

Synthesis and Characterization of Azo-Based Methacrylate Polymers with Methoxy and Nitro End Groups for Nonlinear Optical Applications

K. Sadagopan, A. S. Rekha, D. Ratna, A. B. Samui

Naval Materials Research Laboratory, Ambernath 421506, Maharashtra, India

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ABSTRACT: One new and three already described azo-based methacrylate monomers with methoxy and nitro end groups and spacer length 2 and 6 were synthesized. These monomers were copolymerized with methyl methacrylate and the monomers as well as copolymers were characterized by classical spectroscopy techniques (FTIR, NMR, and UV-VIS), gel permeation chromatography (GPC), elemental analysis and thermal analysis (TGA and DSC). The glass transition temperature of the polymers was found to be above room temperature and thermal decomposition temperatures above 100°C. All the polymers were amorphous in nature and formed excellent homogeneous films

with good optical transparency. The polymer films coated on indium tin oxide glass slides were poled and their order parameters were calculated to check the stability of oriented dipoles. Few samples were also studied for their second harmonic generation properties. Temporal stability, checked up to 120 h at room temperature, was found to be quite satisfactory. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 3497–3504, 2007

Key words: nonlinear optical (NLO) polymer; order parameter; azo-based polymer; second harmonic generation

INTRODUCTION

There has been a considerable interest in the synthesis and characterization of second-order nonlinear optical (NLO) polymers due to their potential applications in photonic devices. These applications include frequency doubling, light modulation, optical switching, information storage, etc.¹ Azobenzene based NLO polymers have drawn considerable attraction because of their optical properties that allow various applications triggered by light.^{2–6} Conventionally, NLO chromophores were physically blended with glassy polymer hosts.^{7,8} The drawbacks of such guest-host systems are limited solubility of dopant (resulting in phase separation), loss of orientation, and poor temporal stability of poled films.

Polymeric systems where chromophores are covalently attached to polymer backbone were found to have advantages over such chromophore dispersed polymer blends.⁹ In such azo polymers, the chromophore consisting of a donor and acceptor groups linked by a π -electron unit is attached to the polymer backbone via methylene units (spacer). The ability of the chromophoric side chain to align in a

noncentrosymmetric fashion under dc-field (poling) gives the property of second-order NLO response to these polymers. The challenge in designing such NLO materials is to attain high stability of the aligned dipoles after removal of the external field. Also, the NLO polymers should be easy to process (solubility in common solvents) and should have good optical transparency and thermal stability. Other factors of particular importance are the intrinsic NLO activity of the chromophore, the strength of donor and acceptor groups, and the length of spacer joining the chromophore to the polymer backbone. It has been observed that though longer flexible chains help in the alignment of chromophores during poling, they reduce the temporal stability of the poled NLO polymer.¹⁰

In the journey of making high efficient NLO azo polymers, several efforts were made in tailoring these polymers with efficient chromophores, strong donor-acceptor groups, etc. by various researchers viz. Ho et al.,¹¹ Meyers et al.,¹² Vohra et al.,¹³ Yu Sui et al.,¹⁴ Beltrani et al.¹⁰

Also several studies have shown that the fast relaxation behavior of poled NLO polymers could be controlled to a better extent by either crosslinking^{15–17} the aligned dipoles during poling or by interpenetrating networks.^{18–22}

A great number of reports is available on synthesis and characterization of azo containing monomers and copolymers.^{23–29} The reports cover both

Correspondence to: A. B. Samui (asit_samui@rediffmail.com).

physically mixed azo compounds, as well as, chemically attached azo functionality. A good number of reports are concentrated on liquid crystalline photoactive polymers, particularly on synthesis and LC properties.^{27,30–32} The most important functionality responsible for NLO activity is the azo group. Over the years, efforts were made to incorporate thermal and temporal stability and enhance molecular hyperpolarizability by varying the chromophore, end group, and spacers.^{33,34} A detailed study is must for understanding the inherent characteristics of methacrylate copolymers containing azo functionality in terms of NLO characteristics. Our literature search did not notice any detailed report on study of azo containing methacrylate copolymers having methoxy/nitro end group for its NLO properties.

