

DIELECTRIC PROPERTIES OF 1,2-POLYBUTADIENES

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ABSTRACT

The dielectric permittivity and loss tangent of 1,2-polybutadienes with different chain structures were determined as a function of temperature from -180°C to 100°C at different frequencies, and the frequency and structure dependence of the dielectric properties of 1,2-polybutadienes have been investigated. It is found that a maximum of the permittivity occurs in the glass-transition region. The width of the glass-transition peak increases with increasing frequency while its height has little change. With a rise in the content of 1,2-units, the permittivity decreases and the height of the glass-transition peak slightly grows. A maximum of the width of the glass-transition peak appears when the content of 1,2-units is about 45%. Both the permittivity and dielectric loss drop down as the growth of the content of syndiotactic 1,2-units.

INTRODUCTION

1,2-polybutadienes have a variety of chain structure, leading them to possess many properties useful in the fields of rubber, plastics, coating and so on^[1-3]. Therefore, 1,2-polybutadienes have recently attracted a large volume of research works concerning their synthesis, structure, mechanical properties, processing, utilization, etc. However, up to now there has not been a detailed report about their dielectric properties. This may be due to a fact that 1,2-polybutadienes are synthesized from non-polar monomer, butadiene, and therefore, they may be considered as having low dielectric activity. But it is not the case. In fact, although the polarity of 1,2-polybutadienes is weak, it is still sufficient to render them a fair dielectric activity for dielectric study. This is because 1,2-polybutadienes contain vinyl side group, the structure of which is corresponding to that of propylene with a dipole moment of 0.35 Debye^[4], and besides, it is hard to avoid containing a trace amount of carbonyl group in the polymers^[5] as other hydrocarbon polymers do, especially those containing unsaturated $\text{C}=\text{C}$ bonds^[6]. Such trace amount of carbonyl group make the polymers dielectrically active without seriously disturbing other properties^[7].

Dielectric measurements have proven to be a valuable tool in the study of polymer physics. The investigation of dielectric properties of a polymer over a wide frequency and temperature ranges would provide a lot of information about the structure and molecular motion of the polymer^[6,8,9], with both theoretical and practical significance.

The purpose of this paper is to present the results of dielectric measurements of 1,2-polybutadienes with different contents of 1,2-units and different chain configurations over a temperature range from -180°C to 100°C and frequency range of 30Hz to 100KHz.

EXPERIMENTAL

1. Samples

1,2-polybutadiene samples used in this work were prepared in our laboratory. Those labelled 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 Li(*n*-Bu) as a catalyst and the microstructure was regulated by tetrahydrofuran. The microstructure of the samples was determined by IR method and the configuration was estimated by ^{13}C -NMR spectroscopy. Intrinsic viscosity was measured in toluene at 30°C. The structural parameters of the samples are given in Tables 1 and 2. The samples were further purified in order to remove impurities as completely as possible. The specimen being used for dielectric measurements were made at 100°C using a laboratory press. The applied pressure is 100kg/cm².

Table 1 The structural parameters of the samples

Sample	L-3	V-38	D-4	4-61	V-7	L-6
1,2-unit(%)	7	21	36	45	57	71
<i>cis</i> -1,4-unit(%)	41	28	32	26	19	16
<i>trans</i> -1,4-unit(%)	52	51	32	29	24	13
$[\eta]$ (dl/g)	3.06	3.22	3.01	3.39	3.77	2.99

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

Configuration(%)	Syndiotactic	Isotactic	Atactic	$[\eta]$ (dl/g)
S-8	18	41	41	3.46
S-10	33	25	42	3.39

