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Synthesis and electro-optical properties of methacrylate polymers containing hexyl sulfone stilbene chromophore

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SUMMARY: Methacrylate polymers bearing pendant stilbene chromophore containing 4'-dialkylamino electron donor and 4-hexylsulfonyl electron acceptor has been synthesized. Owing to the introduced flexible alkyl chain to the NLO chromophore terminal group, soluble polymers was obtained up to 64 mol % of chromophore monomer portion in the copolymer. These amorphous polymers exhibited good film-forming abilities, thermal stability, and excellent optical clarity. The electrooptic coefficient (r_{33}) as high as 6.4 pm/V were measured at 1.3 μm by reflection method. These polymers were easily photobleached by irradiation of light at 350 ~ 450 nm wavelength for lateral confinement in channel waveguide.

Introduction

Recently, nonlinear optical (NLO) materials are being actively studied because of their potential to serve as the active components of ultrafast and highly efficient devices for optical communications, electrooptic (EO) modulation, and switching (1,2). Organic poled NLO polymers, in particular, are thought to possess many potential advantages over existing inorganic materials in view of their fast response time, modification capability, and easy processing for integrated assembly (3). For the practical optical device fabrication, these organic materials require the thermal stability, film forming properties of multi-layer thin films, low loss of propagation light, and as well as large electrooptic coefficients. There are many of the NLO polymers developed, nevertheless; little polymers such as amino-nitro stilbene based methacrylate successfully used for the EO devices like Mach-Zehnder modulator or directional coupler (4, 5, 6). These are due to their ease of polymer synthesis, transparency, and suitable polymer properties such as glass transition temperature (Tg).

Our previous work on electrooptic materials containing sulfonyl acceptor has been extended to the synthesis of long alkylated sulfonyl stilbene chromophore and the characterization of their doped polyimide as a host polymer (7, 8). In these systems, we found that the long alkylated chromophore with sulfonyl acceptor has enhanced solubility to the host polyimide and increase thermal stability of oriented dipole. In this

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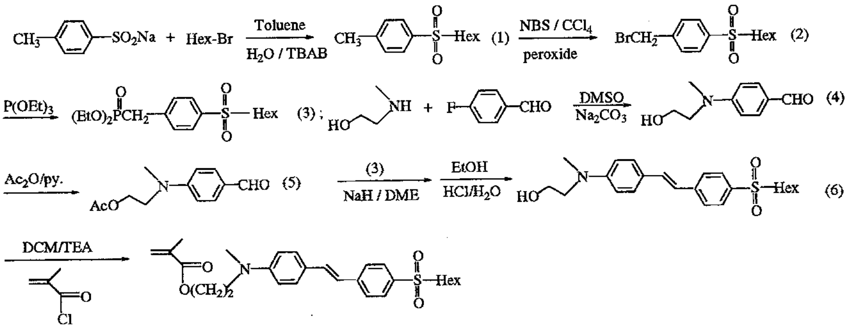
paper, we describe the synthesis and electrooptic properties of the methacrylate polymers bearing chromophore with a long alkyl sulfonyl acceptor.

Experimental Section

Materials. Solvents and starting materials were purchased from Aldrich Chemical Co. and used without further purification. Diethyl [(4-hexylsulfonyl) benzyl] phosphonate **(3)** and 4-[N-(2-hydroxyethyl)-N-methylamino] benzaldehyde **(4)** were synthesized according to the published literature procedures in references 8 and 9, respectively.

