

Synthesis and Characterization of Azo-Based Acrylate Polymers for Use as Nonlinear Optical Materials

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ABSTRACT: In this work, high molecular weight azo polymers were synthesized by incorporating the azo monomer into a base polymer through their reactive functional groups. Copolymers of methyl methacrylate and methacrylic acid (with varying concentrations of carboxylic acid group) were synthesized. These were then reacted with epoxy-terminated azo molecule by carboxylic acid–epoxy reaction. The functionalized systems show excellent film homogeneity and optical clarity. The series of copolymers were characterized using FTIR, NMR, UV–vis spectrometry, gel permeation

chromatography, elemental analysis, thermogravimetric analysis, and differential scanning calorimetry. The polymer films coated on ITO glass slides were poled and their order parameters were calculated to check the stability of oriented dipoles. Temporal stability, checked up to 120 h under ambient conditions, was found to be excellent. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 425–431, 2007

Key words: NLO polymer; functional polymer; order parameter; nonlinear optical polymer; azo-based polymer

INTRODUCTION

Since the last few decades, nonlinear optical (NLO) materials have drawn considerable research interest because of their potential commercial applications in optical communication, optical data storage, optical switching, and frequency modulation.^{1,2} All the research carried out in nonlinear optics aims at developing a material with good nonlinear properties and satisfying all the technological requirements such as fast response, high damage threshold, and wide transparency range.^{3,4}

Organic polymers are better choice for NLO applications when compared to the inorganic crystal. They are cheap, flexible, easy to fabricate, show better mechanical properties, have good film-forming properties, and are compatible with existing technologies.^{5–7} The main condition for providing second-order nonlinearity in polymer films is the existence of noncentrosymmetry.^{8–10} Polymers with NLO properties must possess large molecular nonlinearity as well as optical transparency at the required wavelength, good processibility, and good thermal and temporal stability.^{11,12}

For decades, several guest-host systems have been considered for NLO studies. However, such systems suffer from severe drawbacks—the poled NLO moiety in the polymer matrix tends to relax easily lead-

ing to a loss of second-order parameters,¹³ the concentration of NLO moiety that can be conveniently used as dopant is limited; also the NLO moiety tends to leach out of the host matrix at higher temperatures resulting in phase separation.¹⁴ One solution for the stability problem could be the use of polymers with high glass transition temperatures covalently bonded to the NLO moiety.^{15,16}

Azobenzene derivatives have widely been investigated as promising NLO materials^{17,18} because of their high hyperpolarizability, easy methods of preparation, and better processibility. Regarding synthesis strategies, still the synthesis of chromophore-containing monomer followed by polymerization remains the most convenient route.^{17–20} However, most of the time, this method fails to realize high molecular weight and very often requires the use of comonomer that further complicates the situation. As the relaxation of oriented dipoles is the most important criteria for selection toward device fabrication, it is obvious that high molecular weight polymer is a must. To overcome this problem, the strategy of synthesizing high molecular weight functional polymer can be used. This polymer can be reacted further with chromophore-containing molecules to make the required polymer.

In the present report, copolymer of methyl methacrylate and methacrylic acid was synthesized as high molecular weight functional polymer. Azo moiety was attached through the carboxyl function of the copolymer. The series of copolymers were characterized and their order parameters were calculated to check the stability of oriented dipoles.

