

# Azo-naphthol dyes based polymethacrylate films and their substituent effects in the holography investigations

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A new series of azo-naphthol dye based poly(alkyloxymethacrylate)s with various electron withdrawing and donating substituents in the aromatic ring were synthesized for holographic grating formation studies. These polymers were characterized by UV, IR, <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectroscopy. The photoisomerization studies were performed for all the polymers. The glass transition temperature and thermal stability of the polymers were investigated by DSC and TGA respectively. The optical characterization of the polymers was investigated using Nd-YAG laser. The diffraction grating efficiency was found to depend on the time of exposure and intensity ratio of the incident beam.

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## 1. Introduction

The promising development in optoelectronics has greatly increased the demand for new nonlinear optical materials in recent years. In this regard, organic materials are most attractive owing to the known rich variety of organic compounds and the inherent flexibility in synthesizing such compounds with desired properties [1]. Organic materials offer advantages of large susceptibilities, high laser damage threshold, faster response time and versatility of molecular structural modifications [2-4]. Aromatic azo groups serve as the parent molecule to a wide range of dyes, indicators and nonlinear optic chromophores. The absorption maxima strongly depends on ring substituents and can be tailored to absorb anywhere from the UV to visible region [5]. Azo polymers are interesting due to their photoresponsive behavior which can be utilized in optical switches, optical data recording or optical information storage [6, 7]. Although great efforts have been extended on the investigation of the relationships that exist between the molecular structure of an organic material and the resulting third order nonlinearities, the understanding of these dependences is scarce. The study of linear and NLO coefficients is fundamental for increasing the ability to tune NLO properties by appropriate design of organic systems at the molecular level. The structure of the azo chromophore ascertains some properties such as the absorption maxima and the *cis-trans* isomerization rate, as well as the orientation ability. It has been reported that large surface modulations can be reversibly photo induced on surfaces of azo polymer films [8-10]. The photo induced surface-relief-gratings (SRGs) are formed upon exposure to an interference pattern of Ar ion laser beams at modest intensities [11]. The surface relief structures formed are stable below the glass transition temperatures (Tg's) of the polymers and can be removed by heating

samples to their Tg's or erased optically even below the Tg's [12,13].

The aim of the present investigation is to synthesize photo addressable polymers for holographic grating formation studies. To achieve this, azo dyes with various substituents like electron withdrawing, electron donating and unsubstituted one were synthesized by coupling with 1-naphthol. On the other hand, p-hydroxybenzoic acid (HBA) was alkylated and consequently methacrylated with methacrylic acid. The monomers were prepared by coupling the substituted and unsubstituted p-phenylazo- $\alpha$ -naphthol and the p-HBA analogue, and were polymerized using free-radical polymerization technique. Due to the highly asymmetric nature of this polymer structure and high conjugation in the backbone, they are anticipated to be nonlinear materials suitable for optical storage applications. The synthetic method and characterization of monomers/polymers using various spectroscopic techniques, thermal and optical studies are discussed.

## 2. Experimental

### 2.1. Materials

$\alpha$ -Naphthol, benzene, acetone, chloroform, dichloromethane, N, N'-dimethyl formamide, ethanol, methanol and tetrahydrofuran were purified by the usual procedure and dried before use [14]. HBr 47% (SRL), 1, 6-hexanediol (Merck), triethylamine (SD fine) were distilled before use. p-Hydroxybenzoic acid (SRL), aniline (Spectrochem), 4-nitroaniline (Merck), 4-aminobenzonitrile (Aldrich), 4-chloroaniline (Merck), 4-bromoaniline (Spectrochem), 4-fluoroaniline (Spectrochem), 4-iodoaniline (Fluka) p-anisidine (SD fine), 4-aminobenzonitrile (Aldrich) and p-toluidine (Merck) were used as received. Silica gel (60-120 mesh,

SRL) was dried in an oven at 110°C for 1 h and cooled in a desiccator before use. 2, 2'-Azobis(isobutyronitrile) (AIBN) was used after recrystallization in chloroform-methanol (1:1). 6-Bromohexanol was prepared following procedure reported elsewhere [14].

## 2.2. Measurements

Infrared spectra were recorded on a Nicolet IR (Impact 440) spectrophotometer using KBr pellets. High-resolution <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were recorded on a Bruker spectrometer (300 and 75.4 MHz, respectively). Deuterated DMSO was used as a solvent for <sup>1</sup>H-NMR spectra, unless otherwise mentioned. The photoisomerization studies of the polymers were carried out by UV irradiation between 240-600nm wavelengths. Trans-cis photochemical isomerization of polymers was investigated by irradiating with Spectroline (New York) low-pressure mercury pencil lamp in a spin-coated quartz plate for 1 min and the UV absorption measured immediately on a Shimadzu UV-260 spectrophotometer. The experiment was repeated until no change in absorbance. TGA and DSC studies were carried out on a Mettler Toledo STAR<sup>c</sup> system under nitrogen atmosphere. The heating rate of TGA analysis was performed at 20°C min<sup>-1</sup> with a nitrogen flow of 20mL min<sup>-1</sup>. The optical set-up for recording the grating in the polymer film samples is explained as follows. The beam from an Nd-YAG laser output wavelength 532 nm was used to record the grating. The beam from the laser was split into two beams of equal intensity using a dielectric coated beam splitter and they were allowed to interfere. The interfering angle was adjusted to 10 degrees. The polymer coated glass plates prepared were kept at the region of superposition of the two writing beams. The experiment was performed on a vibration isolation table. The growth of the grating was monitored by illuminating the region of superposition with a beam of 30 mW He-Ne laser at 632.8 nm (05-LHP-928, Melles Griot). The intensity of the first order-diffracted beam was monitored with a photo detector combined with digital power meter (Coherent model Fieldmaster GS).

## 2.3. Synthesis of precursors

The precursors such as 4-(6-hydroxyhexyloxy)benzoic acid and 4-(6-(methacryloyloxy)hexyloxy)benzoic acid (MHBA) were synthesized by the reported procedures [15].

### 2.3.1. Synthesis of 4-(4'-X-phenylazo)-1-naphthol (X=H, CH<sub>3</sub>, OCH<sub>3</sub>, F, Cl, Br, I, NO<sub>2</sub>, CN)

A typical procedure adopted for the preparation of 4-(4'-X-phenylazo)-1-naphthol is as follows. Substituted anilines were diazotized using sodium nitrite in the presence of hydrochloric acid followed by coupling with  $\alpha$ -naphthol substrate to produce 4-(4'-X-phenylazo)-1-naphthol dye in good yield (80-86%). Its purity was examined by thin layer chromatography and purified by column chromatography over silica gel using chloroform/methanol mixture.

