

FREQUENCY DEPENDENCE OF THE DIELECTRIC RELAXATION OF 1, 2-POLYBUTADIENES

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ABSTRACT

The dielectric loss factor and permittivity of a series of 1, 2-polybutadienes with different contents of 1, 2-units and different contents of syndiotactic 1, 2-units were determined over a frequency range from 30Hz to 100KHz at different temperatures. The WLF equation was evaluated for various samples with T_g at 100KHz as a reference temperature and the master curves of various samples have been constructed, which are in accordance with those calculated by Havriliak-Negami equation. The frequency dependence of the dielectric relaxation of 1, 2-polybutadienes was investigated over a frequency range from 10^0 Hz to 10^{12} Hz in terms of the experimental data and the master curves.

INTRODUCTION

The relaxation of polymers is in nature a rate process and so that it is dependent upon the frequency of the alternating electric field exerted. The relationship between the complex permittivity and the frequency is usually expressed as follows^[1,2]

$$\frac{\epsilon^*(\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = F(\omega) \int_0^\infty - \left[\frac{d\phi(t)}{dt} \right] [\exp(i\omega t)] dt \quad (1)$$

$$F(\omega) = [\epsilon^*(2\epsilon_0 + \epsilon_\infty)] / [\epsilon_0(2\epsilon^* + \epsilon_\infty)]$$

where ϵ^* is complex permittivity, ϵ_0 and ϵ_∞ are the limiting low and high-frequency dielectric constants, respectively, $\phi(t)$ is dipolar autocorrelation function, ω is angular frequency and $F(\omega)$ is called the internal-field function and its value is close to unity so that it is negligible in most cases.

A dipolar autocorrelation function $\phi(t)$ is a function of describing the structural change and molecular motion, and it can be obtained by dielectric experimental data or theoretical models. Some empirical dipolar autocorrelation functions are usually employed in interpretation of the dielectric relaxation behaviours of polymers because those from theoretical models are much complex to be used. An empirical equation used most frequently is Havriliak-Negami equation^[3,4]

$$\frac{\epsilon^*(\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \frac{1}{[1 + (i\omega\tau)^{1-\alpha}]^\beta} \quad (2)$$

where τ is the mean relaxation time, and α and β are parameters related to the width and shape of relaxation time distribution curve.

It can be seen from Eqs. 1 and 2 that the macroscopic dielectric relaxation behaviours of a polymer are dependent on its microscopic structure and molecular motion, so a lot of information related to the microstructure and chain dynamics of polymers can be obtained by studying dielectric relaxation behaviours over a wide frequency range. On the other hand, polymers are often used as dielectric or magnetic materials, so it is of practical significance to investigate the behaviours of polymers under the effect of an alternating electric field.

This paper is to present the results of investigation on the frequency dependence of the dielectric relaxation of 1, 2-polybutadienes.

EXPERIMENTAL

1, 2-Polybutadiene samples used in this work were prepared in our laboratory, those that are denoted by letter S were prepared with molybdenum catalyst system and the others were prepared with *n*-butyl lithium. The structural parameters of the samples are given in Tables 1 and 2, which the samples S-8 and S-10 have close contents of 1, 2-units but different contents of syndiotactic 1, 2-units.

Table 1 The structural parameters of the samples

Sample	V-38	V-61	L-6	S-8	S-10
1, 2-unit(%)	21	45	71	82	84
<i>cis</i> -1,4-unit(%)	28	26	16	3	3
<i>trans</i> -1,4-unit(%)	51	29	13	15	13
$[\eta]$ (dl/g)	3.22	3.39	2.99	3.46	3.39

The microstructures were determined by IR and $[\eta]$ were measured in toluene at 30°C.

Table 2 The configuration of 1, 2-units in samples S-8 and S-10

Configuration(%)	Syndiotactic	Isotactic	Atactic
S-8	18	41	41
S-10	33	25	42

The configuration were determined by ^{13}C -NMR.

The samples were carefully purified in order to remove impurities as completely as possible before the dielectric measurement is performed. The dielectric measurements were made on type TRS-100 dielectric loss measuring set from Japan Ando Electric Co..