In this article, we report the synthesis, characterization, and NLO response of azo/methacrylate copolymers containing methoxy and nitro end groups of spacer lengths 2 and 6. Attempt is made to analyze the effect of spacer length and end group on thermal stability and NLO activity. We also report here the order parameter to get first hand information about the stability of poled NLO polymer films.

EXPERIMENTAL

Materials

4-Nitroaniline, 2-chloroethanol, 1-chloro-6-hydroxyhexane, and methacryloyl chloride (ACROS Organics, Belgium), *p*-anisidine (MERCK Schuchard, Germany) were used as received. Phenol, and Triethylamine (Analytical Grade) obtained from sdfine Chemicals, India, were freshly distilled before use. All solvents (AR) were distilled before use. Other chemicals were of analytical grade and used as received.

Synthesis

Synthesis of the azo/methacrylate copolymers were done in three steps following the method of Suk et al.²³ as given in Figure 1.

Step I: Synthesis of 4-methoxy-4'-hydroxyphenylazobenzene (AzoOMe)/4-nitro-4'-hydroxyphenylazobenzene (AzoNO₂)

p-Anisidine (10 g, 0.081 mol)/4-nitroaniline (11.2 g, 0.081 mol) were dissolved in 50 mL of concentrated hydrochloric acid and 20 mL of water was added to it. The resulting solution was stirred for half an hour at room temperature and then cooled to 0°C. To this cooled solution, sodium nitrite (10 g, 0.145 mol) dissolved in 15 mL ice water was slowly added

by maintaining the temperature in the range 0–5°C. After the addition was over, the resulting mixture was stirred for half an hour and slowly added to phenol (11.2 g, 0.12 mol) in sodium hydroxide solution (15 g, 0.375 mol in 30 mL water) at 10–15°C. The solution was stirred at 0°C for 2 h. The solution was then acidified and the precipitated product was filtered, dried, and recrystallized twice from ethanol solution (Ethanol:water = 2 : 1, v/v).

Yield: AzoOMe: 45% (mp: 128.4°C)

AzoNO₂: 45% (mp: 213.6°C)

Synthesis of 4-hydroxyhexyloxy-4'-methoxyphenylazobenzene (Azo6OMe)/4-hydroxyhexyloxy-4'-nitrophenylazobenzene (Azo6NO₂)/4-hydroxyethoxy-4'-methoxyphenylazobenzene (Azo2OMe)/4-hydroxyethoxy-4'-nitrophenylazobenzene (Azo2NO₂)

To 11.1 g of AzoOMe/12.15 g of AzoNO₂ (0.05 mol) in 100 mL of DMF was added 13.8 g (0.1 mol) of anhydrous potassium carbonate and 0.5 g of potassium iodide. The resulting mixture was stirred for half an hour at 100°C. To this 10.25 g of 6-chloro-1-hexanol (0.075 mol) was added drop-wise and the stirring was continued. The completion of the reaction was checked by thin layer chromatography using ethyl acetate, hexane mixture (1 : 1.5 v/v) as eluant. The reaction was continued for 24 h. After cooling to room temperature, the reaction mixture was poured in to 1.2 L of ice water under stirring. The precipitated product was filtered, dried, and recrystallized twice from ethanol.

Yield: Azo6OMe: 65% (mp: 117.6°C)

Azo6NO₂: 68% (mp: 127.9°C)

4-hydroxyethoxy-4'-methoxyphenylazobenzene (Azo2OMe) and 4-hydroxyethoxy-4'-nitrophenylazobenzene (Azo2NO₂) were synthesized in the same way as described above; the reaction duration was 48 h.

