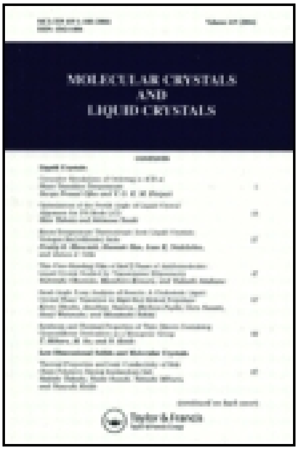

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Second-Order Nonlinear Optical Properties of A Novel Poly α-Methylstyrene Analogue

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SECOND-ORDER NONLINEAR OPTICAL PROPERTIES OF A NOVEL POLY α-METHYLSTYRENE ANALOGUE

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Abstract Employing the conventional second-order nonlinear optical (NLO) chromophore such as nitrostilbene derivative, we synthesized a polymer composed of poly α-methylstyrene structure. New α-methylstyrene polymer containing piperazyl nitrostilbene in the side chain was designed and synthesized in an attempt to enhance both the electro-optic coefficient, r_{33} and its temporal stability. The polymer showed the high glass transition temperature (T_g) implying better temporal stability of the second-order NLO property. This polymer film was corona-poled under 3.5 - 5 kV at the temperature which was either close to the T_g or higher than that. The electro-optic coefficient of this polymer was measured to be 23 - 28pm/V at 632.8 nm of He-Ne laser.

INTRODUCTION

The strong potential of organic materials with large second- and third-order oprical nonlinearities for a wide range of frequency application has been highlighted compared to bandwidth limitations of conventional inorganic electro-optic materials. A study on the second-order nonlinear optical (NLO) properties of dye attached polymers has drawn much interest as an active research area. [1-4]

Particularly, side-chain polymers have been intensively studied in recent years as potential candidates for application in electro-optic and photonic devices. [5-8] Ease of processability, high damage threshold, fast response, and large NLO properties are the advantages to utilize them for NLO devices such as frequency doubler, light modulators, and logic gates. Unfortunately, one difficulty with second-order NLO materials is that most of the organic polymers are likely to crystallize in a centrosymmetric manner. The required noncentrosymmetry for macroscopic second-order optical nonlinearity is usually induced in the materials by external effect of poling process. In this study, using our newly synthesized poly α-methylstyrene analogue, the second-order NLO property was investigated by virtue of electro-optic coefficient measurement. In an attempt to develop NLO organic materials with high optical nonlinearity and good temporal stability, we designed and synthesized a poly α-methylstyrene analogue containing carbamate group and piperazyl nitrostilbene chromophore at the side chain.

EXPERIMENTAL

1. Materials

Nitrophenyl acetic acid, 1-(2-hydroxyethyl)piperazine, dibutyltin dilaurate, and hydroquinone were purchased from Aldrich Chem. Co., and used without further purification. All solvents used in this study were distilled and stored over molecular sieves (4A). m-Isopropenyl-α,α-dimethylbenzyl-isocyanate (American Cyanamide Co.) was used without further purification. Methylmethacrylate(MMA) from Aldrich. Chem. Co. was distilled over calcium hydride. Azobisisobutyronitrile from Junsei Chem. Co. was recrystallized from acetone. Dimethylformamide was dried just before polymerization.

2. Synthesis

4-[N-(2-hydroxyethyl)piperazyl]benzaldehyde (I) and 4-[N-(2-hydroxyethyl) piperazinyl]-4'-nitrostilbene (II) were prepared by reported methods.[9] The syntheses of α-methylstyrene analogue and its copolymer with MMA are illustrated as follows.