RESULTS AND DISCUSSION

1. Variation of the dielectric loss and permittivity with frequency

The variation of the dielectric loss and permittivity of samples V-38 and L-6 are shown in Figs. 1 and 2. A relaxation region over a wider frequency range and with higher intensity appears in the samples within the experimental temperature range and the location of the relaxation region shifts toward to higher temperature with raising frequency. It is obvious that this relaxation is the glass-transition of the samples. Besides, a tail part of a low frequency relaxation emerges within the experimental temperature and frequency ranges in which it may correspond to the T_H transition of the samples.

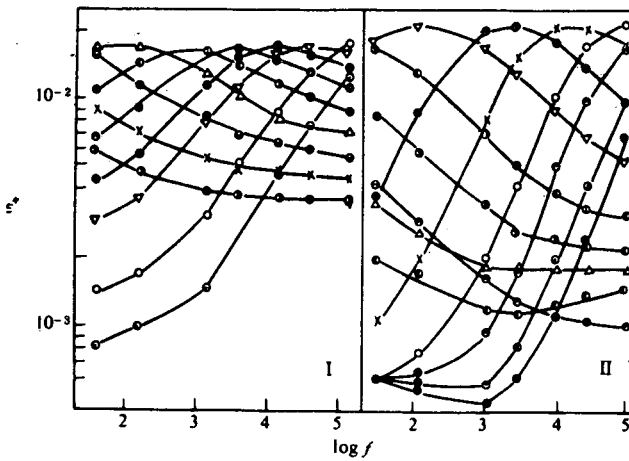


Fig. 1 Variation of dielectric loss with frequency

- I. V-38, ○: -110°C; X: -100°C; ⊖: -95°C; △: -90°C; ⊕: -85°C
●: -80°C; ●: -75°C; ∇: -70°C; ○: -60°C; ⊙: -50°C
- II. L-6, ⊖: -100°C; ●: -70°C; △: -40°C; ●: -35°C; ⊕: -30°C;
∇: -20°C; ●: -10°C; X: 0°C; ○: 10°C; ●: 17°C; ⊙: 25°C; ⊕: 30°C.

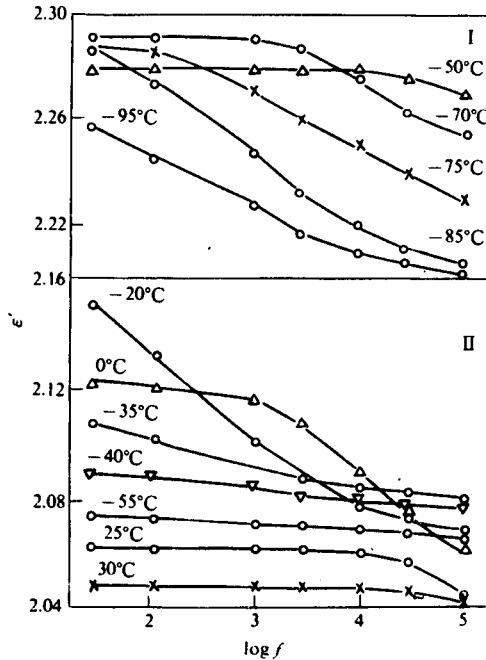


Fig. 2 Variation of permittivity with frequency

I. V-38; II. L-6

2. Master curves

Obviously, the relaxation curves measured within the experimental frequency range are not complete. To achieve a complete relaxation curve over a wide frequency range, it is necessary to construct a master curve from the limited experimental data determined within a narrower frequency range according to the frequency-temperature superposition principle. In this work, the master curves for various samples were drawn with the T_g at 100KHz as a reference temperature. It

is considered that master curves are of practical importance since polymer materials are mostly used at about room-temperature and the T_g of these samples are near to the room-temperature at 100KHz.

