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Nonrelaxing Second-Harmonic Generation From A Poly(2-Methoxy-5-Nitro-1,4-Phenylenevinylene-Co-2-Methoxy-1,4-Phenylenevinylene)

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NONRELAXING SECOND-HARMONIC GENERATION FROM A POLY(2-METHOXY-5-NITRO-1,4-PHENYLENEVINYLENE-CO-2-METHOXY-1,4-PHENYLENEVINYLENE)

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ABSTRACT We have succeeded in preparing a new poled poly[(2-methoxy-5-nitro-1,4-phenylenevinylene)-co-(2-methoxy-1,4-phenylenevinylene)](poly(MNPV-co-MPV)) in thin film via an organic soluble precursor route. The precursor copolymer was prepared by partial nitration of an organic soluble precursor homopolymer synthesized by the polymerization of 2-methoxyphenylene-1,4-bis(tetrahydrothiophenium bromide) followed by reaction with methanol. The random copolymer consists of 67.5 mole % of 2-methoxy-5-nitro-1,4-phenylenevinylene unit and 32.5 mole % of 2-methoxy-1,4-phenylenevinylene unit. The precursor polymer film was heated stepwise in an electric field of 10^5 V/cm and transformed to the final polyconjugated polymer of 1.48 μm thick. This film shows a large second-harmonic generation($\chi^{(2)}=1\times10^{-8}$ esu) when it is measured in transmission with the Nd:YAG laser beam of the wave length of 1.064 μm at an angle of 90° to the film. Moreover, the film exhibits no decay in the SHG activity for more than 3 months even when the sample has a thermal history up to 100 ℃.

INTRODUCTION

Recently, nonlinear optical properties of thin films of organic polymers with delocalized π-electron systems are attracting a great deal of interests because they may exhibit extremely large nonlinear responses and are easy to be varied structurally to optimize materials properties such as processability, mechanical and thermal stability, and laser damage threshold.[1-5]

In spite of much efforts, it is, however, rather disappointing that there has not been an easy method to obtain organic polymers that show nondecaying second-harmonic generation(SHG) activities for a prolonged period of time. As well known, the nonlinear second order optical susceptibility $\chi^{(2)}$ vanishes in the materials that possess a center of symmetry.

$$P=\chi^{(1)}E+\chi^{(2)}EE+\chi^{(3)}EEE+\cdots\cdots$$

where **P** stands for the polarization of a material placed in an applied electric field **E**. Therefore, organic polymers consisting of structural units having high dipole moments are, in general, poled in a high electric field(10^4~10^6 V/cm) to align the dipoles and, thus, to attain a noncentrosymmetric structure. Poling is usually conducted near the glass transition temperatures(T_g) of the polymers. The polymer chains become partially mobile at or near T_g. But maintenance of the poled state is extremely difficult even at room temperature because of the relaxation of the polymer chains, which destroys the orientation of poled dipoles. One of the attractive methods to prevent the relaxation of poled chains is to crosslink them after or during poling to form three-dimensional networks.[6-9] This approach could produce materials of very high $\chi^{(2)}$ values that keep the nonlinear optical activities for a lengthy period of time. An unavoidable drawback for this method, however, lies in the fact that crosslinking reaction is always very difficult to control, and achievement of uniform crosslinks is even more difficult, if not impossible. Therefore, crosslinking of polymer chains is considered inappropriate to obtain materials of high optical grade with uniform quality. Wu and coworkers[10,11] recently reported the poling process of highly thermally stable electro-optic polyimides that are not crosslinked, but the nonlinear optical activity of the materials needs much improvement for practical applications.

