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Relaxation Behavior of a Nonlinear Optical Polyimide/Inorganic Composite

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Polymeric materials with large nonlinear optical (NLO) coefficients are of interest for their potential use in electrooptic applications.[1-3] The chromophores in the polymer matrix are oriented in a noncentrosymmetric fashion by poling for bulk second-order NLO properties.[4-7] A major shortcoming of poled polymeric materials is the lack of long-term stability of the NLO properties. Promising schemes to overcome this problem include the incorporation of the aligned chromophores into cross-linked network structures or polymers with rigid backbones.[7-11]

Aromatic polyimides possess high glass transition temperatures, high temperature resistance, and excellent electrical properties.[12,13] Wu et al. have reported poled organic host/guest systems using aromatic polyimides.[14-17] These systems demonstrated stable electrooptic response at high temperatures because of their high T_g and excellent thermal stability. Recently, we reported on a polymer/inorganic composite of polyimide/alkoxysilane dye (ASD) as a second-order NLO material.[18] A sol–gel reaction, which takes place during the preparation of this type of composite, consists of hydrolysis of an alkoxysilane compound, followed by polycondensation of the hydrolyzed compound.[19] Water released during the imidization of polyamic acid (a precursor of polyimide) assists the hydrolysis of the ASD,[20] leading to the formation of linked dye molecules uniformly distributed in a dense polyimide matrix. The poled polyimide/ASD film displayed a large second-order NLO effect (d_{33} = 28 pm/V)[21] with excellent temporal stability at 120 °C.

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(21) In ref 18, the d_{33} is reported to be 13.7 pm/V. The corrected d_{33} value of this polyimide/ASD composite at 1.064 μm is 28 pm/V.

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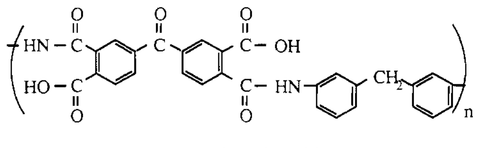
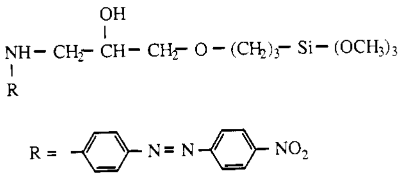


(a) Polyamic acid



(b) Alkoxysilane dye

Figure 1. Chemical structures of the aromatic polyimide and the alkoxysilane dye.

The stability of the poled order is linked to the relaxation of the chromophores and the polymer matrix.[22,23] An understanding of the molecular motions in the NLO polymers is essential for the development of better NLO materials. Study of the relaxation behavior for the sol–gel/polymer composites have been reported by a number of researchers.[24–27] In our previous study, we were unable to obtain information about the thermal relaxation of the polyimide/ASD system using differential scanning calorimetry. Here, we report the relaxation behavior of this polymer/inorganic composite using dynamic mechanical and dielectric spectroscopies, and its correlation to the stability of the NLO properties.

Polyamic acid (PAA, Figure 1a) solution (19.5 wt % in 1-methyl-2-pyrrolidinone), Skybond 705, which is based on 3,3′,4,4′-benzophenonetetracarboxylic dianhydride and 3,3′-methylenedianiline, was obtained from Monsanto Chemical Co. The synthesis of the ASD (Figure 1b) of (3-glycidoxypropyl)trimethoxysilane and 4-(4′-nitrophenylazo)aniline was reported earlier.[10,28,29]

For the pristine polymer film, polyamic acid solution was filtered through 5-μm membranes. The solution was cast on microscope slides using a Gardner knife. For the preparation of doped PAA films, a mixture of the polymer solution and the dye was prepared with a weight ratio of 4:0.15. Casting of the PAA/ASD films was done in the same manner as for the pristine polymer film. However, a silanized glass slide was used to ease the removal of the polymer film. The films were left overnight under the hood, and were gradually heated under vacuum to 120 °C. The temperature was maintained at 120 °C for an additional 24 h. Typical thicknesses of the films were 50–60 μm. The imidization temperature was selected to be 220 °C throughout this study based on our previous investigation.[18] IR study earlier established that the imidization reaction was essentially complete after 4 h at 220 °C.[18]