Synthesis of [1-[4-(N-ethylenepiperazyl)-4'-nitrostilbene]-N-[(1,1-dimethyl-m-isopropenyl)benzyl]]carbamate (III)

4-[N-(2-hydroxyethyl)piperazyl]-4'-nitrostilbene (II) (2.9 g, 8.21mmole) was dissolved by stirring in dry dimethylformamide (DMF, 200ml) at 25°C under nitrogen atmosphere. Then, a trace of dibutyltin dilaurate (0.15 mole %) was added into the mixture. This was followed by dropwise addition of m-isopropenyl-α,α-dimethylbenzyl-isocyanate (m-TMI, 1.65 g, 8.21 mmole) which was diluted in DMF (10ml) over a period of

15 minutes. The mixture was heated at 70°C for 8 hours. After cooling, the resultant solution was poured into the cold water (1 liter). Red solid was precipitated and dried under vacuum at 70°C for 24 hours. It was dissolved into chloroform and dried over sodium sulfate. The solid which exhibited two spots on TLC plate was purified using liquid column chromatography as an eluent of ethylacetate. The solid (R_f - 0.9) was isolated from the crude solid. After concentrating the final solution, it was recrystallized into the ethanol. Percent yield, 60%(wt.) m.p. 120-121°C

Poly [1-[4-(N-ethylenepiperazyl)-4'-nitrostilbene]-N-[(1,1-dimethyl-m-isopropenyl)benzyl]]carbamate-co-methylmethacrylate (50/50)

[1-[4-(N-ethylenepiperazyl)-4'-nitrostilbene]-N-[(1,1-dimethyl-m-isopropenyl)benzyl]]carbamate (III) (1 g, 2.26 mmole) was dissolved in 8.9 ml of freshly dried dimethylformamide in a vacuum ampule. To the solution, are added 0.67 g of methylmethacrylate and 5 mole percent of azobisisobutyronitrile. The mixture was degassed by standard freeze-vacuum-thaw technique and heated in a sealed vacuum ampule at 60°C for 64 hours. Then the resultant mixture is poured into methanol to precipitate the copolymer. The copolymer was purified by reprecipitation from chloroform into methanol and was dried *in vacuo* at 100°C for 48 hours.

3. Others

Melting temperature of the monomer was determined by using a Melt-Temp II Capillary-melting-point apparatus and is reported here uncorrected. DSC (differential scanning calorimetry) thermogram of the polymer was taken to define the glass transition temperature and melting temperature by using a Perkin Elmer DSC-7 instrument under nitrogen. Absorption spectra were recorded with a Shimadzu UV240 (204-58000) spectrometer.

4. Material Processing

Polymer film was spin coated at 3000 rpm onto Indium Tin Oxide glass using filtered solution (ca. 8 % wt.) in chloroform. The film was thoroughly dried in vacuum at 100°C for more than 96 hours. The thickness of the polymer film was measured by a Talysurf 10 (Taylor Hobson). All films were poled using the corona poling technique in a wire-to-plane geometry. [10] The film was placed on a planar aluminum electrode which was heated by two cartridge heaters. The temperature of the sample was continuously monitored with a thermocouple. When the temperature was either close to the glass transition temperature (T_g) or higher than that, a large positive (3.5 - 5 kV) voltage was applied to the top electrode which was suspended 1 cm above the planar electrode. The sample was slowly cooled down to room temperature in the presence of the applied electric field. The applied voltage was varied according to the dielectric breakdown strength of the polymer.

5. Measurement of Electro-optic Coefficient, r_{33}

We measured the electro-optic coefficients by way of the simple reflection technique recently reported by C. C. Teng et. al.[11] The film was mounted on the stage and the incident angle of the beam was adjusted to 22.5°. A laser beam was incident on the back of the glass substrate at an angle 22.5°. The polarization of the input beam was set at 45° to the plane of incidence. The reflected beam propagated through a quarter wave plate, an analyzer, and into a detector. The modulating signal in the beam was measured using lock-in amplifier (Stanford Research Model 510). The beam propagated through the quarter wave retarder which can make a bias of the beam power (I_c). Using this retarder, we checked the maximum power first at a biased intensity to obtain a linear response. The sine wave modulating voltage (~ 10 V_{rms}) was applied to the sample. In order to measure the I_m value, a lock-in-amplifier was utilized to obtain the small signal due to the phase retardation. The reasonable value of I_m, the modulating amplitude signal could be observed by using this amplifier. Since in equation 1 and 2, the other parameters were already known, once the value of I_c and I_m were measured, the electro-optic coefficient "r_{33}" could be calculated by the following equations

$$\frac{I}{I_c} \approx \delta \psi_{sp} \qquad [1]$$

$$r_{33} = \frac{3\lambda I_m}{4\pi V_m I_c n^2} \frac{(n^2 - \sin^2\theta)^{\frac{3}{2}}}{(n^2 - 2\sin^2\theta)} \frac{1}{\sin^2\theta} \qquad [2]$$

where I_m is the amplitude of modulation, V_m is the modulating voltage applied to the sample, and I_c is half the maximum intensity of modulation. The value determined will correspond to r_{33} provided that the electro-optic optic coefficient is dispersionless and the poled polymer belongs to the point group (α, ∞,∞)

