

## Effects of Number-Average Molecular Weight of Liquid Hydroxyl-Terminated Polybutadiene on Physical Properties of the Elastomer

KATSUHIRO ONO, HIDETOSHI SHIMADA, and TOSHIHIDE NISHIMURA, *Idemitsu Petrochemical Co., Ltd., Tokyo 100, Japan*, SHINZO YAMASHITA, *Department of Chemistry, Faculty of Polytechnic Sciences, Kyoto Institute of Technology, Kyoto 606, Japan*, HIROSHI OKAMOTO, *Department of Applied Chemistry, Aichi Institute of Technology, Toyota 470-03, Japan*, and YUJI MINOURA, *Department of Chemistry, Research Institute for Atomic Energy, Osaka City University, Osaka 558, Japan*

### Synopsis

The relationships between the molecular weight of liquid hydroxyl-terminated polybutadiene (HTPB) and the physical properties of the elastomers were investigated. HTPB having various molecular weights were cured with 4,4'-diphenylmethane diisocyanate (MDI) by the one-shot method and the physical properties of these elastomers obtained were measured. The tensile strength, modulus, tear resistance, and hardness decreased with increase in the molecular weight of HTPB, and this phenomenon was remarkable in the low molecular weight HTPB (below about 3000). On the other hand, the ultimate elongation increased linearly with increase in the molecular weight of HTPB. The effects of incorporating a short-chain diol, N,N-bis(2-hydroxypropyl)aniline, on the physical properties of the elastomers are also discussed.

### INTRODUCTION

Liquid hydroxyl-terminated polybutadiene (HTPB) can be crosslinked with chain extension by the reaction of the terminal hydroxyl groups with a variety of diisocyanates and yield vulcanizates comparable to those from conventional butadiene rubbers.<sup>1-6</sup> Although the properties of elastomers of HTPB vary widely depending on the physical properties of liquid polymers such as molecular weight, molecular weight distribution, functionality, degree of branching, and microstructure,<sup>7</sup> very little in the way of experimental results has yet been reported.

In this paper, the relationships between the number-average molecular weight ( $\bar{M}_n$ ) of HTPB and the physical properties of the elastomers are discussed. For this purpose, the elastomers were prepared by the one-step reaction of HTPB ( $\bar{M}_n$  of about 1000-8000) with 4,4'-diphenylmethane diisocyanate (MDI). The effects of  $\bar{M}_n$  of HTPB on the properties such as tensile strength, modulus, ultimate elongation, and hardness were investigated. At the same time, the

change in the properties of the elastomers of HTPB compounded with a short-chain diol known as reinforcing agent was also studied with respect to  $\bar{M}_n$  of HTPB.

## EXPERIMENTAL

### Materials

Liquid hydroxyl-terminated polybutadiene (HTPB) having a molecular weight of about 1000–8000 was prepared on a laboratory scale according to the patents<sup>8</sup> and used for the preparation of the elastomers by a one-step reaction with diisocyanate (MDI) (hereinafter referred to one-shot elastomers). Poly bd R-45HT and R-45M from ARCO Chemical Co. were also used for comparison. The physical properties of prepared HTPB and commercial R-45HT and R-45M are illustrated in Table I.

4,4'-Diphenylmethane diisocyanate (MDI) as curing agent and N,N-bis(2-hydroxypropyl)aniline (HPA) from Upjohn Co. as reinforcing agent were used without further purification. Solvents and other reagents were also used without further purification.

### Vulcanization

The one-shot elastomers were obtained using MDI as vulcanizing agent and di-*n*-butyltin dilaurate (DBTDL) as catalyst. The vulcanization of HTPB was carried out by compression molding at 120°C for 60 min.

### Measurements

**Physical Properties of Liquid Polybutadiene.** The molecular weight measurement was carried out with a vapor pressure osmometer (Knauer Co.) using benzene as the solvent. Molecular weight distribution was measured by high-speed liquid chromatography (HLC-802 Toyo Soda Co.) and gel-permeation chromatography (GPC-1AR Shimadzu Co.). Measurement of the microstructure was carried out by the infrared method of Morero.<sup>9</sup> The hydroxyl content was determined by the analytical procedure<sup>10</sup> suggested by ARCO Chemical Co., and the H<sub>2</sub>O content was determined according to the Carl Fisher method. Bulk viscosity was measured with a B-type viscometer at 30°C.

**Properties of One-Shot Elastomers.** Dumbbell-shaped specimens for measuring tensile strength, modulus, and elongation and B-type specimens for tear resistance testing (0.5-mm thick, respectively) were die cut from the elastomer sheets which were stored at room temperature for one week. The physical properties were measured at room temperature using an IS-500 Autograph (Shimadzu Co.) at a strain rate of 500 mm/min.

