Memory Effects above T_g in Poled Guest/Host Polymers

Stephan Schüssler,[†] Uwe Albrecht,[†] Ranko Richert,[*,‡] and Heinz Bässler[†]

Fachbereich Physikalische Chemie und Zentrum für Materialwissenschaften,
Philipps-Universität Marburg, 35032 Marburg, Germany, and Max-Planck-Institut für
Polymerforschung, Ackermannweg 10, 55128 Mainz, Germany

Received July 21, 1995; Revised Manuscript Received November 22, 1995[⊗]

ABSTRACT: We present systematic experiments of electric field poling and relaxation of 4-(dimethylamino)-4′-nitrostilbene doped at 1 wt % in poly(isobutyl methacrylate) in a sandwich configuration of ITO electrodes using the second harmonic generation technique. A novel ultraslow relaxation mode at temperatures far above the glass transition temperature T_g has been identified qualitatively with a special repoling technique. Isothermal alignment and relaxation of the chromophore orientations show significant differences in their mean rates and in their sensitivity to variations of the field strength and the presence of small amounts of plasticizer molecules. A tentative qualitative model is proposed in which the necessity for considering nonlinear responses is postulated.

Introduction

An important impediment to the realization of the technological potential of poled guest/host polymer systems is their inherent thermal instability of the alignment of hyperpolarizable dopant molecules once the poling field is removed. The lack of centrosymmetry is indispensable for second harmonic generation (SHG) or other second-order nonlinear optical effects.[1] Therefore, the impact of orientational relaxation of the bulk polymer on the centrosymmetry of the dopant molecules and concomitantly on the SHG efficiency has received much attention.[2−8] At present, it is still a matter of controversy whether the SHG-efficiency onset and decay of a guest/host polymer is quantitatively coupled to the relaxation behavior of the undoped polymer counterpart system.[7,8] A previous detailed investigation of such materials led us to the conclusion that orientational motion of the chromophoric dopants is strongly decoupled from that of the polymer constituents.[7] For the presently studied system DANS/PIBMA it was found that the relaxation times of the bulk polymer follow the expected Vogel−Fulcher[9] like temperature dependence, whereas the SHG decay exhibits simple activation behavior of the Arrhenius type, so that the SHG relaxation is slower than the polymer dynamics above the glass transition T_g and faster below T_g.[7] The latter feature is clearly undesirable in the context of persistent optical nonlinearities for technical applications. Although the SHG technique selectively monitors the alignment of the chromophoric molecules, this method also yields information regarding the dynamic properties of the surrounding matrix cages, if one assumes that $\langle \cos\,\theta \rangle$ of the hyperpolarizable molecules is the only time- and temperature-dependent factor acting on the SHG intensity.

In this contribution we focus on the comparison of both the relaxation and the poling kinetics at a given temperature using electrode-poled films of 4-(dimethylamino)-4′-nitrostilbene dissolved at 1 wt % in poly(isobutyl methacrylate). We first examine the realignment kinetics as a function of the foregoing extent of relaxation of the SHG efficiency and for various delay times between relaxation and the poling process. Secondly, we explore the impact of the dc poling field strength and of plasticizers on the temperature dependence of poling and relaxation rate constants. Following previous work,[6,10] these average rates are obtained by assuming a static Gaussian distribution of energy barriers characterized by a mean rate $<r>$ and Gaussian width σ of the distribution as fit parameters.

Experimental Section

Poly(isobutyl methacrylate) (PIBMA) films of 25 μm thickness doped with 1 wt % 4-(dimethylamino)-4′-nitrostilbene (DANS) were cast from HPLC-grade toluene (Merck) solutions and placed in an ITO sandwich-electrode architecture. A 76 MHz mode-locked Nd-YAG laser operated at 1064 nm was used as a light source. Guided by our previous success with respect to the reproducibility of SHG signals, the sample's thermal history was erased by heating to 170 °C for 1 h prior to each measurement. The experimental details regarding detection and sample preparation and the method of kinetic analysis have been described previously.[7]

Results

Numerical fits to the SHG decay data were achieved by following eq 1 based on a static Gaussian distribution of energy barriers with the parameters $<r>$ and σ which quantify the mean relaxation rate and the Gaussian width, respectively. This model, presented in detail elsewhere,[10] turned out to yield satisfactory results when applied to SHG relaxation data:[6,7]

$$I(t) = (2\pi\sigma^2)^{-1/2} \int_{-\infty}^{+\infty} \exp(-\epsilon^2/2\sigma^2 - \nu_0 e^{-\epsilon} t)\, d\epsilon \quad (1)$$

From such an approach to dispersive kinetics a mean rate $<r> = \nu_0 \exp(\sigma^2/4)$ can be deduced from the slope of $I(t)$, i.e. $<r> = -dI(t)/dt|_{t=0}$. Note that this definition of $<r>$ via the slope applies to decay data in general; i.e. it is not model specific.

