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Communications to the Editor

Orientational Relaxation in Electric Field Poled Guest–Host and Side-Chain Polymers below T_g

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The use of polymeric materials requires understanding of the underlying mechanisms responsible for the slow structural relaxation processes that result in changes in physical properties associated with aging. This is especially critical for second-order nonlinear optical polymers in which polar order has been created by electric field poling near the glass transition temperature. For application in frequency doubling or electrooptic devices, these poled polymers must maintain a substantial degree of poled order and associated bulk nonlinearity at operating temperatures at least as high as 80 °C and at processing temperatures that may exceed 250 °C for short periods of time.

In this paper, relaxation of poled order is measured by following the decay of the second-harmonic generation signal in a variety of nonlinear optical polymer with glass transition temperatures varying from 90 to 225 °C. The nonlinear chromophores have been incorporated into the polymer hosts either as dissolved guests or by covalent attachment to the polymer backbone as a side chain. In the guest–host case, it will be shown that there is a strong correlation between the characteristic poled order relaxation time τ at a particular temperature and the glass transition temperature T_g of the guest–host system. This relationship has been observed over 6 decades in τ for several large chromophores and in a variety of polymer hosts. The poled order decay in side-chain polymers is consistent with this "universal relationship" over a limited temperature range just below T_g but deviates from it at lower temperatures.

The guest chromophores and side-chain polymer systems used in this work are presented in Figure 1. The synthesis of and measurements on the lophines have been described previously.[1,2] For the guest–host systems, the chromophores have been dissolved in the polymers at concentrations up to 26 wt % without any evidence of crystallization or phase separation. Host polymers used in this work are as follows: Ultem, an amorphous soluble poly(ether imide) (from General Electric);[3] poly(methyl methacrylate) (PMMA; Aldrich, MW 90K); Bisphenol A polycarbonate (PC; Aldrich, M_w = 20–25K); polystyrene (PS; Polysciences, M_w = 250–300K); PIQ-2200, a soluble poly(amic acid)–polyimide precursor (from Hitachi). The side-chain polymers studied were DR1-PMMA and NAT-PMMA *in which* the chromophores Disperse Red 1 (DR1) and 4-amino-4′-nitrotolan (NAT) are covalently attached to the methacrylate as indicated in Figure 1 at a loading level of 10%. The polymers were dissolved in appropriate solvents, and thin films were spun onto transparent conducting substrates. The films were then baked in a vacuum oven above T_g to give solvent free 1–4-μm-thick films. The films made from PIQ-2200 were imidized at 250 °C. The T_g's of all the doped and cured films were determined by differential scanning calorimetry (DSC).

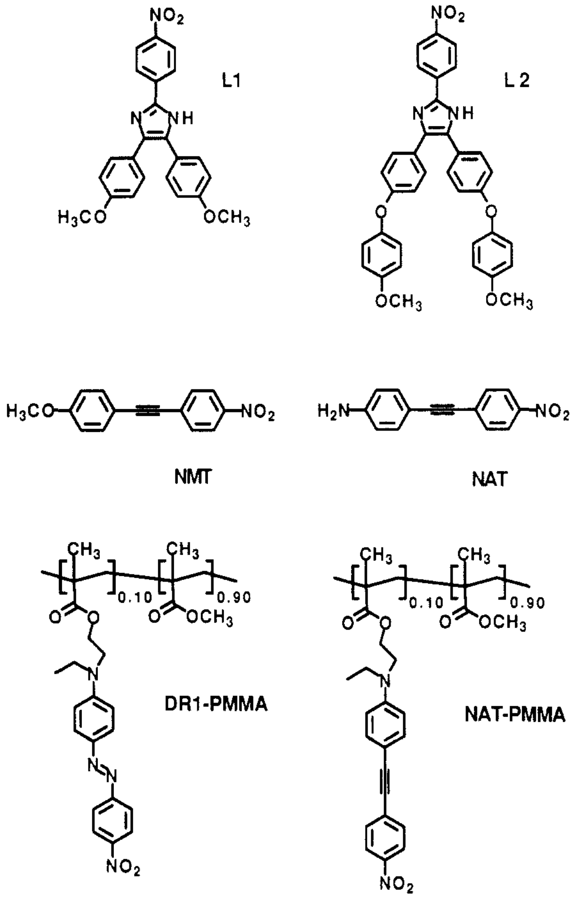

Figure 1. Chromophores and side-chain polymers used.

The electric field poling and subsequent relaxation of the poled order were monitored by following the decay of the second-harmonic generation (SHG) signal.[1,2] The poling field was applied and the sample was heated slowly to a point just below T_g while monitoring the SHG signal. The sample was held at this poling temperature for several minutes and then slowly cooled over a period of 20–40 min to room temperature. Residual surface charge was at least partially removed by wiping the polymer surface with either alcohol or water before any further measurements were made.

