Small conformationally mobile molecules as probes for molecular mobility in glassy polymers

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A new method for studying molecular mobility in glassy polymers—the method of conformationally inhomogeneous probes—is described. A small quantity of a low-molecular-weight compound (probe) having unidentical conformations with different vibrational spectra is introduced into a polymer. The thermodynamic and activation parameters responsible for the concentrations of the conformers and the rates of conformational transitions are connected with both the intramolecular interactions and the properties of the medium (e.g. polymer). Information about the kinetics and equilibria of the conformers could be obtained by investigating the vibrational spectra. This information may be the key to understanding the molecular mobility and free-volume distribution in polymers. The following compounds were used as probes: 1,2-bromofluoroethane, methyl dichlorophosphate and *trans*-1,2-dichlorocyclohexane. The polymers polystyrene, poly(vinyl chloride), poly(methyl methacrylate), poly(vinyl acetate), poly(vinylbutyral), polypropylene and polybutadiene were investigated. The temperature dependences of the absorption-band intensities of the probes were studied. Freezing of the conformational transitions in the probe molecules was found at temperatures T_f characterizing specific polymer–probe systems. The T_f are close to the temperatures of the relaxation transitions in the pure polymers. The possibilities of the method are discussed.

(Keywords: glassy polymers; molecular mobility; conformationally mobile probes)

INTRODUCTION

Molecular mobility and the distribution of free volume in glassy polymers have been intensively studied by different physical methods. The methods of dielectric, mechanical and acoustic relaxation[1–12] and differential scanning calorimetry[13,14] are the most developed. The spectroscopic methods (n.m.r.[1,15,16], excimer fluorescence spectroscopy[17], far-i.r. spectroscopy[18,19]) are also widely used. Methods based on the use of molecular probes are numerous. The mobilities of spin[20], electrochromic[21,22], fluorescence[23,24], excimer-forming[25,26] and photochromic[27,28] probes, the kinetics of proton transfer in polymers[29,30] and the kinetics of ring closure of merocyanine[31] have been studied. The great number of approaches indicates, on the one hand, that interest in studying molecular mobility in polymers grows and, on the other hand, that a universal approach to this problem is absent. The various physical methods are aimed at investigating different aspects of molecular mobility, and their data are complementary.

Earlier[32] we proposed a new approach to study molecular mobility in glassy polymers, which is based on the investigation of the conformational mobility of small molecules introduced into polymers. The present paper is devoted to describing the approach and discussing the results obtained up to now.

METHOD OF INVESTIGATION

The basis of the approach is as follows. A small quantity of low-molecular-weight compound (probe) having at least two unidentical stable conformations A and B in dynamic equilibrium:

$$A \overset{K}{\rightleftharpoons} B \qquad (1)$$

is introduced into the polymer. Here K is a conformation equilibrium constant. Classic examples of the compounds in question are 1,2-disubstituted ethanes having two stable conformers, *trans* and *gauche*. The value of the equilibrium constant is determined by the relation:

$$K = \exp(-\Delta H_0/RT + \Delta S_0/R) \qquad (2)$$

where ΔH_0 and ΔS_0 are the enthalpy and entropy differences of the conformers. The rate of the conformational transitions is determined by activation free enthalpy $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$, where $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are the enthalpy and entropy of activation. The values ΔH_0, ΔS_0, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are connected with both the intramolecular interactions and the properties of the medium (e.g. polymer). Hence, information about the structure and molecular mobility of the polymers may be obtained by investigating the thermodynamic and kinetic parameters of the probe conformations.

The shift of the conformational equilibrium and the rate of the conformational transitions may be registered by infra-red spectra. According to the Lambert–Buger–

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Beer law, one may write for the integral intensities I_A and I_B of the absorption bands of the conformers:

$$\ln(I_A/I_B) = \ln(\alpha_A/\alpha_B) - \Delta H_0/RT + \Delta S_0/R \qquad (3)$$

where α_A and α_B are the integral absorption coefficients of analytical bands. It is seen from (3) that if there are conformational transitions in the system and $\Delta H_0 \neq 0$, then the experimental value $\ln(I_A/I_B)$ must depend on temperature.

