

Conformational mobility of 1,2-di-(*p*-bromophenyl)ethane dispersed in polymer matrices: correlations with relaxation transition phenomena and free volume distribution in glassy polymers

A. A. Stolov^{a,*}, D. I. Kamalova^a and A. B. Remizov^b

^aDepartment of Chemistry, Kazan State University, Kremlevskaya St. 18, Kazan 420008, Russia

^bKazan State Technological University, Karl Marx St., 68, Kazan 420015, Russia

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Conformational mobility of 1,2-di-(*p*-bromophenyl)ethane (DPBPE) introduced into glassy poly(vinyl chloride) (PVC) and poly(methyl methacrylate) (PMMA) matrices has been studied by infrared absorption spectra. For both systems under investigation the freezing of the *trans*–*gauche* conformational transitions in DPBPE has been found. The temperatures of freezing of the conformational equilibrium (T_f) have been determined: 276 ± 8 K (PVC) and 326 ± 18 K (PMMA). The T_f values are correlated with the secondary relaxation transition temperatures of the pure polymers. In the view of the obtained data, the processes responsible for the relaxation transitions in PVC and PMMA are analysed. The volume of the conformationally mobile group of DPBPE (108.2 \AA^3) was found to be close to the free volume entity sizes of the polymers, measured at T_f temperatures by positron annihilation lifetime spectroscopy. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Behaviour of small molecules introduced into polymer matrices is extensively studied by different physical methods^{1–4}. The interest in this problem is based on the fact that the mobility of low molecular weight compounds serves as a tool for investigating the segmental and local molecular dynamics of bulk polymers. The other motivation of such studies is a desire to develop new nonlinear optical materials using amorphous polymers^{5,6}.

Two different types of molecular mobility can be identified: (i) the mobility of molecules as a whole (i.e. translational and rotational diffusion), and (ii) the intramolecular transformations. A variety of approaches exists for studying each type of molecular motion. Translational and rotational diffusion has been investigated by gas diffusivity⁷, spin^{4,8}, electrochromic⁹, hydrogen-bond-forming^{10,11}, and some fluorescence^{6,12,13} and photochromic probes⁵. The intramolecular transformations have been studied for excimer-forming¹⁴, various kinds of fluorescent^{15–17}, phosphorescent¹⁸ and photochromic^{19–21} probes. For the majority of the probes belonging to the latter group the transformations are achieved by photoexcitation of the molecules. There are also methods which provide information on the different types of molecular motion. Thus, dielectric relaxation spectroscopy was successfully used for studying the intramolecular rotational relaxation

and the orientational diffusion of the whole molecules embedded in glassy polymers^{22–24}.

In our recent works we studied the conformational behaviour of some low molecular weight compounds introduced into amorphous glassy polymers^{25,26}. It has been proposed to investigate the temperature shift of the conformational equilibrium for analysing the relaxation transition phenomena and free volume distribution of the polymers. The decrease of the temperature causes the concentration redistribution over the conformers, if there is an equilibrium between them. However, if the conformational equilibrium is frozen, the concentrations of the conformers do not change with the temperature. It was reported²⁵ that each polymer/probe system is characterised by a certain temperature (T_f) below which the conformational equilibrium is frozen. The T_f values were found to be dependent both on the polymer and the probe. For the same polymer the freezing temperature increases, as a rule, with the size of the conformationally mobile part of the probe molecule. It was also noted that T_f values are close to the temperatures of the secondary relaxation transitions of the polymers. Thus, it was supposed that the freezing of the conformational equilibrium reflects some processes taking place in the polymers at the temperatures close to T_f . Comparing the structure of the probe and the polymer, one may propose a process, responsible for the observed relaxation transition. The distinctive feature of the method is that it does not use photoexcitation of the probe molecules.

