The Effect of Preparation Process of PMDA–ODA–DR1 Polyimide on Its Second Harmonic Generation Characteristics

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SYNOPSIS

In situ second harmonic generation (SHG) observation of PMDA–ODA–DR1 polyimide films prepared by different preparative procedures were studied to understand the effects of the residual acid and the imidization byproduct and the extent of imidization on the SHG characteristics of the PMDA–ODA–DR1 polyimides. PMDA–ODA–DR1 polyimides with or without removal of salt were also investigated to study the influence of remaining triethyl hydrogen ammonium chloride salt on the SHG characteristics and reliability of the polymers. A blue shift in the UV/vis spectrum during poling was observed for the low-temperature-baked film, but did not occur for the high-temperature-baked film. Both high-temperature imidization and removal of the byproduct organic salt did not only improve the poling efficiency of PMDA–ODA–DR1 polyimide as a SHG material, but also slowed down the relaxation of the film and made the film more reliable. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Second-order nonlinear optical (NLO) polymers are one of the most promising materials with potential applications in optical information processing and telecommunications.[1,2] Such materials also exhibit large susceptibilities and versatility of molecular structure modifications.[3] There are presently many types of NLO polymeric materials, with the following three kinds being the most popular: (1) guest–host materials,[4] (2) linear polymers covalently attached with NLO chromophores,[5] and (3) crosslinked polymers covalently functionalized with NLO chromophores.[6,7–19] The NLO chromophore covalently bonded onto the polymer chain has been used to improve the stability of the NLO characteristics by a slowing down of its relaxation of the orientation.[20,21]

In situ second harmonic generation (SHG) observation is a useful tool for studying the NLO properties of the polymer under the poling process. It may also be used to study the variation of NLO characteristics of the polymer upon simultaneous reaction under poling. As has been demonstrated by Wu et al.,[7,8] polyamic acid doped with a nonlinear chromophore can be imidized during poling. Stahelin et al.[10] showed that the poling process is a physical and chemical process because the imidization simultaneously involves the evolution of water and the formation of imide groups with the reduction of the amic acid group. During the poling process, the residual solvent in the polymer also gradually gases out from the polymer under heating. It has been confirmed that such water evolution resulted in an increase in conductivity of the film and reduced the effective electric field for poling. The SHG signal dropped during the heating procedure of the poling process until 150°C because of a decrease of the effective applied field. The SHG characteristics and relaxation properties of the guest–host polyimide

NLO have been extensively studied, but few studies on the preparation and SHG properties of the chromophore chemically bonded polyimide are reported.

In this study, we focused on the preparative parameters essential for the development of DR1 (dispersed red 1; an NLO organic compound) chemically bonded polyimide with good optical properties. There are some difficulties in preparing this type of NLO polyimide which displays stable NLO characteristics even at elevated temperature (122°C). Also, the poling process, accompanied by heating and cooling, caused dynamic structural changes in the polyimide. Thus, in situ observation was used to characterize the dynamic nonlinear optical properties of the polyimide. Its decay behavior at elevated temperature and its SHG signal response speed, with or without removal of the organic salt before the in situ poling, were used to study the influence of hydrogen chloride–amine salt on those SHG properties. In addition, a biexponential approximation[22-24] with long-time relaxation and short-time relaxation was modeled to predict the SHG stability of the PMDA–ODA–DR1 polyimide at elevated temperature.

EXPERIMENTAL

Preparation of the Polyamic Acid (PAA)–DR1

4.4′-Diamino diphenyl ether (ODA) was dissolved in N-methylpyrrolidone (NMP) and then pyromellitic dianhydride (PMDA) was added to the solution. After no solid PMDA was found in the solution, the mixture was further stirred at room temperature under nitrogen atmosphere for 1 more h. The solid content of the PAA solution was 5 wt %. Thionyl chloride, with a 15% molar ratio relative to the carboxylic acid, was then added dropwise into the PAA solution kept in an ice bath. The resulting solution was further stirred for 2 more h for the reaction. The excess thionyl chloride and the byproduct hydrogen chloride in the PAA solution were removed by vacuum pumping. DR1 was purified by recrystallization from ethanol. The purified DR1, with a 10% molar ratio relative to the original carboxylic acid, was dissolved in NMP and then added dropwise into the acid chloride containing the PAA solution. The mixture was stirred for 24 h at room temperature. Triethylamine was then added into the polymer solution to neutralize the byproduct hydrogen chloride. Polymer solutions both with or without triethylamine were prepared for study.

