

# Synthesis and characterization of styrene/maleimide copolymers with high poling stability of dipolar chromophore

S. ARORA, S. KUMAR<sup>a\*</sup>

*Department of Chemistry, Kurukshetra University, Kurukshetra - 136 119, India*

*<sup>a</sup>Department of Chemistry, S.D. College, Ambala Cantt - 133 001, India*

Styrene/maleimide copolymers with N-(4-nitrophenyl) maleimide and N-(4-benzoylphenyl) maleimide as dipolar chromophores have been synthesized and characterized by thermal and spectral techniques. The weight-average molecular weights of these polymers, as determined by GPC using THF as the eluent, were 10480-12550. The resulting polymers have been found to possess good thermal stabilities (decomposition temperatures 292-308 °C) and high glass transition temperatures (192-205 °C). The vacuum deposited thin films of these polymers were subjected to corona poling to induce polar order. Under the poling conditions (5 kV, 180 °C, 30 min.), the order parameter values for polymeric thin films were estimated to be 0.312-0.355. The relaxation behaviour of aligned dipoles was studied at room temperature as well as at high temperatures using UV/Vis absorption spectroscopy. At room temperature, the decayed amounts of order parameter were found to be 7.2-8.5 % even after 60 days of poling. It was further observed that after heating for 200 h, polymeric thin films retained 75-80 % of initial polar order at 80 °C and 70-76 % at 90 °C.

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## 1. Introduction

The development of poled polymeric thin films [1-10] with dipolar chromophore, that are suitable for the fabrication of high-speed integrated optical devices, has become a major focus of research in recent years. Depending on the applications, the dipole alignments in these polymers can be achieved either by corona poling or by parallel-electrode poling. To achieve noncentrosymmetric alignment of dipolar chromophores, electrical poling is a common procedure for breaking the centre of symmetry of randomly oriented chromophores. However, in the absence of poling electric field, the dipolar orientation in poled polymers tends to relax to the thermodynamically more stable random structure through polymer chain segmental motions leading to the decay of the nonlinearity. Therefore, the successful implementation of poled polymer films in electrooptic devices depends mainly on the outcome of research aimed at developing materials in which dipole orientation will be retained over an extended period of time in the operating temperature range. The polar groups responsible for electrooptic applications are introduced in the material as doped guests (guest-host systems) [11-13] or by covalent bonding [1-10]. Guest-host systems have some advantages in the simplicity of preparation but the poling induced alignment of dipolar chromophores is poor. Thermal stability of poling-induced chromophore dipole alignment can be improved by covalent incorporation of dipolar

chromophores into various polymeric systems. It can be further increased by the design of high glass transition polymers like polyimides [14-18] or maleimide based copolymers [19-21].

Copolymers of maleimide and styrene, which are synthesized from free radical copolymerization, possess high glass transition temperatures usually greater than 200 °C [19,21]. Maleimide based polymers functionalized with dipolar chromophores give high thermal stability of nonlinear optical effects [22]. Moreover, these polymers possess good solubility in most of the common organic solvents and easily form the thin films. Keeping in view the significance of these copolymers, efforts were directed to synthesize Styrene/maleimide copolymers with N-(4-nitrophenyl) maleimide and N-(4-benzoylphenyl) maleimide as dipolar chromophores. This paper also reports the temporal stability of poling induced aligned dipoles in the vacuum-deposited thin films of these synthesized polymers.

## 2. Experimental

### 2.1 Chemicals

Tetrahydrofuran (THF), acetic anhydride and toluene were purified by distillation. Maleic anhydride, 4-aminobenzophenone, 4-nitroaniline and styrene were

purchased from Across Organics Co. and used as received unless otherwise stated.