Scheme 1



Preparation of monomers. 4-[N-(2-Acetoxyethyl)-N-methylamino] benzaldehyde (5); (4) was dissolved in 78 mL of pyridine and 102 g of acetic anhydride (1 mol), and the solution was heated at reflux for 16 h. After cooling, the reaction mixture was poured onto 1 L of 5 % HCl in water, and the resulting mixture was extracted with ethyl acetate. The combined organic extracts were washed with aqueous $NaHCO_3$ and again with water, and dried over $MgSO_4$, and the solvent was removed at reduced pressure. The residue was fractionally distilled in vacuo to provide 112 g (51 %) of a pale yellow oil: b.p. 142 °C/0.2 mmHg; ^{1}H-NMR ($CDCl_3$) δ 1.97 (s, 3H), 3.06 (s, 3H), 3.67 (t, 2H), 4.24 (t, 2H), 6.74 (d, 2H), 7.72 (d, 2H), 9.71 (s, 1H).

4-[(2-Hydroxyethyl)methylamino]-4-(hexylsulfonyl) stilbene (6); To a vigorous stirred suspension of sodium hydride (2.6 g, 54 mmol, 60 % dispersion in mineral oil), 4-[(2-acetoxyethyl)-methylamino] benzaldehyde (5) (6 g, 27 mmol), and 60 mL of dry, freshly distilled 1,2-dimethoxyethane (DME) under nitrogen at room temperature was added diethyl [(4-hexylsulfonyl) benzyl] phosphonate (3) (10.3 g, 27 mmol) in 50 mL of DME. The mixture immediately turned yellow. The reaction mixture was heated at reflux for 3 h under nitrogen. The yellow solution was then poured over 400 g of crushed ice. A yellow solid was filtered and air dried. The resulting solid was dissolved in 150 mL of 10% (v/v) HCl in the mixture of ethanol and water (1:1), and the solution was heated at reflux for 10 h. After cooling, the solution was neutralized to pH 7 by the slow and careful addition of sodium carbonate. The yellow solid thus formed was collected by filtration, washed with water, and air dried. Recrystallization from ethanol yielded 7 g (58 %) of a bright yellow solid, mp 129 °C. ^{1}H-NMR ($CDCl_3$) δ 0.83 (t, 3H), 1,23 (m, 6H), 1.67 (m, 2H), 3.04 (m, 5H), 3.51 (t, 2H), 3.80 (t, 2H), 6.76 (d, 2H), 6.92 (d, 1H), 7.19 (d, 1H), 7.41 (d, 2H), 7.59 (d, 2H), 7.81 (d, 2H).

4-[(2-Methacryloxyethyl)methylamino]-4'-(hexylsulfonyl) stilbene: A stirred mixture of 4-[(2-hydroxyethyl)methylamino]-4'-(hexysulfonyl) stilbene (6) (8.7 g, 22 mmol), distilled triethylamine (3.3 g, 33 mmol), and 200 mL of dry, distilled dichloromethane was treated dropwise with methacryloyl chloride (3.5 g, 33 mmol) at 23 °C under nitrogen. After 72 h, the resulting solution was washed with saturated aqueous sodium bicarbonate, the solution was dried over $MgSO_4$ and the solvent was removed at reduced pressure. The product was recrystallized from tetrahydrofuran (THF)/hexane to yield 7.4 g (72%) of a yellow solid, m.p. 110 °C.; Elem. anal. Calcd for $C_{27}H_{35}NO_4S$: C, 69.05; H, 7.51. Found: C, 69.0; H, 7.49. ^{1}H-NMR ($CDCl_3$) δ 0.83 (t, 3H), 1,24 (m, 6H), 1.67 (m, 2H), 1.90 (s, 3H), 3.04 (s, 3H), 3.06 (t, 2H), 3.67 (t, 2H), 4.32 (t, 2H), 5.55 (t, 1H), 6.05 (d, 1H), 6.75 (d, 2H), 6.93 (d, J=16.27, 1H), 7.20 (d, J=16.23, 1H), 7.43 (d, 2H), 7.61 (d, 2H), 7.82 (d, 2H). ^{13}C-NMR ($CDCl_3$) δ 13.86 (-CH_3), 18.2 (-CH_3C), 22.2, 22.7, 27.9, 31.1 (methylene), 38.7 (NCH_3), 50.8 (NCH_2-) 56.4 (CH_2SO_2), 64.7 (CH_2O), 112.0, 122.0, 124.7, 125.9, 126.2, 128.3, 128.4, 132.6, 135.9, 136.2, 143.6, 149.1 (stilbene, vinyl), 167.3 (CO_2). IR (cm^{-1}): 1715 (C=O),

Polymerization. The polymerization was carried out with 2,2-azobis(2-methylpropionitrile (AIBN) in chlorobenzene at 70 °C for 48 h as discribed in the literature (10).

