

# Study of rotational mobility of stable nitroxide radicals in solid polymers

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The rotational mobility of stable nitroxide radicals in PS, PMMA, PVC, PP and PE has been studied over a wide temperature range by the e.s.r. method. At temperatures  $T$  lower than  $T_g$ , spin probes act as kinetically independent particles, the rotational frequency of which is determined mainly by the micropore dimensions of the polymer and depends indirectly on the mobility of segments or side groups.

## INTRODUCTION

The spin probe method has recently aroused increasing interest because of its wide possibilities for the investigation of molecular motions and changes in polymer systems<sup>1-3</sup>. The method provides valuable information at a molecular level on crystallization and orientation, structure and degradation, compatibility and other properties.

These quantitative investigations represent only one aspect of the application of the method. Of the same importance is the use of the technique for studying the frequencies of rotational motion of low molecular particles, namely stable organic radicals in polymers. This is interesting because according to current ideas<sup>4</sup> and experimental results<sup>5</sup> the rotational mobility of particles is no less significant in the kinetics of reactions in polymers than translational diffusion. Since the present knowledge of translational diffusion in polymers is satisfactory and less is known about rotational mobility, the spin probe method appears to present a new approach to the study of the latter.

The basic problem arising from the use of this method is the relationship between the motions of a low molecular particle and those of the kinetic elements of macromolecules. A few studies<sup>2,6,7</sup> in this field have shown that the motions of spin probes in the high elastic state are determined by the short range segmental motions. The motions in the temperature range below  $T_g$  are not so clear.

The aim of the present paper was to analyse the frequencies of rotation of spin probes in a series of polymers differing in structure and properties with regard to the dynamics of rotation of low molecular particles and to explain the mechanism of their motion over a wide temperature range.

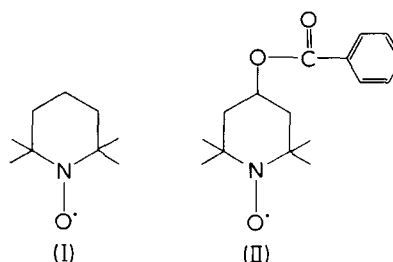
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## EXPERIMENTAL

The polymers used are characterized in *Table 1*.

Synthetic zeolites, types NaX and CaA were used as porous sorbents. Zeolites were dehydrated at 350°C.

Stable nitroxide radicals were employed as spin-probes:



The radical I was introduced into polymers and zeolites by absorption of its vapours at 100°C up to concentrations between  $10^{-3}$  and  $10^{-4}$  mol<sup>-1</sup>. The polymers were then heated at this temperature for several hours to distribute the radicals evenly. The spin probe (II) was introduced into samples by swelling the polymer in a benzene solution of the radical. The samples were then dried carefully *in vacuo* at  $10^{-3}$  torr and 100°C until no changes were observed in the spectra.

The spectra were recorded on an X-band E-4 Varian spectrometer with a temperature controller E-257. The 100 kHz modulation amplitude used did not exceed 0.1 mT and the microwave power was 0.5 mW.

The rotational correlation time<sup>†</sup>,  $\tau$ , in the rapid motion region ( $6 \times 10^{-11} < \tau < \times 10^{-9}$ ) was calculated according

Table 1 Characterization of polymers

Polymer	Density (g/cm <sup>3</sup> )	$M_w$	Sample form	Name	Producer
Polypropylene (isotactic), PP	0.896		Granules	Tatren	Slovnaft, Cz.
Polyethylene, PE	0.921		Granules	Bralen	Slovnaft, Cz.
Polystyrene (atactic), PS	1.043	$2.7 \times 10^4$	Flake	Vestyrol N	Hoechst, W. Germany
Poly(vinyl chloride), PVC	1.412	$8.9 \times 10^4$	Powder	E-PVC1	Chemical Works, Cz.
Poly(methyl methacrylate), PMMA	1.18	$3.0 \times 10^6$	Flake	Plexiglass 233	Rhöm and Haas Co, W. Germany

to equation (1) based on the theory of Freed–Fraenkel<sup>8</sup>:

$$\tau = 6.7 \times 10^{-10} \Delta H_{+1} \left[ \left( \frac{I_{+1}}{I_{-1}} \right)^{1/2} - 1 \right] \text{ (sec)} \quad (1)$$

where  $\Delta H_{+1}$  is the linewidth (in gauss) of the low field component and  $I_{+1}$  and  $I_{-1}$  are the intensities of the low and high field components of the spectrum, respectively.