## 2.2 Measurements

Molecular weights of these polymers were calculated with the help of GPC technique against polystyrene standard using THF as the solvent. I.R. spectra were recorded on BUCK SCIENTIFIC M 500 spectrometer.  $^1\text{H}$  NMR spectra were recorded on BRUKER DRX 300 MHz NMR spectrometer with TMS (tetramethylsilane) as the internal reference. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed by Perkin Elmer (Pyris Diamond) thermal analyzer at the heating rate of  $10\text{ }^\circ\text{C}/\text{min}$  under nitrogen atmosphere using alumina as the reference material. UV/Vis absorption spectra of the polymers were recorded with the help of Shimadzu UV-2500 PC spectrophotometer attached to integrated sphere assembly (ISR-240 A). Thin films of these polymeric materials were grown on the cleaned quartz glass slides by vacuum deposition technique at a vacuum of  $10^{-6}\text{ mm/Hg}$  with the help of high vacuum coating system (NIRVAT EU-300). The thickness of these polymeric thin films was controlled with the help of thickness monitor and kept about  $1000\text{ \AA}$ . The vacuum deposited thin films of these polymers were poled under different poling conditions using optimized high potential multi-point corona poling technique. Optical band gaps for polymeric materials have been measured [23] using UV/Vis absorption spectroscopic technique.

## 2.3 Synthesis [19] of N-(4-nitrophenyl) maleimide C1

2.0 g (20 mmol) of maleic anhydride and 2.8 g (20 mmol) of 4-nitroaniline were dissolved in distilled toluene. The reaction mixture was refluxed for 3 hrs. After refluxing, the toluene was removed under reduced pressure resulting into yellow coloured maleic amic acid. This maleic amic acid was used directly for the next reaction. The prepared maleic amic acid and 2.0 g (25 mmol) of sodium acetate were dissolved in 20 ml of distilled acetic anhydride. The reaction mixture was refluxed for 2 hrs. with constant stirring using mechanical stirrer. The resulting solution was naturalized using sodium bicarbonate to get precipitate of N-(4-nitrophenyl) maleimide **C1**. The resulting precipitates were washed with water, dried and recrystallized with ethanol. Using the same procedure, N-(4-benzoylphenyl) maleimide **C2** was prepared by taking 4-aminobenzophenone in place of 4-nitroaniline.

### C1

Yield: 3.0 g (69 %).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) = 4.86 (d, 2H, imide ring CH), 7.54 (d, 2H, Ar H), 7.98 (d, 2H, Ar H).

IR (KBr,  $\text{cm}^{-1}$ ): 1770 (C=O asym. str., imide ring), 1726 (C=O sym. str., imide ring), 1610 (C=C str.), 1528 & 1355 (N=O str.), 1378 (C-N str.).

Mass (m/z): 219 ( $\text{M}^++1$ )

### C2

Yield: 65 %.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) = 4.94 (d, 2H, imide ring CH), 7.53-7.85 (m, 9H, Ar H).

IR (KBr,  $\text{cm}^{-1}$ ): 1776 (C=O asym. str., imide ring), 1720 (C=O sym. str., imide ring), 1692 (C=O str., aryl conjugated), 1612 (C=C str.), 1372 (C-N str.).

Mass (m/z): 278 ( $\text{M}^++1$ )

## 2.4 Synthesis of polymer P1 (Fig. 1)

2.2 g (10 mmol) of chromophore (monomer) **C1** and 1.1 ml (10 mmol) of styrene were dissolved in THF taken in 100 ml two-necked round bottom flask fitted with condenser. The polymerization was initiated by using azobis (isobutronitrile) [AIBN] taken in the ratio 40:1 w/w (monomer: AIBN). The reaction mixture was heated for 24 hrs. at  $60\text{ }^\circ\text{C}$  with continuous stirring under  $\text{N}_2$  atmosphere. The polymer was precipitated by pouring the reaction mixture drop wise into excess of methanol. The polymer was purified by repeated precipitation and finally dried. The polymer **P2** was prepared using the above procedure by taking **C2** in place of **C1**.

### P1

Yield: 2.3 g (72 %).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) = 2.82 (dd,  $\text{CH}_2$ ), 3.43 (t, Ph CH), 3.82-3.88 (m, imide ring CH), 6.96-7.12 (m, Ar H), 7.82 (dd, Ar H)

IR (KBr,  $\text{cm}^{-1}$ ): 1776 (C=O asym. str., imide ring), 1722 (C=O sym. str., imide ring), 1595 (C=C str.), 1525 & 1345 (N=O str.), 1385 (C-N str.).

