

# Glass Transition Temperature and Chain Flexibility of 1,2-Polybutadiene

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## Synopsis

The solubility parameter and glass transition temperature of 1,2-polybutadiene with different 1,2-unit content have been measured.  $T_g$  increases with increasing 1,2-unit content, whereas no essential change of solubility parameter has been observed. So, it may be concluded that chain flexibility arising from internal rotation about single bond is the sole factor which determines glass transition. Chain flexibility was then studied by computation of energy of rotational isomerization  $\epsilon$  and the steric factor  $\epsilon$  characterizing hindrance to internal rotation. Finally, the potential barrier to internal rotation  $U$  was obtained by correlating  $\delta$  and  $\epsilon$  via  $T_g$ . The results are shown in Table VI.  $\sigma$ ,  $\epsilon$  and  $U$  all increase with increasing 1,2-unit content indicating rising of  $T_g$  is a result of increasing chain stiffness. Determination of the solubility parameter of 1,2-polybutadiene by viscometry with toluene-cyclohexane (similar molar volume) as mixed solvent was examined and proved to be reliable. The exponent  $\alpha$  in the Mark-Houwink equation for 1,2-polybutadiene-toluene system was estimated from the solubility parameter of polymer and solvent according to the method of van Krevelen and Hoftzer<sup>16</sup> and found to be 0.725. This value of  $\alpha$  was used as a first approximation for the calculation of molecular weights from GPC data. The Mark-Houwink equations finally established for the system, 1,2-polybutadiene-toluene (30°C) with different 1,2-unit contents are given in eqs. (8)-(10).

## INTRODUCTION

The glass transition temperature  $T_g$  of 1,2-polybutadiene increases with increasing 1,2-unit content,<sup>17</sup> but no insight work into such a phenomenon has been reported. It is generally accepted that there are two main factors determining the glass transition of an amorphous polymer, i.e., intermolecular interaction characterized by cohesion energy density and intramolecular interaction arising from internal rotation or flexibility of the chain. The purpose of this paper is to make clear which factor is more determinant in the dependence of glass transition temperature on 1,2-unit content. For this purpose the solubility parameters which indicate cohesion energy densities and also the  $T_g$ 's of some 1,2-polybutadiene samples were measured. No essential change of solubility parameter with different 1,2-unit content was observed. Accordingly, a thorough study on the internal rotation of the molecular chain of 1,2-polybutadiene was planned. The energy of rotational isomerization  $\epsilon$  was computed from  $T_g$  and  $\Delta\alpha$ , the difference in the thermal coefficients of volume expansion above and below  $T_g$ , by the method cited in Ref. 25. On the other hand, the steric factor  $\sigma = (r_0^2/M)^{1/2}(r_{0f}^2/M)^{1/2}$ , a parameter characterizing the hinderance to internal rotation, was calculated.  $(r_0^2/M)^{1/2}$ , the unperturbed dimension, was

obtained from  $K_\theta$  which was estimated by the Stockmayer-Fixman equation.<sup>26</sup>  $(r_{0f}^2/M)^{1/2}$ , the unperturbed dimension of a freely rotation chain, was calculated according to Ref. 27. Finally,  $\sigma$  and  $\epsilon$  were correlated through  $T_g$  to compute the potential barrier to internal rotation  $U$ .

In the measurement of the solubility parameters of the 1,2-polybutadiene samples by viscometry, we found that the use of binary mixture of solvents with similar molar volume such as toluene and cyclohexane is convenient and more precise than the use of pure solvents. Besides the intrinsic viscosities of the samples which were measured, the  $\overline{M}_w$ 's for the application of the Stockmayer-Fixman equation were computed from GPC data where the exponent  $\alpha$  in the Mark-Houwink equation needed in the computation is estimated from the solubility parameter of polymer and solvent by the van Krevelen method.<sup>16</sup> Mark-Houwink equations for the 1,2-polybutadiene-toluene system with 8, 30, and 90% 1,2-unit, respectively, are presented.