Preparation of Three Types of Polyimide–DR1 Films

The PAA–DR1 solution was coated on the surface of clean ITO glass. The film was dried at 80°C for 1 h (soft bake) in a vacuum oven, then imidized by two different procedures—First type: The film was imidized at 150°C for 5 h; and second type: besides the low-temperature baking, the polymer film was further heated at 200°C for 1 h (high-temperature baking). The third type of polyimide–DR1 film was prepared by immersing the high-temperature-baked film in deionized water for 5 h to remove the organic salt. The third type of polyimide film was then vacuum-dried at 150°C overnight.

Second Harmonic Generation (SHG) Study

In Situ *Poling SHG Study*

The NLO signals during poling were measured *in situ* by the setup reported by Liao et al.[25] shown in Figure 1. The light source used as the fundamental light is a Q-switched Nd : YAG laser operating at 1.064 μm. The transmitted beam was passed through colored glass filters and an interference filter to remove all traces of the fundamental light before the second harmonic signal at 532 nm was detected with a photomultiplier detector. A reference signal was generated using SHG from a quartz crystal. The sample was poled in a temperature-controllable chamber with an optical window. The temperature was gradually raised to slightly above the T_g of the polymer film for several minutes. It was then gradually cooled down to room temperature before the electric field was removed.
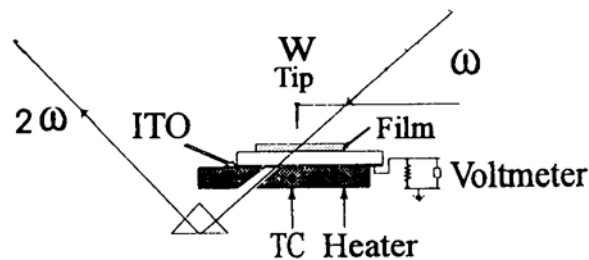

Figure 1 Experimental setup for the *in situ* measurements of the second harmonic intensity and temperature of polymer films during the corona poling process. W tip, tungsten tip; TC, thermocouple; ITO, indium tin oxide film.

Decay Studies of SHG Signal on PMDA–ODA–DR1 Polyimide Film

Decay of the SHG signal was measured both at room temperature and elevated temperature.

Decay at Room Temperature

The decay of the SHG signal at room temperature was observed through the UV absorption change.[15] Assuming that the predominant second-order polarizability tensor component (β_{zzz}) is parallel to the molecular dipole (μ), the dipole can be related to an order parameter (Φ)[1,15-16]:

$$\Phi = (3\langle \cos^2\theta \rangle - 1)/2$$

where $\langle \rangle$ is the expected value, and θ, the angle between the molecular dipole moment (μ) and the applied electric field (E). If the transition dipole moment is parallel to μ, it follows[9] the equation

$$\Phi = 1 - A_1/A_0$$

where A_0 is the absorbance of the nonpolarized film, and A_1, the absorbance of the polarized film measured with the optical electric fields polarized perpendicular to the plane of the film. The absorbance of the film decreased after poling. The lower the A_1/A_0, the higher the order parameter.

Meanwhile, θ approached zero as the order parameter became higher, i.e., the molecular dipole moment got closer to the applied electrical field. The decay of the order parameter is an indication of the decay orientation at room temperature.

Decay at Elevated Temperature

To compare the difference between the relaxation behavior of the high-temperature-baked film and the low-temperature-baked film, the decay of the alignment at elevated temperature was measured. The polyimide film was obtained as in the room-temperature decay study, except that it was heated at the desired temperature for the decay study. The desired temperature was chosen as the temperature at which the SHG signal reaches a plateau during the cooling procedure. For the decay behavior of an NLO polymer, a biexponential model has been proposed[22-24] of the following form:

$$\frac{I(t)}{I(0)} = Ae^{-t/\tau_1} + (1 - A)e^{-t/\tau_2}$$

in which long-time relaxations are characterized by τ_2, and short-time relaxations, by τ_1. As illustrated by Torkelson et al.,[22] the SHG intensity decay is a combined measurement of the surface charge decay and the loss of chromophore orientation due to mobility and local free volume of the polymer matrix. The relaxation time τ_2 may be related to the chromophore mobility in the polymer matrix. By curve fitting, the coefficient "A" and both characteristic relaxation times, τ_1 and τ_2, were calculated to understand the different relaxation behaviors of various types of PMDA–ODA–DR1 polyimides.