Each probe can be characterised by its molecular volume

* To whom correspondence should be addressed

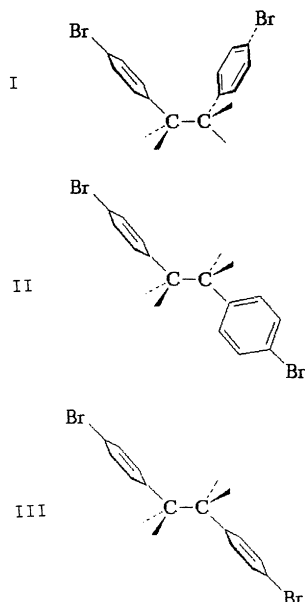


Figure 1 Some of the stable conformations of DPBPE

(V_p) and activation volume (V_p^\ddagger). The latter means an extra volume necessary for the intramolecular transition to occur. These two characteristics are the most important ones controlling the dynamics of probes in polymer matrices.

The activation volume (V_p^\ddagger) can be defined as a volume swept out by the atoms during the conformational transition process. In our previous works with probes more simple than DPBPE^{25,26} we calculated the volumes swept out while rotating the smallest conformationally mobile parts of the molecules. The rest of the molecules were assumed to be fixed. For all the probes used it has been found that the 'swept out volumes' are close (within 10–20%) to the van der Waals volumes of the rotating groups. However, one should note that a conformational transition in confined media can be a result of a very complex motion, including rotational, translational motions of the molecule as a whole, and the internal rotation of both its parts. Unfortunately, taking into account all the degrees of freedom, it becomes almost impossible to determine the V_p^\ddagger magnitudes exactly. It should be also noted that the activation of certain degrees of freedom depends on the temperature and shapes of the free volume entities of the polymers. Therefore, it seems more reasonable to use a more simple approach for estimating the V_p^\ddagger magnitudes, i.e. as has been done previously^{25,26}, to assume, that they are close to the van der Waals volumes of the smallest conformationally mobile groups. In the view of this, the volumes of the conformationally mobile groups instead of the V_p^\ddagger ones are used below.

The V_p and V_p^\ddagger values of the probes studied in Refs. 25 and 26 (1,2-bromofluoroethane, methyl dichlorophosphate and 1,2-dichloroethane) are relatively low: $71.5 \leq V_p \leq 96.8 \text{ \AA}^3$ and $13.0 \leq V_p^\ddagger \leq 26.3 \text{ \AA}^3$, respectively. It was of interest to investigate a probe with a larger molecular volume. The molecule studied in the present paper is 1,2-di-(*p*-bromophenyl)ethane ($\text{BrC}_6\text{H}_4\text{-CH}_2\text{-H}_2\text{C-C}_6\text{H}_4\text{Br}$, DPBPE). There are three axes of internal rotation in this molecule (Figure 1). First, similar to other ethane-like molecules, the rotation about $\text{C}_{\text{aliph}}\text{-C}_{\text{aliph}}$ bond gives rise to appearance of *gauche* and *trans* forms. One of the *gauche* conformers (I) and two different *trans* conformers (II and III) are shown in Figure 1. Secondly, the rotation of two

phenyl rings about the $\text{C}_{\text{aliph}}\text{-C}_{\text{arom}}$ bonds is also possible (compare conformers II and III). The van der Waals volume of the whole molecule (V_p), calculated by the additive scheme²⁷ is equal to 242.0 \AA^3 . The activation volume necessary for the *trans-gauche* transition was estimated as the van der Waals volume of the *p*-bromophenyl group plus the volume of two hydrogen atoms attached to aliphatic carbon: $V_{p(t-g)}^\ddagger = 108.2 \text{ \AA}^3$. Rotation of one phenyl ring about the $\text{C}_{\text{aliph}}\text{-C}_{\text{arom}}$ bond means the motion of four aromatic carbon and four attached hydrogen atoms: $V_{p(\text{arom})}^\ddagger = 58.5 \text{ \AA}^3$.

The aim of the present work is the investigation of conformational mobility of DPBPE in two glassy polymers: poly(methyl methacrylate) (PMMA) and poly(vinyl chloride) (PVC).