In order to obtain  $\tau$  in the region of slow motions ( $8 \times 10^{-10} < \tau < 3 \times 10^{-8}$ ) the parameter  $\kappa(\tau)$  was calculated according to ref 9:

$$\kappa(\tau) = \frac{H_{+1}(\tau) - H_{+1}(\tau \rightarrow 0)}{H_{+1}(\tau \rightarrow \infty) - H_{+1}(\tau \rightarrow 0)} \times 100 \quad (2)$$

where  $H_{+1}(\tau)$  is the position of the maximum of the first derivative absorption line in a low field and  $H_{+1}(\tau \rightarrow 0)$ , are the positions of these maxima for the two limiting values (rapid and slow) of  $\tau$ . The values of  $\tau$  were determined according to the calibration plot of  $\kappa(\tau)$ <sup>9</sup>.

## RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of the rotational correlation time for radical I in various polymers.

The deviation from the linear Arrhenius plot towards higher activation energies (point of break,  $T_B$ ) is characteristic of all polymers. In order to be able to analyse the results in Figure 1 the curves are shifted in the temperature range so that the points of break should lie one below the other.

The points of break,  $T_B$ , glass transition temperatures,  $T_g$ , activation energies  $E_1$  and  $E_2$ , pre-exponential factors,  $f_{01}$  and  $f_{02}$ , for both temperature ranges are summarized in Table 2.

Table 2 shows that  $T_B$  are close to  $T_g$  for all the polymers studied. The value of  $T_B$  depends slightly on the dimensions of the radical. The values of  $\tau$  at the point  $T_B$  depend on the polymer and vary from  $10^{-8}$  sec in PVC to  $1.6 \times 10^{-9}$  sec in PS. Thus the temperature  $T_g$  is not an isofrequency point for rotation of the low molecular particles in polymers.

† Uncertainties in  $\tau$  arise from inhomogeneous broadening due to unresolved hyperfine structure which leads to deviation from the Lorentzian form of the observed line and from possible anisotropy of the rotational diffusion tensor.

This is the main cause of difficulties arising by the use of the constant  $\tau$  values or their corresponding parameters for determining the  $T_g$  of various polymers. In previous papers<sup>11,12</sup> the quantity  $T_{50G}$  employed for this purpose is the temperature at which the distance between extrema of the components of the e.s.r. spectra of nitroxide radicals reaches 50 G. The results indicate that the differences between  $T_{50G}$  and  $T_g$  can be substantial, e.g. this difference can amount to 136°C for PS for radical I (Table 2).

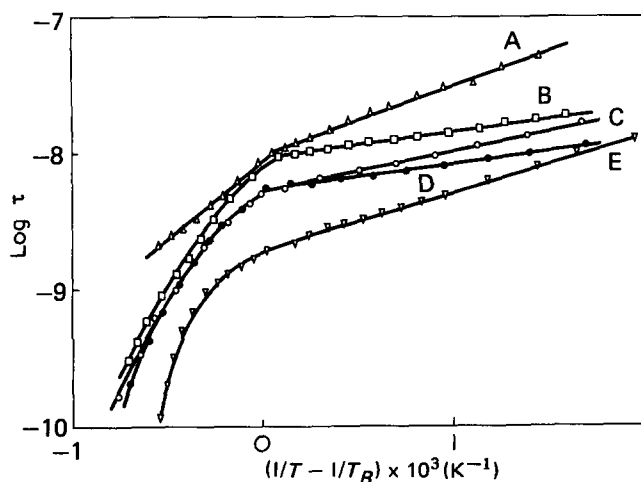


Figure 1 Plot of the logarithm of the correlation time ( $\log \tau$ ) against shifted ( $T_B$ ) reciprocal temperature of radical I in: A,  $\Delta$ , PVC; B,  $\square$ , PMMA; C,  $\circ$ , PP; D,  $\bullet$ , PE; E,  $\triangle$ , PS

