

## Relaxation Phenomena in a Polymer Matrix Including a Tautomeric Complex with a Proton Transfer

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When studying molecular-ionic tautomerism due to the reversible transition of a proton in complexes with a hydrogen bond, it is very important to determine the effect of the medium properties on the equilibrium position



The results of the works [1]–[4] revealed the substantial effect of processes of rearrangement of the molecular environment on the transition of a proton in a complex with a hydrogen bond and on the formation of an ion pair. Equilibrium (1) shifts to the right when the temperature is lowered, but in vitrifying solvents the concentration of the ionic forms stops growing near the glass transition temperature  $T_g$ , the ratio of the concentrations of the two complex types no longer depends on the temperature, and the state of the system becomes thermodynamically unstable. When high-molecular compounds (a polymer matrix) are used as the solvent, the nonequilibrium nature of process (1) manifests itself not near the glass transition temperature (an  $\alpha$  relaxation transition), but at lower temperatures corresponding to the freezing out of small-scale movements (a  $\beta$  transition).

This work is concerned with studying the kinetics of the establish-

ment of molecular complex-ion pair equilibrium in a glass medium within the temperature interval in which deviation from van't Hoff's equation begins to be observed. It can be expected that in this temperature interval the measured relaxation time of a tautomeric proton transition will be great enough and amenable to measurement with conventional equipment employed in static spectroscopic studies. The temporal resolution of such a procedure is determined by the time needed for a specimen to acquire a constant temperature, and is  $(2-3) \times 10^2$  s under our conditions. The objects studied were films of a copolymer of methacrylic acid (3.1 mol %) with styrene and containing dibutylamine. It has been shown in Ref. [1] that deviations from the equilibrium relation between the molecular and the ionic forms of the complex arise in this system when the temperature is lowered in the region of 60–40°C. The temperature at which freezing of the tautomeric equilibrium occurs depends on the cooling rate and the specimen "prehistory".

In the IR spectrum of a copolymer film containing a three-fold excess of amine relative to the number of acid units there were observed a band  $\nu$  (C=O) of the molecular complex at  $1710\text{ cm}^{-1}$  and bands  $\delta(\text{NH}_2^+)$  and  $\nu_{as}(\text{CO}_2^-)$  of an ionic pair at 1620 and  $1550\text{ cm}^{-1}$ , respectively (see Fig. 2b in Ref. [1]). When a specimen was cooled to 50°C, the intensity of the molecular form bands dropped, and that of the ionic one increased. With a further lowering of the temperature, the spectrum stopped changing, and equilibrium was frozen.

Kinetic measurements were carried out in the interval 55–35°C on the  $\nu$  (C=O)  $1710\text{ cm}^{-1}$  band because in this interval equilibrium was shifted greatly in the direction of the ion pair, and minor changes in the concentration of both forms of the complexes could be registered with a high accuracy according to the change in the intensity of the molecular complex band. Moreover, in this region the absorption of light by styrene units is comparatively low, which enabled us to use films of considerable thickness. Identical films ~300  $\mu\text{m}$  thick of the copolymer containing dibutylamine were placed in both channels of a UR-20 spectrometer. The films were prepared from a solution in chloroform and were dried in vacuum at ambient temperature. The temperature of the film in the specimen channel was controlled by means of an electric heater (it remained constant at 23–25°C in the reference channel). The variations in

transmittance were registered at the maximum of the band  $\nu$  (C=O) at  $1710\text{ cm}^{-1}$ . The film in the specimen channel was first held at  $t \sim 100^\circ\text{C}$  (the glass transition temperature of the copolymer specimens studied was lower owing to the presence of the amine, which has a plasticizing effect). The temperature was then lowered to the preset value, and the transmittance was measured in relation to the time for plotting a kinetic curve.

Figure 1 shows the temperature dependence of the optical density  $\Delta D$  for the  $1710\text{ cm}^{-1}$  band, registered in a differential spectrum, for two cooling regimes—rapid (10 K/min) and slow (1 K/min). In the interval  $100\text{--}60^\circ\text{C}$ , the specimen cooling rate did not affect the behavior of the temperature dependence of  $\Delta D$ . Consequently, the procedure used in our work allowed us to observe the position of the molecular complex-ion pair equilibrium in this temperature region. Below  $60\text{--}50^\circ\text{C}$ , the value of  $\Delta D$  was independent of the temperature, and tautomeric equilibrium (1) was frozen. Here the asymptotic value of  $\Delta D$  was higher and the departure of the system from equilibrium was greater at a higher cooling rate (the equilibrium values of the optical density at  $t < 60^\circ\text{C}$  can be estimated by extrapolation of the experimentally established temperature depend-

