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Relaxation of Polar Order in Poled Polymer Systems: A Comparison between an Isothermal and a Thermally Stimulated Experiment

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ABSTRACT: The relaxation of polar order in a poled polymer system which had been designed in the context of nonlinear optical (NLO) materials was investigated. The isothermal relaxation of the Pockels effect as measured by the modulation of waveguide modes for different temperatures are best described by a symmetric Havriliak−Nagami relaxation time distribution. The width of the distribution increases with decreasing temperature. The temperature dependence of the mean relaxation time followed a modified version of the Vogel−Tamann−Fulcher equation. Thermally stimulated discharge current (TSDC) experiments were carried out in order to verify the proposed time−temperature behavior. The modified Vogel−Fulcher description of relaxation times describes the TSDC spectra well using the same relaxation time distributions as found for the isothermal relaxation.

Introduction

The future of poled polymers for applications in devices that exploit the NLO properties of these materials is strongly correlated to a further understanding of the processes which cause the temporal decay of the electrooptical effect in these systems.[1] The temperature dependence of the relaxation times is of particular interest for practical reasons as well as for the assessment of NLO polymers based on different design concepts, e.g. guest−host systems or systems in which the NLO-active chromophores are attached in different ways to a flexible or rigid backbone. The isothermal relaxation of polar order in poled materials is often fitted to multiexponential or Kohlrausch−Williams−Watts (KWW) stretched exponential function. However, the assignment of specific decay characteristics from the isothermal experiment is tedious if only minor relaxation occurs in the considered time interval.

Time−temperature characteristics have been explained by the WLF equation[2,3] and Arrhenius-like behavior,[4−6] as well as by empirical equations[7,8] depending on the type of chromophore and its linkage to the polymer chain. The validity of these interpretations can only be manifested by the analysis of the relaxation process over a wide temperature range. Improvement has recently been achieved in recording fast decays of polar order even above the glass transition temperature.[9] In the following we present results obtained by isothermal decay experiments utilizing the method of attenuated total reflection (ATR)[8,10] and measurements of thermally stimulated discharge currents (TSDC)[11,12] on the same poled polymer samples. Since TSDC is an almost background-free method, even weak polar decay processes (especially in the low-temperature region) can be studied. By comparing the two experiments, which measure different physical quantities and probe different time−temperature regions of polar relaxation, conclusive information about the activation process and the relaxation time distribution can be gained. TSDC experiments on NLO-active materials have previously been performed and compared with the thermally induced decay of SHG intensity,[13,14] but to our knowledge a comparison of data derived from isothermal decay with TSDC experiments and their simulation, based on a specific temperature dependence of relaxation times, does not exist for the decay of polar order in NLO poled polymers.

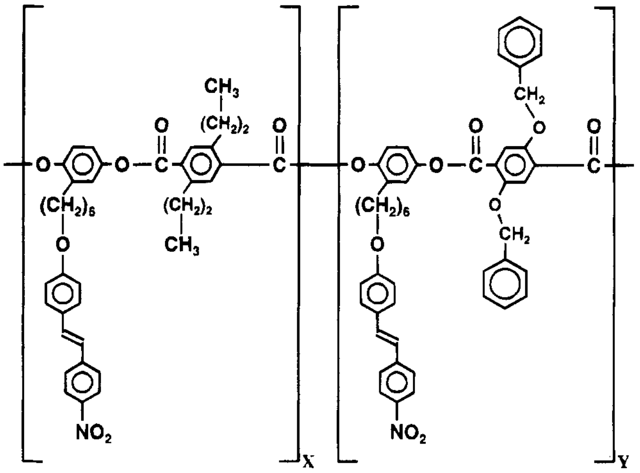

Figure 1. Rigid-rod-like polyester with alternately attached NLO chromophores ($X/Y = 1$).

Experimental Section

The polymer under investigation is based on a rigid-rod-like polyester backbone to which the NLO chromophores are attached via a flexible spacer. The polymer structure[15] is shown in Figure 1.

