Free volume structure and spin probe dynamics in solid polymers

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Analysis of the structure of nine polymers, in terms of the average size of free volume at T_{50G} for spin probe Tempo, reveals an empirical connection between this microstructural characteristic of matrices and the change in reorientational regime of the spin probe.

Introduction

The concept of free volume plays a dominant role in the interpretation of dynamic phenomena in the physics and physical chemistry of disordered systems. In the case of amorphous polymers, this relatively simple idea is used successfully for correlations and sometimes predictions in the segmental dynamics of macromolecules[1], reorientational dynamics of photochromic, fluorescence[2-4] and spin probes[5,6] as well as diffusion of penetrants[7]. In spite of a clear basis for the relation between free volume and numerous dynamic parameters, the correlations have, at best, semiempirical character. The main reasons for this are the operational character of free volume definitions[8] as well as problems with the experimental measurement of free volume. However, during the last decade significant progress has been made in the development of positron annihilation spectroscopy (p.a.s.), allowing quantitative characterization of disordered materials in free volume terminology through analysis of the lifetime and relative intensity of positron and two forms of positronium[9].

Spin probe dynamics in polymers, as detected by electron spin resonance (e.s.r.) spectroscopy, is a useful indirect microscopic tool for studying the structural and dynamic state of a matrix[10]. A common feature of reorientational dynamics of nitroxyl probes is a transition from slow motion to the rapid reorientational regime. According to the free volume hypothesis, this transition at T_{50G} takes place if a certain critical free volume about the probe is reached[5,6]. This idea is basically intuitive and should be tested. We believe that by considering the structural and dynamic characteristics simultaneously an empirical relation may be found between them; this will contribute to an understanding of molecular aspects of the structure–dynamics relation of particles in polymers. This contribution presents a new empirical connection between the average size of free volume entities and a change of reorientation dynamics of the spin probe from slow to rapid motion regime measured by e.s.r. in a series of polymers.

Experimental

Materials. The model substances used were polymers with a wide range of glass transition temperatures

(T_gs): 1,4-polybutadiene (1,4-PB), polyisobutylene (PIB), isotactic polypropylene (iPP), poly(vinyl acetate) (PVAc), atactic polystyrene (a-PS), atactic poly(methyl methacrylate) (a-PMMA), polycarbonate (PC), polysulfone (PSU) and poly(ether sulfone) (PES). T_g values were measured by d.s.c. and are shown in *Table 1*.

E.s.r. measurement. Spin probe 2,2,6,6-tetramethylpiperidine-1-oxyl (Tempo) was introduced into the individual polymers by diffusion from vapour at high temperature. E.s.r. spectra were measured in a wide temperature range that included both motion regimes of reorientation dynamics; the instrument used was an EPR spectrometer Varian E-4 with temperature variator E-257.

Results and discussion

The $2A_{ZZ}-T$ dependences (i.e. the distance of extreme peaks of triplet spectra from temperature) have an identical sigmoidal form in all polymers[11]. A general feature of reorientational dynamics is the transition from the slow motion regime ($2A_{ZZ} \approx 60-70G$) to the rapid motion regime ($2A_{ZZ} \approx 30-40G$). This dynamic change is characterized[11] by temperature parameter T_{50G} at which the correlation time of the probe is 3×10^{-9} s. *Table 1* shows that T_{50G} values depend on the quality (i.e. chemical structure) of the polymer matrix. For polymers with relatively low T_g, the T_{50G} lies above these temperatures, while for polymers with a high T_g the change of motion of the probe takes place below these temperatures. The dynamics of the probe is generally connected with the existence of fluctuation about the probe. In some cases a correlation was found between probe dynamics and certain secondary relaxations for polymers with various chemical compositions[11]. The question is, what is the common feature causing the change in probe dynamics in these polymers with different chemical structures? From a general point of view it may be a local fluctuation of density or a free volume fluctuation close to the probe.

The results of standard measurement of a polymer by means of p.a.s., i.e. the temperature dependence of the average lifetime of *ortho*-positronium $\bar{\tau}_3$, are identical for all polymers. Its form is similar to the temperature dependence of macroscopic volume with the change of slope at T_g[12-19]. The *ortho*-positronium is the most stable

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Table 1 Temperature characteristics of polymers, polymer–Tempo systems and geometrical characteristics of free volume in polymer matrices

| Polymer	T_g (°C)	T_{50G} (°C)	$\bar{\tau}_3(T_{50G})$ (ns)	Ref.	$\bar{R}_f$ (Å)	$\Delta\bar{R}_f$ (Å)	$\bar{v}_f$ (Å^3)	$\Delta\bar{v}_f$ (Å^3)
1,4-PB	−102	−4	2.12	12	2.96	−0.39	109	−60
PIB	−70	7	2.06	13	2.91	−0.44	103	−66
iPP	−3	10	2.20	14	3.03	−0.32	117	−52
PVAc	33	65	2.25	15	3.08	−0.27	122	−47
a-PS	105	−12	2.10	16	2.95	−0.40	108	−61
a-PMMA	115	63	2.08	17	2.93	−0.42	105	−64
PC	150	50	2.15	18	2.95	−0.40	112	−57
PSU	185	55	2.16	19	3.00	−0.35	113	−56
PES	220	60	2.18	19	3.02	−0.33	115	−54

form of bound positron in condensed materials and its lifetime is directly linked to the size of holes in the matrix. According to the quantum-mechanical model in spherical approximation, the following relation is valid[20]:

$$\tau_3 = \frac{1}{2}\left[1 - \frac{R_f}{R_0} + \frac{1}{2\pi}\sin\left(\frac{2\pi R_f}{R_0}\right)\right]^{-1} \quad (1)$$

where R_f is the radius of a spherical hole, and $R_0 = R_f + \Delta R$, with ΔR an empirical parameter obtained by fitting measurements on zeolites with well-defined holes ($\Delta R = 1.656$ Å). In the case of amorphous polymers as complicated disordered systems, equation (1) may be used in the sense of average lifetime and corresponding average size of free volume entity. This approximation was recently verified by p.a.s. measurements of free volume distribution in epoxy samples[21].