1. Memory Effects. The basic scope of this work is to investigate the temporal course of SHG recovery upon reapplying the external poling field after a partial relaxation at a constant temperature $T > T_g$ ($T_g \approx 63$ °C). An important prerequisite for such an experiment is highly reproducible SHG signals.[6,7] The temporal pattern of the poling traces can be compared if each scan is normalized after inverting the SHG recovery data. Figure 1 shows the results for $T = 90$ °C ($T_g + 27$ K) and a dc field of 0.14 MV/cm, where trace 1 corresponds to the normalized SHG decay. The remaining (inverted) curves (2−5) show the SHG recovery signals when reapplying the poling field after a decay of ~50% (2) and

---

[†] Philips-Universität Marburg.

[‡] Max-Planck-Institut für Polymerforschung.

[⊗] Abstract published in *Advance ACS Abstracts,* January 15, 1996.

0024-9297/96/2229-1266$12.00/0

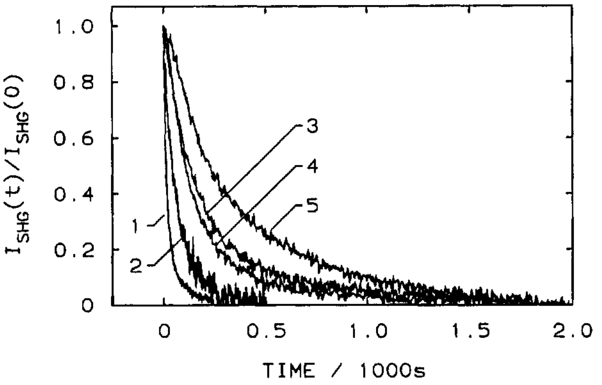

Figure 1. Normalized SHG decay (1) and inverted curves of realignment (2–5) of 1 wt % DANS dissolved in PIBMA at T = 90 °C (T_g + 27 K). Curves 2–4 show the SHG recovery signals when reapplying the poling field after a decay of ~50% (2) and after complete reorientation with no (3) or a further delay of 1/2 h (4). Trace 5 corresponds to poling of a freshly prepared sample.

after complete reorientation with no (3) or a further delay of 1/2 h (4). Trace 5 corresponds to the alignment by poling at T = 90 °C directly after standardization. A similar behavior is observed at T = 120 °C, but with an overall acceleration in the kinetics. It is obvious that (1) reorientation and alignment kinetics of the dipolar chromophores do not coincide and (2) although working in the viscoelastic region this system reveals a memory on a time scale of hours.

2. Dependence on dc Field Strength and Temperature. Especially the direct comparison of traces 1 and 5 in Figure 1 points toward the basic difference of isothermal relaxation and poling response functions in this system. A further investigation of this discrepancy as a function of temperature, poling field strength, and power density of the incident laser appears in order. The relevant results gained by either applying different dc fields or varying the laser power on the sample by readjustment of the focus are depicted in the form of Arrhenius plots in Figures 2 and 3, respectively.

Despite a retardation by about 1.5 orders of magnitude, a similar temperature dependence of poling and relaxation is observed, whereas little variations of the intensity of the excitation beam cause no effect (Figure 2). Lowering the poling field by a factor of ~7 yields a significant decrease of both the orientational alignment and relaxation kinetics. Thereby the Arrhenius-like behavior (E_{act} ~ 120 ± 10 kJ/mol) is preserved, with only minor changes in the activation energies (Figure 3).

3. Influence of Plasticizers. Further information on the above features stems from the impact of small amounts of unpolar molecules of low molecular weight as plasticizers on the dopant orientational mobility. A series of temperature-dependent traces for alignment (E = 0.14 MV/cm, open circles) and relaxation (open squares) was recorded by choosing a 1 wt % DANS/PIBMA film which also contained 3 wt % biphenyl. Figure 4 summarizes these results including the corresponding data obtained in the absence of plasticizers (filled symbols).

Adding only very low concentrations of biphenyl does not cause significant changes of the bulk material properties, whereas the dopant mobility is more sensitive to the presence of biphenyl: As demonstrated in Figure 4, a molar ratio DANS:biphenyl of ~1:5 causes the kinetics of poling to coincide with those of the relaxation process, while the former remains practically unchanged relative to the unplasticized sample. It is important to note that in this case plasticizing additives result in a decreased mean rate of the SHG efficiency relaxation.