If a low-molecular-weight compound is added to a polymer as a probe (an admixture) and the temperature of the sample is decreased, then the values ΔH_0, ΔS_0, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ may be a function of the processes taking place in the polymer. In particular, starting from some temperature T_f, freezing of conformational mobility in probe molecules may occur. The temperature T_f is easily fixed in an experiment by the change in the slope of the dependence $\ln(I_A/I_B) = f(1/T)$. If the ratio α_A/α_B does not depend on temperature, then at $T < T_f$ the dependence $\ln(I_A/I_B) = f(1/T)$ becomes parallel to the abscissa.

Thus, when comparing the structure of the probe and the studied polymer, one may propose the processes that take place in polymers at temperatures close to T_f.

EXPERIMENTAL

The following polymers were used to prepare the systems that were then experimentally analysed: atactic polystyrene (PS), emulsion polymerized, viscosity-average molecular weight $M_\eta = 1.1 \times 10^5$; poly(vinyl chloride) (PVC), suspension polymerized, trademark C-70; poly(vinyl acetate) (PVA), emulsion polymerized, with $M_\eta = 4.4 \times 10^4$; poly(methyl methacrylate) (PMMA), blend polymerized, with melt viscosity index 0.5, and thermostability according to Vika 380 K; polybutadiene (PBD), with $M_\eta = 4 \times 10^4$; poly(vinylbutyral) (PVB), product of Lauson; and atactic polypropylene (PP). All polymers were commercially available non-fractionated products and were used as obtained. We determined the isomeric composition of PBD using the method[33]: 67% 1,4-*trans*, 27% 1,4-*cis* and 6% 1,2 isomer. Its glass transition temperature measured by d.s.c. is 200 K.

Polymer films having a thickness of 0.03–0.15 mm were prepared by evaporating the solvent from the solution of polymer: PS and PVA by evaporating chloroform, and PVC by evaporating tetrahydrofuran. PMMA, PP and PVB films were prepared by milling.

1,2-Bromofluoroethane ($CH_2Br–CH_2F$, BFE), methyl dichlorophosphate ($P(O)Cl_2–OCH_3$, MDCP) and *trans*-1,2-dichlorocyclohexane ($C_6H_{10}Cl_2$, DCCH) were used as probes. The compounds were synthesized according to refs. 34–36. Structural and spectral parameters of the probes are given in *Table 1*.

A probe was introduced into a polymer from the gaseous phase. The duration of the saturation was varied depending on the polymer–probe pair in the range from 10 min to 10 h. Then, in order to get a homogeneous distribution of a probe in a polymer, the samples were kept at room temperature for a few hours. The time was much larger than that calculated taking into account the diffusion coefficient of a probe in a polymer[40]. In addition, the homogeneity in the distribution of a probe along the thickness of the film was controlled by a.t.r. spectroscopy.

The concentration of the probe and the thickness of the absorbing layer were calculated by i.r. spectra using the Lambert–Buger–Beer law. The necessary absorption coefficients were determined beforehand from i.r. spectra of solutions of a probe (or a polymer) in solvents having dielectric constants close to that of the polymers studied. As a result, the concentration of a probe was equal to 1–4% (~0.1 mol l^{-1}).

The i.r. spectra were registered with a Specord M 80 spectrometer and processed by computer. The low-temperature measurements were carried out with a one-beam cryostat cooled by liquid nitrogen. Temperature was measured with a copper–constantan thermocouple with an accuracy of ±0.5 K. The average cooling rate was 0.07 K s^{-1}. During the experiment (8–10 h), 25–30 i.r. spectra were recorded at different temperatures.

RESULTS AND DISCUSSION

As an example, parts of the spectra of DCCH in PP at various temperatures are given in *Figure 1*. Redistribution of the absorption-band intensities of the conformers occurs as the temperature is varied. An example of the quantitative treatment of spectra is given in *Figure 2*. All dependences $\ln(I_A/I_B) = f(1/T)$ consist of two linear branches. Such curves indicate that freezing of the conformational equilibrium of the probes takes place at the intersections of the branches (at temperatures T_f).

Statistical treatment of experimental data was carried out according to ref. 41. The error in T_f was determined to be the extreme left and extreme right points in the intersection of confidence ranges of straight lines.

It was found that the variation in concentration of a probe within 1–4 vol% does not lead to variations in T_f exceeding the limits of accidental experimental errors.