Yield: Azo2OMe: 60% (mp: 135.0°C)

Azo2NO₂: 65% (mp: 188.4°C)

Synthesis of 4-methacryloyloxyhexyloxy-4'-methoxyphenylazobenzene (M6OMe)/4-methacryloyloxyhexyloxy-4'-nitrophenylazobenzene (M6NO₂)

To 6.6 g of Azo6OMe/6.9 g of Azo6NO₂ (0.02 mol) in 50 mL of tetrahydrofuran (THF) was added 2.43 g of triethylamine (0.024 mol) and 0.5 g of hydroquinone. To the solution, 2.5 g of methacryloyl chloride (0.024 mol) in 10 mL of THF was added drop-wise under nitrogen atmosphere. The resulting solution was stirred for 20 h at room temperature. (The completion of the reaction was checked by TLC using

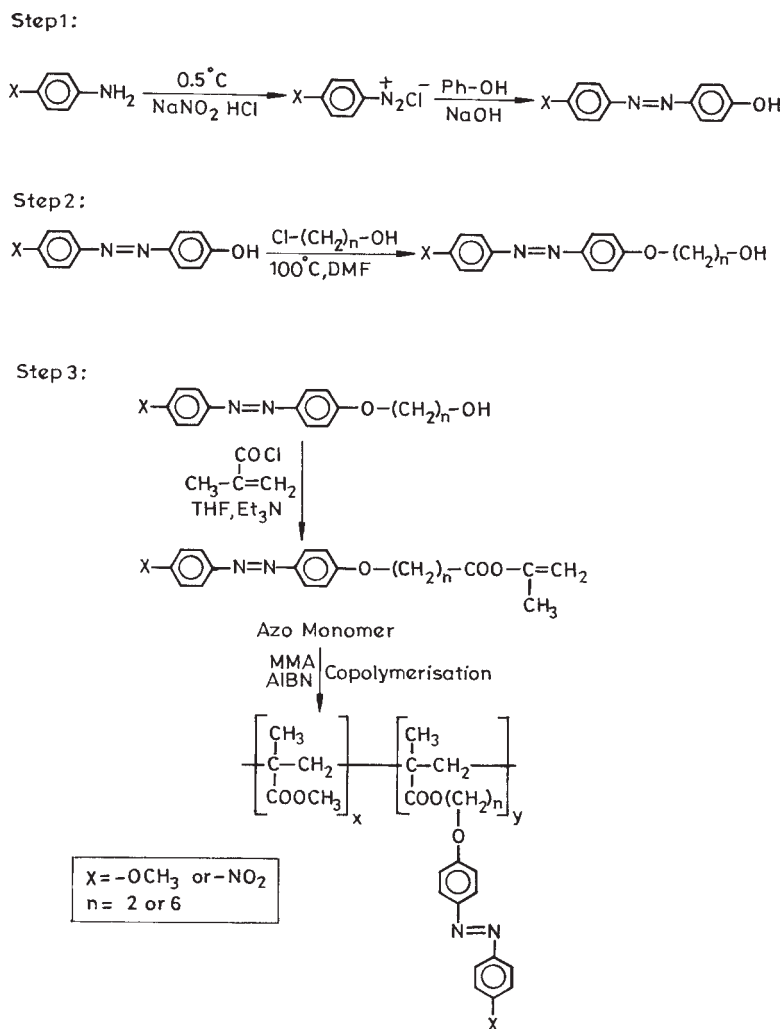


Figure 1 Copolymer synthetic scheme (3 steps).

ethyl acetate, hexane mixture (1 : 1.5, v/v as eluant.) The reaction mixture was cooled, excess chloroform was added, and washed several times with distilled water. The organic layer was separated and dried over anhydrous sodium sulfate. The solvent was evaporated under vacuum and the obtained residue was recrystallized from ethanol/chloroform mixture (1 : 1.5, v/v).

M6OMe: Yield: 30%; mp: 70.5°C; λ_{max} : 354 nm; FTIR (cm^{-1}): 1498 (ν N=N), 1737 (ν C=O), 1597 (ν_{arom} C=C), 1656 (ν_{alif} C=C), 2935, 2860 (ν_{alif} C-H), 1251 (ν C-O-C).

