

# Multiple Transitions in Atactic 1,2-Polybutadienes Observed from Dynamic Mechanical and Dielectric Relaxation Data

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## Synopsis

Detailed investigation by dynamic mechanical, dielectric and  $^{13}\text{C}$ -NMR relaxation spectroscopies over a temperature range from  $-180$  to  $100^\circ\text{C}$  reveals the multiple transitions in atactic 1,2-polybutadienes, which are denoted as  $T_{11}$ ,  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$  in conformity with reducing temperature. The spectroscopic data obtained show that  $\alpha$  transition is the glass transition of the samples,  $\beta$ - and  $\gamma$ -relaxations are likely to be related to the flexibility of the main chain and the side chain motion, respectively, and  $\delta$  loss process seems to be associated with the defects and inhomogeneity in structure.  $T_{11}$  transition observed in the dielectric relaxation spectra may be manifested by the abrupt broadening of the resonance peaks in solid-state  $^{13}\text{C}$ -NMR spectra.

## INTRODUCTION

There is a great variety of chain structures in 1,2-polybutadienes, which gives rise to many kinds of physical and mechanical properties.<sup>1-3</sup> However, most studies on 1,2-polybutadienes reported so far are focused on the synthesis, structure, property, processing, and applications. Investigations on the multiple transitions of atactic 1,2-polybutadienes have received less attention.

In this paper, the multiple transitions of atactic 1,2-polybutadienes observed from dynamic mechanical, dielectric, and solid-state  $^{13}\text{C}$ -NMR relaxation data are represented, and the relationship between the multiple transitions and the chain structure is investigated. The assignation of the various transitions is tentatively discussed.

## EXPERIMENTAL

### Materials

1,2-Polybutadiene samples, except S-1, used in this work were prepared with *n*-BuLi as catalyst and the percentages of 1,2- units in the polymers were regulated by addition of tetrahydrofuran using a procedure reported in Ref. 4. Sample S-1 was prepared with a molybdenum catalyst system: the details of the procedure were presented in our previous paper.<sup>5</sup> The structural parameters of the samples are given in Table I. The samples were purified before

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TABLE I  
The Structural Parameters of Samples<sup>a</sup>

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

<sup>a</sup>The percentages of *cis*-1,4-, 1,2- and *trans*-1,4- units were determined by the relative intensities of 734, 911, and 967  $\text{cm}^{-1}$  bands in the IR spectrum, respectively, and  $[\eta]$  was measured in toluene at 30°C.

measurements by the following procedures: the samples were dissolved in toluene and the solutions filtered through a G1 sintered crucible after complete dissolution; the samples were dried after they are deposited out from the solution by addition of methanol, and then extracted with acetone for 48 h in a Soxhlet apparatus. The toluene, methanol, and acetone used are all analytically pure. After the extraction the samples are dried in a vacuum desiccator to a constant weight.

### Instruments

Dynamic mechanical measurement was performed on a torsional pendulum apparatus designed in our laboratory.<sup>6</sup> Dielectric measurement was made on Japan Ando Electric Co., Type TRS-10C dielectric loss measuring set, and the effective diameter of the electrode used was 38 mm. NMR measurement was carried out by a Varian XL-200 NMR spectrometer.

### Measurements

The specimens for measurements were modeled at 100°C using a laboratory press; the applied pressure was 100  $\text{kg}/\text{cm}^2$ . The dimension of the specimen for dynamic mechanical measurement was  $30 \times 2 \times 0.5$  mm. Those for dielectric measurement were circular with a diameter of 0.5–0.7 mm. In order to closely attach the specimen with the electrode surface, a copper foil with a thickness of  $2.2 \times 10^{-2}$  mm was placed on the two sides of the specimen. The samples for NMR measurement had a length of 25 mm and a diameter of 10 mm.

For dynamic mechanical and dielectric measurements, the specimen was first cooled with boiling liquid nitrogen, and then the measurements were carried out with warming at a rate of 1–2°C/min. For solid-state NMR measurement below room temperature, the sample was cooled by boiling liquid nitrogen to a specific temperature, and then the measurement was performed at that temperature.

