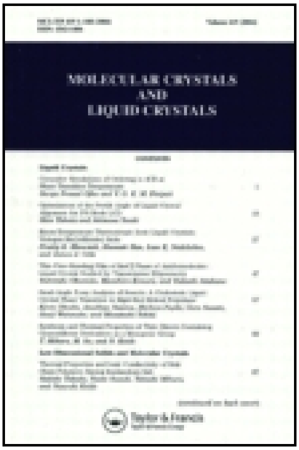

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Nonlinear Optical Properties of Polymeric Thin Films

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Nonlinear Optical Properties of Polymeric Thin Films

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The orientation of chromophores (dipoles), introduced into polymer matrices covalently or dispersed molecularly, under the electric field (poling), has been discussed from the *in situ* observation of optical absorbance. The second harmonic generation of these polymer systems has also been observed. From depoling dynamics measurement, it is suggested that the orientational relaxation of chromophores due to thermal motion can be suppressed by the introduction of covalent bonding into the side chain, not the molecularly dispersion into the polymer matrix.

Keywords: optical absorbance, second harmonic generation, poling dynamics, corona poling, PMMA/DR1 system, polyurethane derivative

1. INTRODUCTION

Organic photonics is the booming research area of opto-electronic application of organic materials in the field of optical computing and/or communications.[1,2] From the materials viewpoint, the intramolecular charge transfer through π-electron conjugation gives large optical nonlinearities in the molecular level, whereas the centro-symmetry of the crystal structure determines the macroscopic second order nonlinearity $(\chi^{(2)}_{ijk}(-\omega_3; \omega_1, \omega_2))$; if the crystal is centro-symmetric, then $\chi^{(2)}$ becomes zero. On the other hand, the third order optical nonlinearity $\chi^{(3)}_{ijkl}(-\omega_4; \omega_1, \omega_2, \omega_3)$ does not depend on the crystal symmetry but on the microscopic third order susceptibility $\gamma_{ijkl}(-\omega_4; \omega_1, \omega_2, \omega_3)$ of the constituent molecular unit. It is suggested that in conjugated linear chain structures such as polyenes and polydiacetylenes the π-electrons are delocalized in their motion only in one dimension along the chain axis.[3] The major contribution to γ_{ijkl} is the dominant chain axis component. In the widely spread two dimensional π-conjugation systems, other tensor components also contribute to $\langle\gamma\rangle$.[4]

The inversion center of polymeric systems can be removed by aligning dipolar chromophores using an external electric field.[5] The resulting materials show second order nonlinear optical responses and these are suitable for guided-wave electro-optic devices. Enhancement of the orientational order and the stabilized poled state are key issues in poling of polymeric systems. We have already reported the molecular design of ID/2D π-conjugated systems,[6] e.g., polyalkylthiophenes,[7] polydiynes[8] and phthalocyanine derivatives,[9] for third order nonlinearities. In this paper we will discuss the homogeneous polar alignment by corona-poling for second order nonlinearities. The poling dynamics will also be discussed in two kinds of polymeric systems: a molecularly doped polymer and a covalently attached polymer.