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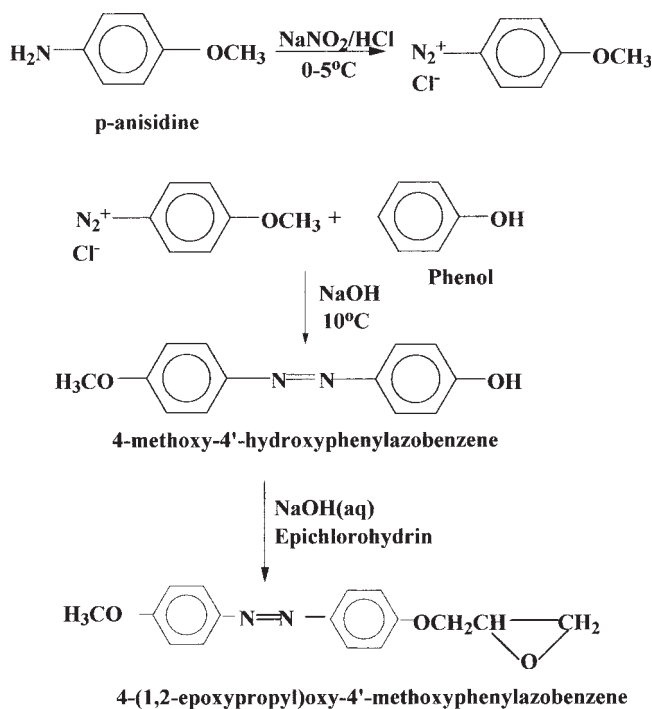


Figure 1 Reaction scheme for the synthesis of EPMPA.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA) (M/s, S.D. Fine Chemicals, India) was purified by washing with aqueous NaOH solution followed by distillation under reduced pressure. Methacrylic acid (MA) (M/s, Fluka Laboratories) was distilled through copper turning-filled condenser under vacuum. *p*-Anisidine, epichlorohydrin, and triphenyl phosphine were used as received (S.D. Fine Chemicals, India). All solvents were distilled before use.

Synthesis

Synthesis of the azo-containing NLO unit [4-(1,2-epoxypropyl)oxy-4'-methoxyphenylazobenzene (EPMPA)] was done in two steps as given in Figure 1.

The product obtained in the first step [4-methoxy-4'-hydroxyphenylazobenzene (MHPA)] was isolated, washed well with water, dried and recrystallized

from aqueous ethanol solution (2 : 1 v/v). It crystallized as brown crystals. Yield: 84% (m.p.: 134.1°C).

Synthesis of 4-(1,2-epoxypropyl)oxy-4'-methoxyphenylazobenzene

4-(1,2-Epoxypropyl)oxy-4'-methoxyphenylazobenzene (EPMPA) was synthesized by following conventional epoxidation method.²¹ In a typical method, in a round bottom flask equipped with a condenser, a nitrogen inlet, and a stirrer, MHPA (11.4 g, 0.05 mol) was placed. Sodium hydroxide (3.6 g, 0.09 mol) was added as a 10% aqueous solution and heated to 45°C. Epichlorohydrin (7.4 g, 0.08 mol) was added rapidly with stirring. The mixture was heated at 95°C for 2 h. Upon completion of the reaction, unreacted epichlorohydrin and water were distilled out under vacuum. The mass obtained was dissolved in *N,N*-dimethylformamide and precipitated by pouring into excess distilled water. The precipitate obtained was filtered, washed well with water, dried and recrystallized from ethylacetate. It crystallized as brown crystals. Yield: 70% (m.p.: 121.1°C).

Synthesis of methyl methacrylate-*co*-methacrylic acid polymer

Methyl methacrylate-*co*-methacrylic acid (MMA-MA) copolymer was synthesized by following the method of Samui et al.²² The feed ratio was taken as calculated from the copolymerization equation considering the reactivity ratio values for MMA and MA as $r_1 = 0.98$ and $r_2 = 0.68$.²³ MMA and MA at various mole ratios dissolved in *N,N*-dimethylformamide (65% solution) was taken in a round-bottom flask fitted with a condenser, nitrogen inlet, and stirrer. The reaction mixture was heated to 70°C and AIBN (10^{-2} mol/L) was added. Reaction was allowed to continue for 4 h, cooled to room temperature, and then poured into cold distilled water. The polymer precipitated was filtered and purified (made monomer free) by reprecipitation thrice using DMF/water. Purified polymer was dried at 60°C under vacuum.

Five different batches of this polymer were synthesized with varying equivalent weights as shown in Table I.

