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Nuclear Motions in Polyisobutylene by NMR

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Résumé.

Les mesures de temps de relaxation spin-réseau et spin-spin des protons dans le polyisobutylène sont interprétées ainsi que les valeurs des largeurs de raies et celles du second moment. Les résultats obtenus en résonance magnétique nucléaire sont reliés aux valeurs des pertes mécaniques et diélectriques ainsi qu'à la viscosité. On trouve que les résultats ne sont interprétés correctement que si on introduit deux mouvements moléculaires principaux, différant en fréquence par un facteur d'environ 10^3. Chaque mouvement implique une distribution des fréquences de relaxation.

Les mesures de résonance magnétique nucléaire confirment l'opinion déduite des données de viscosité, de pertes diélectriques et mécaniques que la bande de fréquences de corrélation la plus élevée est associée à un mouvement des chaînes moléculaires, ne mettant en jeu qu'un petit nombre de chaînons. La fréquence la plus basse est probablement associée avec le mouvement de plus grandes sections de la chaîne de polyisobutylène.

Proton magnetic resonance relaxation in polyisobutylene has been measured in the temperature range — 196° C to 220° C. Steady state and transient signal nuclear magnetic resonance results are correlated with other relaxation measurements.

The sample of polyisobutylene (PIB) was part of a special batch [3], which has been used in a number of mechanical, dielectric and nuclear magnetic resonance studies [1, 2, 3, 4, 5, 6, 7].

The low temperature region was investigated by means of a steady state nuclear magnetic resonance apparatus [5]. In the region above room temperature the pulse technique was used to measure T_1 and T_2 [6, 8]. The results obtained are summarised in figure 1. There is a minimum in T_1 of 24.1 msec at 50° C. T_2 is considerably smaller than T_1 even at the highest temperatures. Also, in the high temperature region the decay of the transverse nuclear magnetisation is consistent with a two-term exponential decay, $h_1 \exp(-t/T_{21}) + h_2 \exp(-t/T_{22})$, where $h_1 : h_2 \simeq 9 : 1$; and $T_{21} : T_{22} \simeq 1 : 3$. It is important to note that the ratio of (T_1/T_2) at the

minimum of T_1 is 73 as opposed to 2.25 as predicted by the single relaxation time theory due to Bloembergen, Purcell and Pound [9] (called here the BPP theory). Values of T_2 obtained from the line width and second moment measurements are also included in figure 1. In converting from

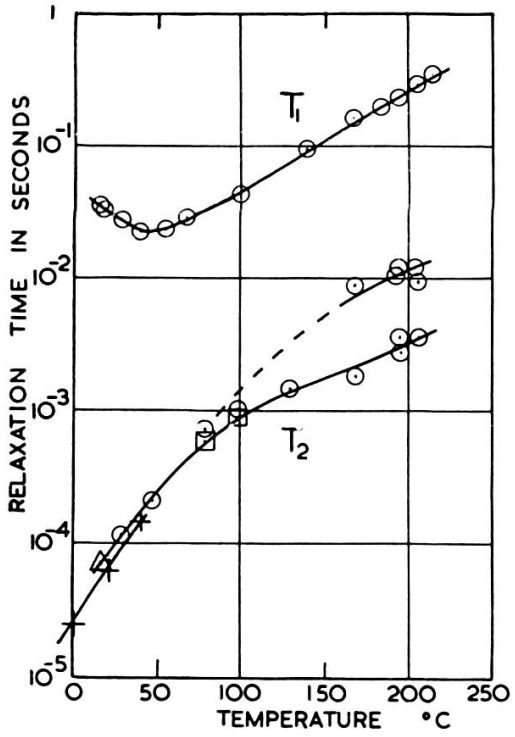

Fig. 1.

The experimental results. T_1 and T_2 versus temperature for PIB determined by the following methods [8].

⊙ — T_2 — from 90°, τ, 180°; pulse sequence.
⊙ — T_1 — from 180°, τ, 90°; pulse sequence.
□ — T_2 — from 90°, τ, 180°, 2τ, 180°, etc. sequence.
△ — T_2 — from ' Bloch decay '.
\+ — T_2 — from line width measurements [5].

Above 170° C the decay of the transverse nuclear magnetisation is consistent with two $T_2's$, as explained in the text.

the line width (δH) to T_2 it has been assumed, without much error, that the line shape is Lorentzian, in which case,

$$T_2 = \frac{2}{\sqrt{3}\,\gamma\,\delta H} \tag{1}$$

where γ is the proton gyromagnetic ratio.

Application of the BPP theory to our results reveals serious discrepancies between the correlation frequencies, $\nu_c(T_1)$, $\nu_c(T_2)$, and $\nu_c(\Delta H_2)$ derived independently from T_1, T_2 and the second moment (ΔH_2^2) values respectively. We therefore concluded that T_1 and T_2 (or ΔH_2) are con-