M6NO₂: Yield: 40%; mp: 105.9°C; λ_{max} : 376 nm; FTIR (cm^{-1}): 1507, 1339 (ν -NO₂), 1715 (ν C=O), 1593 (ν_{arom} C=C), 1665 (ν_{alif} C=C), 2940, 2864 (ν_{alif} C-H).

The monomers 4-methacryloyloxyethoxy-4'-methoxyphenylazobenzene (M2OMe) and 4-methacryloyloxyethoxy-4'-nitrophenylazobenzene (M2NO₂) were synthesized in the same way as described earlier.

M2OMe: Yield: 35%; mp: 60.2°C; λ_{max} : 364 nm; FTIR (cm^{-1}): 1499 (ν N=N), 1726 (ν C=O), 1596

(ν_{arom} C=C), 1666 (ν_{alif} C=C), 2929, 2863 (ν_{alif} C-H), 1252 (ν C-O-C).

M2NO₂: Yield: 38%; mp: 140.5°C; λ_{max} : 372 nm; FTIR (cm^{-1}): 1519, 1342 (ν -NO₂), 1716 (ν C=O), 1597 (ν_{arom} C=C), 1663 (ν_{alif} C=C), 2932, 2864 (ν_{alif} C-H).

Synthesis of azomethyl methacrylate copolymers

All the four monomers were copolymerized with methyl methacrylate (1 : 1, mol : mol).

A representative procedure of copolymerization of M6OMe with MMA is as follows :

One gram (0.0025 mol) of M6OMe and 0.25 g (0.0025 mol) of MMA were taken in an ampule. *N,N*-dimethylformamide was added to prepare a 25% solution. 1% (w/w) of AIBN was added as initiator. The resulting solution was degassed 5 times by freeze-thaw cycle and sealed under vacuum. The polymerization was carried out at 70°C for 48 h. The solution was then poured into 200 mL of methanol.

The precipitated polymer (P6OMe) was filtered and purified by repeated dissolution/precipitation using chloroform/warm *n*-hexane till the polymer was free from excess monomer. The pure polymer (P6OMe), thus obtained, was dried in the vacuum oven at 60°C for 24 h.

The other three copolymers P6NO₂, P2OMe, and P2NO₂ were also synthesized by following similar procedure. The yield was around 75–85% in all cases.

Characterization

Numerical average molecular weight of the copolymers was determined by gel permeation chromatography (GPC) 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 475000 Da.

IR spectra were acquired on a Perkin–Elmer IR spectrometer (Model : 1650) using KBr pellet. ¹H and ¹³C-NMR spectra were recorded on a 500 MHz FT-NMR instrument (Bruker Avance-500) with deuterated chloroform as solvent for P2OMe, P6OMe and P2NO₂, and dimethylsulfoxide in the case of P6NO₂. The solvent peaks in the obtained spectrum were used to calibrate the spectrum. 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 done in the wavelength range of 200–800 nm.

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 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 ambient temperature to 600°C at a heating rate of 20°C/min under a flow of nitrogen gas.

Indium tin oxide (ITO)-coated glass (1" × 3") 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 8 h. 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^{35,36}

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

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

The order parameters of the final polymer films were calculated from the UV absorption spectra at their respective λ_{max} values.

The second-order NLO properties of the poled polymer films (spun cast on ITO-coated glass) were studied by using a polarized Q-switched Nd : YAG laser beam of wavelength 1064 nm with a pulse width of 10 ns and a frequency of 20 Hz. The samples were mounted on a rotational stage that could be rotated around an axis perpendicular to the surface. The laser beam after passing through the polymer film was blocked by a 532 nm interference filter. The SHG signal was detected by a photomultiplier tube, amplified and then averaged with a boxcar integrator. The relaxation pattern (decrease in SHG signal) was also studied with time at room temperatures.

