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SYNTHESIS OF POLYMERS CONTAINING AZOBENZENE SIDE GROUPS BOUND TO THE MAIN CHAIN THROUGH AN ELECTRON DONOR OR AN ELECTRON ACCEPTOR SUBSTITUENT

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Dedicated to the memory of our special friend, Professor Sukant K. Tripathy.

ABSTRACT

Two new amorphous high-Tg azobenzene-containing polymers: poly{4-[(2-(methacryloyloxy)ethyl)ethylamino]-4'-(methylsulfonyl)azobenzene} (p**DRSAM**) and poly{4-[(2-(methacryloyloxy)ethylsulfonyl]-4'-(diethylamino)azobenzene}(p**DRASM**), having side group dipoles of the same strength but differently bound to the main chain, and a series of copolymers of various compositions, have been synthesized.

Key Words: Azobenzene polymers; Synthesis; Amino-bound azobenzene; Sulfone-bound azobenzene; Side group polarity

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INTRODUCTION

Previous studies demonstrated that amorphous azo-polymers films with high glass transition temperature can be used for photoinduced birefringence and surface relief gratings, as a consequence of the photoinduced trans-cis-trans isomerization of the azobenzene groups [1]. The birefringence level depends on many structural factors, including the type of azobenzene, its polarity and bulkiness, the type of binding the chromophore to the main chain, the azo concentration in the polymer, as well as the intrinsic tendency to form ordered domains [2]. Some amorphous copolymers show cooperative motion, which is mainly determined by the polarity of the azobenzene and similar groups. Polar azobenzene groups can associate, usually in an anti-parallel fashion, and the photoinduced motion can then coerce other groups to move in concert [3-5].

The obvious questions raised by the above findings are: how important is that the azobenzene chromophore be always bound to the main chain through the electron-donor (amino) site? What would happen if the chromophore were bound through the electron-accepting site? And how would a copolymer, that contains azobenzenes bound both ways behave under irradiation with linearly polarized light? In order to answer there questions, we present here the synthesis and characterization of two homopolymers having side group azo dipoles of the same strength but differently bound to the main chain, and three copolymers of various compositions. These polymers are designed specially for the study of the relationship between the orientation of azobenzene groups and their dipole direction. Side-chain polymers with alternating donor-attached and acceptor-attached NLO-phores have been reported by Nagase *et al.* [6] for nonlinear optics by taking advantages to the noncentrosymmetric alignment of NLO-phores. They used two kinds of non-azo chromophores, one is [4-(dihexylamino)phenyl sulfonyl] propyl, the other is 2-[N-methyl-4-(octylsulfonyl)amino]ethyl. We chose amino as the electron donor group and sulfone as the electron acceptor group. The amino-sulfone azobenzene chromophore was chosen because of its high dipole moment as well as its possibility to functionalize at either end of the chromophore. This class of chromophores has been reported for nonlinear optical applications [7, 8]. Several kinds of modified amino-sulfone azobenzene chromophore have been reported for NLO applications [9-11]. 4-aminophenyl 6-hydroxyhexyl sulfone and 4-[di(2-hydroxyethyl)amino]-4'-((6-hydroxyhexyl) sulfonyl)azobenzene were used by Dalton *et al*. for synthesis of main-chain polymers [9] or cross-linked polymers [10]. Ulman *et al.* have introduced a single functionality at each end of an amino-sulfone azobenzene chromophore, from which they have synthesized several head-to-tail main-chain NLO polymers [7]. They also synthesized some acrylic polymers bearing azobenzene chromophores containing 4'-dialkylamino electron donor and 4-methylsulfonyl electron acceptors with different spacers.