RESULTS AND DISCUSSION

1. Synthetic Consideration

The synthesis of the α-methylstyrene polymer is illustrated in the following FIGURE 1. Well known reaction for urethane formation from isocyanate can give us to prepare the monomer III.[12] In this reaction, dibutyltin dilaurate was used as a catalyst for the carbamate formation. A high reaction yield was easily achieved. From the literature [13], in the case of copolymerization of m-isopropenyl-α,α-dimethylbenzyl isocyanate (m-TMI) with methylmethacrylate (MMA), the reactivity ratios were

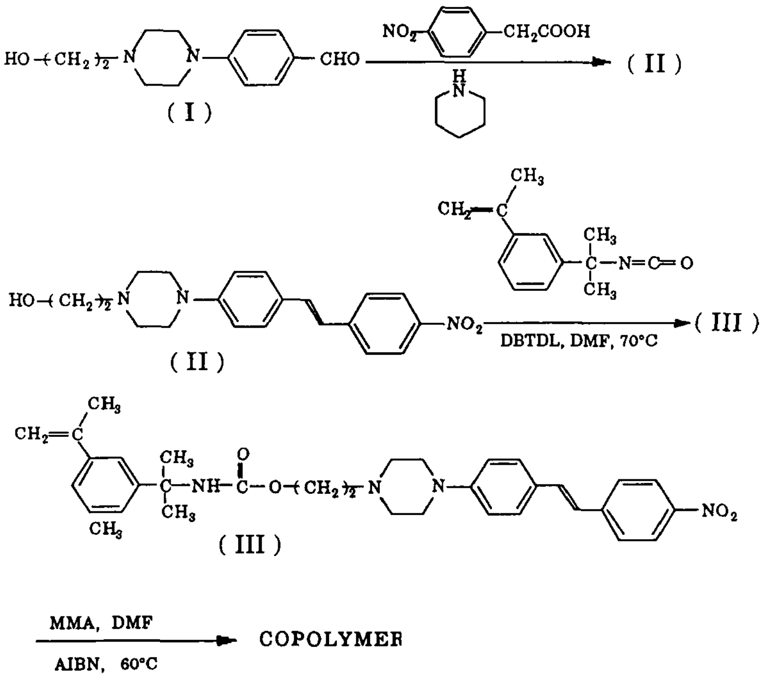

FIGURE 1. Synthetic scheme for new poly α-methylstyrene analogue

postulated to be 0.62 and 0.31. Referring this preliminary data, we can design our synthesis and presumed the proper monomer feeding ratio for our synthesis. At least 50% of NLO active group was expected to be contained in this polymer structure.

Nuclear magnetic resonance spectrum let us calculate the exact ratio of NLO unit and MMA in the structure, which was calculated 1:1 resulting from the feeding ratio of 1:3. When we use the three equivalent of methylmethacrylate into the reaction mixture, the monomer ratio was determined to be 1:1 ratio against m-TMI.

2. Thermal Properties of Polymers

DSC was utilized for studying the thermal transition behavior of the polymer. Clear glass transition temperature (124- 126 °C) was observed over third cycle of heating and cooling. As expected, very small melting behavior can be observed due to a little extent of the crystallizable portion. The T_g was determined 124- 126 °C so that we could confirm the possibility of improvement of the second-order NLO stability. (See FIGURE 2)