### P2

Yield: 75 %.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) = 2.78 (dd,  $\text{CH}_2$ ), 3.46 (t, Ph CH), 3.80-3.87 (m, imide ring CH), 6.92-7.06 (m, Ar H), 7.34-7.72 (m, Ar H)

IR (KBr,  $\text{cm}^{-1}$ ): 1770 (C=O asym. str., imide ring), 1718 (C=O sym. str., imide ring), 1688 (C=O str., aryl conjugated), 1615 (C=C str.), 1380 (C-N str.).

## 3. Results and discussion

Styrene/maleimide copolymers were synthesized by radical copolymerization of N-(substituted phenyl) maleimide and styrene using AIBN as free radical initiator in THF solvent at  $60\text{ }^\circ\text{C}$  (Fig. 1). The resulting polymers were found to possess good solubility in most of the common organic solvents.

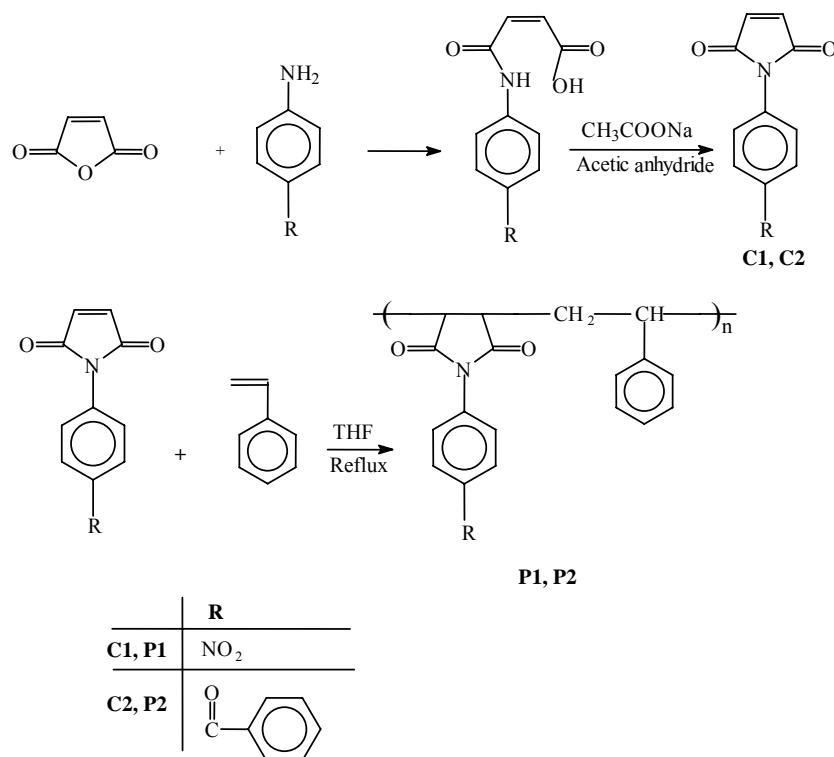


Fig. 1. Synthetic scheme for chromophores and polymers.

The weight-average molecular weights,  $M_w$  of these two polymers **P1** and **P2** as determined by GPC using THF as the eluent were 12550 and 10480 respectively.

