

CARBON-13 NMR STUDY ON MOLECULAR MOTION OF 1,2-POLYBUTADIENE—TEMPERATURE DEPENDENCE OF MOLECULAR MOTION

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ABSTRACT

Proton-decoupled, ^{13}C FT-NMR (operating at 50.3 MHz) is used to determine spin-lattice relaxation time (T_1), nuclear Overhauser enhancement (NOE), linewidth and chemical shift of 1,2-polybutadiene as a function of temperature in CDCl_3 solution and the temperature dependence of molecular motion of 1,2-polybutadiene has been investigated with these NMR relaxation parameters. It is found that jumps of NOE and linewidth vs. temperature appear between -10°C and -30°C . The minimum of nT_1 vs. temperature for all carbons occur at about -45°C .

The molecular motion of polymers is intensely dependent upon temperature. However, in a polymer there are many kinds of motion units, each of them has itself temperature dependence of motion different from that of other units. It is of great significance to study the particular temperature dependence of dynamics of individual motion unit in polymers. For this purpose, high-resolution NMR technique is a very powerful tool. The NMR relaxation parameters for individual nucleus in a molecule can be determined as functions of temperature, structural parameters and other factors and this makes it possible to microscopically search dynamics of single atom in a polymer^[1,2]. In this paper, the carbon-13 spin-lattice relaxation times (T_1), nuclear Overhauser enhancement factors (NOE), linewidths and chemical shifts for various carbons in 1,2-polybutadiene in CDCl_3 solution were measured as a function of temperature from -70°C to 30°C on 200 MHz pulse FT-NMR spectrometer (^{13}C operating frequency is 50.3 MHz), and the temperature dependence of the molecular motion of 1,2-polybutadiene has been investigated.

EXPERIMENTAL

1,2-Polybutadiene sample used in this work is prepared with molybdenum catalyst^[3]. The content of 1,2-units in the sample is 80%, the intrinsic viscosity is 4.14 and the M_w/M_n is 1.31. T_1 is determined by $180^\circ-t-90^\circ$ pulse sequence and NOE is estimated by comparison between the intensities of the resonance peaks with proton-decoupled and proton-

coupled.

RESULTS AND DISCUSSION

1. Variation of NOE values with temperature

According to NMR theory^[4], if ^{13}C - ^1H dipolar interaction is predominant, and segmental motion is isotropic, ^{13}C NOE can be given by

$$\text{NOE} = 1 + \frac{R}{\alpha} \left(\frac{6\tau_c}{1 + (\omega_H + \omega_C)^2 \tau_c^2} - \frac{\tau_c}{1 + (\omega_H - \omega_C)^2 \tau_c^2} \right) \quad (1)$$

where $R = \frac{\gamma_H}{\gamma_C}$, and

$$\alpha = \frac{\tau_c}{1 + (\omega_H - \omega_C)^2 \tau_c^2} + \frac{3\tau_c}{1 + \omega_C^2 \tau_c^2} + \frac{6\tau_c}{1 + (\omega_H + \omega_C)^2 \tau_c^2}$$

γ_H , γ_C and ω_H , ω_C are gyromagnetic ratios and the Larmor frequencies for ^1H and ^{13}C , respectively, τ_c is the average rotational correlation time for the carbon of interest. If temperature is high enough to make molecular motion satisfying the extreme narrowing condition, that is,

$$(\omega_H + \omega_C)\tau_c \gg 1 \quad (2)$$

then NOE will reach its theoretic maximum

$$\text{NOE} = 1 + \frac{1}{2}R = 2.988 \quad (3)$$

NOE values will fall down from the theoretic maximum with reducing temperature in spite of the relaxation mechanism, and when temperature is reduced to the value so low that the term $\omega\tau_c$ is far larger than unity, the NOE will fall down to the theoretic minimum

$$\begin{aligned} \text{NOE} &= 1 + R[6(R-1)^2 - (R+1)^2] / [6(R-1)^2 + (R+1)^2 + 3(R-1)^2(R+1)^2] \\ &= 1.153 \end{aligned} \quad (4)$$

NOE values will vary over a range from 2.988 to 1.153 with temperature, of course, on condition that dominant relaxation mechanism responsible for T_1 and NOE is ^{13}C - ^1H dipolar interaction. The variation of NOE with temperature is associated with molecular motion, so that some information about molecular motion can be drawn out from the temperature dependence of NOE.