## EXPERIMENTAL

### Sample Preparation

1,2-Polybutadienes were prepared in our laboratory with *n*-butyllithium as initiator, cyclohexane and tetrahydrofuran as solvent, and microstructure regulating agent.<sup>1</sup> Other samples prepared with molybdenum and iron catalytic system were kindly supplied by Professors Xienming Tang and Gouzhi Liu of this Institute. The content of 1,2-units of all the samples, ranging from 8 to 90%, was determined by IR.

### Intrinsic Viscosity Measurement

The intrinsic viscosity of 1,2-PBs were measured at  $25 \pm 0.05^\circ\text{C}$  in a series of solvents with various solubility parameters and the intrinsic viscosities of samples with different molecular weight for the determination of Mark-Houwink coefficients were measured in toluene at  $30 \pm 0.05^\circ\text{C}$ . Since the Ubbelohde viscometer used has been adjusted according to the literature,<sup>2</sup> the kinetic energy and end-effect correction were neglected in the measurements.

### Gel Permeation Chromatography

The GPC instrument used in this work was operated at  $30^\circ\text{C}$  using toluene as solvent with a steady flow rate of 0.36 cc/min. Polystyrene standards were used for universal calibration. The value of  $M[\eta]$  for each polystyrene standard was calculated from a knowledge of its molecular weight and the appropriate Mark-Houwink coefficients for polystyrene. The retention volumes for the set of standards were obtained, and the effect of peak broadening due to diffusion was corrected.

### Glass Transition Temperature Measurement

The glass transition temperature of samples was determined with a linear dilatometer. The cooled samples at low temperature were heated steadily to higher temperature at a rate of 1.4°C/min. The thermal coefficients of volume expansion of the samples were taken as three times of their linear coefficients which were measured experimentally.

## RESULTS

### Solubility Parameter of 1,2-PB

Gee<sup>3</sup> determined the solubility parameter of rubber via equilibrium swelling measurement in various solvents. However, this method needs a series of solvents, and the swelling experiment is time-consuming. In this work, we have adopted the method of viscosity measurement developed by Mangaraj et al.<sup>4</sup> for the determination of the solubility parameter  $\delta_p$  of a polymer. In this method, the solubility parameter  $\delta_s$  of the solvent in which the polymer exhibits maximum intrinsic viscosity is taken as the solubility parameter of the polymer.

From the open points in Figure 1, plotting intrinsic viscosity of sample  $[\eta]$  vs. solubility parameter  $\delta_s$  of pure solvent in which  $[\eta]$  was measured,

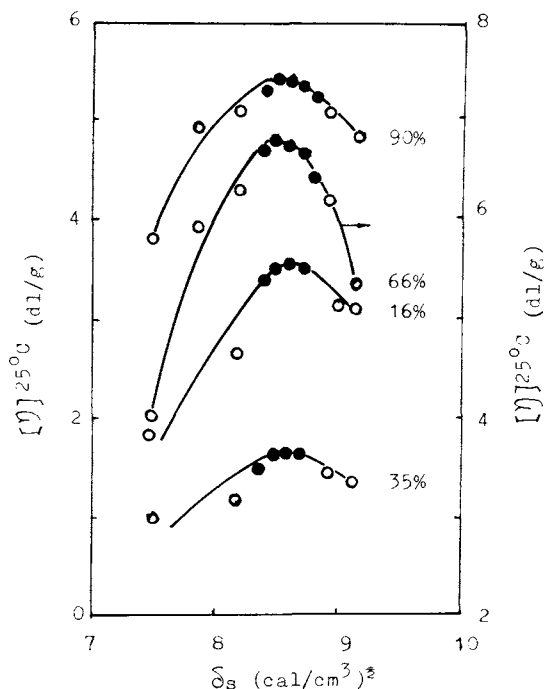


Fig. 1. Plot of intrinsic viscosity of 1,2-PB vs. solubility parameter of solvent  $\circ$  pure solvent;  $\bullet$  mixed solvent of cyclohexane and toluene.

it can be seen that there is a wide gap of  $\delta_s$  value ranging from 8.2 to 8.9  $(\text{cal}/\text{cm}^3)^{1/2}$  whereupon the peak is so uncertain that no precise value of  $\delta_p$  can be estimated. Thus, the use of binary-mixed solvent has been considered for such determinations.