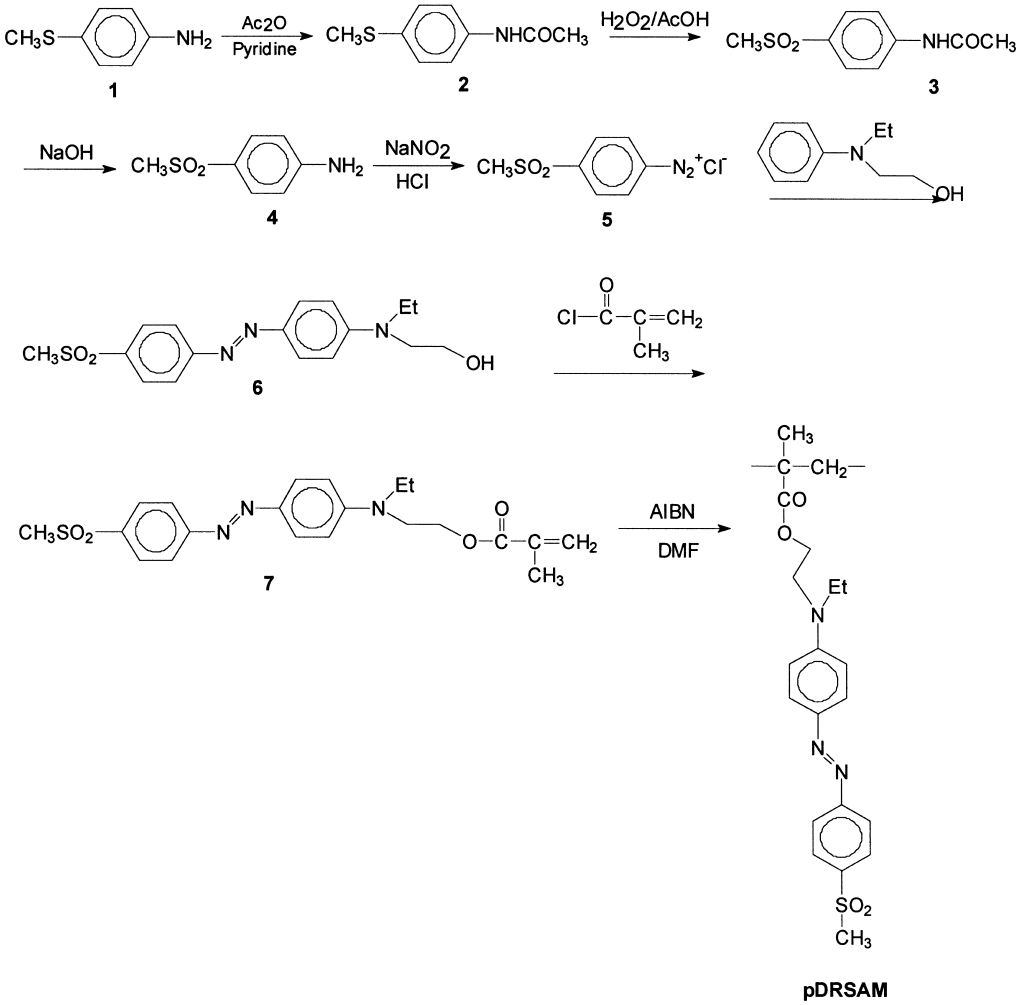
EXPERIMENTAL

Melting points were determined on a Mel-tep II laboratory device and are uncorrected. Proton NMR spectra were recorded on a Bruker AC-F 200 NMR spectrometer. Carbon-13 NMR spectra were obtained on a Bruker AM-400 spectrometer with gated decoupling and a 6-s delay between pulses. UV-Vis absorption spectra were obtained from Hewlett-Packard 8452A diode array spectrophotometer. The molecular weights (relative to polystyrene) of the resulting polymers were obtained by gel permeation chromatography (GPC) on a Water Associates liquid chromatograph equipped with a Model 440 absorbance detector and a Model R401 differential refractometer. The glass transition temperatures of the polymers were measured by differential scanning calorimetry (DSC) with a Mettler TA 3000 thermal analysis system equipped with a TC10A TA processor and a DSC30 head. Dry dichloromethane, triethylamine and pyridine were obtained by distillation from CaH_2 prior to use. Methacryloyl chloride was purchased from Fluka and was distilled before use. 4-Aminothiophenol, 4-(methylmecapto)-aniline, 2-(*N*-ethylanillino)ethanol and 2-hydroxyethyl chloride were used as purchased from Aldrich. The synthetic routes for the monomers and polymers are shown in Schemes 1 and 2.

RESULTS AND DISCUSSION

For the synthesis of monomer **7**, we started with 4-(methylmercapto)-aniline that was protected with acetic anhydride. The sulfide **2** was oxidized using hydrogen peroxide to give the sulfone compound **3**. Deprotection of **3** to give **4** was readily accomplished by treatment with sodium hydroxide solution. The 4-(methylsulfonyl)aniline **4** was converted into azobenzene derivative **6** by treatment with sodium nitrite and hydrochloric acid mixture followed by coupling with *N*-ethyl-*N*-(2-hydroxyethyl)aniline. Reaction of **6** with methacryloyl chloride gave the monomer **7**.

