                 | 0.5                         | 6          | 0.7                         | 11         |
| Diethylphthalate        | 198.4                             | 10.0                                                | 0.3                         | 0          | 0.6                         | 7          |
| Ethylene glycol         |                                   |                                                     |                             |            |                             |            |
| Monoethyl ether         | 91.0                              | 10.5                                                | 0.6                         | 4          | 0.6                         | 9          |
| Dimethyl sufoxide       | 72.2                              | 12.0                                                | 0.7                         | 0          | 0.2                         | 1          |

<sup>a</sup>Based on  $d_4^{20}$ .

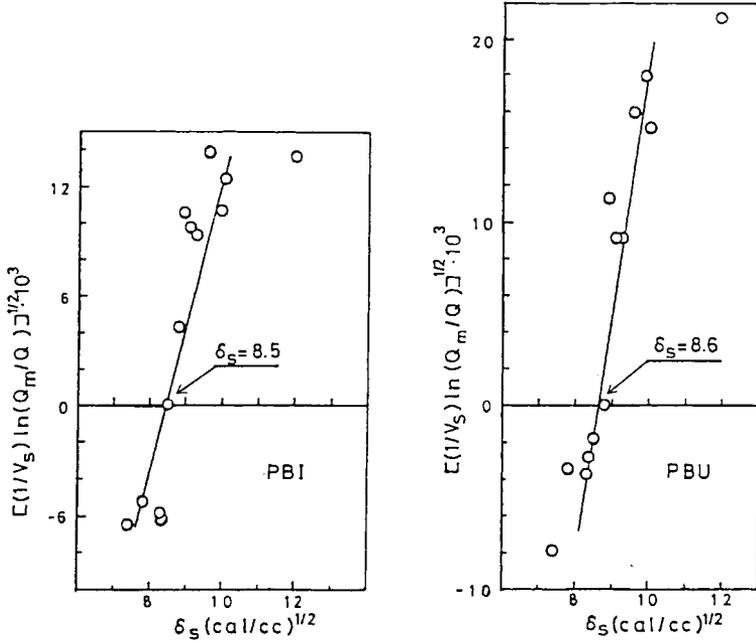


Fig. 3. Estimation of  $\delta_p$  for (A) PBI and (B) PBU.

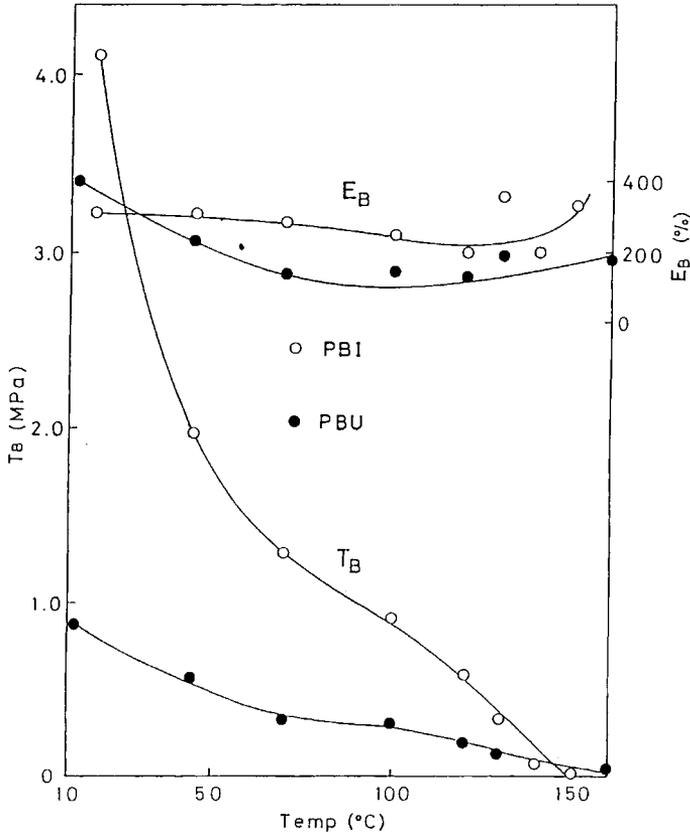


Fig. 4. Temperature dependence of tensile properties. (○) PBI; (●) PBU.