### 4-(4'-Phenylazo)-1-naphthol

IR (KBr) cm<sup>-1</sup>: 1414 (-N=N-), 1316 (C-C), 3239 (-NH/-OH), 1618 (C=O), 1154 (Ar-N=). <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>)  $\delta$ : 11.25 (s, 1H, OH), 7.08-8.81 (m, 10H, ArH). <sup>13</sup>C-NMR (DMSO-d<sub>6</sub>)  $\delta$ : 136.80 (ArC-OH), 131.65 (ArC-H), 148.96 (ArC-N=), 116.14 (ArC-C). Elemental anal: C<sub>16</sub>H<sub>12</sub>N<sub>2</sub>O (248.09) calculated: C, 77.40; H, 4.87; N, 11.28. Found: C, 77.37; H, 4.84; N, 11.25

### 4-(4'-Methylphenylazo)-1-naphthol

IR (KBr) cm<sup>-1</sup>: 1418 (-N=N-), 1315 (C-C), 3244 (-NH/-OH), 1600 (C=O), 1157 (Ar-N=). <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>)  $\delta$ : 11.22 (s, 1H, OH), 7.04-8.79 (m, 10H, ArH). <sup>13</sup>C-NMR (DMSO-d<sub>6</sub>)  $\delta$ : 159.84 (ArC-OH), 24.30 (ArC-CH<sub>3</sub>), 143.95 (ArC-N=), 114.05 (ArC-C). Elemental anal: C<sub>17</sub>H<sub>14</sub>N<sub>2</sub>O (262.11): calculated: C, 77.84; H, 5.38; N, 10.68. Found: C, 77.81; H, 5.36; N, 10.64

### 4-(4'-Methoxyphenylazo)-1-naphthol

IR (KBr) cm<sup>-1</sup>: 1407 (-N=N-), 1317 (C-C), 3044 (-NH/-OH), 1597 (C=O), 1153 (Ar-N=). <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>)  $\delta$ : 10.17 (s, 1H, OH), 6.67-8.42 (m, 10H, ArH). <sup>13</sup>C-NMR (DMSO-d<sub>6</sub>)  $\delta$ : 160.06 (ArC-OH), 54.73 (ArC-OCH<sub>3</sub>), 143.75 (ArC-N=), 114.05 (ArC-C). Elemental anal: C<sub>17</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub> (278.11) calculated: C, 73.37; H, 5.07; N, 10.07. Found: C, 73.35; H, 5.04; N, 10.03

### 4-(4'-Fluorophenylazo)-1-naphthol

IR (KBr) cm<sup>-1</sup>: 1411 (-N=N-), 1315 (C-C), 3217 (-NH/-OH), 1613 (C=O), 1149 (Ar-N=). <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>)  $\delta$ : 11.06 (s, 1H, OH), 7.05-8.76 (m, 10H, ArH). <sup>13</sup>C-NMR (DMSO-d<sub>6</sub>)  $\delta$ : 159.58(ArC-OH), 165.18 (ArC-F), 143.81 (ArC-N=), 116.22 (ArC-C). Elemental anal: C<sub>16</sub>H<sub>11</sub>FN<sub>2</sub>O (266.09) calculated: C, 72.17; H, 4.16; N, 10.52. Found: C, 72.13; H, 4.13; N, 10.46.

### 4-(4'-Chlorophenylazo)-1-naphthol

IR (KBr) cm<sup>-1</sup>: 1414 (-N=N-), 1314 (C-C), 3243 (-NH/-OH), 1623 (C=O), 1152 (Ar-N=). <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>)  $\delta$ : 11.2 (s, 1H, OH), 7.03-8.88 (m, 10H, ArH). <sup>13</sup>C-NMR (DMSO-d<sub>6</sub>)  $\delta$ : 159.58 (ArC-OH), 137.05 (ArC-Cl), 143.10 (ArC-N=), 115.81 (ArC-C). Elemental anal: C<sub>16</sub>H<sub>11</sub>ClN<sub>2</sub>O (282.06) calculated: C, 67.97; H, 3.92; N, 9.9. Found: C, 67.93; H, 3.87; N, 9.86.

### 4-(4'-Bromophenylazo)-1-naphthol

IR (KBr) cm<sup>-1</sup>: 1413 (-N=N-), 1312 (C-C), 3241 (-NH/-OH), 1622 (C=O), 1152 (Ar-N=). <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>)  $\delta$ : 11.21 (s, 1H, OH), 6.96-8.80 (m, 10H, ArH). <sup>13</sup>C-NMR (DMSO-d<sub>6</sub>)  $\delta$ : 159.55 (ArC-OH), 124.83 (ArC-Br), 143.71 (ArC-N=), 116.61 (ArC-C). Elemental anal: C<sub>16</sub>H<sub>11</sub>BrN<sub>2</sub>O (326.01) calculated: C, 58.74; H, 3.39; N, 8.56 Found: C, 58.70; H, 3.33; N, 8.51.

### 4-(4'-Iodophenylazo)-1-naphthol

IR (KBr) cm<sup>-1</sup>: 1412 (-N=N-), 1314 (C-C), 3231 (-NH/-OH), 1624 (C=O), 1151 (Ar-N=). <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>)  $\delta$ : 10.7 (s, 1H, OH), 7.04-8.86 (m, 10H, ArH). <sup>13</sup>C-NMR (DMSO-d<sub>6</sub>)  $\delta$ : 160.60 (ArC-OH), 96.681 (ArC-I), 143.88 (ArC-N=), 114.02 (ArC-C). Elemental anal: C<sub>16</sub>H<sub>11</sub>I<sub>2</sub>N<sub>2</sub>O (373.99) calculated: C, 51.36; H, 2.96; N, 7.49. Found: C, 51.30; H, 2.94; N, 7.44.

### 4-(4'-Nitrophenylazo)-1-naphthol

IR (KBr) cm<sup>-1</sup>: 1412 (-N=N-), 1320 (C-C), 3267 (-NH/-OH), 1627 (C=O), 1166 (Ar-N=). <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>)  $\delta$ : 11.95 (s, 1H, OH), 7.07-8.44 (m, 10H, ArH). <sup>13</sup>C-NMR (DMSO-d<sub>6</sub>)  $\delta$ : 159.64 (ArC-OH), 124.86 (ArC-NO<sub>2</sub>), 143.88 (ArC-N=), 114.24 (ArC-C).

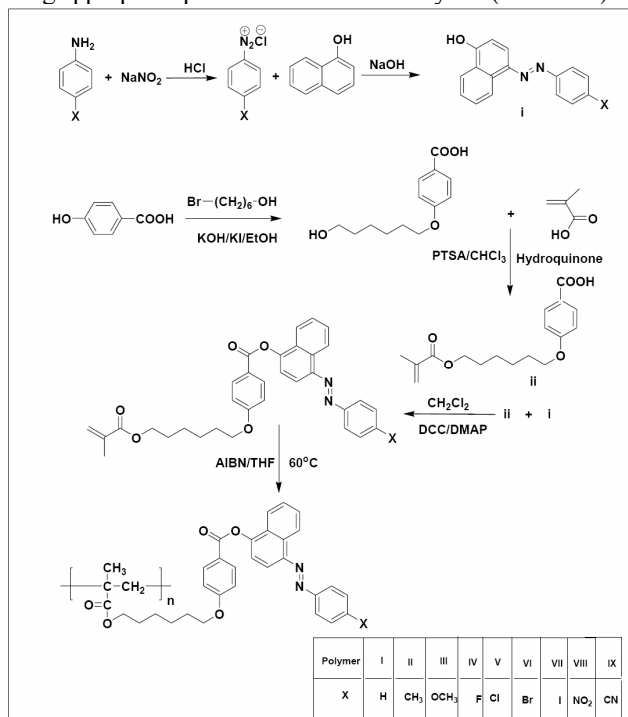
Elemental anal: C<sub>16</sub>H<sub>11</sub>N<sub>3</sub>O<sub>3</sub> (293.08) calculated: C, 65.53; H, 3.78; N, 14.33. Found: C, 65.47; H, 3.72; N, 14.29.