2. EXPERIMENTAL

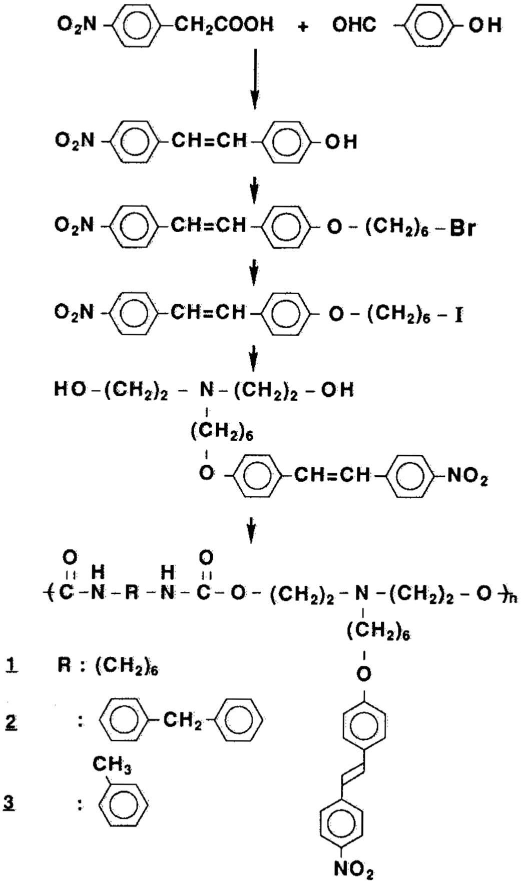
2.1 Materials

Two kinds of polymer thin films were prepared: the one is polymethyl methacrylate (PMMA) doped with azo-dye disperse red 1 (DR1)[10] and the other is polyurethane with 4-nitrostilbene derivatives in the side chain (PU-NS).[11] DR1 (Eastman Kodak Co.) was purified by the column chromatography and precipitation methods. The mixture of PMMA (optical grade) and DR1 in $CHCl_3$ was spin-coated on the glass substrate. The film thickness was well controlled homogeneously in the range of 1-3 μm. In the case of PU-NS, on the other hand, three types of polymers $\underline{1}$-$\underline{3}$ were synthesized as shown in Scheme 1. The glass transition temperatures T_g of these polymers were 20.6°C, 50.3°C and 64.4°C, respectively. We used PU-NS $\underline{3}$ mainly in this study because of higher T_g and no absorption at a second harmonic wavelength. The film was also prepared by a spin-coating method.

2.2 Poling

Since azo-dyes and/or stilbene derivatives with functional groups at *para* position have the second order hyperpolarizability in parallel to the molecular dipole, then it is important for the second order nonlinear optics to align the dipoles in the side chains (PU-NS) or of guest molecules (PMMA/DR 1) in one direction, especially perpendicular to the film surface. The high electric field was applied across the film by a corona poling technique. As shown in Figure 1, the needle electrode (W or Ta) was set above the film sample placed on the glass substrate, and applied high potential for the corona discharging. The grid was inserted in between the needle electrode and the sample to uniform the electric field. The substrate temperature was controlled by the heater during the poling process.

The alignment of dipoles can be estimated by the change of optical absorption, that is, when the dipoles align well perpendicular to the film surface along the electric field applied, the cross section of optical absorption due to chromophore molecules decreases.[12] It follows the decrease in theoretical absorbance of the film. The relationship between the decrease in optical absorbance and the increase in the intensity of second harmonic generation (SHG) will be discussed later.



SCHEME 1 Polyurethane 1-3 for nonlinear optics.

2.3 In Plane Distribution of Poling

Poled polymer films were fixed on the translational (x-y) stage, and the optical absorption spectra at an arbitrary point (x, y) were measured by the spectrophotometer (Shimadzu UV 3100S). The uniformity of poling was checked by changing the point (x, y).

2.4 Poling Dynamics Measurement

The sample was placed between two tungsten (W) wires and heated by the panel heater. During the poling of the film, the change of optical absorption and transient SHG were measured.

3. RESULTS AND DISCUSSION

3.1 Poling

The PMMA/DR1 film has a single optical absorption peak in the visible region of which maximum locates around 480 nm. After the corona poling of the film, the

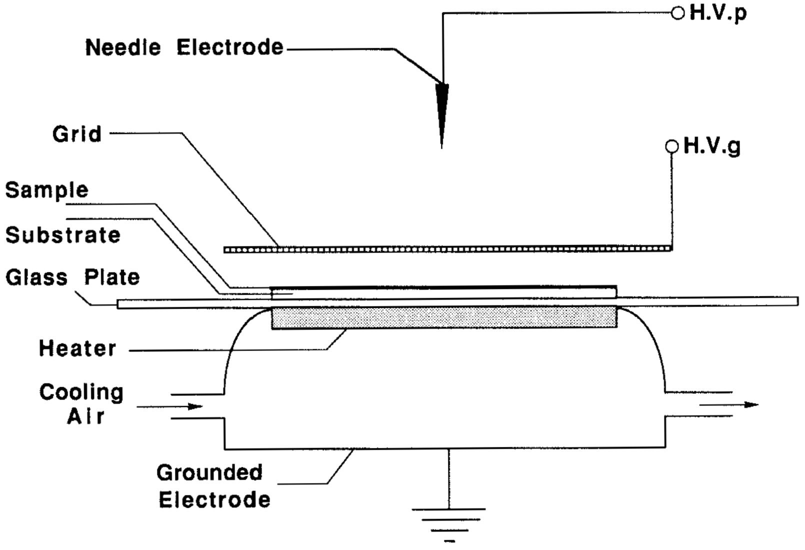


FIGURE 1 Corona-poling apparatus.

