

# Study of the molecular mobility in isotactic polypropylene by the spin-probe method

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*Dedicated to Professor Ing. A. Hrivík, CSc., in honour of his 60th birthday*

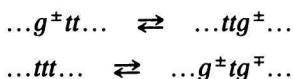
On the basis of the measured values for  $T_{50G}$  for four probes, quantities in isotactic polypropylene related to the molecular mobility are calculated from relations of free volume theory. We have determined: (i) average free volume at the temperature  $T_g$  ( $9 \times 10^{-30} \text{ m}^3$ ) and its temperature dependence and (ii) volume of a moving segment at  $T_g$  ( $3.54 \times 10^{-28} \text{ m}^3$ ).

На основе измеренных величин температуры  $T_{50G}$  для четырех зондов рассчитаны параметры характеризующие молекулярную подвижность в изотактическом полипропилене. Для расчетов были использованы формулы свободно-объемной теории. Были определены: (i) средний свободный объем при температуре  $T_g$  ( $9 \cdot 10^{-30} \text{ м}^3$ ) и его зависимость от температуры и (ii) объем движущегося сегмента при температуре  $T_g$  ( $3,54 \cdot 10^{-28} \text{ м}^3$ ).

In spite of an extensive experimental material and great theoretical efforts in the studies of the molecular mobility in polymer systems, there are still a vast number of problems to be solved. The knowledge of motions at molecular level and their characterization for concrete polymers is very important for understanding the mechanism of individual transitions in polymers. The investigation of the mobility has in most cases been concentrated on the changes in the rotational state of bonds [1]. The bond lengths and angles are considered to be fixed. The problem is in this case reduced to three specific rotational angles which show on the curve of the potential energy three minima — *trans* ( $t$ ), *gauche*<sup>-</sup> ( $g^-$ ), and *gauche*<sup>+</sup> ( $g^+$ ).

Conformational transitions in polymers must have a special character. If only a rotational motion about a bond of the polymer chain took place and all other bonds remained fixed, the tails would have to undergo a wide swinging motions, which would be strongly opposed by viscous and inertial forces. Several possibilities have arisen which eliminate this situation; they have been discussed in detail earlier [2] mainly in view of the cooperativeness of motions. An important finding of this paper is that immediately after rotation about one bond there was strong increase in the transition rate of its second-neighbour bonds, lasting for a short period of

time. The dominant types of transitions (occurring ten or more times as often as the other types) are



In both cases the first two and the last two bonds translate relative to each other. This type of motions, together with crankshaft and crank motions [3—5] cause fluctuation in free volume distribution and are associated with spin probe motions.

Spin probes which diffuse into the amorphous part of a polymer follow to some extent the motion of the polymer system [6] especially at  $T_g$  and above it, where fluctuation occurs in the free volume distribution because of the mentioned molecular motions [1, 5]. The volume and shape of the probe is also important for its motion. The frequency of the probe rotation can then be expressed as a function of the volume of the moving macromolecular segment ( $v_m$ ), volume of the probe ( $v_p$ ), and temperature [7, 8].

$$\ln(v_0/v) = \frac{c'_{1g} c_{2g}}{c_{2g} + T - T_g} B \quad (1)$$

Here  $c'_{1g}$ ,  $c_{2g}$  are the WLF parameters ( $c'_{1g} = 2.303c_{1g}$ ),  $v_0$  is the frequency of the free probe rotation (molecular constant) and  $v$  is the frequency of the probe rotation in the polymer matrix.

$$B = \frac{v_p}{v_m} = \frac{v_p^*}{v_m^*} \quad (2)$$

where  $v_m^*$  ( $v_p^*$ ) is the minimum free volume required by the segment (probe) to jump (rotate). If we choose for the temperature  $T$  the temperature at which the distance of the boundary lines of the EPR spectrum of the probe ( $2A_{zz}$ ) is just 5.0 mT ( $T_{50G}$ ) (Fig. 1), we can write eqn (1) in the form

$$T_{50G} - T_g = \left( \frac{c'_{1g} B}{\ln(v_0/v)} - 1 \right) c_{2g} \quad (3)$$

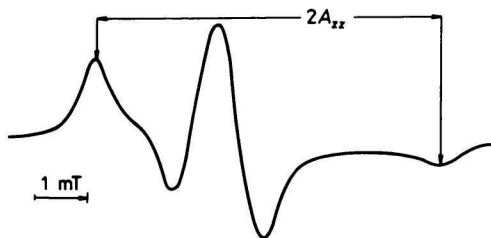


Fig. 1. EPR spectrum of the spin probe I in i-PP at 10 °C.  $2A_{zz}$  parameter.