Swelling was measured as follows: specimens of the elastomers (20 × 20 × 0.5 mm) were weighed and then immersed in benzene. After 72 hr at room temperature, the specimens were wiped with filter paper, weighed again, and then exposed for 72 hr in the atmosphere. Benzene was removed, by placing the specimens under vacuum for 24 hr, and the samples were reweighed. The differences between the weights after benzene removal and the initial weight

TABLE I  
Chemical Structure and Molecular Weight of Liquid Hydroxyl-Terminated Polybutadiene

HTPB mol. wt <sup>a</sup>	Hydroxyl content, meq/g	$\bar{A}_n^b$	$\bar{A}_w^b$	$\bar{A}_w/\bar{A}_n$	Function- ality	Bulk viscosity (30°C) poises	Microstructure, % <sup>d</sup>			H <sub>2</sub> O content, wt-%
							Cis	Trans	Vinyl	
1350	1.69	87	160	1.83	2.28	24	15.7	58.7	25.5	0.05
1530	1.44	94	219	2.32	2.20	42	15.4	57.0	27.6	0.07
1740	1.35	113	238	2.11	2.35	47	16.0	59.2	24.8	0.05
2220	0.99	135	232	1.72	2.20	39	15.0	57.8	27.2	0.05
2310	0.98	—	—	—	2.26	37	16.6	58.3	25.1	0.05
2460	0.86	150	256	1.71	2.12	42	14.2	58.1	27.6	0.05
2550 <sup>e</sup>	0.85	136 <sup>c</sup>	315 <sup>c</sup>	2.31 <sup>c</sup>	2.17	54	15.6	57.9	26.4	—
2690	0.72	—	—	—	1.94	63	15.6	57.4	26.9	0.05
2810 <sup>f</sup>	0.70	—	—	—	1.95	53	—	—	—	—
3710	0.55	—	—	—	2.04	131	15.6	57.5	26.8	0.05
4210	0.49	—	—	—	2.06	—	—	—	—	—
5500	0.28	—	—	—	1.60	—	—	—	—	—
8040	0.25	371	770	2.08	2.01	891	16.1	58.7	25.3	0.08

<sup>a</sup> Number-average molecular weight determined by vapor pressure osmometer using benzene as solvent.

<sup>b</sup> Number- and weight-average chain length determined by high-speed liquid chromatograph (HLC-802 Toyo Soda Co.).

<sup>c</sup> Determined by gel permeation chromatography (GPC-IAR Shimadzu Co.).

<sup>d</sup> Obtained by the infrared method of Madero.<sup>9</sup>

<sup>e</sup> Commercial Poly bd R-45HT from ARCO Chemical Co.

<sup>f</sup> Commercial Poly bd R-45M from ARCO Chemical Co.

of the samples were regarded as the amount of sol. The sol fraction was determined as

$$S = [(W - W_A)/W] \times 100$$

and the swelling ratio  $1/V_R$  was expressed by the equation

$$1/V_R = 1 + [(W_B/W_A - 1)\rho_2]/\rho_1$$

where  $W$  is the initial weight,  $W_A$  is the weight after removing benzene,  $W_B$  is the weight of the swollen sample,  $\rho_1$  is the density of benzene, and  $\rho_2$  is the density of the sample after removing benzene.

## RESULTS AND DISCUSSION

### Physical Properties of Liquid Polybutadiene

Some of the data on the structure of polybutadiene obtained by radical polymerization were reviewed by Condon<sup>11</sup> and Richardson.<sup>12</sup> An important conclusion was that a *trans*-1,4 structure was energetically more favorable than *cis*-1,4 and vinyl structures because of the low energy requirement for *trans*-1,4 addition. The microstructure of HTPB was investigated using the infrared method of Morero.<sup>9</sup> The key bands for *cis*-1,4, *trans*-1,4, and vinyl structures of HTPB gave very good agreement with those proposed by Morero. As shown in Table I, the microstructures of all HTPB were almost the same, and the *trans*-1,4 structure was most predominantly consistent with the conclusion of Condon<sup>11</sup> and Richardson.<sup>12</sup> The content of the vinyl structure was about 27% and hence smaller than that of conventional polybutadiene obtained by ionic polymerization. This may lead to a higher performance of the elastomers at low temperature.<sup>13</sup> In fact, the higher performance at low temperature of cured HTPB has been verified.<sup>14</sup> As can be seen from Table I, the ratio of weight-average chain length to number-average chain length,  $\bar{A}_w/\bar{A}_n$ , ranging from 1.71 to 2.32, is independent of the  $\bar{M}_n$  of HTPB. It may be easily understood that the molecular weight distribution of HTPB is relatively narrow and close to a Gaussian distribution.