EXPERIMENTAL

Blend polymerised, with melt viscosity index 0.5, and thermostability according to Vika 380 K PMMA, and suspension polymerised, trademark C-70 PVC were used in the study. DPBPE was synthesised according to Ref. 28, and purified by recrystallisation from ethanol. The purity of the final product was checked with thin-film chromatography. The indirect confirmation of the product's purity was obtained when comparing its infrared spectrum with the documented one²⁸.

The samples were prepared as follows. The mixtures of the polymers with DPBPE were prepared by weight, each containing approximately 5 wt.% of the probe. The mixtures were dissolved in chloroform (PMMA) and tetrahydrofuran (PVC). The films with approximate thickness 0.5 mm were cast on KBr plates and kept at room temperature for 10–15 days in order to remove the solvent. Then the films were dried *in vacuo* at 120–170°C over several hours. The absence of the solvents in the samples was controlled by i.r. spectra, using 680- and 900- cm^{-1} intense absorption bands of chloroform and tetrahydrofurane, respectively. The concentration of DPBPE in the samples, following from the weight measurements was 1.5 vol.% (approximately 0.15 mol l^{-1}).

The infrared (i.r.) spectra were registered with a Specord M80 spectrometer combined with a computer. The low-temperature measurements were carried out with a Carl Zeiss one-beam cryostat cooled by liquid nitrogen. The measurements above room temperature were performed using the self-made high-temperature cell. Temperature was measured with a platinum resistor with an accuracy $\pm 0.5 \text{ K}$. The average cooling rate was 0.07 K s^{-1} . All other experimental details have been described previously²⁵.

RESULTS AND DISCUSSION

Chiu *et al.*²⁸ were the first to establish the fact of conformational inhomogeneity of DPBPE. They have studied i.r. spectra, dipole moments and the molar Kerr constants of DPBPE. It has been shown that solutions of DPBPE contain comparable quantities of *trans* and *gauche* conformers. However, the possible isomerism due to rotations of the phenyl rings around the $\text{C}_{\text{aliph}}\text{-C}_{\text{arom}}$ bond has not been considered, and the relative stability of the conformers has not been studied in the cited work.

To obtain more data on the conformational isomerism of DPBPE we have reinvestigated its i.r. spectra, and performed molecular mechanics and normal coordinate calculations²⁹. The molecular mechanics study gives six unequivalent minima on the potential energy hypersurface,