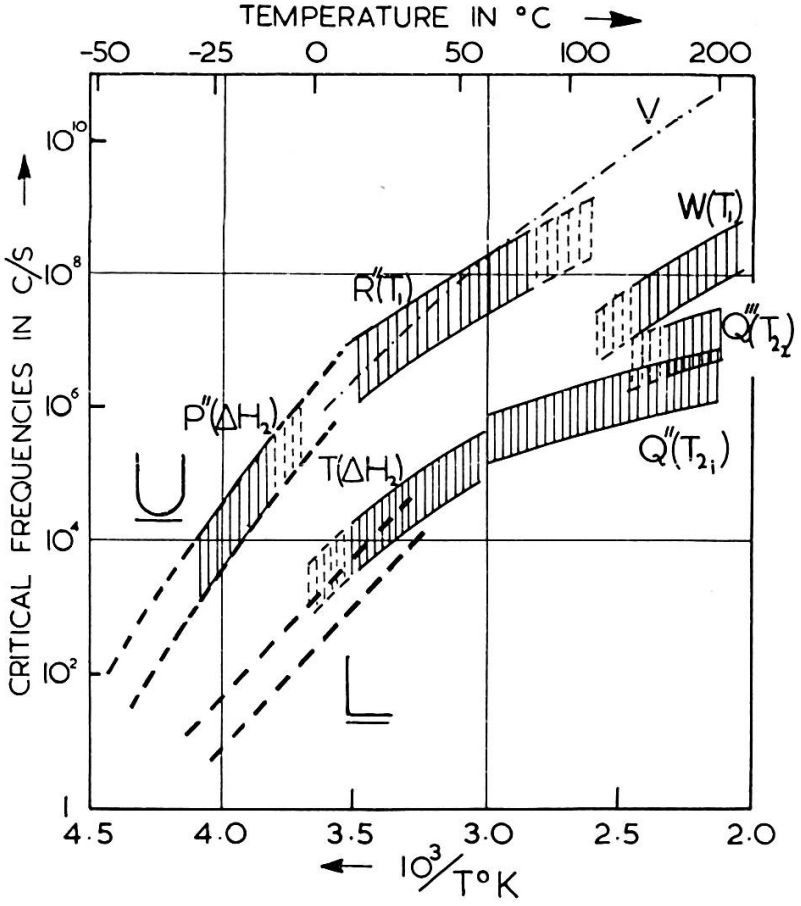

Fig. 2.

Transition map for PIB showing correlation of nuclear magnetic resonance results with mechanical, dielectric and flow viscosity measurements.

Bands $P''(\Delta H_2)$ and $T(\Delta H_2)$ are deduced from ΔH_2.
Bands $Q''(T_{21})$ and $Q'''(T_{22})$ are deduced from T_{21} and T_{22} respectively.
Bands $R''(T_1)$ and $W(T_1)$ are deduced from T_1.

Mechanical and dielectric results fall into two bands *U* and *L*. Curve V represents a plot of $\left(\frac{\eta}{T°K}\right)$ vs. $\frac{1}{T°K}$, where η is the flow viscosity of PIB.

trolled by separate processes in some temperature ranges and we have called on other data on PIB in support of our hypothesis.

Our expectations were verified because, as shown in figure 2, the dielectric and mechanical measurements show two absorption bands, *U*

and L, with their characteristic frequencies in the ratio of about 1000: 1, at a given temperature. However, variation of critical frequency with temperature derived from the NMR results differs considerably from those of band U and L [6]. On further analysis we have concluded that there are at least two basic motions each with a distribution of relaxation frequencies, which correspond in their centre frequencies to bands U and L [6].

In the choice of certain parameters of the two motions we were guided by mechanical and dielectric measurements. Thus, the spectrum of each motion was taken to consist of two discrete lines of equal intensity, and in the frequency ratio of 9: 1 for the fast process in band U, and 6: 1 for the slow process in band L. Details of this type of distribution are discussed in reference 6, but it may be mentioned here that unambiguous results for ν_c can only be obtained in temperature regions where one of the motions has a predominant influence on the nuclear signal. For example, below — 10° C ΔH_2 is controlled mainly by the faster motion; this region corresponds to band P″ (ΔH_2) in figure 2. On the other hand above + 10° C the slower motion determines ΔH_2; hence it is possible to deduce band T (ΔH_2). There is an analogous situation in the case of T_1. The result of this analysis is shown in figure 2 where the source of each frequency band in the figure is indicated by its symbol [6].

Figure 2 shows that bands P″ (ΔH_2) and R″ (T_1) refer to the mechanism which is associated with band U, and with the flow viscosity curve V, and bands T (ΔH_2) and W (T_1) belong to the lower frequency absorption band L. However Q″ (T_{21}) and Q‴ (T_{22}) show some divergence from the extrapolated band L and are not entirely consistent with W (T_1). In spite of these discrepancies a reasonable explanation of the behaviour of ΔH_2, T_2 and T_1 has been achieved over a wide range of temperature. The large ratio of (T_1/T_2) at the minimum of T_1 is satisfactorily explained because at this particular temperature T_1 is determined almost entirely by the fast motion, whereas T_2 is governed by the slow process.

Line width and second moment measurements show that intensities of interaction expressed in terms of the second moment values for a rigid lattice are between 11 and 19 gauss^2 for the faster motion and about 2 gauss^2 for the slower motion. These figures suggest that at about — 35° C where narrowing of the line is observed the CH_3 groups probably reorient very rapidly about their C_3 axes and that this narrowing is produced by motion of links in the PIB chain and is that associated with the band U. The low intensity of interaction for the slower motion in band L indicates probably

that the nuclear magnetic interaction is external to the molecule and most likely takes place between separate chains, or parts of the same chain. The low frequency of the motion is taken to mean that the entities involved in the process are segments of the PIB chain considerably larger than one link.

A more precise interpretation of the present results would be possible if nuclear magnetic resonance measurements were extended into the high temperature region both with the pulse and the high resolution steady state apparatus. Mechanical and ultrasonic absorption data in this region would also be very valuable.

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