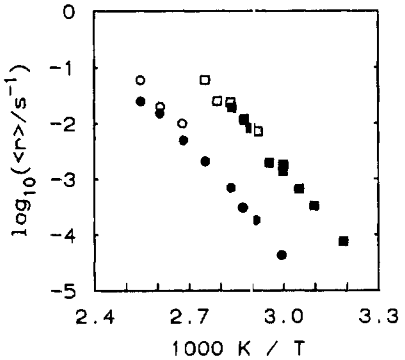

Figure 2. Arrhenius plot of the mean rate of isothermal SHG poling (●) and relaxation (■) of a PIBMA sample doped with 1 wt % DANS. Open symbols refer to poling (○) and relaxation (□) with increased laser focus on the sample. The poling field was E = 0.14 MV/cm.

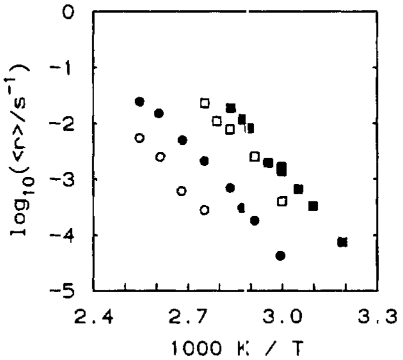

Figure 3. Temperature dependence of the mean rate of isothermal SHG poling (●, ○) and orientational relaxation (■, □) of a PIBMA sample doped with 1 wt % DANS using dc fields of 0.14 MV/cm (●, ■) and 0.02 MV/cm (○, □).

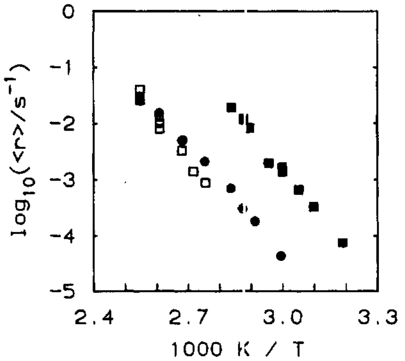

Figure 4. Temperature dependence of the mean rate of isothermal SHG poling (●, ○) and orientational relaxation (■, □) of a PIBMA sample doped with 1 wt % DANS. The plot compares data for unplasticized samples in Figures 2 and 3 (●, ■) with the results for samples containing 3 wt % biphenyl (○, □). For the plasticized sample the rate for poling (○) and relaxation (□) coincide within symbol size.

Discussion

Observing a memory effect associated with a time scale of hours at temperatures significantly above T_g contradicts intuition because the structural α-relaxation of the pure matrix has been shown to proceed on a microsecond time scale under these conditions.[7] Usually, tracer diffusion (e.g. ionic conduction) follows the temperature dependence of the α-process to a good approximation, so that impurity diffusion should also proceed on short time scales in this case. Moreover, the observed asymmetry regarding onset and decay of the SHG efficiency is counterintuitive and not paralleled by common experimental techniques for detecting rotational dynamics of molecular probes. Together with the field-dependent SHG kinetics, it follows that a departure from the linear response regime for poled guest/host systems has to be considered. This nonlinear response obtained from poling at a field of 0.14 MV/cm is most probably the cause for the discrepancy between SHG kinetics and dielectric relaxation found previously,[7] where the latter technique customarily employs fields around 100 V/cm which yield linear responses.

The history dependence of chromophore orientation on the time scale of hours implies that a relaxation other than the α-process is active, which might be identified as a long-range structural relaxation of the *bulk polymer* PIBMA, whose dependence on temperature is bound to remain unresolved at present. This hypothesis is underlined by the results of Spiess et al.[11] who have reported on the anisotropic behavior of a similar matrix material in the T range just above T_g. The existence of a slow relaxational mode in the viscoelastic regime of polymers has been a matter of controversy.[12] However, in a recent light-scattering study on organic low-molecular weight glass-forming liquids Fischer[13] has reported on a similarly slow relaxation processes interpreted in terms of long-range density fluctuations at temperatures well above T_g and for systems which exhibit a Vogel–Fulcher-like temperature dependence of the relaxation times, as for the present material PIBMA.

