

Applicability of the superposition principle during polarization of nonlinear optical polymer films

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Isothermal polarization and depolarization currents in polystyrene doped with DR1 chromophore molecules have been measured and analyzed in order to study the electrical relaxation of the poled order in this guest-host system. It has been shown that the superposition principle is applicable to the doped polystyrene at temperatures lower than the glass transition temperature indicating that the polymer system under study can be considered electrically as a linear one with a negligible electric conductivity. The response function was not exponential one, but characterized by a broad distribution of relaxation times.

Key words: superposition principle, non-linear optical polymers.

Introduction.

According to scientific predictions, organic polymers will gradually replace their inorganic counterparts in optoelectronic devices with non-linear optical (NLO) polymers being one of the most promising new materials [1–4]. The system must not possess a center of symmetry in order to have the NLO properties. Therefore, in *guest-host* materials, the NLO chromophores dissolved in a glassy polymer matrix must be permanently aligned for breaking the symmetry and producing the residual polarization. This is the most easily accomplished by applying a DC electric field to a polymer at the elevated temperature, at which the chromophore dipoles can be readily oriented, and the subsequent cooling under the applied electric field. The thin polymer film is usually placed between two parallel electrodes with the polar axis perpendicular to the film planes (sandwich poling) [5].

Performance of the poled material is limited by the structural relaxation inherent to all glassy polymers leading to eventual randomization of the preferential orientation of the chromophore molecules [6–8]. The constraints on the degree, to which the poling-induced orientation of the chromophores can be maintained over long periods of time above room temperature, are not well understood. It is also not clear what theoretical description is appropriate for the polymer relaxation below the glass transition temperature (T_g). One does not understand what poling and physical aging protocols and methods are most appropriate for obtaining the maximum microstructural alignment and the increased temporal stability, because the phenomena of formation and relaxation of the poled order in NLO polymers are far from being comprehensively studied and understood.

The dipole orientational relaxation is often probed by

the second-harmonic generation (SHG) [2, 8]. Results obtained by this method are normally do not fit to a simple exponential Debye model corresponded to one relaxation time, therefore either the Kohlrausch-Williams-Watts (KWW) stretched exponential function, or the bi-exponential function is used, both characterizing a broad distribution of relaxation times.

At the same time, we believe that the relaxation processes in NLO polymers can be studied by purely electrical methods adopted from the well developed field of the electret research [5]. As an example, in this paper we report on application of isothermal polarization and depolarization current measurements to investigate formation and relaxation of the poled order in amorphous polystyrene (PS) doped with the Disperse Red (DR1) chromophore molecules. We consider this system as a model one, on which some features of the relaxation typical for all *guest-host* NLO polymers can be obtained. Electrical relaxation and related phenomena have been previously studied only in pure PS, but even these data are not comprehensive [9, 10].

Experimental procedures.

Atactic amorphous PS ($M_w=250\ 000$) was obtained by purification of a commercial resin. Samples were prepared from a mixture of PS and the Disperse Red 1 (DR1) dissolved in chloroform. The solution was spread over a glass plate and after drying the film was treated at 100 °C for 24 h under vacuum. Then the film was removed by immersing the plate into water. The content of the dye was controlled from 0,5 to 2,5 % in the films whose thickness was about 20 mm.

Doped samples of 20 μm thick PS with Al electrodes deposited on both sides by vacuum evaporation were

placed in a temperature-controlled surrounding. The samples were initially heated to 120 °C, then slowly cooled to room temperature in a short circuit conditions to remove the random polarization or space charge. Then the samples were kept for 15 min at the required temperature and polarized at 100 V during different times ranging from 4 to 3000 s. The current measured at the longest time of polarization was used as $E_o \cdot \varphi(t)$ for further calculations according to Eq. (4). Depolarization currents were measured automatically, and the results are shown in Figs. 1–3 together with the calculated currents.

Results and discussion.