For the first time, we have succeeded in the preparation of a PPV copolymer (5 in SCHEME 1) in a poled state and found that a thin film of this polymer exhibits a very high SHG activity. Moreover, the thin polymer film keeps the activity for more than three months even when it has a thermal history up to 100 ℃. We would like to describe the synthetic method of this polymer and discuss the details of our findings on the SHG properties thereof. Third-haromic generation from unpoled PPV and some of PPV derivatives have been reported earlier by us[12,13] and others.[14-17]

EXPERIMENTAL

Synthesis

Synthesis of 1,4-Bis(tetrahydrothiopheniummethyl)-2-methoxybenzene Dibromide, 1. 2,5-Bis(bromomethyl)anisole(20.0 g ; 6.8×10^{-2} mole) and tetrahydrothiophene (48.0 g ; 0.544 mole) were dissolved in 300 ml of methanol. The mixture was stirred for

24 hours at 50 ℃, after which the solution was concentrated by distilling out methanol. The residue was poured into dry acetone at 0 ℃, and the white precipitate formed was thoroughly washed with dry acetone and dried. The product yield was 19.2 g(65.0 %). The structure was confirmed by its IR- and ^{1}H-NMR spectra.

Preparation of Poly[2-methoxy-1,4-phenylene-(1-methoxy)ethylene], 3.[18-22] Monomer 1(15.0 g ; 3.19×10^{-2} mole) was dissolved in 150 ml of distilled water. An aqueous solution(0.918 M) of tetramethylammonium hydroxide(34.75 ml; 3.19×10^{-2} mole) was added to the monomer solution at 0 ℃. The mixture was stirred at 0 ℃ for 20 minutes to synthesize the water soluble precursor polymer 2. The reaction mixture was neutralized with 1M-HCl. The conversion was found to be 67.2 %. After neutralization, the mixture was dialyzed against distilled water for 3 days using a dialysis tube of molecular weight cutoff at 12,000. The dialyzed mixture was again dialyzed against methanol for 2 days. The mixture was heated to and maintained at 50 ℃ for 2 days and cooled. The precipitate was collected and washed with methanol. The product yield was 2.57 g(49 %). The inherent solution viscosity value of the polymer 3 measured at 30 ℃ for 0.2 g/dL solution in N,N-dimethylacetamide was 0.60.

Nitration of Polymer 3. Polymer 3(1.20 g ; 7.31 mmole) was disoolved in 120 ml of CH_2Cl_2. The mixture was cooled to -42 ℃ using a dry ice/acetonitrile bath. To this solution was added 25.97 g(0.254 mole) of acetic anhydride. With fast stirring 7.5 ml of fuming nitric acid was added dropwise. After being stirred for 2 hours at -42 ℃, the reaction mixture was poured into cold methanol. The precipitate was thoroughly washed with cold methanol and dried. The copolymer 4 thus prepared was found to contain 67.5 mole % of the nitrated unit by elemental analysis(N content) and ^{1}H-NMR spectroscopy. The inherent solution viscosity value measured at 30 ℃ for 0.20 g/dL solution in N,N-dimethylacetamide was 0.69. ^{1}H-NMR($CDCl_3$): δ8.1(aromatic H ortho to NO_2), 6.5-7.2(aromatic H) 4.5(-CH-), 3.75(ϕ-CH_3), 3.2 ppm(CH_2 and CH-OMe). IR(film): 3020(aromatic C-H stretching), 1508 and 1353(N-O stretching), 1096cm^{-1}(C-O stretching). Anal. Found: C 62.70, H 5.72, N 4.52 %. Cacld. for the composition containing 67.5 mole % of nitrated unit: C 62.53, H 5.97, N 4.52 %.

Preparation of Poly[(2-methoxy-5-nitro-1,4-phenylenevinylene)-co-(2-methoxy-1,4-phenylenevinylene)], 5. Polymer 4(1.00 g) prepared above was dissolved in 50ml of 1,2-dichloroethane. The solution was filtered through a Teflon syringe filter (Aldrich, hole size: 0.45 μm) and the filtrate was poured into n-hexane. The

