

# Dielectric and Dynamic Mechanical Behaviors of 1,2-Polybutadienes

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## Synopsis

The dielectric relaxation behavior of 1,2-polybutadienes is analyzed in terms of the experimental data and master curves. The dielectric measurement data were fitted to the empirical relaxation time distribution model of Havriliak and Negami over a frequency range from  $10^0$  to  $10^{12}$  Hz. The constants of the WLF equation,  $C_1$  and  $C_2$ , were evaluated with  $T_g$  at 100 kHz as a reference temperature for some samples, and the master curve of a sample was constructed. The dynamic mechanical measurements for a series of 1,2-polybutadienes with different chain structures were performed over a temperature range from  $-150$  to  $50^\circ\text{C}$ . A qualitative comparison of the dielectric and dynamic mechanical behaviors of 1,2-polybutadienes has been made.

## INTRODUCTION

In our previous paper<sup>1</sup> we presented the results of investigation on the multiple transitions of atactic 1,2-polybutadienes revealed by dynamic mechanical, dielectric, and NMR spectroscopic methods. In this work, we continue to present the other results of the dielectric and dynamic mechanical measurements of 1,2-polybutadienes.

On the dynamic mechanical behavior of 1,2-polybutadienes, there have been a few reports<sup>2,3</sup>; however, the detailed studies of the relationship between the dynamic mechanical behavior and structure of these polymers over the wide temperature and frequency ranges do not appear so far. The same is true with the dielectric behavior of 1,2-polybutadienes. In this work, the dielectric relaxation behavior of 1,2-polybutadienes was analyzed in terms of experimental data and master curves as well as fitting the empirical equation of Havriliak and Negami<sup>4,5</sup> over a frequency range from  $10^0$  to  $10^{12}$  Hz and a temperature range from  $-180$  to  $100^\circ\text{C}$ . The dynamic mechanical data of a series of 1,2-polybutadienes with different chain structures were determined over a temperature range from  $-150$  to  $50^\circ\text{C}$ , and the qualitative comparison of the dielectric with dynamic mechanical behaviors of 1,2-polybutadienes has been made.

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TABLE I  
The Structural Parameters of the Samples with Different Contents of 1,2-Units

Sample	V-1	V-2	V-3	V-4	V-5	V-6	V-7	V-8	V-9
1,2-Unit (%)	7	21	36	45	49	57	71	74	82
<i>Cis</i> -1,4-unit (%)	41	28	32	26	23	19	16	13	10
<i>Trans</i> -1,4-unit (%)	52	51	32	29	26	24	13	13	8
$[\eta]$ (dL/g)	3.06	3.22	3.01	3.39	3.21	3.77	2.99	3.51	3.47

TABLE II  
The Structural Parameters of the Samples with Different Contents of Syndiotactic 1,2-Units

Sample	S-0	S-1	S-2	S-3	S-4	S-5	S-6
1,2-Unit (%)	80	82	83	88	86	86	82
Isotactic (%)	48	42	36	29	26	24	18
Syndiotactic (%)	12	18	22	29	32	35	41
Atactic (%)	40	40	42	42	42	41	41
$[\eta]$ (dL/g)	4.14	2.74	2.78	2.64	2.78	2.09	3.46

## EXPERIMENTAL

### Samples

1,2-Polybutadiene samples used in this work were prepared in our laboratory. Those labeled by letter S were prepared with molybdenum catalyst system in hexane and the chain configuration of the polymers was regulated by addition of allyl bromide. The others were prepared with *n*-BuLi as a catalyst, and the microstructure of the polymers was regulated by tetrahydrofuran. The determination of the microstructure and configuration of the samples were performed by means of IR and  $^{13}\text{C}$ -NMR spectroscopies. The intrinsic viscosity was measured in toluene at 30°C. The structural parameters of the samples are given in Tables I and II. The samples were further purified to remove impurities in them as completely as possible by the following procedure: The samples were dissolved in toluene, the solutions were filtered by a cinder filter after complete dissolution, and then the samples were deposited out of the solutions by methanol; after drying they were extracted by acetone for 48 h. The toluene, methanol, and acetone used are all analytically pure. After extraction the samples were dried in a vacuum desiccator to constant weight.

### Dielectric and Dynamic Mechanical Measurements

The specimens used for dielectric and dynamic mechanical measurements were modeled at 100°C using a laboratory press. The applied pressure is 100 kg/cm<sup>2</sup>.