RESULTS AND DISCUSSION

The DSC diagram of the PMDA–ODA–DR1 polymer imidized at two different temperatures is shown in Figure 2. The glass transition temperature (T_g = 150°C) of PMDA–ODA–DR1 polyimide baked at 150°C is lower than that (T_g = 165°C) of the polyimide baked at 200°C. It is well known[26] that under the same imidization time polyamic acid imidized at lower temperature will have a lower degree of imidization than that imidized at higher temperature. Therefore, it is reasonable to surmise that the lower T_g of the polymer PMDA–ODA–DR1 imidized at 150°C resulted from the lower degree of imidization. On the other hand, the glass transition temperature (T_g = 165°C) of the PMDA–ODA–DR1 imidized at 200°C is much lower than that (T_g > 300°C) of PMDA–ODA imidized under the same imidization condition. This much lowering of the T_g in DR1-polyimide may be due to the lowering in the number of imide rings on the main chain and the presence of longer spacer units between the imide rings.

The UV/vis spectrum changes of the low-temperature-baked and high-temperature-baked films, measured before and after poling, are shown in Figures 3 and 4, respectively. The UV/vis spectrum shifting of these two types of polyimide upon poling was quite different. In the case of the low-temperature-baked film, the wavelength of maximum absorption (λ_{max}) shifted from 509 to 486 nm upon poling. The blue shift of the absorption band was attributed to the structure change resulting from the imidization reaction during the poling process. Before the poling process, there were some hydrogen-bond interactions between the residual carboxyl groups of PAA and the lone-pair electrons on the nitrogen atom of DR1. Such interaction may hinder the resonance among the lone-pair electrons on the nitrogen atom of DR1 and the π electrons on the
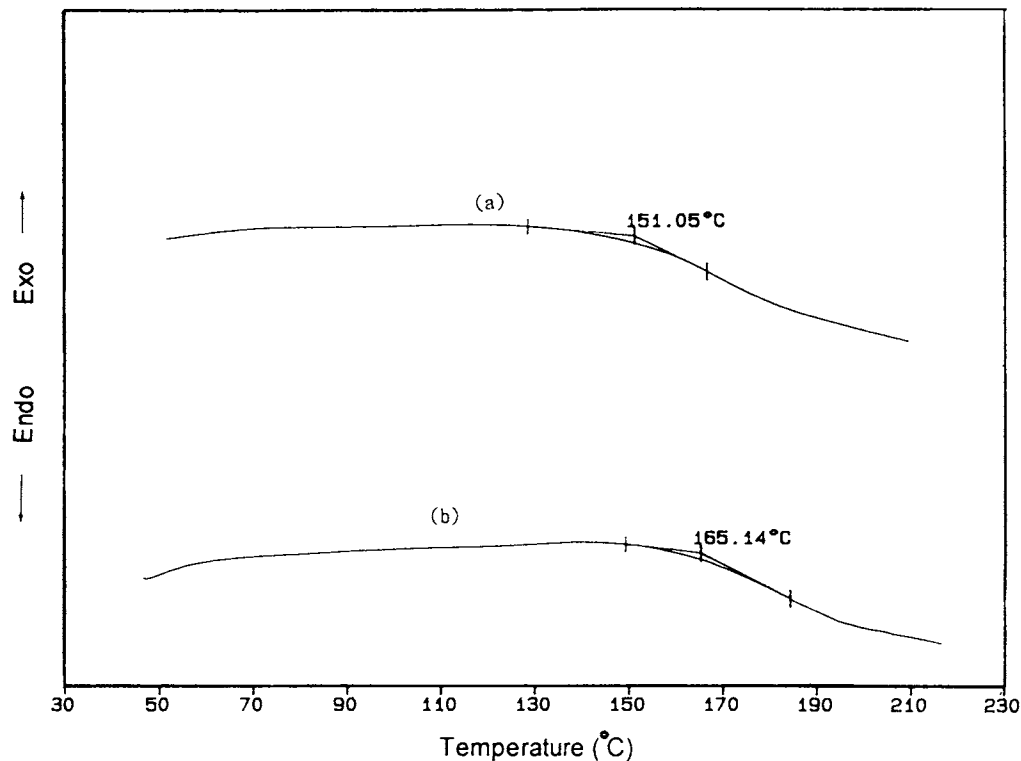
Figure 2 DSC diagram of (a) low-temperature-baked film and (b) high-temperature-baked film.

benzene ring and the diazo bond. During the poling process, more acid groups reacted with amide groups of the low-temperature-baked polyimide to form imides. Therefore, the resonance among the lone-pair electrons on the nitrogen atom of DR1 and the π electrons on the benzene ring and the diazo bond became more significant, resulting in lowering the energy level of the ground state of DR1 in the low-temperature-baked polyimide upon poling, enlarging

the energy gap between the ground state and the excited state.