RESULTS AND DISCUSSION

In the present study, it has been planned that a series of copolymers (containing azo comonomer) will be synthesized with varying other comonomers and attachment of some other functionality so that cross-linking can be achieved during poling. This report is first in the series. Attempts have been made to concentrate on the synthesis and characterization of copolymers made from simple azo monomers and methyl methacrylate.

Detailed report on synthesis of copolymer of methyl methacrylate and azo containing methacrylate having NLO properties is not available in literature. Although, quite a good number of NLO polymers having various chromophores other than azo have been reported, it is believed that with suitable selection of azo molecule, stable NLO polymer can be made. In the present study, azo polymers have been synthesized and NLO properties evaluated. Two types of end group such as methoxy and nitro were introduced in the azo molecule. As spacer length plays an important role in deciding the thermal property, ease of poling, and stability of poled polymer, we have selected two spacer lengths—2 and 6. The database can be utilized to develop azo copolymers with better stability in the poled state.

The azo monomers were synthesized following conventional methods of etherification (for attachment of spacer) and vinyl group attachment (reaction of methacryloyl chloride with hydroxyl

TABLE I
Elemental Analysis and Gel Permeation Chromatography Results and the Mole Ratio of MMA and Azo Monomer in the Copolymers

Polymer	C (%)	H (%)	N (%)	Azo monomer:	
				MMA	Mole ratio
P6NO ₂	63.79	5.79	7.34	0.6 : 1	19545
P2NO ₂	60.57	5.08	8.74	0.8 : 1	13436
P6OMe	65.6	6.86	5.6	1 : 1	26981
P2OMe	64.27	6.01	6.17	0.9 : 1	8396

terminated azobenzene compounds to yield the monomers). All the monomers showed good solubility in common organic solvents like chloroform, THF, DMF, etc.

The monomers were copolymerized with MMA using AIBN as initiator by radical polymerization in DMF solvent. The polymerization was completed after 48 h with good yields. All the synthesized copolymers except P6NO₂ were soluble in common organic solvents like chloroform, THF, etc.; P6NO₂ was found to be sparingly soluble in these solvents at room temperature. It was readily soluble in *N,N*-dimethylformamide and dimethylsulphoxide. All the copolymers formed thin homogeneous films of good optical quality when spun coat on glass slides.

The monomers show a λ_{\max} of around 355–360 nm for the methoxy-terminated azo molecules and around 370–377 nm for the nitro-terminated azo molecules. The structure of the monomers were confirmed by FTIR from the appearance of vinylic stretching and ester bands in all the monomers. This was further confirmed by the NMR spectra. The vinylic proton peaks were observed at around 5.5 and 6.1 ppm in the ¹H-NMR spectrum and at around 162 ppm in ¹³C-NMR spectrum. The purity of the azo monomers was established by elemental analysis. The obtained values match with the theoretical values showing acceptable purity of the monomers.

The FTIR spectra of the monomers and the polymers were compared for confirmation of complete polymerization. Most of the IR bands of the monomers, except the vinyl band at 1660–1650 cm⁻¹, remain unchanged upon polymerization. The band disappeared due to copolymer formation. The FTIR spectrum of the poled polymer was also carried out and no change was observed after poling.

The ratio of the azo monomer and MMA in the copolymers was determined from elemental analysis. The results are summarized in Table I. The feed ratio in each case was maintained at 1 : 1 (mol/mol). The ratio of the monomers in the copolymer was found to be in the range of 0.6 : 1–1 : 1 (mol/mol).

The number average molecular weight of the copolymers obtained by GPC is summarized in Table I. The molecular weight lies in the range of 8000–27,000 Da.

¹H-NMR and ¹³C-NMR spectral data of the polymers are given in Table II. The vinylic proton observed in ¹H-NMR of the monomers (5.55 ppm, s and 6.10 ppm, s) disappeared in case of the polymers. In the ¹³C-NMR spectra of the polymers, an additional peak at 177 ppm is observed besides that already present in the monomers at 162 ppm. This additional peak at 177 ppm can be attributed to the ester linkage of MMA; the 162 ppm peak was attributed to the ester group of the azo monomer.

