Pressure Dependence of the Depoling Temperature in Nonlinear Optical Polymers

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ABSTRACT: Second harmonic generation (SHG) was used to monitor the pressure dependence of the depoling temperature (T_d) in dye-doped, corona-poled poly(methyl methacrylate), polystyrene, and polycarbonate. The decay of the SHG signal emitted from these systems was monitored at fixed hydrostatic pressures up to 3000 atm while the temperature was ramped at 10 °C/min. The depoling temperature increased 21−27 °C in the three systems, for every 1000 atm of applied hydrostatic pressure. The width of the transition also increased as a function of pressure. The shift in T_d as a function of pressure is used to interpret previous relaxation data in poled polymers, leading us to conclude that chromophore reorientation in nonlinear optical polymers is coupled to long range α-type relaxations near and above the glass transition temperature, T_g, and to secondary motions well below T_g.

Introduction

For the last several years, there has been considerable research on nonlinear optical (NLO) polymers.[1] These materials have potential applications as the active material in electrooptic (EO) modulators, switches, and frequency doubling devices.[2] In conjunction with efforts to increase the nonlinearity in these materials through novel synthesis[3] and processing, significant effort has been devoted to modifying their structures to enhance their thermal and temporal stability.[4] In an effort to understand the mechanisms behind the decay of the induced second order susceptibility in NLO polymers, several experimental techniques have been used to characterize the relaxations in these materials.[5,6]

Recently, we have developed a method using hydrostatic pressure and second harmonic generation (SHG) to determine the pressure dependence of $\chi^{(2)}$ in poled polymers.[7] Using that method, we have extracted the activation volumes associated with the reorientation of the nonlinear optical chromophore dopants in one side-chain and several guest−host systems.[8] Briefly, we have found that the relaxation characteristics of a doped system depend on the relative sizes of the dopants and the side groups on the polymer. Specifically, we found that for dopants near the size of Disperse Red #1 (DR1) and larger, the reorientation was coupled to α-type relaxations associated with the glass transition. Whereas, for small dopants, we found that the reorientation can also be coupled to secondary or β-type relaxations. More importantly, we found that, for all systems, the coupling of chromophore reorientation to sub-glass transitions increased as the applied pressure increased.[9] Since the application of pressure is similar to reducing the temperature, these results may have important implications for applications of these materials at temperatures well below the glass transition at atmospheric pressure.

The motivation for the work presented in this paper came from an unexplained aspect of the pressure dependence of the decay times in our previous work. Figure 1 shows some typical data from experiments that measured the decay of $\chi^{(2)}$ in corona-poled guest−host polymers as a function of applied hydrostatic pressure.

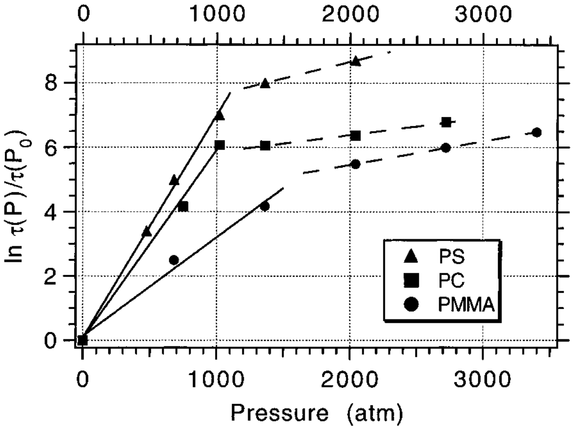

Figure 1. Logarithm of the pressure shift factor ($a_p = \tau(P)/\tau(P_{atm})$) vs pressure for 10 wt % DR1 in PMMA, PC, and PS. The experiment was performed at $T_g + 5$ °C for each system.

All 21 of the guest-host systems we have looked at so far have exhibited behavior similar to that seen in Figure 1, wherein the initial slope was sharply decreased around 1000−1500 atm. The slope of these curves is proportional to the activation volume associated with the chromophore reorientation that is responsible for the decrease in $\chi^{(2)}$. The cause for the sharp change in slope raises questions about the actual state of the system at these pressures. This paper presents the method we used to determine the glass transition temperature of three guest−host systems, and hence the state, at various pressures using SHG. We then use that information to explain the features of Figure 1 and to make some general comments about the state of the art concerning relaxation studies of NLO polymers.