For the construction of master curve, the first thing to be done is to calculate shift factor by WLF equation, and therefore, the coefficients C_1 and C_2 of WLF equation must be evaluated from the experimental data. For achieving this, the WLF equation is rearranged as

$$-(T - T_s)/\log b_T = C_2/C_1 + (1/C_1)(T - T_s) \quad (3)$$

where b_T is dielectric shift factor and T_s is reference temperature. Then, C_1 and C_2 can be evaluated from the slope and intercept of the plotting of $-(T - T_s)/\log b_T$ against $(T - T_s)$. The WLF plotting so drawn for samples L-6 and S-8 are shown in Fig.3. And the C_1 and C_2 values with T_g at 100KHz as a reference temperature for various samples are given in Table 3.

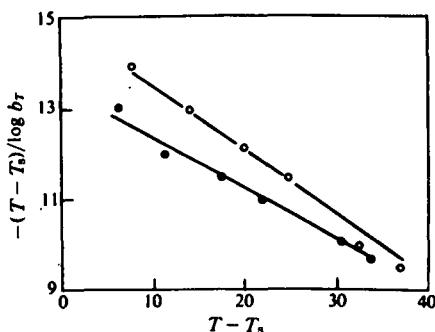


Fig. 3 The WLF plottings for samples L-6 and S-8

● L-6, $T_s = 282^\circ\text{K}$; ○ S-8, $T_s = 296^\circ\text{K}$.

Table 3 The C_1 and C_2 of various samples with T_g at 100°K as T_s

Sample	V-38	V-61	L-6	S-8	S-10
C_1	9.67	9.09	8.89	8.71	8.56
C_2	112.0	112.0	112.0	106.0	75.8

When constructing a master curve, in addition to horizontal shift according to WLF equation, the experimental data must be vertically shifted according to the following relationships^[5,6]

$$\epsilon'_s = \epsilon'_T \left[\frac{T\rho_s}{T_s\rho_T} + \frac{\epsilon_\infty}{\epsilon'_T} \left(1 - \frac{T\rho_s}{T_s\rho_T} \right) \right] \quad (4)$$

$$\epsilon''_s = \epsilon''_T \frac{T\rho_s}{T_s\rho_T} \quad (5)$$

$$\omega_s = \omega_T b_T \quad (6)$$

where ρ is the density of the samples and the subscripts T and s indicate the values at temperature T and reference temperature T_s , respectively. It is a bit troublesome to measure the density of the samples at various temperatures, while the measurement of volume expansion coefficient is relatively convenient, and so the volume expansion coefficient was used instead of the density in calculation of ϵ'_s and ϵ''_s .

The master curves constructed following the above procedure for sample L-6 are shown in Fig.4, which are similar in shape to that constructed from dynamic mechanical data of 1, 2-polybutadiene by Yanovsky^[1]. It should be checked by calculation theoretically whether the master curve constructed is in accordance with the objective one. In this work, ϵ' and ϵ'' values of sample L-6 were calculated by Havriliak-Negami equation as follows

$$\frac{\epsilon(\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = A^{-1} \cos \beta \theta \quad (7)$$

$$\frac{\epsilon''(\omega)}{\epsilon_0 - \epsilon_\infty} = A^{-1} \sin \beta \theta \quad (8)$$

$$A = [1 + (\omega\tau)^{1-\alpha} \sin(\alpha\pi/2)]^2 + [(\omega\tau)^{1-\alpha} \cos(\alpha\pi/2)]^2$$

$$\theta = [(\omega\tau)^{1-\alpha} \cos(\alpha\pi/2)] / [1 + (\omega\tau)^{1-\alpha} \sin(\alpha\pi/2)]$$

The five parameters in the equation were evaluated by complex plane analysis of the dielectric measurement data, in which ϵ_0 is 2.098; ϵ_∞ , 2.012; α , 0.22; β , 0.38 and τ , 1.59×10^{-6} sec. The calculated results are also plotted in Fig.4 (Solid line), it can be seen that the calculated values are consistent with the master curve in the glass transition range. This shows that the master curve constructed reflects approximately the objective case of the change in $\epsilon'(\omega)$ and $\epsilon''(\omega)$ with frequency in the glass-transition region.