The influence of imidization during poling on the low-temperature-baked film was remarkable. Therefore, the blue shift in the UV/vis absorption spectra is significant in Figure 3, while the UV/vis spectra of the high-temperature-baked film illustrated in Figure 4 shows a negligible blue shift after poling. The imidization extent of the high-temper-
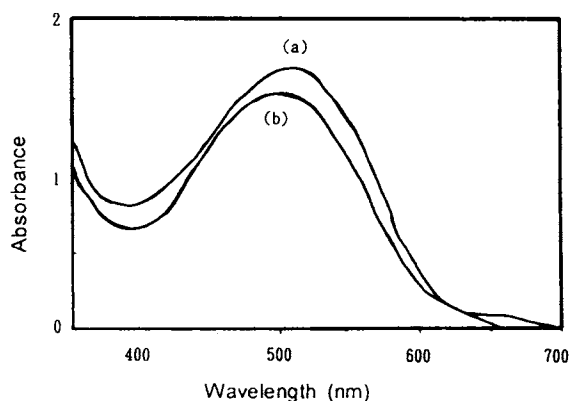

Figure 3 UV/vis spectra of the low-temperature-baked film (a) before poling and (b) after poling.
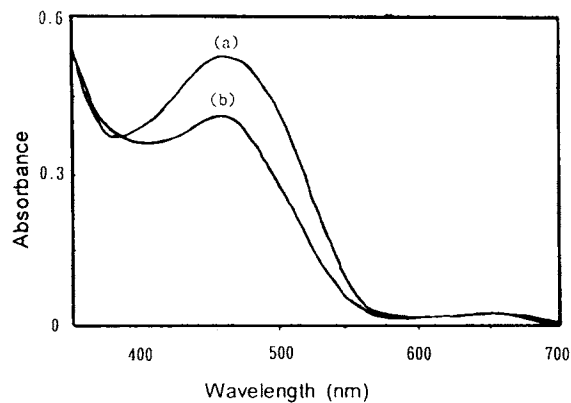

Figure 4 UV/vis spectra of the high-temperature-baked film (a) before poling and (b) after poling.

ature-baked film was relatively higher than that of the low-temperature-baked film. Further imidization during poling was less remarkable, so the change in the resonance and the hydrogen-bonding interaction attributed to the change of the molecular structure became negligible.

Figure 5 shows the FTIR spectra of the PMDA–ODA–DR1 polyimide without treating with triethylamine before and after poling. The benzene ring absorption at 1600 cm^{-1} is an invariant peak during the poling treatment. The N—H absorbance should decrease after the imidization reaction because the N—H functional groups should be converted to imide groups. To the contrary, the N—H absorption at 3400–3500 cm^{-1} increased after poling. Meanwhile, the diazo absorption at 1482 cm^{-1} decreased after poling. Primarily, this was probably due to the reaction between the residual hydrogen chloride and the diazo bond under the high temperature and high electric field during the poling process. Such a reaction resulted in the formation of —NH—NH— functional groups and the destruction of the N=N groups. It disrupted the structure of the NLO chromophores and led to the insignificant SHG intensity.

For PMDA–ODA–DR1 polyamic acid, treated with triethylamine to neutralize the residual hydrogen chloride after polymerization, the FTIR spectra of the polymer film baked at 150°C is shown in Figure 6. Both the cyclic imide ring bending absorption

peak at 725 cm^{-1} and the imide ring C—N stretching absorption peak at 1380 cm^{-1} increased after poling. The N—H absorption peak at 3400–3500 cm^{-1} decreased after poling, due to the formation of imide groups during the poling process.