2. Dielectric measurements

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

RESULTS AND DISCUSSION

1. Multiple dielectric dispersion regions

The curves of dielectric loss(ϵ'' or $\tan\delta$) and permittivity (ϵ') versus temperature are usually called dielectric relaxation spectra while the curve of ϵ'' and $\tan\delta$ vs. temperature is called the dielectric loss spectrum and that of ϵ' vs. temperature the dielectric dispersion spectrum. Fig.1 shows the dielectric spectra of sample S-10 at different frequencies. Two well-defined relaxation regions are observed in the dielectric loss spectra. One having higher intensity and locating at higher temperature is certainly attributed to the glass-transition of the sample, and the other having very low intensity and over a broader temperature range is a secondary relaxation. There seems to be another secondary relaxation region between -60°C and -20°C, but it is not quite sure

for the moment. Besides, a $T > T_g$ relaxation process, called T_{II} transition, appears between 40°C and 90°C, which although rather vague, is consistent with a report by Sidorovitch^[10] who was the first to observe T_{II} transition in 1,2-polybutadienes. It is very interesting to notice that more relaxation regions are revealed in the dielectric dispersion spectra, denoted by α , β , γ , δ in the order of decreasing temperature. The assignments of various relaxation processes observed here will be discussed in another paper.

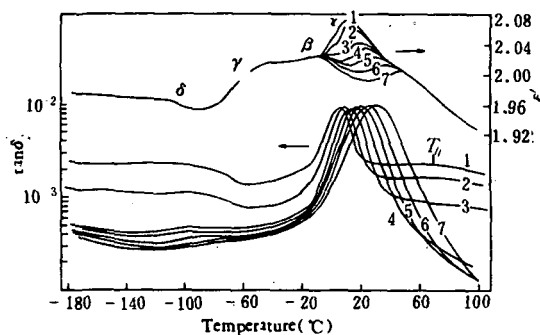


Fig.1 Dielectric spectra of sample S-10 at different frequencies

1, 30Hz; 2, 110Hz; 3, 1KHz; 4, 3KHz; 5, 10KHz; 6, 30KHz; 7, 100KHz

It is found that in some relaxation regions permittivity peaks occur and differ from those of typical non-polar hydrocarbon polymers such as polyethylene, atactic polypropylene, and polystyrene, in which no ϵ' peaks can be observed in the glass-transition region^[6]. But they are quite similar to those of isotactic vinyl polymers and some other polymers with a weak polarity.

2. Frequency dependence of the dielectric properties

Fig.1 also shows the frequency dependence of the dielectric properties of 1,2-polybutadienes. In the α relaxation region, with increasing frequency the permittivity peak decreases and shifts toward higher temperature. This mainly arises from the decrease in the concentration of the dipoles oriented with the alternating electric field. Below the α relaxation region, ϵ' has little change with varying frequency, implying that the segmental motion of the polymers is frozen and so the orientation of dipoles is hard to take place at this time and only an electronic and atomic polarization are responsible for the dielectric properties. Above α relaxation range, ϵ' is also independent of frequency, due to the fact that the frequency of the orientation of dipoles become larger than that of the alternating electric field applied. As to the dielectric loss, $\tan\delta$, it can be seen from Fig.1 that both below and above the α relaxation range, $\tan\delta$ decreases with increasing frequency while the intensity of $\tan\delta$ peak keeps little changed with frequency within the α relaxation region.

3. Relationship between the dielectric properties and the content of 1,2-units

The dielectric dispersion spectra of the samples with different contents of 1,2-units are shown in Fig.2. As can be seen, with the increase of content of 1,2-units, ϵ' values decrease although the magnitude of the decrease is a little low. Above α relaxation region, the ϵ' values of the various samples except one with 21% content of 1,2-units tends to coincide with rising temperature.

Fig.3 shows the dielectric loss spectra of the samples with different contents of 1,2-units. It can be seen that with the increase of content of 1,2-units, the intensity of the dielectric loss peak

becomes higher within the glass-transition region, and the dielectric loss decreases below the glass-transition region.

