Styrene/Maleimide Copolymer with Stable Second-Order Optical Nonlinearity

PO-HOU SUNG,[1,*] CHUNG-YUNG CHEN,[1] SHIN-YU WU,[1] and JUNG Y. HUANG[2]

[1]Department of Chemistry, Fu-Jen Catholic University, Hsinchung, Taipei, Taiwan, Republic of China, [2]Institute of Electro-Optical Engineering, National Chiao-Tung University, Hsinchu, Taiwan, Republic of China

SYNOPSIS

Radical copolymerization of *N*-(azo dye) maleimide or *N*-(substituted phenyl) maleimide and styrene were carried out using 2,2′-azobis-isobutyronitrile as an initiator in THF at 60°C. These copolymers exhibit high solubility in most of the organic solvents and excellent thermal stability up to 280°C under nitrogen atmosphere. The copolymer films which were heated at 200–240°C under high corona field exhibit d_{33} = 3–5 pm/V, in the Maker-fringe measurement. Experimental results also showed that the copolymer with azo dye as chromophore did not decay in second harmonic response even at 130°C. © 1996 John Wiley & Sons, Inc.

Keywords: styrene • maleimide • copolymer • NLO • thermal stability

INTRODUCTION

Organic chromophores with large second-order nonlinear optical properties have recently received immense attention.[1,2] In particular, poled amorphous polymers with incorporation of nonlinear optical chromophores have attracted a large number of scientists due to its easy processability to fabricate thin film for optical applications.[3-5] However, because of the rotational freedom of the chromophore and relaxation of the main chain, second-order nonlinear optical properties are generally not very stable when the temperature approaches the glass transition temperature of the matrix. Efforts to increase the thermal stability entails selecting high glass transition temperature (T_g) matrices, e.g., crosslinking,[6,7] main chain chromophores,[8] or high glass transition polymers.[9]

Alternating copolymers of maleimide and styrene which are synthesized from free radical copolymerization show excellent thermal stability. Their T_gs are usually higher than 200°C.[10-12] In addition, the polymers show excellent solubility properties in various common organic solvents. The work of Gunter et al. examined the electrooptical properties of styrene/maleimide copolymer with chromophores as side chains. They were able to obtain stable and large second-order optical nonlinearity. To increase the poling efficiency, they incorporated a spacer $[\!-\!(\!-CH_2\!-\!)\!-_n]$ between the chromophore and the imide ring which drastically decreased the T_g.[13] Dalton et al. utilized diamine containing chromophore to crosslink styrene/maleic anhydride copolymer in 1995.[14] Similar chromophores with spacer were used in their study.

In this study, two types of second-order nonlinear optical styrene/maleimide copolymer without spacer were synthesized. The chain was expected to be more rigid than the published results. Their main chain structures were comparable. Thus, the difference in the long-term stability of second harmonic response between these two copolymers would depend on the rotational freedom and size of the chromophores.

EXPERIMENTAL

Preparation of Chromophores and Monomers

3-Nitro-4-aminoacetanilide (Compound 1)

Acetic anhydride was added dropwise to a solution of an equimolar amount of 2-nitro-1,4-phenylene

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[*] To whom all correspondence should be addressed.