The expression  $\ln(v_0/v)$  can here be replaced by a universal constant [7, 8] (13.8), or by a constant for the probe used [9] or it can be determined from the measurements of the rotational correlation times.

The value of  $T_{50G}$  in eqn (3) was determined by the EPR measurement. If  $T_g$  for the polymer is known, the parameter  $B$  can be found which is connected with the probe volume and the volume of the moving segment of the polymer chain. Spin probes allow then to look into the mechanism of the molecular mobility in polymer systems. In this paper we will point to (i) the application of free volume approach to the interpretation of the results of the EPR measurements of spin probes and to (ii) the connection between these results and the molecular mobility in isotactic polypropylene.

### Experimental

Isotactic polypropylene (i-PP), Tatren (Slovnaft, Bratislava) with the relative molecular mass  $M_r \approx 200\,000$ ,  $\rho$  (296 K) =  $0.905\text{ g cm}^{-3}$  was used for measurement. Stable nitroxide radicals of the type I, II, III, IV were introduced into the polymer from benzene solution of the concentration of  $1 \times 10^{-3}\text{ mol dm}^{-3}$ . Impregnation was done at room temperature for 48 h. The samples were then carefully dried at diminished pressure  $\approx 0.13\text{ Pa}$  and at 373 K till the measured spectrum started to change.

The EPR spectra were recorded on an X-band E-4 Varian spectrometer.

### Theoretical

In the first place we should note that eqn (1) derived by *Kusumoto* [8] and *Bullock* [7] from the ideas of *Bueche* [10] very simply follows from the known Doolittle eqn [11]

$$\ln\left(\frac{\tau_r}{\tau}\right) = B\left(\frac{1}{f_r} - \frac{1}{f}\right) \quad (4)$$

Here  $f$  is the free volume fraction and  $\tau$  is the rotational correlation time of the spin probe,  $r$  is the reference state.  $B$  is constant (in the case of the translational diffusion  $B \approx 1$  [11]). With respect to the relation (1) and (3), we are interested in the ratio between the correlation times corresponding to the temperature  $T_{50G}$  and the free rotating probe ( $T \rightarrow \infty$ ). At  $T \rightarrow \infty$ ,  $f \rightarrow \infty$  using relation (A8) eqn (4) assumes the form identical with (1)

$$\ln(\tau(T_{50G})/\tau(\infty)) = \ln(v_0/v) = \frac{B}{f(T_{50G})} = \frac{c'_{1g}c_{2g}}{c_{2g} + T_{50G} - T_g} B \quad (1a)$$

A similar relationship was found by *Vrentas* and *Duda* [12] in their study of the diffusion in the system polymer—solvent.

The expression  $\ln(v_0/v)$  in eqn (3) is not always determined from experimental measurements and is often replaced by the universal constant [7, 8]. However, since it should reflect specific features of the probe used, it is more useful to replace it by various values belonging to individual probes. The values have been determined in an earlier paper [9] where the dependence of  $RT \ln(v_0/v)$  on the mass of spin probes has been reported.

From the definition of the parameter  $B$  (eqn (2)) it also follows that  $v_m^* = kv_m$  and  $v_p^* = kv_p$  ( $k$  is constant). According to eqn (A4)

$$kv_m = c'_{ig}v_{tg} \quad (5)$$

and from eqn (A5) then

$$k = \frac{c'_{ig}}{c'_{ig} - 1} \quad (6)$$

This allows to quantify the ideas about free volume based on the EPR measurements of the spin-probe motions. From eqns (5) and (2) for  $v_{tg}$  then follows

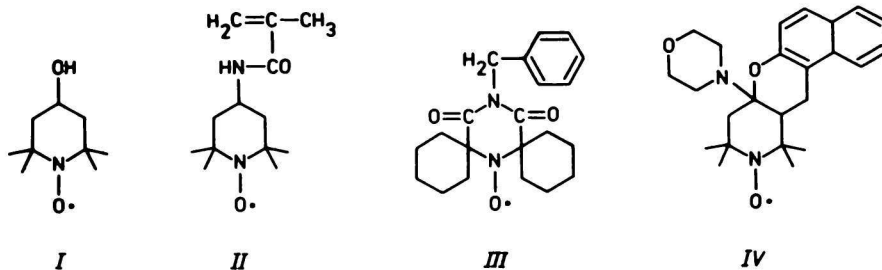
$$v_{tg} = \frac{v_p}{B} \cdot \frac{1}{c'_{ig} - 1} \quad (7)$$

The temperature dependence of  $v_t$  derived in Appendix (eqn (A7)) can be determined from eqn (7).