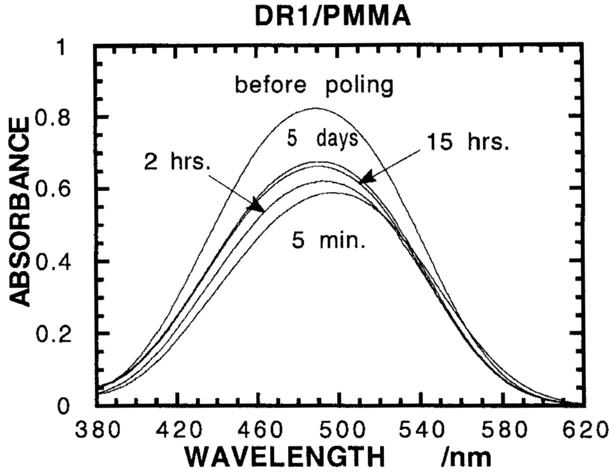


FIGURE 2 Absorption spectra of PMMA doped with 10 wt% DR1 films: Before poling, 5 min., 2 hrs., 15 hrs., and 5 days after poling.

peak shifts toward red and decreases its intensity (height) due to the decrease of absorption cross section. The peak height increases gradually to the initial value due to the thermal relaxation of oriented dipoles (molecules) as shown in Figure 2. The degree of orientation of dipoles in the film strongly depends on the poling field (applied potential), temperature (thermal history of poling), local field (potential energy fluctuation around the molecule), and so forth.

Defining the molecular charge transfer axis of chromophore as z axis, we can determine a macroscopic second order susceptibility $\chi^{(2)}_{zzz}$ of the poled polymer film as follows:[13]

$$\chi^{(2)}_{zzz} = N f^{\omega}_{z} f^{\omega}_{z} f^{2\omega}_{z} \beta_z L_3(p) \tag{1}$$

where N is the number of chromophore molecules in the unit volume, β_z the second order molecule hyper-polarizability in the z direction, f^{ω}_{z} the correction factor of local field at the angular frequency of ω, $L_3(p)$ the third order Langevin function, $p = \mu E/kT$, μ the molecular dipole moment, E the external electric field, k the Boltzmann constant, and T the temperature. Under the condition of small μ and E, $L_3(p)$ is nearly equal to $\mu E/5kT$. In order to enhance $\chi^{(2)}_{zzz}$, therefore, we should pole the film just above T_g.

A PMMA/DR1 film, for example, was poled at 100°C as a function of applied (poling) voltage. Figure 3 indicates the absorbance change ΔA ($= A_{\text{poled}} - A_{\text{non-poled}}$) with poling voltage. It shows the threshold voltage around 4 kV. Poling time (duration) is also an important factor. As shown in Figure 4, $-\Delta A$ increases gradually when the substrate temperature is well lower than T_g, but saturates at higher temperatures. It is suggested that the thermal annealing after the poling saturation just below T_g enhances ΔA.

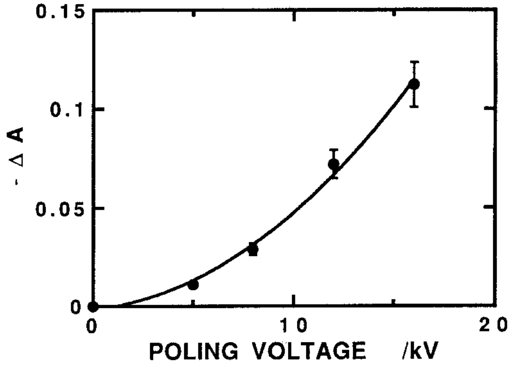


FIGURE 3 Absorbance change at 100°C as a function of poling voltage.