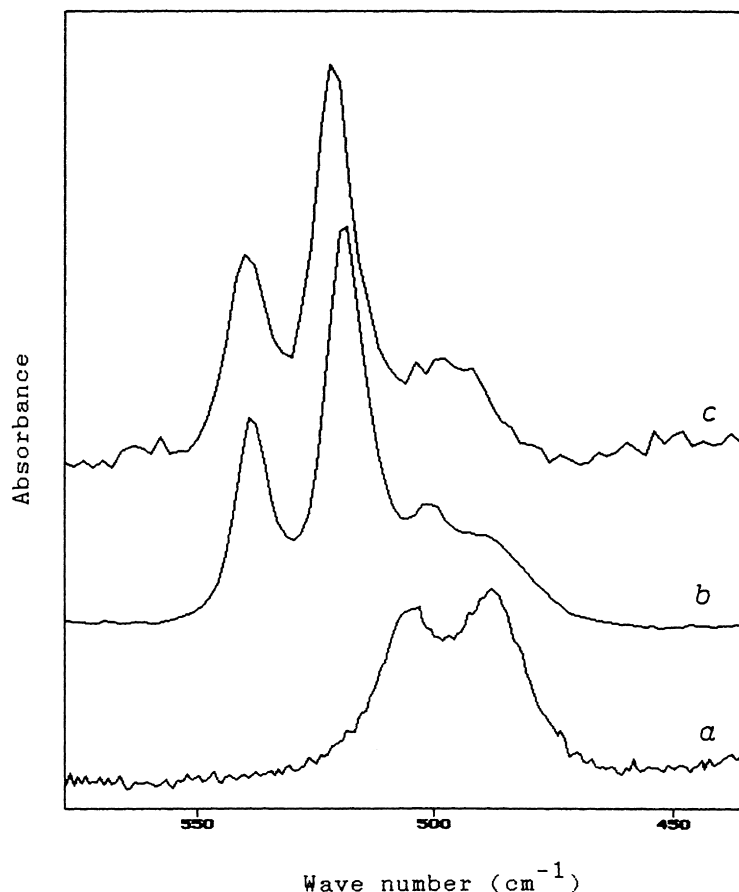


Figure 2 I.r. spectra of: (a) crystalline DPBPE; (b) its solution in chloroform; and (c) DPBPE dispersed in PMMA. All the spectra are registered at 295 K

which correspond to three *trans* and three *gauche* conformations. Only one conformer exists in the most stable crystalline modification. It has been found²⁹ that this conformer has the *p*-bromophenyl groups in *trans* positions, the phenyl rings being nearly orthogonal to the $C_{\text{arom}}-C_{\text{aliph}}-C_{\text{aliph}}'-C_{\text{arom}}'$ plane (conformer III in *Figure 1*).

Figure 2 shows part of the i.r. spectra of crystalline DPBPE (*a*), and its solution in liquid chloroform (*b*). One can see that new bands at 538 and 518 cm^{-1} appear when passing to the spectrum of the solution. It follows that one or several new conformers of DPBPE appear in the liquid media. The assignment of the new bands to conformers was performed on the basis of the solvent and temperature behaviour of the band intensities, normal coordinate analysis and molecular mechanics calculations²⁹. It has been shown that the phenyl rings have two stable orientations with respect to the $C_{\text{arom}}-C_{\text{aliph}}-C_{\text{aliph}}'$ plane: (i) close to parallel and (ii) close to orthogonal, the former being less stable. Conformers I and II (*Figure 1*) were found to be mainly responsible for the bands at 538 and 518 cm^{-1} , respectively (though several other conformers contribute to the both bands as well).

It should be noted that the *trans* and *gauche* conformers of DPBPE essentially differ in their dipole moments: $\mu_t = 0$, $\mu_g \cong 3.3 \text{ D}^{29}$. Owing to this, the *gauche* conformers should be better stabilised in polar media³⁰. In our previous work²⁹ the solvent effect on the conformational equilibrium of DPBPE has been studied, the dielectric constants of the solvents being in the range from 1.9 (hexane) up to 36.6 (dimethylformamide). It has been shown that the influence of the solvent polarity really does occur. However, such influence was found to be fairly weak in comparison, for

instance, with the similar effects on 1,2-dichloroethane³¹ or 1,2-dibromoethane³² conformers. The weakness of the effect is definitely due to the relatively large molecular volume of DPBPE³⁰. The dielectric constants of PVC (3.2) and PMMA (3.2) fall in the above-mentioned range of the dielectric constants of the liquid solvents. Therefore, no special effect due to the polymer's polarity (in comparison with the liquid solutions) has been expected.

I.r. spectra of DPBPE in glassy polymers (*Figure 2c*) are really similar to those obtained for the liquid solutions (*Figure 2b*). Note, that the spectrum shown in *Figure 2b* corresponds to the solution in chloroform, the dielectric constant of which (4.7) is close to those of PVC and PMMA. It follows from *Figure 2* that the mixture of the DPBPE conformers, but not just one of them alone, is present in the polymer matrices.

The bands at 538 and 518 cm^{-1} were found to be the most convenient for investigating the *trans-gauche* conformational equilibrium in DPBPE. The intensity ratio of these bands (D_{518}/D_{538}) is proportional to the conformational equilibrium constant, and the temperature variation of this ratio indicates the presence of the conformational transitions in the studied system. *Figure 3* shows the dependence of $\ln(D_{518}/D_{538})$ on T^{-1} for DPBPE embedded in PVC. As has been found before^{25,26}, such dependencies consist of two linear branches, intersecting at a certain temperature T_f . At $T < T_f$ the band intensity ratio does not vary with the temperature, hence the conformational transitions do not occur below T_f . The obtained T_f values (temperatures of freezing of the conformational equilibrium) for DPBPE/polymer systems are given in *Table 1*.