### 3.1 IR and <sup>1</sup>H NMR studies

IR and <sup>1</sup>H NMR data of **P1** and **P2** supported their proposed structures. IR spectrum of **P1** shows characteristic absorption peaks at 1776 and 1722 cm<sup>-1</sup> attributed to the asymmetric and symmetric stretching vibrations, respectively, of carbonyl groups in imide ring [16]. For polymer **P2**, the similar peaks due to carbonyl groups were observed at 1770 (asym.) and 1718 (sym.) cm<sup>-1</sup>. The absorption peak observed at 1385 cm<sup>-1</sup> (C-N str. of imide ring) together with obvious bands at 1525 and 1345 cm<sup>-1</sup> due to the nitro group further support the proposed structure of the polymer **P1**. The peaks at 1380 and 1688 cm<sup>-1</sup> in the IR spectrum of **P2** are attributed to the C-N str. (imide ring) and aryl conjugated carbonyl group respectively. <sup>1</sup>H NMR spectra of these polymers show several characteristic peaks. The methylene group in the polymeric backbone of **P1** and **P2** appears at 2.82 and 2.78 ppm respectively. The proton in -CH- group attached to phenyl ring appears as triplet at 3.43 (**P1**) and 3.46 ppm (**P2**). The multiplet due to proton in imide ring appeared at 3.82-3.88 ppm (**P1**) and 3.80-3.87 ppm (**P2**). The signal due to aromatic protons of polymers **P1** and **P2** appears as multiplet at 6.92-7.82 ppm and 6.92-7.72 ppm respectively.

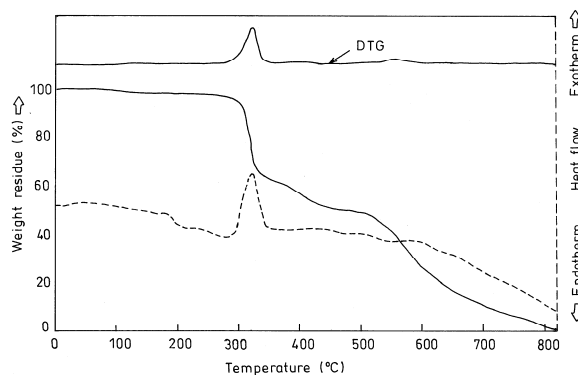


Fig. 2. DSC, TG and DTG thermograms of polymer **P1**.

### 3.2 Thermal studies

Fig. 2 shows DSC, TGA and DTG (differential thermogravimetric analysis) thermogram of polymers **P1**. DSC thermogram indicates that **P1** exhibits a  $T_g$  around 192 °C. Therefore, **P1** is expected to possess high orientational stability. Because the thermal relaxation process of the dipole orientation is directly related to the free volume in the polymer, a critical free volume is required for the relaxation of the orientation of dipoles. This critical free volume is related to the glass transition temperature; a high glass transition temperature implies a higher orientational stability. TGA thermogram indicates that polymer **P1** exhibits decomposition temperature value

(initial) of 292 °C. The exothermic peak (maxima) observed at 322 °C in DSC thermogram suggests decomposition of the polymeric system. DTG curve reveals maximum weight loss around 322 °C, in consistent with DSC results. DSC, TGA and DTG thermograms for polymer **P2**.

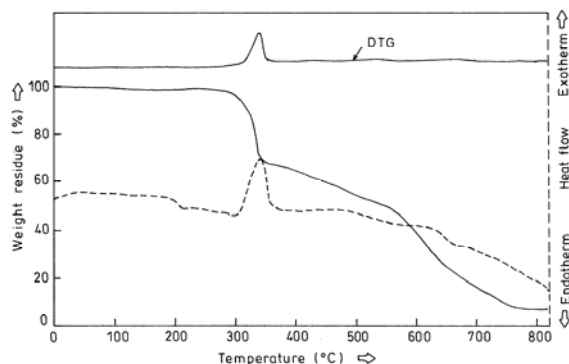


Fig. 3. DSC, TG and DTG thermograms of polymer **P2**.

are shown in Fig. 3. The glass transition temperature value of 205 °C was observed for the polymer **P2**. For similar styrene/maleimide copolymer, Sung *et al.* [16] have observed glass transition temperature more than 200 °C. The glass transition temperature value of polymer **P2** is 13 °C higher than that of polymer **P1** since chromophore **C2** has larger size as compared to chromophore **C1**. The incorporation of larger groups is expected to increase glass transition temperature value of the polymer. For polymer **P2**, the maximum weight loss occurs at 340 °C as suggested by DTG curve. The decomposition temperature for polymer **P2** is 308 °C. DSC curve, indicating exothermic peak (maxima) around 340 °C, further supports the TG results. The results suggest maximum weight loss (41 % for **P1** and 34 % for **P2**) in the temperature range 200-400 °C. The percentage weight loss for polymer **P2** is lower as compared to polymer **P1**. At 800 °C, the residue weight of polymer **P2** is 7 % whereas it is 2 % for **P1**. Furthermore, the decomposition temperatures of these polymers are 100-103 °C higher than the respective  $T_g$ 's. Hence upon poling near  $T_g$ , decomposition is not expected to occur.