#### 4-(4'-Cyanophenylazo)-1-naphthol

IR (KBr) cm<sup>-1</sup>: 1407 (-N=N-), 1310 (C-C), 3239 (-NH/-OH), 1618 (C=O), 1155 (Ar-N=). <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>) δ: 10.5 (s, 1H, OH), 6.66-8.42 (m, 10H, ArH). <sup>13</sup>C-NMR (DMSO-d<sub>6</sub>) δ: 159.64 (ArC-OH), 116.22 (ArC-CN), 143.81 (ArC-N=), 116.20 (ArC-C). Elemental anal: C<sub>17</sub>H<sub>11</sub>N<sub>3</sub>O (273.09) calculated: C, 74.71; H, 4.06; N, 15.38. Found: C, 74.65; H, 3.99; N, 15.30.

#### 2.3.2. Synthesis of (4-X-phenyl){[4-[4-(6(methacryloyloxy)hexyloxy)benzoyloxy]naphthyl]diazene}(X=H, CH<sub>3</sub>, OCH<sub>3</sub>, F, Cl, Br, I, NO<sub>2</sub>, CN)

A solution of N,N-dicyclohexylcarbodiimide (3.71 g, 0.018 mol) and dichloromethane (50mL) was added drop wise to a stirred solution of 4-(6-(methacryloyloxy)hexyloxy)benzoic acid (5.61 g, 0.018 mol), 4-(4'-phenylazo)-1-naphthol (4.469, 0.018 mol) and 4-(dimethylamino)pyridine (2.19g, 0.018 mol) in dichloromethane (50mL). This reaction was monitored using thin layer chromatography (TLC) until completion and was stirred overnight at room temperature. The solution was then filtered and the solvent was removed under reduced pressure. The residue was then purified by using column chromatography on silica gel (chloroform and methanol) to yield the desired monomer. The remaining monomers were prepared in a similar manner using appropriate precursors with 70-76% yield (Scheme 1).



Scheme 1. Synthesis of monomers and polymers.

{[4-(4-(6-Methacryloyloxyhexyloxy)benzoyloxy)naphthyl]phenyldiazene}

IR (KBr) cm<sup>-1</sup>: 1414 (-N=N-), 1729 (-C=O), 1654 (-C=C-), 1262 (Ar-O-C). <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>) δ: 1.24 (s, 3H, CH<sub>3</sub>-C), 1.76 (s, 2H, CH<sub>2</sub>=C), 3.63 (t, 2H, Ar-O-CH<sub>2</sub>), 7.25- 7.82 (m, 9H, ArH), 8.86 (d, 1H, ArH). <sup>13</sup>C-NMR (DMSO-d<sub>6</sub>) δ: 20.06 (CH<sub>3</sub>-C), 111.64 (C=CH<sub>2</sub>), 164.51 (ArC-O-C), 64.91 (-O-CH<sub>2</sub>), 145.42 (ArC-N=). Elemental anal: C<sub>33</sub>H<sub>32</sub>N<sub>2</sub>O<sub>5</sub> (536.23) Calculated: C, 73.86; H, 6.01; N, 5.22. Found: C, 73.79; H, 5.96; N, 5.19.

(4-Methylphenyl){[4-[4-(6-(methacryloyloxy)hexyloxy)benzoyloxy]naphthyl]diazene}

IR (KBr) cm<sup>-1</sup>: 1411 (-N=N-), 1735 (-C=O), 1613 (-C=C-), 1266 (Ar-O-C), 1212 (Ar-CH<sub>3</sub>). <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>) δ: 1.37 (s, 3H, CH<sub>3</sub>-C), 1.77 (s, 2H, CH<sub>2</sub>=C), 3.46 (t, 2H, Ar-O-CH<sub>2</sub>), 7.25-7.63 (m, 9H, ArH), 3.80 (s, 3H, Ar-CH<sub>3</sub>). <sup>13</sup>C-NMR (DMSO-d<sub>6</sub>) δ: 25.42 (CH<sub>3</sub>-C), 114.94(C=CH<sub>2</sub>), 166.15 (ArC-O-C), 64.49 (-O-CH<sub>2</sub>), 146.71 (ArC-N=).

Elemental anal: C<sub>34</sub>H<sub>34</sub>N<sub>2</sub>O<sub>5</sub> (550.25) calculated: C, 74.16; H, 6.22; N, 5.09. Found: C, 74.13; H, 6.18; N, 5.05.

(4-Methoxyphenyl){[4-[4-(6-(methacryloyloxy)hexyloxy)benzoyloxy]naphthyl]diazene}

IR (KBr) cm<sup>-1</sup>: 1415 (-N=N-), 1712 (-C=O), 1639 (-C=C-), 1264 (Ar-O-C), 1258 (Ar-OCH<sub>3</sub>). <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>) δ: 1.25 (s, 3H, CH<sub>3</sub>-C), 1.77 (s, 2H, CH<sub>2</sub>=C), 3.98 (t, 2H, Ar-O-CH<sub>2</sub>), 7.10-7.93 (m, 9H, ArH), 8.88 (d, 1H, ArH), 3.89 (s, 3H, Ar-OCH<sub>3</sub>). <sup>13</sup>C-NMR (DMSO-d<sub>6</sub>) δ: 26.00 (CH<sub>3</sub>-C), 114.98 (C=CH<sub>2</sub>), 167.63 (ArC-O-C), 64.52 (-O-

CH<sub>2</sub>), 144.38 (ArC-N=). Elemental anal: C<sub>34</sub>H<sub>34</sub>N<sub>2</sub>O<sub>6</sub> (566.64) calculated: C, 72.07; H, 6.05; N, 4.94. Found: C, 72.04; H, 6.01; N, 4.88.

(4-Flouropheryl){[4-[4-(6-methacryloyloxy)hexyloxy)benzoyloxy]naphthyl]diazene}

IR (KBr) cm<sup>-1</sup>: 1413 (-N=N-), 1712 (-C=O), 1639 (-C=C-), 1264 (Ar-O-C), 1268 (Ar-F). <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>) δ: 1.29 (s, 3H, CH<sub>3</sub>-C), 1.69 (s, 2H, CH<sub>2</sub>=C), 3.71 (t, 2H, Ar-O-CH<sub>2</sub>), 7.03-7.97 (m, 9H, ArH), 8.89 (d, 1H, ArH). <sup>13</sup>C-NMR (DMSO-d<sub>6</sub>) δ: 20.12 (CH<sub>3</sub>-C), 111.77 (C=CH<sub>2</sub>), 167.90 (ArC-O-C), 65.20 (-O-CH<sub>2</sub>), 151.40 (ArC-N=). Elemental anal: C<sub>34</sub>H<sub>31</sub>FN<sub>2</sub>O<sub>5</sub> (554.22) calculated: C, 71.47; H, 5.63; N, 5.05. Found: C, 71.42; H, 5.57; N, 5.03.

