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# Effect of Pressure during Poling on the Relaxation of a Guest−Host NLO Polymer

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## Introduction

A polymer glass that is cooled from the melt at a finite rate through its glass transition temperature ($T_g$) is in a nonequilibrium thermodynamic state. In this state, the polymer undergoes substantial relaxation toward equilibrium even well below $T_g$. The relaxation rate and distribution of relaxation times qualitatively reflect the stability of the polymer glass. Recently, considerable efforts[1−7] have been invested in understanding the effects of various kinetic and thermodynamic variables on sub-$T_g$ relaxation in polymers. Understanding of the relation between the stability of a polymer glass and these variables is essential to the development of a processing protocol that can produce a stable polymer glass. Among these variables, evidence of pressure densification on the stability of a polymer glass at the molecular level is significantly lacking in the literature while the effect of pressure densification remains unanswered, even though it is of prime importance to practical processing techniques such as injection molding.

In our previous work using measurements of the decay of the second-order optical susceptibility in electric field poled nonlinear optical (NLO) polymers, [7−10] we observed that the application of pressure on previously poled samples increases the $T_g$ and retards the relaxation of the polymer. The applied pressure reduces the free volume to some degree, causing low-frequency molecular motion such as rotational transitions or long-range cooperative motions to be greatly suppressed since these molecular motions require relatively large free spaces for the rearrangement of several atoms. However, we did not test whether the improved temporal stability could be achieved by applying pressure during poling at elevated temperatures and then removing the pressure at temperatures well below $T_g$ so that the polymer glass could be densified somewhat. It is known that the free volume of a pressurized polymer glass is smaller than that in a nonpressurized polymer glass even after removal of the pressure.[11] Recent positron annihilation studies[12] indicate that the free volume fraction and the size of free volume pockets in pressurized polymers are smaller than those in nonpressurized polymers. Theoretically, DiMarzio et al.[13]predicted that the introduction of pressure during glassification can make a permanently densified polymer glass. In light of the free volume concept, one might expect that the temporal nonlinear optical stability of pressurized polymer films would be better than nonpressurized polymer films. This would be true if the reorientation of dopant chromophores is independent of polymer motion. It would also be true if the pressure does not increase the conformational energy but only decreased the free volume fraction. Since the relaxation of the polymer can also be responsible for dopant reorientation, a microscopic technique that can distinguish between these two mechanisms must be used.

The second-order optical susceptibility in poled polymers is a function of the amount of ordering achieved during electric field poling. The ordering of dopants in the polymer can be achieved by applying an electric field near or above the $T_g$ where the polymer has sufficient mobility to change its configuration, allowing the dopants to acquire a preferential alignment along the poling field. The polar order can be frozen by cooling the film below $T_g$, where the polymer motions are greatly suppressed, while retaining the poling field. Once the temperature reaches room temperature, the poling field is removed. However, substantial reduction of the second-order susceptibility has been observed even at temperatures well below $T_g$ due to polymer relaxation. Monitoring the second harmonic generation (SHG) signal with time can provide qualitative information on the stability of the polymer on a molecular level.[14−18]

In this work, we studied the effect of applying pressure during poling and glassification on the sub-$T_g$ relaxation of poly(methyl methacrylate) (PMMA) doped with Disperse Red #1 (DR1). The thermal stability of $\chi^{(2)}$ in this guest−host system was studied using SHG decay techniques. The depoling temperature was also determined as a function of the poling pressure. Since many polymeric materials are processed near $T_g$ under pressure and subsequently cooled to sub-$T_g$ resulting in nonequilibrium conditions, this study can provide useful information not only for NLO polymer device fabrication but also for polymer processing.

