

Dimerization of Fluorescent Molecular Probes on a Polystyrene Surface

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Abstract—Fluorescent spectroscopy is used to demonstrate the effect of vitrification of the surface layer of polystyrene on the mobility and dimerization of probe molecules in the layer. The results of this work agree well with the data obtained earlier using an independent technique.

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INTRODUCTION

Much current attention is focused on studying the relaxation processes (vitrification among them) occurring in the surface layers of high-molecular compounds since the structure and condition of the surface layer are the most responsible for the adhesion and friction properties of polymers, their biocompatibility, etc. In addition, composite materials, in which ordered ensembles of metal nanoparticles are stabilized in a thin surface layer of a glassy polymer, find increasingly wide application in optoelectronics and catalysis. In this case, vitrification may be of key importance in the formation of nanocomposites with design properties [1, 2].

In recent years, a variety of experimental and theoretical methods have been employed to study vitrification in polymer surface layers. The results of studies in this area are rather contradictory, which may be explained both by purely experimental difficulties and by the absence of a unified approach to the description of the vitrification process, as well as by a lack of understanding of its nature, even for the bulk polymer. Nevertheless, there are a number of studies [3–10] indicating that, for many polymers, the vitrification temperature T'_v at the air–polymer surface is lower than the corresponding bulk temperature, T_v .

In [10], an original method is proposed for studying polymer surface structure and the special features of the vitrification process. It is based on the use of atomic scanning microscopy to monitor the immersion of metal nanoparticles into the polymer layer on which they were preliminarily adsorbed from a colloidal solution as the system was subjected to stepwise annealing. Using polystyrene as an example, the authors managed not only to demonstrate that $T'_v < T_v$ but also to rather

accurately determine the value of T'_v for polystyrene samples with $M_w = 270000$, 51000, and 9600 (prepared by the same method and under the same conditions as the samples used in this study).

Table 1 lists the values of the vitrification temperature T'_v along with the corresponding bulk values, T_v , for different M_w .

This study extends the work started in [11]. The investigation of the relaxation processes in a polystyrene surface layer is continued using the so-called method of fluorescent molecular probes. This optical method has already proved efficient for studying phase transitions in thin polymeric films [12, 13]. In essence, the method is based on the study of fluorescence spectra of dye molecules introduced into a polymer (or adsorbed on its surface) and linked to the host molecules by weak van der Waals forces. In this case, the parameters of the fluorescence spectra of photoexcited dye molecules (peak position, intensity, spectral structure, spectral line width, etc.) depend considerably on the state of their nearest environment, i.e., of the polymeric matrix.

Table 1. The bulk (T_v) and surface (T'_v) vitrification temperatures for polystyrene with different molecular masses M_w , according to [10]

M_w	T_v , K	T'_v , K
270000	380 ± 3	318 ± 5
51000	375 ± 3	308 ± 5
9600	365 ± 3	<293

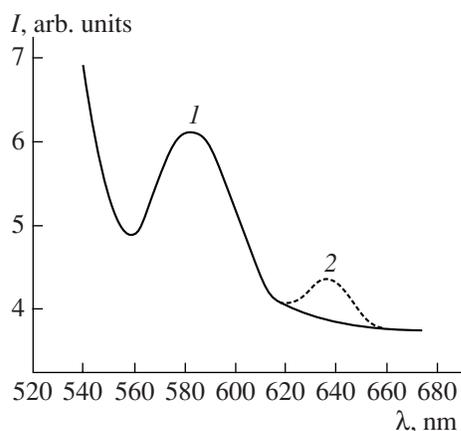


Fig. 1. The typical fluorescence spectrum of rhodamine B molecules adsorbed on polystyrene surface: (1) monomer and (2) dimer bands. Decay of the excitation line is shown in the left part of the figure.