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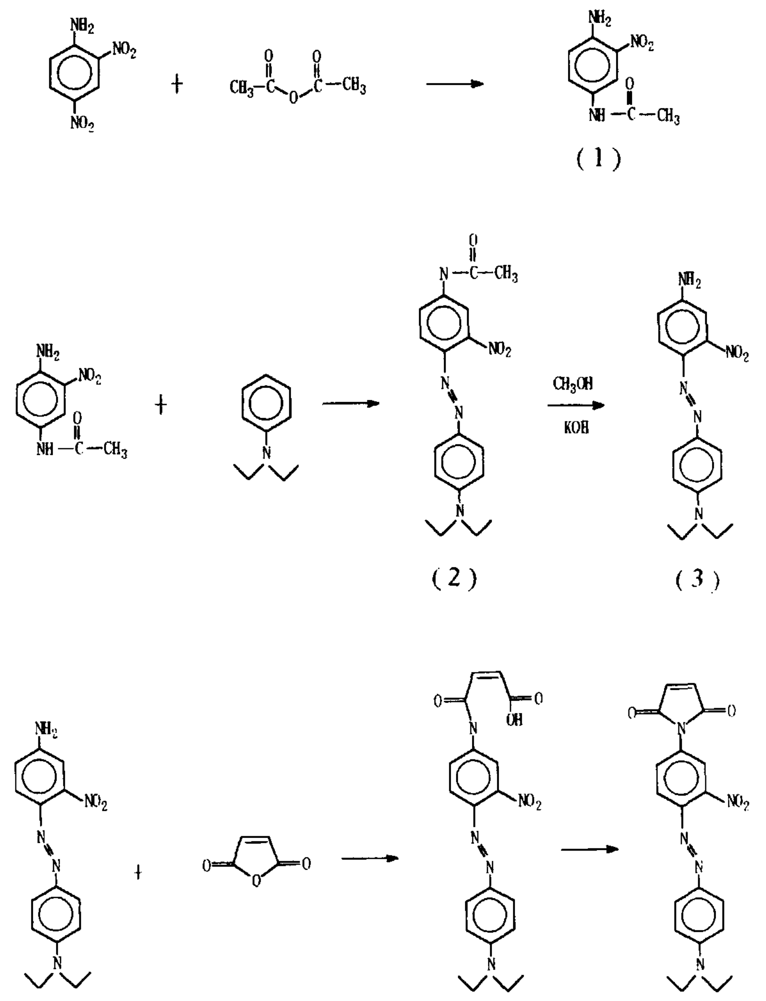


Monomer B

Scheme 1. Synthesis of monomer.

diamine in dry acetone at 5°C for 8 h. The monoacetanilide derived from diamine was prepared following these experimental conditions. The product was purified by recrystallization from ethyl acetate (mp 184–186°C).

^{1}H-NMR (DMSO-d_6): $\delta = 1.99$ (s, 3H); 6.94 (d, $J = 9.0$ Hz, 1H); 7.30 (s, 2H); 7.48 (dd, $J = 2.1$; 9.0 Hz, 1H); 8.35 (d, $J = 2.1$ Hz, 1H); 9.88 (s, 1H).

2-Nitro-4-amino-4′-N,N-diethyl Amino Azobenzene (Compound 3)

Compound **1** (1.997 g) was dissolved in 6 mL of 6*N* HCl by gentle warming, then sodium nitrite (0.708 g) dissolved in 8 mL of water was quickly added at a temperature below 5°C. To the cooled solution, 0.683 g of glacial acetic acid and 1.572 g of *N,N*-diethylaniline were added. After stirring for 1 h at 5°C and then 2 h at room temperature, the solution was neutralized by adding 10% $NaOH_{(aq)}$. The product, 2-nitro-4-acetamido-4′-N,N-diethyl amino azobenzene (compound **2**), was filtered, washed with water, and dried under vacuum at 60°C (72%, mp 159–160°C).

^{1}H-NMR (DMSO − d_6): $\delta = 1.13$ (t, $J = 7.0$ Hz, 6H); 2.10 (s, 3H); 3.46 (q, $J = 7.0$ Hz, 4H); 6.79 (d, $J = 9.2$ Hz, 2H); 7.74–7.65 (m, 4H); 8.30 (d, $J = 1.6$ Hz, 1H); 10.60 (s, 1H).

Compound **2** was dissolved in 150 mL hot methanol and 20 mL $KOH_{(aq)}$ (50% w/w) was added. The mixture was heated at the refluxing temperature for 3.5 h. Methanol was removed by distillation and the residual solution was poured into the crushed ice. The precipitate (mp 122–125°C) was collected and washed with water. The disapperance of carbonyl group absorption ($\sim$1700 cm^{-1}) in FT-IR revealed that the protected group was removed successfully.