TABLE I
Acid Value, Equivalent Weight, and Molecular Weight of the Polymer (MMA-MA)

| Polymer | Equivalent weight | MMA : MA mole ratio | Acid value | M_w | M_n |
|---------------|-------------------|---------------------|------------|---------|--------|
| (MMA-MA) I | 1990 | 95 : 5 | 28.2 | 56,210 | 29,419 |
| (MMA-MA) II | 720 | 86 : 14 | 77.9 | 163,201 | 36,506 |
| (MMA-MA) III | 504 | 80 : 20 | 111.3 | 112,295 | 31,786 |
| (MMA-MA) IV | 377 | 75 : 25 | 148.8 | 86,608 | 34,679 |
| (MMA-MA) V | 267 | 65 : 35 | 210.1 | 96,619 | 26,350 |
| (MMA-MPMA) II | 22440 | – | 2.5 | – | – |

Synthesis of methyl methacrylate-co-4-methoxyphenyl methacryloyloxy-(2-hydroxypropyl)oxy azobenzene polymer

The reaction scheme for the modification of polymer (MMA-MA) is shown in Figure 2.

Mixture of EPMPA and MMA-MA copolymer (1.2 : 1 by equivalent weight) were placed in a round-bottom flask fitted with a condenser, nitrogen inlet, and stirrer. *N,N*-dimethylformamide was added to prepare a 25% solution. Triphenylphosphine (1% w/w) was added as a catalyst. The reaction mixture was heated at 100°C and stirring continued for 4 h. The reaction mixture was cooled and poured into cold distilled water. The precipitate obtained was filtered and purified by repeated dissolution in chloroform followed by reprecipitation in warm *n*-hexane till the polymer was free from excess EPMPA. The polymer (MMA-MPMA), thus obtained, was dried in the vacuum oven at 60°C for 24 h.

Fabrication of sample for poling

Indium tin oxide (ITO)-coated glass (1 in. × 3 in.) with a sheet resistance of ~ 30 ohms was taken for poling studies. It was sequentially cleaned in an ultrasonic bath using water and methanol. The NLO polymer solution (3%) in THF was filtered and then spin-coated (at a rotation speed of 1200 rpm for 60 s) on the ITO glass to obtain a thin NLO polymer layer. This was then dried at 60°C for 1 h.

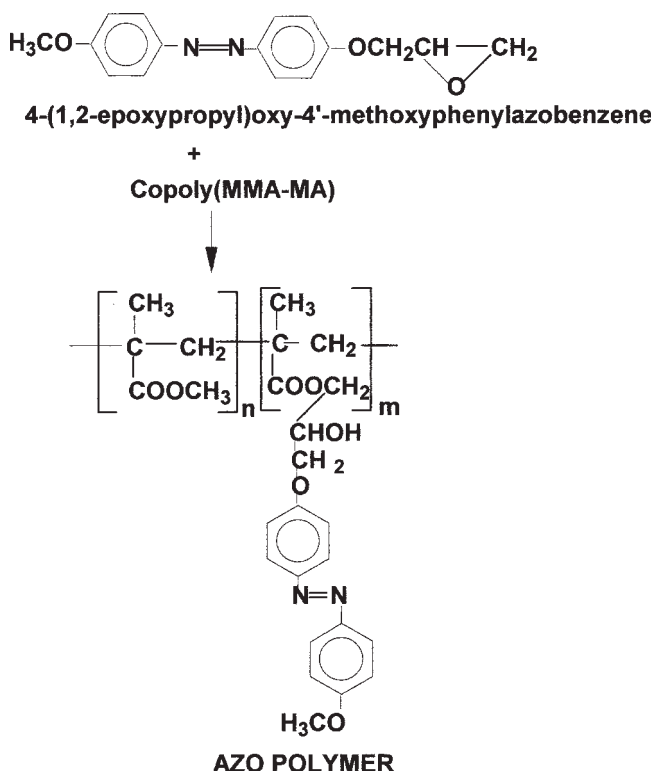


Figure 2 Reaction scheme for modification of polymer (MMA-MA).

Characterization

Acid value/equivalent weight/molecular weight

The acid value, equivalent weight, and molecular weight of the copolymers (MMA-MA) and the azo polymer (MMA-MPMA) was determined as per the ASTM Standards²⁴ and by gel permeation chromatography using THF as eluent (flow rate 0.7 mL/min). The GPC-system was calibrated with polystyrene standards with a molecular weight range from 371 to 475,000.