The λ_{\max} of the polymers P2OMe and P6OMe are around 355–360 nm and of P2NO₂ and P6NO₂ are around 370–377 nm. The λ_{\max} values for the polymers are summarized in Table IV. This observed λ_{\max} is because of the intramolecular charge-transfer band of the azo chromophore. The bathochromic shift in λ_{\max} of the nitro compounds can be attributed to the increased conjugation due to the presence of nitro end group.

The DSC and TGA results for all the four polymers are summarized in Table III. From the DSC

TABLE II
NMR Data of the Copolymers

Polymer series	Chemical shift values (in delta scale)
P2OMe	¹ H-NMR: 1.02 (s), 1.25 (s), 1.55 (s), 3.50(s), 3.55 (s), 3.83 (s), 3.88 (s), 6.99 (m, aromatic, 4H), 7.86 (m, aromatic, 4H), 7.25 (CDCl ₃); ¹³ C-NMR: 16.66, 18.1, 18.8 (–CH ₃), 24.7, 25.4 (–CH ₂ –), 44.64, 44.95 (quaternary carbon), 51.75, 54.4, 55.5 (–CH ₂ –O–), 63.2, 66.0 (Ph–O–CH ₂ –), 114.2, 114.8, 120.9 (aromatic), 160.3, 161.7, 177.7, 178.0 (ester groups), 7.0 (CDCl ₃)
P6OMe	¹ H-NMR: 0.85 (s, 3H), 1.01 (s, 3H), 1.22 (s, 3H), 1.47 (s, 3H), 1.82 (m, 8H), 3.67 (t, 2H), 4.04 (t, 2H), 6.99 (m, aromatic, 4H), 7.86 (m, aromatic, 4H); ¹³ C-NMR: 16.5, 18.0, 18.7 (–CH ₃), 25.5, 25.9, 28.07, 28.5, 29.2 (–CH ₂ –), 44.6, 44.9 (quaternary carbon), 51.7, 54.4 (–CH ₂ –O–), 62.9, 65.0, 68.2 (Ph–O–CH ₂ –), 114.2, 114.7, 124.3, 125.9 (aromatic), 161.1, 161.6, 177.8 (ester groups), 77.0 (CDCl ₃)
P2NO ₂	¹ H-NMR: 1.03 (s), 1.25 (s), 3.5 (s), 3.6 (s), 4.25 (s), 4.32 (s), 6.99 (m, aromatic, 4H), 7.9 (m, aromatic, 4H), 7.25 (CDCl ₃); ¹³ C-NMR: 16.64 (–CH ₃), 18.93 (–CH ₂ –), 44.7 (quaternary carbon), 51.8 (–CH ₂ –O–), 63.1, 65.6 (Ph–O–CH ₂ –), 115.0, 123.1, 124.7, 125.6 (aromatic), 162.07, 177.6, 178.0 (ester groups), 77.0 (CDCl ₃)
P6NO ₂	¹ H-NMR: 1.07 (s, 3H), 1.74 (s, 3H), 1.87 (m), 3.44 (s, 2H), 4.2 (s, 2H), 6.99 (aromatic, 2H), 7.7 (aromatic, 4H), 8.2 (aromatic, 2H), 2.5, 3.3 (DMSO)

TABLE III
Thermal Properties of the Copolymers

Polymer	T_g (°C)	Tdi (°C)
P6NO ₂	48	120
P2NO ₂	64	110
P6OMe	76	180
P2OMe	116	200

analysis of the polymers, we found that the glass transition temperatures (T_g) of the four polymers, viz. P2OMe, P6OMe, P2NO₂, P6NO₂ are 116.0, 76.3, 64.0, and 46°C, respectively. As observed, the polymers with spacer length 6 show a lower T_g than those with spacer length 2. This reduction in T_g is due to the plasticizing effect of the longer spacer on the polymer chain. The T_g of all the polymers are well above room temperature.