^{1}H-NMR (DMSO-d_6): δ = 1.12 (t, J = 7.0 Hz, 6H); 3.42 (q, J = 7.0 Hz, 4H); 6.30 (s, 2H); 6.75 (d, J = 9.2 Hz, 2H); 6.82 (dd, J = 2.5 and 10.3 Hz, 1H); 6.91 (d, J = 2.5 Hz, 1H); 7.56–7.60 (m, 3H).

N-*(2-methoxy-5-nitrophenyl)maleimide (Monomer A)*

A typical imidization reaction was used to synthesize monomers. Maleic anhydride was dissolved in toluene and mixed with an equimolar amount of 2-methoxy-5-nitroaniline. After refluxing for 1.5 h, toluene was removed under reduced pressure. The yellow powder obtained was maleic amic acid. This compound was used directly for next reaction. Maleic amic acid prepared and sodium acetate were dissolved in acetic anhydride. The solution was stirred for 30 min at refluxing temperature, then sodium hydrogen carbonate solution was added gradually to neutralize the solution. The precipitate was collected, washed with water, and dried under vacuum at 90°C.

^{1}H-NMR ($CDCl_3$): δ = 3.92 (d, J = 4.5 Hz, 3H); 6.90 (d, J = 2.2 Hz, 2H); 7.09 (d, J = 9.2 Hz, 1H); 8.13 (d, J = 2.7 Hz, 1H); 8.35 (dd, J = 2.7; 9.2 Hz, 1H). UV-Vis(THF): $\lambda_{max/nm}$ = 302. Exact mass: Calcd: 248.0433; Found: 248.0432.

N-*(2-nitro-4′-diethyl amino azophenyl)maleimide (Monomer B)*

Following the same procedure as described for preparation of monomer **A**, monomer **B** was obtained as red powder from compound **3**, maleic anhydride, and acetic anhydride.

^{1}H-NMR ($CDCl_3$): δ = 1.24 (t, J = 7.1 Hz, 6H); 3.48 (q, J = 7.1 Hz, 4H); 6.73 (d, J = 8.1 Hz, 2H); 6.92 (s, 2H); 7.70 (dd, J = 2.2; 8.7 Hz, 1H); 7.88–7.82 (m, 3H); 7.97 (d, J = 2.2 Hz, 1H). UV-Vis(THF): $\lambda_{max/nm}$ = 466. Exact mass: calcd: 393.1437; Found, 393.1436.

Preparation of Copolymers

Copolymerization were carried out in THF at 60°C using AIBN as initiator. An equimolar amount of monomer **A** or **B** and styrene were mixed in a round bottom flask and purged with N_2. After 20 h, the contents were poured into a large excess of methanol. The polymers were purified by repeated precipitation and finally dried under vacuum.