Spectroscopic analysis

IR spectra were acquired on a Perkin-Elmer IR spectrometer (Model: 1650) using KBr pellet. NMR spectra were recorded on a BrukerAC200 spectrometer using CDCl_3 solvent. UV-vis analysis was carried out using UV-vis spectrophotometer Varian (Cary 500). The samples were dissolved in chloroform, placed in the UV cell at room temperature, and scanning was done in the wavelength range of 200–800 nm.

Elemental analysis

Elemental analysis was obtained by employing a CHN analyzer (Perkin-Elmer, 2400 series II) using helium as a driving gas and oxygen as a combustion gas.

Thermal analytical techniques

Thermal analytical techniques like TGA and DSC were carried out using TGA-2950 and DSC-Q100 (TA Instruments), respectively. DSC analysis was carried out by taking the sample in a sealed aluminum pan and heating under nitrogen atmosphere at a heating rate of 5°C/min.

TGA for all the samples were typically carried out from room temperature to 600°C at a heating rate of 20°C/min under a flow of nitrogen gas.

Corona poling and determination of order parameter

The NLO polymer films (coated on ITO-coated glass) were poled by application of a voltage of about 7.5 kV for 2 h at temperatures above their glass-transition temperatures.

The order parameter of a poled NLO film is defined by^{25,26}

$$\Phi = 1 \frac{A_2}{A_1}$$

where A_2 = absorbance of the poled polymer films and A_1 = absorbance of the unpoled polymer films.

The order parameters of the final polymer films were calculated from the UV absorption spectra at 359 nm.

RESULTS AND DISCUSSION

Synthesizing high molecular weight NLO polymer is difficult by free radical polymerization method. Simple polymerization or even copolymerization of the azo monomer with conventional monomers does not yield high molecular weight polymers. Mostly molecular weight remains on the lower side. It is expected that if the molecular weight of the NLO polymer is sufficiently high, the properties can be enhanced. Therefore, we first synthesized a high molecular weight functional polymer and then incorporated the azo monomer through the reaction of side groups. Thus, this method uses a high molecular weight functional polymer, which is then derivatized to arrive at the NLO polymer. This technique has a distinct advantage over the conventional method of copolymerization as the molecular weight built up will not remain a problem any more. Further, a crosslinking moiety can also be attached as side group for making the system thermoset. Also, the molecular mobility is restricted, which leads to increased stability.²⁷ Further, concentration of the NLO moiety in the functionalized polymer can be varied as per requirement. Of course, the processing of the high molecular weight polymer, to make a film with acceptable optical quality, should be experimentally viable. The functionalized systems usually show excellent film homogeneity and optical clarity.

Synthesis

Introduction of epoxy group to the azo moiety was done using epichlorohydrin. Excess of epichlorohydrin was used to ensure completion of reaction. The liberated HCl (by reaction of —OH of azo molecule with Cl of epichlorohydrin) was removed by reaction with excess NaOH solution. Aqueous NaOH thus acts both as a medium to dissolve the reactants and carry out the reaction as well as an HCl eliminator. A fairly high yield of the product was obtained.

Copolymer MMA-MA contains carboxyl group. This has been selected as the base polymer and the epoxy function of the azo monomer has been attached to the carboxyl group as has been utilized by Ratna et al. for modification of epoxy resins.^{28,29} This route is more convenient compared to standard esterification route.

Chemical analysis

Acid values of copolymers MMA-MA and MMA-MPMA are given in Table I. As expected, there is a

gradual increase of acid value as the ratio of MMA : MA increases.

The final polymers (MMA-MPMA) were also characterized for their acid value. One value is incorporated in the table. The value is less than 3 in all the samples.

Gel permeation chromatography

The average molecular weight of the MMA-MA copolymers obtained by gel permeation chromatography is summarized in Table I. The minimum molecular weight (M_w) obtained was 0.56×10^5 for polymer I and the maximum was 1.6×10^5 for polymer II.

