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Poly(methyl methacrylate)/ 1,2-dichloroethane system: freezing of conformational mobility in the low-molecular component

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The conformational dynamics in 1,2-dichloroethane (DCE)/poly(methyl methacrylate) (PMMA) mixtures has been studied at different concentrations of DCE. The intensities of the infrared absorption bands belonging to the *trans* and *gauche* conformers have been measured in the 77–300 K temperature range. Besides, the glass transition temperatures of the mixtures T_g were determined by the differential scanning calorimetry. For all the systems under investigation the freezing of the conformational transitions has been found: below a certain temperature T_f the *trans/gauche* ratio becomes temperature independent. The T_f value for the lowest volume fraction of DCE ($C = 0.01$) was found to be close to the temperature of one of the secondary relaxation transitions of pure PMMA (195 K). At this temperature the free volume entities in PMMA should have the volume close to that of the conformationally mobile groups of DCE (~25 Å^3). The concentration dependence of T_f consists of two branches. At low concentrations of the diluent ($C < 0.6$) T_f slowly decreases with the concentration of DCE, reflecting the concentration behaviour of the relaxation transition temperature. At the higher concentrations the freezing of the conformational equilibrium in DCE occurs at the glass transition of the mixtures, and the T_f values are close to the T_g ones. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

The local dynamics and free volume distribution in polymers have been extensively studied by different physical methods. A significant part of the data, published during the last 20 years, was obtained using various molecular probes introduced into the polymers[1-3]. All the probes used can be subdivided into two groups, according to their behaviour in the polymer matrix. First, there are probes for which the rotational or translational dynamics of the molecules as a whole is investigated. This group includes spin[4], some of fluorescent[5,6], electrochromic[7] and hydrogen-bond-forming probes[8,9]. Second, there are probes for which the internal rotation is under investigation. For the most part of such probes the internal rotation is achieved by the photoexitation of the molecules. This group includes excimer-forming[10], various kinds of fluorescent[11-13] and photochromic[14,15] probes.

The probes included in the latter group differ both in their molecular volumes (V_p) and in the volumes needed for the photoisomerization ($V_p^{\neq}$). The larger is V_p, the larger are the distortions of the polymer matrix caused by the introduced molecule. In this connection, the sizes of the probes should be as small as possible. The volumes of conformationally mobile groups of the probes correspond to the scale of molecular mobility in polymers which could be investigated by using these probes. Here, the smaller is $V_p^{\neq}$ of a probe, the smaller is the size of the free volume entities which could be testified by it, and the smaller are the molecular fragments of the polymer, which motions could be modelled by similar motions of the probe.

Recently, a new method of studying the molecular mobility in polymers was proposed[16]. It is based on the investigation of the conformational equilibrium in a low-molecular-weight compound (probe) introduced into a polymer. The decrease of the temperature causes the concentration redistribution over the conformers, if there is equilibrium between them. However, if the conformational equilibrium is frozen, the concentrations of the conformers do not change with temperature. It was reported[16], that each polymer/probe system is characterized by a certain temperature (T_f) below which the conformational equilibrium is frozen. The T_f values were found to be dependent both of 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 proposed, that the freezing of the conformational equilibrium reflects some processes

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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 V_p and $V_p^{\neq}$ values of the probes used in ref. 16 (1,2-bromofluoroethane, methyl dichlorophosphate and *trans*-1,2-dichlorocyclohexane) lie in the following ranges: $71 < V_p < 133\,Å^3$ and $13 < V_p^{\neq} < 100\,Å^3$. These values are significantly smaller than those of the excimer-forming, fluorescent and photochromic probes[10–15]. As an example, the volumes needed for the isomerization of the photochromic probes[15] are in the 127–575 Å^3 range. Therefore, in comparison with the well known probes[10–15], the conformational behaviour of the ones used in ref. 16 reflects the mobility of smaller molecular units of the polymers, and, as a result, the freezing of the conformational equilibrium should be observed at lower temperatures.