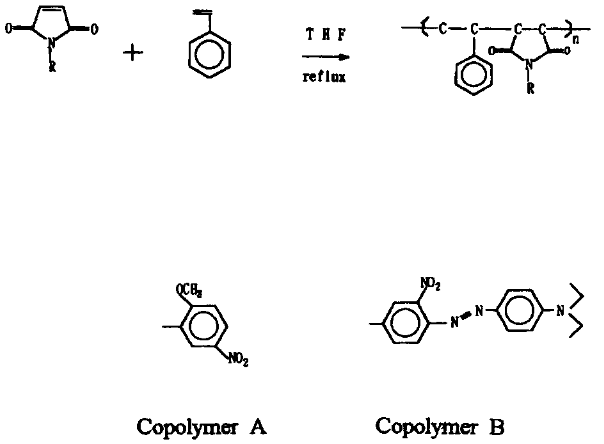
Measurements

Infrared spectra were recorded on Analet ATC-750 spectrophotometer. ^{1}H-NMR spectra were recorded on a Bruker AC-F300 NMR spectrometer and TMS was used as the internal reference. The molecular weights (M_n and M_w) of the polymers were determined by gel permeation chromatography (Waters M-410) and calibrated with polystyrene standards. A differential scanning calorimeter (DuPont DSC-910) was used to measure the glass transition temperature (T_g) of the specimen. The measurements were carried out from RT to 300°C under N_2 atm. at a heating rate 10°C/min. Thermogravimetric analysis was performed in DuPont TGA-951 thermal analyzer at the heating rate of 10°C/min under N_2 atm. Second harmonic generation (SHG) measurements were performed by using a Nd:YAG laser at a wavelength of 1.06 μm. The second harmonic coefficients of the copolymers were then calculated in comparison with the second harmonic intensity generated by the quartz sample.

RESULTS AND DISCUSSION

Chemical structures of starting materials and the reaction sequence are shown in Schemes 1 and 2. The advantages of choosing alternating copolymers of maleimide and styrene are that they (1) contain large amount of the active molecules; (2) have an extremely high T_g, usually higher than 200°C; (3) exhibit high solubility in most of the organic solvents; and (4) easily form the thin films.

The copolymer composition curve plotted in terms of the mol % of styrene in copolymer (data obtained from EA and NMR) against that in the



Scheme 2. Synthesis of second-order NLO styrene/maleimide copolymers.

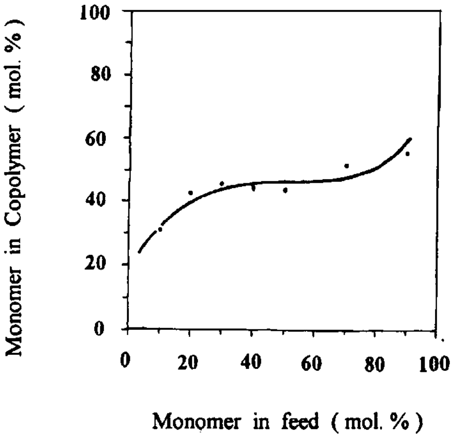


Figure 1. Copolymerization composition curves of monomer **A** with styrene in THF at 60°C.

styrene monomer feed is shown in Figure 1., from which a highly alternating tendency is observed over a wide range, as expected.[10-12] Electron-donating or -withdrawing substituents on the aromatic ring of maleimide are likely to play an important role in the formation of alternating copolymer. A series of monomers with different polarities was examined in our laboratory. Those results will be published in the future.

The number- and weight-average molecular weight of these two copolymers as determined by gel permeation chromatography are given in Table I. The relative low molecular weight indicated that the chain transfer reaction between the free radical and THF has a significant effect.

The thermal properties of the copolymer **A** and **B** were determined by DSC and TGA. As shown in Figures 2–4, the DSC scan of copolymer A revealed a T_g around 225°C, and TGA showed the copolymer to be stable up to 328°C. However, there were no obvious glass transitions in the DSC traces for the copolymer **B** up to 200°C. The exothermic peaks observed at 277°C represent the decomposition of azo dye, which were consistant with the TGA results.

The order parameter is defined by $\Phi = 1 - (A_{\perp}/A_0)$ (where $A_{\perp}$ and A_0 are UV-visible absorption of poled and unpoled films, respectively).[15] It can be used to estimate the degree of the chromophore orientation. In corona discharge poling condition (6 μA/7 kV, 240°C, 2 h for copolymer **A**, and 2 μA/7 kV, 200°C, 1.5 h for copolymer **B**), the order parameters for copolymers **A** and **B** are 0.55 and 0.32, respectively. UV-visible absorption of unpoled and poled copolymers are shown in Figures 5 and 6. For copolymer **A**, the absorption increased significantly after 90°C aging. However, copolymer **B** showed no measurable change at the identical condition. This observation reveals that the relaxation of the nonlinear optical properties of copolymer **B** at a temperature up to 90°C is negligible.

Table I. Molecular Weight Data for the Styrene/Maleimide Copolymers

Copolymer	M_w	M_n	M_w/M_n
A[a]	14,995	11,609	1.292
B[b]	4835	3454	1.400

[a] DMF as eluent.
[b] THF as eluent.