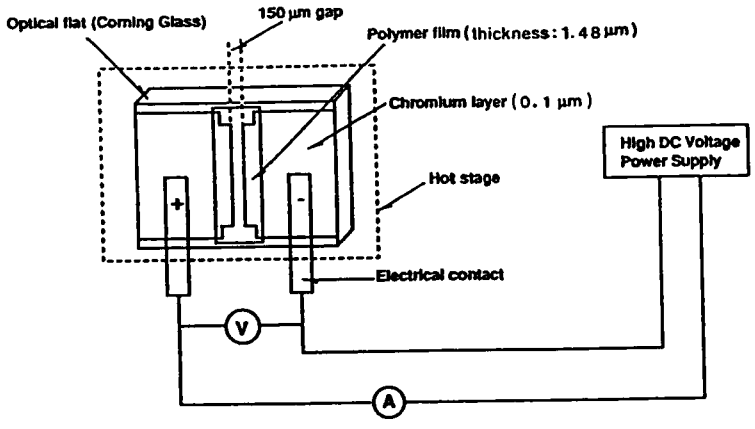


FIGURE 1 Schematic diagram of thin film poling experiment.

precipitate was redissolved in 10 ml of 2-ethoxyethyl acetate. The solution was again filtered through a Teflon syringe filter and was spread on a KOH-washed Corning glass(7059) plate(2.5×2.5 cm and 1 mm thick) on which a thin layer of chromium had been deposited to a thickness of 1000 Å in a thermal evaporator of 10^{-6} torr pressure. The optical flat was separated by 150 μm gap in the middle of the plate, see Figure 1. The two electrodes were attached onto the chromium layer and were fixed with a epoxy resin. The cell was attached to a spin coater and a thin film of polymer 4 was coated in the central gap.

The whole cell was placed in a hot stage (Mettler FP82) and heated stepwise as shown below while the applied electric field onto the two electrodes was maintained constant at 1.0×10^5 V/cm. The heating rate was kept constant at 10 ℃ /min under nitrogen atmosphere. The thickness of the final film was 1.48 μm.

25℃ → 130℃/30min → 160℃/30min → 180℃/10min
→ 210℃/30min → room temperature

The above mentioned heating and poling condition was selected after many trial and errors. Thermogravimetric analysis of polymer 4 reveals that thermolysis occurs from about 120 ℃ to 250 ℃ when a sample was heated steadily from room temperature at a heating rate of 10 ℃/min. We, however, observed that a sample thermally treated as above did not show any weight loss up to 270 ℃. Figure 2 compares UV-vis spectra of polymer 4 and 5.

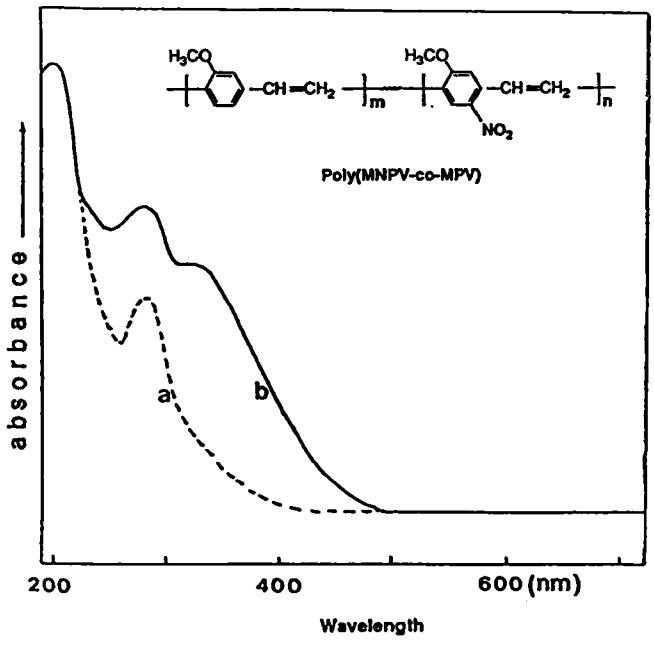


FIGURE 2 UV-vis spectra of a) precursor polymer(4) of poly(MNPV-co-MPV) and b) poly(MNPV-co-MPV)(5) after elimination.