The aim of the present work is the application of the method, proposed in ref. 16, to a polymer/diluent system. The dependence of T_f upon the concentration of the diluent is investigated. Poly(methyl methacrylate) (PMMA) and 1,2-dichloroethane (DCE) are taken as the objects of the study. DCE is used both as the probe and the diluent: its volume fraction in the mixtures with PMMA is varied from 0.01 up to 1.00. The *trans–gauche* conformational equilibrium of DCE in the liquid solutions has been extensively studied[17–19]. The conformational transition in DCE involves the rotation of one of the CH_2Cl groups around the C–C bond. The van der Waals volume of the DCE molecule, calculated by additive scheme[20] is equal to $V_p = 75.2\,Å^3$. The estimated swept out volume needed for the conformational transition was found to be close to the van der Waals volume of the CH_2Cl group minus the increment of the carbon atom: $V_p^{\neq} = 23.5\,Å^3$. The conformational dynamics in the polymer/diluent systems was examined by the infrared (i.r.) spectra of the samples.

EXPERIMENTAL

Blend polymerized, with melt viscosity index 0.5, and thermostability according to Vika 380 K PMMA was used. Commercially available 1,2,-dichloroethane was purified according to ref. 21.

The samples were prepared in two ways. (i) PMMA films having the thickness 0.03–1.0 mm were prepared by milling. Then DCE was introduced into the polymer from the gaseous phase at room temperature. The duration of the saturation was varied depending on the anticipated concentration in the range from 10 min to 1 h. Then, in order to get a homogeneous distribution of the probe in the polymer and to remove the excess of DCE in the film, the samples were kept at room temperature for several days. The concentration (volume fraction, *C*) of DCE in the samples, prepared in such a way were not larger than 0.3. (ii) The samples having larger concentrations were prepared from solutions of PMMA in DCE. The drop of the solution was kept between two KBr windows for several days in order to obtain the necessary concentration of DCE.

The volume fraction of DCE in the sample and the thickness of the absorbing layer were calculated from the i.r. spectra using the Beer's law. The necessary absorption coefficients were determined beforehand from i.r. spectra of solutions of DCE in acetone and PMMA in chloroform. In addition, the concentrations of DCE were evaluated by weight. A good agreement was found between the two ways of measurement.

The i.r. spectra were registered with a Specord M 80 spectrometer combined with a computer. The low temperature measurements were carried out with a one-beam cryostat cooled by liquid nitrogen. Temperature was measured with a platinum resistor with an accuracy ±0.5 K. The average cooling rate was 0.07 K s^{-1}.

Special attention was paid to the possibility of the phase separation in the systems under study. The absence of the phase separation was supported by three facts. First, the transparency of the samples was stable during the time much larger than the time of the experiments. Second, if the phase separation takes place the domains with the high concentration of DCE should appear. Then, crystallization of DCE should be observed in these domains at temperatures below its melting point (238 K). However, no evidence of crystallization was found both in the i.r. spectra and visually, in the crossed polarizers. Third, as will be shown below, the temperature of freezing of the conformational transitions in DCE was found to be dependent on its concentration. This is possible only if there is no phase separation in the systems.

The glass transition temperatures (T_g) of pure PMMA and some of the samples were determined by differential scanning calorimetry. The measurements were carried out with the Perkin Elmer DSC-2 device at the cooling rate 0.3 K s^{-1}.

RESULTS AND DISCUSSION

It is well known, that in the liquid state and solutions of DCE the equilibrium between *gauche* (g) and *trans* (t) conformers exists[17,18]. Vibrational spectra of DCE were studied in detail in refs 22 and 23. The band pair 710 (t) and 655 cm^{-1} (g) was found to be the most convenient for the investigations, as these bands fall in the transparency