Table 1 contains $\bar{\tau}_3$ values for our series of polymers at the corresponding T_{50G} taken from literature data[12–19]. In general, it was found that $\bar{\tau}_3(T_{50G})$ and $\bar{R}_f(T_{50G})$ lie in a relatively narrow interval of about 2.14 ± 0.08 ns and 2.98 ± 0.05 Å, respectively. A volume representation of holes in accordance with equation (1) is the alternative. In this case $\bar{v}_f$ lies at about 112 ± 10 Å^3. The comparison of average size of holes with van der Waals' characteristics of the probe Tempo, i.e. $R_P^W = 3.35$ Å and $v_P^W = 169$ Å^3, in the framework of the simplified average free volume theory of polymer media, may suggest that the given probe is a defect in the matrix. *Table 1* expresses this fact in the form $\Delta\bar{R}_f = \bar{R}_f - R_P^W$ and $\Delta\bar{v}_f = \bar{v}_f - v_P^W$. Values of these quantities lie in a relatively narrow interval of -0.37 ± 0.1 Å and -58 ± 9 Å^3, respectively. A further finding is that $\bar{R}_f$ and $\bar{v}_f$ at corresponding T_{50G} values for the given probe in a series of polymers are approximately constant, regardless of the chemical structure and dynamic state of the polymer matrix characterized by T_g values and by individual secondary relaxations. Our tentative explanation of this finding is illustrated in *Figure 1*.

From a general point of view it is necessary to consider polymers as systems with a free volume distribution rather than with a uniform hole size. It was found that this distribution has a Gaussian form[21,22]. According to the free volume theory of particle mobility in liquids and glasses[23], the change in the motional regime of spin probes requires the achievement of a critical free volume fluctuation around the moving particle, $\Delta R^* = R^* - R_P^W$, which should be a constant characteristic for a given probe, independent of the quality of the polymer. Below
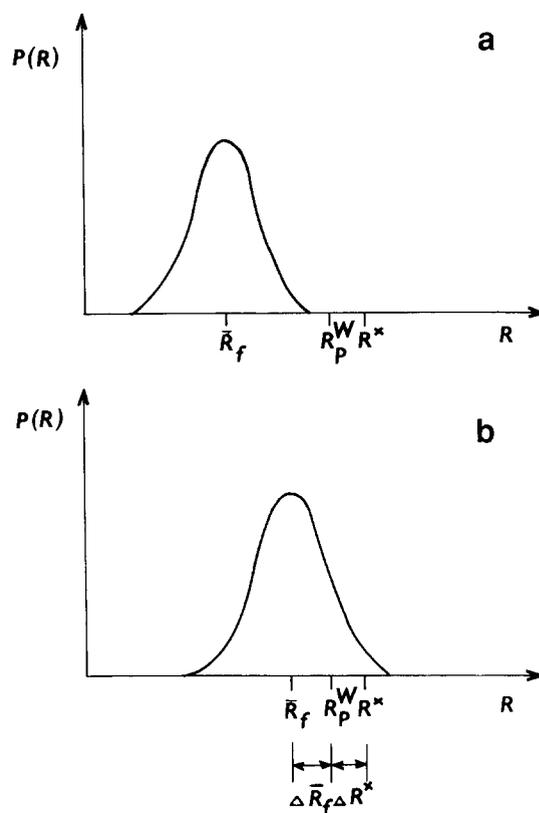
Figure 1 Schematic interpretation of the relation between free volume structure and spin probe dynamics: (a) $T < T_{50G}$; (b) $T > T_{50G}$

T_{50G}, $\bar{R}_f$ is relatively small and the right tail of the free volume radius distribution does not reach the critical radius R^* for rapid motion. In this temperature region the probes can be considered as defects in the polymer matrix which reorient slowly due to small fluctuations of chains in their surroundings (*Figure 1a*). With increasing temperature the free volume distribution function is shifted to higher $\bar{R}_f$ values[21]. When the right tail reaches the R^* value, non-zero probability exists for rapid reorientation of part of the spin probes. Then one can expect the superposition of fast and slow triplets, in agreement with experiment. At T_{50G}, defined as the temperature at which all probes reorient in the rapid regime, the right tail of distribution overcomes the critical value. Our empirical finding, i.e. the approximate constancy of $\bar{R}_f(T_{50G})$ and $\Delta\bar{R}_f(T_{50G})$, parallels the above-mentioned condition ΔR^*, as can be seen from

Figure 1b. Slight deviations from a strictly constant value can be ascribed partly to the use of spherical approximation as well as to potential intermolecular interactions between probe and medium. Nevertheless, we may conclude that the main condition for the change of motional regime is the presence of a certain size of average free volume, with the associated free volume fluctuation allowing the rapid reorientation of spin probes.

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