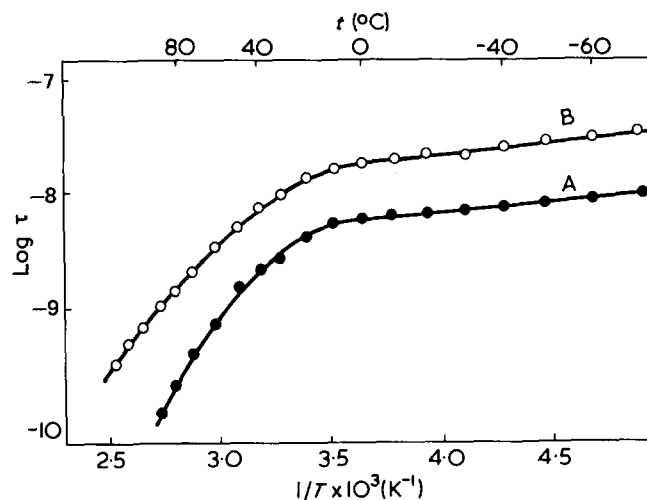


Figure 2 Plot of  $\log \tau$  against  $1/T$  for radicals I ( $\bullet$ ) and II ( $\circ$ ) in PP

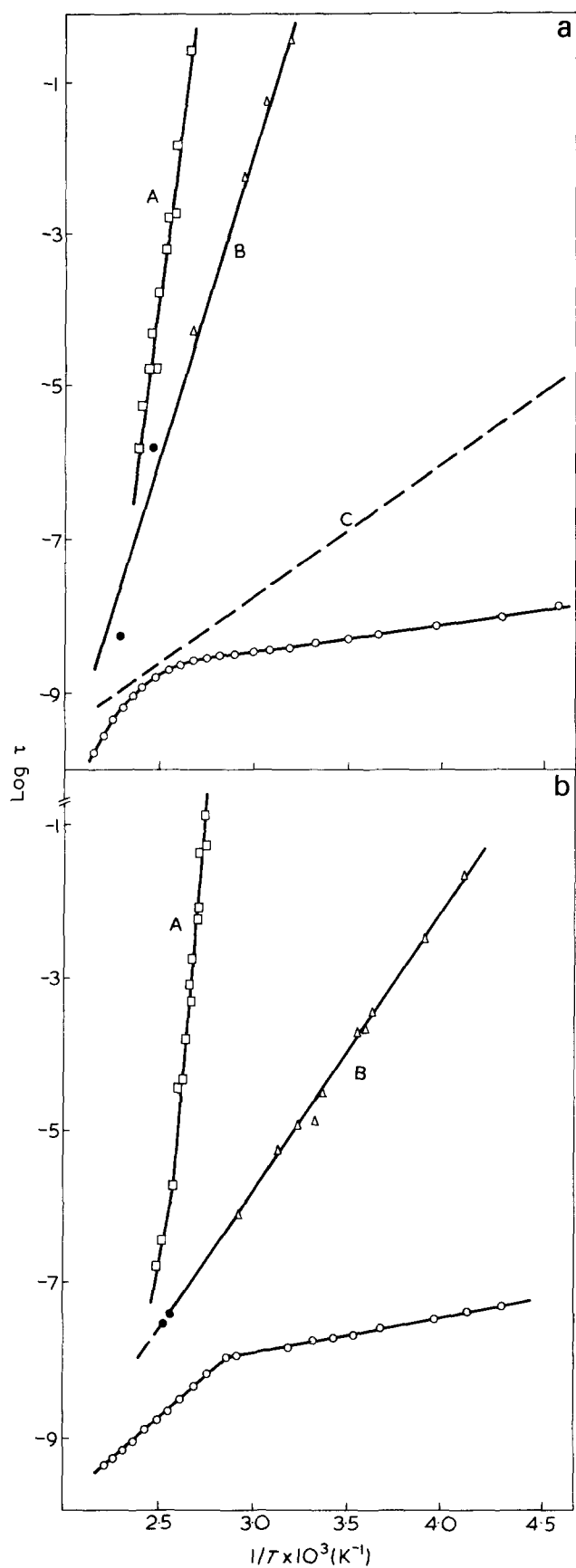
Table 2 Characteristic temperatures and Arrhenius parameters from the data obtained by the spin probe technique in polymers