## RESULTS AND DISCUSSION

### Dynamic Mechanical and Dielectric Relaxation Spectra

The dynamic mechanical spectra for samples V-4 and S-1 are shown in Figure 1. Two transitions can be observed, the one having higher peak

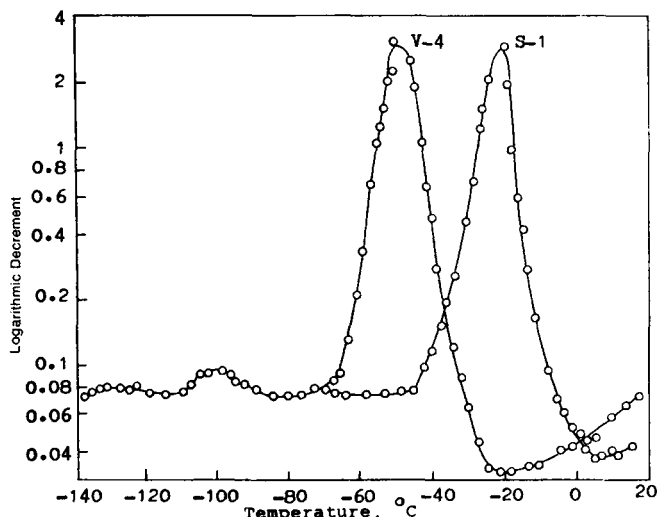


Fig. 1. Dynamic mechanical spectra for samples V-4 and S-1.

intensity and located at higher temperature is the glass transition of the samples; the other, occurring between  $-110$  and  $-90^{\circ}\text{C}$ , is a secondary relaxation.

The dielectric spectra of sample S-1 are shown in Figure 2. In the dielectric loss spectra ( $\tan \delta$  vs. temperature), a  $T > T_g$  transition, i.e.,  $T_{11}$  transition, can be observed between  $40$  and  $80^{\circ}\text{C}$ , although its intensity is very weak, in addition to the glass transition between  $-40$  and  $20^{\circ}\text{C}$  and a secondary relaxation between  $-120$  and  $-70^{\circ}\text{C}$ , which corresponds to those observed in dynamic mechanical spectra. It is of interest to notice that more transitions can be observed in the dielectric dispersion spectra ( $\epsilon'$  vs. temperature) than in the dynamic mechanical and the dielectric loss spectra. As shown in Figure 2, in addition to the glass transition, two secondary relaxations can be obviously revealed in the dielectric dispersion spectra. Also, there seems to be another relaxation between  $-160$  and  $-100^{\circ}\text{C}$  (see Figs. 3 and 5).

In summary, five transitions are observed in the dynamic mechanical and dielectric relaxation spectra, denoted as  $T_{11}$ ,  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$  in conformity with

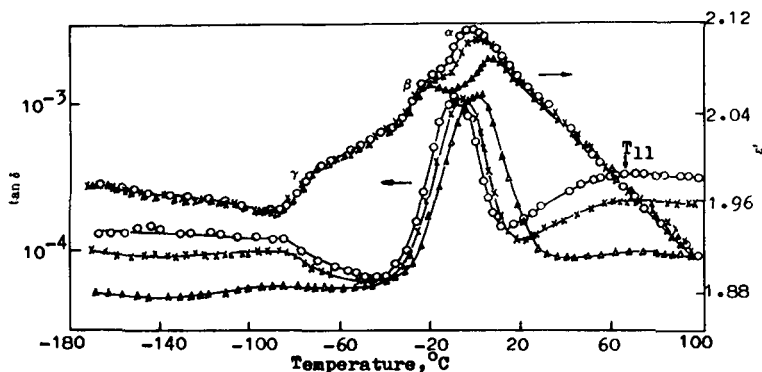


Fig. 2. Dielectric spectra of sample S-1: (○) 30 Hz; (×) 110 Hz; (Δ) 1 kHz.