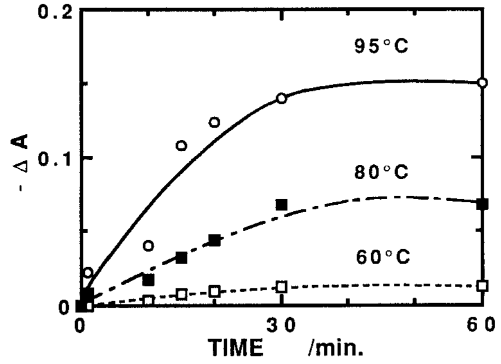


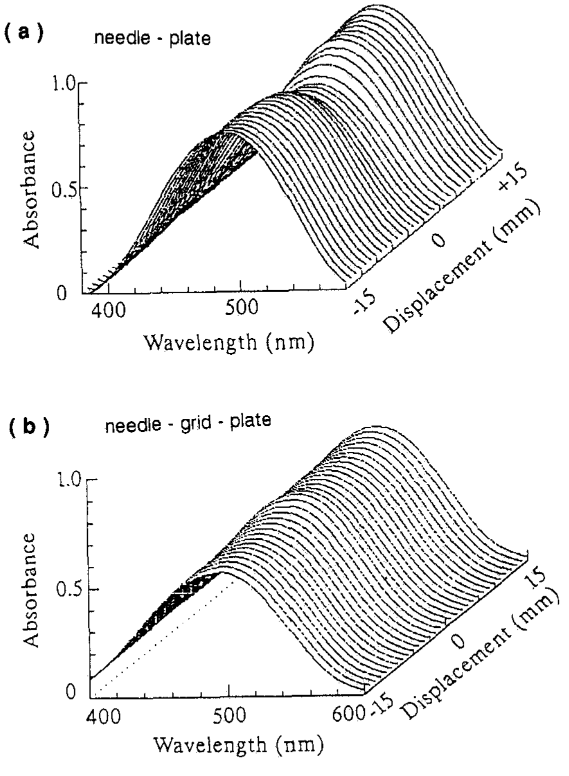
FIGURE 4 Absorbance change at various fixed temperatures as a function of time.

3.2 In Plane Distribution of Poling

The needle-plane electrodes configuration or corona poling without grid electrode gives a non-uniform poling of the polymer films. As shown in Figure 5(*a*), the absorbance change ΔA becomes larger in the vicinity of the needle electrode (displacement = 0 corresponds to the needle position) than in other parts, that is, just below the needle electrode the film is better poled. On the other hand, introducing the grid electrode in between two electrodes, the uniformity of poling was improved. The distribution depends strongly on the needle-grid distance and the grid potential. The best distribution was obtained under the conditions of the needle-grid distance 2 cm and the grid potential 12 kV, as shown in Figure 5(*b*). It should be noted here that the uniform poling of the film is most important for the light propagation measurement or waveguide application in order to determine origins of the dispersion and/or scattering of light due to either artifacts or the fluctuation of refractive index in position.

3.3 Second Harmonic Generation of PU-NS Film

Second harmonic generation (SHG) was measured in the film of PU-NS at a fundamental wavelength of 1.064 μm. The second harmonic (SH) coefficients are



Absorption spectra vs displacement

FIGURE 5 Absorption spectra of PMMA/DR1 film as a function of displacement: Corona poling with (a) needle-plate electrode configuration and (b) needle-grid-plate electrode configuration.

determined by measuring the SH intensity as a function of incident angle in transmission through the film. Figure 6 indicates the change of SH intensity with the incident angle. The components d_{33} and d_{31} can be determined independently by measuring *p*-polarized SH with *s*- and *p*-polarized fundamental lights (*s*-*p* SH and *p*-*p* SH, respectively).