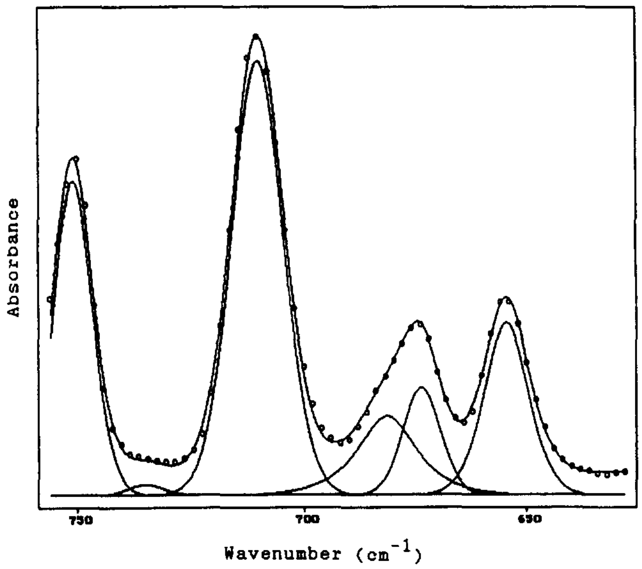

Figure 1 I.r. spectrum of DCE/PMMA system at 300 K. The volume fraction of DCE is 0.35. The experimental spectrum (circles) is fitted by the sum of components (continuous curve)

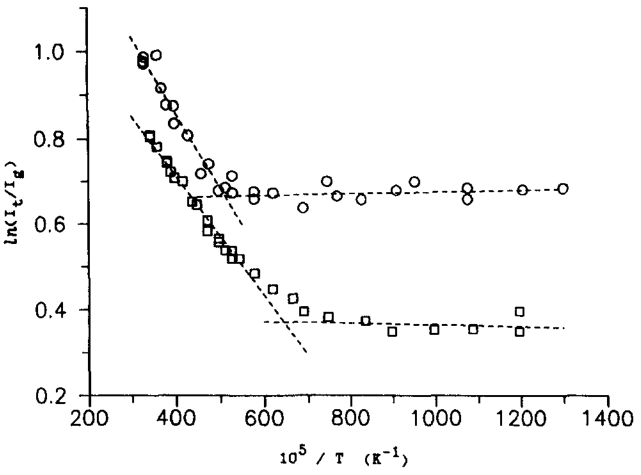

Figure 2 The temperature dependencies of $\ln(I_t/I_g)$ for the bands at $710\,cm^{-1}$ (t) and $655\,cm^{-1}$ (g) of DCE. The volume fraction of DCE is 0.033 (circles) and 0.60 (squares). The dashed lines show the least square approximation of the high- and low-temperature branches. The intersection points correspond to $T_f = 195\,K$ ($C = 0.033$) and 155 K ($C = 0.60$)

range of PMMA. As an example, the i.r. spectrum of one of the samples is shown in *Figure 1*. The spectra in the range $756-628\,cm^{-1}$ were fitted by the sum of the components with the form of the multiplication of Lorentzian and Gaussian functions. In addition to the above mentioned band pair two bands of PMMA at 751 and $735\,cm^{-1}$ and two more bands of DCE at 682 and $674\,cm^{-1}$ fall in this range. One can see, that the bands at 710 and $655\,cm^{-1}$ are isolated enough from their neighbours and therefore their peak and integrated intensities could be evaluated reliably. As the peak intensities (I_t, I_g) were determined with a higher accuracy, they were used below when considering the conformational equilibrium in DCE.

The dependencies of $\ln(I_t/I_g)$ upon T^{-1} for the samples with the volume fractions of DCE 0.033 and 0.60 are shown in *Figure 2*. Each of the obtained dependencies consists of two branches. The high-temperature branches reveal the temperature redistribution of the conformers. It is well known that all thermodynamic parameters of the conformational equilibrium in DCE are strongly dependent on the solvent[17–19]. The *trans* conformer is more stable in the gas phase, while the *gauche* one is more stable in polar solvents[17,18]. As far as we know, the enthalpy differences of the conformers of DCE dissolved in glassy polymers has not been yet measured. In the case of DCE/PMMA system the *gauche* conformer is found to be more stable for all the samples (cf. *Figure 2*). We have determined the enthalpy difference of the conformers ΔH, using the van't Hoff equation for the high-temperature branches. The ΔH value was found to be independent of the concentration of DCE within the following limits: $\Delta H = 0.22 \pm 0.07\,kcal\,mol^{-1}$.

The low-temperature branches show the absence of the temperature redistribution of the conformers: the curves are nearly parallel to the abscissa. Thus, freezing of the conformational equilibrium takes place in the temperature ranges where the branches are intersected.

