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Dipolar Relaxation in a Second-Order Nonlinear Optical Interpenetrating Polymer Network

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Second-order nonlinear optical (NLO) materials are of much interest for applications such as electrooptic modulation and frequency conversion.[1–3] Polymeric second-order NLO materials have been studied extensively in recent years[4–9] due to their low dielectric constant, large nonlinearity, and ease of processability compared to inorganic NLO materials. In these polymeric systems, the noncentrosymmetric alignment of NLO chromophores achieved by the poling technique[3] is responsible for the NLO properties. However, the decay of the poled order as the material is subjected to high temperatures is still an outstanding problem. In order to use these materials in practical applications, the long-term NLO stability at temperatures up to 100 °C with spikes to higher temperatures is required during device fabrication and operation. Therefore, an understanding of this decay process is the key to the development of stable polymeric NLO materials.

The relaxation of aligned NLO chromophores is often characterized by monitoring the decay of second harmonic (SH) generation as a function of time at different temperatures.[10,11] In a typical guest/host system where chromophores are dispersed in an amorphous polymer, Stähelin et al. were able to fit the temporal relaxation to a Kohlrausch–Williams–Watts (KWW) equation, establishing that the decay of the dipole alignment is explained by a single relaxation phenomenon.[11] A fit of the relaxation times to the Williams–Landel–Ferry (WLF) equation pointed out that relaxation of the second-order NLO properties is mainly related to the glass transition temperature (T_g) of the media. Thus, high-T_g polymers are sought for stability at elevated temperatures. In other reports,[4,6,7] increased cross-linking has been used as a vehicle to enhance the NLO stability. Cross-linking networks reduce the mobility of the polymer chains which further prevent the aligned NLO chromophores from relaxing to a random orientation. Improved stability of the nonlinear response was established in a system with a higher cross-linking density.[7] However, polymers which possess high T_gs as well as high cross-linking densities still exhibit slow decay of the NLO properties at elevated temperatures. Although qualitatively the relaxation behavior of cross-linked systems at elevated temperatures seems similar to guest/host systems, a detailed experimental comparison of the relaxation behavior of the two systems has not been reported.

The important issues we address in this paper are the role of cross-linking in the stabilization of the NLO properties and the differences in the relaxation behaviors between the cross-linked network and a classic guest/host system. An interpenetrating polymer network (IPN) containing aligned NLO chromophores is selected to test these issues. An IPN is a structure in which two or more networks are physically combined.[12–14] The IPN is known to be able to remarkably suppress the creep and flow phenomena in polymers. The motion of each type of polymer in the IPN is reduced by the entanglements between the networks.

The IPN system consists of an NLO active epoxy-based polymer network and an NLO active phenoxy–silicon polymer network.[15,16] The epoxy-based NLO network is prepared from the epoxy prepolymer (BPAZO) based on the diglycidyl ether of Bisphenol A and 4-[(4′-nitrophenyl)-azo]aniline functionalized with cross-linkable acryloyl groups.[7] The second NLO network of a phenoxy–silicon polymer is based on an alkoxysilane dye (ASD)[17] of (3-glycidoxypropyl)trimethoxysilane and 4-[(4′-nitrophenyl)-azo]aniline and the multifunctional phenoxyl molecule 1,1,1-tris(4-hydroxyphenyl)ethane (THPE).[9] The chemical structures of BPAZO, ASD, and THPE are shown in Figure 1. The IPN is formed simultaneously upon heating, where the epoxy-based polymer network is formed through a double bond reaction and the phenoxy–silicon polymer network is formed through a sol–gel reaction.

The T_g of the IPN was determined to be 176 °C by differential scanning calorimetry. The corona poling technique[3,4,7] was employed to align the NLO chromophores. Poling and curing were performed simultaneously at 200 °C for 1 h. The second-order NLO properties of the poled IPN samples were measured by second harmonic generation from 1.064-μm laser radiation. The relaxation behavior of the second-order NLO properties was studied by monitoring the decay of the SH intensity as a function of time at different temperatures (from 110 to 170 °C) 24 h after poling and curing to avoid any space charge effect. The NLO coefficient, d_{33}, of the poled IPN sample was measured to be 33 and 5.5 pm/V at incident fundamental wavelengths of 1.064 and 1.542 μm, respectively.