Experimental Section

The three host polymers, poly(methyl methacrylate) (PMMA) (MW 145 000), polycarbonate (PC) (MW 20 000), polystyrene (PS) (MW 280 000), and the dopant Disperse Red #1 (DR1) were each obtained from Aldrich Chemical and used as received. Dimethyl-*p*-nitroaniline (DpNA) was obtained from Kodak and used as received. DR1/PMMA, DpNA/PMMA, and DR1/PC were dissolved in chloroform to 8% by weight. DR1/PS was dissolved in pyridine. The number density of the dye in each host was approximately 2×10^{20}/cm^3. Thin films were spread on microscope slides using a knife edge technique. Films 10 ± 2 μm thick (Ono Soki DG-525 digital gauge) were

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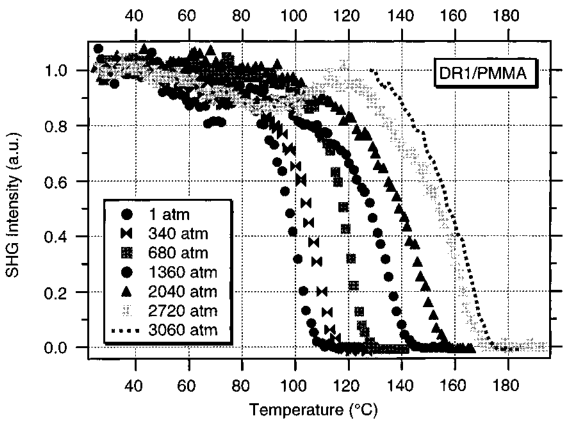

Figure 2. Decay of the SHG intensity as a function of temperature and pressure in DR1/PMMA.

Table 1. Glass and Atmospheric Pressure Depoling Transition Temperatures in PMMA, PS, and PC

material	DSC determined T_g (°C)	SHG determined T_d (°C)
DpNA/PMMA	80	77
DR1/PMMA	94	97
DR1/PS	93	108
DR1/PC	119	135

typical. The solvent was removed by air-drying the films for 24 h, followed by baking the films near T_g for 3 h at atmospheric pressure and then for 3 h more under vacuum. The glass transition temperatures of the dried materials, measured at 10 °C/min with a Dupont 2100 differential scanning calorimeter, are given in Table 1.

A nonzero $\chi^{(2)}$ was induced in each sample by corona poling[10] at $T_g + 10$ °C for 10 min at a voltage of 4–6 kV, drawing a current of 2 μA. The samples were cooled at 3 °C/min for 5 min with the field on and then removed from the corona apparatus and cooled to room temperature at ~15 °C/s. This procedure results in a low level of poling but also minimizes the amount of charge injected into the samples during poling. The samples were then stored at room temperature for 2 days to allow the bulk of the remaining charge to dissipate. The films were removed from the microscope slide prior to insertion into the optical cell.

The apparatus used to measure the SHG from the doped, oriented polymer systems as a function of pressure is described in detail elsewhere.[9] Briefly, it consists of an enclosed optical cell filled with a pressure transmitting fluid of light silicone oil (Dow Corning Co., 200 Fluid, 50 cSt) that is placed in a standard SHG arrangement. The cell is equipped with an internal thermocouple to monitor the temperature of the sample. The heating rate was controlled to ±1 °C/min (Omega CN76000) while the pressure was manually controlled (±34 atm) during each run. For each run, free standing films, prepared as above, were placed into the pressure cell after which the pressure was raised to the experimental pressure while the temperature remained at room temperature. Subsequently, the sample was heated at 10 °C/min and the SHG signal recorded until the temperature was well above that of the transition. A different film with an identical poling and thermal history was used for each run at a new pressure.