Statistical treatment of the data was carried out according to ref. 24. The T_f values were determined as the intersection points of the straight lines, approximating the rectilinear parts of the high- and low-temperature branches. The accuracy of the determination was ±10 K. It is seen from *Figure 2* that the dilution of PMMA by DCE leads to the decrease of T_f. In addition, it should be noted that the temperature region intermediate between the rectilinear left and right parts of the curves becomes broader. This may be due to the fact, that the increase of the DCE concentration leads to an additional inhomogeneity of the surrounding of the DCE molecules.

Table 1 The T_f values (K) for some of the PMMA/DCE systems

Volume fraction of DCE	T_f^a	Volume fraction of DCE	T_f^a
0.012	193	0.46	167
0.033	195	0.60	155
0.10	193	0.74	126
0.35	173	1.00	109^b

[a] The accuracy of the evaluation ±10 K
[b] Ref. 36

Some of the obtained T_f values are presented in Table 1, and all the data are shown in *Figure 3*.

It has been well established, that both intra- and intermolecular interactions may be responsible for the freezing of conformational equilibria[25–27]. When the conformational transitions take place in a liquid medium, the freezing of the conformational equilibrium is primarily due to the intramolecular forces. For such systems it has been found that the T_f values are proportional to the heights of the barriers to internal rotation[25,27]. Using the barrier height for DCE ($5.15\,kcal\,mol^{-1}$)[28] and the data of ref. 27, we estimated the hypothetical T_f value, for which only the intramolecular interactions are responsible. $T_f = 70\,K$. Comparing this temperature with those in *Table 1* one can see that freezing of the conformational transitions for the PMMA/DCE systems is not governed by the intramolecular barrier to internal rotation.

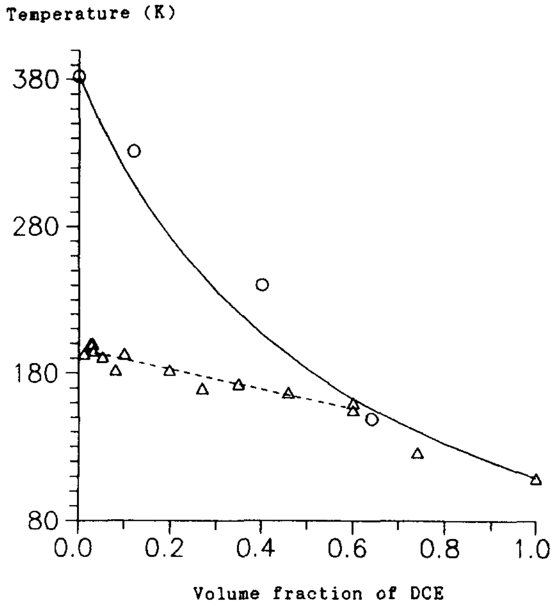

Figure 3 The dependence of T_f (triangles) upon the volume fraction of DCE. A part of the dependence in the range $0 < C < 0.6$ is fitted by a straight line (dashed). Circles correspond to the glass transition temperatures, measured by differential scanning calorimetry. The continuous line is drawn according to the relationship (1)

At low concentrations of DCE in PMMA the determined value of $T_f = 195 \pm 10\,K$ is close to the relaxation transition temperatures of pure PMMA, obtained by different methods: 188–198 K (temperature dependence of rigidity[29]); 190 K (measurement of Young's modulus[30]) and 198 K (measurement of velocity of sound[31]). Thus, it seems likely, that the freezing of the conformational equilibrium of DCE is due to the freezing of a certain type of mobility in the polymer matrix, taking place within this temperature range. Note also, that the T_f values obtained for the other conformationally-inhomogeneous probes introduced into PMMA[16] are close to the above mentioned ones: 190 K (1,2-bromofluoroethane); 190 K (methyl dichlorophosphate) and 210 K (*trans*-1,2-dichlorocyclohexane).