The T_g of the polymer is 68 °C as measured by DSC (Mettler DSC 30) at a heating rate of 10 °C/min. Films were spin coated from a polymer/tetrachloroethane solution onto a 40 nm thick gold layer deposited on a BK7 glass substrate. Spinning conditions were chosen to obtain a film thickness of about 2 μm. After the films were dried for 24−48 h in a vacuum oven at 80 °C, a 100 nm top gold electrode was evaporated onto the polymer. Electric field poling was performed at $T_{pol} = 95$ °C, with poling fields of $E_{pol} = 40$ V/μm. The poling temperature is well above T_g, so the dynamic and orientational properties of the material are in thermal equilibrium and the previous thermal history is extinguished. Poling and relaxation studies were carried out in a nitrogen atmosphere. Following the commonly used poling procedure, a cooling rate of 0.1 °C/min was used from T_{pol} to room temperature. After cooling, the

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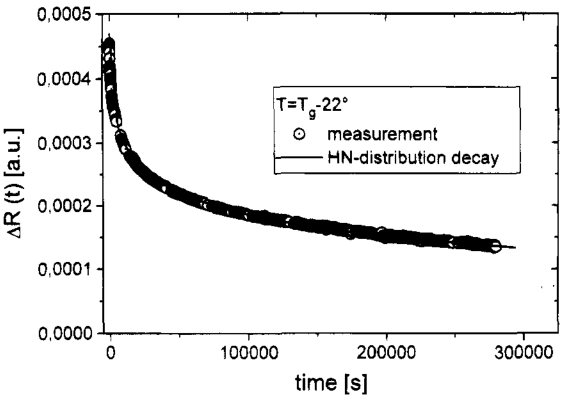

Figure 2. Isothermal decay of polar order at $T = T_g - 22$ °C fitted according to eq 6 with $\alpha = 0.59$, $\beta = 1$, and $\tau_m = 72300$ s.

samples were heated in less than 5 min to the relaxation temperature. At that temperature the poling field was removed and the relaxation measurement started immediately. The electrooptical response of the poled polymer films was determined by ATR. In the waveguide modulation experiment the refractive index of the poled polymer is changed due to the Pockels effect. This causes a shift of the angular position of the waveguide modes which corresponds to a change in reflectivity at a fixed angle. The amplitude of the modulation signal is proportional to the polar order in the polymer:

$$\Delta R \sim \chi^{(2)}_{333}(-\omega;\omega,0) \sim \langle \cos^3 \theta \rangle \tag{1}$$

where θ is the angle between the poling field direction and the direction of the dipole moment of the chromophore.

The same poling procedure and conditions were used for the TSDC experiment to obtain samples with identical thermal history. Constant heating rates between 1 and 10 °C/min were used during depolarization of the samples. This is comparable to the heating rates used to heat the samples to the relaxation temperature in the isothermal experiments. The resulting depolarization current was measured using a Keithley 617 electrometer.

Results and Discussion

The decay of $\Delta R(t)$ is shown in Figure 2 for a fixed temperature $T = T_g - 22$ °C. For a first approximation, the relaxation curves can be fitted by a biexponential decay. As has been already reported for a similar polymer with short alkyl side chains,[8] the slow and fast relaxation components showed almost identical temperature dependencies which followed an empirical equation:

$$\tau(T) = \tau_0 \exp\left[\frac{E}{k(T_g + 50 - T)}\right] \tag{2}$$

introduced by Stähelin et al.[7] as a modified version of the Vogel–Tamann–Fulcher (VTF) equation. In this equation τ is the relaxation time at temperature T, T_g is the glass transition temperature of the polymer, k is the Boltzmann constant, and E is a parameter with the dimension of energy. The prefactor τ_0 is necessary to obtain the correct units.

While a biexponential description implies the coexistence of two distinct physical processes causing the relaxation, previously reported results[8] indicate that the general description can be based on a continuous distribution of relaxation times. The KWW[16] distribution is extensively used to describe the polar order decay curves. This function has been shown to be related to the fractal properties of diffusion processes of materials in the glassy state.[17] However the representation by the KWW function has two disadvantages. First, it represents an asymmetric distribution function. Secondly, an exact computational method for the calculation of KWW decay functions does not exist.[18] Therefore, we favor the use of the more general distribution introduced by Havriliak and Negami (HN),[19] which contains both symmetric and asymmetric types of distributions:

Table 1. Relaxation Times and Distribution Parameters as Obtained from the Fits to the Isothermal Decay Curves

T (K)	$-\ln(\tau_m)$ (s)	α
298	−13.8 ± 1	0.97 ± 0.3
308	−13.3 ± 1	0.47 ± 0.3
314	−11.9 ± 0.5	0.62 ± 0.1
319	−11.1 ± 0.5	0.59 ± 0.1
327	−7.7 ± 0.2	0.28 ± 0.05
334	−5.8 ± 0.2	0.10 ± 0.05

$$G(u,\alpha,\beta) = \frac{1}{\pi} u^{(1-\alpha)\beta} \sin(\beta\phi)\, [u^{2(1-\alpha)} + 2u^{1-\alpha} \cos[\pi(1-\alpha)] + 1]^{-\beta/2} \tag{3}$$

$$\phi = \arctan\left[\frac{\sin[\pi(1-\alpha)]}{u^{1-\alpha} + \cos[\pi(1-\alpha)]}\right] \tag{4}$$

with the mean relaxation time τ_m and

$$u = \tau/\tau_m \tag{5}$$

The time dependence of the isothermal relaxation is thus given by

$$\Delta R(t) = \Delta R(0) \int_{-\infty}^{\infty} G(u,\alpha,\beta) \exp\left[-\frac{t}{\tau(u,T)}\right] du \tag{6}$$

