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A STUDY OF LOCAL MOBILITY IN POLY(ISOBUTYLENE) BY THE SPIN PROBE METHOD

J. BARTOŠ[1]* and Z. HLOUŠKOVÁ[2]

[1]Research Institute of Rubber and Plastic Technology, CS-764 22 Gottwaldov, Czechoslovakia

[2]Polymer Institute, Centre of Chemical Research of the Slovak Academy of Sciences, CS-842 36 Bratislava, Czechoslovakia

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Abstract—A detailed study has been made of the rotation of the spin probe 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (TANOL) in the regime of fast motion in poly(isobutylene) using the activation energy; a free volume model of the probe mobility in the condensed phase is described. Results of the applications of exact and approximate treatments of the generalized free volume model are compared. An analysis of the geometrical and energy parameter of α-mobility has shown that the motion of the probe in the elastic state of the amorphous phase is controlled by local conformational mobility of small segments of the macromolecules.

INTRODUCTION

The problems of the dynamics of macromolecules in solid polymers are of great importance in polymer physics and chemistry. Their solution at molecular level governs the extent of understanding of a series of physical and physico-chemical processes, such as relaxation and phase transition, diffusion of molecules and macromolecules and chemical reactivity in polymer matrices.

An indirect way for study of the dynamics of chains in solid polymers is the spin-probe method using the ESR technique [1]. Essentially it consists of monitoring of the changes with temperature of ESR spectra of a relatively stable nitroxide radical dispersed between chains, as a result of changes in molecular motions of a polymer. The ESR spectrum of the radical is sensitive to change in basic characteristics of the probe motion with correlation time τ_R between 10^{-6}–10^{-11} sec. This interval is usually divided into two regions (1) slow regime (10^{-6}–10^{-8} sec) at lower temperatures and (2) fast regime (10^{-8}–10^{-11} sec) at higher temperatures. The second characteristic of the probe motion (distance of the boundary lines of the triplet signal $2A'_{zz}$) monotonously decreases with decreasing τ_R and thus with increasing temperature. In the region of the slow motion regime, $2A'_{zz} \simeq 60$–70 G, while in the regime of fast motion $2A'_{zz} \simeq 30$–40 G. The value $2A'_{zz} = 50$ G is sometimes used for characterizing the probe–polymer system. The transition between the two regimes occurs at this value, to which the parameter T_{50G} [2] corresponds.

The main problem in investigation of the molecular mobility of the medium by the spin probe is elucidation of the relation between the dynamics of the probe and of its surroundings. Some authors have reported that, for the fast regime, the probe motion is strongly influenced by the segmental mobility of the polymer [3,4].

According to the present ideas on mobility in the solid phase, the probe motion may be explained in two ways. In agreement with the activation energy approach, the motion of the probe is conditioned by energetic fluctuations in the close vicinity of the probe. Then the temperature dependence of the correlation time may be described by an Arrhenius equation:

$$\tau_R(T) = \tau_{\infty,R} \cdot \exp(-E_R/RT), \qquad (1)$$

where $\tau_{\infty,R}$ and E_R are respectively the pre-exponential term and the activation energy of the probe motion, and R is a universal constant. However, wide application of equation (1) in the regime of fast motions led to anomalously low values of $\tau_{\infty,R}$ (10^{-15}–10^{-22} sec) [5].

An alternative approach is based on the free volume concept [6, 7]. The re-orientation of the probe proceeds for sufficient fluctuation of the local free volume in its close vicinity, caused by molecular motions of the polymer. All versions of the free volume model of probe mobility in polymeric systems are based on the Bueche free volume treatment of the segmental mobility in polymer [8]. The original Kusumoto version [6] proposed for interpretation of $T_{50G} - Tg$ correlation, as well as the improved Bullock [9] and modified Tiňo versions [10], describe segmental mobility by the Williams–Landel–Ferry equation and provide size parameters for segmental motion. Recent generalization of these versions [7] using the modified Arrhenius equation, i.e. the Vogel–Fulcher–Tamman–Hess (VFTH) equation for the temperature dependence of relaxation frequency of α-mobility at $T > T_g$,

$$\phi_\alpha(T). = \phi_{\infty,\alpha} \cdot \exp[-B/(T - T_0)], \qquad (2)$$

where $\phi_{\infty,\alpha}$ is a pre-exponential factor, i.e. hypothetic frequency at $T \to \infty$, usually 10^{12}–10^{14} 1/sec; $B = E_\infty/R$ = empirical energy parameter of the mobility, E_∞ being the hypothetical activation energy of