The functionality  $F_n$  of HTPB is shown by eq (1):

$$F_n = \frac{\bar{M}_n}{\text{equivalent weight}} \quad (1)$$

Hence, eq. (2) is derived from eq. (1) using the relation that the equivalent weight is the reciprocal of the hydroxyl content per gram of polymer:

$$\text{hydroxyl content} = F_n \times (1/\bar{M}_n) \quad (2)$$

Figure 1 shows the relationship between  $1/\bar{M}_n$  and the hydroxyl content of HTPB; and from the slope,  $F_n$  is found to be 2.2. This value is slightly greater than 2.0, which is consistent with the results reported by other investigators.<sup>15-18</sup> Therefore, it was suggested that these HTPB molecules have little branching.

The relationship between  $\bar{M}_n$  and the bulk viscosity of HTPB measured with a B-type viscometer is linear (Fig. 2). Expressed in formula form, the experimental equation is

$$\log \eta = 1.16 + 0.22 \times 10^{-3} \bar{M}_n \quad (3)$$

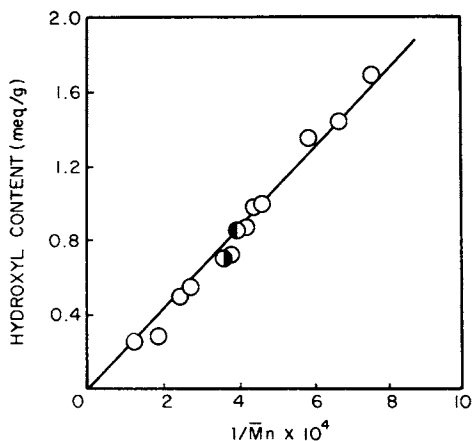


Fig. 1. Relationship between hydroxyl content and number-average molecular weight of liquid hydroxyl-terminated polybutadiene: (●) commercial Poly bd R-45HT; (●) commercial Poly bd R-45M.

where  $\eta$  is the bulk viscosity at 30°C. This result may be taken to indicate that the structures (especially microstructures), functionalities, and molecular weight distributions of all HTPB are essentially equal. The relation obtained in this work is similar to that of broad-distribution hydroxyl-terminated polybutadiene.<sup>19</sup>

#### Effects of Number-Average Molecular Weight of Liquid Polybutadiene on Mechanical Properties of Elastomers

It has been considered that mechanical properties of the elastomers based on liquid polymers may be varied widely depending on the physical properties of prepolymers such as molecular weight, molecular weight distribution, func-

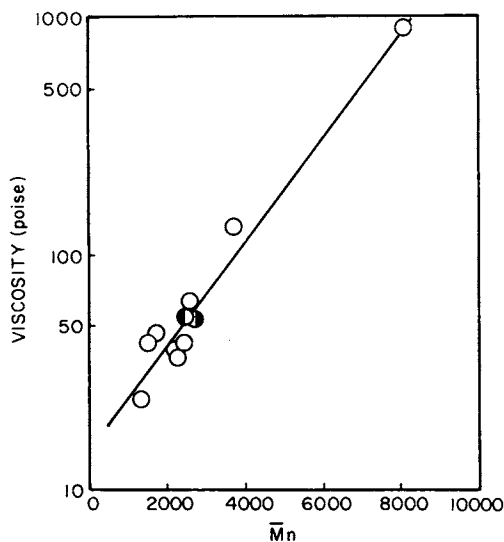


Fig. 2. Relationship between bulk viscosity and number-average molecular weight of hydroxyl-terminated polybutadiene (B-type viscometer, 30°C): (●) commercial Poly bd R-45HT and R-45M.