To monitor the decay of the poled order at a given temperature, the film was heated as quickly as possible to the desired temperature and the start of the decay (t = 0 s) was taken as the time at which the film had reached and stabilized at the desired temperature (typically 100–200 s after turning on the temperature controller). Decay times reported here refer to the decay of the effective second-order nonlinear optical coefficient d, proportional to the square root of the measured SHG intensity using p-polarized light at an incidence angle of 45° to the polymer film surface. These decay times are typically determined

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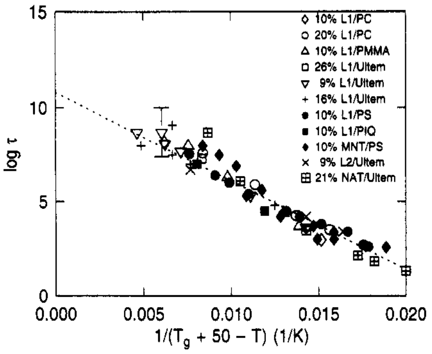

Figure 2. Semilog plot of the stretched exponential relaxation time t as a function of $1/(T_g + 50 - T)$ for a variety of chromophores and a number of host polymers. The dashed line is a linear least-squares fit to all of the plotted points. A typical error bar is indicated for one of the data points.

from the experimental data at times longer than ≈500 s and shorter than ≈6×10^4 s, although some decays have now been monitored for as long as ≈3×10^6 s.

Decays for both the guest–host systems and side-chain polymers are nonexponential. The time decay can in general be described by a stretched exponential (Kohlrausch–Williams–Watts) function:[4]

$$d = d_0 \exp(-t/\tau)^{\beta} \qquad (1)$$

This functional form is consistent with a continuous distribution of exponential decay times with the width of the distribution characterized by β and the peak by τ. The decays can also be described adequately using the sum of two exponentials.[2] For guest–host systems the SHG decay data can be fit to eq 1 using β values in the range from 0.25 to 0.5, consistent with results obtained by previous workers.[5,6] For the side-chain systems the value of β was observed to increase monotonically with temperature reaching a value of 1 as T_g was approached. This implies that the distribution of relaxation times narrows to a single value as the temperature is increased for these systems. It must be emphasized that there is a large degree of uncertainty in the values for the longest τ's ($\tau > 10^6$ s) since they have been obtained by extrapolation after monitoring for only ≈10^5 s. Experiments in which the decay is monitored over longer time periods ($>3 \times 10^6$ s) yield τ values that are longer than the values obtained from extrapolation after shorter times, indicating that eq 1 does not completely describe extremely slow relaxation processes.

The temperature dependence of the decay time τ does not in general exhibit an energy-activated Arrhenius type of behavior.[2] Rather the temperature-dependence agrees with the following functional form for a wide variety of guest–host systems:[1,2]

$$\tau(T) = A \exp[-B/(T_0 - T)] \qquad (2)$$

where A and B are positive constants independent of polymer host and the guest molecule for the larger chromophores investigated. In addition, T_0 is simply related to the glass transition by:

$$T_0 = T_g + (50 \pm 10)\ {}^{\circ}\mathrm{C} \qquad (3)$$

This relationship is illustrated in Figure 2 for lophine 1 (L1) in a variety of different polymer hosts and at a range of concentrations. In addition, decay times for lophine 2 (L2) in Ultem, 4-amino-4′-nitrotolan (NAT) in Ultem, and 4-nitro-4′-methoxytolan (NMT) in polystyrene are also presented (see Figure 1). Despite the widely varying T_g's (90–224 °C) of the systems studied, all the data lie near the same line. From the plot in Figure 2 it is possible to obtain a rough estimate for τ knowing only the T_g of the guest–host system. It must be pointed out that not all guest chromophores fit on or near the straight line in the figure. The chromophore size and perhaps the aspect ratio also seem to be important. Several investigations of the effect of chromophore size on poling relaxation have been carried out.[7–9] We have studied smaller chromophores such as substituted styrenes and benzenes and found that the SHG signal relaxed to zero faster than could be followed in the present experiment (<1–2 s). These chromophores do not fall on or near the line in Figure 2.