Although we have no rigorous support in favor of a correlation between the memory effect of the SHG efficiency and possible long-range density fluctuations, such an interpretation would be in accord with the following picture: For a freshly prepared sample the kinetics of DANS alignment is governed by the temperature as well as the dc field strength only. The isothermal relaxation at $T \gg T_g$ has turned out not to depend on a waiting period under the applied field once a steady state signal intensity has been achieved, while the time scale involved in repoling is sensitive to the delay between the beginning of relaxation and poling onset. Since the time scale for aligning the chromophores is field-dependent (cf. Figure 3), the electrostatic forces acting on the chromophore dipoles are no longer negligible relative to the thermal energy. Therefore, the polymer vicinity of a particular dye molecule might suffer a nonequilibrium structural distortion which relaxes only slowly. Within the lifetime of this distortion, orientational motion of the dye can be relatively fast. However, if the distortion is small (low fields) or if it has relaxed (long delay periods), orientational motion is more frustrated, in accord with the data in Figures 1 and 3. In any case the chromophore dynamics are not directly linked to the α-process of the polymer, since even low poling fields do not shift the SHG kinetic time scale toward that of the dielectric α-relaxation.[7] Due to the long lifetime of such a distorted configuration, the length scale associated with these structural changes should exceed that of the α-relaxation, which is a more local process at these elevated temperatures. Within this picture, the difference in the kinetics of poling and relaxation of the SHG active subensemble of molecules can easily be regarded as a highly material-specific property, as inferred earlier.[3] The possible role of chromophore–chromophore interactions can be addressed only if analogous experiments with dopant concentrations well below 1 wt % were available, which is not feasible without setup. In previous experiments, however, concentrations of 1 and 0.5 wt % DANS in a PEMA matrix gave identical results.[6]

We finally address the effect of plasticizers on the poling and relaxation times of the SHG kinetics compiled in Figure 4. Although plasticizer molecules tend to decrease the glass transition of the bulk material, thereby accelerating the α-process at a given temperature, the effect of 3 wt % biphenyl in the DANS/PIBMA samples is to further retard the orientational motion of the dopants, as documented in Figure 4. This observation underlines the notion of a highly material-specific discrepancy between the poling and relaxation processes, which is virtually zero for the plasticized sample. It follows that alignment-induced distortion of the type mentioned above is either suppressed by the presence of plasticizing molecules or short lived in this case.

Conclusions

Through a systematic combination of electric field poling and relaxation experiments of DANS in PIBMA, the main goal of this study is to rationalize the controversial issue of dopant orientational mobility in poled guest/host polymers. Isothermal realignment traces with variable time delays after a relaxation step have hinted at the contribution of a novel ultraslow relaxation mode of the system at temperatures well above T_g, which resembles the phenomenology of long-range nonequilibrium structural relaxations, similar to those discussed by other authors. The tentative picture of structural distortion accompanying the alignment of dopants turns out to be in accord with the observations regarding the delay time relative to the foregoing relaxation, the dependence on the electric field strength, and the effect of plasticizers at moderate concentrations. In contrast to the dielectric α-relaxation, the temperature dependences of the SHG kinetics are well approximated by Arrhenius laws, with similar activation energies for the very different absolute times scales related to different experimental situations. Finally, we note that the observed field dependence implies a departure from the linear response regime, so that the fluctuation-dissipation theorem does not apply in this situation. As a consequence, the temporal instability of the SHG efficiency in these poled guest/host polymers is not solely a signature of equilibrium fluctuations.

References and Notes

(1) Prasad, P. N.; Williams, D. J. *Introduction to nonlinear optical effects in molecules and polymers*; Wiley: New York, 1991.
(2) Goodson, T.; Wang, C. H. *Macromolecules* **1993**, *26*, 1837.
(3) Guan, H. W.; Wang, C. H.; Gu, S. H. *J. Chem. Phys.* **1994**, *100*, 8454.
(4) Stähelin, M.; Burland, D. M.; Ebert, M.; Miller, R. D.; Smith, A.; Twieg, R.; Volksen, W.; Walsh, C. A. *Appl. Phys. Lett.* **1992**, *61*, 1626.
(5) Eich, M.; Sen, A.; Looser, H.; Bjorklund, G. C.; Swalen, J. D.; Twieg, R.; Yoon, D. Y. *J. Appl. Phys.* **1989**, *66*, 2559.
(6) Schüssler, S.; Richert, R.; Bässler, H. *Macromolecules* **1994**, *27*, 4318.
(7) Schüssler, S.; Richert, R.; Bässler, H. *Macromolecules* **1995**, *28*, 2429.
(8) Dhinojwala, A.; Wong, G. K.; Torkelson, J. M. *Macromolecules* **1993**, *26*, 5943.
(9) Vogel, H. *Phys. Z.* **1921**, *22*, 645. Fulcher, G. S. *J. Am. Ceram. Soc.* **1923**, *8*, 339.
(10) Richert, R. In *Optical techniques to characterize polymer systems*; Bässler, H., Ed.; Elsevier: Amsterdam, 1989.
(11) Kulik, A. S.; Beckham, H. W.; Schmidt Rohr, K.; Radloff, D.; Pawelzik, U.; Boeffel, C.; Spiess, H. W. *Macromolecules* **1994**, *27*, 4746.
(12) Keinath, S. E., Miller, R. L., Rieke, J. A., Eds. *Order in the amorphous state of polymers*; Plenum Press: New York, 1987.
(13) Fischer, E. W. *Physica A* **1993**, *201*, 183.

MA951051X