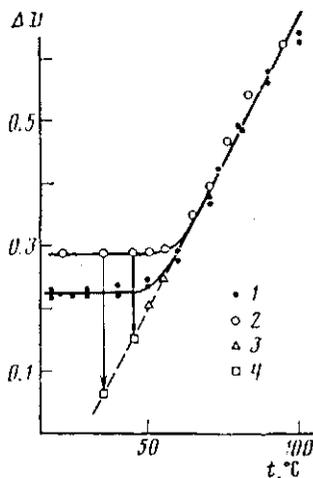


FIGURE 1 Temperature dependence of the optical density of the  $1710\text{ cm}^{-1}$  band measured in a differential spectrum for a cooling rate of (1) 1 K/min and (2) 10 K/min; (3) experimental values of  $\Delta D_{\infty}$ ; (4) extrapolated values of  $\Delta D_{\infty}$ .

ence of  $\Delta D$  to the region of lower temperatures as shown by the dashed line in Figure 1). In the intermediate temperature interval 60–50°C, where the curve of  $\Delta D$  versus  $t$  has a kink (Figure 1), the relaxation time of molecular motion in the polymer, which limits the kinetics of the proton transition process, becomes comparable with the characteristic time of an experiment. Under conditions of a rapidly relaxing environment, the characteristic time of proton transfer in complexes with a hydrogen bond  $\text{OH}\dots\text{N} \rightleftharpoons \text{O}^-\dots\text{NH}^+$  did not exceed  $\sim 10^{-6}$ – $10^{-7}$  s. Hence, such a tautomeric complex can be an effective probe allowing one to obtain useful data on the features of thermal motion in polymers.

To determine the rate of approach of the system to equilibrium, a rapidly cooled specimen was held at a fixed temperature (55, 50, 45, 35°C). The transmittance at  $1710\text{ cm}^{-1}$  was measured in relation to the time. The results of these measurements are presented in Fig. 2. The kinetic curves were approximated by the exponential equation

$$(\Delta D_t - \Delta D_\infty) / (\Delta D_0 - \Delta D_\infty) = \exp(-t/\tau), \quad (2)$$

where  $\Delta D_0$  and  $\Delta D_\infty$  are the optical densities at  $t=0$  and  $t=\infty$ ,  $\Delta D_t$  is the instantaneous value of the optical density, and  $\tau$  is the relaxation time. For 55 and 50°C, we succeeded in determining the values of  $\Delta D_\infty$  by direct experiments. The duration of an experiment was 4–6 and 25–30 h, respectively. The values of  $\Delta D_\infty$  obtained closely fit a curve of  $\Delta D$  versus  $t$  (Fig. 1) corresponding to the equilibrium state and extrapolated to low temperatures (the dashed line). For lower temperatures, the required experiment time increases so that the value of  $\Delta D_\infty$  being measured begins to be affected by accidental factors difficult to control, and the accuracy of measurement drops substantially. Therefore the extrapolated values of  $\Delta D_\infty$  indicated in Fig. 1 by arrows were used to determine the relaxation time  $\tau$  for 45 and 35°C.

Figure 3 shows plots of function (2) for four temperatures. The results were processed in a "Mir-2" computer. The values of  $\tau$  obtained were  $(2.1, 4.2, 8.2, 37.0) \times 10^3$  s for 55, 50, 45, and 35°C, respectively. The accuracy of determining  $\tau$  was  $\sim 20\%$ .

The temperature dependence of the relaxation time usually has the form  $\tau = \tau_0 \exp(U/RT)$ . The values of  $\tau$  obtained fit this relation satisfactorily. The value of the activation energy is  $U = (27 \pm 4)$