The T_f values for polymer–probe pairs determined in this way are given in *Table 2*. The blank spaces in the table correspond to situations when the absorption bands

Table 1 Structural and spectral parameters of the probes

Compound	V_p[a]	$V_p^{\ddagger}$[b]	Conformations	Analytical i.r. bands (cm^{-1})	Ref.
BFE	71.5	13.0	*trans* (*t*) *gauche* (*g*)	680 450	36
MDCP	96.8	26.3	*trans* (*t*) *gauche* (*g*)	586, 518 608, 548	34, 38
DCCH	132.3	~100	diaxial (*aa*) diequatorial (*ee*)	1006, 699, 616, 498 909, 747, 514, 448	35, 39

[a] V_p = van der Waals molecular volume ($Å^3$) calculated by additive scheme[37]

[b] $V_p^{\ddagger}$ = van der Waals volume ($Å^3$) of the smallest mobile group of the molecules (e.g. H_2F, CH_3 and volume close to volume of DCCH) calculated by additive scheme[37]

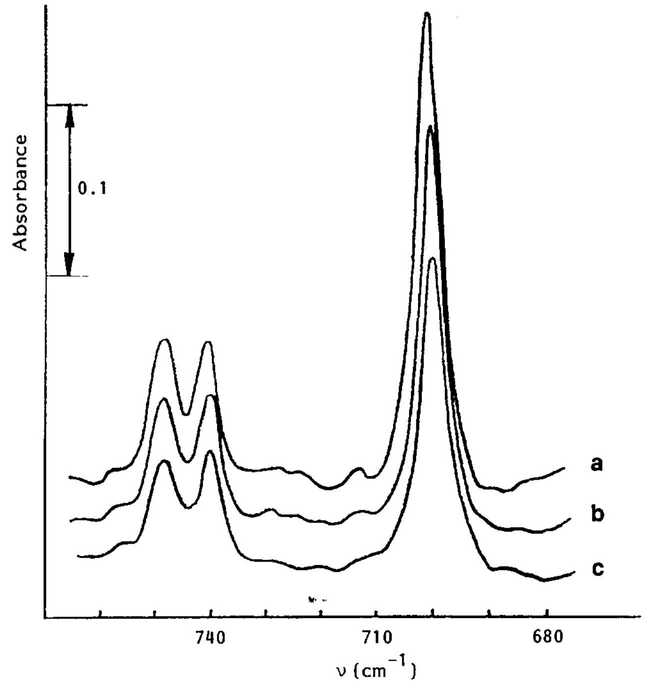

Figure 1 I.r. spectrum of *trans*-1,2-dichlorocyclohexane (DCCH) in PP: (a) $T=145$ K; (b) $T=203$ K; (c) $T=297$ K

of the probe do not fall in the spectral range in which the polymer investigated is transparent.

The values of the activation energy of conformational transitions in probe molecules are such that in liquid solutions the molecules keep their conformational mobility right down to 150 K (DCCH)[42] and 40–70 K (BFE and MDCP)[43]. Since the freezing of conformational mobility for probes introduced into polymers occurs at essentially higher temperatures, one may state that the freezing of conformational transitions is due to processes occurring in the polymers.

It should be noted that T_f values are significantly lower than the glass transition temperatures T_g (α transition) of the most pure polymers[40] (except PBD). It is well known[44] that addition of 1–4% of low-molecular-weight compound can shift T_g by 5–30 K. Study of some of our systems by differential scanning calorimetry enabled us to confirm the above evaluation. Straight-line dependences of $\ln(I_A/I_B)$ upon $1/T$ indicate the absence of distortions in homogeneous distribution of low-molecular-weight compounds in samples. Thus, freezing of conformational transitions does not reflect plasticized glass transitions in the systems under investigation.

We compared the T_f values with the temperatures of relaxation transitions T_{rel}. The T_{rel} values closest to the

Table 2 Freezing temperatures T_f (K) of conformational transitions

	T_f(K)						
Polymer	BFE	MDCP	DCCH	T_{rel} (K)	Assignment	Method*	Ref.
PS	–	144±10	183±21	130–170	Rotations of phenyl (Ph) groups	a	1
				145	β_1 transition (rotation of Ph groups)	b	8
				178	–	b	1
				164	Vibration mobility of Ph groups	c	7
				193	Vibration mobility of Ph groups	b	7
				197	Vibrations of phenyl groups	d	1
				120, 190	–	e	1
				132	γ transition	f	18
PVC	–	169±7	192±17	120–130	Hindered motion of Cl atoms	e	1
				150	–	g	1
				220	β transition	f	19
				203	Hindered motion of Cl atoms	d	5
PMMA	190±20	190±14	210±12	188–198	Main-chain methyl groups motion	h	10
				190	–	g	1
				198	Main-chain methyl groups motion	d	5
				170	γ transition	f	18
PVA	170±20	200±13	218±13	173, 233	γ and β transitions	b	1
				195	–	d	5
				200–240	β transition	c	13
PVB	193±25	–	213±20	–	–	–	–
PP	157±12	–	201±26	147	Motions of methyl groups	i	1
				203	Twisting vibrations of CH_3, CH_2, CH groups	b	1
				160	Rotation of CH_3 groups	e	1
				170–200	β transition	c	13
PBD	–	148±7	170±15	129–138	β transition	b	12
				154–188	β_1 transition	b	12