In Situ SHG Measurement

In Figure 7, the SHG signal of the low-temperature-baked film increased due to the electric field-induced alignment at the initial poling state. The SHG signal started to drop as the poling temperature reached 50°C, dropped to zero at about 100°C, and remained zero during the latter heating process. Similar phenomena were observed in the in situ poling and imidization process of the dye-doped polyimide film mentioned by Stahelin et al.[10] during the poling period between room temperature and 150°C. Stahelin et al. showed the SHG variation observed during poling as being interpreted by the change of the applied poling field limited by the leakage current. Such an interpretation agrees with the phenomena observed in this study. The decrease in the SHG signal resulted from the decreased effective electric field applied on the film and was attributed to the water evolution-induced increasing conductivity, as the imidization extent of the low-temperature-baked polyimide film was relatively low before poling.
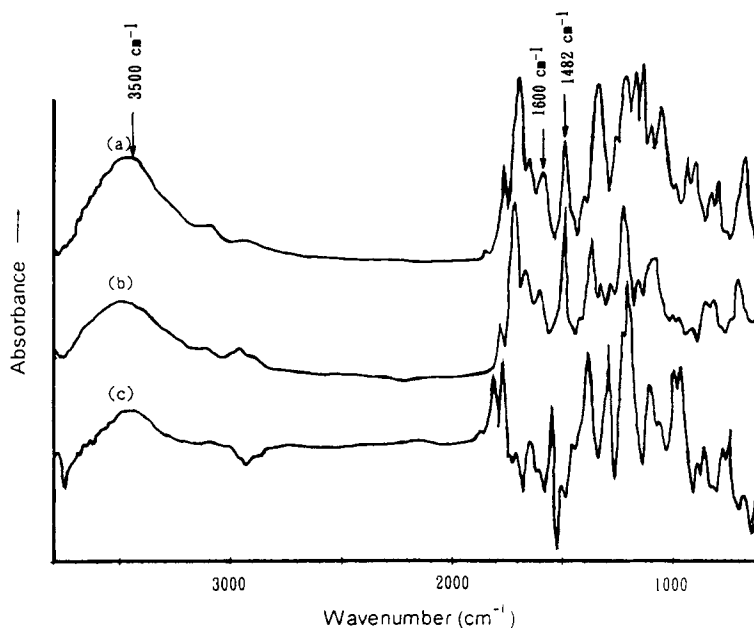

Figure 5   FTIR spectra of the low-temperature-baked film (a) before and (b) after poling (without tertiary amine treatment); (c) c = b − a.
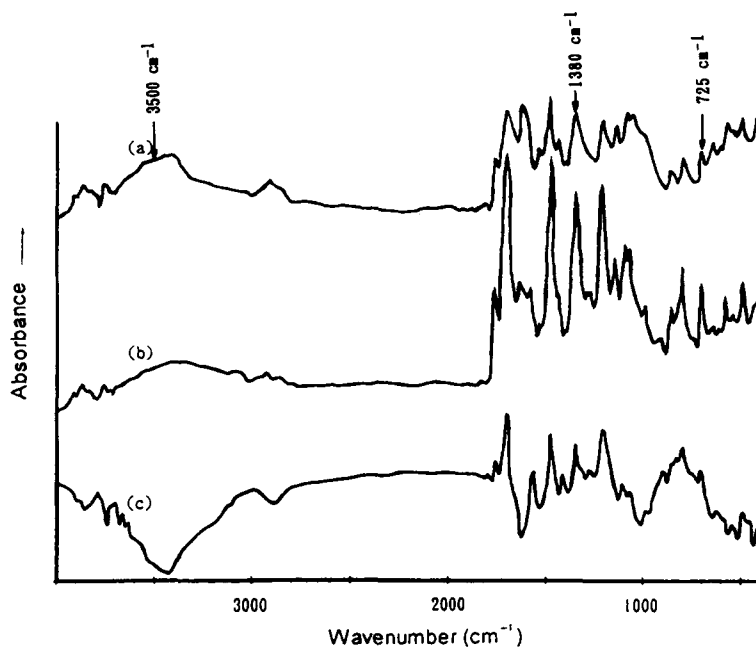
Figure 6 FTIR spectra of the low-temperature-baked film (a) before and (b) after poling (with tertiary amine treatment); (c) $c = b - a$.

Therefore, the low-temperature-baked polyimide film can be imidized further and evolve water and residual NMP during poling. Such evolution, together with increase in mobility of the ions at higher temperature, increased the conductivity of the film and decreased the effective applied electric field. After the sample had been held at 180°C for 15 min and then cooled to room temperature with the electric field still on, the SHG signal of the sample started to increase during cooling. The SHG signal reached a maximum value at about 40°C, then began to decrease with decreasing
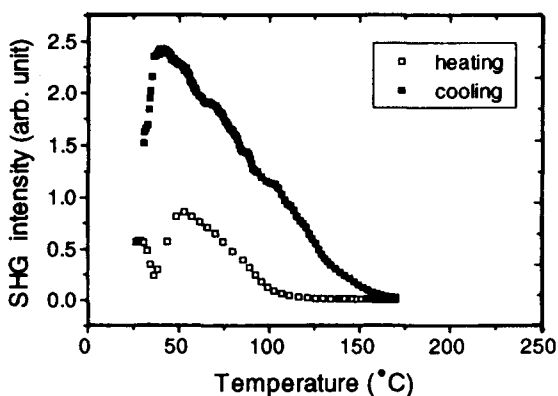