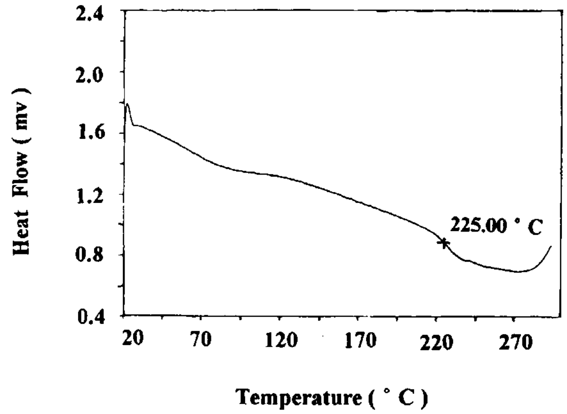


Figure 2. DSC trace of copolymer **A**.

The main chain structures of these two types of copolymers are almost identical. Thus, the relaxation rate of orientational order in these systems therefore depends on the size and degree of rotational movement of the chromophores.[16] Thus, it is reasonable to predict that the retention of SHG response of the small spherical molecule (2-methoxy-5-nitrobenzene) in the copolymer matrix should be

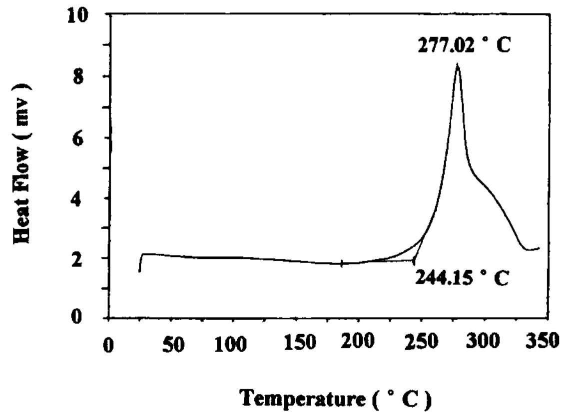


Figure 3. DSC trace of copolymer **B**.

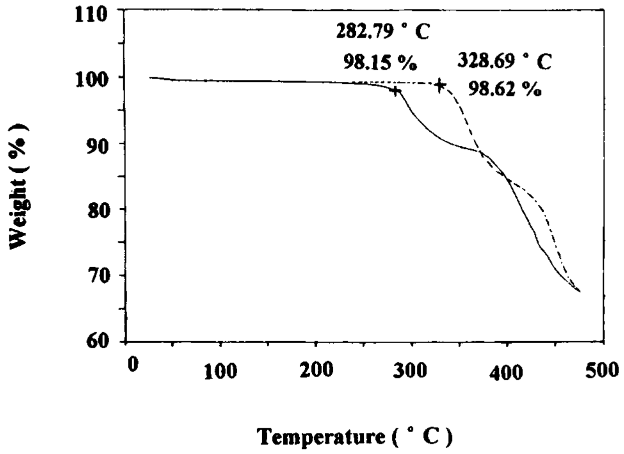


Figure 4. TGA trace of styrene/maleimide copolymers: (· · · · · ·) copolymer **A**, (—) copolymer **B**.