The segment volume ( $v_m$ ) varies with temperature. The increase in the occupied volume ( $v_m(\text{occ})$ ) corresponding to the volume at 0 K takes place in two ways: (i) By homogeneous expansion of the material ( $v_i$ ) as a result of the increasing amplitude of anharmonic vibrations with temperature and (ii) by the formation of holes ( $v_t$ ) distributed discontinuously throughout the material at any instant [12–14]. The volume distribution belonging to vibrations — interstitial — is uniform and cannot contribute to molecular mobility. In their free volume studies, *Vrentas* and *Duda* incorporate it into proper volume [12]. In this sense we also understand this volume in the present paper; we consider it implicitly in the volume  $v_m$  ( $v_m = v_m(\text{occ}) + v_i$ ). *Brostow* [14] has developed a method that allows calculation of both types based on the choice of the so-called critical volume  $v_c$ , which is somewhere between  $v_i$  and  $v_t$ . His illustrative calculation of these volumes for toluene shows that (i)  $v_i$  is much smaller than  $v_t$  and their mutual difference increases with increasing temperature. If we neglect  $v_i$  as being very low,  $v_m(\text{occ})$  will be identical with  $v_m$  used by us.

## Results

We used four probes (Scheme 1) and measured the corresponding values for  $T_{50G}$  for i-PP. Table 1 shows molecular masses of the probes, their volumes, the



Scheme 1

Table 1

Molecular masses, spin probe volumes, and other characteristics connected with the rotation of individual spin probes in i-PP

| Probe                                       | I     | II    | III   | IV    |
|---|-------|-------|-------|-------|
| $M_r \cdot 10^{-2}$                         | 1.72  | 2.39  | 3.65  | 3.84  |
| $v_p \cdot 10^{28}/\text{m}^3$ <sup>a</sup> | 1.77  | 2.47  | 3.37  | 3.89  |
| $v_{\text{eff}} \cdot 10^{28}/\text{m}^3$   | 1.77  | 2.23  | 2.58  | 3.04  |
| $\ln(v_0/v)$ <sup>b</sup>                   | 10.6  | 11.08 | 12.1  | 12.3  |
| $K$   | 194.7 | 186.3 | 170.6 | 167.8 |
| $T_{50G}$                                   | 317   | 335   | 343   | 362   |
| $B$   | 0.50  | 0.63  | 0.73  | 0.86  |
| $f(T_{50G})$                                | 0.047 | 0.055 | 0.058 | 0.067 |
| $v_t(T_{50G}) \cdot 10^{30}/\text{m}^3$     | 17.2  | 20.7  | 22.0  | 25.5  |

a) Volumes calculated according to Ref. [15].

b) Determined on the basis of the data from Ref. [9].

corresponding values for  $\ln(v_0/v)$ ,  $T_{50G}$  values and other results discussed later. Eqn (3) can be written as

$$T_{50G} - T_g + c_{2g} = \frac{c'_{1g} c_{2g}}{\ln(v_0/v)} B = KB \quad (8)$$

When using various values for  $\ln(v_0/v)$  for individual probes taken from [9] (Table 1), the constant  $K$  will also have various values. In the calculations of the constant  $K$  (Table 1) and in other calculations we will assume that  $c_{1g} = 17.4$  and  $c_{2g} = 51.6$  K [7, 8]. The values for  $T_{50G}$  were calculated from the temperature dependence of the EPR spectra belonging to the individual probes. The values are reported in Table 1. If we take for  $T_g$  of i-PP the value of 270 K [15], we determine

from relation (8) the values for the parameter  $B$  (Table 1), which, according to eqn (2) gives the ratio between the volume of the used probe and the volume of the moving segment.

In an earlier paper [15] effective volumes of the probes with respect to the probe  $I$  have been calculated. It was assumed there that by using another probe the volume of the segment ( $v_m$ ) does not vary. We shall use the same approach in this paper. Since we use other values of  $\ln(v_0/v)$ , the method will give different values

for probe volumes  $v_p(i) = \frac{B(i)}{B(I)} \cdot v_p(I)$  ( $i = II, III, IV$ ). The obtained values are

listed in Table 1 as  $v_{eff}$ . On the other hand, from the known volume of the probe and the parameter  $B$  one can determine the volume of the moving segment. For i-PP  $v_m = 3.54 \times 10^{-28} \text{ m}^3$ . In view of the molecular mobility it is interesting to know the number of monomeric units in i-PP to which this volume corresponds. We shall determine it as follows. The method used for calculation of the probe volumes ([16]) will be employed for determining the volume of one monomeric unit  $v_{i-PP} = 0.51 \times 10^{-28} \text{ m}^3$ . The volume  $v_m$  then corresponds to the segment volume with seven monomeric units. This result is consistent with the discussion on the possible types of motions in polymers [1] according to which and also according to other authors crankshaft motions take place through segments with seven monomeric units.