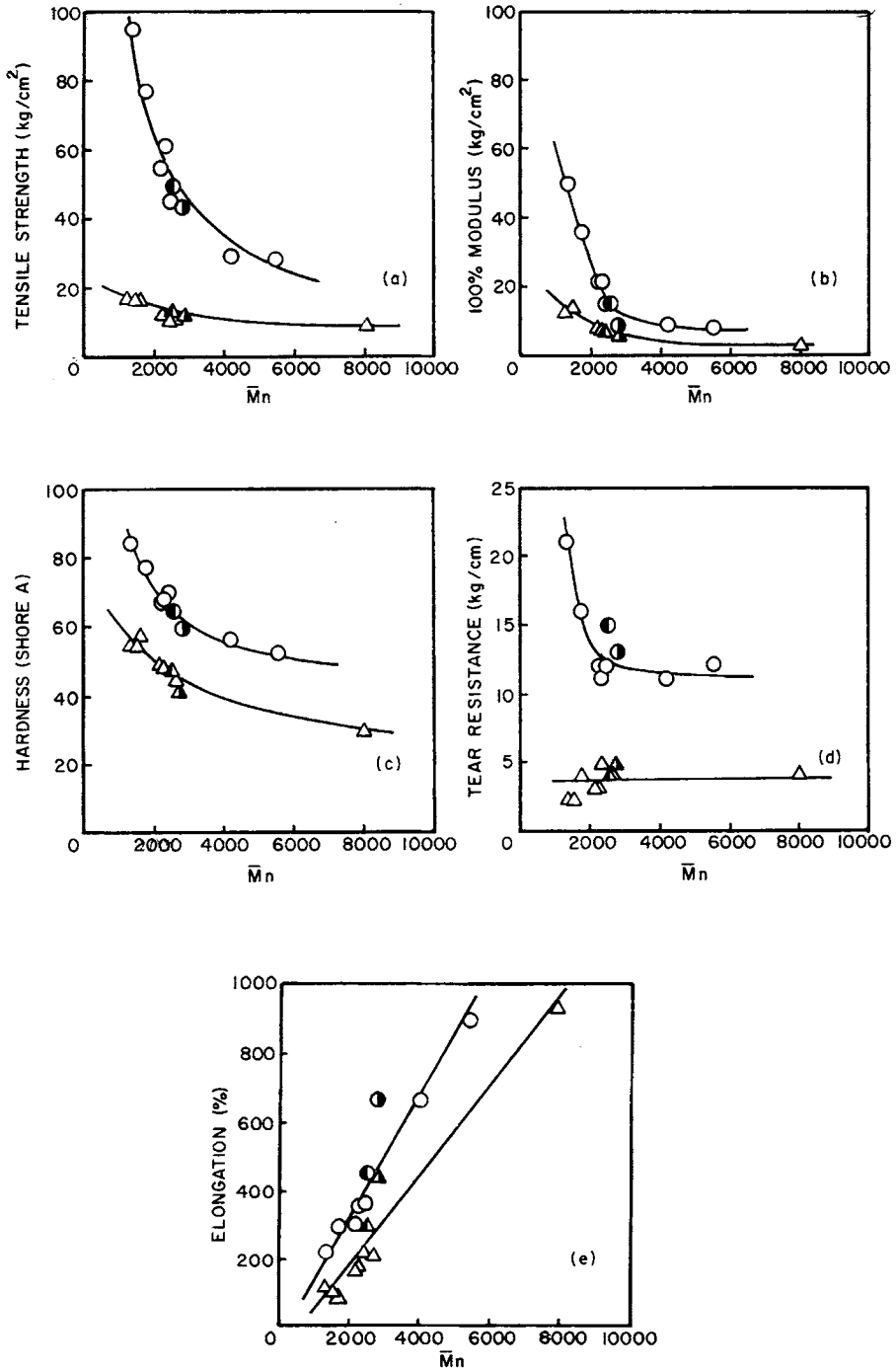


Fig. 3. Effect of number-average molecular weight of hydroxyl-terminated polybutadiene on mechanical properties of elastomers obtained by one-shot method: ( $\Delta, \blacktriangle, \blacktriangle$ ) elastomers obtained by one-shot method, NCO/OH = 1.0; (O,  $\bullet$ ,  $\bullet$ ) one-shot elastomers reinforced by short-chain diol N,N-bis(2-hydroxypropyl)aniline (HPA), HTPB/HPA = 1.0, NCO/OH = 1.0; ( $\bullet, \blacktriangle$ ) commercial Poly bd R-45HT; ( $\bullet, \blacktriangle$ ) commercial Poly bd R-45M. Vulcanizing agent, 4,4'-diphenylmethane diisocyanate; catalyst, di-*n*-butyltin dilaurate.