In Fig. 1 is shown the temperature dependence of NOE for some carbons in the sample. As is seen from Fig. 1, the NOE values for all carbons considered are about 2.6 at 30°C , lower than the theoretic maximum 2.988. This indicates that the segmental motion of the sample has deviated from the extreme narrowing condition at this temperature. The NOE values for all carbons decrease with a drop in temperature and the theoretic minimum of 1.15 is reached for methylene carbon, $-\text{CH}_2-$, in *trans*-1,4-units at -30°C while those for other carbons do not fall down to that value even at -70°C .

It can be observed in Fig. 1 that a jump of NOE vs. temperature appears between -10°C and -30°C and this implies that there is a transition over this temperature range. But it is impossible to assign this transition only on the NOE data.

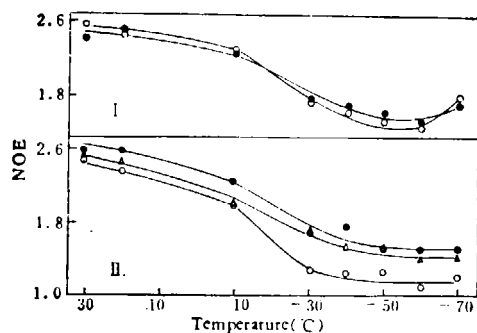


Fig. 1 Variation of NOE values with temperature

I. Vinyl group, $\bullet$ $=\text{CH}_2$; $\circ$ $-\text{CH}=\text{}$

II. Skeletal chain, $\circ$ $-\text{CH}_2-(\text{T})$; $\triangle$ $-\text{CH}-(\text{V})$; $\bullet$ $-\text{CH}_2-(\text{V})$

T and V represent *trans*-1,4- and 1,2-units, respectively.

2. Variation of nT_1 with temperature

If the ^{13}C - ^1H dipolar interaction dominates the ^{13}C -NMR relaxation and segmental motion can be described in terms of the single correlation time model, then T_1 can be expressed as

$$\frac{1}{T_1} = \frac{h^2}{40\pi^2} \gamma_H^2 \gamma_C^2 \sum r_i^{-6} [f(\omega_H - \omega_C) + 3f(\omega_C) + 6f(\omega_H + \omega_C)] \quad (5)$$

where $f(\omega) = \tau_c / (1 + \omega^2 \tau_c^2)$, h is Plank constant. Because of the second-power dependence on τ_c , there must be minimum of T_1 vs. temperature corresponding to transition associated with certain mode of molecular motion.

In Fig. 2 is shown the variation of nT_1 values of various carbons in 1,2-units with temperature. The minimum of nT_1 vs. temperature for all carbons occur at about -45°C . And this means that there is a transition over a temperature range around -45°C , furthermore, the molecular process of this transition can also be deduced from the fact that the nT_1 minimums are observed for all carbons in both skeletal chain and vinyl group within the same temperature range, which imply that the transition is related to the motions of both skeletal chain and vinyl group. So it is reasonable to say that this transition is corresponding to the β and γ transitions observed by dielectric relaxation method presented in our previous work^[5].