(4-Chlorophenyl){[4-[4-(6-(methacryloyloxy)hexyloxy)benzoyloxy]naphthyl]diazene}

IR (KBr) cm<sup>-1</sup>: 1413 (-N=N-), 1745 (-C=O), 1639 (-C=C-), 1264 (Ar-O-C), 752 (Ar-Cl). <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>) δ: 1.30 (s, 3H, CH<sub>3</sub>-C), 1.62 (s, 2H, CH<sub>2</sub>=C), 3.59 (t, 2H, Ar-O-CH<sub>2</sub>), 7.13-8.01 (m, 9H, ArH), 8.93 (d, 1H, ArH). <sup>13</sup>C-NMR (DMSO-d<sub>6</sub>) δ: 20.16 (CH<sub>3</sub>-C), 111.58 (C=CH<sub>2</sub>), 163.21(ArC-O-C), 65.31(-O-CH<sub>2</sub>), 151.40 (ArC-N=). Elemental anal: C<sub>33</sub>H<sub>31</sub>ClN<sub>2</sub>O<sub>5</sub> (570.19) calculated: C, 69.41; H, 5.47; N, 4.91. Found: C, 69.36; H, 5.46; N, 4.88.

(4-Bromophenyl){[4-[4-(6-(methacryloyloxy)hexyloxy)benzoyloxy]

naphthyl]diazene}

IR (KBr)  $\text{cm}^{-1}$ : 1428 (-N=N-), 1700 (-C=O), 1654 (-C=C-), 1260 (Ar-O-C), 516 (Ar-Br).  $^1\text{H-NMR}$  (DMSO- $d_6$ )  $\delta$ : 1.41 (s, 3H,  $\text{CH}_3\text{-C}$ ), 1.49 (s, 2H,  $\text{CH}_2\text{=C}$ ), 3.86 (t, 2H, Ar-O- $\text{CH}_2$ ), 7.23-7.89 (m, 9H, ArH), 8.94 (d, 1H, ArH).  $^{13}\text{C-NMR}$  (DMSO- $d_6$ )  $\delta$ : 25.52 ( $\text{CH}_3\text{-C}$ ), 114.38 ( $\text{C=CH}_2$ ), 166.15 (ArC-O-C), 64.44 (-O- $\text{CH}_2$ ), 146.16 (ArC-N=). Elemental anal:  $\text{C}_{33}\text{H}_{31}\text{BrN}_2\text{O}_5$  (614.14) calculated: C, 64.39; H, 5.08; N, 4.55. Found: C, 64.33; H, 5.04; N, 4.49.

(4-Iodophenyl){[4-[4-(6-methacryloyloxy)hexyloxy]benzoyloxy]naphthyl]diazene}

IR (KBr)  $\text{cm}^{-1}$ : 1389 (-N=N-), 1708 (-C=O), 1636 (-C=C-), 1260 (Ar-O-C), 472 (Ar-I).  $^1\text{H-NMR}$  (DMSO- $d_6$ )  $\delta$ : 1.32 (s, 3H,  $\text{CH}_3\text{-C}$ ), 1.62 (s, 2H,  $\text{CH}_2\text{=C}$ ), 3.83 (t, 2H, Ar-O- $\text{CH}_2$ ), 6.99-7.68 (m, 9H, ArH), 8.90 (d, 1H, ArH).  $^{13}\text{C-NMR}$  (DMSO- $d_6$ )  $\delta$ : 20.20 ( $\text{CH}_3\text{-C}$ ), 111.77 ( $\text{C=CH}_2$ ), 167.12 (ArC-O-C), 65.12 (-O- $\text{CH}_2$ ), 151.40 (ArC-N=). Elemental anal:  $\text{C}_{33}\text{H}_{31}\text{IN}_2\text{O}_5$  (662.13) Calculated: C, 59.83; H, 4.72; N, 4.23. Found: C, 59.78; H, 4.71; N, 4.19.

(4-Nitrophenyl){[4-[4-(6-methacryloyloxy)hexyloxy]benzoyloxy]naphthyl]diazene}

IR (KBr)  $\text{cm}^{-1}$ : 1319 (-N=N-), 1718 (-C=O), 1636 (-C=C-), 1259 (Ar-O-C), 1212 (Ar- $\text{NO}_2$ ).  $^1\text{H-NMR}$  (DMSO- $d_6$ )  $\delta$ : 1.14 (s, 3H,  $\text{CH}_3\text{-C}$ ), 1.52 (s, 2H,  $\text{CH}_2\text{=C}$ ), 3.41 (t, 2H, Ar-O- $\text{CH}_2$ ), 6.99-7.68 (m, 9H, ArH), 8.90 (d, 1H, ArH).  $^{13}\text{C-NMR}$  (DMSO- $d_6$ )  $\delta$ : 25.74 ( $\text{CH}_3\text{-C}$ ), 28.74 ( $\text{C=CH}_2$ ), 165.72 (ArC-O-C), 64.28 (-O- $\text{CH}_2$ ), 144.36 (ArC-N=). Elemental anal:  $\text{C}_{33}\text{H}_{31}\text{N}_3\text{O}_7$  (581.22) calculated: C, 68.15; H, 5.37; N, 7.22. Found: C, 68.10; H, 5.34; N, 7.16.

(4-Cyanophenyl){[4-[4-(6-methacryloyloxy)hexyloxy]benzoyloxy]naphthyl]diazene}

IR (KBr)  $\text{cm}^{-1}$ : 1329 (-N=N-), 1708 (-C=O), 1636 (-C=C-), 1260 (Ar-O-C), 2367 (Ar-CN).  $^1\text{H-NMR}$  (DMSO- $d_6$ )  $\delta$ : 1.19 (s, 3H,  $\text{CH}_3\text{-C}$ ), 1.37 (s, 2H,  $\text{CH}_2\text{=C}$ ), 3.53 (t, 2H, Ar-O- $\text{CH}_2$ ), 7.02-7.88 (m, 9H, ArH), 8.48 (d, 1H, ArH).  $^{13}\text{C-NMR}$  (DMSO- $d_6$ )  $\delta$ : 18.28 ( $\text{CH}_3\text{-C}$ ), 28.53 ( $\text{C=CH}_2$ ), 167.51 (ArC-O-C), 64.72 (-O- $\text{CH}_2$ ), 145.53 (ArC-N=). Elemental anal:  $\text{C}_{34}\text{H}_{31}\text{N}_3\text{O}_5$  (561.23) calculated: C, 72.71; H, 5.56; N, 7.48. Found: C, 72.66; H, 5.53; N, 7.44.

### 2.3.3. Polymerization

All the polymers (I-IX) were synthesized by a free radical solution polymerization method from the corresponding monomers using AIBN as an initiator in THF at 60°C. The typical procedure for the synthesis of polymer I is as follows: (4-X-phenyl){[4-[4-(6-methacryloyloxy)hexyloxy]benzoyloxy]naphthyl]diazene} (X=H) (0.01 mol) and AIBN (0.001 mol) were dissolved in dry THF and a gentle stream of nitrogen was passed into the solution. The solution was kept in an oil bath at 60°C for 24 h. Then the solution was cooled and poured into excess of methanol to precipitate the product. The crude polymer thus obtained was reprecipitated twice

using chloroform and methanol. The purified polymer was dried at 40°C under vacuum for 48 hours (yield 75%). The remaining polymers (II-IX) were prepared by adopting the similar procedure using the respective monomers with good yield of 70-73%.