After the analysis by Singer *et al*,[13] the relations $d_{33} = 3d_{31}$ and $d_{ijk} =$

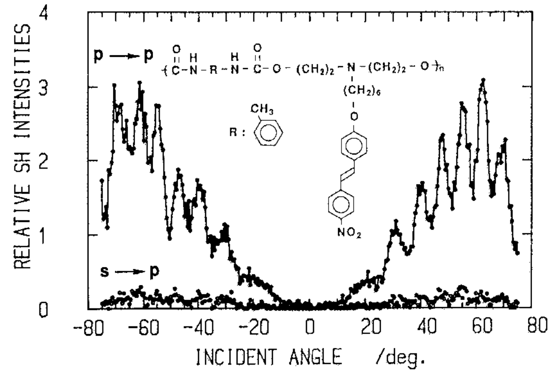
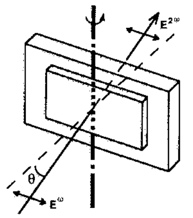


FIGURE 6 SHG Maker fringes as a function of incidental angle: *p*-polarized SHG with *s*- and *p*-polarized fundamental lights.



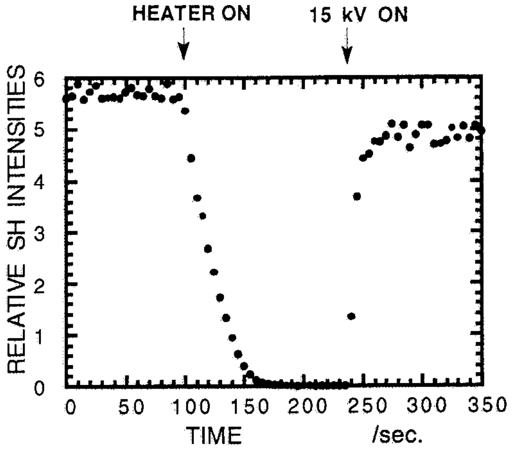


FIGURE 7 Transient SHG during poling and depoling: *p*-polarized SHG with *p*-polarized fundamental light at θ = 45°.

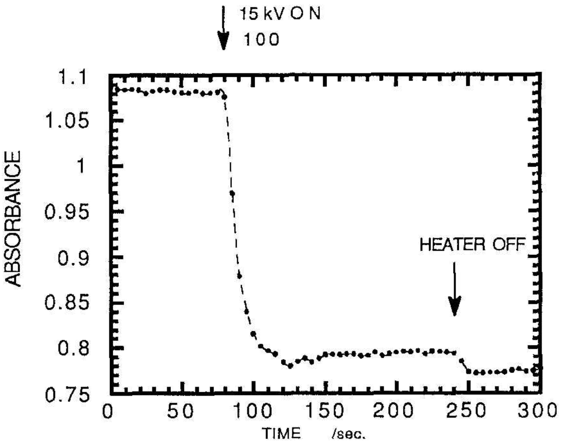


FIGURE 8 Absorbance change at a wavelength of 380 nm during poling of PU-NS film.

$(1/2)\chi^{(2)}_{ijk}$ were obtained from Figure 6. This result suggests that the orientational model of chromophores with one-dimensional charge transfer is applicable to the poling of PU-NS film. When the permanent dipole differs in direction with the polarization axis due to intramolecular charge transfer, off-diagonal components of β tensor contribute to the enhancement of $\chi^{(2)}$. It should be noted that this type of enhancement in nitro-carbazole derivatives as chromophores is under investigation in our group. The result will be appeared elsewhere in the near future.

3.4 Poling Dynamics

For the *in situ* observation of chromophore orientation under the electric field, we can measure the absorbance change[14] and/or the SH intensity change[15] during the poling or depoling process. Figure 7 shows an example of SH intensity change of PU-NS film for the *p*-polarized fundamental YAG laser (1.064 μm) with the incident angle of 45°. By heating the film (heater ON), the SH intensity decreases due to randomization of chromophores. On the other hand, by applying the electric field (15 kV ON), the SH intensity increases due to orientation of chromophores in one direction. Figure 8 shows the absorbance change of PU-NS film during the poling. The SH intensity depends on the second order susceptibility and coherence length, whereas the absorbance change reflects directly the orientational behavior of chromophores. Therefore the absorbance change measurement is better (and easier) than the SH intensity measurement for the analysis of poling dynamics.