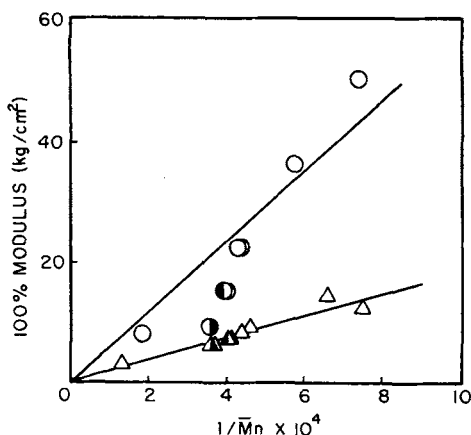


Fig. 4. Relationship between 100% modulus of elastomers obtained by one-shot method and  $1/\bar{M}_n$  of liquid hydroxyl-terminated polybutadiene: ( $\Delta, \blacktriangle, \triangle$ ) elastomers obtained by one-shot method, NCO/OH = 1.0; ( $\circ, \bullet, \odot$ ) one-shot elastomers reinforced by short-chain diol N,N-bis(2-hydroxypropyl)aniline (HPA), HTPB/HPA = 1.0, NCO/OH = 1.0; ( $\bullet, \blacktriangle$ ) commercial Poly bd r-45HT; ( $\odot, \blacktriangle$ ) commercial Poly bd R-45M.

tionality, degree of branching, microstructure, etc.<sup>7</sup> Tables II and III show the mechanical properties of the elastomers prepared by the reaction of HTPB and MDI, and the effect of the added short-chain diol in relation to  $\bar{M}_n$  of HTPB. These results are shown in Figure 3. As is illustrated in Figure 3(a), tensile strength of the one-shot elastomer decreased with increase in  $\bar{M}_n$  of HTPB, and this phenomenon was most pronounced below  $\bar{M}_n$  of about 3000. The 100% modulus, hardness, and tear resistance illustrated in Figures 3(b)–3(d), respectively, decreased with increase in  $\bar{M}_n$  in a manner similar to tensile strength. On the other hand, ultimate elongation of one-shot elastomers [Fig. 3(e)] increased linearly with increase in  $\bar{M}_n$  of HTPB.

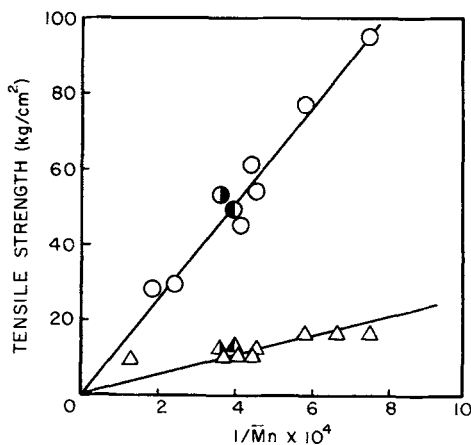


Fig. 5. Relationship between tensile strength of elastomers obtained by one-shot method and  $1/\bar{M}_n$  of liquid hydroxyl-terminated polybutadiene: ( $\Delta, \blacktriangle, \triangle$ ) elastomers obtained by one-shot method, NCO/OH = 1.0; ( $\circ, \bullet, \odot$ ) one-shot elastomers reinforced by short-chain diol N,N-bis(2-hydroxypropyl)aniline (HPA), HTPB/HPA = 1.0, NCO/OH = 1.0; ( $\bullet, \blacktriangle$ ) commercial Poly bd R-45HT; ( $\odot, \blacktriangle$ ) commercial Poly bd R-45M.

TABLE II  
Mechanical Properties of Elastomers from HTPB, HPA, and MDI by One-Shot Method<sup>a</sup>

HTPB mol. wt	Grams HPA per 100 g HTPB	Grams MDI per (100 g HTPB + HPA)(g)		Tensile strength, kg/cm <sup>2</sup>	Elongation, %	Modulus, kg/cm <sup>2</sup>			Tear re- sistance, kg/cm	Hardness	
		HTPB	MDI			100%	200%	300%		Shore A	Shore D
1350	16.7	42.3	95	220	50	85	—	21	84	28	
1740	13.3	33.8	77	290	36	54	—	16	77	28	
2220	9.8	24.8	54	300	22	37	54	12	67	21	
2310	9.7	24.5	61	350	22	36	50	11	68	21	
2460	8.5	21.5	45	360	15	24	36	12	70	18	
2550 <sup>b</sup>	8.4	21.3	49	450	15	22	30	15	64	19	
2810 <sup>c</sup>	6.9	17.5	53	660	9	12	15	13	59	15	
4210	3.6	9.0	29	660	9	11	14	11	56	15	
5500	2.7	7.0	28	890	8	9	11	12	52	14	

<sup>a</sup>HTPB = liquid hydroxyl-terminated polybutadiene; HPA = N,N-bis(2-hydroxypropyl)aniline (from Upjohn Co.); MDI = 4,4-diphenylmethane diisocyanate. HTPB/HPA = 1.0; NCO/OH = 1.0; cure cycle, 60 min at 120°C; catalyst, di-*n*-butyltin dilaurate (0.05 phr).