Poly{[4-(4-(6-methacryloyloxy)hexyloxy)benzoyloxy]naphthyl]phenyldiazene}(I)

IR (KBr)  $\text{cm}^{-1}$ : 1509 (-N=N-), 1734 (ester C=O), 1467 (-OCH<sub>2</sub>), 1254 (Ar-O-C).  $^1\text{H-NMR}$  (DMSO- $d_6$ )  $\delta$ : 1.29 (s, 3H,  $\text{CH}_3\text{-C}$ ), 1.2-1.3 (s, 2H, C- $\text{CH}_2$ ), 4.08 (t, 2H, Ar-O- $\text{CH}_2$ ), 7.03-7.99 (m, 10H, ArH).  $^{13}\text{C-NMR}$  (DMSO- $d_6$ )  $\delta$ : 25.71 ( $\text{CH}_3\text{-C}$ ), 20.0 ( $\text{CH}_2\text{-C}$ ), 163.64 (ArC-O-C), 64.91 (-O- $\text{CH}_2$ ), 153.07 (ArC-N=).

Poly[(4-methylphenyl){[4-[4-(6-methacryloyloxy)hexyloxy]benzoyloxy]naphthyl]diazene}(II)

IR (KBr)  $\text{cm}^{-1}$ : 1509 (-N=N-), 1733 (ester C=O), 1474 (-OCH<sub>2</sub>), 1253 (Ar-O-C), 1214 (Ar- $\text{CH}_3$ ).  $^1\text{H-NMR}$  (DMSO- $d_6$ )  $\delta$ : 1.25 (s, 3H,  $\text{CH}_3\text{-C}$ ), 1.1-1.4 (s, 2H, C- $\text{CH}_2$ ), 3.95 (t, 2H, Ar-O- $\text{CH}_2$ ), 6.83-7.93 (m, 10H, ArH), 3.95 (s, 3H, Ar- $\text{CH}_3$ ).  $^{13}\text{C-NMR}$  (DMSO- $d_6$ )  $\delta$ : 25.84 ( $\text{CH}_3\text{-C}$ ), 20.60 ( $\text{CH}_2\text{-C}$ ), 164.21 (ArC-O-C), 64.21 (-O- $\text{CH}_2$ ), 152.80 (ArC-N=).

Poly[(4-methoxyphenyl){[4-[4-(6-methacryloyloxy)hexyloxy]benzoyloxy]naphthyl]diazene}(III)

IR (KBr)  $\text{cm}^{-1}$ : 1508 (-N=N-), 1735 (ester C=O), 1476 (-OCH<sub>2</sub>), 1253 (Ar-O-C), 1242 (Ar-OCH<sub>3</sub>).  $^1\text{H-NMR}$  (DMSO- $d_6$ )  $\delta$ : 1.25 (s, 3H,  $\text{CH}_3\text{-C}$ ), 1.0-1.4 (s, 2H, C- $\text{CH}_2$ ), 3.92 (t, 2H, Ar-O- $\text{CH}_2$ ), 7.07-8.04 (m, 10H, ArH), 4.01 (s, 3H, Ar-OCH<sub>3</sub>).  $^{13}\text{C-NMR}$  (DMSO- $d_6$ )  $\delta$ : 25.76 ( $\text{CH}_3\text{-C}$ ), 20.58 ( $\text{CH}_2\text{-C}$ ), 163.96 (ArC-O-C), 64.30 (-O- $\text{CH}_2$ ), 152.94 (ArC-N=).

Poly[(4-fluorophenyl){[4-[4-(6-methacryloyloxy)hexyloxy]benzoyloxy]naphthyl]diazene}(IV)

IR (KBr)  $\text{cm}^{-1}$ : 1510 (-N=N-), 1735 (ester C=O), 1466 (-OCH<sub>2</sub>), 1254 (Ar-O-C), 1228 (Ar-F).  $^1\text{H-NMR}$  (DMSO- $d_6$ )  $\delta$ : 1.46 (s, 3H,  $\text{CH}_3\text{-C}$ ), 1.1-1.3 (s, 2H, C- $\text{CH}_2$ ), 3.99 (t, 2H, Ar-O- $\text{CH}_2$ ), 6.92-7.99 (m, 10H, ArH).  $^{13}\text{C-NMR}$  (DMSO- $d_6$ )  $\delta$ : 25.71 ( $\text{CH}_3\text{-C}$ ), 19.90 ( $\text{CH}_2\text{-C}$ ), 164.12 (ArC-O-C), 64.80 (-O- $\text{CH}_2$ ), 153.10 (ArC-N=).

Poly[(4-chlorophenyl){[4-[4-(6-methacryloyloxy)hexyloxy]benzoyloxy]naphthyl]diazene}(V)

IR (KBr)  $\text{cm}^{-1}$ : 1602 (-N=N-), 1743 (ester C=O), 1467 (-OCH<sub>2</sub>), 1255 (Ar-O-C), 513 (Ar-Cl).  $^1\text{H-NMR}$  (DMSO- $d_6$ )  $\delta$ : 1.42 (s, 3H,  $\text{CH}_3\text{-C}$ ), 1.2-1.4 (s, 2H, C- $\text{CH}_2$ ), 3.99 (t, 2H, Ar-O- $\text{CH}_2$ ), 6.99-8.01 (m, 10H, ArH).  $^{13}\text{C-NMR}$  (DMSO- $d_6$ )  $\delta$ : 25.60 ( $\text{CH}_3\text{-C}$ ), 20.20 ( $\text{CH}_2\text{-C}$ ), 163.82 (ArC-O-C), 65.12 (-O- $\text{CH}_2$ ), 151.40 (ArC-N=).

Poly[(4-bromophenyl){[4-[4-(6-methacryloyloxy)hexyloxy]benzoyloxy]naphthyl]diazene}(VI)

IR (KBr)  $\text{cm}^{-1}$ : 1508 (-N=N-), 1734 (ester C=O), 1477 (-OCH<sub>2</sub>), 1253 (Ar-O-C), 760 (Ar-Br).  $^1\text{H-NMR}$  (DMSO- $d_6$ )  $\delta$ : 1.25 (s, 3H,  $\text{CH}_3\text{-C}$ ), 1.2-1.3 (s, 2H, C- $\text{CH}_2$ ), 3.98 (t, 2H, Ar-O- $\text{CH}_2$ ), 6.88-7.93 (m, 10H, ArH).  $^{13}\text{C-NMR}$

(DMSO- $d_6$ )  $\delta$ : 28.64 (CH<sub>3</sub>-C), 20.16 (CH<sub>2</sub>-C), 163.78 (ArC-O-C), 65.06 (-O-CH<sub>2</sub>), 151.48 (ArC-N=).

Poly[(4-iodophenyl){[4-[4-(6-(methacryloyloxy)hexyloxy)benzoyloxy]naphthyl]diazene}] (VII)

IR (KBr)  $\text{cm}^{-1}$ : 1508 (-N=N-), 1718 (ester C=O), 1475 (-OCH<sub>2</sub>), 1252 (Ar-O-C), 476(Ar-I). <sup>1</sup>H-NMR (DMSO- $d_6$ )  $\delta$ : 1.31 (s, 3H, CH<sub>3</sub>-C), 1.0-1.3 (s, 2H, C-CH<sub>2</sub>), 3.97 (t, 2H, Ar-O-CH<sub>2</sub>), 6.93-7.96 (m, 10H, ArH). <sup>13</sup>C-NMR (DMSO- $d_6$ )  $\delta$ : 25.68 (CH<sub>3</sub>-C), 19.82 (CH<sub>2</sub>-C), 163.56 (ArC-O-C), 65.12 (-O-CH<sub>2</sub>), 153.12 (ArC-N=).