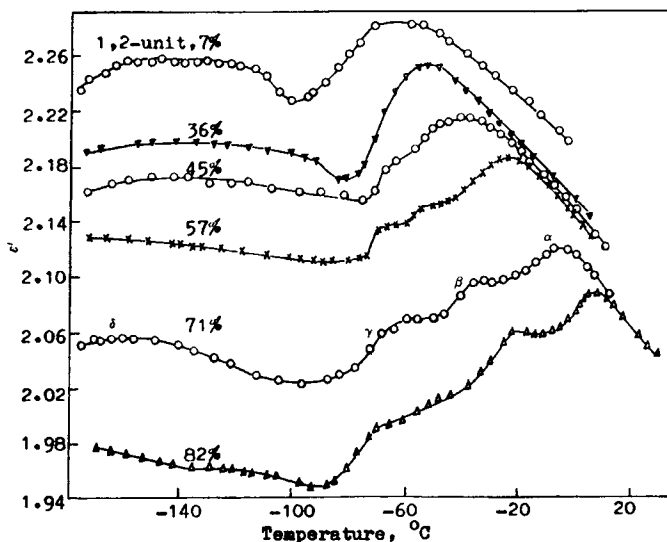


Fig. 3. Dielectric dispersion spectra of the samples with different percentages of 1,2- units at 3 kHz.

reducing temperature. The fact that more transitions can be revealed in the dielectric dispersion spectra than in the dielectric loss spectra for 1,2-polybutadienes implies that some vicinal transition peaks are overlapping in the latter. So far as we know, there have been no other reports on the secondary transitions of atactic 1,2-polybutadienes.

### Transitions Assignments

In Figure 3 are shown the dielectric dispersion spectra of the samples with different percentages of 1,2- units. As indicated, there is a trend between percentage of 1,2- units and the intensity and location of these transitions. The possible molecular origins of these transitions of 1,2-polybutadienes are as follows.

#### *α Transition*

As was seen in the figures, the intensity of  $\alpha$  transition is much higher than that of the other transitions in both the dynamic mechanical and dielectric loss spectra. The 1,2-polybutadienes prepared with *n*-BuLi are noncrystalline as shown in Figure 4. Our earlier work<sup>5</sup> has shown that sample S-1 is also noncrystalline; thus no transitions associated with crystalline properties would appear. This  $\alpha$  transition is most likely the glass transition of the sample.

#### *β Transition*

$\beta$  transition cannot be observed in the dielectric loss spectra and seems to have an overlap with other transition peaks. In the dielectric dispersion spectra,  $\beta$  transition is not observed when the percentage of 1,2- units is lower than 57%, but, with increasing percentage of 1,2- units, the  $\beta$  transition becomes more and more obvious and the location of the transition peak shifts

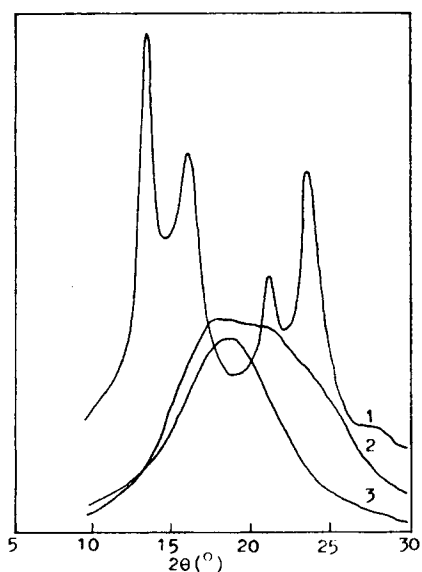


Fig. 4. X-ray diffraction curves of 1,2-polybutadienes: (1) syndiotactic 1,2-polybutadiene<sup>7</sup>; (2) sample V-5; (3) sample V-3.

to higher temperature. It is likely that the  $\beta$  transition is related to the flexibility of the main chain, because the flexibility of the main chain of 1,2-polybutadienes decreases with increasing the percentage of 1,2- units.<sup>8</sup> However, the exact molecular origin of the  $\beta$  transition cannot be determined from the present data.

#### *$\gamma$ Transition*

$\gamma$  transition is not observed in the dielectric dispersion spectra in the case that the percentage of 1,2- units is lower than 45%, and with increasing percentage of 1,2- units, the intensity of the  $\gamma$  transition increases, but its location has not shift significantly, unlike the case of the  $\beta$  transition. Thus, it does not seem that the  $\gamma$  transition is related to the flexibility of the main chain as does the  $\beta$  transition, but seems to be associated with the motion of vinyl group noncooperative with the skeletal bonds.