The process taking place in PMMA at these temperatures may involve freezing of internal rotation of one of the lateral groups. The possible types of internal rotation of PMMA groups are analysed in detail in ref. 32. We calculated the van der Waals volumes of the movable groups of PMMA using the additive scheme[20]. They should be close to the volumes needed for the conformational transitions. The volume of the ether group (-C(O)OCH$_3$) minus the increment of the carbon atom linked to the main chain equals 33.6 Å^3; the corresponding values for the alkoxy group (-OCH$_3$) is 26.3 Å^3 and for both methyl groups are 6.0 Å^3. It seems likely, that the group which internal rotation is frozen at 195 K should have the volume close to $V_p^{\neq}$ of the probe (23.5 Å^3). One can see, that the alkoxy group fits this condition. Therefore, it seems reasonable to assume that the relaxation process in question is due to the rotations of the alkoxy group around the C–O bond. The attribution of this process to the motion of the main chain methyl groups[29,31] seems questionable, if one takes into account the volumes and the intramolecular barriers to internal rotation of these groups ($\sim$7 kcal mol^{-1})[32].

It also follows from the obtained results, that the free volume entities in PMMA at 195 K should have the volume comparable with $V_p^{\neq}$. The parameters of the free volume distribution in polymers can be estimated from the data of positron annihilation lifetime spectroscopy[33–35]. As far as we know, the data for PMMA at low temperatures has not been obtained yet. However, the values in the range 35–120 Å^3, which were obtained when investigating the temperature dependencies of the average hole sizes in polycarbonate and polyoxymethylene[35], are in satisfactory agreement with our estimations.

It is seen from *Figure 3*, that the dependence of T_f upon C is approximately linear up to $C = 0.6$. This, probably, reflects the concentration behaviour of the corresponding relaxation transition.

In order to correlate the obtained T_f values with the glass transition temperatures (T_g), the latter were determined by differential scanning calorimetry for several concentrations of DCE. The following magnitudes were obtained (K): 382 (pure PMMA); 331 ($C = 0.12$); 240 (0.40) and 149 (0.64). The determined glass transition temperatures are shown in *Figure 3*.

The limitations of the experimental procedure precluded the measurements of T_g for the concentrations of DCE higher than 0.64. However, the glass transition temperature of the pure DCE can be estimated on the basis of the data of ref. 36. The amorphous films, obtained by condensing the vapour of DCE on a KBr plate at 77 K were found to contain both *trans* and *gauche* conformers[36]. Subsequent heating of the samples did not lead to the redistribution of the concentrations of the conformers up to the temperature 109 K, at which crystallization of DCE, accompanied with conformational transitions, started. Earlier it was shown that conformational equilibria of low-molecular-weight liquids freeze at their glass transition temperatures[26]. Therefore, the value 109 K may be considered as the glass transitions temperature of pure DCE.

It is evident that the concentration behaviour of T_g in the mixtures is due to the plasticization of PMMA by DCE. There are several approaches to describe the dependence of T_g upon C for polymer/diluent systems[37]. The most easy-to-use is the relationship, proposed by Kelley and Bueche[38], because all the parameters used in it are available. According to ref. 38:

$$T_g = \frac{\beta_p(1-C)T_{gp} + \beta_d C T_{gd}}{\beta_p(1-C) + \beta_d C} \qquad (1)$$

where β_p and β_d are the coefficients of the thermal expansion of the polymer and diluent respectively, T_{gp} and T_{gd} are their glass transition temperatures. The values $\beta_p = 5.5 \times 10^{-4}\,K^{-1}$ (ref. 39) and $\beta_d = 14.9 \times 10^{-4}$ (the average for chloroform and chloroethane)[40] were used in the calculations. The obtained curve is shown in *Figure 3*. One can see that there is a significant deviation from the experimental points at low concentrations of DCE. However, the T_g value measured at $C = 0.64$ appeared to be close to that predicted by equation (1). It seems likely, that for the PMMA/DCE system the concentration dependence of T_g has a 'dual behaviour', as has been found for some other systems[41,42].

At low concentrations of DCE the temperatures of freezing of the conformational equilibrium are significantly lower than T_g. However, the distance between T_g and T_f decreases with the dilution of PMMA, and the two dependencies become undistinguishably close at $C \sim 0.6$. At $C > 0.6$ freezing of the conformational transitions of DCE occurs due to the glass transition of the system.

Thus, the concentration dependence of T_f consists of two branches. At low concentrations of the diluent the system behaves as a plasticized polymer, and T_f values reflect one of the secondary relaxation transitions. At higher concentrations one obtains a solution of the polymer in the low-molecular-weight liquid. In the latter case the T_f values are close to the T_g ones.

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