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Influence of the strength of polarizing electric field on free relaxation of electric birefringence in poly(butyl-isocyanate) solutions

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ABSTRACT

Free relaxation of electric birefringence in tetrachloromethane solution of high molecular weight poly(butyl-isocyanate) was studied. The effect of electric field strength on the average relaxation time was observed. The relaxation spectrum was analyzed using the Rouse and Zimm theories. With increase in the electric field strength, the contribution of fast (deformation) relaxation modes also increased significantly. It is assumed that certain changes in intramolecular mobility occur under the influence of electric field.

1. Introduction

Electric birefringence (EB, the Kerr effect) is widely used in the studies of conformational, electro-optical and kinetic properties of polymer molecules and micellar structures in solutions [1–9]. A considerable number of publications are devoted to the studies of electro-optical properties of polyelectrolytes in solutions [9–14]. In the case of the polymers possessing rather high equilibrium rigidity, the study of dependence between stationary birefringence and molecular weight of polymer and use of the theories for the Kerr constant of worm-like chains [15,16] allow making some conclusions about dipole and anisotropic structure of polymers as well as the persistent length (the Kuhn segment) of a macromolecule [16–19]. In a number of publications [17,20,21], the authors discuss significant influence of solvent polarity on the value of the equilibrium EB in polymer solutions. At the same time, studies of non-equilibrium EB give some information about dynamic characteristics of macromolecules independently of solvent polarity [20]. Therefore, non-equilibrium EB can be efficiently used in the analysis of dynamic characteristics of macromolecules belonging to various classes, including strongly charged polyelectrolytes (e.g., DNA) [6,22–28]. The data obtained by non-equilibrium EB may be interpreted using theories of dynamic properties of particles and worm-like chains, and among them the theories taking into account kinetic flexibility of macromolecules [29–31].

The use of strong electric fields provides a means to obtain more information about a macromolecule (its two very important characteristics, i.e., dipole moment and optical anisotropy). High electric field strength (E) provides the energy of interaction between macromolecule and electric field which is comparable to the energy of thermal motion; the ratio between potential energy of a molecule μE (where μ is the constant dipole moment) and thermal energy kT ($\mu E/kT$) varies from the values which are much lower than 1 to the values which are significantly higher than 1 (in the latter case, the Δn vs. E^2 dependence departs from linearity and tends toward saturation).

In our previous works, equilibrium EB in solutions of high molecular weight poly(butyl-isocyanate) (PBIC) in tetrachloromethane (CCl_4) was investigated. The departure of the Δn vs. E^2 dependence from linearity was revealed and explained [32,33]. It is important to note that in strong square pulsed electric fields, increase in EB cannot be described by a simple set of exponents [34–39]; however, the decline of birefringence after switching off electric field occurs according to the simple exponential law in the case of monodisperse ensemble of rigid molecules or particles [40,41]. The goal of the present work is to study the influence of electric field strength on dynamic characteristics of macromolecules obtained by free relaxation of electric birefringence.

2. Experimental

2.1. Materials

In the present work, EB relaxation in solutions of high molecular weight PBIC was studied. Molecular weight (M) of this fraction was 770 000 Da; it was determined from the value of intrinsic viscosity and the known Mark–Kuhn–Houwink equation [16]. Polydispersity index of the polymer was 1.5 (determined by size-exclusion chromatography measurements which were performed in benzene as an eluent and with the use of polystyrene standards for

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calibration). In EB experiments, tetrachloromethane was used as a solvent; its dielectric permittivity ε_0 is 2.238, refractive index $n_0 = 1.4607$, $T = 298$ K.

2.2. Methods

Prolonged exposure of a solution to strong electric field may cause undesirable consequences, e.g., breakdown, conductivity, overheating, etc.

We have suggested the method for EB measurement involving the use of a single electric pulse which allows measuring both induced anisotropy and free relaxation after switching off electric field [32,42–44].

Rectangular electric field pulses with amplitudes up to 140 kV/cm and a duration 16.5 ms were applied. The relaxation time of electric field when it is switched on is equal to ~50 μs, and when it is switched of does not exceed 1 μs. The Kerr cell was a glass tube with sealed-in titanium electrodes 3 cm in length placed along the light path; the width of a gap between electrodes was 0.022 cm.

EB was measured with the use of polarization-optical setup consisting of a light source (He–Ne laser with a wavelength λ of 632.8 nm), a polarizer and analyzer crossed with it, the Kerr cell and compensator.

In general, the luminous flux $I(t)$ passing through the birefringent system (Kerr cell and the compensator) during a single pulse supply time t is given by the expression:

$$I(t) = \frac{I_0^2}{2}\left[\left(\sin 2\eta \sin\frac{\delta}{2}\right)^2 + \left(\sin 2\eta_{cell}\sin\frac{\delta_{cell}(t)}{2}\right)^2 + 2\sin 2\eta \sin 2\eta_{cell}\sin\frac{\delta}{2}\sin\frac{\delta_{cell}(t)}{2}\times\left[\cos\frac{\delta}{2}\cos\frac{\delta_{cell}(t)}{2} - \sin\frac{\delta}{2}\sin\frac{\delta_{cell}(t)}{2}\cos 2(\eta_{cell}-\eta)\right]\right] \quad (1)$$

where I_0 is the intensity of light incident upon birefringent system, δ, δ_{cell} (t) – are the phase shift, and η, η_{cell} – are the azimuth of a compensator and a cell, respectively.

$$\delta_{cell}(t) = \frac{2\pi l \Delta n(t)}{\lambda}, \quad (2)$$

where l is the length of optical path in the Kerr cell, $\Delta n(t)$ – electric birefringence induced in Kerr cell.