For the simulation, the numerical stability of the integration was insured and the whole procedure was implemented together with a nonlinear fitting routine. The fit for $T = T_g - 22$ °C is compared to the experimental data in Figure 2.

The parameters obtained for the different relaxation temperatures are listed in Table 1. In all cases we found β close to 1 indicating a symmetric relaxation time distribution. The higher uncertainty for the relaxation time and the width of the distribution at lower temperatures is due to a minor amount of relaxation during the time interval of the measurements. Within the experimental uncertainty the width of the distribution increases with decreasing temperature. This agrees with observations on guest–host systems where best fits to the isothermal decay data were obtained by using a symmetric Gaussian distribution of activation energies.[4] Again, an increase in the width of the distribution with decreasing temperature has been observed. The mean relaxation time τ_m in eq 5 is plotted versus $1/(T_g + 50 - T)$ in Figure 3. The experimental data conform well to the modified Vogel–Fulcher eq 2 with $\tau_{0,m} = 1.8 \times 10^{12}$ s and $E = -10.6$ kJ/mol. From this a relaxation time of $\tau = 15$ s can be predicted at the glass transition temperature, which agrees rather well with the relaxation time of the α-process at T_g. This result indicates that the observed decay of the electrooptical response must be associated to the angular reorientation of the chromophores.

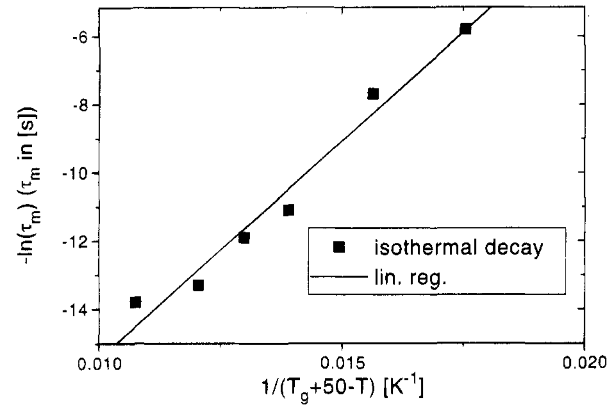

Figure 3. Thermal activation behavior of the mean relaxation time according to eq 2.

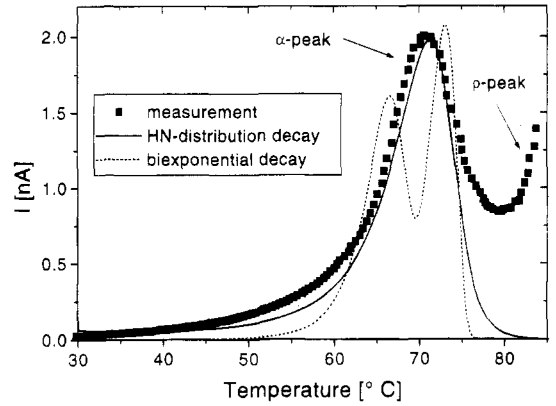

Figure 4. Comparison between the experimental and simulated TSDC spectra. Theoretical spectra have been computed for a biexponential relaxation mode (dashed line) and a relaxation mode involving a continuous relaxation time HN distribution (solid line).

In order to verify these results we performed TSDC experiments on samples treated in the same way as those studied for isothermal relaxation. Figure 4 shows an experimental TSDC spectrum for a heating rate of $h = 5$ °C/min. As observed by others,[13] we detect two different processes, one of which can be associated to the glass transition of the polymer and is therefore designated as α-peak. The second has been attributed to the motion of space charges induced during the poling process and is labeled ϱ-peak. While the shape and the area of the α-peak were well reproducible, the ϱ-peak showed irreproducible variations.