<sup>b</sup>Commercial Poly bd R-45HT from ARCO Chemical Co.

<sup>c</sup>Commercial Poly bd R-45M from ARCO Chemical Co.



TABLE III  
Mechanical Properties of Elastomers from HPTB and MDI by One-Shot Method<sup>a</sup>

HPTB mol. wt.	Grams MDI per 100 g HTPB	Tensile strength, kg/cm <sup>2</sup>	Elongation, %	Modulus, kg/cm <sup>2</sup>			Tear re- sistance, kg/cm	Hardness	
				100%	200%	300%		Shore A	Shore D
1350	21.1	16	120	12	—	—	2	54	17
1530	18.0	16	100	14	—	—	2	54	17
2220	12.4	12	160	9	—	—	3	49	13
2310	12.3	10	170	8	—	—	3	48	13
2460	10.8	10	220	7	9	—	5	47	12
2550 <sup>b</sup>	10.6	13	290	7	10	—	4	47	13
2810 <sup>c</sup>	8.8	12	430	6	8	10	5	41	11
8040	3.1	9	920	3	4	5	4	29	8

<sup>a</sup>HPTB = Liquid hydroxyl-terminated polybutadiene; MDI = 4,4'-diphenylmethane diisocyanate. NCO/OH = 1.0; cure cycle, 60 min at 120°C; catalyst, di-*n*-butyltin dilaurate (0.05 phr).

<sup>b</sup>Commercial Poly bd R-45HT from ARCO Chemical Co.

<sup>c</sup>Commercial Poly bd R-45M from ARCO Chemical Co.

According to Flory,<sup>20</sup> the retractive force per unit initial cross-sectional area at the rubbery state is described as

$$\sigma = \nu RT(\alpha - 1/\alpha^2)(1 - 2\bar{M}_c/M) \quad (4)$$

where  $\sigma$  is retractive force per unit initial cross-sectional area,  $\nu$  is the concentration of crosslinked units,  $R$  is the gas constant,  $T$  is absolute temperature,  $\alpha$  is a relative length given by  $l/l_0$  ( $l_0$  is the initial length and  $l$  is the tensile length),  $\bar{M}_c$  is the number-average molecular weight of the network chain, and  $M$  is the molecular weight of the primary molecules. Yamashita<sup>7</sup> predicts that when the liquid rubbers, which have a functional group on each terminal, are cured with trifunctional vulcanizing agents,  $M$  in eq. (4) becomes infinite, and therefore  $\sigma$  is proportional to  $\nu$ . The value of  $\nu$  is inversely proportional to  $\bar{M}_c$  according to the following equation:<sup>21</sup>

$$\nu = \rho/\bar{M}_c \quad (5)$$

where  $\rho$  is density. For one-shot elastomers based on HTPB, it can be easily predicted that  $\sigma$  is inversely proportional to  $\bar{M}_c$ . Hence,  $\sigma$  is given by eq. (6) by postulating that  $\bar{M}_n$  of HTPB is proportional to  $\bar{M}_c$ :

$$\sigma = A/\bar{M}_n \quad (6)$$

where  $A$  is constant.

Figure 4 is a plot of 100% modulus versus reciprocal number-average molecular weight of HTPB. An approximately linear relationship can be observed between them. This result is satisfactorily consistent with eq. (6).

A plot of tensile strength versus reciprocal  $\bar{M}_n$  of HTPB is shown in Figure 5. The tensile strength is inversely proportional to  $\bar{M}_n$  in a manner similar to 100% modulus. Equation (7) was therefore obtained:

$$T_B = B/\bar{M}_n \quad (7)$$

where  $B$  is constant.

From these results, it can be inferred that the tensile strength and 100% modulus of the elastomers will be dependent on  $\bar{M}_c$  and  $\nu$ .

Apart from the usual butadiene rubbers, the elastomers prepared with HTPB have, however, urethane linkage in their main chains. We must consider the effect of urethane groups on the properties of the elastomers. In one-shot elastomers obtained under the condition of NCO/OH = 1.0, the reaction forming urethane linkage may be most favorable compared to the reactions producing allophanate and biuret linkages. The concentration of urethane linkage increases with decreasing  $\bar{M}_n$  of HTPB, followed by an increase in intermolecular hydrogen-bonding sites<sup>22</sup> which leads to the growth of pseudo-crosslinks. Because of the reasons mentioned above, tensile strength, 100% modulus, and hardness will increase with a decrease in  $\bar{M}_n$  of HTPB. This consideration fully explains the results of Figures 3(a)–3(d).