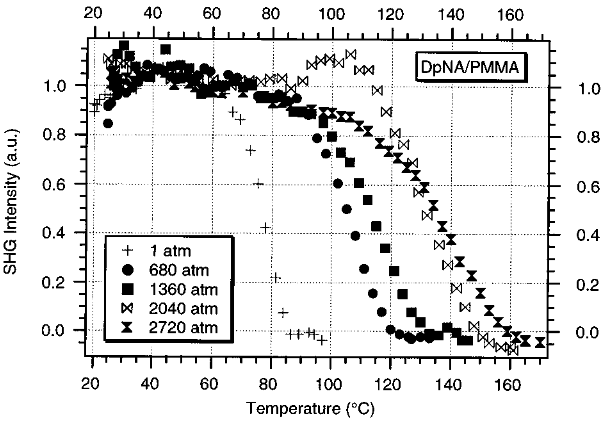

Figure 3. Decay of the SHG intensity as a function of temperature and pressure in DpNA/PMMA.

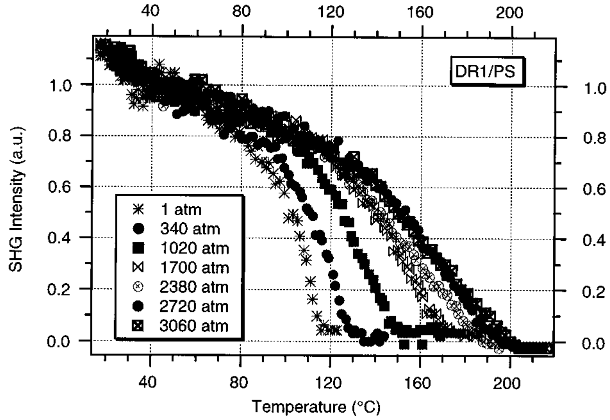

Figure 4. Decay of the SHG intensity as a function of temperature and pressure in DR1/PS.

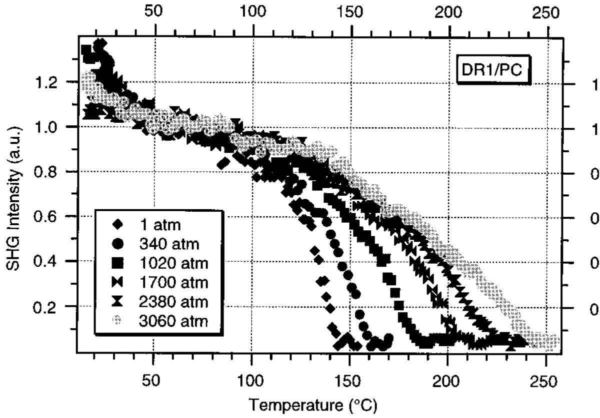

Figure 5. Decay of the SHG intensity as a function of temperature and pressure in DR1/PC.

Results and Discussion

Figures 2–5 show the decay of $\chi^{(2)}$ in the three polymer systems at various pressures. The general features are the same for each. At temperatures below the T_g of the matrix, the SH signal is relatively constant or decays slightly whereas above T_g, the signal falls off rapidly. We use the inflection point of these transitions to define a "depoling" temperature T_d. This depoling temperature corresponds to the temperature where the nonlinear optical chromophore acquires significant reorientational mobility. Since the heating rate (10 °C/min) was the same for both the optical and differential scanning calorimetry (DSC) methods, we would expect to get the same result for each method if the reorientation of the chromophore in the doped samples is coupled to the same relaxation that gives rise to the calorimetric transition seen by DSC. The atmospheric pressure depoling temperatures T_d are given in Table 1.

For the cases of DR1/PMMA (Figure 2) and DpNA/PMMA (Figure 3) T_d and T_g are in closed agreement. For DR1/PS (Figure 4) and DR1/PC (Figure 5), T_d is about 15 °C higher than the T_g determined by DSC. These data suggest that the reorientation of DR1 and DpNA in PMMA is strongly coupled to the same relaxation process responsible for the DSC determined glass transition, the α relaxation. This conclusion is supported by the fact that the SH signal from the PMMA samples is essentially constant up to the transition region and then exhibits a sharp decrease, even at elevated pressures. For both DR1/PS and DR1/PC, the SH signal exhibits a slow decay before the onset of the transition followed by a much faster decay after the onset. This behavior suggests that more than one mechanism is responsible for the reorientation of the chromophore in these systems. It is also interesting to note that the decay of the SHG signal near room temperature in PS and PC is nearly independent of pressure, a feature indicative of secondary relaxation processes in polymers.[11]