#### *$\delta$ Transition*

$\delta$  transition is characterized by a rather wide temperature range from  $-180$  to  $-100^{\circ}\text{C}$  for all the samples. It was found that the intensity of  $\delta$  transition drops down or even becomes null after subjecting the sample to an alternating electric field as shown in Figure 5. Curve 2 in Figure 5 is the result of repeat dielectric measurement with the same specimen of V-5, that is, the specimen is recooled to  $-180^{\circ}\text{C}$  after the first measurement is completed from  $-180$  to  $50^{\circ}\text{C}$ , and then the measurement is repeated. The two curves coincide above  $-30^{\circ}\text{C}$ , but below  $-30^{\circ}\text{C}$ , as shown in Figure 5,  $\delta$  transition vanishes in curve 2 while it is evident in curve 1. The same is true with all the other samples. This indicates that the  $\delta$  transition is sensitive to the effect of an

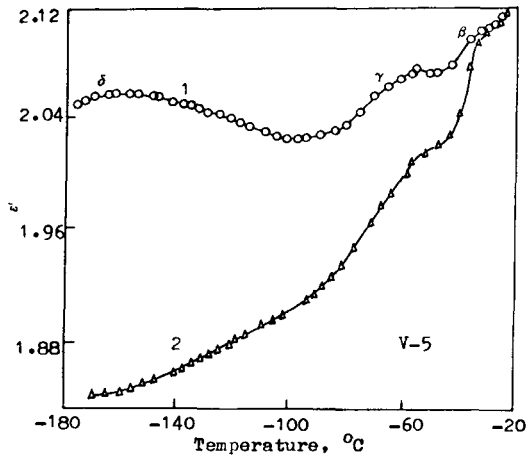


Fig. 5. The result of repeat dielectric measurements: (○) first; (Δ) repeat measurement.

external field. It was reported that polystyrene has also a transition between  $-180$  and  $-100^{\circ}\text{C}$ , which would disappear after heat treatment for 30 min at  $280^{\circ}\text{C}$ ; this transition was supposed to arise from the defects and imperfection in structure.<sup>9,10</sup> This transition of polystyrene has a feature similar to the  $\delta$  transition of 1,2-polybutadienes. Thus it appears reasonable to assume that the  $\delta$  transition of 1,2-polybutadienes is possibly related to the defects and inhomogeneity in structure.

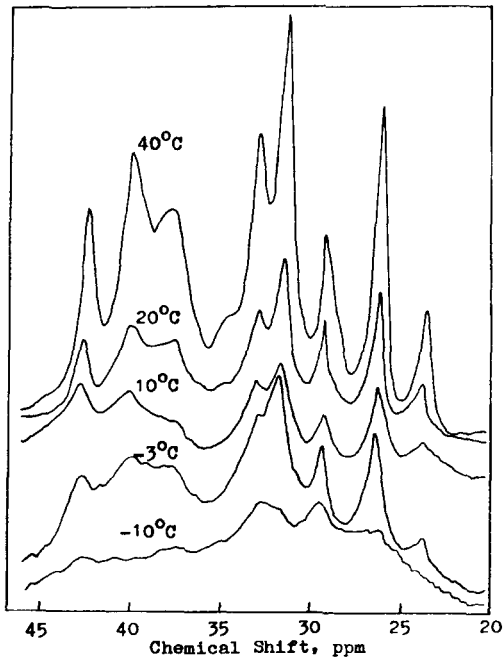


Fig. 6. Solid-state  $^{13}\text{C}$ -NMR spectra for sample V-3 at different temperatures.