As observed, the molecular weight is quite high (of the order of 10^5) in all the samples. The relaxation of the oriented dipoles is expected to be minimum for this polymer.

Elemental analysis

The purity of the final azo copolymers was determined from elemental analysis. The results are summarized in Table II. Theoretical values are presented within brackets. The obtained values match with the theoretical values showing acceptable extent of reaction.

FTIR spectra

Figure 3 shows the characteristic FTIR spectra of EMPMA, and copolymers MMA-MA and MMA-MPMA. In Figure 3(a) (FTIR spectra of EMPMA), the —N=N— (azo) linkage is indicated by the peak at 1599 cm^{-1} and the —O— epoxy linkage is shown by the 839 cm^{-1} peak. The peaks at 1658 and 1731 cm^{-1} for copolymer MMA-MA [Fig. 3(b)] indicate the presence of carboxyl and ester group, respectively.

Similarly, for copolymer MMA-MPMA [Fig. 3(c)], the —N=N— (azo) linkage is indicated by the peak at 1597 cm^{-1} . The disappearance of the carboxyl peak at 1658 cm^{-1} and the epoxy peak at 839 cm^{-1}

TABLE II
Elemental Analysis Results of EPMPA, Polymer (MMA-MA), and Polymer (MMA-MPMA)

| Sample | Elemental analysis | | |
|----------------|--------------------|-----------|-----------|
| | % C | % H | % N |
| EPMPA | 65.3 (67.6) | 5.0 (5.6) | 9.5 (9.8) |
| (MMA-MA) I | 58.8 (59.6) | 7.6 (8.0) | — |
| (MMA-MPMA) I | 59.4 (60.7) | 7.3 (7.7) | 1.0 (1.2) |
| (MMA-MA) II | 57.9 (59.2) | 7.6 (7.9) | — |
| (MMA-MPMA) II | 60.5 (61.5) | 7.1 (7.3) | 2.7 (2.8) |
| (MMA-MA) III | 58.1 (58.8) | (7.7) 7.9 | — |
| (MMA-MPMA) III | 61.2 (61.9) | 6.9 (7.1) | 3.4 (3.5) |
| (MMA-MA) IV | 57.8 (58.3) | 7.6 (7.9) | — |
| (MMA-MPMA) IV | 61.2 (62.3) | 6.7 (6.9) | 4.1 (4.1) |
| (MMA-MA) V | 57.0 (57.7) | 7.7 (7.8) | — |
| (MMA-MPMA) V | 61.5 (62.8) | 4.1 (4.9) | 4.8 (5.0) |