We used two methods to determine the transition temperatures from the data in Figures 2−5. In the first method, the minimum in the derivative of the SHG intensity curves was identified as the depoling temperature. For the second method, we used a graphical approach where the tangents to the onset and completion of the transitions were used to locate the midpoint of the transition. Each method gave similar results. Figure 6 shows the change in T_d as a function of applied pressure using the graphical technique for determining T_d . The effect of pressure on the depoling temperature (dT_d/dP), determined with our nonlinear optical technique, should be compared with the work of other researchers who used different techniques to measure dT_g/dP. In order to compare transition temperatures and the effects of pressure on them, we first must realize that these transitions are affected by the formation history of the glass. The doped nonlinear glasses studied here were formed by cooling from the melt at 1 atm during the poling procedure. These types of glasses are known as “low-pressure or constant formation” glasses (LPG).[12] Unfortunately, most studies of dT_g/dP to date have been done on glasses formed by pressurizing the melt isothermally. These types of glasses are known as “high-pressure” glasses (HPG). The chief methods used to determine dT_g/dP have been dilatometry, dielectric relaxation, and Brillouin scattering. Our result (22 °C/1000 atm) for doped PMMA is similar to the results reported by Shishkin (17−21 °C/1000 atm) and Olabisi and Simha (24 °C/1000 atm) for undoped PMMA determined by dilatometry,[13] although their results were for HPG. For doped PS, our result (21 °C/1000 atm) is again similar to dilatometry measurements by Shishkin (17−21 °C/1000 atm), Oels and Rehage[14] (31 °C/1000 atm), and Quach and Simha (32 °C/1000 atm) on HPG versions of PS. Quach and Simha also report a value of 74 °C/1000 atm for a LPG version of PS whereas Stevens et al.,[15] using Brillouin scattering, report a value of 31 °C/1000 atm for both LPG and HPG polystyrene. For doped PC, our result (27 °C/1000 atm) is much lower than the HPG value (50 °C/1000 atm) that Zoller[16] obtained using dilatometry. These discrepancies have not been explained yet but may have to do with the difference between doped and undoped systems or the difference in the heating and cooling rates of the various experiments.

At the highest pressures, we see (Figure 6) a slight deviation from a linear relationship between T_d and the applied pressure. An unbounded, linear relationship, between T_g and pressure is predicted by the free volume model whereas DiMarzio and Gibbs[17] predict that the transition temperature should increase with pressure but reach a finite asymptote. They predict that the leveling off should be easily observable at 10 000 atm. The data for PS and PMMA are not very different from what one would expect from the free volume theory. While the PC data are more in line with the DiMarzio prediction, higher pressure data are needed to conclusively choose between the two predictions.

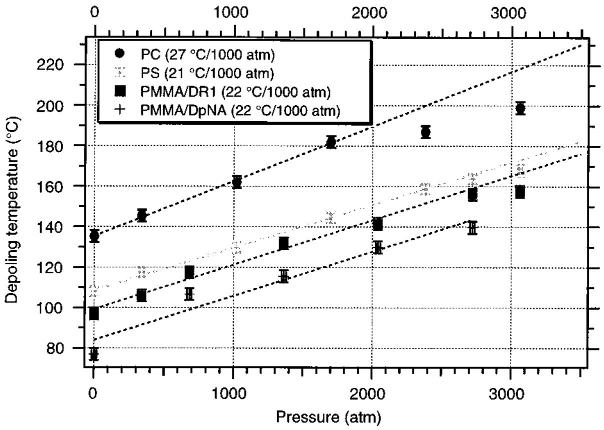

Figure 6. Pressure dependence of the depoling temperature T_d in DR1/PMMA, DR1/PS, and DR1/PC. The dotted lines are linear fits to the low-pressure data and represent the prediction given by the free volume theory.

The width of the transitions (Figures 2−5), as determined from the difference between the onset and completion temperatures or from the full-width-at-half-maximum (fwhm) of the derivative of the SHG intensity curves, increased with increasing pressure for all of the samples. Figures 2−5 show a broader transition for PS and PC than for the two PMMA systems. The pressure dependence of the transition width could be interpreted as an indication of the amount of cooperativity needed for the reorientation of the chromophore or could be a reflection of possibility that the heating rate was too fast compared to the chromophore reorientation time at the higher pressures.