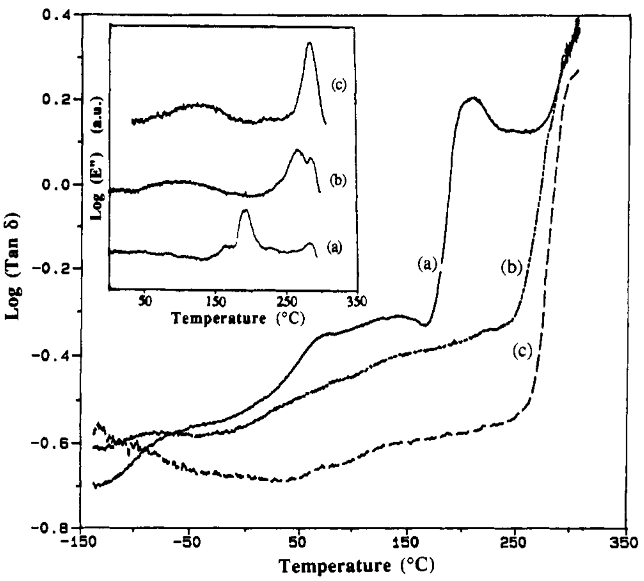


Figure 2. Mechanical loss (tan δ) as a function of temperature of undoped polyamic acid samples which were subjected to heat treatment for (a) 0 min, (b) 30 min, and (c) 4 h at 220 °C. The inset shows the relative loss modulus (E″) of the same samples vs. temperature.

Dynamic mechanical analysis was performed using a dynamic mechanical analyzer (DMA 983, TA Instrument Co.) with low-mass vertical clamps at a frequency of 1.0 Hz using a heating rate of 2.5 °C/min. The dielectric analysis was carried out by using a TA Instrument Dielectric Analyzer model 2970. Gold electrodes, 300 Å thick, were vacuum evaporated on both sides of the polymer films. Dielectric measurements were performed with a thin film parallel plate sensor from −150 to 350 °C at a heating rate of 2.5 °C/min and frequency scan range from 1 to 1000 Hz. For clarity of representation, only the 1000-Hz data are reported.

Figure 2 shows temperature dependence of the mechanical loss for the PAA samples. The PAA sample a (curve a) was dried at 120 °C for 24 h under vacuum. Prior to the dynamic mechanical measurement, this sample was heated to 120 °C on a hot stage for 5 min and rapidly quenched to room temperature. For samples b and c (curves b and c) imidization was carried out on a hot stage at 220 °C for 30 min and 4 h, respectively. Imidization of PAA causes a shift of the α relaxation to higher temperatures. The tan δ value of the highly imidized sample (c) is significantly lower than those of the less imidized sample (b) and the untreated sample (a). This result is expected as the imidization results in ring formation which increases the stiffness of the polymer backbone and reduces the main-chain mobility. The inset in this figure shows the loss modulus as a function of temperature and clearly illustrates how the α relaxations change upon imidization. The α relaxation of polyamic acid (a) is at 190 °C. The second relaxation peak at 288 °C corresponds to the α relaxation of cured polyimide. This implies that some degree of imidization has already taken place during the drying process at 120 °C. E″ maximum for sample b is much broader and indicates a broad distribution of the degree of cyclization throughout the sample. This further demonstrates the incompleteness of the imidization process of the 30-min sample. More

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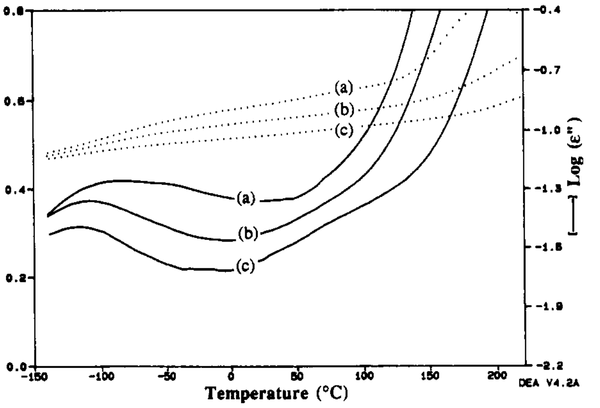