For monomer **14**, we used 4-aminothiophenol as starting material, it was converted to **9** by coupling with 2-chloroethanol using sodium ethoxide as base. Protection of **9** with acetic anhydride produced **10** that was oxidized using hydrogen peroxide to give sulfone compound **11**. To deprotect the acetyl group, we first tried base condition (10% NaOH in ethanol) which is efficient for deprotection of **3**, but it always gave 4-[2-ethoxyethyl)sulfonyl]aniline as the major product. Finally, we found it could be readily deprotected with 10% conc. HCl in ethanol to offer **12** in 95% yield. Compound **12** was converted into the azobenzene derivative **13** by treatment with sodium nitrite and hydrochloric acid mixture followed by coupling with diethylaniline. Reaction of **13** with methacryloyl chloride gave the monomer **14**.

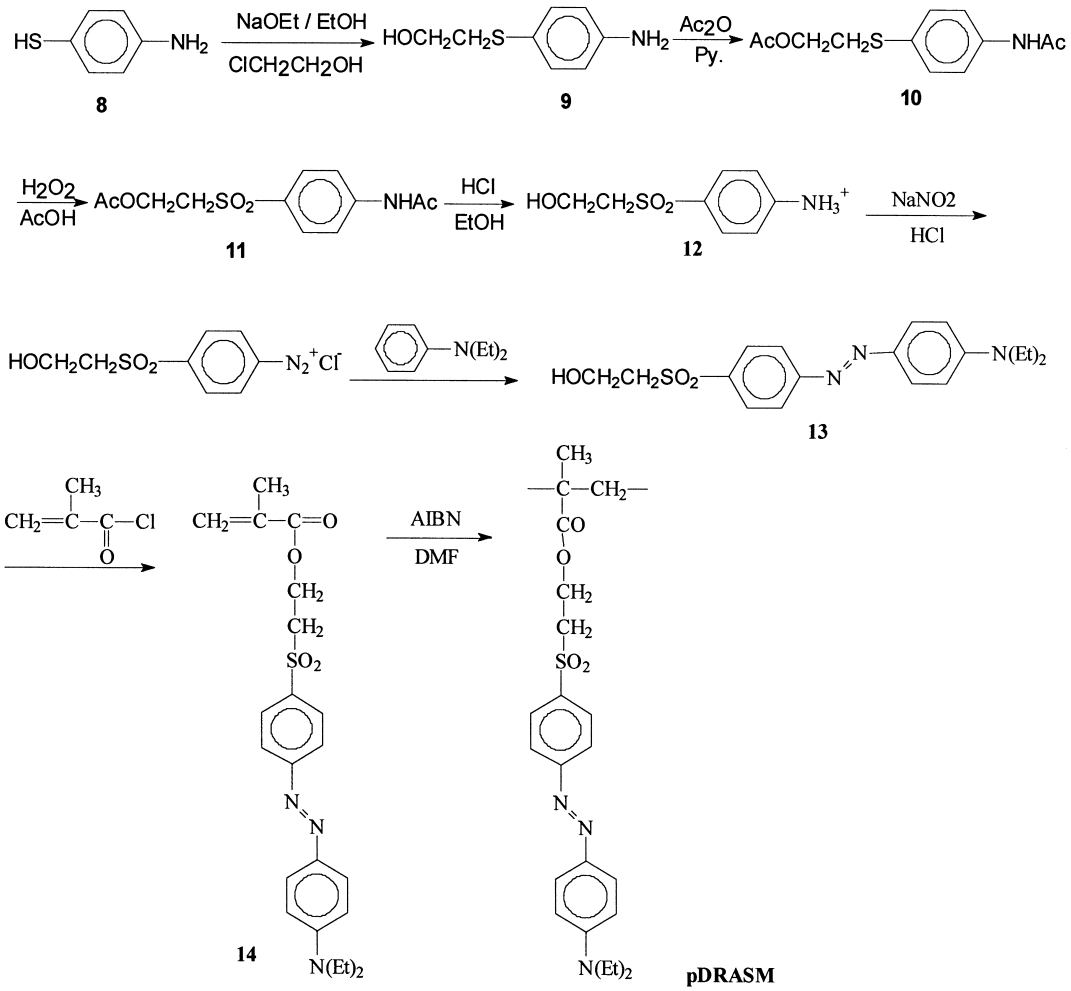


Scheme 1.