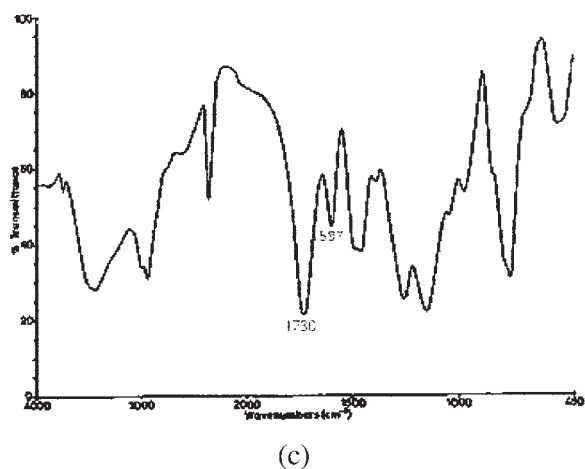
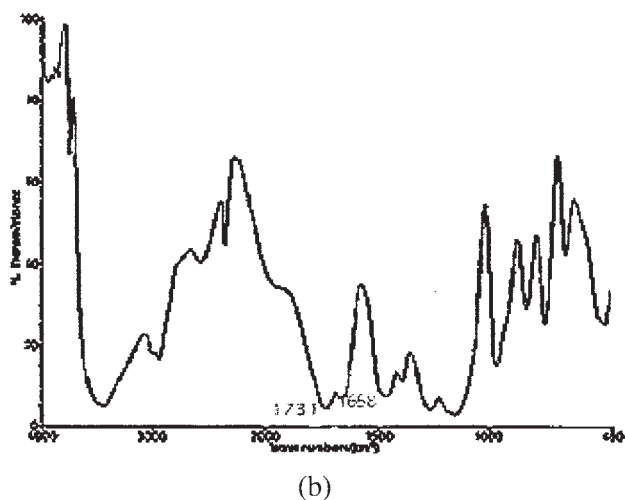
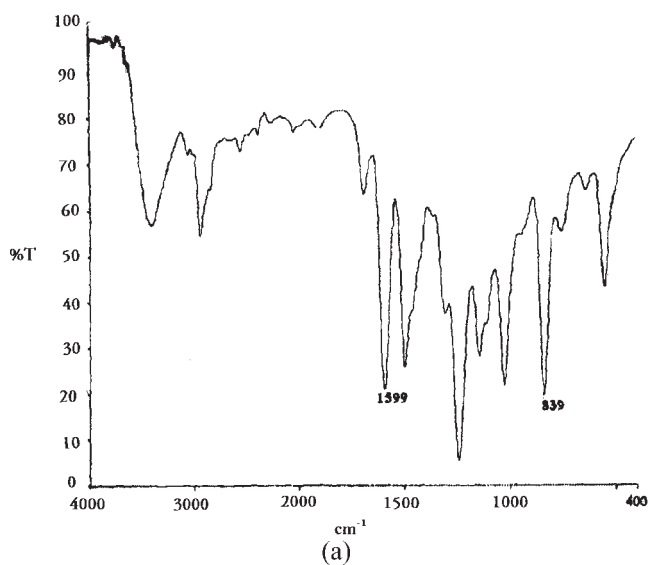


Figure 3 FTIR spectra of (a) EPMPA; (b) Polymer (MMA-MA); (c) Polymer (MMA-MPMA).

confirms the reaction of epoxy with the carboxyl group. The peak of residual carboxyl group (acid value: 2.5) is not noticed in the spectrum. The peak at 1100 cm^{-1} can be attributed to the ether linkages generated during carboxyl-epoxy reaction. The FTIR spectrum of the poled polymer was also carried out and no change was observed after poling.

NMR spectra

The ^1H NMR spectra of EPMPA, MMA-MA-III, and MMA-MPM-III are shown in Figure 4. In Figure 4(a) (EPMPA), the peaks at 2.7, 2.8, and 3.4 ppm are due to protons attached to epoxy ring. The peak at 7.2 ppm is due to solvent CDCl_3 . The peak at 3.9 ppm is due to the protons of methoxy group and doublets at 7.0 and 7.9 ppm are due to aromatic protons. In the spectra of MMA-MA-III [Fig. 4(b)], the peaks at 8, 1.2, and 1.8 ppm can be attributed to carboxyl proton, methyl proton, and methylene proton, respectively. The peak at 3.0 ppm can be assigned to protons of methyl group of ester. In case of MMA-