## Experiment

The PMMA ($M_w$ = 335 000) and guest chromophore DR1 were obtained from Aldrich Chemical Co. The films (10 wt % DR1) were optically clear over the temperature range 20−110 °C, indicating a single phase system and suggesting that the effects of pressure on the stability of the polymer glass measured for these films would be still valid for the neat polymer glass. The PMMA/DR1 mixture was dissolved in a cyclohexane/toluene mixture (4:1) as a 10% concentration. Films of ~30 $\mu$m thickness (Ono Soki DG-525 digital linear gauge) were obtained by solution casting onto ITO-coated glass substrates. The ITO served as the bottom poling electrode. The films were dried under ambient conditions for 2 days, followed by an 8 h bake at 105 °C and then 16 h at 105 °C in a vacuum oven. A 0.25 cm$^2$ gold electrode was then sputtered on the center portion of the film surface to act as the top poling electrode.

The pressure poling cell is similar to our previous optical pressure cell[8] except that one end plug has been modified with electrical feedthroughs instead of an optical window. A new holder was designed to contact the electrodes on the sample to facilitate poling. The new cell allowed us to pole the polymer film while pressure was applied. We employed the following protocol: (1) the NLO polymer was heated to above its glass transition temperature in the pressure cell at atmospheric pressure and held at $T_g$ + 10 °C for 30 min to remove any thermal history, (2) a nonzero $\chi^{(2)}$ was imparted to the film by dc contact poling at $T_g$ + 10 °C (105 °C) for 20 min while drawing a poling current less than ~2 $\mu$A (poling field = 5−6 V/$\mu$m), (3) pressure was applied within a few seconds and maintained within 70 atm for 1 h, using a silicone oil (Dow Corning Co., 200 Fluid, 50 cSt), (4) the cell was cooled by a water jacket, taking about 20 min to reach room temperature, in the presence of the field and pressure, and (5) the poling

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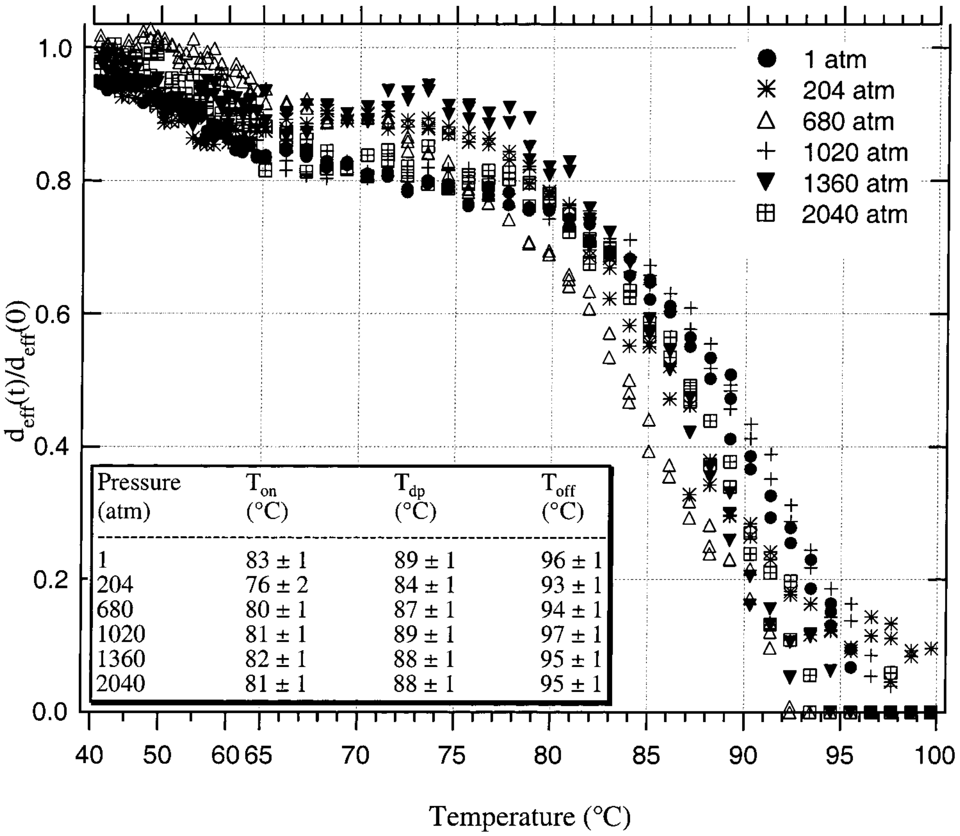