Figure 7 *In situ* SHG intensity of the low-temperature-baked film vs. poling temperature at heating and cooling in the poling process.

temperature. In our other study[25] on the PMDA–DR19 NLO polymer, a similar phenomenon was observed. The phenomenon was well explained by the model calculation of the elastic interaction of the NLO chromophore with the polymer chain below and above T_g. The elastic constant of the interaction below T_g is much greater than that at temperatures above T_g. The orientation of the NLO chromophore at temperature below T_g is more strongly restricted by the polymer chain than above T_g. Therefore, even if the electric field is still on, the SHG signal intensity of the NLO chromophore chemically bonded polymers decreases because the chromophore orientation is restricted by the polymer chain at temperatures below T_g.

Figure 8 shows the SHG signal of the high-temperature-baked film during heating and cooling in the poling process. This film had a higher imidization extent than did the low-temperature-baked film.[26] Fewer functional groups of the high-temperature-baked film could be imidized further in the poling process and, hence, a lesser amount of water was evolved during poling. Therefore, the effective electric field on the film was less affected by heating under the poling process. As the temperature increased upon poling, the NLO chromophore on the polymer chain became more easily aligned under the electric field, resulting in the SHG signal increasing
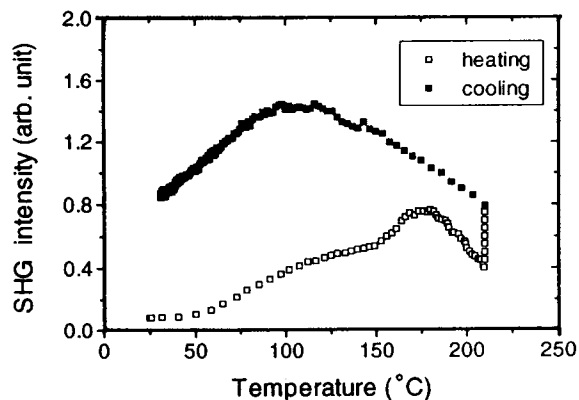
Figure 8 *In situ* SHG intensity of the high-temperature-baked film vs. poling temperature at heating and cooling in the poling process.

Figure 9 *In situ* SHG intensity of the water-immersion-treated film vs. poling temperature at heating and cooling in the poling process.

during the heating process of the poling. After the film was held at 200°C for 10 min, the SHG signal decreased due to Brownian motion at high temperature. On cooling, the SHG signal first increased, reached a maximum, and then decreased. We attribute the increase of the SHG signal at the beginning of the cooling procedure to the decrease in the extent of Brownian motion. At about 115°C, the SHG signal reached its maximum value. Then, the SHG signal decreased as the poling temperature decreased. It may be due to the elastic interaction of NLO chromophores with the polymer chains, as we have explained above. The *in situ* SHG behavior of the salt-removed PMDA–ODA–DR1 polyimide film is shown in Figure 9. The signal behaved like that of the high-temperature-baked film without water-immersion treatment except that the SHG signal reached its maximum value at a lower temperature during the heating step and the percentage drop of the SHG signal at room temperature was less during the cooling procedure. After being washed with water, the concentration of hydrogen chloride–amine salt in the PMDA–ODA–DR1 polyimide film should be much less than that in the polymer film before washing. It is reasonable to infer that at the same working voltage (or applied voltage) the effective electric field across the former film is higher than that across the latter. This may be the reason why the SHG signal reaches its maximum at lower temperature upon heating and the SHG signal drop is less upon cooling.