*Present address: Deutsches Kunststoff Institut, Schlossgertenstnesse 6R, 6100 Darmstadt, F.R.G.

chain motion in an isolated state; and T_0 = empirical temperature parameter of the mobility of the polymer. The following relation for temperature dependence of the correlation time of the spin probe is found,

$$\tau_R(T) = \tau_{\infty,R} \cdot \exp\left(\frac{B \cdot f}{T - T_0}\right), \quad (3)$$

and, after using the approximation [6] $\ln(\tau_{50G}/\tau_\infty) = 13.8$ in a special expression:

$$T_{50G} - T_0 = \frac{B \cdot f}{\ln(\tau_{50G}/\tau_\infty)}. \quad (4)$$

Here $f = v_p^w/v_m^w$ is the ratio of van der Waals volumes of the probe and segment. Our expressions have advantages over previous ones [6, 9] because of a smaller number of parameters and they provide both geometrical and activation energy characteristics of segmental mobility, which controls reorientation of the spin probe. These characteristics allow, after considering the conformational microstructure of the given polymer and the present knowledge of conformational mobility, discussion of segmental mobility in terms of the conformation–segmental motions.

The aim of this paper is to apply both relations for the general version of the free volume model of probe mobility in polymeric systems, compare them and try to discuss segmental mobility in another polyolefin viz. poly(isobutylene) (PIB) in more detail.

EXPERIMENTAL

The samples were prepared from PIB (trade mark Oppanol BASF) and the spin probe 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (TANOL). The probe was introduced into the polymer by diffusion of vapours at 80°C during 6 hr. The ESR measurement was done on a Varian E-4 spectrometer equipped with an additional temperature device E-257. Rotation times τ_R of the spin probe in the region of fast motion were calculated applying the Freed–Fraenkl theory [11] using the relation:

$$\tau_R(T) = 6.7 \times 10^{-10} \cdot \Delta H_{+1} \left(\sqrt{\frac{I_{+1}}{I_{-1}}} - 1\right), \quad (5)$$

where ΔH_{+1} = line width of the low-field component of the spectrum, and I_{+1}, I_{-1} = intensities of the lines of low- and high-field components of the spectrum.

Rotation frequencies of spin probe $\phi_R(T)$ were obtained from:

$$\phi_R(T) = \frac{1}{2\pi\tau_R(T)}. \quad (6)$$

RESULTS AND DISCUSSION

Figure 1 shows the ESR spectrum of the small rigid probe TANOL in PIB at several temperatures. Figure 2 shows the so-called relaxation map of mechanical, dielectric and NMR frequencies in PIB in conventional Arrhenius coordinates log ϕ vs $1/T$ taken from a compilation [4], along with the values of the rotational frequencies of the TANOL probe. The existence of two types of molecular motions in PIB with different temperature variations is evident from the relaxation map: α-molecular motion with non-Arrhenius course assigned to co-operative segmental