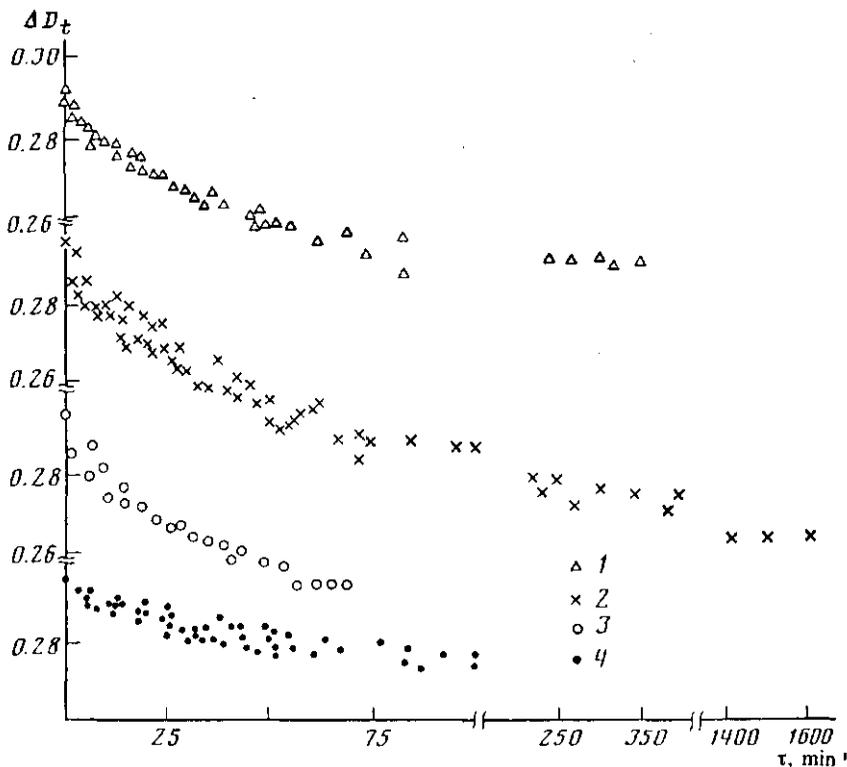


FIGURE 2 Kinetic curves of the time dependence of  $\Delta D_t$ : (1) 55°C, (2) 50°C, (3) 45°C, (4) 35°C.

kcal/mol, while the preexponential factor  $\tau_0 = 10^{-4}$ s has the reasonable meaning of time close in its order of magnitude to the period of natural vibrations of the atoms. The quantity  $U$  is the activation barrier for the relaxation process in the polymer that ensures the rearrangement of the molecular environment of a complex required for the proton transfer [5]. The value of  $U = 27$  kcal/mol found coincides with the activation energy of a  $\beta$  transition in polystyrene measured in Ref. [6] by differential scanning calorimetry. This supports the hypothesis [1] that the rearrangement of the molecular environment of tautomeric complex (1) is due to the motion of the sections of the polymer chain; this motion is frozen out in the  $\beta$  transition.

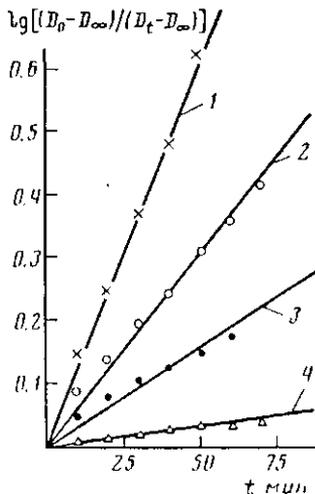


FIGURE 3 Graphs of function (2) for the temperatures: (1) 55°C, (2) 50°C, (3) 45°C, (4) 35°C.

It is customarily assumed that a  $\beta$  transition is associated with the freezing out of small-scale (1–3 units) rotation of polymer chain sections. An assumption was recently advanced in Ref. [6] that the kinetic unit of a chain is commensurate within a broad temperature interval (higher and lower than  $T_g$ ) with a Kuhn segment (eight monomer units for polystyrene [7]), and, consequently, the  $\alpha$  and  $\beta$  relaxation processes are of the same nature, namely, the  $\alpha$  process is due to the cooperative motion of contacting segments of neighboring chains, while the  $\beta$  process is due to the noncooperative motion of the same segments at sites of free volume fluctuations.

When analyzing this question, it is advisable to take into account that the freezing out of tautomeric equilibrium (1) at the  $\beta$  transition temperature occurs if, and only if one of the interacting partners (a carboxyl group) is bound chemically to the polymer chain as is observed in the copolymer of methacrylic acid with styrene (the active matrix) containing a dissolved amine. For a complex formed by a low-molecular acid and an amine dissolved in a polymer containing no active groups (a passive matrix), equilibrium (1) is frozen out at appreciably lower temperatures. For complexes of propionic and adamantancarboxylic acids, which differ noticeably in their size

and shape, with ditutyl- and dioctylamine in polystyrene and poly- $\alpha$ -methyl-styrene, no deviations from the equilibrium state are observed on cooling down to 20°C.

It is indicated in the work [8] that in complexes of trimethylacetic acid with dibutylamine in polystyrene equilibrium (1) is frozen at  $t < -90^\circ\text{C}$ . Similar factors are apparently responsible for the considerable differences in the progress of the monomolecular photochemical rearrangement of spiropiran in the active and passive polymer matrices discovered in Ref. [9]. A systematic study of deviations from equilibrium (1) in passive matrices of various nature and in active matrices on variation of the structure of the proton-donor (acceptor) side radical can contribute to a more precise determination of the scope of the relaxation process in a polymer that is associated with the  $\beta$  transition.

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