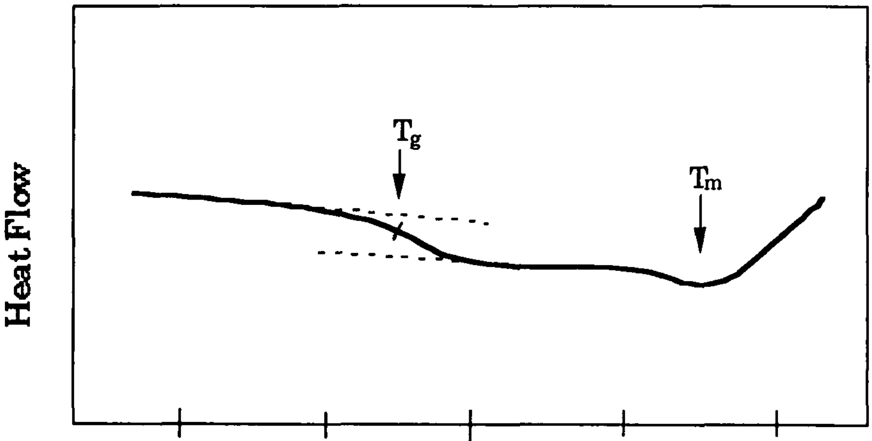

FIGURE 2 Differential scanning thermogram of new poly α-methylstyrene analogue

3. Electro-optic Property

3.1. Electric Field Induced Molecular Alignment

External field- induced molecular orientation is so called "poling process" which implies that a high electric field is applied to a polymeric medium to induce dipolar alignment of the molecules in the direction of the poling electric field at near T_g. In order to remove the noncentrosymmetry in bulk polymeric film, we must employ some external means to rearrange the NLO molecular unit. For our electro-optic measurement, thin film was corona-poled. The applied d.c. voltage and temperature were precisely controlled not to put severe condition. Avoiding the dielectric breakdown and electrical shortage, after fabricating the few micron films, water solution of polyvinyl alcohol (2%wt.) was spin coated on the mother film. It does not interfere the optical quality and cause any scattering phenomena.

3.2. UV- VIS Spectral Analysis

The thin film(~ 1 μm) was fabricated on the quartz plate or borosilicate glass. The cut off region was determined around 600 nm. The absorption maximum (λmax) was observed around 395 nm. In order to investigate the extent of molecular orientation under poling process, UV-VIS spectra of poled and unpoled film were compared. As seen in FIGURE 3, the λmax appeared around 395 nm whose intensity reached to 2.7 (Arb. Unit) before poling. After poling the sample, the λmax was shifted to 402 nm and the intensity was decreased. The absorption spectrum of the poled film exhibited a decrease in their absorbance arising from the dipole rearrangement in the direction of the poling field partially.

3.3. Electro-optic Property of Poly α-methylstyrene Analogue

As a result, use of the piperazyl nitrostilbene dye can lead us to obtain further increase in electro-optic coefficient, r_{33} as compared to conventional nitrostilbene. Therefore, piperazyl group is likely to behave as a good electron donating property in the side chain. Since the upper layer was protected by thin film of poly vinylalcohol (- 500Å), compared to the bare polymeric film, it could stand under 5 kV at 130°C. This means that there was no scattering phenomena or opaqueness resulting from the

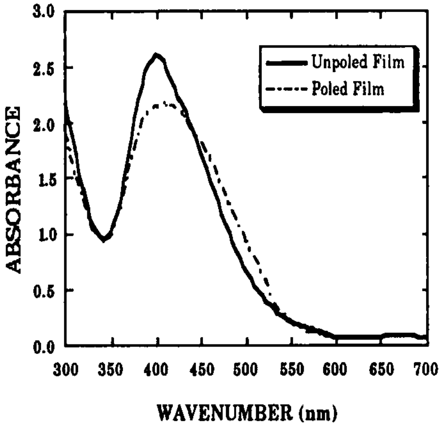

FIGURE 3. UV-VIS spectra of polymer films both after poling and before poling.

dielectric breakdown. After spin coating the polymer solution, the film quality is quite transparent.