Measurement of Refractive Index

Refractive index of polymer 5 was measured by ellipsometry (S2000 Spectroscopic Ellipsometer by Rudolph Co.)[24] over the range of 350-700 nm at the interval of 5 nm. The results are shown in Figure 3. The refractive index value at 1064 nm was estimated using the data for the range of 350-700 nm and the following Sellmeier equation :[25,26]

$$n^2 = C + \frac{\lambda^2 \cdot B}{\lambda^2 - A}$$

where n stands for refractive index and A, B, and C are parameters. The value obtained for 1064 nm was 1.5443, while the experimental value for 532 nm was 1.7048.

Measurement of Second-Harmonic Generation[27-29]

The laser used in the present investigation was a Q-switched Nd:YAG laser (1064 nm; Model SL 800 by Spectron Laser System) with a pulse width of 7ns and a pulse interval of 10 Hz. A photomultiplier tube (R 105 by Hamamatsu Co.) and a BOXCAR

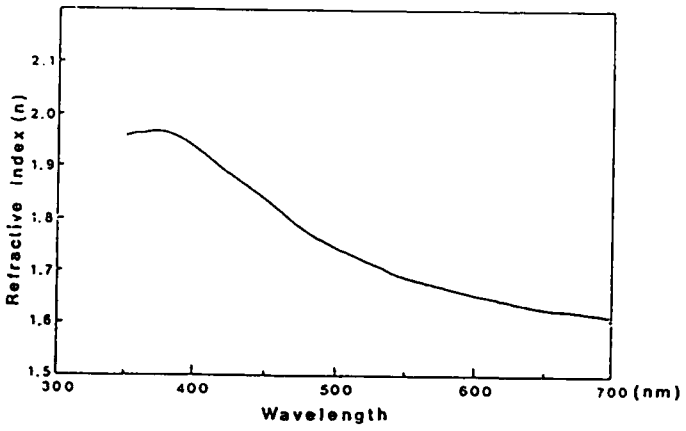


FIGURE 3 Refractive indices of poly(MNPV-co-MPV).

(Model SR 250 by Stanford Res. System) were employed for signal amplification and detection. The sample cell was fixed normal(90°) to the direction of the incident laser beam whose polarization was parallel to the poling direction or the static electric field. In order to check the stability of the laser, SHG by a Y-cut quartz(2.0 mm thick) at 532 nm was recorded. The SHG activity of the polymer film at 532 nm was estimated by comparing its SH intensity with that of the quartz. The experimental setup for the measurement of SHG is shown in Figure 4. The quadratic susceptibility(d_{11}) value of Y-cut quartz was taken to be 0.8×10^{-9} esu.[28]

The coherent length and the relative envelope intensities were determined following literature method.[28] The coherent length of the polymer film was found to be 1.657 μm. For quartz, the value of 20.65 for (011) orientation was utilized.[28]