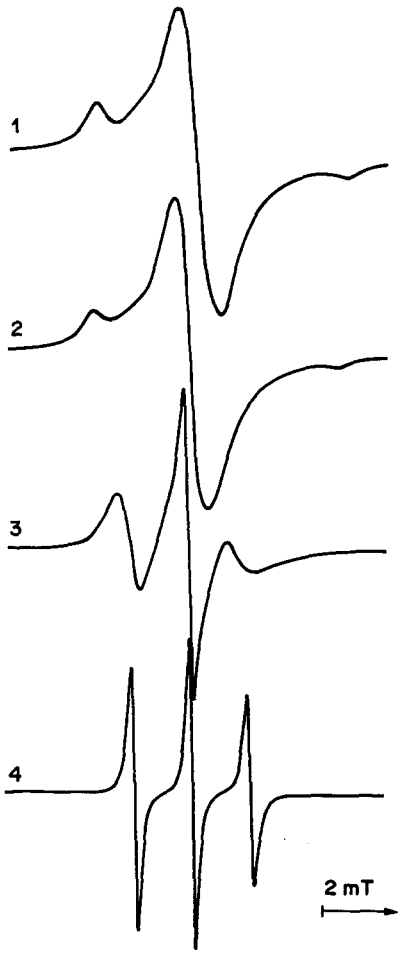

Fig. 1. ESR spectrum of the probe TANOL in PIB at 1, 183 K; 2, 243 K; 3, 303 K; 4, 363 K.

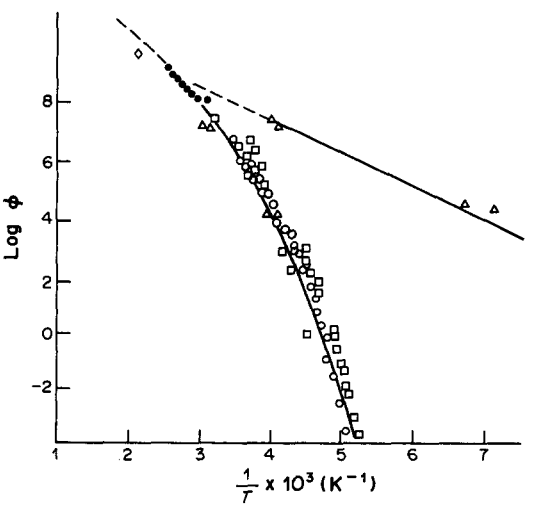

Fig. 2. Relaxation map of mechanical (□), dielectric (○), NMR (△) and hypersonic (◇) relaxation frequencies according to Ref. 4 along with rotational frequencies (●) of TANOL in PIB.

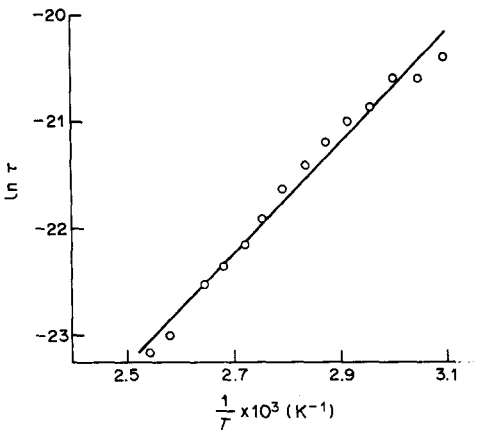

Fig. 3. Arrhenius plot of correlation times of the TANOL probe in PIB.

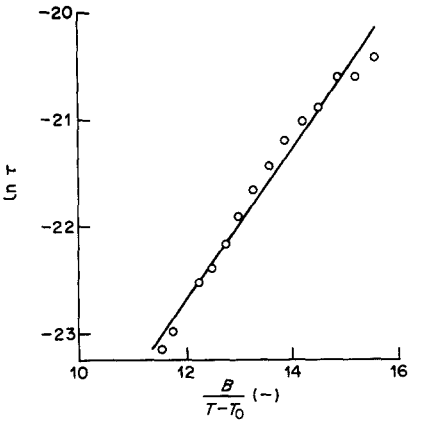

Fig. 5. Test of equation (3) for the TANOL–PIB system.

mobility and β-molecular motion of Arrhenius character attributed to the rotational motions of CH_3 groups. A comparison of the rotational frequencies of the TANOL probe with the frequencies of both types of relaxations shows that the motion of the probe in the region of the fast regime is more associated with the segmental mobility of the polymer.