In the calculation of the volume  $v_m$  and of the effective values of the probe volumes we assumed that over the region of temperatures interesting from the point of view of the EPR measurements of spin probes,  $v_m$  does not vary. A similar assumption has been accepted in Appendix. The assumption is disputable. However, its choice allows to apply the results of the method of spin probes for studying some aspects of the investigation of polymers. In addition, in their recent paper, *Berstein et al.* [17] came to the conclusion that the molecular motion in polymers in the condensed phase proceeds through the basic segment (the authors identify it with Kuhn segment) which does not vary with temperature. This also corresponds to the fact that the value of the parameter  $B$  (calculated from eqn (3)) increases with the increasing volume of the probe (Table 1).

From the known value of  $v_m$  and from the relation (7) we can determine the average free volume per segment in i-PP at  $T_g$ , i.e.  $v_{fg}$ . Its value is  $9 \times 10^{-30} \text{ m}^3$ . Then on the basis of (A7) one can determine the temperature dependence of the average free volume above  $T_g$  and of the value of  $v_f$  corresponding to the respective values of the temperatures  $T_{50G}$  (Table 1).

Using two probes from eqn (8), we have for  $T_g$

$$T_g = \frac{(T_{50G}(II) + c_{2g})K_2(I)V_2(I) - (T_{50G}(I) + c_{2g})}{K_2(I)V_2(I) - 1} \quad (9)$$

where

$$K_2(I) = \frac{K(I)}{K(II)} \quad V_2(I) = \frac{v_p(I)}{v_p(II)}$$

(I) and (II) refer to the quantities corresponding to the probes I and II, respectively.

To be able to determine exactly  $T_g$ , the volumes of the used probes have to be determined exactly and  $c_{2g}$  corresponding to the polymer studied must be used. In these terms we consider the results obtained here as illustrative. This relates, of course, also to other results obtained by the spin-probe method as long as it does not concern qualitative conclusions. In addition, in deriving eqn (3) the energetic aspect of the spin probe rotation has been intentionally neglected. Although *Vrentas and Duda* [12] showed that for temperatures close to the values of  $T_g$  the free volume factor predominates during diffusion, for more precise results, also activation energy of diffusion has to be taken into account which is necessary for overcoming attractive forces as has been reported by *Bullock et al.* [7].

### Appendix

In this Appendix we will point to the application of WLF universal constants in expressing some temperature dependences. We will use generally valid relations

$$v_f = v_{fg} + v_{mg} \Delta \alpha (T - T_g) \quad [7] \quad (A1)$$

where  $v_{fg}$  and  $v_{mg}$  are the values for free volume ( $v_f$ ) and the total volume of the segment, respectively, at  $T_g$  ( $v_{mg} = v_m + v_{fg}$ ),  $\Delta \alpha$  is the difference in thermal expansion coefficient above and below  $T_g$ .

$$f = f_g + \Delta \alpha (T - T_g) \quad [11] \quad (A2)$$

$f$  is the free volume fraction,  $f_g$  is its value at  $T_g$ .

$$\frac{v_{fg}}{v_{mg} \Delta \alpha} = c_{2g} \quad [7, 8] \quad (A3)$$

$$\frac{v_m^*}{v_{fg}} = c'_{1g} \quad [7, 8] \quad (A4)$$

If we use an assumption that the critical volume for segment rotation ( $v_m^*$ ) equals the overall segment volume ( $v_{mg}$ ), then from the relationship  $v_m^* = v_m + v_{fg}$  and eqn (A4), we obtain for  $v_m$

$$v_m = (c'_{1g} - 1)v_{fg} \quad (A5)$$

and for  $f_g$  (from eqn (A4))

$$f_g = \frac{v_{fg}}{v_{mg}} = \frac{1}{c'_{1g}} \quad (\text{A6})$$

From the expressions (A1) and (A3) it follows directly

$$\frac{v_f}{v_{fg}} = 1 + \frac{T - T_g}{c_{2g}} \quad (\text{A7})$$

and for  $f$  with respect to the relations (A2), (A3), and (A6) we can write

$$f = \frac{1}{c'_{1g}} + \frac{T - T_g}{c_{2g}} \cdot \frac{1}{c'_{1g}} = \frac{c_{2g} + T - T_g}{c'_{1g}c_{2g}} \quad (\text{A8})$$

By comparing relations (A8) and (A2) we obtain

$$\Delta\alpha = \frac{1}{c'_{1g}c_{2g}}$$

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