poorer than the large rod-like molecule (azo dye) in the matrix. Indeed, the second harmonic coefficient, $d_{33}(t)$, of copolymer **A** decayed rapidly to 44% within 9 h at 90°C. For copolymer **B**, the relative $d_{33}(t)/d_{33}(0)$ values remained unchanged even at 130°C, (Fig. 7). These results were in good agreement with UV-visible measurements. The rather low second harmonic coefficients are observed for both copolymers which were in the 3–5 pm/V range. It can be explained by considering the chromophore structure. First, there were two electron-withdrawing and one electron-donating groups in the chromophore. Since the molecular dipole is the vectorial sum of local dipoles, the dipole moment of these two electron withdrawing groups will cancel each other. The decrease of the dipole moment in the ground state would reduce the hyperpolarizability of the molecule. Second, Cheng et al. have shown the substitution pattern effect in disubstituted stilbene on charge transfer interactions between the donor and acceptor groups. They concluded that the β values of the different substitution pattern were in the order of para $\gg$ ortho $>$ meta. In the case of weak donors such as methyl and bromo group, the order was para $>$ meta $>$ ortho.[17–18] It is reasonable to accept these concepts in azo dye structure. The main contribution of electron-withdrawing group ($-\mathrm{NO_2}$) in the azo dye of this study was in the ortho position, which did not allow a strong charge-transfer interaction between donor and acceptor groups and might strongly influence their optical nonlinearity.

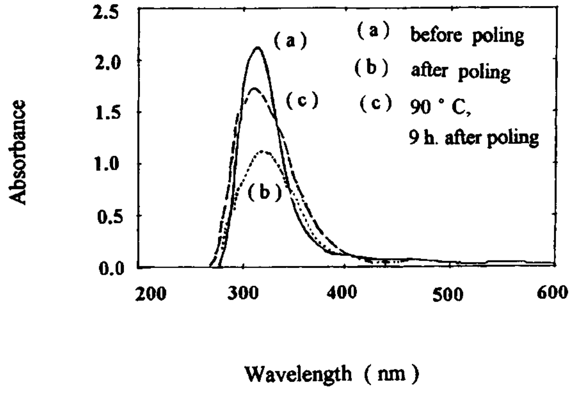


Figure 5. UV absorption spectra of copolymer **A** before and after poling.

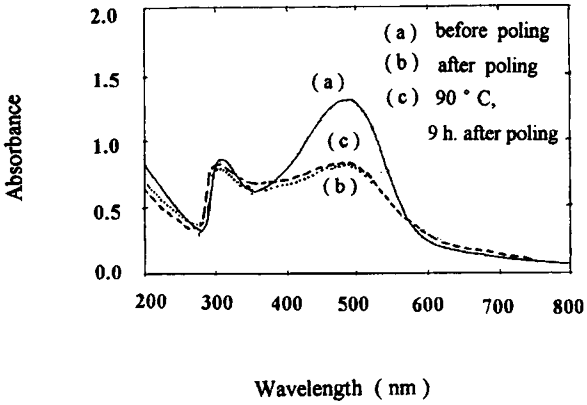


Figure 6. UV absorption spectra of copolymer **B** before and after poling.

CONCLUSIONS

We have shown that it is possible to synthesize soluble maleimide/styrene copolymers containing a high content of pendant chromophore molecules. The copolymers have excellent thermal stability up to 280°C. Preliminary investigations indicate that

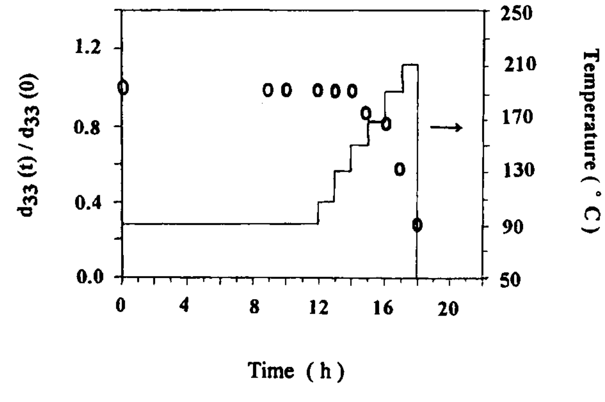


Figure 7. Thermal aging test of styrene/maleimide copolymer **B**. There is virtually no decay in the relative SHG response at 130°C.

the copolymer with large molecular size and rodlike azo dye chromophore, show excellent poling orientation stability even at 130°C. Although the d_{33} values are not very large, it is reasonable to consider that this reaction has great potential for the future. Further study on maleimide/styrene copolymer system with large second order nonlinearity is in progress.

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