It is of interest to compare the T_f values with those

Table 1 Temperatures of freezing of conformational equilibria (T_f (K)) for various polymer/probe systems

Polymer	Probe	V_p^a	$V_p^\ddagger^a$	T_f	Ref.
PVC	DPBPE	242.0	108.2	276 ± 8	This work
	Methyl dichlorophosphate	96.8	26.3	169 ± 7	²⁵
PMMA	DPBPE	242.0	108.2	326 ± 18	This work
	Methyl dichlorophosphate	96.8	26.3	190 ± 14	²⁵
	1,2-Dichloroethane	75.2	23.5	195 ± 10	²⁶
	1,2-Bromofluoroethane	71.5	13.0	190 ± 20	²⁵

^aThe van der Waals volumes (\AA^3) obtained by the additive scheme²⁷

Table 2 The T_f values and the relaxation transition temperatures (K) obtained for PVC and PMMA

Polymer	T_{rel}	Method ^a	Assignment	Ref.
PVC	276 ± 8		T_f for DPBPE	This work
	230–250	a	Segmental mobility including <i>trans-gauche</i> transitions in the regions with lower density (β -relaxation)	³³
	243	b	β -Relaxation	³⁴
	220	c	Freezing of conformational transitions in pure polymer	³⁵
	270	b	Rupture of dipole-dipole physical units in disordered amorphous phase (π -transition)	³⁶
	278	b	β -Relaxation	³⁷
PMMA	326 ± 18		T_f for DPBPE	This work
	280–290	a	Segmental mobility including <i>trans-gauche</i> transitions in the regions with lower density (β -relaxation)	³³
	278	b	Motions of C(O)OCH ₃ groups (β -relaxation)	³⁸
	260–295	b	β -Relaxation	³⁹
	250	c	Freezing of conformational transitions in pure polymer	³⁵
	291	d	Reorientational or vibrational motions of –OCH ₃ groups (β -relaxation)	⁴⁰
	277	e	Reorientational or vibrational motions of –OCH ₃ groups (β -relaxation)	⁴⁰
	345	e	Rotation of C(O)OCH ₃ groups around the main chain	⁴⁰
	313	b	Rotation of C(O)OCH ₃ groups around the main chain (β -relaxation)	⁴¹
333	b	Mobility of the fragments smaller than statistical segments	⁴¹	

^aMethods: (a) differential scanning calorimetry; (b) mechanical relaxation; (c) far infrared spectroscopy; (d) acoustic relaxation; (e) measurement of velocity of sound

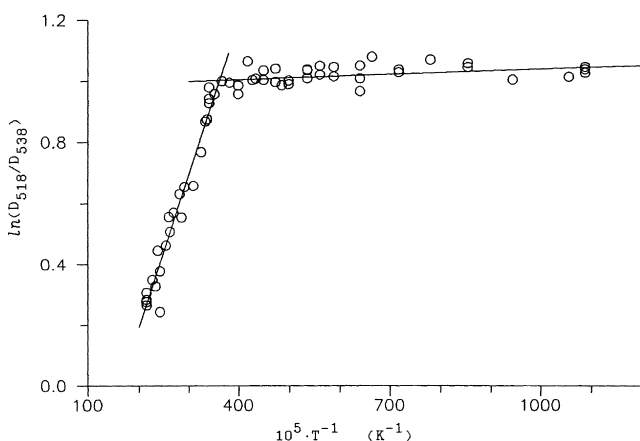


Figure 3 The dependence of $\ln(D_{518}/D_{538})$ upon T^{-1} for DPBPE in PVC. The lines show the least-square approximation of the high- and low-temperature branches. The intersection points correspond to $T_f = 276 \pm 8$ K

obtained previously^{25,26}, and the literature data on relaxation transition temperatures of the polymers.