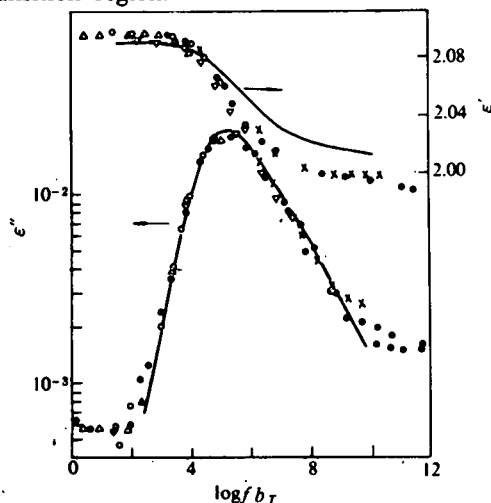


Fig.4 The master curve of sample L-6

● - 40°C; ○ - 35°C; X - 30°C; ⊕ - 20°C; ▽ - 10°C
 ⊖ 0°C; Δ 10°C; 0 25°C; ⊗ 30°C.

The solid line is the calculated values, $T_g = 282^\circ\text{K}$.

3. Structure dependence of the dielectric relaxation

The master curves for three samples with different contents of 1, 2-units are shown in Fig.5. It is evident that the intensity of the glass-transition increases with the increase in the content of 1, 2-units and the width of the transition peak is the greatest for sample V-61 with 45% 1, 2-units. The same is true in the curves of dielectric loss vs. temperature of the samples. For sample L-6 with 71% 1, 2-units, an increase in dielectric loss with reducing frequency below 100Hz can be observed, which may be the tail part of a low-frequency transition. When frequency is higher than

10^9 Hz, there seems to have a decrease in dielectric loss with the increase in the content of 1, 2-units.

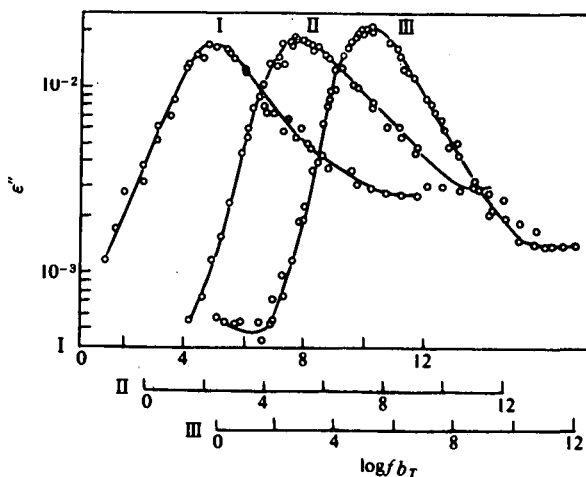


Fig. 5 The master curves for the samples with different contents of 1, 2-units
I. V-38; II. V-61; III. L-6

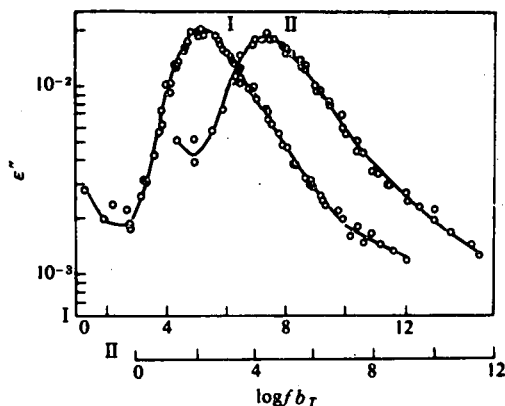


Fig. 6 The master curves for the samples with different contents of syndiotactic 1, 2-units
I. S-8; II. S-10

In Fig.6 are shown the master curves for the samples with different configuration of 1, 2-units. It appears that the intensity of the glass-transition is lower for the sample with higher content of syndiotactic 1, 2-units than for the one with lower content of syndiotactic 1, 2-units.

Keywords:

1, 2-Polybutadiene; Dielectric Properties; Permittivity

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