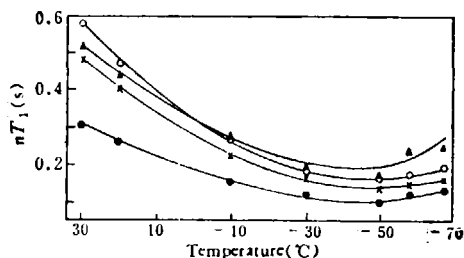


Fig. 2 Variation of nT_1 values of the carbons in 1,2-units with temperature

$\circ$ $-\text{CH}=\text{}$; $\triangle$ $-\text{CH}_2-$; $\times$ $=\text{CH}_2$; $\bullet$ $-\text{CH}-$

It can be seen from Fig. 2 that the variation of nT_1 values with temperature for methylene carbon in skeletal chain is not as sharp as those for other carbons, this may be attributed to the high mobility of methylene group. Between 30°C and -40°C the differences between the nT_1 values of various carbons become smaller.

In Fig. 2 no breaks of the curves of nT_1 values vs. temperature appear between -10°C and -30°C as do in the curves of NOE values vs. temperature and this shows that the transition observed in the curves of NOE values vs. temperature does not arise from short-range molecular motion.

3. Temperature dependence of linewidth

For Lorentz NMR line shape, the linewidth at half height is in inverse proportion to spin-spin relaxation time T_2 ^[6],

$$\Delta H_{1/2} = 2/T_2 \quad (6)$$

where $\Delta H_{1/2}$ is the linewidth at half height in Hz. It has been well known that T_2 depends on the molecular motion at low frequencies, so that it can be employed to characterize the long-range molecular motion of polymers. The linewidth can play the same role as T_2 for investigating molecular motion because of simple inverse proportional relationship between them.

The temperature dependence of ^{13}C -NMR linewidths for various carbons in the sample is shown in Fig. 3. It can be seen from Fig. 3 that above 10°C the temperature effect on the linewidths of two carbons in vinyl group is very weak while the linewidths of other carbons slightly increase with decreasing temperature. This appears to indicate that the temperature effect is stronger on the motion of vinyl group than on the motion of skeletal chain. Below -30°C the linewidths of all carbons except the methylene carbons in *trans*-1,4-units increase slightly with reducing temperature. It is of interest to note that the linewidth of two carbons in *trans*-1,4-units is approximate to those of other carbons in skeletal chain above -10°C, but below -10°C the increase in the linewidths of the carbons in *trans*-1,4-units with reducing

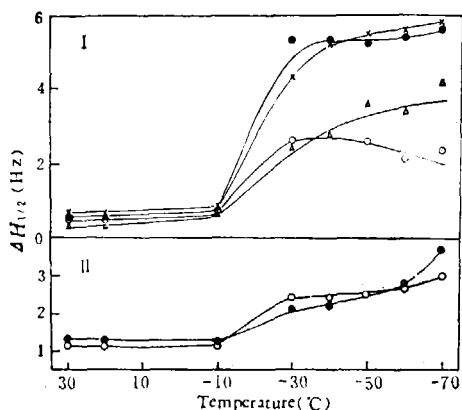


Fig. 3 Temperature dependence of ^{13}C -NMR linewidth

- I. Skeletal chain, ● $-\text{CH}=\text{C}$; × $-\text{CH}=\text{V}$; △ $-\text{CH}=\text{T}$; ○ $-\text{CH}_2-\text{T}$
 II Vinyl group, ● $=\text{CH}_2$; ○ $-\text{CH}=\text{}$

temperature are far smaller than those in the linewidths of other carbons. This may suggest that the mobility of *trans*-1,4-units is higher than that of other units at the temperature low enough. Schaefer^[7] had also observed the similar phenomenon in polyisoprene and he proposed that this is associated with the greater freedom of the extended *trans* configuration.

In Fig. 3 jumps in the curves of linewidth vs. temperature for various carbons are observed between -10°C and -30°C , being in accordance with the jumps of NOE vs. temperature in Fig. 1. As linewidth is characteristic of long-range molecular motion, it could be inferred that the transition between -10°C and -30°C arises from some larger motion units. Comparing it with the glass-transition of the bulk sample determined by means of dynamic mechanics which also appears between -10°C and -30°C (Fig. 4), it is concluded that the transition observed between -10°C and -30°C in the plotting of NOE and linewidth against temperature are corresponding to the glass-transition of the sample.