First, it should be noted that the T_f values determined for polymer/DPBPE systems are significantly higher than those obtained when 1,2-bromofluoroethane, methyl dichlorophosphate and 1,2-dichloroethane were used as the probes in the same polymers (Table 1). Table 1 also shows the van der Waals volumes of the probes (V_p) and their activation volumes (V_p^\ddagger). Since the studied bands of DPBPE belong

mainly to conformers I (*gauche*) and II (*trans*), the activation volume necessary for the *trans-gauche* transition ($V_{p(t-g)}^\ddagger = 108.2 \text{ \AA}^3$) is taken as a characteristic value for the polymer/DPBPE systems. The data of Table 1 confirm the finding of our previous studies, that the higher the V_p and V_p^\ddagger magnitudes are, the higher the freezing temperature for its conformational equilibrium is.

Second, it is seen that the T_f values fall below the glass transition temperatures (T_g) of the polymers: 353 (PVC) and 380 K (PMMA). Hence the freezing of the conformational mobility in the probe cannot be attributed to the glass transition. The effect of plasticisation should be neglected because of relatively small concentrations of the probe (1.5 vol.%), and the fact that DPBPE is a crystalline solid far above the obtained T_f values.

It is widely accepted, that β -relaxation occurs in PVC and PMMA at 230–250 and 280–290 K, respectively³³. Some of the β -relaxation transition temperatures (T_β), obtained by differential scanning calorimetry³³, mechanical relaxation^{34,36,38,39}, far infrared spectroscopy³⁵, acoustic relaxation⁴⁰ and measurement of velocity of sound⁴⁰ are given in Table 2. It is seen that the T_f magnitudes fall above the T_β -values for both DPBPE/PVC and DPBPE/PMMA systems.

Nevertheless, some relaxation processes taking place at temperatures between T_β and T_g have been registered in the polymers under study as well (Table 2). Thus, the maxima found in mechanical and acoustic relaxation spectra of PVC^{36,37} and PMMA^{40,41} fall in the vicinity of the T_f values for the polymer/DPBPE systems. Thus, freezing of the

conformational mobility of DPBPE, probably, reflects some of the secondary relaxation transitions of the polymers.

The processes responsible for secondary relaxation of PVC and PMMA are an object of extensive discussions^{33–48}. Table 2 shows the assignments of the β -process which has been given in some of the cited works. In addition to the data of Table 2 it should be noted that the β -process in PVC was attributed to: vibrational motions of C–Cl groups⁴²; vibrations of small chain fragments, including several carbon atoms⁴³; segment reorientations (flips)⁴⁷. The β -relaxation transition in PMMA was interpreted as the result of bending motions or rotations of the main chain along its axis⁴⁴, and the hindered rotation of the C(O)CCH₃-groups about C–C bonds linking to the main chain⁴⁵. One can see that these assignments are somehow contradictory. In addition it should be noted that, in some of the papers^{37,41}, the processes which occur at temperatures higher than 230–250 for PVC and 280–290 K for PMMA were denoted as ‘ β -relaxation’ as well.

To our mind, the contradictions in interpreting the β -relaxation process are mainly due to the fact that the methods of mechanical, acoustic and dielectric relaxation do not allow one to make an unambiguous assignment of the observed effects. Apparently, the behaviour of probes can throw some more light on that problem. It is obvious that the scale of motions that are frozen at T_f correspond to the activation volume of the probe used in this work: $V_{p(t-g)}^\ddagger = 108.2 \text{ \AA}^3$.

It seems interesting to compare $V_{p(t-g)}^\ddagger$ with the van der Waals volumes of the lateral groups of PMMA. The volume of the –C(O)OCH₃ group minus the increment of the carbon atom linked to the main chain equals 33.6 \AA^3 ; the corresponding value for the alkoxy group (–OCH₃) is 26.3 \AA^3 (all the values were calculated by the additive scheme²⁷). It follows that the internal rotation of both –OCH₃ and –C(O)OCH₃ groups can not be considered as an origin of the relaxation process found in PMMA at $326 \pm 18 \text{ K}$.