From the TGA analysis of the polymers (Table III), it was observed that the initial decomposition temperature of all the polymers lies above 100°C. This result ensures reasonable thermal stability of the copolymers.

The order parameters of the final polymer films were calculated from the UV absorption spectra at their respective λ_{\max} values. Figure 2 is a representative plot of the change in absorbance before and after poling of polymer P6OMe. The corresponding data for all the other polymers are given in Table IV. As expected, the absorbance of the polymer decreased after poling. Polymer P6NO₂ showed the highest order parameter value of 0.39. This can be attributed to two reasons: the ease of alignment of the dipoles due to increased spacer length and the strong electron withdrawing nature of the —NO₂ group leading to a good donor–acceptor combination across the conjugated π bond system. P6NO₂ is therefore expected to show maximum SHG. Polymer P2OMe showed the least order parameter value of 0.02.

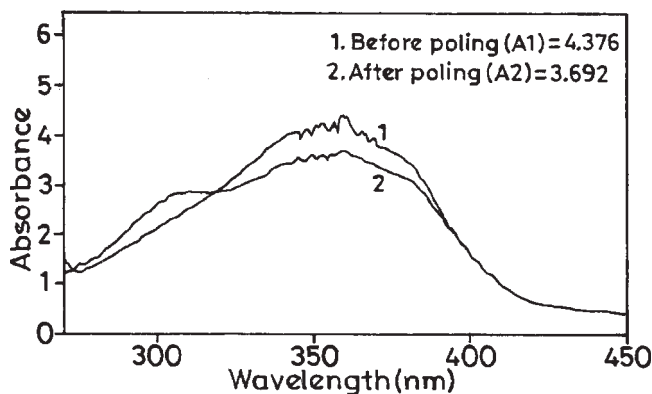


Figure 2 Plot of the change in absorbance before and after poling of polymer P6OMe.

TABLE IV
UV-VIS Data, Change in Absorbance (After Poling), and Order Parameter Values of the Copolymers

Polymer	λ_{\max} (nm)	Absorbance		Order parameter
		Before poling	After poling	
P6NO ₂	377	2.202	1.325	0.39
P2NO ₂	370	3.971	3.381	0.15
P6OMe	360	4.376	3.692	0.16
P2OMe	356	1.479	1.449	0.02

Stability of the poled polymer samples was monitored over a period of time by measuring their absorbance by UV-VIS spectrophotometer. Figure 3 shows the variation of order parameter of the poled NLO polymer (P6OMe) with time at room temperature. After an initial drop, the order parameter is stable for at least 100 h after poling.

The second harmonic generation (SHG) signal intensity of the polymer films were measured after poling. A representative plot of the observed SHG signal (au) versus temperature (for polymer P6NO₂) is shown in Figure 4. As expected, polymer P6NO₂ showed high SHG intensity. This is because of the high difference in the dipole moment between the donor and acceptor groups of the azo moiety in this polymer. Also a spacer length of 6 makes the polymer molecule more flexible allowing better orientation of the dipoles on poling. Both these factors contribute to the high SHG signal intensity shown by P6NO₂. P2NO₂ also showed good SHG signal though not as high as that for P6NO₂. However, the temporal stability of P6NO₂ was found to be on the lower side. As shown in Figure 5, the SHG signal shows an initial dip within 200 min and then remains constant to above 3000 min. This is probably because of the low glass transition temperature of the polymer, which allows faster relaxation of the poled dipoles. The effort to improve the temporal stability by introducing crosslinking is in progress and will be presented in a later communication.