Poly[(4-nitrophenyl){[4-[4-(6-(methacryloyloxy)hexyloxy)benzoyloxy]naphthyl]diazene}] (VIII)

IR (KBr)  $\text{cm}^{-1}$ : 1510 (-N=N-), 1735 (ester C=O), 1472 (-OCH<sub>2</sub>), 1254 (Ar-O-C), 1315 (Ar-NO<sub>2</sub>). <sup>1</sup>H-NMR (DMSO- $d_6$ )  $\delta$ : 1.01 (s, 3H, CH<sub>3</sub>-C), 0.9-1.2 (s, 2H, C-CH<sub>2</sub>), 3.41 (t, 2H, Ar-O-CH<sub>2</sub>), 6.58-8.09 (m, 10H, ArH). <sup>13</sup>C-NMR (DMSO- $d_6$ )  $\delta$ : 25.72 (CH<sub>3</sub>-C), 20.46 (CH<sub>2</sub>-C), 163.72 (ArC-O-C), 64.50 (-O-CH<sub>2</sub>), 151.98 (ArC-N=).

Poly[(4-cyanophenyl){[4-[4-(6-(methacryloyloxy)hexyloxy)benzoyloxy]naphthyl]diazene}] (IX)

IR (KBr)  $\text{cm}^{-1}$ : 1508 (-N=N-), 1719 (ester C=O), 1471 (-OCH<sub>2</sub>), 1259 (Ar-O-C), 2220 (Ar-CN). <sup>1</sup>H-NMR (DMSO- $d_6$ )  $\delta$ : 1.18 (s, 3H, CH<sub>3</sub>-C), 1.2-1.3 (s, 2H, C-CH<sub>2</sub>), 3.66 (t, 2H, Ar-O-CH<sub>2</sub>), 6.78-7.99 (m, 10H, ArH). <sup>13</sup>C-NMR (DMSO- $d_6$ )  $\delta$ : 25.62 (CH<sub>3</sub>-C), 19.80 (CH<sub>2</sub>-C), 164.16 (ArC-O-C), 64.61 (-O-CH<sub>2</sub>), 152.96 (ArC-N=).

## 2.4. Film preparation

The typical procedure adopted for the preparation of film for optical property studies is as follows: The polymer I (6 wt %) was dissolved in THF and centrifuged for about 30 minutes, the supernatant solution was decanted, filtered through a 0.2  $\mu\text{m}$  polyethersulfone membrane filter and then spin coated on a pre-cleaned (washed with dilute chromic acid) glass slides and annealed at 50°C in vacuum for 2 hours. The thickness of the film obtained was found to be 0.53  $\mu\text{m}$ . The remaining polymers II-IX films were also prepared in a similar manner [16].

## 3. Results and discussion

### 3.1. Synthesis and characterization of polymers

The synthetic approach used to prepare the monomers and polymers containing azo naphthol moieties are shown in Scheme I. The starting material is 4-substituted aniline, in which the amino group was diazotized with sodium nitrite in the presence of three equivalent of hydrochloric acid. The diazonium salt was converted into p-phenylazo- $\alpha$ -naphthol by coupling with  $\alpha$ -naphthol.

The flexible spacer was introduced by alkylation of the compound p-hydroxybenzoic acid with 6-bromohexanol gave the corresponding 4-(6-hydroxyhexyloxy)benzoic acid. Esterification of the above hydroxylated compound with methacrylic acid yield the 4-(6-(methacryloyloxy)hexyloxy)benzoic acid. This was again coupled with p-phenylazo- $\alpha$ -naphthols to yield the polymerizable monomer,

(4-X-phenyl){[4-[4-(6-(methacryloyloxy)hexyloxy)benzoyloxy]naphthyl]diazene}. This was polymerized by free radical solution polymerization with AIBN as an initiator in THF. The polymers were characterized by spectral techniques and all the spectral values are in accordance with the structure. Fig. 1 shows the representative <sup>1</sup>H-NMR spectrum of the polymer II.

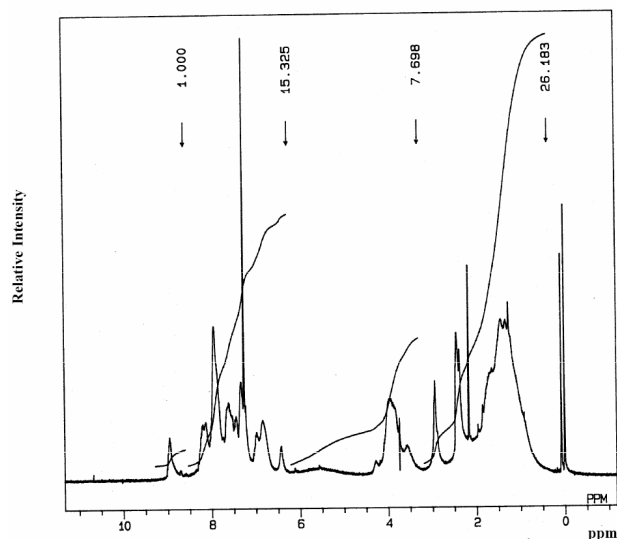


Fig. 1. <sup>1</sup>H-NMR spectrum of polymer II.

### 3.2 Thermal Properties

#### 3.2.1 Thermogravimetric Analysis

Thermogravimetric analysis was performed on a Seiko model SSC 5200H thermal analyzer in nitrogen atmosphere at a heating rate of 10°C min<sup>-1</sup>. The TGA traces of the polymers are shown in Fig. 2 and their data are given in Table 1. The thermal stability of the polymers was evaluated by 10% and 50% weight loss at minimum temperature. All the polymers were stable up to 230°C and start to decompose around 370°C under a 'two-stage' decomposition process. The 'first stage' decomposition may be ascribed to the evolution of nitrogen gas by the cleavage of side chain azo group [17]. The final decomposition around 370-570°C, may be due to the pyrolytic cleavage of ester linkage of the aromatic backbone. The decomposition of the polymers was almost complete at 700°C and no further weight loss was observed.

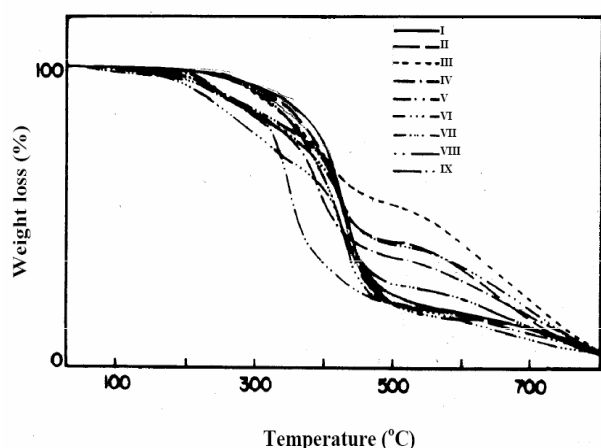


Fig. 2. TGA thermograms of polymers I-IX.