Polymer	Radical	$T_g^*$ (°C)	$T_B$ (°C)	$T_{50G}$ (°C)	$E_1^\dagger$ (kJ/mol)	$f_{01}^\dagger$ (sec)	$E_2^\ddagger$ (kJ/mol)	$f_{02}^\ddagger$ (sec)
PMMA	I	70–105	70	42	21	$5.0 \times 10^{-12}$	4.2	$2.0 \times 10^{-9}$
	II		85	150	21	$2.0 \times 10^{-11}$		$4.0 \times 10^{-9}$
PVC	I	74	78	83	42	$6.9 \times 10^{-15}$	8.8	$4.2 \times 10^{-10}$
PS	I	100	104	–32	84	$1.1 \times 10^{-19}$	8.0	$1.6 \times 10^{-10}$
	II		10	38	46	$3.2 \times 10^{-16}$		$2.9 \times 10^{-9}$
PP	I	0	10	–60	46	$5.0 \times 10^{-17}$	3.8	$1.1 \times 10^{-9}$
PE	I	–20	–43	–65	42	$1.6 \times 10^{-17}$	6.3	$3.2 \times 10^{-10}$

\* From dielectric relaxation measurements;

† calculated for the range  $T > T_B$  from the maximum deviation of curves;

‡ calculated for the range  $T < T_B$



**Figure 3** Rotational correlation times of the spin probe (○) and those of  $\alpha$ ,  $\beta$  and  $\gamma$  relaxation processes: A,  $\alpha$ ; B,  $\beta$ ; C,  $\gamma$  obtained from the maxima of the dielectric loss peak (□), mechanical loss peak ( $\Delta$ )  $\tau = 1/2\pi\gamma_m$  and from n.m.r. data (●) in logarithmic coordinates plotted against reciprocal temperature in PS (a) and PVC (b). (The dashed line represents the  $\gamma$  process in PS obtained by extrapolation at very low temperature)

Kumler *et al.*<sup>12</sup> determined the relation between  $T_{50G}$  and  $T_g$  for radical II. The value  $T_{50G}$  depends strongly on the radical size. The difference in  $T_{50G}$  between the radicals I and II is 108°C in PMMA. Evidently, for determining  $T_g$  it is better to use the correlation between the points of break,  $T_B$ , on the plots of  $\tau$  vs. temperature.

Let us analyse the correlation times and their temperature dependence in more detail. Apparent activation energies for points above  $T_B$  are between 21 and 84 kJ/mol (Table 2) and for the low temperature region between 4.2 and 8.8 kJ/mol. These values are independent of the choice of radical used as a spin probe.

For a series of polymers a characteristic deviation from the linear dependence is observed in the high temperature region. In Figure 3a, the correlation times of radical I in PS, measured over a wide temperature range, are compared with the quantities obtained by the methods of dielectric and mechanical relaxations and n.m.r.<sup>10,13-15</sup>. In atactic PS three basic relaxation processes are observed: the  $\alpha$  process associated with the motion of the main chain segments; the  $\beta$  process related to the rotational motion of the benzene rings about the bonds by which they are attached to the main chain; and the  $\gamma$ -process attributed to the mobility of the structural chain defects or to rotational vibrations of benzene rings.

Figure 3a shows that at  $T_g$  the frequencies of rotation of spin probes are higher by 8 orders of magnitude than the frequencies of the  $\alpha$  process and by 3-4 orders of magnitude higher than those of the  $\beta$  process. Their activation energies are 352 and 167 kJ/mol, respectively, and are considerably higher than those characteristic of the rotation of the spin probes. We found no break for PS in the temperature dependence at the transition temperature of 30°C (Figure 1).

The times of the  $\gamma$  relaxation approach the values for  $\tau$ . On this basis it is often assumed that the motion of the spin probe is determined mainly by these relaxation processes. But in polymers having no side groups as well as no low temperature maxima of dielectric loss, the same type of temperature dependence is observed.

Figure 3b shows a similar plot for PVC. In this polymer only two relaxation processes were found and attributed to segment motion and motion of the side groups or impurities<sup>10,14</sup>. The relation between the relaxation times and  $\tau$  for the spin probe is the same as for PS and analogous for all other polymers investigated. The results obtained lead to the conclusion that the parameters determining the temperature dependence of  $\tau$  are not influenced by the structure of the polymer chain, existence of the side groups and crystalline regions. The values presented in Figure 1 are related to various structures of the chain: without side groups (PE and PVC), with methyl side groups (PP, PMMA), ether (PMMA) and phenyl (PS) side groups, amorphous and crystalline. The value for  $\tau$  at the point  $T_g$  is not connected with the existence of side groups. Thus, for example  $\tau_g$  in PVC and PMMA as well as in PE and PP are similar (Table 3). The rotational mobility of the spin probes is not associated with segmental motions of polymers at low temperatures. The authors of a previous paper<sup>15</sup> came to the analogous conclusion by investigating dielectric relaxation of low molecular admixtures in polymers.