In order to clarify the role of polymer main chains for the orientation and relaxation of chromophores, two types of polymer systems were studied; the guest-host polymer system (PMMA/DR1) and the side chain type polymer (PU-NS). In the case of polyurethanes which have flexible main chains, the glass transition temperature T_g is adjustable by modifying the main chain structure. Both PU-NS and PMMA/DR1 films used in this study have almost the same T_g (65°C). They were corona-charged as a function of temperature, poling potential and time using two-wire electrode configuration. After corona-poling, the films were heated to

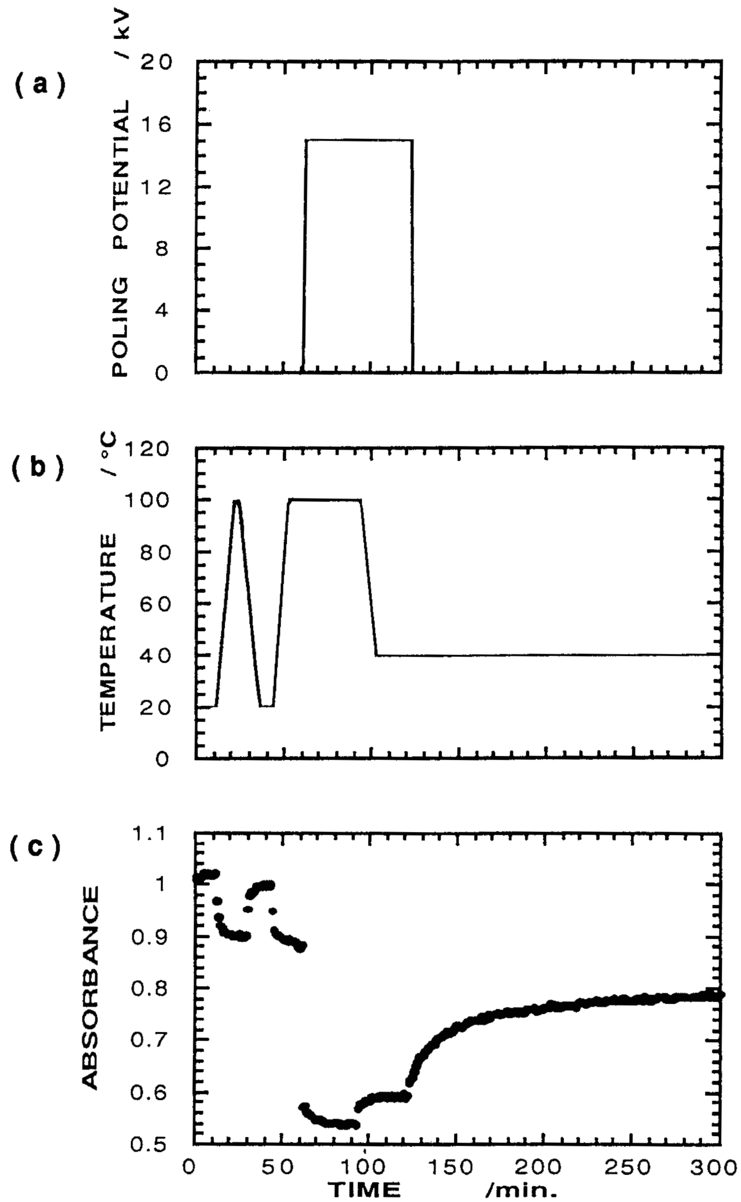


FIGURE 9 Relaxation dynamics: (a) potential and (b) thermal evolution, and (c) absorbance change.

relax the chromophore orientation. Figure 9 (*a*)–(*c*) indicate the poling dynamics measuring procedures. The large absorbance decrease was observed on poling (high temperature under applied potential), followed by a slow relaxation (depoling) due to thermal randomization of chromophores after the poling (below T_g without applied potential). Time evolution of absorbance A(t) after the poling suggests the orientational relaxation dynamics, as shown in Figure 10. Above T_g, both polymer systems show the rapid relaxation. Below T_g, however, the relaxation in PU-NS