Thermal analysis plays an important role in the study of the structure and stability of the polymers. The results reveal that these polymers possess good thermal stability. The electron withdrawing groups displayed enhanced stability. On the other hand, electron donating group brought down the stability. The methyl pendant materials (**II**) displayed slightly lower thermal stability than all their aromatic counterparts. The polymers containing electron acceptor substituents (**VIII**, **IX**) withdraws the electrons on the ring and increases the positive charge on the diazonium ion.

Among the halogen containing polymers, the thermal stability follows the inductive effects of halogens that are apparently overwhelmed by the polarizability and electron repulsion factors. The char yield of the polymers was in between 22 -42 %, except for polymer **II**, which shows that these polymers could play an important role in the self-extinguishing properties of engineering thermoplastics.

### 3.2.2 Differential scanning calorimetry

DSC analysis was performed under nitrogen atmosphere at a heating rate of  $20^{\circ}\text{C min}^{-1}$ . The DSC traces of all the polymers are shown in Fig.3 and the data are shown in Table1. All the polymers showed two endothermic peaks, one at lower temperature attributed to glass transition temperature ( $T_g$ ), and another at high temperature due to melting transition temperature ( $T_m$ ). It is noteworthy to mention that adding a benzene group between the polymer main chain and acrylic group resulted in an increase in  $T_g$ . As a result, the polymer is more stable at high temperature [18,19].

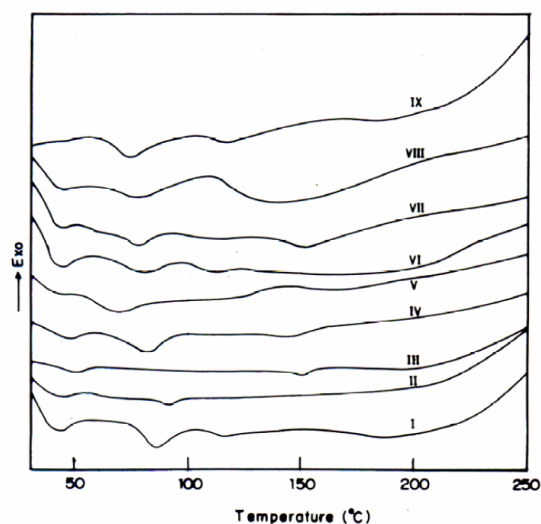


Fig. 3. DSC thermograms of polymers I-IX.

Table 1. TGA and DSC thermal data of the polymers I-IX.

Polymer	X	TGA				DSC	
		Weight loss corresponds to(°C)		Total weight loss at 700°C (%)	Char Yield at 700°C (%)	$T_g$ (°C)	$T_m$ (°C)
		10%	50%				
I	H	355	440	70	30	46	85
II	CH <sub>3</sub>	270	455	95	5	40	75
III	OCH <sub>3</sub>	230	430	78	22	71	115
IV	F	325	430	78	22	42	95
V	Cl	330	455	64	36	50	150
VI	Br	340	455	74	26	46	79
VII	I	310	570	58	42	40	70
VIII	NO <sub>2</sub>	265	420	72	28	43	85
IX	CN	260	370	66	34	41	77

The introduction of substituent at the terminal position of the molecule, that separate the ring structures from one another, depends on the nature of the corresponding substituent (**X**). When the size of the substituent is increased, the long molecular axis was separated by the amount of the ring-X bond length. Hence the thermal stability and attraction of the molecules were altered according to the nature of substituent [20].

The transition temperatures of the electron donating group containing polymers were comparable to those of the electron withdrawing group containing polymers. Among the electron donating substituents the melting transition temperatures of the methoxy substituent (**III**) are significantly higher than those of the other polymers. It may be due to the polar and bulky nature of the methoxy group. A decreasing trend in transition temperature was observed while comparing the other halogens from chlorine to iodine. The low transition temperature exhibited by polymer **IV** may be due to the small size of the terminal fluorine atom which leads to a minimal steric effect in comparison to all other substituents [21]. While comparing the electron withdrawing substituent containing polymers, polymer **VIII** has high transition temperatures.

### 3.3. Photochemical properties

The photoisomerization study was performed for all the polymer films on the spin-coated quartz plate. The UV-visible absorption spectra of the polymer **III** is shown in Fig. 4. The *trans* azobenzene shows an absorption around 375 nm, due to the  $\pi$ - $\pi^*$  transition, and its transition moment lies along the molecular long axis of the azobenzene moiety. An increasing trend of *cis* isomer was also observed at  $\lambda_{\text{max}}$  438 nm due to  $n$ - $\pi^*$  transition of azobenzene moiety. After completion of irradiation with visible light ( $>350$  nm), the absorbance was restored for azobenzene moiety owing to *trans*-*cis* photochemical back isomerization.

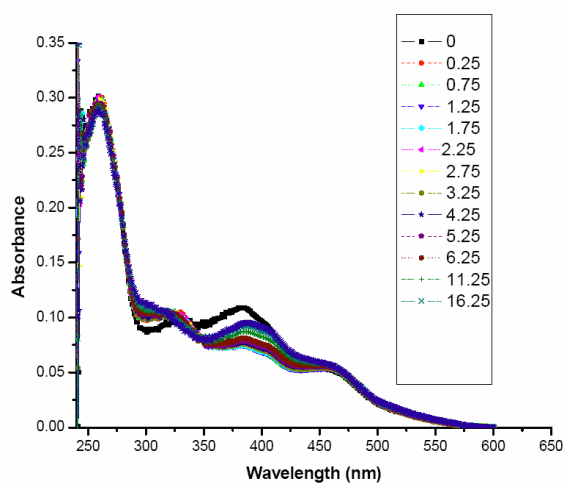


Fig. 4. UV-irradiation pattern of the polymer **III**.

It is attributed that the terminal substituent depends on the size and the effect of withdrawing/donating nature of the resonance. The time taken for total *cis* transformation depends on the nature and size of the terminal substituent in the side chain azo moiety. Among all the polymers, the bulky terminal substituent containing polymer took longer time for the completion of photoisomerization process than the smaller terminal substituents. This reveals that a steric factor hindered two terminal carbons coming closer. If the substituents were small, the steric hindrance was consequently less; hence the time taken was minimal for *cis* transformation [22]. Based on the above observations, the rate of switching time for terminally substituted polymers are in the following order:

$$\mathbf{I > II > VIII > IX > III}$$

For the halogen substituted polymers, the rate of switching time are in the following order:

$$\mathbf{V > IV > VI > VII}$$

### 3.4. Holographic Grating Formation

The optical set up for recording the grating in the polymer sample is shown in Fig. 5. The mechanism of formation of surface relief grating is as follows: When the films are exposed to interference pattern, in the bright region, the dye molecule absorbs the light energy and get excited to singlet state, which decays rapidly to triplet states. Since the energy is high enough, the molecules in the triplet state are further excited and dissociated into free radicals of high volatility. Due to this type of “homolytic fission of carbon-carbon single bonds”, the concentration of dye molecules in the bright region decreases reducing the thickness of the film. Surface relief formation can be attributed to dissociation of dye molecules. This results in inscribing of permanent surface relief structure. The recording is in the form of thickness modulation as well as amplitude modulation [23]. High density optical data storage technique using Fourier transform holography is used to carry out the diffraction efficiency studies in these polymers.