EXPERIMENTAL PROCEDURE

Polystyrene (PS) films with molecular masses $M_w = 270000$, 51000, and 9600 were fabricated on the surface of silicon wafers by drop casting from a 2 wt % toluene solution. The film-coated samples were maintained in air for 1–2 days and, then, annealed in air at $120 \pm 1^\circ\text{C}$ for 6 h. This procedure, first, provided for a more complete evaporation of solvent from the surface layer so that the structures formed in the surface layer were close to equilibrium and, second, made it possible to prepare samples with a similar thermal history, which has a considerable influence on the polymer properties.

Rhodamine B dye molecules were used as the fluorescent probes. The dye molecules were adsorbed on the PS surface by immersing the samples into an ethanol solution of rhodamine B (0.4 mg/ml) for 15 min with subsequent drying in air for no less than 24 h. According to the estimates made with a piezoelectric resonance microbalance [13], a submonolayer of dye molecules (less than 0.5 of the monolayer) was formed on the surface. This result was also confirmed by the shape of the fluorescence spectra. In these conditions, the influence of the dye molecules on the polymer properties is negligibly small.

Fluorescence spectra were measured by an automated spectrofluorimeter comprised of an MDR-12 monochromator and an MDR-6 double monochromator and operated in the photon-counting mode. A DKSeL-1000 xenon lamp was used to induce fluorescence at 515 nm. The spectrofluorimeter was equipped with a cell holder kept at ± 0.5 K with a thermostat. The frequency was set with an accuracy no worse than ± 0.5 nm.

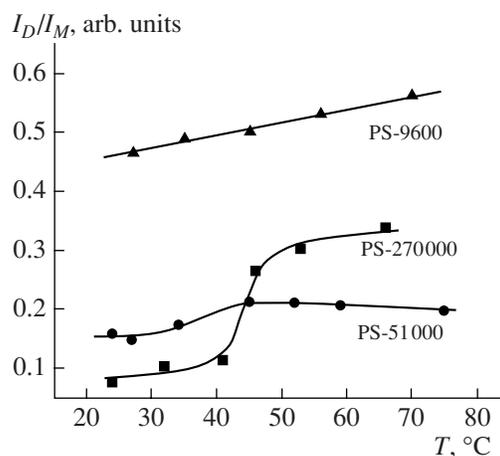


Fig. 2. Temperature dependences of the ratio between the dimer and monomer band intensities (I_D/I_M) for polystyrene with molecular mass $M_w = 270000$, 51000, 9600.

RESULTS AND DISCUSSION

The typical fluorescence spectrum of rhodamine B molecules on the PS surface is shown in Fig. 1. Two bands can be discerned: the peaks at approximately 580 nm (solid curve) and 640 nm (dashes) correspond to the fluorescence of rhodamine B monomers and associates, respectively. The latter appear in the spectrum only if rhodamine B dimers or more complex associates are formed. Note that immediately after the deposition of rhodamine B onto the PS-51000 and, especially, PS-270000 surfaces, only a short-wavelength band was actually observed; that is, no dimers resulted from the adsorption of dye in the concentrations used in this study.

We studied the temperature dependences of the fluorescence spectra of the rhodamine B molecules adsorbed on the surface of PS with molecular masses of $M_w = 270000$, 51000, and 9600 in the temperature range 297–348 K (i.e., considerably below the bulk vitrification temperatures T_v for all the PS samples under study, see Table 1).

Analysis of the temperature behavior of the fluorescence indicates that the peak corresponding to the rhodamine B monomers decreases with an increase in the sample temperature. Concurrently, the dimer band with a longer wavelength appears and grows in intensity (see Fig. 1). Similar variations in the luminescence spectrum are typically observed in solutions of some organic substances and may be attributed to the formation of excited dimers (excimers) there [14]. In this study, we deal with the rhodamine B molecular solution in a thin PS surface layer.