When using the $\lambda/4$ ($\delta = \pi/2$) mica plate as a compensator, and taking into account the orientation of the Kerr cell $\eta_{cell} = 45^\circ$ we obtain the expression:

$$I(t) = \frac{I_0^2}{4}\left[1 - \cos\delta_{cell}(t) + \sin 2\eta \sin\delta_{cell}(t) + \sin^2 2\eta\cos\delta_{cell}(t)\right] \quad (3)$$

Then, using the following change of variables (where r and Ω depend only on the compensator azimuth η):

$$r = \sqrt{\sin^4 2\eta - \sin^2 2\eta + 1} \quad \frac{\sin 2\eta}{r} = \sin\Omega \quad (4)$$

we obtain:

$$I(t) = \frac{I_0^2}{4}[1 + r\cos(\delta_{cell}(t) - \Omega)] \quad (5)$$

Also, the noise signals (I_{noise}) of the installation are included in Eq. (5) as an additional term:

$$I(t) = \frac{I_0^2}{4}[1 + r\cos(\delta_{cell}(t) - \Omega)] + I_{noise} \quad (7)$$

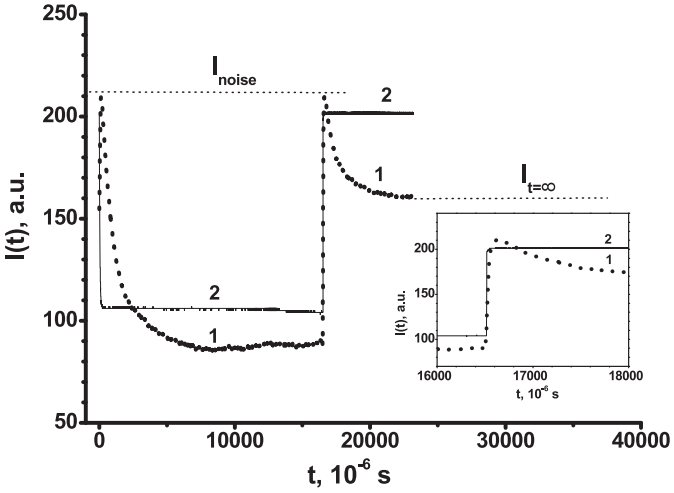

Figure 1. Time dependences of luminous flux intensity (1) and the applied electric pulse (2) at $E = 58.2$ kV/cm, compensator azimuth $\eta = 11^\circ 6'$.

The dependence of the electric birefringence on time after switching off the applied electric field is described by the following formula:

$$\frac{\Delta n(t)}{\Delta n_0} = \int_0^\infty \psi(\tau) e^{-t/\tau} d\tau, \quad (8)$$

where $\psi(\tau)$ is the EB distribution function plotted against relaxation times.

Thus, defining $\delta_{cell}(t)$, we can obtain the distribution function $\psi(\tau)$.

To avoid the direct detection of I_0 and I_{noise} one can set the compensator azimuth η (and thus, the r and Ω) and thus, create a phase difference of the compensator δ smaller than of a cell at the maximum applied voltage and of an opposite sign. Then, at the direct moment of time (at the process of the impulse rise as well as at its decay) will be a position of a compensation (a minimum of luminous flux Figure 1), which corresponds to the equality to zero of the derivative of the expression (7).

In this case, we have the system of equations:

$$I_{min} = \frac{I_0^2}{4}(1 + r) + I_{noise}$$
$$I_{t=\infty} = \frac{I_0^2}{4}(1 + r\cos\Omega) + I_{noise} \quad (9)$$

and, consequently, the ability to determine both the magnitude of the incident flux I_0 as well as I_{noise}.

Substituting the obtained values in Eq. (7) we get a direct link between the registered $I(t)$ and the magnitude of δ_{cell} (t) during the measurements.

3. Results and discussion

According to molecular hydrodynamics data [16], the equilibrium rigidity of PBIC A is equal to $(80 \times 10) \times 10^{-7}$ cm; therefore, in the polymer with a molecular weight of 770 000 Da, one macromolecule includes 20 Kuhn segments. Thus, macromolecules of the studied PBIC exist in a coil conformation. Equilibrium electrooptical properties of this fraction were studied earlier [33,45].

Figure 1 presents the measured time dependences of luminous flux intensity at $E = 58.2$ kV/cm and compensator azimuth $\eta = 11^\circ 6'$. Similar dependences were observed at other values of electric field.

Normalized time dependences of anisotropy $\Delta n(t)/\Delta n_0$ after switching off the pulse for various electrical field amplitudes are presented in Figure 2.