The solubility parameter  $\bar{\sigma}$  of a solvent mixture where the components have similar molar volumes is related to their volume fractions  $\phi_i$  and their solubility parameters  $\delta_i$  by the expression<sup>5</sup>

$$\bar{\delta} = \sum_i \phi_i \delta_i \quad (1)$$

Although the above expression is by no means quantitatively accurate,<sup>6</sup> it has been used widely with reasonable success.<sup>7-10</sup>

The components of binary solvent mixture used in this work are cyclohexane and toluene, which have nearly the same molar volume of 108.7 and 106.8  $\text{cm}^3$ , respectively.

From the intrinsic viscosities of samples in cyclohexane-toluene mixtures (the full points in Fig. 1) the maximum values of  $[\eta]$  and, then, the solubility parameters of the samples were determined easily. All the samples, except that with 16% 1,2-unit, have the same solubility parameter of 8.5  $[(\text{cal}/\text{cm}^3)^{1/2}]$ .

The solubility parameter of polymer  $\delta_p$  can be derived more accurately from an expression correlating the molar volume  $V_s$  of each solvent to its solubility parameter  $\delta_s$ , as shown by Matsuo<sup>11</sup>:

$$\frac{1}{V_s} \left[ 1 - \frac{[\eta]}{[\eta]_{\max}} \right]^{1/2} = C^{1/2} (\delta_p - \delta_s) \quad (2)$$

where  $C$  is a constant. Hence, a plot of the left side of eq. (2) vs.  $\delta_s$  should give a straight line having an intercept on the abscissa equal to  $\delta_p$ . The value of  $[\eta]_{\max}$  were estimated from Figure 1 and a plot according to eq. (2) is shown in Figure 2. The straight lines in Figure 2 were determined by

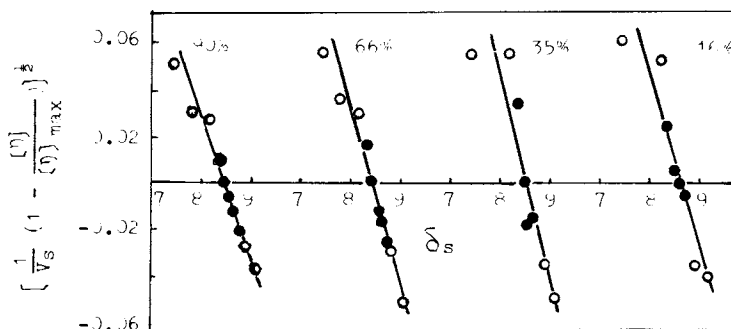


Fig. 2. Plot of  $\left[ \frac{1}{V_s} \left( 1 - \frac{[\eta]}{[\eta]_{\max}} \right) \right]^{1/2}$  vs  $\delta_s$  in eq. 2 for various solvents:  $\circ$  pure solvent;  $\bullet$  mixed solvent of cyclohexane and toluene

the least-squares method. The results obtained from Figures 1 and 2 which are in agreement with each other, are listed in Table I.