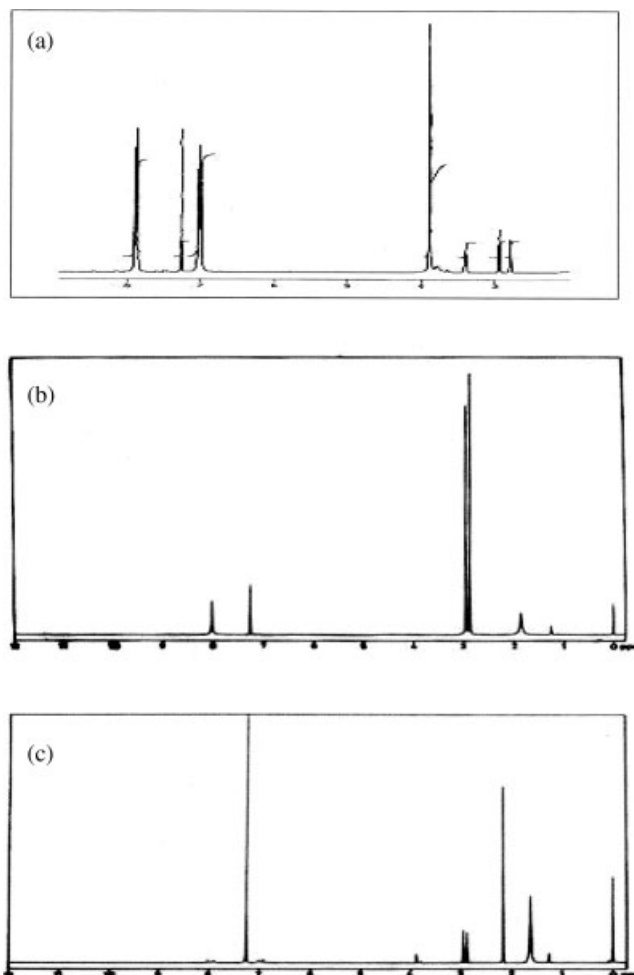


Figure 4 ^1H NMR spectra of (a) EPMPA; (b) Polymer (MMA-MA); (c) Polymer (MMA-MPMA).

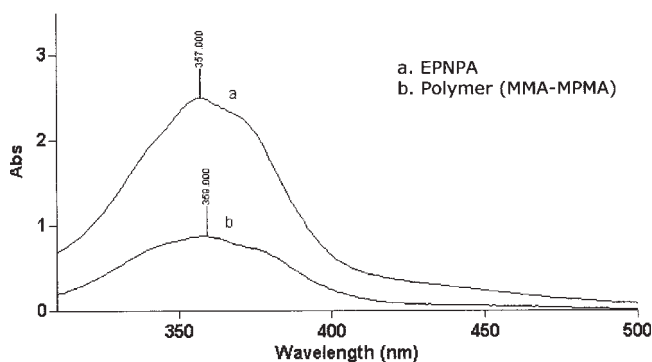


Figure 5 UV-vis spectra of (a) EPMPA; (b) Polymer (MMA-MPMA).

MPMA-III [Fig. 4(c)], the characteristic peak of carboxyl proton disappeared indicating the completion of the carboxyl-epoxy reaction.

UV-vis spectra

A representative UV-vis spectra of EPMPA and the final (MMA-MPMA) polymers is shown in Figure 5. EPMPA exhibited a UV absorption band with λ_{\max} at 357 nm because of the intramolecular charge-transfer band of the azo chromophore. All the final polymers exhibited a UV absorption band with λ_{\max} at 359 nm.

Differential scanning calorimetry

Glass transition temperature (T_g) of the polymer is a crucial factor in determining the stability of NLO property of the poled polymer. T_g of the various polymers synthesized are summarized in Table III. All the final polymers exhibited glass transition temperature between 120 and 150°C. The T_g of the copolymer MMA-MA changes after introduction of the azo moiety. In each case, the T_g of the polymer increases after modification with the azo moiety. This is due to the presence of aromatic structure in the modified polymer. T_g value above 120°C indicates that the polymers will be quite useful for offering reasonable stability to the poled dipoles.

TABLE III
Thermal Analysis Results of Polymer (MMA-MA) and Polymer (MMA-MPMA)

| Polymer number | T_g of polymer (MMA-MPMA) (°C) | Initial decomposition temperature (°C) of polymer (MMA-MPMA) |
|----------------|----------------------------------|--|
| I | 1120 (135) ^a | 172 |
| II | 147 (128) ^a | 230 |
| III | 131 (91) ^a | 181 |
| IV | 128 (104) ^a | 167 |
| V | 134 (111) ^a | 171 |

^a Indicates T_g of parent MMA-MA copolymer.