In the case of the electric field E applied to a dielectric, the superposition principle establishes that if the response function $\varphi(t)$ for a unit step variation of the electric field, as well as the time dependence of the electric field are known, then it is possible to calculate the current $I(t)$ at any moment according to the following equation

$$I(t) = A \int_{-\infty}^t \varphi(t-\tau) \frac{dE(\tau)}{d\tau} d\tau, \quad (1)$$

where A is the surface area of the sample. Suppose a step voltage is applied producing a constant electric field E_o during a period of time t_o from $t = -t_o$ to $t = 0$ and after that the sample is short circuited. In this case one can write

$$\frac{dE}{dt} = E_o \delta(t+t_o) - E_o \delta(t), \quad (2)$$

where $\delta(t)$ is Dirac's delta function. Therefore, the Eq. (1) for the transient current can be rewritten for $t > 0$ as

$$I(t) = AE_o \left[\int \varphi(t-\tau) \delta(\tau+t_o) d\tau - \int \varphi(t-\tau) \delta(\tau) d\tau \right]. \quad (3)$$

After integration and considering the depolarization current as a positive one we obtain

$$I(t) = AE_o [\varphi(t) - \varphi(t+t_o)]. \quad (4)$$

It is clear from Eq. (4) that if the poling time t_o is very long ($t_o \rightarrow \infty$), then $\varphi(t+t_o) \rightarrow 0$ and $I_s(t) = A \cdot E_o \cdot \varphi(t)$. Therefore, if the superposition principle is applicable, it is possible to calculate the depolarization current corresponded to any poling time t_o from only one experimental curve $I_s(t)$. Thus, the opposite is also correct, i.e. if the experimentally measured and calculated isothermal depolarization currents match with each other, then the superposition principle is valid and the system is linear.

Corresponding calculations were performed for samples of PS+1,5 % DR1 at different temperatures below T_g and results of the calculations were compared with experimental $I_d(t)$ curves. As an example, the curves obtained at 75 and 90 °C are shown in fig. 1 and fig. 2. To obtain the experimental curves we applied the poling voltage of 100 V for a definite time t_o in the range from 4 s to about 1000-2000 s and then measured the depolarization current. The current corresponded to the longest poling time was taken as $I_s(t) = A \cdot E_o \cdot \varphi(t)$ for further calculations according to Eq. (4).

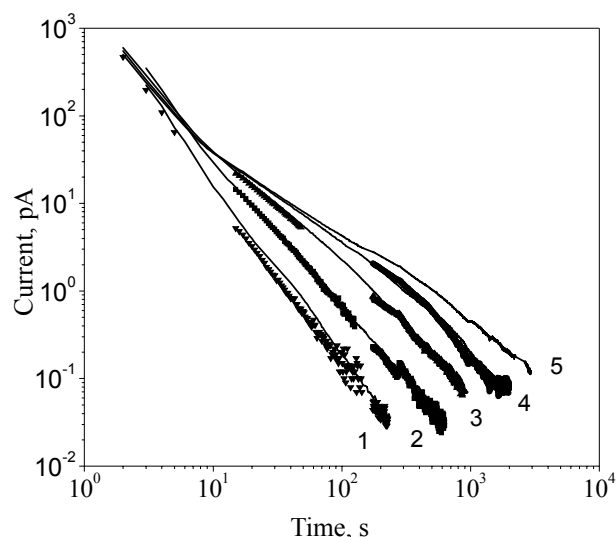


Fig. 1. Isothermal depolarization currents at 75 °C in isothermally poled PS+1,5 % DR1 samples with different poling times. Solid lines – calculations, points – experiment

It is clear from fig. 1 and fig. 2 that even for a very short poling time of 4 s good agreement is observed between experimental and calculated data proving validity of the superposition principle for a given system. This result is neither obvious, nor trivial, because the polymer under study possesses nonlinear optical properties. At the same time, as our results have proven, doped PS can be considered electrically as a linear system. From the data shown in fig. 1 and fig. 2 one can conclude also that the response function $\varphi(t)$ deviates considerably from the often postulated power law of $\varphi(t) = t^{-n}$, but at low and medium poling times the curve $I_d(t)$ is very close to the straight line in logarithmic coordinates.