The dielectric measurements were made on Japan Ando Electric Co., type TRS-10C dielectric loss measuring set, the effective diameter of the electrode is 3.8 cm. In order to have a close attachment of the specimen with the surface of the electrode, a copper foil with thickness of  $2.2 \times 10^{-3}$  cm was stuck on

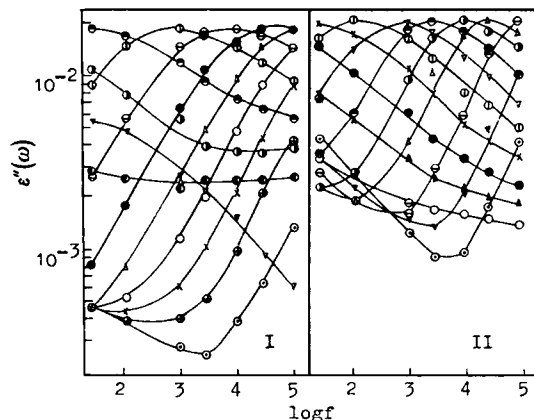


Fig. 1. The plots of  $\epsilon''(\omega)$  against frequency ( $f$ ) at different temperatures ( $^{\circ}\text{C}$ ) for samples V-4 and S-6: (I. V-4) ( $\nabla$ )  $-100$ ; ( $\bullet$ )  $-80$ ; ( $\circ$ )  $-70$ ; ( $\ominus$ )  $-60$ ; ( $\oplus$ )  $-50$ ; ( $\ominus$ )  $-40$ ; ( $\bullet$ )  $-30$ ; ( $\Delta$ )  $-20$ ; ( $\circ$ )  $-10$ ; ( $\times$ )  $0$ ; ( $\oplus$ )  $10$ ; ( $\odot$ )  $25$ . (II. S-6) ( $\circ$ )  $-25$ ; ( $\blacktriangle$ )  $-20$ ; ( $\bullet$ )  $-15$ ; ( $\times$ )  $-10$ ; ( $\oplus$ )  $-5$ ; ( $\nabla$ )  $0$ ; ( $\ominus$ )  $5$ ; ( $\oplus$ )  $10$ ; ( $\Delta$ )  $15$ ; ( $\ominus$ )  $20$ ; ( $\blacktriangledown$ )  $35$ ; ( $\odot$ )  $45$ .

the two sides of the specimen. The dynamic mechanical measurements were carried out on a homemade torsional pendulum. The length, width, and thickness of the specimen are 2, 0.2, and 0.05 cm, respectively.

## RESULTS AND DISCUSSION

### Dielectric Relaxation Spectra

The plots of the real and imaginary components of complex dielectric permittivity  $\epsilon'(\omega)$  and  $\epsilon''(\omega)$  against frequency at different temperatures for samples V-4 and S-6 are shown in Figures 1 and 2. Within the experimental frequency range, a relaxation process can be observed at some temperatures. This is ascribed to the glass transition of the samples, but it is evident that the relaxation curves at any temperature are all incomplete. That means that the glass transition loss peak has a width larger than the experimental frequency range in this work.

### WLF Equation and Master Curve

To obtain a complete glass-transition curve and investigate the dielectric behavior over a broad frequency range of the polymers, the master curves for some samples were constructed using the experimental data. The shift along frequency axis of the data was performed according to the WLF equation. The constants of the WLF equation,  $C_1$  and  $C_2$ , were determined from the dielectric measurement data. To determine  $C_1$  and  $C_2$ , the equation is written in following form:

$$-(T - T_s)/\log b_T = C_2/C_1 + (1/C_1)(T - T_s) \quad (1)$$

where  $b_T$  is the dielectric shift factor and  $T_s$  is a reference temperature. Then, the  $C_1$  and  $C_2$  can be evaluated from the slope and intercept of the plotting of