Figure 2 shows the decay of the d_{33} coefficient as a function of time at different temperatures for the IPN samples. The time $t = 0$ was defined as the time when the samples were brought to the desired temperatures for the relaxation study. The IPN system shows no measurable decay of SH intensity after being heated at 110 °C for 168 h. An attempt was made to fit the experimental data at higher temperatures to the KWW equation which is often used to characterize the orientational relaxation in polymers.[18] The KWW equation can be written as[11]

$$d_{33}(t)/d_{33}(0) = \mathrm{e}^{-(t/\tau)^{\beta}} \qquad 0 < \beta \le 1$$

where β determines the width of the distribution of relaxation times about some central value. The characteristic relaxation time τ is the time required for the system to decay to 1/e of its initial value. The equation fits the decay curves very well only for temperatures in the vicinity of T_g (range from 140 to 170 °C) shown as solid lines in Figure 2, with β values falling in a range of 0.3–0.4 and the τ values in a range of 10^4-10^6 s. The data from experiments at 120 and 130 °C do not fit the KWW equation, and attempted fits result in large deviations from the data. The extremely slow decay of d_{33} at temperatures lower than 130 °C corresponds to very long relaxation times.

Figure 3 shows a plot of log τ as a function of $1/(T_g - T)$ using the following equation:

$$\tau = \tau_0 \mathrm{e}^{B/(T_g - T)}$$

The dashed line represents the data for the guest/host type samples reported by Stähelin et al.[11] An arrow indicates the temperature at 110 °C, at which no decay of the SH coefficient was observed after a period of 168 h.

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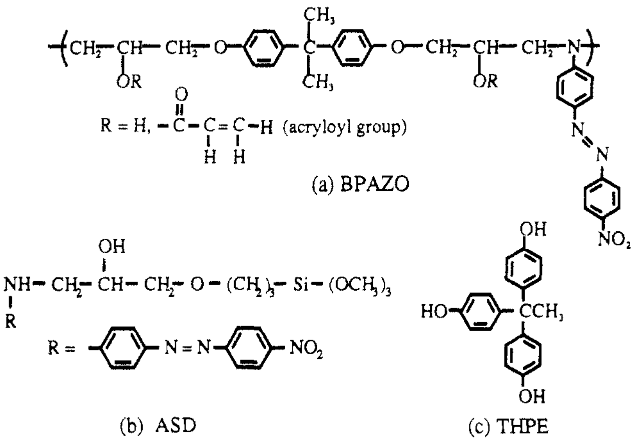

Figure 1. Chemical structures of BPAZO, ASD, and THPE.

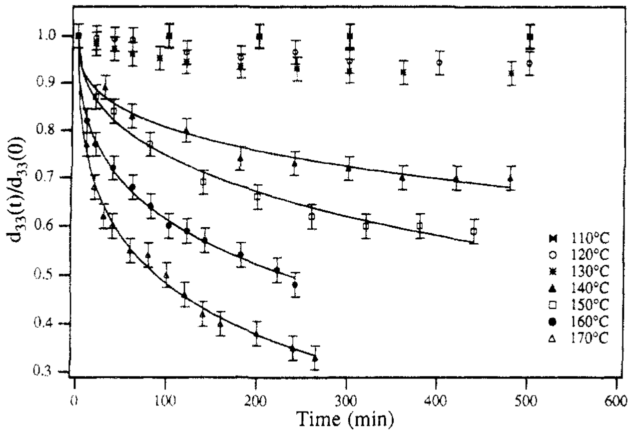

Figure 2. Temporal behavior of the second harmonic coefficient of the IPN at different temperatures.