Figure 3. Plot of dielectric constant (ε') and loss (ε'') at 1000 Hz vs temperature for polyamic acid films with different heating times. Curve (a) refers to polyamic acid films which were dried at 120 °C for 24 h under vacuum. Curves (b) and (c) refer to dried polyamic acid films which were subjected to heating at 220 °C for 30 min and 4 h, respectively.

complete imidization leads to a narrowing of the E'' peak and a peak shift toward higher temperatures (c). The β relaxations around 50–100 °C are related to the vibrational mobility of the aromatic and benzimide rings.[12] A shift of the relaxation peaks toward higher temperatures due to the imidization reaction is caused by the restriction of the mobility of the aromatic rings.

Dielectric spectra in Figure 3 show the molecular relaxation of polyamic acid and the effect of imidization. Due to imidization, ε' and ε'' values decrease. This behavior is in agreement with the result from dynamic mechanical analysis. The β relaxation peaks were not resolved in the dielectric analysis due to a high concentration of ionic impurities.

In contrast to β relaxation, the γ relaxations (−150 to −50 °C) move toward lower temperatures as the imidization time increases (Figures 2 and 3). The activation energies of the γ relaxations calculated from the dielectric measurements (from peak temperatures of ε'') were 54, 39, and 32 kJ/mol for 0, 30 min, and 4 h heated samples, respectively. These energy values correspond to small-scale mobilities. The observed peak shift may be associated with the loss of water and water–polymer interaction.[12,30]

The dielectric spectra (Figure 4) show the effects of imidization on the dynamics in the polymer/inorganic composite. Adding ASD to the PAA matrix (Figure 4a) dramatically increased the magnitude of the γ relaxation, and the peaks became better resolved compared to undoped PAA. In the doped system the movements of the ASD overshadow the typical γ relaxation of the PAA. The β relaxations also shift toward higher temperatures. These relaxations are more prominent than those of undoped PAA, but the effect of ionic impurities still contributes heavily to this region.

For the 30-min imidized sample (Figure 4b), surprisingly a splitting of the γ relaxations into two peaks (in the range of −150 to 25 °C) is observed. The peak at the lower temperature (−111 °C) is the characteristic peak of polyimide which was also observed in Figure 3b. The peak at higher temperature (−32 °C) is the relaxation associated with the sol–gel reaction of the ASD molecules, which is only partially complete after 30 min of heating. The interaction between the ASD network and polyimide may play an important role for this relaxation.

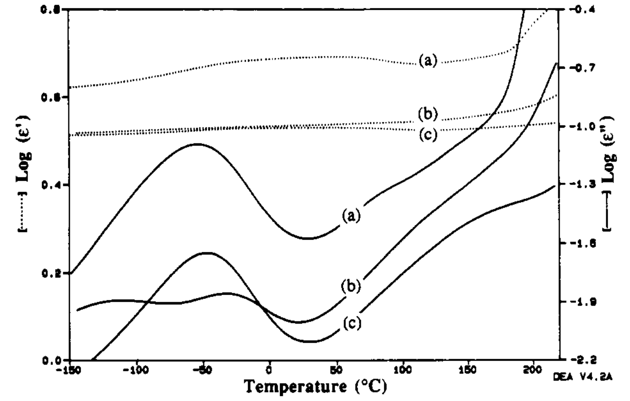

Figure 4. Plot of dielectric constant (ε') and loss (ε'') at 1000 Hz vs temperature for doped polymers. Curve (a) refers to polyamic acid doped with ASD and dried at 120 °C for 24 h under vacuum. Curves (b) and (c) refer to doped polamic acid films which were subjected to heating at 220 °C for 30 min and 4 h, respectively.

