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

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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 (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 Å^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 diffusivity[7], spin[4,8], electrochromic[9], hydrogen-bond-forming[10,11], and some fluorescence[6,12,13] and photochromic probes[5]. The intramolecular transformations have been studied for excimer-forming[14], various kinds of fluorescent[15–17], phosphorescent[18] and photochromic[19–21] probes. For the majority of the probes belonging to the latter group the transformations are achieved by photoexitation 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 molecu embedded in glassy polymers[22–24].

In our recent works we studied the conformatio behaviour of some low molecular weight compoun introduced into amorphous glassy polymers[25,26]. It l been proposed to investigate the temperature shift of t conformational equilibrium for analysing the relaxati transition phenomena and free volume distribution of t polymers. The decrease of the temperature cau the concentration redistribution over the conformers, there is an equilibrium between them. However, if t conformational equilibrium is frozen, the concentrations the conformers do not change with the temperature. It w reported[25] that each polymer/probe system is characteris by a certain temperature (T_f) below which the conform tional equilibrium is frozen. The T_f values were found to dependent both on the polymer and the probe. For the sa polymer the freezing temperature increases, as a rule, w the size of the conformationally mobile part of the pro molecule. It was also noted that T_f values are close to t temperatures of the secondary relaxation transitions the polymers. Thus, it was supposed that the freezing of t conformational equilibrium reflects some processes taki place in the polymers at the temperatures close to Comparing the structure of the probe and the polymer, o may propose a process, responsible for the observ relaxation transition. The distinctive feature of the meth is that it does not use photoexitation of the probe molecul

Each probe can be characterised by its molecular volu

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