### Effect of Number-Average Molecular Weight on Swelling of the Elastomers

The effect of  $\bar{M}_n$  of HTPB on the physical properties of the one-shot elastomers is also illustrated in the results of swelling measurements using benzene.

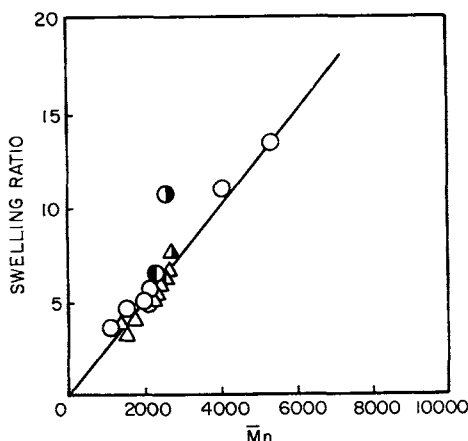


Fig. 6. Relationship between swelling ratio of elastomers obtained by one-shot method and  $\bar{M}_n$  of liquid hydroxyl-terminated polybutadiene: ( $\Delta, \blacktriangle, \triangle$ ) elastomers obtained by one-shot method, NCO/OH = 1.0; ( $\circ, \bullet, \circ$ ) one-shot elastomers reinforced by short-chain diol N,N-bis(2-hydroxypropyl)aniline (HPA), HTPB/HPA = 1.0, NCO/OH = 1.0; ( $\circ, \blacktriangle$ ) commercial Poly bd R-45HT; ( $\bullet, \blacktriangle$ ) commercial Poly bd R-45M.

The swelling ratio  $Q$  linearly increased as  $\bar{M}_n$  increased (Fig. 6). This result will also be explained by taking into account the urethane group content of the elastomers.

The experimental relation between  $Q$  and  $\nu$  was given by Lorenz<sup>23</sup> as follows;

$$Q \propto 1/\nu \quad (8)$$

From eq. (5) and the assumption that  $\bar{M}_c$  is proportional to  $\bar{M}_n$  of HTPB, relation (9) is obtained:

$$Q \propto \bar{M}_n \quad (9)$$

At this point, it should be noted that  $\nu$  is proportional to the concentration of urethane linkage in the HTPB-based elastomer.

On the other hand, sol fraction equalled approximately 10% in any of the elastomers. Because of the relatively high sol fraction of the elastomers, it seems that unre reacted HTPB will exist to some extent in these elastomers. Hence, complete vulcanization will lead to improvement of the mechanical properties of the elastomers. From the description mentioned above and the result of Figure 6, it can be easily seen that the urethane group content will greatly affect the physical properties of the one-shot elastomers.

### Reinforcement of Elastomers by Short-Chain Diol

The reinforcement by short-chain diol in urethane chemistry is well known. N,N-Bis(2-hydroxypropyl)aniline (HPA) was used as reinforcing agent. Ryan<sup>4</sup> has investigated the reinforcing effect of HPA on commercial Poly bd R-45M and concluded that when the amount of HPA used as a modifier was increased (Poly bd R-45M/HPA ratio from 1 to 0.5), the properties of the elastomer were greatly improved. In this work, HPA was mixed at a HTPB/HPA ratio of 1.0.

As can be seen from Figures 3(a)–(d), tensile strength, 100% modulus, hardness, and tear resistance decreased with increase in  $\bar{M}_n$  of HTPB, and the phenomenon was marked below  $\bar{M}_n$  of about 3000 as well as for the elastomers without HPA. By incorporating HPA into the elastomers, these properties increased over the wide range of HTPB  $\bar{M}_n$  and, therefore, the diol appears to impart the reinforcing effect to the elastomers. This reinforcing effect was obvious in low molecular weight HTPB (below about 3000). Ultimate elongation of one-shot elastomers reinforced by HPA, however, linearly increased as  $\bar{M}_n$  of HTPB increased. The effect of the diol on ultimate elongation was observed in accordance with other properties of the elastomers.

The reinforcement by short-chain diol may be explained by taking into account an increase in the urethane linkage from HTPB with MDI and that from HPA with MDI. Hence, the remarkable reinforcing effect of the diol on the elastomers at HTPB low molecular weight may be due to a higher urethane group content according to the higher volume of the diol under the constant condition where the HTPB/HPA ratio equals 1.0. On the other hand, in the case of the reinforcement by short-chain diols, it should also be considered an auxiliary effect based on the stiffness of the elastomer backbone by the aromatic ring of short-chain diols (in the case of aromatic ones), except for the urethane linkage.