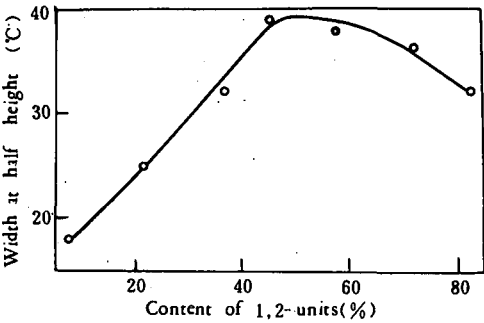


Fig.2 The dielectric dispersion spectra of the samples with different contents of 1,2-units at 1KHz

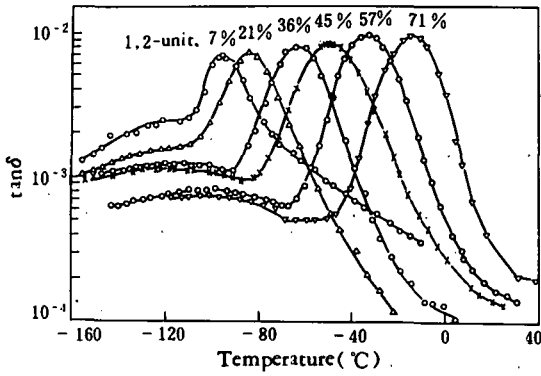


Fig.3 The dielectric loss spectra of the samples with different contents of 1,2-units at 1KHz

From Fig.3 it is also found that the change in the width of the glass-transition peaks with the content of 1,2-units is not monotone but shows a maximum. As shown in Fig.4, the maximum of the width of the glass-transition peaks appears when the content of 1,2-units is about 45%.

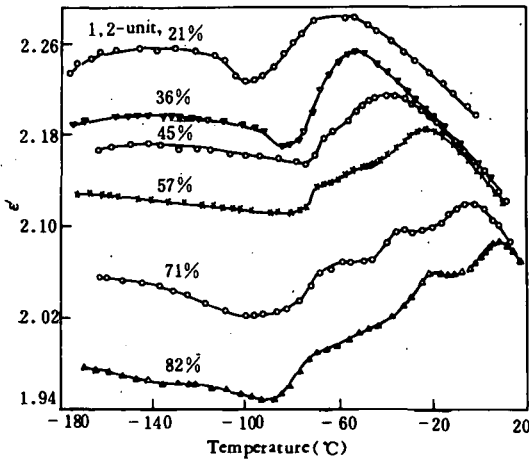


Fig.4 Relationship between the width of the glass-transition peaks and the content of 1,2-units

4. Stereochemical dependence of the dielectric properties

The dielectric spectra of the samples with different contents of syndiotactic 1,2-units are shown in Fig.5. With the increase of the content of syndiotactic 1,2-units, the permittivity decreases throughout the whole experimental temperature range, and the intensity of the glass-transition becomes lower and its location shifts to higher temperature. Below the glass-transition range, the dielectric loss values are close to each other for the two samples. In the syndiotactic configuration, the directions of the dipole vectors on vinyl groups are opposite to each other and this will lead to a counteraction of the part of the dipoles so that the effective dipole moment, a vector sum of all dipoles, will become smaller or even tend to null. Besides, the inter- and intramolecular interactions of the polymers all increase with a rise in content of syndiotactic 1,2-units, which will cause a growth of the potential barrier for the orientation of dipoles accompanying the applied alternating electric field. It is a joint result from the two kinds of effect mentioned above that the decrease in dielectric loss and permittivity with the increase of the content of syndiotactic 1,2-units.

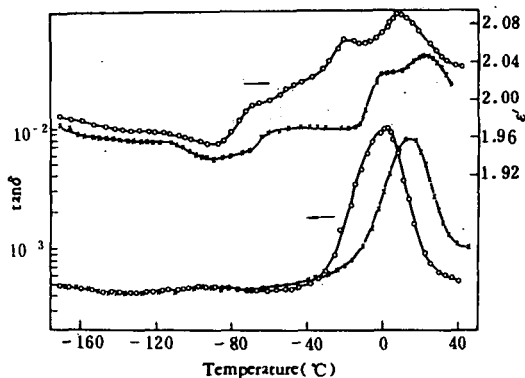


Fig.5 The dielectric spectra of the samples with different contents of syndiotactic 1,2-units at 3KHz.

Keywords:

1,2-polybutadiene; Dielectric properties; Permittivity; Loss tangent

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