Synthesis

4-Acetamidophenyl Methyl Sulfide **(2)**

A solution of 4-(methylmercapto)-aniline (**1**) (15 mL, 120 mmol) and acetic anhydride (13.7 mL, 144 mmol) in 30 mL pyridine was refluxed for 2 hours. The solution was poured onto ice-water (500 mL), and the precipitated product was collected by filtration and washed with water, 5% HCl, and again with water. The product was recrystallized from methanol/water to produce 18.64 g (86%) of a slightly yellow solid **2**. ^{1}H NMR ($CDCl_3$) δ (ppm) 2.11 (s, 3H, -$COCH_3$), 2.42 (s, 3H, -SCH_3), 7.16 (d, 2 aromatic H, ortho to NH), 7.41 (d, 2 aromatic H, meta to NH), 8.37 (s, 1H, D_2O exchangeable, NH).



Scheme 2.

4-Acetamidophenyl Methyl Sulfone **(3)**

A solution of 4-acetamidophenyl methyl sulfide (**2**) (18.04 g, 100 mmol) in glacial acetic acid (100 mL) was heated to reflux with stirring. Hydrogen peroxide (30 ml of 30% solution) was added in small portions, and the resulting mixture was stirred at reflux for 3 hours. The reaction mixture was concentrated, and the residue was dissolved in dichloromethane. The solution was washed with water, dried (Na_2SO_4) and evaporated. The residue was crystallized from ethanol/water to afford **3** (17.68 g, 83%). ^{1}H NMR (DMSO-d_6) δ (ppm) 3.40 (s, 3H, -$COCH_3$), 3.12 (s, 3H, -SO_2CH_3), 7.80 (AB, 4 aromatic H), 10.37 (s, 1H, D_2O exchangeable, NH).

4-(Methylsulphonyl)aniline **(4)**

The mixture of 4-acetamidophenyl methyl sulfone (17.5 g, 82.2 mmol), 25.0 g NaOH, 120 mL ethanol and 120 mL water was refluxed with stirring for 12 hours. The resulting solution was extracted with CH_2Cl_2. The extract was washed with brine, dried (Na_2SO_4) and evaporated. The residue was recrystallized from ethanol/water to produce **4** (10.65 g, 76%). mp 132-133°C; ^{1}H NMR (DMSO-d_6) δ (ppm) 3.40 (s, 3H, -SO_2CH_3), 6.02 (s, 2H, D_2O exchangeable, NH_2), 8.02 (d, 2 aromatic H, meta to NH_2).

4-[(2-Hydroxyethyl)ethylamino]-4'-(methylsulfonyl)azobenzene **(6)**

4-(Methylsulphonyl)aniline (10.5 g, 61.4 mmol) was added to a stirred solution of conc. HCl (15.7 mL, 193 mmol) in water (45 mL). The temperature was maintained below 10°C using an ice-bath. To the mixture, a solution of $NaNO_2$ (4.33 g, 73 mmol) in H_2O (60 mL) was added. After 15 minutes of stirring, a mixture of 2-(N-ethylanilino)ethanol (10.2 g, 61.4 mmol) and sodium acetate (18.2 g, 220 mmol) in H_2O (75 mL) was cooled in ice and added to the diazonium salt slowly with stirring. The reaction was immediate and the precipitate formed was filtered and washed with water. The crude product was purified by silica gel column chromatograph using 0-3% CH_3OH in CH_2Cl_2 as eluent to afford **6** (15.2 g, 71%). ^{1}H NMR ($CDCl_3$) δ (ppm) 1.23 (t, 3H, CH_3 of Et), 1.82 (s, 1H, D_2O exchangeable, OH), 3.06 (s, 3H, -SO_2CH_3), 3.56 (m, 4H, -NCH_2-), 3.87 (t, 2H, -CH_2O-), 6.78 (d, 2 aromatic H, ortho to NR_2), 7.83-8.01 (m, 6 aromatic H).