### 3.3 Optical studies

The results of the UV/Vis study of thin films of polymers **P1** and **P2** showed an absorption maxima at 360 and 380 nm respectively due to  $\pi$ - $\pi^*$  transition in the dipolar chromophores. The optical direct band gaps for polymer **P1** and **P2** were found to be 3.36 eV and 3.12 eV respectively, indicating their insulating behaviour. After the molecular dipoles were aligned along the direction of the electric field by corona poling, the maximum absorbance was reduced. Poling efficiency has been determined in terms of order parameter defined by

$$\phi = 1 - A_{\perp} / A_0 \quad (1)$$

where  $A_0$  and  $A_{\perp}$  are the absorbances of the polymer film before and after corona poling.

It was observed that order parameter increased with poling temperature as well as poling voltage (Figs. 4 and 5). Under the conditions of 5 kV poling voltage applied to the corona needle 180 °C for 30 minutes, the order parameter values for polymer **P1** and **P2** were estimated to be 0.355 and 0.312 respectively (Fig. 4).

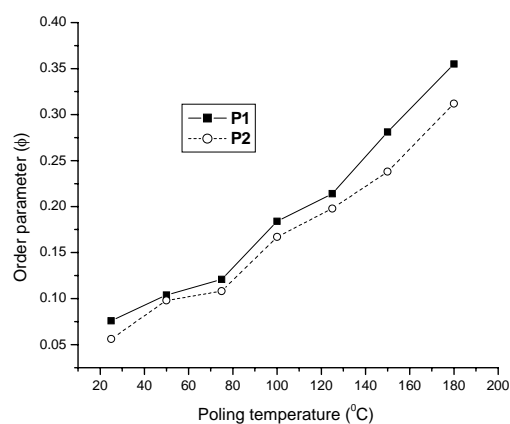


Fig. 4. Variation of order parameter of polymers with temperature under poling conditions (5 kV, 30 min.)

#### 3.3.1 Relaxation behaviour of aligned dipoles

The temporal stability of aligned dipolar chromophores has been measured using UV/Vis measurements. Sung *et al.* [16] studied relaxation behaviour of styrene/maleimide copolymers using second-harmonic generation measurements and reported that the results were in good agreement with UV/Vis measurements.

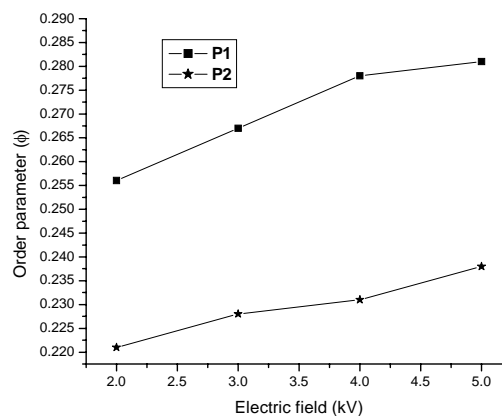


Fig. 5. Variation of order parameter of polymers with voltage under poling conditions (150 °C, 30 min.)

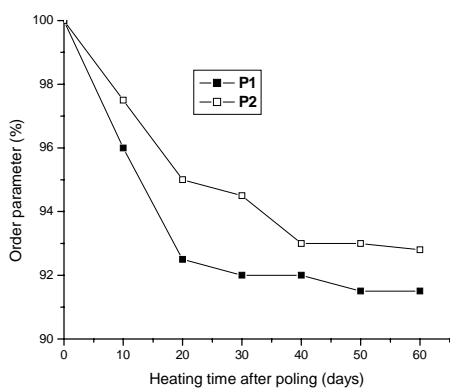


Fig. 6. Relaxation behavior of aligned dipoles in polymeric thin films at room temperature after poling at (5 kV, 180 °C, 30 min.).