To account for the peculiarities of the rotational mobility of the low molecular particles we have to take into account defects and porosity in the structure of the glassy polymers. All this is well known from numerous experiments examining permeability and sorption of vapours and gasses<sup>16-20</sup>.

Table 3 Values  $\tau_g$  and specific surface of polymers  $S_S$ 

Polymer	$\tau_g \times 10^9$ (sec)	$S_S$ (m <sup>2</sup> /g)
PVA*	10	0.5
PVC	10	1.8
PMMA	8.7	—
PP	6.0	—
PE	5.0	2.8
PS	3.2	—
Cellulose	3.5 †	9.0

\* Data from ref 22; † at 100°C

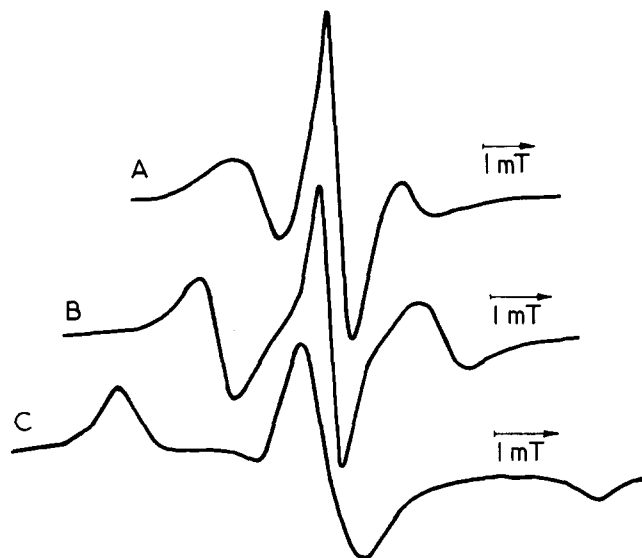


Figure 4 E.s.r. spectra of radical I. A, in cellulose at 100°C; B, radical I and C, II in NaX zeolite at 20°C

The data on sorption of nitrogen vapours in polymer glasses<sup>16,17</sup> and of hydrogenated monomers<sup>18</sup> showed that polymers can be divided into free-meshed macroporous sorbent including PS, cellulose and its derivatives and close-packed microporous sorbents. The existence of the pores enables us to employ such polymers, e.g. on the basis of PS, as sorbents in chromatography. The analysis of the data on gas sorption in PS led the authors<sup>20</sup> to the conclusion that a polymer contains capillary structure with a mean radius of about 10 Å. The existence of this structure must affect the mobility of particles with van der Waals radii of 3.5 Å (spin probe I).

This approach based on consideration of the porosity of polymers helps us to explain the differences in values of  $\tau$  in  $T_g$ . In Table 3 the values for  $\tau_g$  are compared with those for specific surfaces for nitrogen ( $S_S$ )<sup>16,17</sup>.

Table 3 shows that a correlation exists between  $\tau_g$  and parameters characterizing the packing of a polymer. Evidently the rotational mobility of spin probes is closely connected with the existence of micropores in the polymer. Figure 4 shows the e.s.r. spectrum of radical I in cellulose at 100°C for which  $\tau = 3.5 \times 10^{-9}$  sec. It is known<sup>17</sup> that cellulose is a macroporous sorbent; therefore rotation of the radical proceeds at rather high frequency even at a temperature considerably lower than  $T_g$ .

In this connection it was interesting to study rotation of radicals in solid porous sorbents modelling the structure of the glassy polymer. For this purpose we used synthetic zeolites representing crystalline mineral sorbents with pores of known dimensions<sup>23</sup>. Figure 4 shows the e.s.r. spectra of the radicals I and II in type NaX zeolite with a chan-

nel 8 Å in diameter at room temperature. Figure 5 shows  $\tau$  as a function of temperature for radical I. The values for  $\tau$  depend on the radical size and are close to the corresponding values for polymer.

The activation energy in zeolites is 10.5 kJ/mol and is similar to the values of activation energy obtained for polymers below  $T_g$ .

We did not observe the e.s.r. spectra of radicals in the CaA type zeolites since the dimensions of an access window in the zeolite (4 Å) are so small that they hinder the sorption of particles.