For testing the reliability of the  $\delta_p$  values obtained from intrinsic viscosity measurement both in pure and in mixed solvents, the overall interaction parameters of a ternary system (solvent 1-solvent 2-polymer 3)<sup>12</sup> have been studied,

$$\chi_{\text{overall}} = \varphi_1\chi_{13} + \varphi_2\chi_{23} - \varphi_1\varphi_2\chi_{12} \quad (3)$$

where subscripts 1, 2, 3 refer to cyclohexane, toluene, and 1,2-PB, respectively, the  $\varphi$ 's are the corresponding volume fractions and the  $\chi_{ij}$ 's are the interaction parameters of the corresponding binary mixtures. According to literature,<sup>13</sup> the following equation is given for ternary systems:

$$(\delta_1 - \delta_3)^2 V_1 - (\delta_2 - \delta_3)^2 V_2 - (\delta_1 - \delta_2)^2 [(V_1 - V_2)\varphi_1^2 - 2V_1\varphi_1 + V_1] = 0 \quad (4)$$

Using the  $\delta$  and  $V$  values of cyclohexane and toluene, and the  $\delta$  of the sample obtained from Figure 1, we calculated the volume fraction of cyclohexane  $\phi_1$  in such a ternary system. The result is 0.597 which is rather close to the actual  $\varphi_1$ , 0.571, used for the calculation of  $\bar{\delta}$  in eq. (1) to estimate  $\delta_p$  in Figure 1.

### Mark-Houwink Equations of 1,2-PBs

The calculation of molecular weight by universal calibration in GPC technique depends on a knowledge of the Mark-Houwink coefficients  $K$  and  $\alpha$ <sup>14</sup>:

$$[\eta] = K^{1/(1+\alpha)} \sum_i W_i J_i^{\alpha/(1+\alpha)} \quad (5)$$

$$\bar{M}_w = K^{-1/(1+\alpha)} \sum_i W_i J_i^{1/(1+\alpha)} \quad (6)$$

$$\bar{M}_n = K^{-1/(1+\alpha)} / \left( \sum_i W_i / J_i^{1/(1+\alpha)} \right) \quad (7)$$

In the case of a shortage of Mark-Houwink coefficients, a method has been developed for determining the molecular weight of a polymer by a combination of its intrinsic viscosity and GPC data for each series of assumed

TABLE I  
Solubility Parameter of 1,2-PB

Microstructure (%)	16,46,30	35,33,32	66,—,—	90,0,10
1,2-, <i>cis</i> -1,4-, <i>trans</i> -1,4-				
Solubility parameter				
From Figure 1 (cal/cm <sup>3</sup> ) <sup>1/2</sup>	8.6	8.5	8.5	8.5
From Figure 2 (cal/cm <sup>3</sup> ) <sup>1/2</sup>	8.61	8.53	8.44	8.47

value of  $\alpha$  of the Mark-Houwink equation ranging 0.5 to 0.98.<sup>15</sup> Such a method seems to be too tentative.

As is well known, the value of  $\alpha$  in the Mark-Houwink equation depends on the nature of both polymer and solvent. The intrinsic viscosity  $[\eta]$  is a measurement of the size of a polymer molecule in solution, i.e., the higher the  $[\eta]$  value in good solvent, the more extended the molecular chain. On the other hand, the solubility parameter of the solvent in which the polymer exhibits the highest value of  $[\eta]$  is taken as the solubility parameter of the polymer. Based on the above consideration, a method of evaluating the value of  $\alpha$  in the Mark-Houwink equation from the solubility parameters of polymer and solvent was proposed by van Krevelen and Hoftzer.<sup>16</sup> From Figure 7 in van Krevelen and Hoftzer's paper the value of  $\alpha$  in the Mark-Houwink equation for 1,2-PB-toluene system was found to be 0.725 using the solubility parameter of 8.5 and 8.9 (cal/cm<sup>3</sup>)<sup>1/2</sup> for 1,2-PB and toluene, respectively. Then, the values of  $K$  in the Mark-Houwink equation were evaluated by eq. (5) from GPC data and the measured values of  $[\eta]$ . Subsequently, the  $\bar{M}_w$ 's of the samples were calculated by eq. (6) with the same value of  $\alpha$ , i.e., 0.725. The results are listed in Table II. Plotting  $\log [\eta]$  vs.  $\log \bar{M}_w$  (Fig. 3), we obtained the Mark-Houwink equation for 1,2-PB with 8, 30, and 90% 1,2-unit in toluene at 30°C as follows:

8% 1,2-PB:

$$[\eta] = 2.64 \times 10^{-4} \bar{M}_w^{0.73} \quad (8)$$

30% 1,2-PB:

$$[\eta] = 2.32 \times 10^{-4} \bar{M}_w^{0.73} \quad (9)$$

90% 1,2-PB:

$$[\eta] = 2.17 \times 10^{-4} \bar{M}_w^{0.72} \quad (10)$$

Surprisingly, the exponents in eqs. (8)–(10) are very close to the value of 0.725 obtained from solubility parameters of 1,2-PBs and toluene. Suppose 0.6 was arbitrarily selected for the value of  $\alpha$  to repeat the above procedure of calculation for 1,2-PB with 8% 1,2-unit; one would finally obtain a value

TABLE II  
Molecular Weight and Intrinsic Viscosity of 1,2-PB

8%–1,2–,57% c,35% t		30%–1,2–,38% c,32% t		90% 1,2–,10% t	
$[\eta]$ (dL/g)	$\bar{M}_w \times 10^{-4}$	$[\eta]$ (dL/g)	$\bar{M}_w \times 10^{-4}$	$[\eta]$ (dL/g)	$\bar{M}_w \times 10^{-4}$
0.85	6.34	1.85	21.98	1.40	20.12
1.32	11.63	2.50	33.64	1.98	30.94
2.25	24.15	3.16	46.67	2.45	41.66
3.71	48.28	3.79	58.70	2.74	49.20
5.89	90.81	4.42	72.67	3.40	68.41
—	—	—	—	4.27	92.92

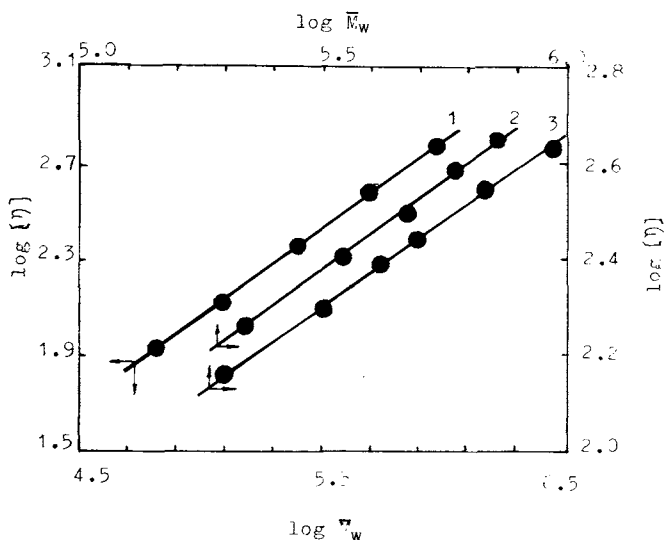


Fig. 3. Plot of intrinsic viscosity vs. molecular weight for 1,2-PBs with various 1,2-unit content: 1-8%; 2-30%; 3-90%.

of 0.66 for  $\alpha$  from the  $\log [\eta]$  vs.  $\log \bar{M}_w$  plot which is much larger than the originally selected value of 0.6. So, we believe that the estimation of the value of  $\alpha$  in the Mark-Houwink equation from solubility parameters of polymer and solvent is practical, and eqs. (8)–(10) are reliable.

### Glass Transition Temperature of 1,2-PB

It is shown in Figure 4 that the glass transition temperature of 1,2-PB increases with increasing content of 1,2-unit. The  $\Delta\alpha$ 's in Table III are the difference in the thermal coefficients of volume expansion of 1,2-PBs above and below glass transition temperature. Similar results have been reported,<sup>17</sup> but no interpretation has been given yet. In this paper, the phenomenon is interpreted in terms of the intra- and intermolecular interaction of 1,2-PB chains (see Discussion, the second subsection).