4-[(2-(Methacryloyloxy)ethyl)ethylamino]-4'-(methylsulfonyl)azobenzene **(7)**

A solution of 4-[(2-hydroxyethyl)ethylamino]-4'-(methylsulfonyl)azobenzene (2.0 g, 5.76 mmol) and triethylamine (1.0 mL, 6.92 mmol) in 40 mL THF at 0°C was treated dropwise with methacryloyl chloride (0.67 mL, 6.92 mmol). The reaction mixture was stirred for 2 hours at 0°C and 16 hours at room temperature, then filtered to remove the triethylammonium chloride. The filtrate was diluted with 150 mL CH_2Cl_2 and washed with brine, saturated $NaHCO_3$ and brine. The organic layer was dried (Na_2SO_4) and concentrated at reduced pressure. The residue was purified over silica gel column using 0-1.5% CH_3OH in CH_2Cl_2 as eluent to afford **7** (1.80 g, 75%). ^{1}H NMR ($CDCl_3$) δ (ppm) 1.24 (t, 3H, CH_3 of Et), 1.92 (s, 3H, allyl CH_3), 3.07 (s, 3H, -SO_2CH_3), 3.52 (q, 2H, CH_2 of Et), 3.71 (t, 2H, -NCH_2-), 4.35 (t, 2H, -CH_2O-), 5.57 (s, 1H, =CH), 6.08 (s, 1H, =CH), 6.80 (d, 2 aromatic H, ortho to NR_2), 7.86-8.04 (m, 6 aromatic H).

4-Acetamidophenyl 2-acetoxyethyl Sulfone **(11)**

Sodium metal (9.6 g, 0.4 mol) was dissolved in absolute ethanol (300 mL) with stirring under nitrogen. 4-Aminothiophenol (**8**) (50.0 g, 0.4 mol) was added

in small portions, then 2-chloroethanol (32.2 g, 0.4 mol) was added. The resulting mixture was heated at reflux for 1 hour and filtered, and the filtrate was concentrated. The residue was dissolved in CH_2Cl_2, and the solution was washed with water, 5% $NaHCO_3$, and again with water. The organic layer was dried (Na_2SO_4) and evaporated. The crude product **9** was used for next step reaction without further purification. It was dissolved in pyridine (80 g, 1.0 mol) and treated with acetic anhydride (100 g, 1.0 mol). The resulting mixture was stirred at room temperature for 16 hours and concentrated. The residue was dissolved in CH_2Cl_2 and washed with water. The organic layer was dried (Na_2SO_4) and evaporated to afford crude product **10** which was dissolved in 300 mL glacial acetic acid and heated to reflux with stirring. Then 30% hydrogen peroxide solution (110 mL) was added in small portions, and the resulting mixture was stirred at reflux for 3 hours. The reaction mixture was concentrated, and the residue was dissolved in CH_2Cl_2 and washed with water. The organic layer was dried (Na_2SO_4) and evaporated to dryness, and the residue was crystallized from methanol to afford **11** (56.0 g, 49% from **8**). ^{1}H NMR (DMSO-d_6) δ (ppm) 1.74 (s, 3H, CH_3CO_2-), 2.09 (s, 3H, CH_3CON-), 3.63 (t, 2H, -CH_2SO_2-), 4.22 (t, 2H, -OCH_2-), 7.80 (s, 4 aromatic H), 10.40 (s, 1H, D_2O exchangeable, -NH-).

4-[2-Hydroxyethyl)sulfonyl]aniline **(12)**

4-Acetamidophenyl 2-acetoxyethyl sulfone (11) (20.0 g, 70 mmol) was suspended in 100 mL 10% conc. HCl in absolute ethanol, and the mixture was refluxed for 5 hours. The crystals of the amine hydrochloride that formed on standing were collected and washed with cold ethanol, dried to afford 13.3 g (94%) product. The free amine **12** was liberated by suspending the solid in 300 mL of saturated aqueous sodium bicarbonate. NMR (DMSO-d_6) δ (ppm) 3.21 (t, 2H, -CH_2SO_2-), 3.56 (t, 2H, -OCH_2-), 4.79 (t, 1H, D_2O exchangeable, -OH), 6.10 (s, 2H, D_2O exchangeable, NH_2), 6.62 (d, 2 aromatic H, ortho to NH_2), 7.44 (d, 2 aromatic H, meta to NH_2).