| Pressure (atm) | $T_{on}$ (°C) | $T_{dp}$ (°C) | $T_{off}$ (°C) |
|---|---|---|---|
| 1 | 83 ± 1 | 89 ± 1 | 96 ± 1 |
| 204 | 76 ± 2 | 84 ± 1 | 93 ± 1 |
| 680 | 80 ± 1 | 87 ± 1 | 94 ± 1 |
| 1020 | 81 ± 1 | 89 ± 1 | 97 ± 1 |
| 1360 | 82 ± 1 | 88 ± 1 | 95 ± 1 |
| 2040 | 81 ± 1 | 88 ± 1 | 95 ± 1 |

**Figure 1.** Decay of the SHG signal as a function of temperature in 10% DR1/PMMA films poled at pressures of 1, 204, 680, 1020, 1360, and 2040 atm.

field was removed and the pressure removed quickly (within 1 s) after the cooling was complete. The sputtered gold electrode on the polymer film was removed using a mixture of $HNO_3/HCl/H_2O$ with the weight ratio of 3:2:5. (Care should be taken handling this mixture.) The acid mixture was removed by deionized water followed by $N_2$ gas purge. SHG decay was measured at 70 °C ($T_g - 25$ °C), with the data collection starting 2 min after the insertion of the film into the oil-filled sample cavity of the optical cell, to allow the film to come to thermal equilibrium. For each sample, the elapsed time from the point of releasing the applied pressure to the point of taking SHG data was ~15 min. Charge injection[19] and thickness changes due to electrostriction can be safely ignored since the poling field was small. In addition to the isothermal decays, identically prepared films were subjected to a temperature ramp study[9] in order to determine the depoling temperature of each pressure poled film.

## Results and Discussion

When a poled film is subjected to a constant heating rate, the SH signal remains relatively constant or decays only slightly at temperatures below $T_g$, whereas near or above $T_g$, the signal falls off rapidly. The depoling temperature, which can be defined as the midpoint of these transitions, corresponds to the temperature where the dopants acquire significant reorientational mobility and provides information about the local dynamics of the polymer. Since the depoling temperature for a given pressure poled sample varied slightly from sample to sample, four to five samples were employed to obtain an average depoling temperature for each pressure. Typical SHG decays during heating for films poled under 1, 204, 680, 1020, 1360, and 2040 atm are shown in Figure 1. The mean values of onset ($T_{on}$), offset ($T_{off}$), and depoling ($T_{dp}$) temperature are listed in the inset. The uncertainties are the standard deviations of the means. Although the differences in $T_{dp}$ and $T_{on}$ between nonpressure poled and pressure poled films are small, one can see that the pressure poled samples have lower $T_{dp}$ and $T_{on}$ especially for the lower pressure poled films (≤680 atm). The lower values of $T_{dp}$ and $T_{on}$ indicate that the pressure poled films are less stable than the pressure-free sample, which might be rather striking. Our results corroborate a similar study of the effect of pressure densification on $T_g$ observed by Wunderlich et al.[20] According to them, the introduction of pressure actually decreases $T_g$, with pressurized PMMA having a lower $T_g$ than that of nonpressurized PMMA even after months of physical aging at a moderately elevated temperature.