Figure 3 shows that, over the limited range 323–393 K, the temperature dependence of the rotational correlation time of the probe in PIB may be described by an Arrhenius equation. Applying this equation, we obtain: $\tau_{\infty,R} = 1.9 \times 10^{-16}$ sec and $E_R = 43.0$ kJ/mol. While that activation energy has a reasonable value, the pre-exponential term has a value lower than expected (10^{-12}–10^{-14} sec). An analogous situation arises for α-mobility. Generally, over the wider temperature interval, the temperature dependence of relaxation frequency obeys the VFTH equation (2). Figure 2 includes the curve calculated from literature data $\phi_{\infty,\alpha} = 2.4 \times 10^{14}$ sec^{-1}, $B = 3125$ K and $T_0 = 122$ K [12]. For a rather narrow temperature interval, we can use for α-mobility the Arrhenius approximation which gives the parameters: $\phi_{\infty,\alpha} = 2.7 \times 10^{17}$ sec^{-1} and $E_\alpha = 60.5$ kJ/mol. Application of the Arrhenius equation for description

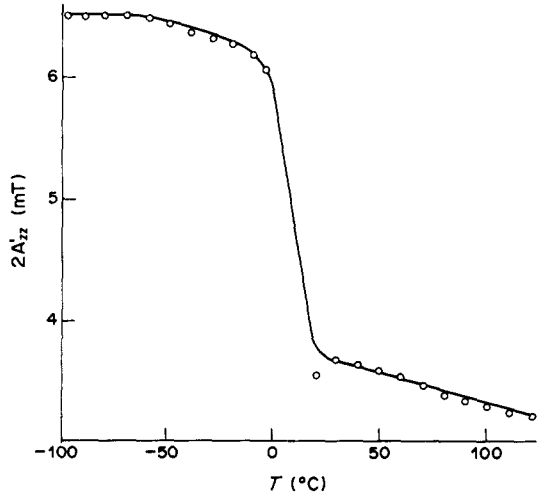

Fig. 4. Temperature dependence of the spectral parameter $2A'_{zz}$ for the TANOL–PIB system.

of α-mobility as well as rotation of the probe leads only to effective activation energies and to effective and unrealistic values of pre-exponential factors. For α-mobility, the effective activation energy given by the relation $E_{eff}(T) = E_\infty - [T/(T - T_0)]^2$ decreases with temperature, i.e. E_{eff} (323 K) = 67.2 kJ/mol and $E_{eff}(393) = 54.8$ kJ/mol and in the limit it reaches the value $E_\infty = 26.1$ kJ/mol. The activation energy approach is thus valid for α-mobility since it leads to plausible values of $\phi_{\infty,\alpha}$ and E_∞ (see below). On the other hand, for the system probe–polymer, it is not possible experimentally to extend the temperature interval of measurement and to record the temperature dependence of both parameters.

The free volume approach is more useful for detailed interpretation of the relationship between the probe and the polymer. Figure 4 shows a typical temperature dependence of the spectral parameter of the probe TANOL in PIB. The value $T_{50G} = 280$ K was determined from this dependence; from an approximate relation (4), we calculated parameter $f = 0.698$. On this basis and by the method of atomic and group contributions to van der Waals volumes [13], one can estimate the segment as having molecular volume $v_m^w = 252.1$ Å^3 or as the number of basic structural units of $N_m = 3.7 \simeq 4 \sim C(CH_3)_2$—$CH_2 \sim$ groups. Figure 5 shows application of the exact equation (3) considering the quality of a polymer through parameters B and T_0 without need of approximation for $\ln(\tau_{50G}/\tau_\infty)$. The geometrical parameter $f = 0.708$ was found by the method of least squares, resulting in $N = 3.6 \simeq 4$ for the structural unit in the segment of the PIB macromolecule. A comparison of f-values shows that, at least in this system, the value of $\ln(\tau_{50G}/\tau_\infty) = 13.8$ is a very good approximation. In addition, application of the general relation of the free volume model (3) leads to a realistic value of the pre-exponential factor of the probe $\tau_{\infty,R} = 2.9 \times 10^{-14}$ sec in contrast with the activation energy model.