## DISCUSSION

### Inter- and Intramolecular Interaction of 1,2-PB Chains

It has been long recognized<sup>18</sup> that high glass transition temperature  $T_g$  is characteristic of polymer with strong intermolecular forces and/or high chain stiffness. In other words, the inter- and intramolecular interactions play a role in the glass transition temperature for common polymers. It is particular in the case of 1,2-PBs studied here, because other factors influencing the glass transition temperature, such as stereoregularity and crystallinity, are absent. The magnitude of  $T_g$  depends on the energy barrier to main chain movement, and the temperature must be raised to achieve movement when the barrier is greater. This energy barrier may be rep-

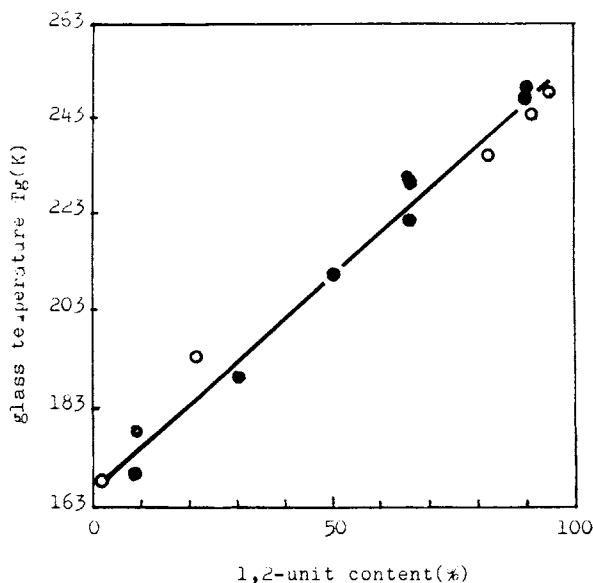


Fig. 4. Dependence of  $T_g$  on 1,2-unit content for 1,2-PB, ● this work; ○ in ref. 17.

resented by the sum of two contributions: first, the potential barrier to internal rotation about bonds, and second, the resistance of the surrounding medium.<sup>19</sup> The first contribution is responsible for the intramolecular interaction and the second, which can be described by cohesion energy density, for the intermolecular interaction.

The solubility parameter or the cohesion energy density of 1,2-PBs with low 1,2-unit content is slightly higher than that with higher content (Table I), which is in agreement with the viewpoint<sup>18,19</sup> that the vinyl side groups provide a flexible sheath around the main chains of 1,2-PBs and lower the hindrance of the surrounding medium to the main chains movement. However, as a matter of fact, the vinyl side groups on the main chain of 1,2-PBs result in raising the glass transition temperature (Table III), which means that the energy barrier to the main chain movement becomes higher and segment movement becomes more difficult. Therefore, vinyl side groups, though they weaken somewhat the intermolecular interaction, highly

TABLE III  
Glass Transition Temperature of 1,2-PB

Microstructure (%)			$T_g$ (K)	$\Delta\alpha \times 10^4$ (deg <sup>-1</sup> )
1,2-	<i>cis</i> -1,4-	<i>trans</i> -1,4-		
8	57	35	169	—
30	38	32	188	4.77
50	45	5	209	4.21
66	—	—	221	3.73
90	0	10	249	3.31



strengthen the intramolecular interaction, that is, lower the flexibility of the chain.

### Internal Rotation of 1,2-PB Chain

The flexibility of the molecular chains of a polymer results from the internal rotations about single bonds. Therefore, the dependence of intramolecular interaction on 1,2-unit content can be investigated in terms of the parameters for internal rotation. According to Gibbs-DiMarzio theory,<sup>20,21</sup> the energy of rotational isomerization, a parameter for the internal rotation of a polymer chain, can be determined from the change in the temperature volume expansion coefficients  $\Delta\alpha$  above and below glass transition temperature.<sup>22</sup> Another method of calculating the energy of rotational isomerization using the same parameters has been reported based on the dependence of internal rotation on the volume change of polymer in the process of glass transition.<sup>23,24</sup>