We also measured the SHG decay to further confirm this observation. The pressure effect on the stability of a polymer glass should be more noticeable in the measurement of SHG decay as a function of time at a given temperature than the depoling temperature measurement, since the relaxation time $\tau$ has been shown to change exponentially with $T_g$ for many guest−host systems.[21,22]

We characterized the isothermal decay of $\chi^{(2)}$ with a KWW stretched exponential expression.[10,18,23] The stability of a polymer glass can be qualitatively studied by determining the average relaxation time and its pressure dependence. Figure 2 shows typical decays of $d_{eff}(t) = {}^1/_2\chi^{(2)}_{eff}(t)$ for films poled under 1, 204, 680, 1020, 1360, and 2040 atm and the stretched exponential fits. Except for the 204 and 680 atm pressure poled films, the SHG decays are well fit by the stretched exponential. The fit parameters ($\tau$, $\beta$, and $\langle\tau\rangle$) are shown in the inset. Since $\tau$ and $\beta$ varied considerably from sample to sample,

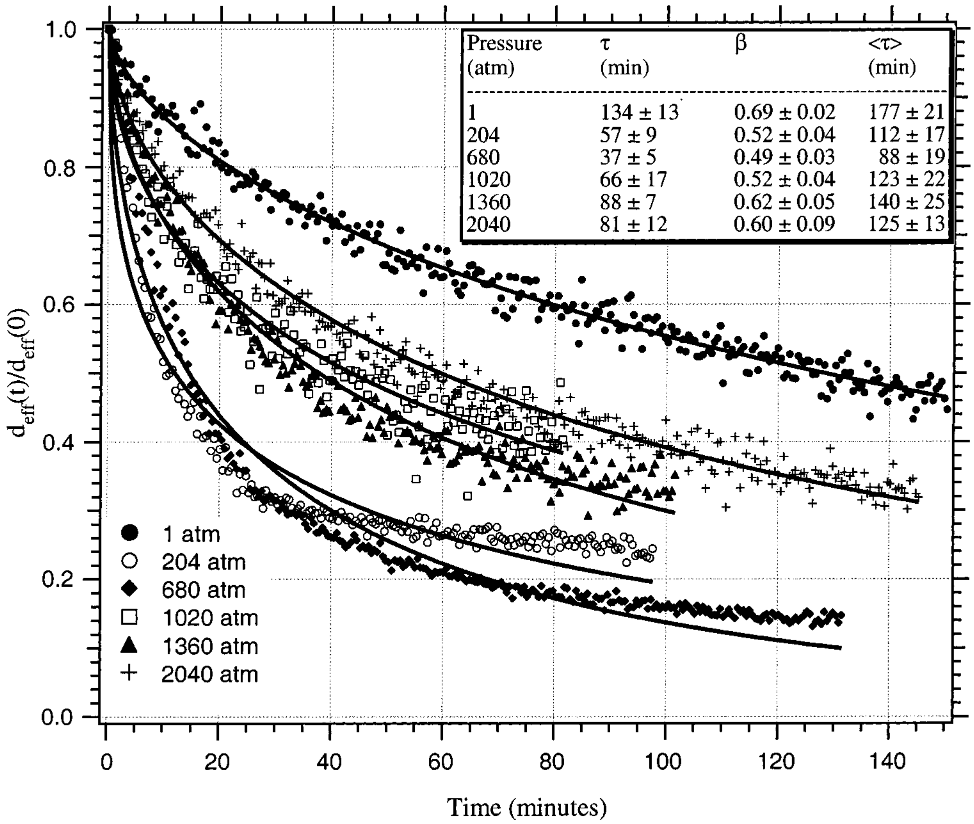

**Figure 2.** Isothermal decay (70 °C) of the SHG signal as a function of time in 10% DR1/PMMA films poled at pressures of 1, 204, 680, 1020, 1360, and 2040 atm.

multiple decay measurements were carried out at each pressure to attain reasonable statistics. From the inset, it is clear that the introduction of pressure during glassification induces faster sub-$T_g$ relaxation and a broader relaxation distribution than for glassification at 1 atm. Another interesting observation is that the relaxation distribution and the relaxation time have two distinct pressure regimes: low pressure (<1020 atm) and high pressure (≥1020 atm).