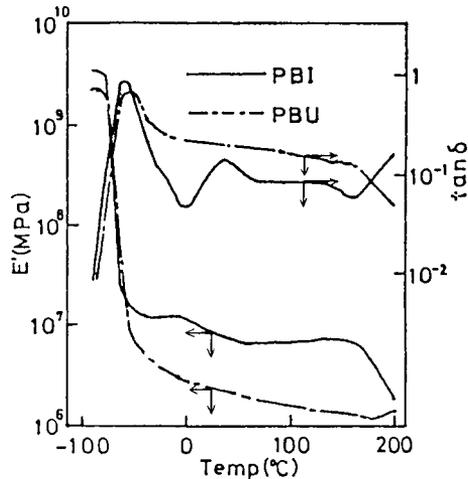


Fig. 5. Dynamic mechanical properties of PBI (—) and PBU (---).

dynamic mechanical properties of PBI and PBU. The difference between PBI and PBU is in  $\tan \delta$ ; a peak at  $40^\circ\text{C}$  and an increase at  $> 170^\circ\text{C}$  of PBI indicate a certain melting behavior suggesting that PBI possesses noncovalent-type crosslinks. It has been proposed that ionic groups in ionomers form some kind of ionic aggregates referred to as ionic clusters. Also in the present case, the differences in the mechanical properties between PBI and PBU could be ascribed to the existence of such ionic clusters of ionene cations in PBI.

Since the reaction between dibromobutane (DB) and AT-PB is not necessarily stoichiometric under the present reaction condition, by varying the amount of DB compounded, we can see how the ammonium ion concentration in PBI, that is, the extent of crosslinking, affects the mechanical properties of PBI. As can be seen in Figure 6, the amount of DB was found to stiffen PBI;

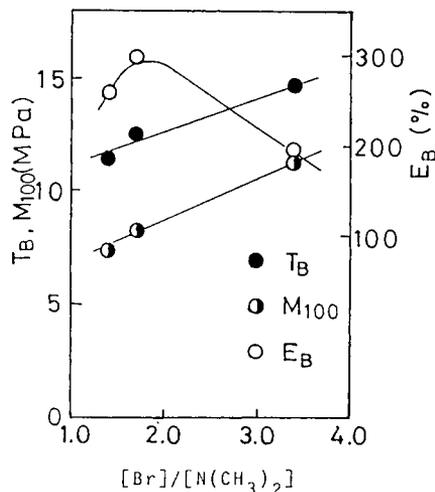


Fig. 6. Tensile properties of PBI plotted against the amount of dibromobutane compounded. (●)  $T_B$ ; (●)  $M_{100}$ ; (○)  $E_B$ .

TABLE IV  
Tensile Properties of the Original and the Remolded Sheets

| Tensile Property | Original Sheet | Remolded Sheet |
|------------------|----------------|----------------|
| $T_B$ (MPa)      | 3.1            | 4.1            |
| $M_{100}$ (MPa)  | 1.9            | 2.6            |
| $E_B$ (%)        | 270            | 240            |

the tensile strength increases with  $[DB]/[N(CH_3)_2]$  while the elongation at break has a maximum.

### Thermoplasticity of PBI

A large temperature dependence of  $T_B$  (Fig. 4) and an increase in  $\tan \delta$  at  $> 170^\circ\text{C}$  (Fig. 5) imply the thermoplastic nature of PBI. In order to check this possibility, we tried to remold the PBI film. After pulverizing the PBI film with a 3-inch two-roll mill, the sample powder was pressed with  $150 \text{ kg/cm}^2$  pressure at  $150^\circ\text{C}$  for 30 min to give a remolded film. Table IV shows the tensile properties of the remolded sample together with those of the original sample, which clearly shows that PBI has a thermoplastic nature. The larger tensile strength of the remolded sample may be due to the orientation of the polymer chains which was caused during the remolding process.

The thermoplasticity of PBI could be ascribed to the following characteristics of the crosslinking mechanism in PBI: (i) The cohesive force originated from the ionene structure of PBI shown in its mechanical properties is a noncovalent type and hence virtually thermoplastic; (ii) Buckler et al.<sup>16</sup> suggested that the quaternary ammonium salt undergoes a thermal decomposition at ca.  $140^\circ\text{C}$  and a reformation at room temperature. Therefore, the crosslinks of the quaternary ammonium salts in PBI are also expected to have thermoplastic nature.

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