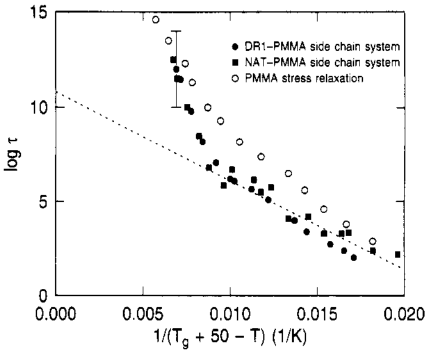

Figure 3. Semilog plot of the stretched exponential relaxation time τ as a function of $1/(T_g + 50 - T)$ for two side-chain polymer systems, DR1-PMMA (●) and NAT-PMMA (■). Also shown are mechanical stress relaxation data for PMMA taken from ref 10 (○). The dashed line is the least-squares fit to the guest–host polymer data shown in Figure 2. A typical error bar for low-temperature points is shown, illustrating the error in extracting a very long lifetime from a short-term experiment.

Figure 3 shows a plot of τ vs temperature for two side-chain polymers. These systems fall on or near the line for guest–host systems at temperatures above about $T_g - 50$ °C but deviate strongly from it below these temperatures. For comparison, stress relaxation data for pure PMMA[10] are also plotted in Figure 3. The stress relaxation data also show such a break near $T_g - 50$ °C.

The empirically determined relationship given by eqs 2 and 3 is similar to the well-known Williams–Landel–Ferry (WLF) or the equivalent Vogel–Fulcher–Tamann (VFT)[11] relationship used to describe the temperature dependence of viscoelastic properties for a variety of amorphous polymers above their glass transition,

$$\tau(T) = C \exp[D/(T - T_0)] \qquad (4)$$

where C and D are constants. For a number of polymers the value of the temperature T_0 is related to T_g by[12]

$$T_0 \approx T_g - 52\ {}^{\circ}\mathrm{C} \qquad (5)$$

in contrast to eq 3.

The WLF equation is frequently explained in terms of a free volume model.[11] In this model polymer relaxation processes are related to the amount of free volume greater than a critical size ν^x. This probability is given by:[13]

$$P \propto \exp[(-\nu^x/\nu_f(T))] \qquad (6)$$

where $\nu_f(T)$ is the total free volume at a given temperature T. For polymers above T_g, $\nu_f(T)$ is assumed to be linearly proportional to temperature and to go to zero at a temperature T_0, often described as the glass transition temperature that would be measured if the polymer could be cooled infinitely slowly so that equilibrium was maintained throughout the process. Relaxation times are directly related to P in this model:

$$\tau \propto 1/P \tag{7}$$

Clearly, relaxation time becomes infinite at the temperature T_0.

Rusch[10,14] has suggested modifying the WLF equation for use at temperatures below T_0 by including an additional nonequilibrium contribution to the free volume $w_f(T)$ that does not disappear at T_0. The total free volume thus becomes $\nu_f(T) + w_f(T)$. This model has been applied to stress relaxation in PMMA and polystyrene[10,14] and recently to the relaxation of poled order in side-chain polymers.[15] Its application can be seen very clearly in Figure 3 for both the stress relaxation and poled order decay data. In both cases as the temperature is lowered, relaxation times increase at one rate above $T \simeq T_g - 50$ °C and at a different, faster rate below this temperature. However, it is difficult to use Rusch's modified WLF equation in a quantitative manner since it requires a knowledge of the thermal expansion coefficient of each material above and below T_g, as well as the thermal expansion coefficient of the equilibrium glassy polymer which cannot be measured directly and becomes an adjustable parameter.

The relaxation of guest–host systems in Figure 2 does not exhibit the change in slope observed for the side-chain systems within the temperature range measured. It should be recalled that the relationship summarized by eqs 2 and 3 applies only to "large" guest molecules, perhaps larger than a significant fraction of the free volume sites. For this situation the poled order relaxation does not exhibit a break at the temperature $T_g - 50$ °C.

Poled order relaxation processes for guest–host and side-chain systems investigated here exhibit both similarities and differences. Above the temperature $T_g - 50$ °C, both types of systems have relaxation times given by eqs 2 and 3. Below this temperature the side-chain systems become significantly more stable. This has important implications for the design of thermally stable second-order optically nonlinear polymers. The PMMA-based side-chain systems investigated here are substantially more stable at lower temperatures that might be in the range of device operating temperatures. On the other hand, at elevated temperatures such as might be encountered during device processing procedures the two types of polymer systems appear to have equivalent thermal stability assuming equal T_g's. Further experiments on different types of side-chain polymers are necessary to ascertain how general this phenomenon may be. The side-chain systems can be described in terms of a modified WLF equation, taking into account the nonequilibrium nature of polymers at lower temperatures. This model does not, however, describe as clearly the guest–host polymers. For these systems the relaxation time τ exhibits the same temperature dependence over the entire range investigated. There is no clear evidence of a break between equilibrium and nonequilibrium dominated behavior, although much longer time-scale experiments are in progress to obtain more accurate decay times in the lower temperature regime.

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