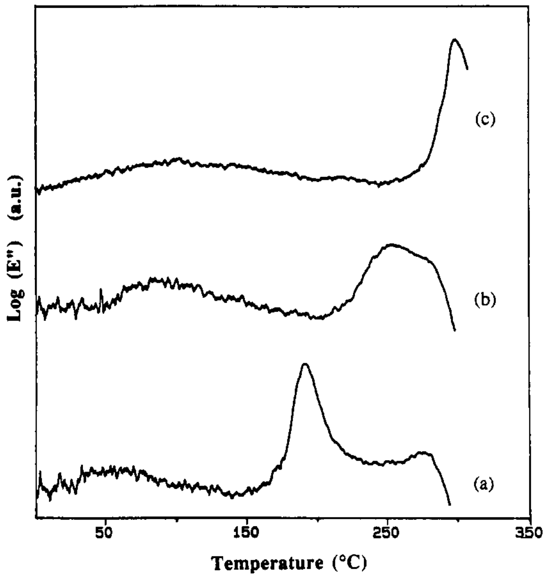

Figure 5. Comparison of loss modulus (E'') as a function of temperature for the polyimide/ASD composite with different extent of heat treatment at 220 °C: (a) 0 min, (b) 30 min, and (c) 4 h.

After 4 h of imidization (Figure 4c), only one peak is revealed in the γ relaxation region (−140 to 25 °C). The ε'' peak value and the magnitude of the relaxation are much higher than that for the 30-min sample. This relaxation (−47 °C) is considered to be resulting from local motions involving some segments of the sol–gel product. The γ relaxation that corresponds to that observed in the undoped 4-h imidized sample does not exist here. This peak could be suppressed or shifted to lower temperature as an effect of the presence of the ASD network.

Results from dynamic mechanical measurements for the composite sample are well correlated with those from dielectric analysis. The γ relaxation region shows a trend similar to that observed from the dielectric analysis. Imidization promotes the shifting of the β and α relaxations toward higher temperatures (Figure 5). tan δ values at high temperature decrease as the imidization time increases. The α relaxation for the 30-min sample is very

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broad since the imidization reaction is not yet complete. The 4 h sample has a sharp α relaxation which is about 10 °C higher than was observed for the 4-h imidized undoped sample. These results were corroborated by the dielectric measurements. The onset points of both, ϵ' and ϵ'' curves at the α relaxation for the doped sample were found to be higher than that for the undoped sample after 4 h of heating. The mobility of the polymer backbones is further restricted after the sol–gel reaction of the ASD dye. The linked dye molecules formed by the sol–gel reaction probably network throughout the polymer matrix and become entangled with the polyimide chains.

Corona poling was performed using a tungsten needle as described elsewhere.[31,32] The imidization, sol–gel reaction, and the alignment of the NLO chromophores took place simultaneously at 220 °C for 30 min under a corona electrode potential of 9 kV. From dynamic mechanical measurements, the α relaxation of the poled/cured sample shifted toward lower temperature (around 10 °C lower) than that of the unpoled/30 min cured sample. This is due to the fact that dipoles of the NLO chromophore as well as those of the polymer are aligned in a thermodynamically unfavorable state as a result of poling.

In our earlier study,[18] the polyimide/ASD composites subjected to thermal treatment for upto 168 h at 120 °C showed a stable d_{33} after a small initial decay. The high α-relaxation temperature and its enhancement in the cured composite is responsible for this excellent temporal stability. Although β relaxation was determined to be 100 °C from the dynamic mechanical measurements, the stability of d_{33} at 120 °C implies that ring vibrational motions which correspond to the β relaxation do not play an important role in the dipolar relaxation process. In contrast to a typical host/guest systems, the α-relaxation temperature of the composite is higher than that of the undoped polymer. This is an attractive feature since a decay of d_{33} is mainly due to the α relaxation which is associated with the main chain motion.

In conclusion, the relaxation behavior of the composite were observed using dielectric and dynamic mechanical analysis. As a result of imidization, the α relaxations shifted to higher temperatures, and the dielectric loss as well as the mechanical loss decreased. The α-relaxation temperature of the polyimide/ASD system was increased by the sol–gel reaction. β relaxation was observed at 100 °C. The motion associated with small segments of the reacted dye molecules was found in the subambient temperature region. The temporal stability of second-order NLO coefficient of this system can be explained by the high α relaxation temperature of the polymer matrix. The linked alkoxysilane dyes and the polyimide have formed a semiinterpenetrating polymer network (semi-IPN-II),[33,34] resulting in a substantial increase in the α-relaxation temperature and superb thermostability of the poled order. Semi-IPN and perhaps heretofore unexplored full interpenetrating polymer network (IPN) systems are good candidates to pursue for stable NLO properties. These investigations involving IPN-NLO polymers are underway in our laboratory.

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