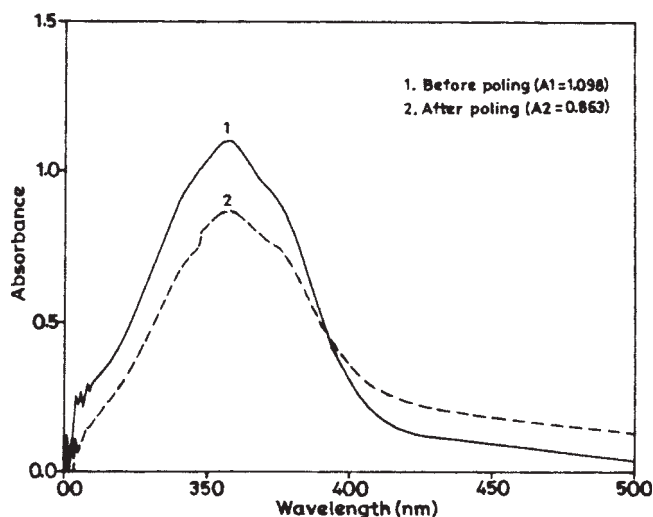


Figure 6 A typical absorbance versus wave length plot showing the change in absorbance before and after poling.

Thermogravimetric analysis

Thermal stabilities of the final five polymers were evaluated by TGA. As shown in Table III, the initial decomposition temperatures (IDT) of the final polymers lie in the range of 167–230°C. The stability is maximum for the copolymer of highest molecular weight (polymer MMA-MPMA-II). This may be due to the presence of higher number of phenyl rings of the azo moiety.

Corona poling and determination of order parameter

The order parameters of the MMA-MPMA polymer films were determined from the UV absorption spectra at 359 nm. Figure 6 shows the change in absorbance before and after poling of polymer (MMA-MPMA). As expected, the absorbance of the polymer

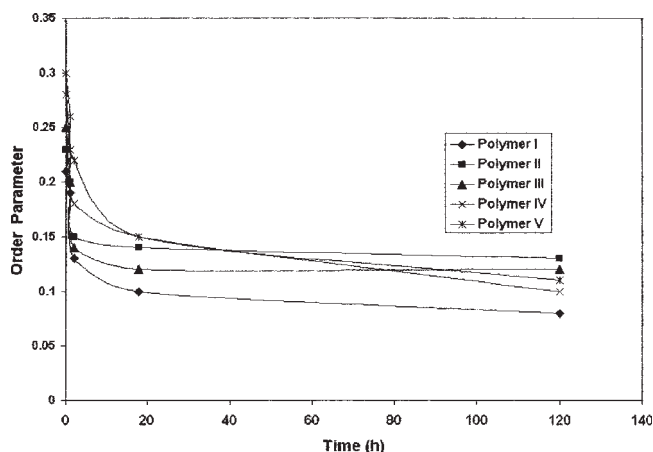


Figure 7 Variation of order parameter of the poled NLO polymers (MMA-MPMA I-V) with time at room temperature.

decreased after poling. The order parameter values for the samples were found to be in the range of 0.2–0.3. Stability of the poled polymer samples was monitored over a period of time by measuring their absorbance by UV–vis spectrophotometer. Figure 7 shows the variation of order parameter of the poled NLO polymers with time at room temperature. As expected the order parameter increases with increase of azo content. It is observed that, after an initial drop, the order parameter is stable for at least 120 h after poling. The stability of order parameter of poled polymer increases with molecular weight and maximum stability is exhibited by polymer II having highest molecular weight (M_w) of 163,201 in the series.

CONCLUSIONS

Epoxy-functionalized azo molecule was synthesized by following conventional route. A series of azo-based NLO polymers were successfully designed and synthesized by modification of functional polymer of desired molecular weight. The yield was found to be satisfactory in each step.

FTIR and NMR spectra have shown that the desired copolymer was formed via polymer modification. DSC data shows that the T_g of the polymers lie in the temperature range between 120 and 150°C. The polymers were found to be stable for a long time after poling. The maximum stability was observed for highest molecular weight polymer. The polymers are easily soluble in common solvents like chloroform, tetrahydrofuran, *N,N*-dimethylformamide, etc. and also show good optical quality and film-forming ability.

This approach can be utilized for synthesizing high molecular weight NLO polymer with varying molecular structure and functionality. If suitably designed, possibility for crosslinking during poling via introduced groups will be an added advantage.

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