As previously [7], the geometrical and energy parameters for α-segmental mobility in PIB may be discussed at a molecular level. Several conformational analysis of model compounds [14–16] of PIB have shown that the most stable conformation of the isolated chain is 8/3 helix formed by distorted pairs

$\sim tg^+\sim$ and $\sim g^-t\sim$, the most stable pairs having combination $\sim t_- g^+\sim$ and $\sim t_+ g^-_+\sim$. A study of the relation between the chain conformation in PIB in the elastic state and α-relaxation by the modified Adam–Gibbs model showed that the conformation of macromolecules in the elastic amorphous phase is predominantly determined by intramolecular interactions that cause the presence of relatively long segments of right- and left- helices [16]. This information on conformational microstructure leads, after considering the mobile criterion, i.e. the assumption of the minimal motion of the remaining parts of the chain out of the segment, to a conclusion on the mechanism of crankshaft motion with a minimum seven-bond segment:

$$Ps_n(tg^+ tg^+ t)\, s_{n+6}Q \rightleftharpoons Ps'_n(tg^+ tg^+ t)^x s_{n+6}Q.$$

This type of motion proceeds by either simultaneous or almost simultaneous crossing of the two rotational barriers s_n and s_{n+6}-th bond; the mobile part of the segment changes its position. From the geometrical point of view, the segment involves seven bonds, i.e. four structural units, in agreement with the ESR result. Another aspect of the dynamics of segmental mobility concerns the energy demands for the particular motion mechanism. The rotation-energy diagram of the model compound for PIB (2,2,4,4,6,6-hexamethylheptane) obtained using the molecular–mechanical method [15] shows that there are three main energy barriers between t,g^+, and g^- rotational states of the bond, with values: $E(g^\pm \rightarrow t) = 22.9$ and 24.5 kJ/mol, $E(g^+ \rightleftharpoons g^-) = 23.8$ kJ/mol, $E(t \rightarrow g^\pm) = 18.8$ kJ/mol; and three low barriers within the rotational bond states as a result of their distortions, $E(g^\pm_\mp \rightarrow g^\pm_\pm) = 2.6$ kJ/mol, $E(g^\pm_\pm \rightarrow g^\pm_\mp) = 1.0$ kJ/mol $E(t_+ \rightleftharpoons t_-) = 4.2$ kJ/mol. Using these data, we can estimate the overall energy barriers as a function of the way of crankshaft motion, viz. of (a) upper limit E_{hl} at strictly simultaneous transition of both barriers through segment end bonds and (b) lower limit E_{ll} corresponding to the consequent crossing of both barriers with s_n and s_{n+6}-th bond. In the first case, there are 42 modes of crankshaft motion as a function of the initial and final state of the rotating bonds [17]. The values of the total energy barrier in the isolated state are determined by an additive rule:

$$E_{hl} = \sum_{n=1}^{2} E_n(s \rightarrow s')$$

and vary between 37.7–48.9 kJ/mol [17]. On the other hand, during non-strictly simultaneous crankshaft motion, rotational motion of one bond is followed by crossing the rotational barrier of the second bond. Then the lower limit of the energy barriers is $E_{ll} = E_n^{max}(s \rightarrow s')$ [18] and can be approximated by the above values of the individual energy barriers between the rotational states of bonds varying between 18.8–24.5 kJ/mol. During rotation of one bond in the long chain, adjacent degrees of freedom are deformed and so the real values of E_{ll} will be a little higher. From a comparison of $E_\infty = 26.1$ kJ/mol from the Vogel equation with estimated limits of energy barriers of crankshaft motion, we have acceptable correlation with the course of consequent transition of both barriers of the segment in crankshaft mobility.

We may conclude from this analysis of geometrical and energy characteristics of segmental mobility in PIB that the rotation of the probe in the elastic state of the amorphous phase in the fast regime is controlled by local conformational mobility of small segments of the macromolecules.

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