On the basis of the analysis of the data obtained we may consider polymer glasses as porous substances with the life time of the cell much greater than  $\tau$  for the rotational motion of the low molecular particle. In this model  $\tau$  is a function of the ratio between the particle size and the pore size as well as of the quantity  $E/kT$ , where  $E$  is the energy characterizing the interaction of the cell with the wall.

Breaks in the temperature dependence are accounted for by an increase in the thermal expansion coefficients above  $T_g$  accompanied by an increase of the free volume and pore dimensions and in the intensity of molecular motion and its participation in reorientation of the low molecular particle. The latter mechanism is significant in the range of high temperatures, where the frequencies of rotation and molecular motion approach each other (Figure 3).

The change in the mechanism of motion at  $T > T_g$  could be the reason for the deviation of  $\tau$  from linear dependence.

## CONCLUSION

Analysis of the data obtained by the spin probe method shows that at temperatures lower than  $T_g$  the low molecular particle is an independent unit. Its rotational frequencies are not associated with the segment mobility but are determined mainly by micropore dimensions in the glassy polymers.

Rotational frequencies of the particles sorbed in the solid matrix depend on the pore dimensions and the energy of interaction with the matrix. For this reason activation energies are low ( $E = 4.2$ – $8.4$  kJ/mol) in the range below  $T_g$  and are close to the temperature energies of desorption of organic molecules from the surface of numerous sorbents<sup>24</sup>.

The lifetime of particles in cavities can be calculated from

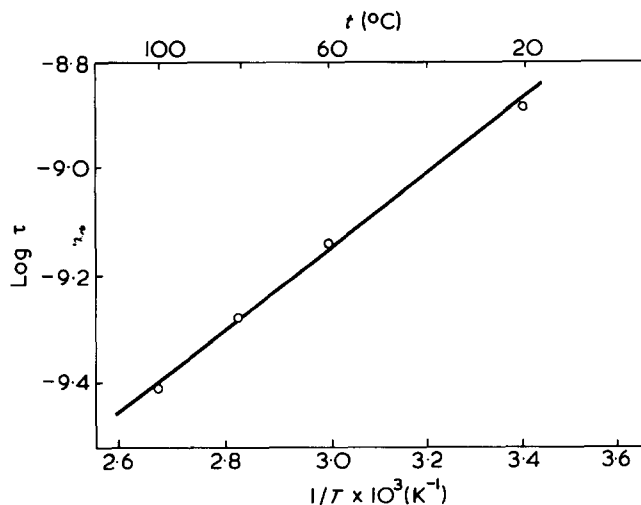


Figure 5 Plot of  $\log \tau$  against  $1/T$  for radical I in NaX zeolite

the data on diffusion. Diffusion coefficients for organic substances in polymers at  $T_g^{25}$  are  $\mathcal{D} = 10^{-11} - 10^{-13}$  cm<sup>2</sup>/sec.

From Einstein's equation  $\tau_D = \bar{x}^2/6\mathcal{D}$  for  $\bar{x} = 10$  Å, we obtain  $\tau_D = 10^{-2} - 10^{-4}$  sec. During this time the particle can change its orientation from  $10^4$  to  $10^6$  times. The values for  $\tau_D$  are, according to diffusion data, close to relaxation times of molecular motions (Figure 3). Thus the rate of the diffusion processes in the polymer is determined by molecular motion but the rotation of the radical proceeds independently. This accounts also for the differences in activation energies for these processes (21–42 kJ/mol).

Above  $T_g$  the molecular motions considerably affect the rotational frequency of particles but the mechanism of rotation in pores can be significant. Thus, for instance, thermo-oxidative degradation in PP results in an increase of the activation energy for diffusion when the activation energy of rotation of the spin probe decreases<sup>26</sup>. This is caused by formation of the solid porous structures in the oxidized polymer.

Using the rotational frequencies of the spin probe I, the polymers can be divided into two groups: (a) PMMA, PVC, poly(vinyl acetate)<sup>22</sup> where  $\tau_g \approx 10^{-8}$  sec; (b) PS, cellulose, PP, PE, polycarbonate<sup>27</sup> where  $\tau_g < 10^{-8}$  sec which are known porous sorbents.

The low molecular particle can be either sorbed in the polymer pores or become one of the defects forming porous structure on transition to the glassy state.

The independence of the activation energy from the spin probe dimensions (Figure 2)<sup>28</sup> supports the validity of the model, i.e. in processes where molecular motions play the main role; for example, in diffusion, the activation energy depends on the particle sizes<sup>29</sup>.

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