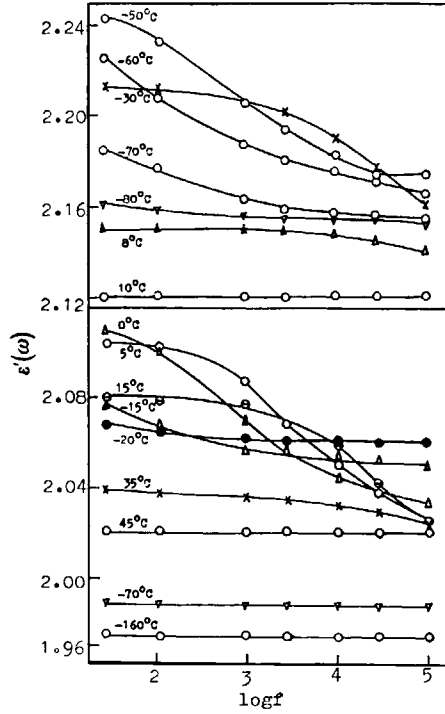


Fig. 2. The plots of  $\epsilon''(\omega)$  against frequency for samples V-4 and S-6.

$-(T - T_s)/\log b_T$  against  $(T - T_s)^{-1}$ . The  $C_1$  and  $C_2$  values with  $T_g$  at 100 kHz as a reference temperature thus obtained for some samples are given in Table III. The variation of the dielectric shift factors obtained both from the WLF equation and shifting  $\epsilon''$  and  $\epsilon'$ , with temperature for sample S-6 are shown in Figure 3.

To construct master curve, in addition to the horizontal shift according to the WLF equation, the experimental data at different temperatures must be vertically shifted according to the following relations<sup>6</sup>:

$$\epsilon_{S'}' = \epsilon_T' \left[ \frac{T\rho_S}{T_S\rho_T} + \frac{\epsilon_\infty}{\epsilon_T'} \left( 1 + \frac{T\rho_S}{T_S\rho_T} \right) \right] \quad (2)$$

$$\epsilon_{S''}'' = \epsilon_T'' \frac{T\rho_S}{T_S\rho_T} \quad (3)$$

$$\omega_S = \omega_T b_T \quad (4)$$

TABLE III  
 $C_1$  and  $C_2$  of Some Samples with  $T_g$  at 100 kHz as a Reference Temperature

Sample	V-2	V-4	V-7	S-6
$C_1$	9.67	9.09	8.89	8.71
$C_2$	112.0	112.0	112.0	106.0

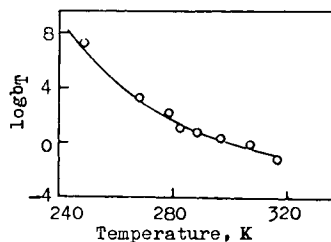


Fig. 3. The variation of the dielectric shift factors of sample S-6 with temperature: (—) obtained from the WLF equation; (○) obtained from shifting  $\epsilon''$  and  $\epsilon'$  to the reference temperature.

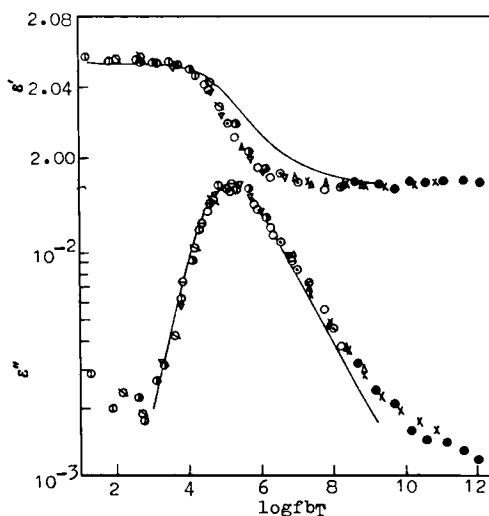


Fig. 4. The master curve of sample S-6 with a reference temperature of 296 K: (●)  $-25^{\circ}\text{C}$ ; (X)  $-20^{\circ}\text{C}$ ; (○)  $-15^{\circ}\text{C}$ ; ( $\Delta$ )  $-10^{\circ}\text{C}$ ; ( $\odot$ )  $-5^{\circ}\text{C}$ ; ( $\ominus$ )  $0^{\circ}\text{C}$ ; ( $\nabla$ )  $5^{\circ}\text{C}$ ; ( $\odot$ )  $10^{\circ}\text{C}$ ; ( $\otimes$ )  $15^{\circ}\text{C}$ ; ( $\bullet$ )  $25^{\circ}\text{C}$ .

where  $\rho$  is the density of the sample, and the subscripts  $T$  and  $S$  indicate the values at temperature  $T$  and the reference temperature  $T_S$ , respectively. Figure 4 shows the master curves of sample S-6 reduced to 296 K. From the figure it can be seen that the superposition of the data is good within the glass-transition range.