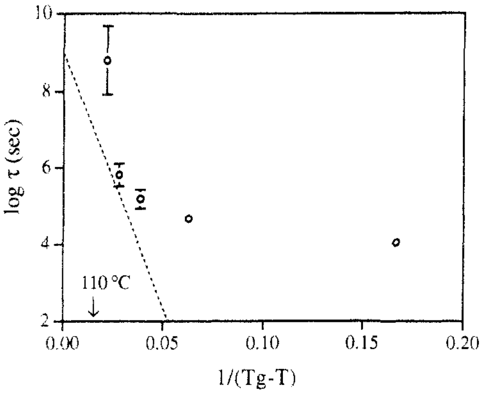

Figure 3. Relaxation time τ as a function of $1/(T_g - T)$ for the IPN samples at 130, 140, 150, 160, and 170 °C. The dashed line is the master curve from ref 11 that is expected to fit the guest/host system.

The error bar for the data point at 130 °C indicates the large deviations in τ values at lower temperatures. The results show that the relaxation behavior of the IPN is significantly different from those of the guest/host type polymers. The stability of the d_{33} coefficient for the IPN samples at low temperatures as well as temperatures close to T_g is substantially superior to the guest/host type samples. An attempt to improve the correlation between τ and T_g, especially when the temperature is close to T_g, was made by plotting log τ vs $1/(T_g + 50 - T)$ as suggested by Stähelin et al.[11] and Walsh et al.[19] The results were not significantly improved, and the nature of departure was similar to that shown in Figure 3.

In contrast to the guest/host systems, the relaxation times τ obtained from the KWW equation at temperatures near T_g for our IPN samples follow Arrhenius type behavior (Figure 4). The Arrhenius equation can be written as[20]

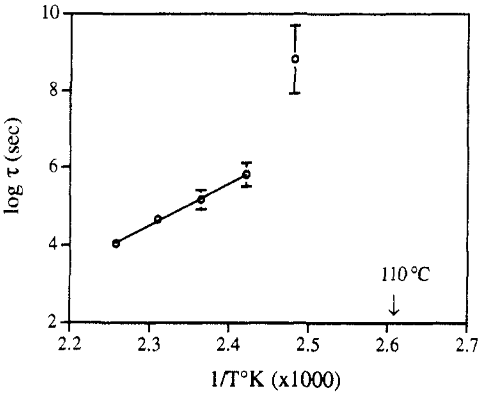

Figure 4. Arrhenius plot for the relaxation of the IPN at 130, 140, 150, 160, and 170 °C. An arrow showing 110 °C indicates the temperature at which no measurable decay of d_{33} could be observed.

$$\tau = Ae^{E_a/RT}$$

where E_a is the activation energy for the relaxation process. The activation energy calculated from the plot for the temperature range of 140–170 °C in Figure 4 is 46 kcal/mol. This is a relatively small value compared to the activation energy that is normally observed for the α relaxation of rigid polymers.[21,22] It implies that the dipolar relaxation in this temperature range follows Arrhenius behavior similar to side-group relaxations in amorphous polymers and is not associated with the main-chain motion. As the temperature decreases to 110 °C, there is a significant increase in the relaxation time at some critical temperature where the relaxation phenomenon may no longer follow Arrhenius behavior. It can be inferred from this result that there are at least two different relaxation mechanisms dominating the SH decay process for the IPN samples.

We have demonstrated that the dipolar relaxation process of the IPN system is essentially different from that of a typical guest/host system. At temperatures lower than 130 °C, the relaxation times significantly increase and deviate from the master line for guest/host systems. In addition, scaling the T_g to T_g + 50 °C does not reduce the data points to the master curve (Figure 3). The decay of nonlinearity of the IPN system at temperatures close to T_g is inherently a slower process than the guest/host system. This property allows for high-temperature spikes, which may be encountered during device fabrication. The extensive cross-linking and chain entanglements in the IPN are responsible for the enhancement of the stability. The combination of high-T_g polymers and the IPN architecture is believed to further improve the temporal stability. This area of research is currently being investigated in our laboratory.

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