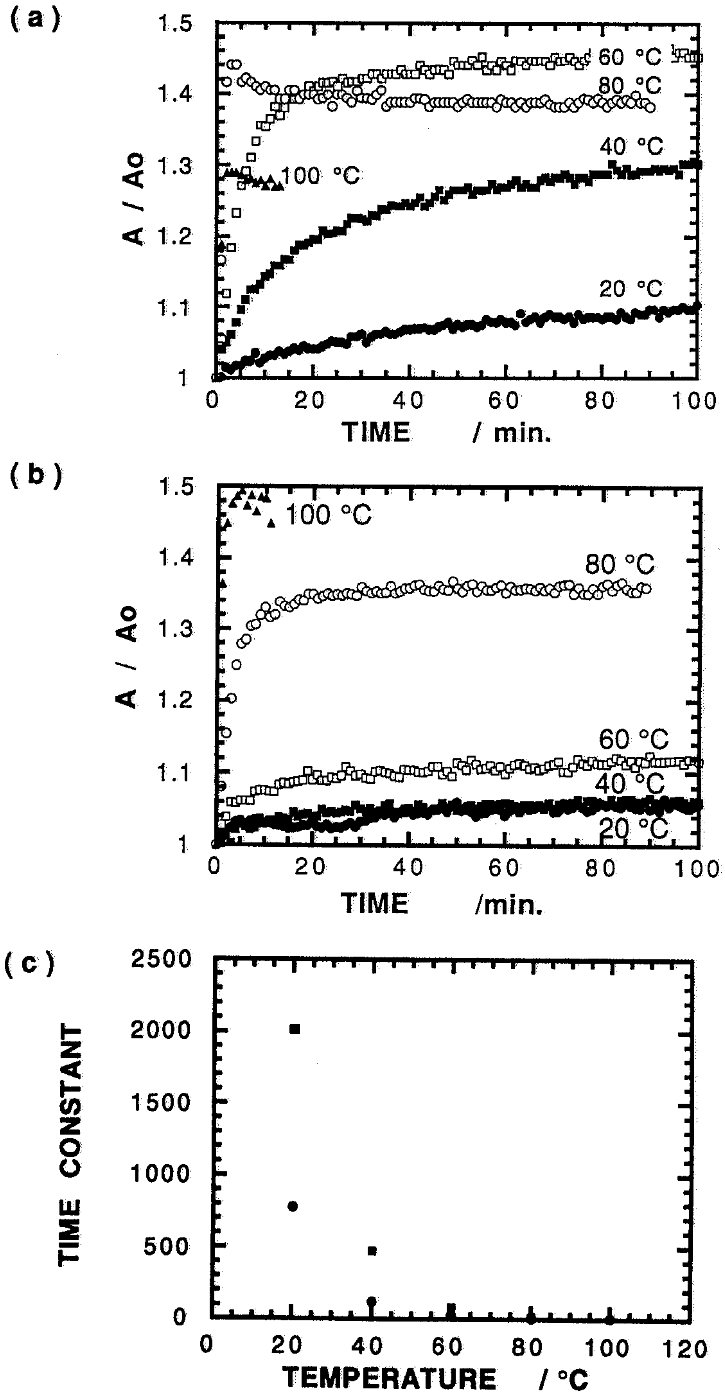


FIGURE 10 Thermal relaxation of (a) PMMA/DR1 and (b) PU-NS films. (c) indicates the temperature dependence of time constant of (●) PMMS/DR1 and (■) PU-NS.

is more suppressed than that in PMMA/DR1. From the curve fitting analysis of the initial decay $A(t)/A(O)$ to $B \exp(-t/\tau)$, where B is the constant, the relaxation time constant τ can be estimated, as indicated in Figure 10(*c*). It is concluded, therefore, that by the introduction of covalently bonded chromophores into side chains the orientational relaxation of dipoles (chromophores) is highly suppressed below T_g.

4. CONCLUSION

The poling (and depoling) dynamics in two different type of polymer systems have been studied; the guest-host polymer (PMMA/DR1) and the side chain type polymer (PU-NS). The optical absorbance is a better measure of dipole (chromophore) orientation in the film than the second harmonic intensity, and fits to the *in situ* observation. The orientational relaxation of chromophores due to thermal motion can be suppressed by the introduction of covalent bonding into the side chain, not the molecular dispersion into the polymer matrix.

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