### Shape of the Dielectric Relaxation Curve

From Figure 4 it can be seen that the dielectric glass-transition loss curve of 1,2-polybutadienes is asymmetrical, implying asymmetrical distribution of the relaxation times. The shape of dielectric relaxation curve of a polymer can be exactly described in terms of some models of relaxation time distribution, in which the empirical Cole-Cole model,<sup>7</sup> Davidson-Cole,<sup>8</sup> and Havriliak-Negami models<sup>4</sup> are used most frequently. Which model fits the shape of dielectric relaxation curve of a particular polymer can be identified by plotting of  $\epsilon''(\omega)$  against  $\epsilon'(\omega)$ , which is a complex plane diagram of the complex dielectric permittivity.<sup>4,5</sup> The complex plane diagrams of sample S-6 at several temperatures in the glass-transition region are shown in Figure 5. As can be seen, the curves of  $\epsilon''(\omega)$  vs.  $\epsilon'(\omega)$  are nearly linear at high frequency

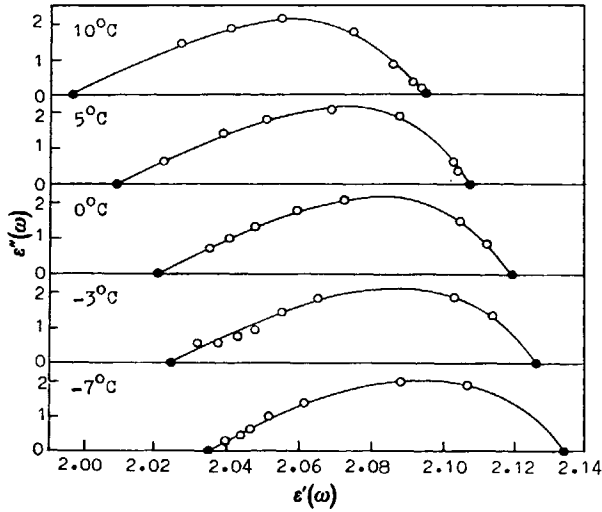


Fig. 5. The complex plane diagrams of sample S-6 in the glass-transition region at several temperatures: (●) extrapolating values.

but circular at low frequency. So the shape of the glass-transition relaxation curve of 1,2-polybutadienes is typically Havriliak-Negami type, and it can be expressed by

$$\epsilon''(\omega) = \epsilon_{\infty} - \frac{\epsilon_0 - \epsilon_{\infty}}{[1 + (i\omega\tau)^{1-\alpha}]^{\beta}} \quad (5)$$

where  $\epsilon_0$  and  $\epsilon_{\infty}$  are, respectively, the limiting low- and high-frequency dielectric constants,  $\omega$  is angular frequency,  $\tau$  is the mean relaxation time, and  $\alpha$  and  $\beta$  are parameters related to the width and shape of the relaxation time distribution. These five parameters can be evaluated from the complex plane diagram of the dielectric permittivity.<sup>4,5</sup> In Table IV are shown these parameters obtained from the complex plane diagrams at different temperatures for sample S-6 (Fig. 5). With these parameters, the complex dielectric permittivity can be calculated by the Havriliak-Negami equation, and thus calculated  $\epsilon'(\omega)$  and  $\epsilon''(\omega)$  as a function of frequency for sample S-6 are also plotted in Figure 4 (solid line). It can be seen the calculated dielectric relaxation curves are roughly in accord with the master curves in the glass-transition region. It indicates that both the master curves and the parameters

TABLE IV  
Dispersion Parameters of the Havriliak-Negami Equation for Sample S-6

Temp (°C)	$\epsilon_0$	$\epsilon_{\infty}$	$1 - \alpha$	$\beta$	$\tau \times 10^3$ (sec)
-7	2.134	2.035	0.65	0.50	6.3
-3	2.126	2.025	0.68	0.43	1.5
0	2.119	2.021	0.73	0.40	0.9
5	2.106	2.008	0.77	0.36	0.2
10	2.095	1.996	0.74	0.38	0.5

of the Havriliak–Negami equation we have obtained are reliable. From Figure 4 the width at half-height of the glass-transition loss peak of the sample is estimated to be about four decades of frequency, being larger than the usual case. It has been found that the width at half-height of glass-transition loss peaks for most amorphous polymers is between 1.7 and 2.5 decades of frequency.<sup>9</sup> The wider glass-transition loss peak means a wider distribution of relaxation times of 1,2-polybutadienes. This is no doubt associated with the great variety of the chain structure of 1,2-polybutadienes. In fact, 1,2-polybutadiene can be regarded as a copolymer of five monomers, i.e., *cis*-1,4-*trans*-1,4-, isotactic 1,2-, syndiotactic 1,2-, and atactic 1,2-units.