Decay of SHG Signal

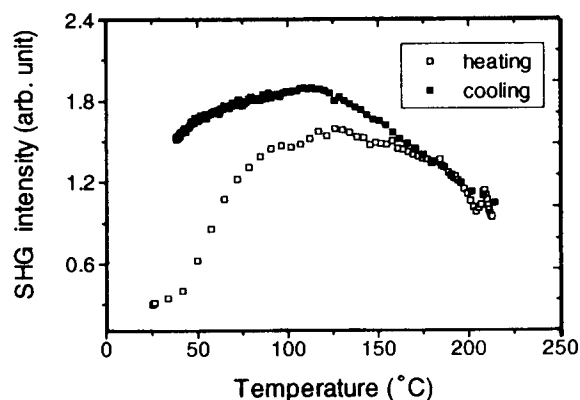The UV/vis absorption spectrum of low-temperature-baked PMDA–ODA–DR1 polyimide film is a

function of poling time as shown in Figure 10. The spectrum shifted significantly after poling, but remained almost the same in the later test. To study the decay behavior of the polyimide film at room temperature after poling, the order parameter of the polyimide was calculated from the absorbance of the baked film as a function of time in Figure 11. The normalized order parameter [$\Phi(t)/\Phi(0)$] was also plotted to illustrate the SHG decay at room temperature. The order parameter dropped 4.5% over 25 min after poling and remained almost constant later on over 10 days.

Although the SHG signal was stable at room temperature, it is still necessary to study the decay behavior at elevated temperature in order to know the reliability of the materials. Two different decay behaviors of the high-temperature-baked film and the low-temperature-baked film were inves-
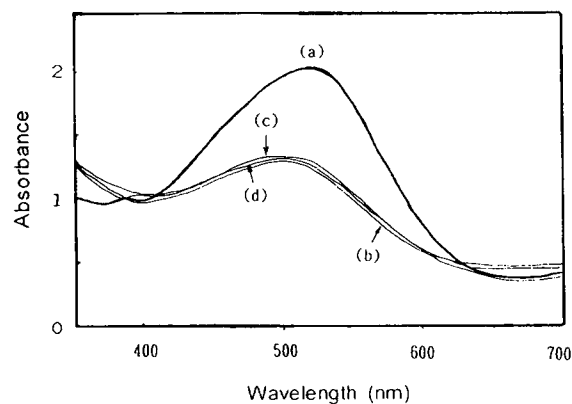

Figure 10 UV/vis spectra of the low-temperature-baked film measured (a) before poling, (b) right after poling, (c) 12 h after poling, and (d) 120 h after poling.
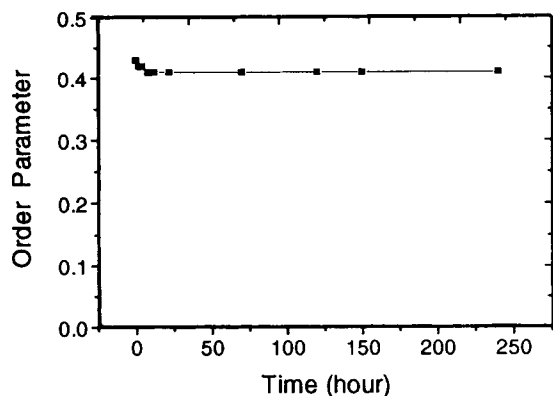
Figure 11 Decay of the order parameter calculated from the changes of UV/vis absorbance of the low-temperature-baked film.

Figure 13 Decay of the SHG intensity of the high-temperature-baked films at elevated temperature (measured at 122°C).

tigated by studying the decay of the *in situ* SHG signal at elevated temperature. A biexponential approximation[22] was made to fit the decay of the SHG signal at elevated temperature with short-time relaxation characterized by τ_1 and long-time relaxation by τ_2, as explained previously. The surface charge decay was related to the short-time relaxation, and the orientational mobility of the chromophore was related to the long-time relaxation.