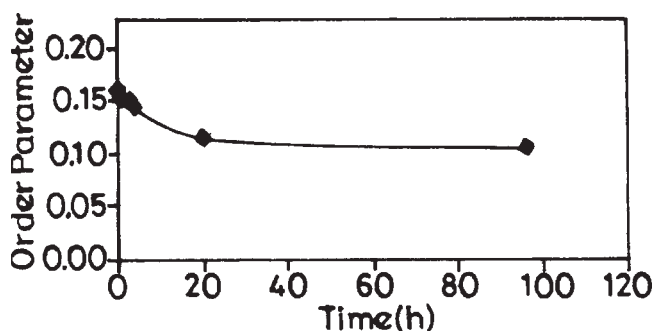


Figure 3 Variation of order parameter of the poled NLO polymer (P6OMe) with time at room temperature.

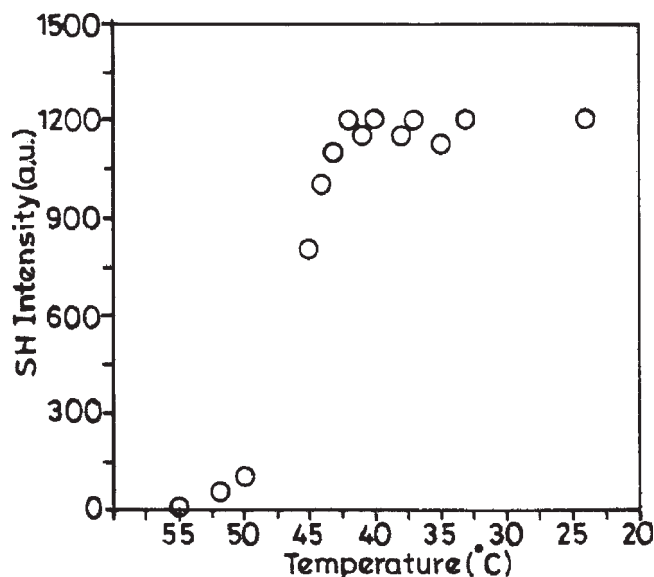


Figure 4 Plot of the observed SHG signal (au) versus temperature (for polymer P6NO₂).

CONCLUSIONS

Azo-based vinyl monomers were synthesized by following conventional route. A series of azobased methacrylate NLO polymers were designed and synthesized by radical copolymerization reaction. The yield was found to be satisfactory in each step.

FTIR and NMR spectra have shown that the desired copolymer was formed as expected. DSC data shows the T_g of the polymers lie in the temperature range of 50–120°C, i.e., well above room temperatures. The initial decomposition temperatures of the polymers lie above 110°C, which indicates that the synthesized polymers are thermally quite stable. The polymers showed fairly high SHG signal intensity and were found to be stable for a long time after

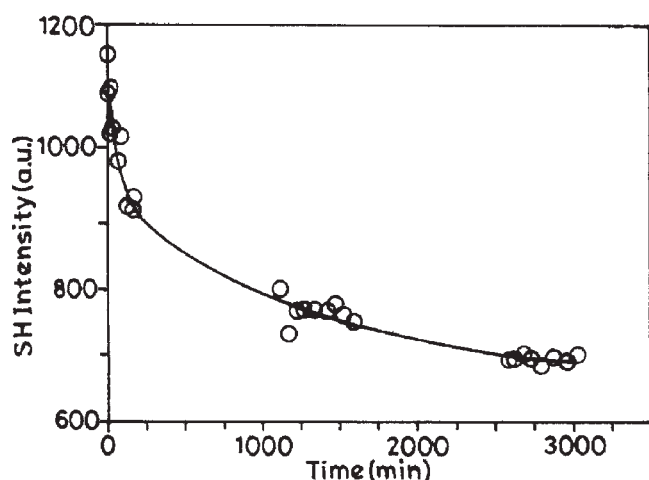


Figure 5 Plot of change in SHG signal versus time at room temperature.

poling. The polymers are easily soluble in common solvents like chloroform, THF, *N,N*-dimethylformamide, etc. and also show good optical quality and film-forming ability.

The attachment of reactive groups for crosslinking (for increased temporal stability) will be reported in a latter communication.

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