### Activation Energy

The plots of  $\log(2\pi f)^{-1}$  against  $1/T$  in the glass-transition region for some samples are shown in Figures 6 and 7. As can be anticipated, these plots are

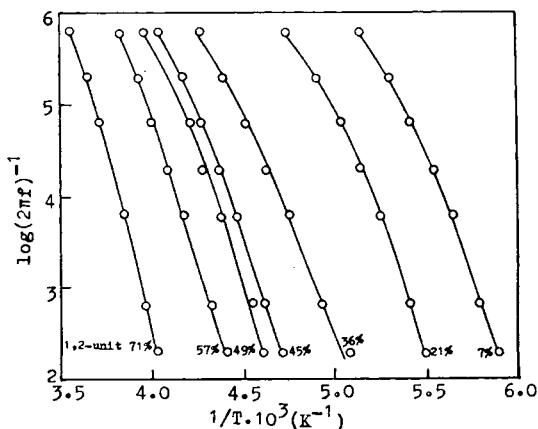


Fig. 6. The plots of  $\log(2\pi f)^{-1}$  against  $1/T$  for the glass transition of the samples with different contents of 1,2-units.

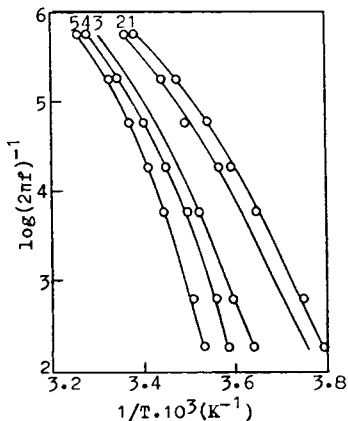


Fig. 7. The plots of  $\log(2\pi f)^{-1}$  against  $1/T$  for the glass transition of the samples with different content of syndiotactic 1,2-units.

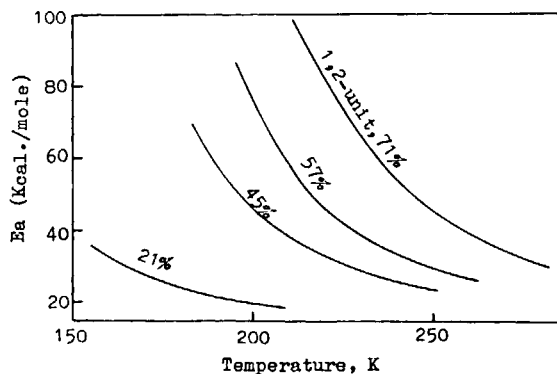


Fig. 8. The variation of  $E_a$  with temperature in glass transition for the samples with different contents of 1,2-units.

not straight lines due to the fact that the apparent activation energy responsible for segmental motion in the glass transition of polymers is not constant but dependent on temperature. The variation of apparent activation energy with temperature in the glass-transition of polymers can be expressed as<sup>10</sup>

$$E_a = 2.303RC_1C_2T^2/(C_2 + T - T_s)^2 \quad (6)$$

In Figure 8 are shown the curves of  $E_a$  vs. temperature calculated according to eq. (6) with  $C_1$  and  $C_2$  values given in Table III for some samples with different contents of 1,2-units. As shown, the change in  $E_a$  with temperature is very sharp at the low temperature side of the glass-transition region. When  $T = T_s$ , eq. (6) has a form as

$$E_a = 2.303R(C_1/C_2)T_s^2 \quad (7)$$

It is found from Table III that the  $C_1/C_2$  values for the various samples are all close to 0.08 and so if  $T_g$  acts as  $T_s$ , the  $E_a$  at  $T_g$  for various samples can be compared by their  $T_g^2$  values. At the high temperature side of the glass-transition region,  $E_a$  tends toward constant and convergence for the various samples. It can also be interpreted by eq. (6). If  $T \gg T_s$ ,  $E_a$  can be expressed as