4-[(2-Hydroxyethyl)sulfonyl]-4'-(diethylamino)azobenzene **(13)**

4-[2-Hydroxyethyl)sulfonyl]aniline (**12**) (5.45 g, 27 mmol) was suspended in a stirred solution of conc. HCl (7 mL) in water (30 mL). The temperature was maintained at below 10°C using an ice-bath. To the mixture, a solution of sodium nitrite (1.6 g, 27 mmol) in water (30 mL) was added slowly. After stirring for 15 minutes, *N*-diethylaniline (4.3 mL, 27 mmol) was added to the diazonium salt mixture slowly with stirring. The mixture was stirred at 0-5°C for 1 hour, and then at room temperature for 2 hours. A solution of NaOAc (9.0 g) in 20 mL water was added, and the resulting mixture was stirred for 1 hours. The precipitate was collected by filtration, washed with water and finally purified with silica gel column using 0-2% methanol in methylene chloride as eluent to afford pure product **13**

(6.83 g, 70%). ^{1}H NMR ($CDCl_3$) δ (ppm) 1.23 (t, 6H, CH_3 of Et), 3.32-3.51 (m, 6H, CH_2 of Et and -CH_2SO2-), 3.99 (t, 2H, -CH_2O-), 6.71 (d, 2 aromatic H, ortho to NEt_2), 7.84-8.01 (m, 6 aromatic H).

4-[(2-(Methacryloyloxy)ethylsulfonyl]-4'-(diethylamino)azobenzene **(14)**

A solution of 4-[(2-hydroxyethyl)sulfonyl]-4'-(diethylamino)azobenzene (**13**) (5.4 g, 15 mmol) and triethylamine (2.6 mL, 18 mmol) in 100 mL THF at 0°C was treated dropwise with methacryloyl chloride (1.74 mL, 18 mmol). The reaction mixture was stirred for 2 hours at 0°C and 14 hours at room temperature, then filtered to remove the triethylammonium chloride. The filtrate was diluted with 250 mL CH_2Cl_2 and washed with brine, saturated $NaHCO_3$ and brine. The organic layer was dried (Na_2SO_4) and concentrated at reduced pressure. The residue was purified over silica gel column using 0-1.5% CH_3OH in CH_2Cl_2 as eluent to afford **14** (4.70 g, 73%). ^{1}H NMR ($CDCl_3$) δ (ppm) 1.22 (t, 3H, CH_3 of Et), 1.75 (s, 3H, allyl CH_3), 3.49 (m, 6H, CH_2 of Et and -CH_2SO2-), 4.49 (t, 2H, -CH_2O-), 5.42 (s, 1H, =CH), 5.80 (s, 1H, =CH), 6.80 (d, 2 aromatic H, ortho to NEt_2), 7.83-8.00 (m, 6 aromatic H).

Polymerization Procedure

A reaction ampoule was charged with 4-[(2-(methacryloyloxy)ethyl)ethylamino]-4'-(methylsulfonyl)azobenzene (**7**) (1.5 g, 3.6 mmol), 5.9 mg of azobisisobutyronitrile (AIBN, 0.36 mmol), and 15 mL of *N,N*-dimethylformamide (DMF, freshly vacuum-distilled). The resulting solution was degassed by bubbling nitrogen through for 25 minutes. The reaction mixture was heated at 65°C for 24 hours and then cooled to room temperature. The polymer was isolated by precipitation into excess methanol followed by reprecipitation twice from methylene chloride into methanol. The polymer was dried in a vacuum oven at 100°C for 24 hours to provide 1.02 g **pDRSAM** (68%):

The above description of the synthesis of polymer **pDRSAM** typifies the procedure employed for all polymers and copolymers described here. For copolymers, suitable mixtures of comonomers (**7** and **14**) were used, and the compositions were obtained by proton NMR.

Yields and characterization data for all of the polymers (**pDRSAM**, **pDRASM** and the copolymers **C1**, **C2** and **C3**) are given in Table 1.