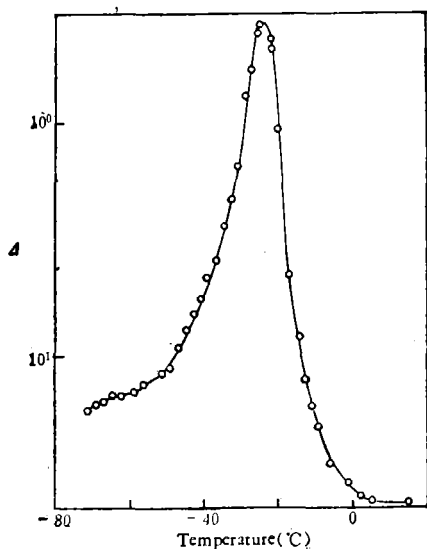


Fig. 4 Dynamic mechanic spectrum of the bulk sample determined by torsional pendulum

4. Temperature effect on chemical shift

It has been known that chemical shift is caused by electronical shielding surrounding the nucleus of interest, and so chemical shift increases with the decrease in the density of electronical cloud surrounding the nucleus. This will be true as in the case of decreasing temperature, because the decrease of temperature must result in slowdown of molecular motion and shortening of the distance between the nucleuses which strengthen the interrepellent of electronical cloud. This will lead to a decrease in electronical shielding and an increase in chemical shift for some nucleuses. The temperature dependence of chemical shift of polymers is related to their structures and molecular motion.

The chemical shift values of various carbons at different temperature are given in Table

1. It is seen from Table 1 that a greater change in chemical shift for the tail-carbon ($=CH_2$) in vinyl group can be observed with decreasing temperature while the chemical shift values for the tertiary carbon ($-CH=$) in vinyl group and methine carbon ($-CH-$) in skeletal chain keep roughly constant. This is because the tail-carbon in vinyl group suffers from a great repellent due to its site on the outside of main-chain, whereas the tertiary carbon in vinyl group and the methine carbon in skeletal chain suffers from a bit constant repelling effect, owing to the fact that they are shielded by other nucleuses around them from the influence of the contract of volume.

Table 1 The chemical shift values of various carbons at different temperature

Temperature (°C)	30	20	-10	-30	-50	-60	-70
$-CH_2-$ (T)	30.0	30.0	30.2	30.2	30.5	30.6	—
$-CH-$ (V) 	38.6	38.5	38.6	38.5	38.6	38.7	38.7
$-CH_2-$ (V)	40.9	40.8	40.4	40.5	—	39.9	40.3
$=CH_2$ (V)	113.6	113.6	113.9	114.1	114.3	114.4	114.3
$-CH=$ (V)	143.3	143.2	143.3	143.3	143.3	143.3	143.3
$-CH=$ (C)	127.9	127.8	127.9	128.0	128.1	128.2	—
$-CH=$ (T)	131.7	131.6	131.7	131.7	131.8	131.8	131.6

REFERENCES

- [1] Heatley, F., *Prog. NMR Spectrosc.*, **1979**, *13*, 47.
- [2] Freeman, R. and Hill, H.D.W., *J. Chem. Phys.*, **1970**, *53*, 4103.
- [3] 倪少儒、唐学明, 化工学报 (*Journal of Chemical Industry & Engineering*), **1983**, *1*, 84.
- [4] Doddrell, D.; Glushko, V. and Allerhand, A., *J. Chem. Phys.*, **1972**, *56*, 3683.
- [5] 倪少儒、沈联芳、余赋生、钱保功, 高分子通讯 (*Polymer Communications*), **1986** (2), 88.
- [6] 王金山, 《核磁共振波谱仪与实验技术》, 机械工业出版社 (Nuclear Magnetic Resonance Spectrometers and Experimental Techniques, Mechanical Industrial Press), **1982**, p. 98.
- [7] Schaefer, J., *Macromolecules*, **1972**, *5*, 427.