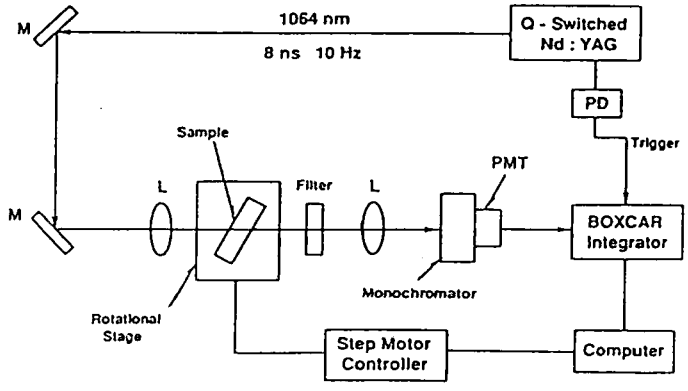


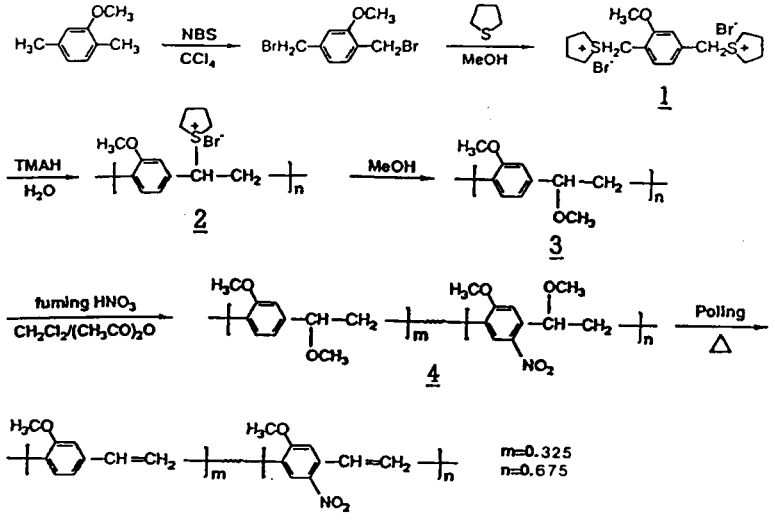
FIGURE 4 Schematic diagram of SHG measurement system.

RESULTS AND DISCUSSION

Synthesis and Poling

Synthetic route to the final polyconjugated polymer 5 is shown in Scheme 1. Bis-sulfonium salt monomer 1 was polymerized in the presence of hydroxide anion at 0 ℃ under a nitrogen atmosphere to produce water soluble polymer 2. The water-soluble polyelectrolyte polymer was dialyzed against distilled water to remove low molar mass species. The molecular weight cutoff of the dialysis tube used was 12,000. This polymerization method was first reported by Wessling and Zimmerman[30] and utilized later by Murase et al.[18,19] and Karasz et al.[20,21] in the preparation of PPV and PPV derivatives. We[22,31-34] also employed the same polymerization method for the synthesis of various PPV derivatives and copolymers.

Polymer 2 was then converted to precursor polymer 3, poly[2-methoxy-1,4-phenylene-(1-methoxy)ethylene], that is soluble in a variety of organic solvents such as methylene chloride and other chlorohydrocarbons. The conversion of the water-soluble polymer into the organic-soluble composition is achieved by nucleophilic substitution of the sulfonium groups by methanol. This method is well-known and was utilized by many others.[23,35,36] The intrinsic viscosity value of this polymer was 0.60, which indicates that its molecular weight is high.

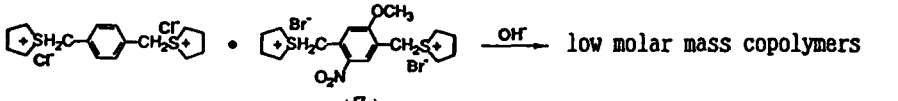


Poly(MNPV-co-MPV), 5

SCHEME 1 Synthetic route to poly(MNPV-co-MPV), 5.

Polymer 3 was reacted with fuming nitric acid at -42 ℃ in a mixed solvent of acetic anhydride and methylene chloride to obtain polymer 4. Since only a part of phenylene rings was nitrated, we obtained a copolymer. According to the nitrogen content and ^{1}H-NMR spectrum, this copolymer contains 67.5 mole % of the nitrated unit. The intrinsic viscosity value of this polymer was 0.69, which is slightly higher than that of polymer 3. This indicates that polymer 3 did not undergo any degradation during nitration. When we conducted the same nitration reaction at 0 ℃, the solution viscosity value decreased to 0.09. Therefore, it is essential to run the reaction at a low temperature to prevent chain breakages.

The synthetic strategy taken by us in this investigation is based on our earlier observation[22,32] that the bis-sulfonium salt monomer bearing the nitro group showed not only poor copolymerization behavior but also decreased sharply the molecular weights of the copolymers formed in the following copolymerization :



(6) (7)

Therefore, we anticipated that copolymerization of the methoxy substituted monomer(compound 1) with the nitrated monomer(compound 7) also would produce only low molar mass precursor polymers especially when a large amount of the nitrated unit is to be included. In fact, our present attempt to nitrate the phenylene rings of polymer 3 and the likes opens an excellent new synthetic approach to obtain a wide variety of polymers, because many different types of aromatic nucleophilic substitution reactions can be applied to this type of polymers.