Conclusions

We have presented a new method to determine the pressure dependence of the glass transition temperature in polymers. In order to use the SHG technique, however, the samples must be noncentrosymmetric and hence must be doped or functionalized with NLO probes or have appropriate orientable dipoles, as in poly(vinylidene fluoride) (PVDF). The probe method is not too restrictive, though, since the technique is sensitive to dopant levels of much less than 1%. The technique can also be applied at atmospheric pressure to obtain the T_g in materials such as cross-linked polymers where traditional DSC methods are difficult.[18]

The SHG technique determines a depoling temperature that is similar to the traditional DSC T_g for systems where the dopant probe reorients via the same mechanism that is responsible for the glass transition seen in DSC scans. The results of this study suggest that the reorientation of DR1 and DpNA in PMMA are strongly coupled to the long range, main chain type relaxations attributed to the glass transition. The coupling is not as strong in the PS or PC matrices as evidenced by the difference between the atmospheric T_d and T_g and the behavior of the SHG decay below the onset of the transitions.

For each of the systems, T_d increased with applied pressure. Using this fact, we can begin to understand the puzzling features of Figure 1. First, recall that the activation volume can be thought of as the volume of the polymer matrix that cooperatively participates in the relaxation. In the "low"-pressure regime (<1000 atm) the larger slope and hence larger activation volume can be attributed to chromophore reorientations that are coupled to long range α-type relaxations. At higher pressures (>1500 atm) the smaller slopes (smaller activation volumes) correspond to smaller rearranging regions and can be attributed to chromophore motion that is affected by secondary relaxations. Using the results of this work (Figure 6), we can calculate the apparent T_g for each pressure in Figure 1. From Figure 6 we see that the T_g of each of the polymers in Figure 1 increases between 21 and 27 °C for every 1000 atm of applied pressure. Therefore, the "low"-pressure region of Figure 1 corresponds to experiments performed 17−22 °C below the glass transition while the "high"-pressure region corresponds to experiments performed 45−72 °C into the glassy state. The two different slopes reflect the fact that the relaxation mechanism is different in the two cases. At high pressures the α-type relaxations appear to be frozen out in these materials. High pressures are qualitatively akin to performing the same experiment at lower temperatures and so it is not surprising to see different activation volumes (Figure 1) in a temperature region normally associated with secondary relaxations. We are currently performing pressure relaxation experiments like the one depicted in Figure 1 for experimental temperatures ranging from $T_g - 35$ °C to $T_g + 35$ °C. Those experiments[19] indicate that reducing the experimental temperature to $T_g - 35$ °C results in a complete quenching of the "low"-pressure or α-type relaxation behavior seen in Figure 1. We observe that only the smaller activation volumes associated with secondary relaxations are responsible for chromophore reorientation when deep in the glassy state.

The above conclusions call to question the conventional interpretation that NLO chromophore reorientations are only a function of α-type relaxations and hence the T_g. Currently, most SHG temperature relaxation experiments on NLO polymers are performed above T_g or only 20−30 °C below T_g at most. Further, dielectric measurements, which are sometimes performed at lower temperatures, are made on unpoled systems. Our results show that these types of experiments are not sensitive to chromophore reorientations that are governed by sub-T_g relaxation processes. Moreover, relaxation experiments performed at temperatures deep in the glass ($< T_g - 30$ °C) take extremely long to complete and are not commonly done; hence, sub-T_g processes responsible for chromophore reorientation may be missed. With relaxation experiments performed at high pressure, which simulates the deep glassy state thermodynamically, and near T_g, the same experiments can be completed in a reasonable amount of time. This is accomplished through the following mechanism. Performing the experiment at an elevated temperature near T_g allows the chromophores to search the available states faster than if the temperature was reduced, but the elevated pressure reduces the volume and hence the amount of configuration or phase space that must be searched in order to achieve the same amount of average reorientation or decay of $\chi^{(2)}$.

Similar experiments as these are planned on technologically promising materials such as guest−host polyimides and polyquinolines.

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