The energy of rotational isomerization,  $\epsilon$ , values for 1,2-PBs calculated from the data in Table III with the equations in the literature<sup>22,25</sup> are shown in Table IV. The lower the 1,2-unit content is, the lower the value of the energy of rotational isomerization and the more flexible the molecular chain of 1,2-PB. As compared to the change of cohesion energy density (square of solubility parameter in Table I) with 1,2-unit content (a decrease of only 2% with 1,2-unit content increasing from 16% to 90%), the energy of rotational isomerization increases 38% when the 1,2-unit content increases from 30% to 90%. So it may conclude that  $\epsilon$  depends on the content of 1,2-unit whereas the dependence of cohesion energy density on 1,2-unit content is negligible. The same reasoning also explains the result in Figure 4. Since the intermolecular interaction is independent of the 1,2-unit content, the change in glass transition temperature with 1,2-unit content (Figure 4) is a characteristic of the dependence of intramolecular interaction on 1,2-unit content, i.e., chain flexibility.

The above-mentioned change in the energy of rotational isomerization of 1,2-PBs with their 1,2-unit content indicates the change in steric hindrance to internal rotation of 1,2-PB chains. Since such a steric effect is usually characterized by the steric factor  $\sigma$ , it is reasonable to assume that there is a relationship between glass transition temperature and the steric factor for 1,2-PBs. From the Stockmayer-Fixman equation<sup>26</sup>

$$[\eta]/M^{1/2} = K_{\theta} + 0.51 \Phi_0 B M^{1/2} \quad (11)$$

a plot of  $[\eta]/M^{1/2}$  vs.  $M^{1/2}$  was obtained using the data in Table II (Fig. 5).

TABLE IV  
Energy of Rotational Isomerization of 1,2-PB's

1,2-Unit content (%)	30	50	66	90
Calculated according to				
Ref. 22 (kcal/mol)	0.82	0.91	0.96	1.08
Ref. 23 (kcal/mol)	0.87	0.97	1.06	1.19

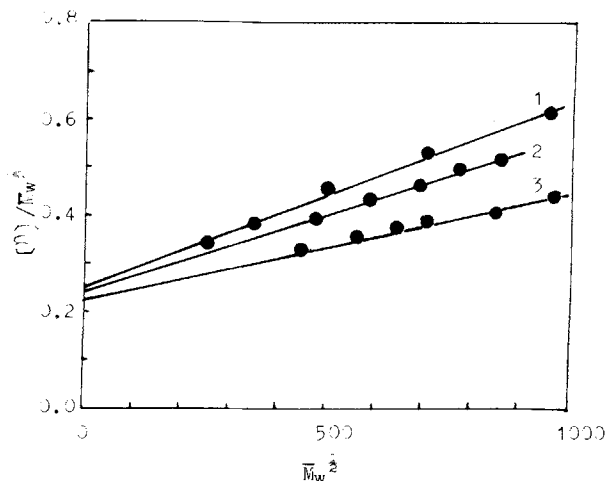


Fig. 5. Plot of  $[\eta] / M^{1/2}$  vs.  $M^{1/2}$  in eq. 11 for 1,2-PBs with various 1,2-unit content: 1-8%; 2-30%; 3-90%.

From the intercepts of the lines in Figure 5 on the ordinate, the unperturbed root-mean-square end-to-end distance  $(\bar{r}_0^2/M)^{1/2}$  was calculated using the equation  $K_\theta = \Phi_0(\bar{r}_0^2/M)^{3/2}$ , where the universal constant  $\Phi_0$  was taken as  $2.3 \times 10^{23}$  (Table V). The root-mean-square end-to-end distance for a model of free rotation chain of 1,2-PB  $(\bar{r}_{0f}^2/M)^{1/2}$  in Table V was estimated using the method of the literature.<sup>27</sup> Comparing the glass transition temperature of 1,2-PBs in Table III with their steric factors in Table V, it is found that

$$T_g = A \cdot (\sigma - b) \quad (12)$$

where  $A = 182$  K and  $b = 0.68$ . In accordance with the results shown in Figure 4, eq. (12) shows that the higher the 1,2-unit content is, the more difficult the internal rotation.