Precursor polymer 4 was heated to 210 ℃ while an electric field of 10^5 V/cm was being applied. The exact heating program was described in Experimental, which was chosen after many experimental conditions were examined. Since polymer 4 undergoes thermolysis from about 120 ℃, it was rather difficult to find an optimum condition. We believe that there is still more room to improve the efficiency of poling, i.e., the degree of dipole orientation. As the eliminitation reaction proceeds, the polymer chains will become stiffer due to the generation of vinylene(-CH=CH-) units along the chain. Therefore, one should try to avoid of a premature elimination to attain a high degree of dipole orientation by poling.

Figure 2 compares the UV-vis spectra of polymer 4 and 5. The precursor polymer shows two absorptions, the positions of whose λ_{max} are located at about 200 and 280 nm, respectively. The first absorption arises from the 2-methoxyphenylene ring and the second from the 2-methoxy-5-nitrophenylene ring. The eliminated, final polymer shows an additional absorption whose λ_{max} appears at about 320 nm. This absorption corresponds to π-π^* transition of the π-system in the main chain. The absorption edge moves to longer wave length from about 400 to 500 nm after thermal elimination. The UV-vis spectrum was obtained for the polymer film that was allowed to go through the exactly same thermal history as that prepared for SHG measurement.

Second-Harmonic Generation

The determination of the relative second-order nonlinear optical susceptibility (d_{33}) in polymer 5 was conducted for a fundamental wave-length of 1.064 μm through an analysis of the Maker fringes.[28,29,37] A detailed theoretical and experimental analysis of this method was described by Jerphagnon and Kurtz.[28,29]

The structure of the sample cell is shown in Figure 1. The polymer film was 1.48 μm thick, and the maximum applied electric field during poling was 1.0×10^5 V/cm. The SHG was measured in a transmission mode with an incidence wave length of 1.064 μm of a Nd:YAG laser at an angle of 90° to the film. The second order susceptibility(d_{33}) value was estimated using the following equation:

$$d_{33} = d_q \left(\frac{I_{M,s}(0)}{I_{M,q}(0)} \right)^{1/2} \left(\frac{l_{c,q}}{l_{c,s}} \right) \left(\frac{\eta_s}{\eta_q} \right)^{1/2}$$

where the subscripts s and q stand for the sample and quartz, respectively. $I_M(0)$ and lc represent the relative envelope intensity at zero degree and coherent length for normal incidence, respectively. The η values were estimated from the following relation :

$$\eta = \frac{(n_\omega + 1)\,(n_{2\omega} + 1)\,(n_\omega + n_{2\omega})}{n_{2\omega} \cdot p^2(0)\, R(0)}$$

where n's are refractive indices at the fundamental and harmonic frequencies. p(0) and R(0) are the projection factor and multiple reflection factor at 0 degree, respectively, and equal to unity.[28,38] The d_{33} value thus obtained is 0.5×10^{-8} esu, thus the $\chi^{(2)}$ value is 1×10^{-8} esu.[2] This value is close to the d_{22} value(0.74×10^{-8} esu) of $LiNbO_3$ and one order of magnitude smaller when compared

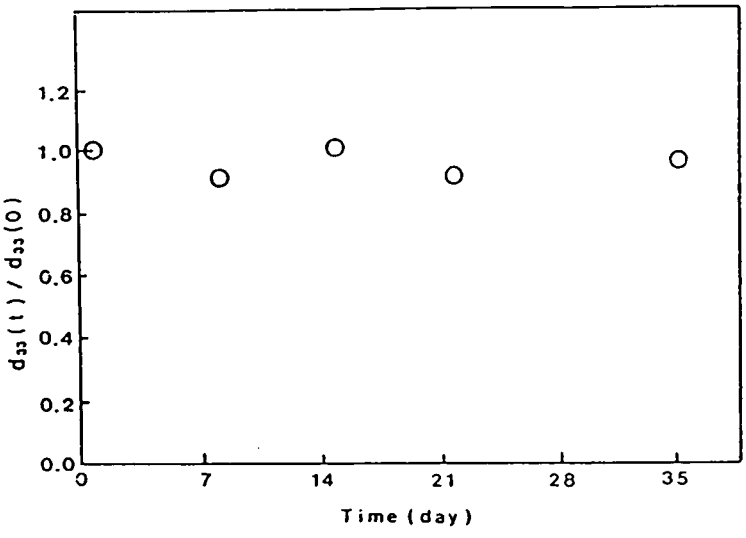


FIGURE 5 SHG intensity of poly(MNPV-co-MPV) plotted as a function of time at room temperature.