We have investigated temporal stability at room temperature as well as at elevated temperatures by measuring absorbance value at different time interval after poling. Fig. 6 shows relaxation behaviour of dipolar chromophore at room temperature after poling under the conditions (5 kV, 180 °C, 30 min.). The decayed amounts of order parameter for polymer **P1** and **P2** are 8.5 % and 7.2 % respectively even after 60 days of poling. After that the polymers **P1** and **P2** showed no measurable change in absorbance value for further one month. Therefore, polymer **P2** possesses better temporal stability of dipolar chromophores. We have also monitored the stability of dipolar chromophores at high temperatures since these materials can be used at elevated temperatures depending on the need of device applications. When a poled film of **P1** was heated at 80 °C, it was observed that after an initial decrease during 5 hrs., the polar order does not significantly change over 200 hrs., which finally results in 75 % of remaining polar order (Fig. 7). Further, it can be seen from Fig. 7 that polymer **P2** retains 80 % of the initial polar order. The main chain structures of these two types of polymers are almost identical. Thus, the relaxation rate of polar order in these systems therefore depends on the size and degree of rotational movement of the chromophores.

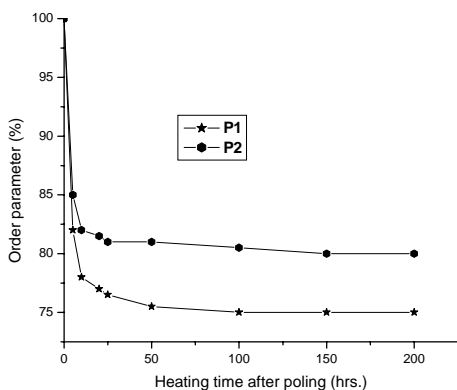


Fig. 7. Relaxation behavior of aligned dipoles in polymeric thin films at 80 °C after poling at (5 kV, 180 °C, 30 min.).

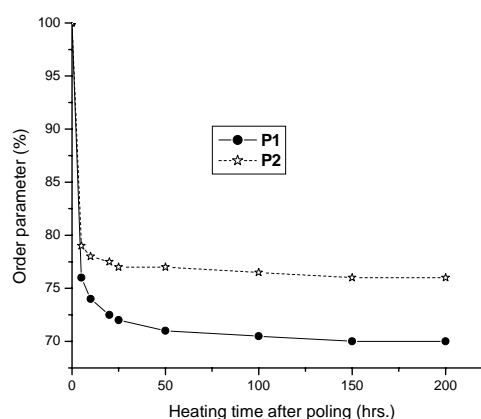


Fig. 8. Relaxation behavior of aligned dipoles in polymeric thin films at 90 °C after poling at (5 kV, 180 °C, 30 min.).

On this basis, it can be predicated that poor retention of polar response of the small dipolar chromophore **C1** in polymer **P1** than comparatively larger size chromophore **C2** in polymer **P2** is reasonable. Fig. 8 dictates the relaxation behaviour of the poled polymeric thin films at 90 °C. At this temperature, polymer **P1** retained 70 % and polymer **P2** retained 76 % of the initial polar order after 200 hrs.

#### 4. Conclusions

Styrene/maleimide copolymers possessing high glass transition temperatures with good temporal stability of aligned dipoles have been synthesized and characterized by thermal and spectral techniques. The optical direct band gaps for these polymers are 3.12-3.36 eV, indicating their insulating behaviour. Under the poling conditions (5 kV, 180 °C, 30 min.), the order parameter values for polymeric thin films were estimated to be 0.312-0.355 suggesting good poling efficiency. After poling under the same poling conditions, the decayed amounts of order parameter were found to be only 7.2-8.5 % at room temperature after 60 days of poling, 75-80 % after heating at 80 °C for 200 h and 70-76 % after heating at 90 °C for the same time period.

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\*Corresponding author: drsushilgoswami@yahoo.com