### Conclusions

1. Tensile strength, 100% modulus, hardness, and tear resistance of one-shot elastomers based on HTPB decreased with increase in HTPB  $\bar{M}_n$ . The phenomenon was pronounced with low molecular weight HTPB (below about 3000). On the other hand, the ultimate elongation increased linearly with  $\bar{M}_n$ .

2. The relationship between 100% modulus ( $\sigma$ ) or tensile strength ( $T_B$ ) and  $\bar{M}_n$  of HTPB could be explained using Flory's equation. The  $\sigma$  or  $T_B$  was expressed by the following equation:

$$\sigma \text{ or } T_B = A/\bar{M}_n$$

where  $A$  is constant.

3. The effects of  $\bar{M}_n$  of HTPB on the physical properties of one-shot elastomers based on HTPB may be interpreted by considering the concentration of the crosslinked chains and the urethane group content of the elastomers.

4. The effects of the short-chain diol (HPA) on the one-shot elastomers should take into account the stiffness of the backbone of the elastomers by the aromatic ring (from HPA) and a succession of the urethane linkage from HPA and MDI, namely, the hard segment.

This work is part of Studies on Liquid Polymers undertaken by the Research Group of Polymer Chemistry and Technology, Japan.

### References

1. Idemitsu Petrochemical Co. Technical Report BD-2 Poly bd liquid Rubber (May, 1973) and ARCO Chemical Co., Product Bulletin BD-1 (March, 1974), BD-2 (March, 1974) and BD-3 (October, 1974).
2. P. W. Ryan, *Br. Polym. J.*, **3**, 145 (1971).
3. P. W. Ryan, *Rubber World*, **163**(4), 47 (1971).

4. P. W. Ryan, *J. Elastoplastics*, **3**, 57 (1971).
5. J. A. Verdol, P. W. Ryan, D. J. Carrow, and K. L. Kund, *Rubber Age* **7**, 57 (1966).
6. J. A. Verdol, P. W. Ryan, D. J. Carrow, and K. L. Kund, *Rubber Age* **8**, 62 (1966).
7. Shinzo Yamashita, *Kobunshi no Bunshi-setsukei*, Part 3, p. 114-147, (1972) Baifukan.
8. U.S. Pat., 3652520. Atlantic Richfield Co., U.S. Pat., 3652520 (March 28, 1972). O. W. Burke, Jr., J. A. Kizer, and P. Davis, U.S. Pat., 3673168 (June 27, 1972).
9. D. Morero, A. Santanbrogio, L. Porri, and F. Clampelli, *Chem. Ind.*, **41**, 758 (1959).
10. ARCO Chemical Co., Analytical Procedure II-20, based on
  - (1) ASTM E-222-65T, Part 31,
  - (2) Scott's *Standard Methods of Chemical Analysis*, Vol. 2, p. 2197,
  - (3) *Anal. Chem.*, **31**, (11), 1809 (1959).
11. K. E. Condon, *J. Polym. Sci.*, **11**, 139 (1953).
12. W. S. Richardson, *J. Polym. Sci.*, **13**, 229 (1954).
13. R. F. Hoffman and R. H. Gobran, *Rubber Chem. Technol.*, **46**, 139 (1973).
14. K. Ono and T. Nishimura, *J. Soc. Rubber Ind. Jpn.* (Nippon Gomu Kyokai-shi), **48**(5), 263 (1975).
15. C. H. Bamford, A. D. Jenkins, and R. P. Wayne, *Trans. Faraday Soc.*, **56**, 935 (1960).
16. W. H. Stubbs, C. R. Gore, and C. S. Marvel, *J. Polym. Sci. A-1*, **4**, 1898 (1966).
17. S. F. Reed, *J. Polym. Sci. A-1*, **9**, 214 (1971).
18. S. F. Reed, *J. Polym. Sci. A-1*, **10**, 649 (1972).
19. D. M. French, *Rubber Chem. Technol.*, **42**, 71 (1969).
20. P. J. Flory, *Ind. Eng. Chem.*, **38**, 417 (1946).
21. S. Yamashita, *Chemistry*, **26**, 804 (1971).
22. Y. Yamaguchi, T. Yokoyama, and T. Tanaka, *J. Chem. Soc. Jpn., Ind. Chem. Sec. (Kogyo Kagaku Zasshi)*, **73**, 1531 (1970).
23. O. Lorenz and C. R. Parks, *J. Polym. Sci.*, **50**, 299 (1961).

Received August 18, 1976