In general, the depolarization current curve consists

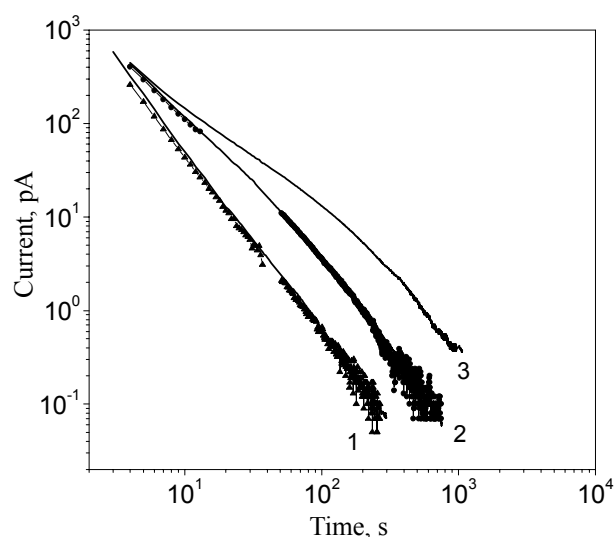


Fig. 2. Isothermal depolarization currents at 90 °C in isothermal poled PS+1,5 % DR1 with different poling times. Solid lines – calculations, points – experiment

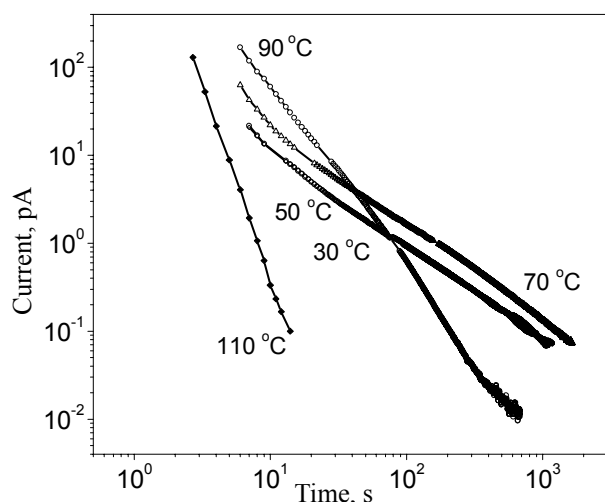


Fig. 3 Isothermal depolarization currents in isothermally poled PS+1,5 % DR1 at voltage 150 V at different temperatures. Solid lines – calculations, points – experiment

of three parts. The current at the first stage (from $t = 0$ till $t = 10$ s) does not depend much on the poling time indicating that it originates from depolarization of dipoles having short relaxation times. In the power law approximation, $n = 2$ is usually observed at this stage. At the second stage (from 10 s to about 100-200 s) the curves obtained at different poling times go apart with n ranging from 2 at very short poling times to $n = 1$ for very long poling times. Therefore, at this stage the shorter poling time, the smaller the power coefficient n . At the third stage, absolute values of the currents corresponded to different poling times are very different, but the coefficient n is almost the same for all curves, which are parallel to each other in logarithmic coordinates with $n = 2$, similarly to that during the first stage.

It follows from Eq. (4) that isochronal values of the depolarization current must be proportional to the poling field. This feature of the superposition principle was examined by comparing experimental depolarization curves obtained after poling for the same time ($t_p = 20$ s in our experiments), but at different poling voltages from 30 to 300 V. The results have shown that the proportionality of the isochronal currents to the poling field is actually observed additionally proving the validity of the superposition principle.

Isothermal depolarization current $I_d(t) = A(dP/dt)$ reflects dynamics of the isothermal relaxation of the residual polarization P . Since the depolarization experiments have been performed under the short circuit conditions ($E = 0$), the conductivity phenomenon did not effect the measurements. Constant voltage was applied for a rather long time and then the sample was short circuited at a definite moment and the depolarization current was recorded. The results are shown in Fig. 3.