The $V_{p(t-g)}^\ddagger$ value is close to the volume of one monomer unit of PMMA (98.75 \AA^3) and approximately two times larger than that for PVC (49.15 \AA^3). Though based on the $V_{p(t-g)}^\ddagger$ value only, it is hardly possible to make an exact interpretation of the processes occurring at T_f values, one should not rule out the internal rotation of monomer units in the both polymers.

The behaviour of one more probe introduced into PMMA reveals the peculiarity in the vicinity of $T_f = 328 \pm 18 \text{ K}$. Thus, one of the photochromic probes (9-hydroxymethyl-10-[(naphthylmethoxy)-methyl]anthracene, HNMA) exhibits freezing of its rotational diffusion at $313\text{--}333 \text{ K}$ ⁴⁹. The van der Waals volume of this probe is 344.0 \AA^3 . Though this value is noticeably larger than the molecular volume of DPBPE (242.0 \AA^3), it seems likely that the activation volume of HNMA molecule rotation as a whole is close to the volume needed for the conformational transition of DPBPE ($V_{p(t-g)}^\ddagger$).

On the basis of the obtained results, the average size of free volume entities of the polymers (V_h), corresponding to T_f temperatures can be estimated. The freezing of the conformational mobility of the probe indicates that no sufficient free volume is present in the vicinity of the introduced molecule. Two extreme situations should be considered: (i) the probe molecule is localised in the free volume hole and does not perturb the matrix; (ii) the probe molecule perturbs the matrix significantly. It is obvious that in the former case the size of free volume entity is close to

V_p at the temperature of freezing of the probe’s conformational mobility. In the latter case the V_h should be close to V_p^\ddagger . Thus, it follows that $V_p^\ddagger \leq V_h \leq V_p$.

The widespread approach to evaluating the free volume entity sizes is the positron annihilation lifetime spectroscopy (PALS). It seems interesting to compare the results obtained by two independent methods. The mean radius of spherical hole for PVC at 295 K has been determined by PALS in Ref.⁵⁰: $R_h(\text{PVC}) = 2.60 \pm 0.05 \text{ \AA}$. Since for the PVC/DPBPE system the T_f value is close to 295 K, the above magnitude of $R_h(\text{PVC})$ may also be extended to the T_f temperature. In Ref.⁵¹ the lifetimes of *ortho* positronium (τ_3) in pure and plasticised PMMA at various temperatures were obtained. Taking the τ_3 value determined for pure PMMA at $T_f = 326 \text{ K}$ ($\tau_3 = 1.98 \pm 0.01 \text{ ns}$), and assuming the validity of the infinite spherical potential model⁵², we calculated the mean hole radius for this polymer: $R_h(\text{PMMA}) = 2.84 \pm 0.05 \text{ \AA}$.

Thus, at the temperatures close to T_f the obtained sizes of the free volume entities obtained by PALS ($V_h(\text{PALS})$) are equal to 73.6 ± 4.4 and $95.9 \pm 5.8 \text{ \AA}^3$ for PVC and PMMA, respectively. One can see that these values are close to the volume of the conformationally mobile fragment of DPBPE, which we assumed to be equal to the activation volume ($V_{p(t-g)}^\ddagger = 108.2 \text{ \AA}^3$). The closeness of V_p^\ddagger to V_h indicates that the probe significantly perturbs the matrix. It should be also noted that the obtained V_h values do not fit one of the above-mentioned relationships, i.e. actually $V_h(\text{PALS}) < V_p^\ddagger$. This discrepancy may be attributed to the assumptions used both in PAL spectroscopy and in the study of the ‘conformational’ probes. To our mind, the main assumption of the latter approach is the way of estimating the activation volume of the conformational probe, V_p^\ddagger . It seems likely, that the true activation volume necessary for conformational transition of the probe is slightly smaller than the size of its conformationally mobile groups. Nevertheless, the satisfactory agreement with the data obtained by PAL spectroscopy indicates that the conformational probes can be used as an independent approach for studying the free volume distribution in glassy amorphous polymers.

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