$$E_a = 2.303RC_1C_2 \quad (8)$$

From Table III it is known that the differences between the  $C_1/C_2$  values of different samples are very small, which is why the  $E_a$  tends toward constant and convergence for different samples with different contents of 1,2-units. It seems to show that the activation of segmental motion of 1,2-polybutadienes at  $T \gg T_g$  is mainly dependent on the intermolecular interaction and less affected by intramolecular interaction. This is in accord with the cohesive energy observation of 1,2-polybutadienes, which shows that the cohesive energy has little change with the content of 1,2-units in 1,2-polybutadienes, although the intramolecular interaction increases with raising the contents of 1,2-units.<sup>11</sup>



### Comparison between the Dielectric and Dynamic Mechanical Behaviors

Figure 9 shows the curves of the dielectric loss factor vs. temperature for the samples with different contents of 1,2-units. It can be seen that with an increase in the content of 1,2-units, the dielectric loss factor becomes higher in and above the glass-transition region, and the width of the glass-transition loss peak has a maximum when the content of 1,2-units is about 45%. The curves of the dynamic mechanical loss vs. temperature for the samples with different contents of 1,2-units are shown in Figure 10. Comparing Figure 10 with Figure 9, it can be found that the variation of the dynamic mechanical

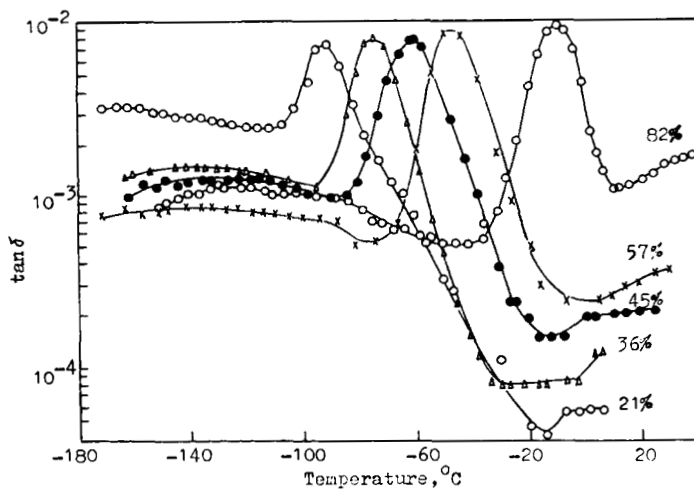


Fig. 9. The plots of the dielectric loss factor against temperature for the samples with different contents of 1,2-units at 30 Hz.

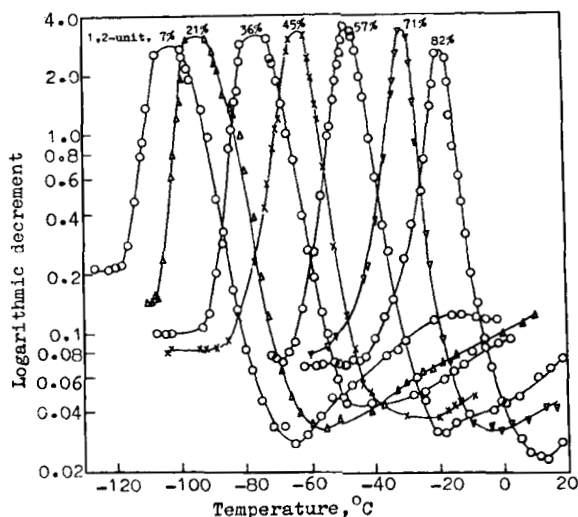


Fig. 10. The plots of the dynamic mechanical loss against temperature for the samples with different contents of 1,2-units.

behavior of 1,2-polybutadienes with the content of 1,2-units is different from that of the dielectric behavior in some aspects. The most outstanding difference between them is that the temperature range covered by the dielectric loss peak is far wider than done by the dynamic mechanical loss peak.