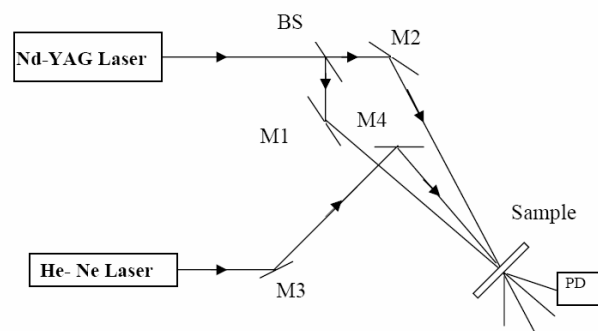


Fig. 5. Experimental set-up for grating formation.

An Nd-YAG laser was employed as a light source of the writing beams in this investigation. Since Nd-YAG laser has a better coherence and also efficient for grating formation, the output of Nd-YAG was used. Two beams of equal intensity (45mW each), obtained using a dielectric coated variable beam splitter, are allowed to interfere on the film. He-Ne laser of 30mW, 633nm was used as read out beam to evaluate the grating formation. The intensity of the first order diffracted beam is measured in real-time using a photo-detector connected to the power meter. The whole experiment was carried out on a vibration isolation table. The diffraction efficiency studies were done by varying the following parameters.

- Time of exposure and
- Intensity ratio of the incident beam

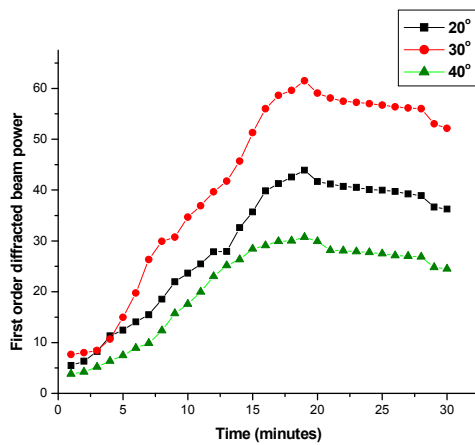


Fig. 6a. First order diffracted beam as a function of interfering angle (50:50 B.S) for polymer IX.

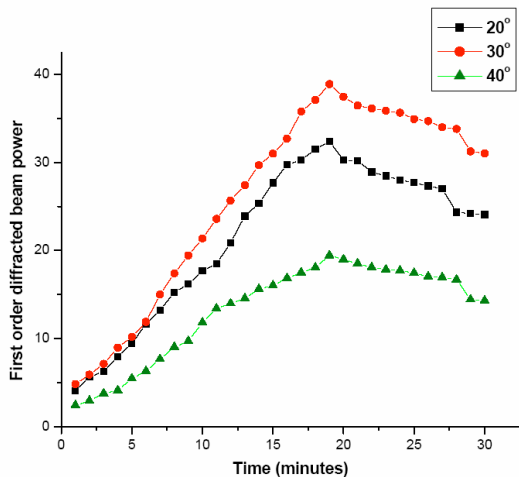


Fig. 6b. First order diffracted beam as a function of interfering angle (70:30 B.S) for polymer IX.

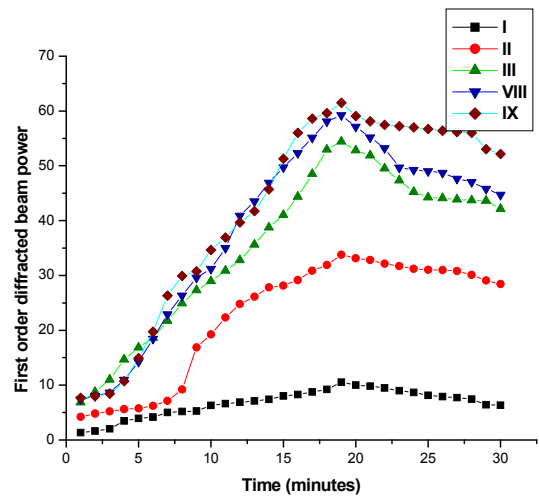


Fig. 7a. Comparison between the polymers (I-III, VIII, IX) for an interfering angle of 30° for the intensity ratio of 50:50.

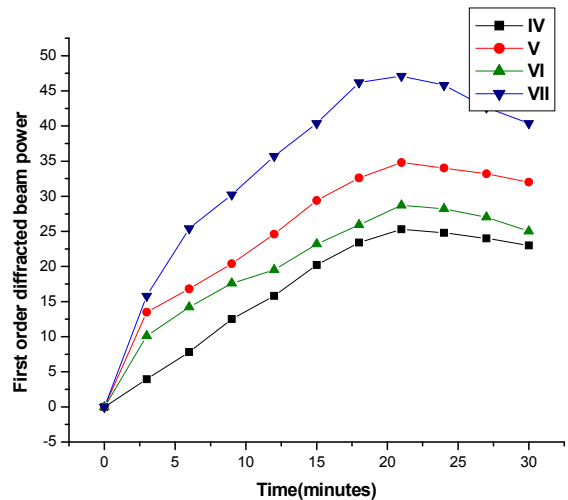


Fig. 7b. Comparison between the polymers (IV-VII) for an interfering angle of 30° for the intensity ratio of 50:50

The time of exposure were varied in minutes. Two different beam splitters (BS) like 50:50 BS and 70:30 BS were used to control the intensity of the incident beam. In general, the Fig. 6-7 show that the signal value of first order diffracted beam rises to a maximum value with time and then decreases on further exposure. The decreasing nature of the maximum value of the diffracted signal could be ascribed to the over exposure of the materials to electromagnetic radiation leading to decrease in the modulation depth of the grating recorded. Further the loss of elasticity of the photo reactive center may also produce a reduction in the power of the first order-diffracted beam [24, 25]. Continuous exposure of high power beam always produces heat due to the interaction of light with



reactive centers and leads to decomposition of polymeric materials [26, 27].

#### 4. Conclusion

A novel free-radical polymerizable methacryloyloxy group containing azo-naphthyl esters were prepared and their photoisomerization properties were studied. All the spectral data are in accordance with the structure. The thermal properties of the polymers were determined by TGA and DSC. TGA data revealed that the polymers were stable up to 355°C. All the polymers were exhibited two stage decomposition that is one at lower temperature due to the cleavage of azo linkage and another at higher temperature due to the pyrolytic cleavage of ester linkage. The DSC results showed that the electron withdrawing substituted polymer showed higher Tg's than the electron-donating substituted polymer. A decreasing trend in transition temperature was observed while comparing the halogens from chlorine to iodine. UV irradiation revealed that the photoisomerization time depends on the dipole moment, size and donor-acceptor characteristics of the terminal substituents. The time taken for the completion of the photoisomerization for the methyl substituted polymer is much longer than the other polymers. All the polymers were investigated for grating formation using Nd-YAG laser at a wavelength of 532 nm for recording and He-Ne laser at a wavelength of 633 nm for reading purpose. The growth of the grating was monitored in real-time using the photo-detector connected to the power-meter. The diffraction efficiency was found to depend on the time of exposure and intensity ratio of the incident beam. It has been found that the grating efficiency of the electron withdrawing substituent polymers is larger than the other polymers. All experimental results show that these polymers have good thermal stability, optical quality film formation, quick optical response and photo stability which make them to be potential optoelectronic materials.

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