It is seen from fig. 3 that the curves at 30 and 50 °C

coincide, while the curve obtained at 70 °C is parallel to those of 30 and 50 °C indicating qualitatively that the relaxation function remained unchanged, but the level of the residual polarization and consequently, the rate of its decay (the depolarization current) increased with temperature in the range from 50 to 70 °C. It is possible that the dipoles are easily oriented at higher temperatures due to decreasing the relaxation time. It means also that the saturated value of the polarization was not reached during poling, because the equilibrium polarization, according to the Langevin-Debye equation, should decrease inversely proportional to the temperature.

However, this in fact happens at $T > T_g$. Due to intensified motion of the polymer chains, the thermal disorienting during poling prevails over the orienting effect of the poling field. As the result, the final value of the residual polarization at the end of poling decreases. Moreover, a large number of the dipoles are disoriented during the short period of time after the short circuiting producing the first part of the depolarization curve characterized by high values of the current and by its fast decrease (curves for 90 and 110 °C in fig. 3).

PS does not show considerable conductivity at temperatures below T_g . On the other hand, at $T > T_g$, the current measured under a constant applied voltage increases showing existence of some conductivity. The origin of this conductivity is not established, but since it is thermally activated, one can suggest that the conductivity current almost certainly originates from the internal emission of intrinsic charge carriers, rather than from the external injection. This suggestion is supported by the linearity of the current - voltage characteristic at $T > T_g$.

It has been found that the temperature dependence of conductivity in doped PS is dissimilar for different content of DR1, so as the higher concentration of the dopant corresponds to the higher conductivity. It is possible that together with the DR1 molecules some other species were added to PS matrix including those producing charge carriers at high temperature. As for the activation energy of conductivity, it has the order of 2,0–2,3 eV. Conductivity of the samples at $T < T_g$ can be neglected, because the saturated steady current was not observed even after application of the poling voltage for a long time. Moreover, polarization and depolarization currents in well poled samples coincide, as seen in fig. 1.

Conclusion.

It has been shown that the electrical relaxation of the poled order in PS doped with DR1 chromophore molecules can be studied by measuring isothermal polarization and depolarization currents. It has been proved that the superposition principle is applicable to the polymer system under study, so as the doped PS can be considered electrically as a linear system with a negligible electric conductivity at temperatures lower than the glass transition temperature.

It has been found that the depolarization current curve

of doped polystyrene consists of three parts with the response function being essentially non-exponential one, but rather characterized by a broad distribution of relaxation times. It means that the behavior of even such a simple system, as PS doped with DR1, is much more complicated than that predicted by known theoretical

models.

By comparing isothermal polarization and depolarization currents one can get practical information on the preferable poling conditions, such as the poling time and temperature required for obtaining the adequate and stable residual polarization.

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Застосування принципу суперпозиції при поляризації нелінійних оптичних полімерних плівок

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Струми ізотермічної поляризації та деполяризації в полістиролі, легованому молекулами хромофору DR1, були виміряні і проаналізовані з метою вивчення електричної релаксації поляризованого порядку в цій guest-host системі. Було показано, що принцип суперпозиції діє в легованому полістиролі за температури, нижчої температури склування, тобто досліджену полімерну систему можна розглядати як електрично лінійну з незначною електричною провідністю. Функція відгуку не експоненціальна і характеризується широким розподілом часів релаксації.

Ключові слова: поляризація, нелінійні оптичні полімери.

Применимость принципа суперпозиции при поляризации нелинейных оптических полимерных пленок

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Токи изотермической поляризации и деполяризации в полистироле, легированном молекулами хромофора DR1, были измерены и проанализированы с целью изучения электрической релаксации поляризованного порядка в этой guest-host системе. Было показано, что принцип суперпозиции применим к легированному полистиролу при температуре ниже температуры стеклования, указывая на то, что исследованную полимерную систему можно рассматривать как электрически линейную с незначительной электрической проводимостью. Функция отклика не является экспоненциальной и характеризуется широким распределением времен релаксации.

Ключевые слова: принцип суперпозиции, нелинейные оптические полимеры.