After corona poling process, we aged the sample at room temperature for several hours in order to remove the surface charge and expose to the first stage relaxation. To deposit the gold electrode on the film, the sample was placed on the mounting holder whose temperature was increased to 60°C during sputtering. Therefore, the electro-optic property we investigated here with our system, was expected to quite stable. As seen in equation (2), I_m, I_c, and the ratio of those values are tabulated as follows. (See TABLE 1) In this calculation, we have assumed a refractive index of 1.50 for n_ω for this polymer. Even though we could trace the decay process of electro-optic coefficient only for 2 days, the relaxation of the second-order NLO property was quite lessened. Stability of the r_{33} was observed to be better than other guest-host systems or many of the other NLO polymers because the T_g of this polymer (125°) was relatively high enough to prevent decay.[14] Additionally, it was presumed that the inter- and intra-molecular hydrogen bond in the carbamate side chain structure contributed some factors preventing the molecular relaxation after poling process. This point is currently being considered and made an attempt to prove employing different polymeric systems in our laboratory.

TABLE 1 Parameters we measured and calculated values of the electro-optic coefficient.

Time (hr.)	I_m (μV)	I_C (mV)	I_m/I_C	r_{33} (pm/V)
5	11.1	27.7	0.40	28
24	10.1	29.6	0.34	23
48	10.2	29.5	0.34	23

CONCLUSION

Newly synthesized polymers exhibiting substantial electro-optic properties has been developed. This polymer incorporates the large molecular second-order nonlinear optical coefficient of a piperazyl nitrostilbene dye processed using a more successful poling process.

Simple reflection method for the measurement of the electro-optic coefficient of polymeric thin film has been utilized to characterize new poly α-methylstyrene derivative containing nonlinear optical chromophore. Covalent bonding of the NLO chromophore to poly α-methylstyrene backbone leads to to an increase in the temporal stability of the nonlinear optical properties. m-TMI was selected to be a good backbone structure and seems to show the strong inter- and intra-molecular hydrogen bonding strength to encourage good temporal stability of molecular rearrangement. The poling efficiency, hence the resulting second-order NLO activity, the film forming properties, and the temporal stability of poling induced orientation of these polymers can be largely enhanced by varying the length of the conjugated bond at the side chain. In our laboratory, we are currently pursuing these endeavors.

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REFERENCES

1. C. Ye, T. J. Marks, J. Yang, G. K. Wong, Macromolecules, 20, 2322 (1987)
2. K. D. Singer, M. G. Kuzyk, W. R. Holland, J. E. Sohn, S. J. Lalama, R. B. Comizzoli, H. E. Katz, and M. L. Schilling, Appl. Phys. Lett., 53, 1800 (1988)
3. A. C. Griffin , A. M. Bhitta, and R. S. L. Hung, in Proceedings of SPIE-The international Society for Optical Engineering on Molecular & Polymeric Optoelectronic Materials, Sandiego, 1986 ed. G. Khanarian Proc. SPIE Bellingham 65 (1987)
4. R. A. Hann and D. Bloor, in Organic Molecules for Nonlinear Optics ,The Royal Society of Chemistry Publication, London, 69 (1989)
5. P. N. Prasad and D. J. Williams, in Introduction to Nonlinear Optical Effects in Molecules and Polymers ; Wiley: New York, 1991.
6. D. J. Williams, in Nonlinear optical Properties of Organic and Polymeric Materials, ACS Symposium. Ser. 233, 1983.
7. D. H. Choi, H. M. Kim, W. M. K. P. Wijekoon, and P. N. Prasad, Chem. Materials, 4, 6, 1253 (1992)
8. A. J. Heeger, J. Orenstein, and D. R. Ulrich, in Nonlinear Optical Properties of Polymers, Mater. Res. Symp. Proceedings, Pittsburgh, 109.,1987
9. R. N. Martino (Hoechst Celanese Corp.), Eur. Pat. 0 294 706 (1988) (Chem. Abstr. , 110, 16. 1989)
10. M. A. Mortazavi, A. Knoesen, and S. J. Kowel, J. Opt. Soc. Am. B. 6, 733 (1989)
11. C. C. Teng and H. T. Mann, Appl. Phys. Lett., 56(18), 30 (1990)
12. C. Hepburn, in Polyurethane Elastomers, 2nd ed., Elsevier Applied Science, London & New York (1992)
13. R. W. Dexter, R. Saxon, and D. E. Fiori, J. Coating Tech., 58, 737, 43 (1986)
14. D. H. Choi and P. N. Prasad, unpublished results (1992).