Another parameter for internal rotation of polymer chain, the potential barrier to internal rotation  $U$ , is often represented as a sum of two contributions, one from the exchange interacting of electrons in adjacent bonds (bond-orientation effect) and the other from interaction of nonbond atoms (steric effect). Combining a parameter  $C = \epsilon/k \cdot T_g$ , where  $\epsilon$  was taken from Table IV, with eq. (12), an expression, like that shown in the literature,<sup>28</sup> was obtained:

$$\epsilon = U - U_0 = A \cdot k \cdot C \cdot \sigma - A \cdot k \cdot C \cdot b \quad (13)$$

TABLE V  
The Steric Factor of Internal Rotation of 1,2-PB

	$K_\theta$ (cm g <sup>-3/2</sup> mol <sup>1/2</sup> )	$(\bar{r}_0^2/M)^{1/2}$ (cm g <sup>-1/2</sup> mol)	$(\bar{r}_{0f}^2/M)^{1/2}$ (cm g <sup>-1/2</sup> mol)	$\sigma$ $(\bar{r}_0^2/M)^{1/2}/(\bar{r}_{0f}^2/M)^{1/2}$
8% 1,2-	0.254	1.034	0.626	1.65
30% 1,2-	0.234	1.006	0.604	1.67
90% 1,2-	0.217	0.981	0.479	2.05

TABLE VI  
Parameters of Internal Rotation of 1,2-PB Chains

	$C$	$\sigma$	$U$	$U_0$ (kcal/mol)	$\epsilon$
30% 1,2-	2.32	1.67	1.40	0.57	0.83
50% 1,2-	2.34	1.83 <sup>a</sup>	1.55	0.58	0.97
66% 1,2-	2.41	1.89 <sup>a</sup>	1.65	0.59	1.06
90% 1,2-	2.41	2.05	1.79	0.59	1.20

<sup>a</sup> Calculated from eq. (12) using the  $T_g$  values in Table III.

where  $k$  is the Boltzmann constant. According to Ref. 28, the quantities  $U$ ,  $U_0$ , and  $\epsilon$  have the physical significance of potential barrier to internal rotation, bond-orientation effect, and steric effect, respectively. The results in Table VI indicate that increasing 1,2-unit content results in the increasing of potential barrier to internal rotation of 1,2-PBs and also the steric effect of the potential barrier, that is, increasing of hindrance to internal rotation of 1,2-PB chains, which is consistent with the results in Table IV.

### CONCLUSION

1. The determination of polymer solubility parameter  $\delta_p$  by viscometry using binary mixture of solvents of similar molar volume is more convenient and more precise than using pure solvents in our case. The results are reliable in the case of 1,2-polybutadienes with toluene-cyclohexane as mixed solvent.

2. The evaluation of the exponent  $\alpha$  in the Mark-Houwink equation from the solubility parameter of polymer  $\delta_p$  and that of solvent  $\delta_s$  by the van Krevelen method as the first approximation for the calculation of molecular weight from GPC data is practical. The Mark-Houwink equations for the 1,2-polybutadiene-toluene system with various 1,2-unit contents so determined are reliable.

3. The increase of  $T_g$  with increasing 1,2-unit content of 1,2-polybutadiene is due to the decreasing of chain flexibility without increasing of intermolecular interaction as demonstrated by the increasing of energy of rotational isomerization  $\epsilon$  and steric factor for internal rotation  $\sigma$  with no essential change of cohesion energy density.

4. Chain flexibility of 1,2-polybutadiene may be characterized by the parameter  $\sigma = (\bar{r}_0^2/M)^{1/2} / (\bar{r}_{0f}^2/M)^{1/2}$  as well as by the energy of rotational isomerization  $\epsilon$ . The correlation of  $\sigma$  and  $\epsilon$  via  $T_g$  gives the potential barrier to internal rotation  $U$ .

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