Figure 2 presents the temperature dependences of the ratio I_D/I_M between the dimer and monomer band intensities in the PS surface layer. The curve for the PS samples with $M_w = 270000$ shows a pronounced step in

the range 314–323 K. For the PS samples with $M_w = 51000$, a similar step is somewhat less pronounced and falls at 307–318 K. Both peaks are observed at temperatures that are close enough to the temperature regions where vitrification of the PS surface layer occurs (see Table 1) and where the nonuniform broadening of the rhodamine B monomer lines is maximum (as determined in [11]) (see Fig. 2). For the low-molecular PS sample with $M_w = 9600$, the I_D/I_M ratio grows slowly and monotonically with temperature.

For dimerization of the adsorbed probe molecules, their concentration and/or mobility in the polymer surface layer should be sufficiently high for them to meet and form excimers during the excited state lifetime [15]. In the experiment, the concentration of the probe molecules could not grow as they diffused into the surface layer; therefore, an increase in dimerization could only be due to an increase in the mobility of the rhodamine molecules in the PS layer. Devitrification of a polymer is associated with the “defrosting” of the segmental mobility of the chains, which leads to a considerable growth of the macromolecule mobility and an increase in the free volume available for diffusion [16]. It is shown in [15] that the coefficient D_n of the translational diffusion of probe molecules in a polymeric matrix relates to free volume as

$$D_n \sim \exp(-V^*/V_f), \quad (1)$$

where V^* is the molecule volume and V_f is the free volume per monomer.

As a result of studying the diffusion of ferrocene and azulene in bulk polyethylene and polystyrene [15], it was demonstrated that the bulk value of V_f varies from 13 to 24 Å³ (i.e., nearly doubles) in the range 293–373 K.

Therefore, the stepwise growth of rhodamine B dimerization in the PS surface layer (for $M_w = 270000$ and 51000) can be explained by a sharp increase in the mobility (diffusion coefficient) of probe molecules owing to the devitrification of the surface layer and an increase in the free volume.

It is known [14, 17] that the translational diffusion coefficient for probe molecules in a solution (polymer matrix) can be estimated by the following formula:

$$D_n \approx 1000(I_D/I_M)/8\pi r N_A \tau_0 C, \quad (2)$$

where r is the probe molecule radius, N_A is Avogadro’s number, τ_0 is the monomer excited state lifetime, and C is the probe molecule concentration in the solution (polymer matrix).

In line with formula (2), the data in Fig. 2 for the PC with $M_w = 270000$ confirms an approximately tenfold increase in the diffusion coefficient D_n during the relaxation process (under assumption that τ_0 and C are constant at 305–326 K).

A slight monotonic growth of the I_D/I_M ratio with temperature on a low-molecular PS sample with $M_w = 9600$ (see Fig. 2) points to the absence of any considerable structural rearrangements that could significantly

Table 2. Temperatures T of the stepwise change in the I_D/I_M ratio for polystyrene with different molecular masses M_w

M_w	T
270000	318 ± 5
51000	312 ± 5
9600	–

change the free volume and the diffusion coefficient of the probe molecules at 300–343 K. In the entire range studied, the fraction of dimers in this sample is considerably higher than that in the high-molecular PS samples. This could obviously be explained by a higher mobility of macromolecules and a larger free volume in the PS with $M_w = 9600$ (a larger fraction of free ends, the absence of cross linking).

Table 2 presents the temperature values at which the nonuniform broadening of the fluorescence spectrum is maximal. Comparing the data of Tables 1 and 2, it is easy to verify that these ranges correlate with the PS vitrification temperatures. This correlation takes place since both changes in the spectral characteristics stem from a change in the properties of the PS surface as a result of its devitrification [11].

CONCLUSIONS

Thus, we have demonstrated the high sensitivity of fluorescent molecular probes to relaxation transitions in the surface layer of polymers. The characteristic temperature regions where the mobility of the probe molecules sharply increases have been determined for polystyrene with different molecular masses. These temperature ranges coincide with the temperature of structural rearrangements in the surface layer of polymers with the respective molecular mass. These results should be taken into account in various applications of polymeric surface layers and thin polymeric films, in particular, in monitoring the vitrification process when polymer surfaces with designed functional properties are required, as well as in synthesizing 2D surface nanocomposites.

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