Our results contradict the simple free volume concept. It appears that the size of the free volume pockets where the dopants are located may not be as important to the reorientation of the dopants as is the relaxation of the host itself. Instead, the stability of the polymer glass should be considered, since host relaxation is a measure of that stability. Wunderlich et al.[20] have observed that the enthalpy of a polymer glass cooled under pressure is higher than that cooled at the same rate under atmospheric pressure. The enthalpy increase indicates that the pressure helps to create relatively high-energy conformers; therefore, the thermodynamic driving force for the relaxation is greater for the pressure poled films. We propose the following model to explain our results. Because of the spatial heterogeneity of the polymer near $T_g$, some regions can be “softer” (less dense, less entangled) than others. Polymer segments in these softer regions may deform more under the applied hydrostatic pressure and hence can be more strained locally. Once the applied pressure is relieved below $T_g$, these strained, high-energy conformers will relax faster than the nonpressurized polymer conformers would relax. When the polymer is heated toward $T_g$, the faster relaxing high-energy conformers facilitate longer range segmental motion; thus, pressure poled films have a lower depoling temperature. For the relatively low pressure poled films, the densification effect (reduction of free volume) is nearly negligible, yet the pressure still creates high-energy conformers. Thus, the relaxation is faster for the relatively low-pressure poled films than for the relatively high-pressure poled films since dopants in the low-pressure films sit in relatively larger cages surrounded by a sufficiently strained host.

While any polymer glass cooled below $T_g$ is in a state of nonequilibrium due to the finite cooling rate, the glasses studied here are further removed from equilibrium due to the applied pressure. Therefore, our observation of the relaxation of the polymer glass is not associated with equilibrium because all the pressurized samples were relaxing toward equilibrium by volume and enthalpy recovery through a sub-$T_g$ relaxation process. In addition, we were not able to observe improved temporal stability of the NLO polymers even for pressure poled films aged several days at room temperature after the removal of pressure. Moreover, it is technically infeasible to measure the relaxation of the pressurized polymer glass in equilibrium using the SHG decay measurement, since several months of physical aging would be necessary, but $\chi^{(2)}$ would decay completely by then.

## Conclusions

An SHG measurement technique has been used to investigate the effect of pressure during poling on the sub-$T_g$ relaxation of a DR1/PMMA guest−host nonlinear optical polymer system. From the depoling temperature measurement technique, the pressure poled samples have relatively lower $T_{on}$ and $T_{dp}$ than nonpressurized films, indicating that the thermal stability of pressure poled NLO films are inferior to nonpressure poled films. For the low-pressure poled films (≤680 atm), the values of $T_{on}$ and $T_{dp}$ are lower than those for high-pressure poled samples (>680 atm). From the isothermal SHG decay measurement, we find that the average relaxation times of pressure poled films are faster than those of nonpressure poled samples, indicating that applying pressure during the glassification produces a less stable polymer glass. Two different pressure regions of the relaxation distribution and relaxation time for the various pressure poled polymers were also observed. For the low-pressure poled films, the relaxation distribution is broader and the relaxation time is faster than those for the higher pressures.

Our observations indicate that dopant reorientation is cooperative with the polymer motions and that the size of the free volume pocket where a dopant is sitting is not as important in determining the reorientation time of the dopants. In addition, we find that the free volume concept is not sufficient to explain the stability of the polymer glass. In fact, use of that concept would (in this case) cause one to incorrectly predict that a pressurized polymer glass has better stability than a nonpressurized one. For the relatively high-pressure poled films (>680 atm), the relaxation is slower than for the low-pressure poled films (≤680 atm). This is an indication that there is sufficient pressure densification at these pressures to reduce the free volume enough to compensate somewhat for the strained high-energy condition of the host.

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