### Structure Dependence of the Dynamic Mechanical Behavior

The effect of the configuration of 1,2-units on the dielectric and dynamic mechanical behaviors of 1,2-polybutadienes is considerable when the content of 1,2-units is higher while such an effect is negligible when the content of 1,2-units is smaller. The effect of the configuration of 1,2-units on the dielectric behavior of 1,2-polybutadienes has been presented in our other paper.<sup>12</sup> The configuration dependence of the dynamic mechanical behavior of 1,2-polybutadienes is shown in Figure 11. As shown, with the increase of syndiotactic 1,2-units, the location of the mechanical loss peak shifts to higher temperatures and the peak height decreases. A linear relationship between the location of the loss peak, i.e.,  $T_g$  (sometimes denoted by  $T_b$ ), and the content of syndiotactic 1,2-units is observed as shown in Figure 12.

Bahary et al.<sup>13</sup> proposed an empirical connection of the  $T_g$  with the content of 1,2-units of atactic 1,2-polybutadienes as follows:

$$T_g = 91V - 106 \quad (9)$$

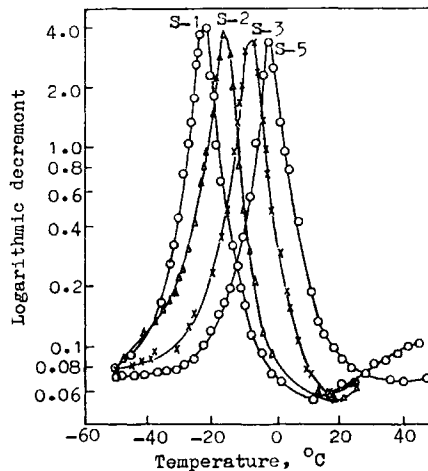


Fig. 11. The plots of the dynamic mechanical loss against temperature for the samples with different contents of syndiotactic 1,2-units.

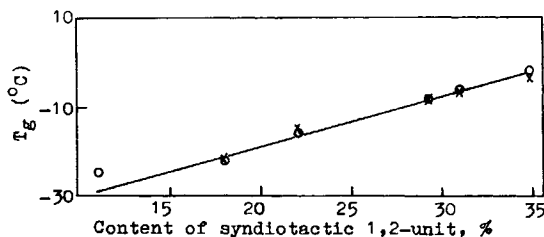


Fig. 12. The relationship between  $T_g$  and the content of syndiotactic 1,2-units.

TABLE V  
The Calculated and Observed  $T_g$  Values of Various Samples

Sample	V-1	V-2	V-3	V-4	V-5	V-6	V-7	V-8	S-0	S-1
1,2-Unit (%)	7	21	36	45	49	57	71	74	80	82
$T_g$ , obs. ( $^{\circ}\text{C}$ )	-104	-96	-77	-64	-58	-48	-31	-27	-20	-19
$T_{gb}$ ( $^{\circ}\text{C}$ ) <sup>a</sup>	-100	-87	-73	-65	-61	-54	-41	-39	-33	-31
$T_{gr}$ ( $^{\circ}\text{C}$ ) <sup>a</sup>						-52	-29	-27	-21	-19

$${}^a T_{gb} = 91V - 106; T_{gr} = 91V + 100S - 106.$$

where  $V$  indicates the content of 1,2-units in 1,2-polybutadiene. In this relation the effect of the configuration of 1,2-units on  $T_g$  is not taken into account, so that it is not applicable to 1,2-polybutadienes with higher contents of 1,2-units unless it is revised by addition of the contribution from the configuration of 1,2-units to  $T_g$ . The samples involved in Figure 12 have similar contents of 1,2-units. Therefore, it might be considered that the rise in  $T_g$  of the samples with higher contents of syndiotactic 1,2-units only arises from the contribution of the configuration of 1,2-units, and the slope of Figure 12 is the varying rate of  $T_g$  with the content of syndiotactic 1,2-units. From Figure 12 this slope is estimated to be about 100. Let  $S$  represent the content of syndiotactic 1,2-units in 1,2-polybutadiene, and, then, the Bahary relation can be revised as

$$T_g = 91V + 100S - 106 \quad (10)$$

The  $T_g$  calculated by eqs. (9) and (10) for some samples are given in Table V together with the observed ones. The deviation of the calculated  $T_g$  values by the Bahary equation from the observed ones becomes larger with a rise in the content of 1,2-units so as to be inapplicable as the content of 1,2-units is higher than 60% while the calculated  $T_g$  values by the revised Bahary relation, eq. (10), are in good accord with the observed ones, as shown in Table V.

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