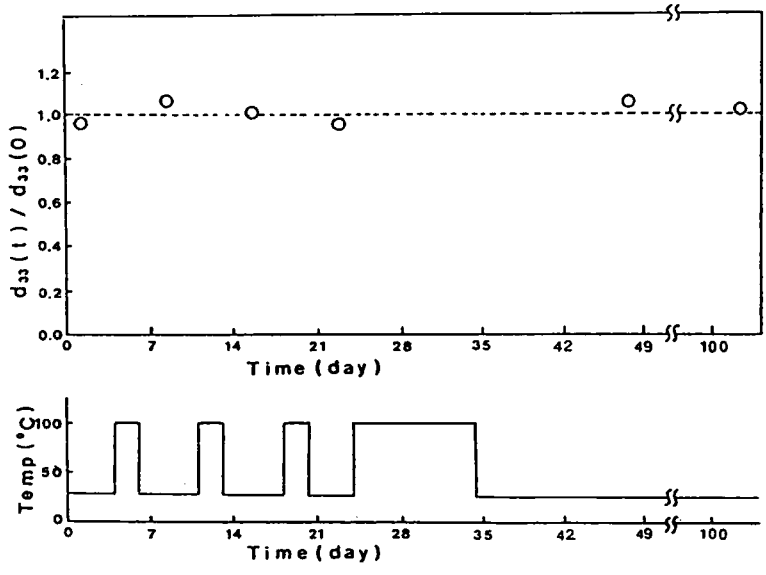


FIGURE 6 SHG intensity of poly(MNPV-co-MPV) plotted as a function of time, whose thermal history is shown by the lower temperature diagram.

with d_{33} value(9.8×10^{-8} esu) of $LiNbO_3$. We believe that betterment of heating program of the polymer film and application of stronger poling electrical field will bring about an improvement in the d_{33} value, at least, to one order of

magnitude greater. We measured the SHG over the period of longer than one month for one specimen kept at room temperature (Figure 5) and more than three months for the other having the thermal history up to 100 ℃ as shown in Figure 6. The results represented in Figure 5 and 6 certainly demonstrate that there is no decay in the SHG properties of the samples. Since thermal elimination of the poled precursor polymer generates vinylene linkages along the main chain, the final polymer is expected to be extremely rigid due to polyconjugation. This rigidity of the polymer chains will exert very high rotational barrier to the aligned dipoles. Therefore, dipole orientation in the present polymers obtained by poling and simultaneous thermolysis of their precursor polymers should be maintained unless the main chain is allowed to make rotational movements by destructing its π-system thermally or by other means. In fact, we did not observe any glass transition for the final polymer(5) up to its decomposition temperature(ca. 420 ℃).

CONCLUSION

We could successfully prepare thin poled films of poly[(2-methoxy-5-nitro-1,4-phenylenevinylene)-co-(2-methoxy-1,4-phenylenevinylene)] by conducting thermolysis of its precursor polymer film in a poling electrical field. The polymer films exhibited non-decaying second-order harmonic generation for the fundamental beam of 1.064 μm, and the $\chi^{(2)}$ value obtained was 1×10^{-8} esu. We have described in this paper a unique approach to obtain thin polymer films of PPV derivatives in a poled state, which reveal high SHG. Nitration of the phenylene rings of the organic soluble precursor polymer allows us to prepare high molecular weight PPV copolymers and opens a new synthetic approach to obtain a wide variety of PPV derivatives. Further modifications of the polymer structure and improvement in poling and thermolysis conditions are expected to enhance the SHG to a degree comparable to or better than that of $LiNbO_3$ producing new materials important to technical applications.

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