The α-peak near the glass transition temperature (DSC-T_g) has been explained by the reorientation of dipoles at the softening point of the material. In this case the area of the α-peak should agree to the value of the frozen-in polarization P_0 calculated according to the commonly used poling theory:

$$P_0 = n\mu f\langle\cos\theta\rangle \tag{7}$$

Where n is the chromophore number density, μ the dipole moment of the chromophore, and $\langle\cos\theta\rangle$ is the average polar order, which can be approximated by $\langle\cos\theta\rangle \approx f[(\mu E_{pol})/(3kT)]$ with the poling field E_{pol} and a local field correction $f = (\epsilon + 2)/3 \approx 1.6$. The numerical integration of the experimental α-peak results in a value of $P_0 = 148\ n$ C/cm^2 which is in very good agreement to the theoretical value for the frozen in polarization $P_0 = 153\ n$ C/cm^2, with $n = 1 \times 10^{21}$ cm^{-3} [15] and $\mu = 4.5$ D.[20]

In the TSDC spectra the low-temperature region (below T_g) of the α-peak is mostly due to the short-time fraction within the continuous relaxation time distribution while the peak appears at temperatures where the mean relaxation time approaches values between minutes and seconds. Because of that the TSDC spectra represents a complicated convolution of the temperature dependence of the relaxation process and the distribution of relaxation times, which itself might alter as function of temperature. A separation of these two contributions from the TSDC spectra only is therefore questionable. TSDC can, however, be used to easily verify models of the time–temperature characteristics of the decay process, as those deduced from the isothermal experiments.

For a single relaxation process the isothermal current density is given by

$$j(t) = \frac{-\mathrm{d}P_0(t)}{\mathrm{d}t} = \frac{P_0(t)}{\tau(T)} \tag{8}$$

The detected depolarization current is $I = jA$, where A is the poled area. The temperature dependence of the current is obtained by connecting the time t with temperature T by the linear heating rate h. Introduction of the distribution function leads to

$$I(T) = P_0A\int_{-\infty}^{\infty}G(u,T)\frac{1}{\tau(u,T)}\exp\left[\frac{-1}{h}\int_{T_0}^{T}\frac{1}{\tau(u,T')}\mathrm{d}T'\right]\mathrm{d}u \tag{9}$$

Here P_0 is the frozen-in polarization at the beginning of the relaxation experiment, T_0 the initial temperature, and $G(u,T)$ the distribution function of relaxation rates.

In Figure 4 the dashed curve represents the theoretical simulation based on a biexponential decay mechanism using the temperature-dependent relaxation rates derived from the isothermal relaxation experiments. The temperature dependence of relaxation times was assumed to follow the modified VTF equation (eq 2). As is seen clearly in Figure 4 this distribution function leads to two distinct maxima in the $I(T)$ curve which is in contrast to the shape of the experimental TDSC spectrum. Even though a biexponential decay explains the isothermal decay curves and the position of the TSDC peak rather well, we can exclude this distribution on the basis of our TSDC data. The solid line in Figure 4 was computed for a symmetric HN distribution with $\tau_{0,m} = 1.8 \times 10^{12}$ s, $E = -9.8$ kJ/mol, and α decreasing linearly with a slope of $\Delta\alpha = -0.008$ °C^{-1} from $\alpha_0 = 0.6$ at $T_0 = 30$ °C according to $\alpha(T) = \alpha_0 + \Delta\alpha(T - T_0)$.

Although a deviation between experiment and theory is observed at higher temperatures (attributed to the space charge effects), there is excellent agreement between experiment and theory for the case of the HN distribution with respect to both the position and shape of the main relaxation peak.

Conclusion

The comparison of isothermal decay measurements and thermally stimulated relaxation experiments has been shown to be a powerful tool to obtain consistent information about the relaxation of polar order in poled polymer systems. The isothermal decay curves could be best fitted, if the relaxation times are distributed according to a continuous and symmetric Havriliak–Negami (HN) distribution with decreasing width at increasing temperature. Minor agreement to the experimental data was achieved on the basis of discrete biexponential representation and an asymmetric Kohlrausch–Williams–Watts distribution of relaxation times. The activation behavior of the relaxation of polar order follows a modified version of the Vogel–Tamann–Fulcher function over a wide temperature region also in NLO polymers based on a rigid-rod-like backbone to which the chromophores are linked via a flexible spacer. However, there is no fundamental theoretical reason at hand for this unusual type of relaxation activation. On the basis of this temperature dependence of relaxation times TSDC spectra have been simulated using different types of relaxation time distribution. By comparison to experimental TSDC spectra the biexponential representation could be clearly excluded, while both the position and the shape of the α-peak could be well explained using the continuous HN distribution. This agreement further proves that the temporal decay of the electrooptical response is due to a reorientation of the NLO active chromophores with only minor contributions from space charge relaxation processes. Further work will be devoted to defining a model which describes both the relaxation rate distribution and the activation behavior based on a reasonable physical picture.

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