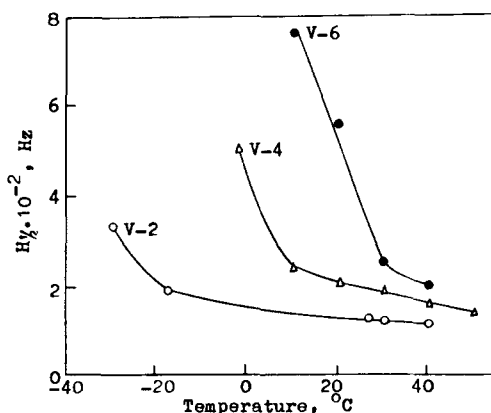


Fig. 7. Solid-state  $^{13}\text{C}$ -NMR line width ( $H_{1/2}$ ) of  $-\text{CH}=\text{}$  in *trans*-1,4- units vs. temperature.

### $T_{11}$ Transition

$T_{11}$  transition of polymers indicates a transition above  $T_g$  from one amorphous state,  $L_1$ , to another amorphous,  $L_2$ . In general, the intensity of  $T_{11}$  transition is very weak for most polymers, so that it is hard to be detected by ordinary methods. Therefore, whether there are  $T_{11}$  transitions is still a matter of dispute.<sup>11</sup> However, it is found that the  $T_{11}$  transition in atactic 1,2-polybutadiene is very obvious. In 1970, Sidorovitch et al.<sup>12</sup> observed with dynamic mechanical relaxation method that 1,2-polybutadienes have an intense  $T > T_g$  transition. Boyer et al.<sup>13</sup> investigated with torsional braid analysis the configuration dependence of the  $T_{11}$  transition in 1,2-polybutadienes and found that the  $T_{11}$  transition exists only in atactic 1,2-polybutadiene; no  $T_{11}$  transition could be observed in either isotactic or syndiotactic forms. This is in agreement with our studies because the 1,2-polybutadiene samples used in this work are all atactic.

The  $T_{11}$  transition of 1,2-polybutadienes can be further manifested by solid-state  $^{13}\text{C}$ -NMR line width measurement. As shown in Figure 6, an abrupt broadening of the resonance bands in solid-state  $^{13}\text{C}$ -NMR spectrum of sample V-3 occurs between  $-10$  and  $-3^\circ\text{C}$ . The linewidth of  $-\text{CH}=\text{}$  in *trans*-1,4- units vs. temperature for some samples are shown in Figure 7, and it can be seen that all of the samples have an abrupt change of slope, indicating that some kind of transitions appears within the corresponding temperature range. It is known that the ratio of  $T_{11}$  transition temperature to  $T_g$  is equal to  $1.2 \pm 0.05$ .<sup>13</sup> The  $T_{11}$  transition temperature range estimated by this

TABLE II  
 $T_{11}$  Transition Temperature Range of Some Samples<sup>a</sup>

Sample	V-2	V-3	V-4	V-6	S-1
$T_{11}^e$ ( $^\circ\text{C}$ )	-75--40	-44-0	-30--13	-6-43	8-50
$T_{11}^r$ ( $^\circ\text{C}$ )	-50--40	-30--10	-20--10	-10-0	0-10

<sup>a</sup>  $e$  = estimated by  $T_{11}/T_g = 1.2 \pm 0.05$ .  $r$  = the abrupt broadening of the solid-state  $^{13}\text{C}$ -NMR line width.

empirical relation and the temperature range in which the abrupt broadening of the solid-state  $^{13}\text{C}$ -NMR line width takes place are given in Table II. As indicated, the transitions found by solid-state  $^{13}\text{C}$ -NMR line width correlate closely to  $T_{11}$  transitions of 1,2-polybutadiene.

### CONCLUSION

At least five transitions in atactic 1,2-polybutadienes can be observed by means of dynamic mechanical and dielectric relaxation spectroscopies over a temperature range from  $-180$  to  $100^\circ\text{C}$ , denoted as  $T_{11}$ ,  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$  transition in the order of decreasing temperature.  $T_{11}$  transition was also detected by solid-state  $^{13}\text{C}$ -NMR line width measurements. The  $\alpha$  transition is the glass transition,  $\beta$  transition is possibly associated with the flexibility of the main chain,  $\gamma$  transition is likely to arise from the motion of vinyl group noncooperative with the main chain, and  $\delta$  transition is suspected of being related to the defects and imperfection in structure. However, it must be pointed out that the above discussion about the assignments of the various transitions of atactic 1,2-polybutadienes are only tentative.

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