*Methods: (a) dielectric relaxation; (b) mechanical relaxation; (c) differential scanning calorimetry; (d) measurement of velocity of sound; (e) measurement of velocity of ultrasound; (f) far-i.r. spectroscopy; (g) measurement of Young's modulus; (h) temperature dependence of rigidity; (i) dilatometry

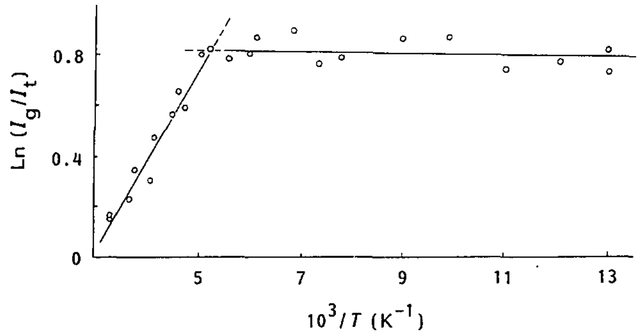

Figure 2 The dependence of $\ln(I_g/I_t)$ upon $1/T$ for 450 cm^{-1} (g) and 680 cm^{-1} (t) absorption bands of 1,2-bromofluoroethane (BFE) in PMMA

measured T_f values have been chosen from literature data. The data are mostly taken from three monographs[1,5,13] (*Table 2*). It is seen that for each T_f value one may get a corresponding relaxation transition discovered by another method. In some papers quoted in *Table 2* attempts have been made to assign the observed relaxation transitions to specific motions in polymers that are frozen (or unfrozen) at the relaxation transition temperatures (see the table). It should be noted that relaxational methods of investigation do not allow one to make an unambiguous interpretation of the observed effects. In this respect methods based on the use of probes can be very helpful.

One may characterize the scale of motions that are frozen in polymers at T_f by the volume of a minimal conformationally mobile fragment of a probe $V_p^{\ddagger}$ (this value is close to the value of the free volume that is necessary for a conformational transition to occur). Obviously, at $T < T_f$ motions requiring a free volume larger than $V_p^{\ddagger}$ are frozen.

One may see the following (*Table 2*): the probe having a smaller volume of conformationally mobile fragment $V_p^{\ddagger}$ has as a rule a smaller T_f value for a given polymer.

The following fact is surprising. In spite of a significant difference in the volumes $V_p^{\ddagger}$ of BFE and DCCH (only the CH_3 group has the size of conformationally mobile fragment smaller than the probe BFE (*Table 1*)), when these molecules are introduced into PMMA and PVB the freezing of conformational transitions occurs practically at the same temperature. At the same time for PP the difference in T_f amounts to 44 K.

In our opinion the difference in the relationship between $V_p^{\ddagger}$ and T_f for different polymers can be explained as follows. The dependence of T_f on $V_p^{\ddagger}$ is probably stepwise, step length being defined by the structure of the polymer. The relaxational process occurring at some temperature T^i_{rel} leads to the freezing of motions requiring free volume within a certain range of values from $V^i_{\max}$ to $V^i_{\min}$. For all the probes having $V^i_{\max} \geqslant V_p^{\ddagger} \geqslant V^i_{\min}$ the freezing of conformational mobility must occur at T^i_{rel}. For the probes having $V_p^{\ddagger} > V^i_{\max}$ or $V_p^{\ddagger} < V^i_{\min}$ the freezing of conformational transitions will occur at the temperatures of another relaxation transition T^i_{rel}. Obviously, for PMMA, the values $V_p^{\ddagger}$ of the probes BFE and DCCH fall in the range of one and the same relaxation transition; however, for PP these probes fall in the range of different transitions.

Thus, by introducing different conformationally inhomogeneous probes into a polymer, one may evaluate the scale of motions that are frozen at temperatures of different relaxation transitions.

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