The SHG signal decay of the low-temperature-baked polyimide film, the high-temperature-baked polyimide film, and the salt-removed polyimide film measured at elevated temperature are shown in Figures 12–14, respectively. The weighing factor A of short-time relaxation and the relaxation times τ_1 and τ_2 derived from curve fitting of Figures 12–14 with a biexponential approximation model[22] are listed in Table I. The influence of short-time re-
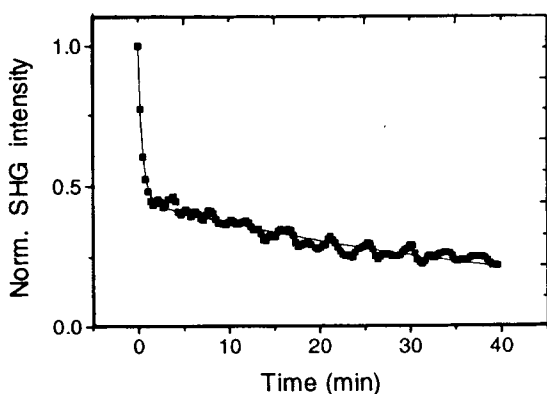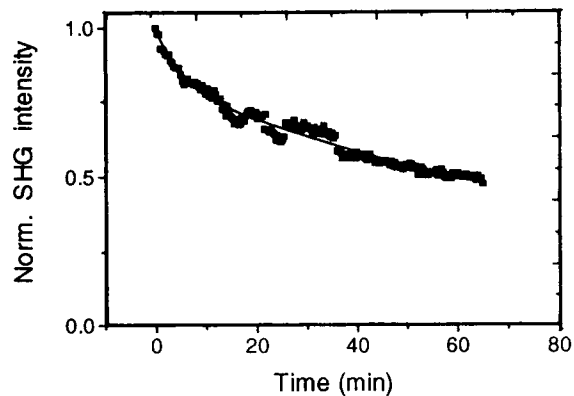
laxation was relatively more important for the low-temperature-baked film than that for either the high-temperature-baked film or the salt-removed film because the weighing factor ($A = 0.33$) of the first film was higher than that of the latter two films (0.10 and 0.12, respectively). The normalized SHG intensity of the low-temperature-baked film dropped to 0.22 after being kept at 85°C for 40 min. The high-temperature-baked film was more stable than was the low-temperature-baked film even at a temperature as high as 122°C. It dropped to 0.5 after being held at 122°C for 65 min. In addition, there was no sharp initial drop of the SHG intensity. Such an increase in stability resulted from an increasing extent of imidization.

Both the relaxation times τ_1 and τ_2 of the salt-removed film (8.78 min, 7.3 h) were larger than those of the high-temperature-baked film without

Figure 12 Decay of the SHG intensity of the low-temperature-baked films at elevated temperature (measured at 85°C).
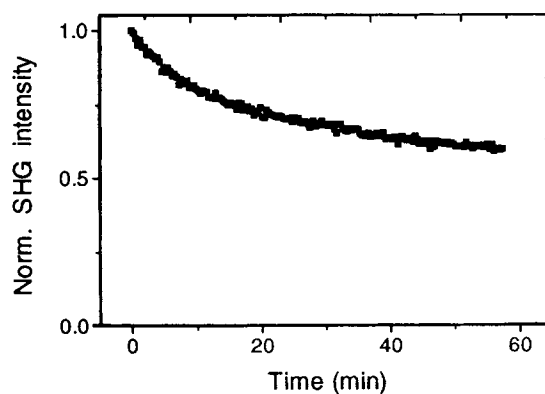

Figure 14 Decay of the SHG intensity of the water-immersion-treated films at elevated temperature (measured at 122°C).

Table I The Coefficient and the Characteristic Relaxation Time of Three PI Films

	Low-temperature-baked Film	High-temperature-baked Film	Water-immersion-treated Film
A	0.33	0.10	0.12
τ_1 (min)	0.52	5.18	8.78
τ_2 (h)	1.83	4.12	7.30
Test temp (°C)	85	122	122

salt removal (5.18 min, 4.125 h). In addition, the normalized SHG signal dropped to 0.6 after being kept at 122°C for 60 min. The relaxation time indicated that the salt removal from the film made the film more reliable. The elimination of the salt from the PMDA–ODA–DR1 polyimide might reduce the plasticization and slow down the orientation relaxation. Therefore, more reliable PMDA–ODA–DR1 film could be obtained by high-temperature imidization and removal of the by-product organic salt.

CONCLUSION

The effects of triethylamine, baking temperature, and salt removal on the SHG characteristics of the NLO chromophore chemically bonded PMDA–ODA–DR1 polyimide films have been studied. The addition of triethylamine in the PAA solution did promote the SHG characteristics of the resulting polyimide film. The polyimide film baked at high temperature showed a higher SHG signal intensity, larger relaxation times τ_1 and τ_2, and a lower weighing factor A of the short time relaxation τ_1 than did the polyimide baked at low temperature. The high-temperature-baked polyimide film with salt removal may even further improve the SHG characteristics. The salt-removed polyimide film displayed an even higher SHG intensity, a lower temperature for maximum SHG signal intensity during the poling process, even higher relaxation times τ_1 and τ_2, and a comparable weighing factor A of the short-time relaxation when the above-mentioned high-temperature-baked polyimide was immersed in water to dissolve out the salt.

According to these studies, a proper preparation process for the NLO chromophore chemically bonded PMDA–ODA–DR1 polyimide can be designed to obtain high SHG intensity and high SHG stability.

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