CONCLUSION

Two new homopolymers, containing amino-sulfone azobenzene moieties as side chain groups, have been synthesized and characterized. The first homopolymer has the azobenzene chromophore bound to the main chain through the amino

Table 1. Synthesis and Properties of the Polymers

Polymer Code	Mol of **14** (%)	Yield (%)	M_n[a]	PD[b]	CH_2Cl_2	λ_{max} (nm) in Tg^C (°C)
pDRSAM	0	68	5700	1.39	436	155
C1	19.6	63	7600	1.95	442	150
C2	52	58	7000	2.03	448	151
C3	79.7	61	5300	1.98	454	149
pDRASM	100	76	5000	1.74	456	144

[a]Number-average molecular weights estimated by GPC.
[b]Polydispersity (Mw/Mn).
[c]Determined by differential scanning calorimetry (DSC).

group, while in the second homopolymer, the chromophore is bound through the sulfone group. The spacer between the chromophore and the main chain consists of two methylene groups. Three copolymers containing these new structural units have also been prepared. These new polymers are amorphous, have high Tg values, and will be used to test the importance of the binding direction of the chromophore in its ability to move and align perpendicular to the polarization of the laser light.

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REFERENCES

1. Natansohn, A.; Rochon, P. Photoinduced Motions in Azobenzene-based Amorphous Polymers. *Adv. Mater.,* **1999**, *11* 1387-1391.
2. Natansohn, A.; Rochon, P. In, *ACS Symposium Series: Photonic and Optoelectronic Polymers*, Samson, K.J.W.; Jenekhe, A., Eds. American Chemical Society: Washington, D. C. 1997; Vol. 672, 236-250.
3. Meng, X.; Natansohn, A.; Barrett, C.; Rochon, P. Azo Polymers for Reversible Optical Storage. 10. Cooperative Motion of Polar Side Groups in Amorphous Ppolymers. Macromolecules **1996**, *29* (3)*,* 946-952.
4. Buffeteau, T.; Natansohn, A.; Rochon, P.; Pezolet, M. Study of Cooperative Side Group Motions in Amorphous Polymers by Time Dependent Infrared Spectroscopy. Macromolecules **1996**, *29* 8783-8790.
5. Natansohn, A.; Rochon, P.; Meng, X.; Barrett, C.; Buffeteau, T.; Bonenfant, S.; Pezolet, M. Molecular Addressing? Selective Photoinduced Cooperative Motion of Polar Ester Groups in Copolymers Containing Azobenzene Groups. Macromolecules **1998**, *31* (4)*,* 1155-1161.

6. Nemoto, N.; Miyata, F.; Nagase, Y.; Abe, J.; Hasegawa, M.; Shirai, Y. Polyamides for Nonlinear Optics: Side-Chain All Donor-Attached NLO-phores vs. Side-Chain Alternating Donor-Attached and Acceptor-Attached NLO-phores. *Chem. Mater.* **1997**, *9* (1), 304-311.
7. Ulman, A.; Willand, C.S.; Kohler, W.; Robello, D.R.; Williams, D.J.; Handley, L. New Sulfonyl-Containing Materials for Nonlinear Optics: Semiempirical Calculations, Synthesis and Properties. J. Am. Chem. Soc. **1990**, *112* 7083-7090.
8. Kohler, W.; Robello, D.R.; Willand, C.S.; Williams, D.J. Dielectric Relaxation Study of Some Novel Polymers for Nonlinear Optics. Macromolecules **1991**, *24* (16), 4589-4599.
9. Xu, C.; Wu, B.; Dalton, L.R.; Ranon, P.M.; Shi, Y.; Steier, W.H. New Random Main-Chain, Second-Order Nonlinear Optical Polymers. Macromolecules **1992**, *25* (24), 6716-6718.
10. Xu, C.; Wu, B.; Todorova, O.; Dalton, L.R.; Shi, Y.; Ranon, P.M.; Steier, W.H. Stabilization of Dipole Alignment of Poled Nonlinear Optical Polymers by Ultrastructure Synthesis. Macromolecules **1993**, *25* (20), 5303-5309.
11. Robello, D.R.; Dao, P.T.; Phelan, J.; Revelli, J.; Schildkraut, J.S.; Scozzafava, M.; Ulman, A.; Willand, C.S. Linear Polymers for Nonlinear Optics. 2. Synthesis and Elecrooptical Properties for Polymer Bearing Pendant Chromophores with Methylsulfonyl Electron-acceptor Groups. Chem. Mater. **1992**, *4* 425-435.