Instruments for Characterization. ^{1}H-, ^{13}C-NMR spectra were recorded on a Bruker AM-300 spectrometer. UV-visible spectra were obtained with a Shimadzu UV-3100S spectrometer. The molecular weights and polydispersity were determined in THF solvent with a Waters GPC-150C calibrated with polystyrene standards. A DuPont 9900 thermal analyzer was used to obtain the DSC thermograms with heating rates of 10 °C/min. The refractive indice were measured with the prism coupler at 1.3 μm. The thickness of the films were confirmed with an α-step surface profiler (Tencor instruments, α-step 300). For the measurement of dielectric constant, a polymer film was coated on indium tin oxide (ITO) coated glass. And then, circular gold electrodes (5-mm diameter) were evaporated on the film. The capacitance (C_p) of the Au-polymer-ITO structure was determined with a HP 4276A LCZ meter at various frequencies. Using electrode area A, capacitance C, and thickness d, the dielectric constant ε was calculated using the relationship $\varepsilon = dC_p/A\varepsilon_0$, where ε_0 is the electric permittivity of free space. The electro-optic coefficient, r_{33}, of the poled polymer films was measured at wavelength of 1.3 μm using a reflection method (11).

Results and Discussion

Synthesis and Characterization. The monomer bearing sulfonyl acceptor was synthesized by convergent methods that involved preparing the doner and acceptor portions of the NLO chromophore separately, as illustrated in Scheme 1. Preparation of the hexyl sulfone acceptor group (**1**) was facilitated through the reaction of p-toluene sulfinic acid sodium salt and 1-bromohexane with a phase transfer catalyst (12). Benzyl bromide (**2**) was achieved by reacting the hexyl sulfonyl toluene with N-bromosuccinimide and then react with triethyl phosphite to produce the benzyl phosphonate (**3**). Preparation of amino donor group was synthesized by reacting the p-fluorobenzaldehyde and amino alcohol through the *ipso* substitution reaction. The methacrylate monomer with methyl sulfonyl stilbene chromophore was not obtained to an isolated product due to spontaneous polymerization after being purified by chromatography, producing an insoluble solid (10).

Table 1.Synthesis and characterization data of NLO polymers

Polym.	m_{feed}[a]	$m_{polymer}$[b]	polymer yield, %	$\overline{M}_w$[c]	$\overline{M}_w/\overline{M}_n$[c]	Tg[d]
P-1	20	19	97	68.7k	3.1	105
P-2	40	37	96	161.2k	3.7	116
P-3	70	64	95	73.2k	2.2	113

[a] Mole fraction (%) of chromophore monomer charge. [b] Mole fraction (%) of chromophore monomer in copolymer determined by ^{1}H-NMR.
[c] Values were obtained by GPC analysis with polystyrene standards.
[d] Determined by differential scanning calorimetry.

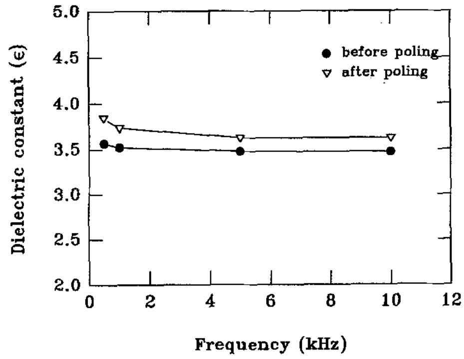
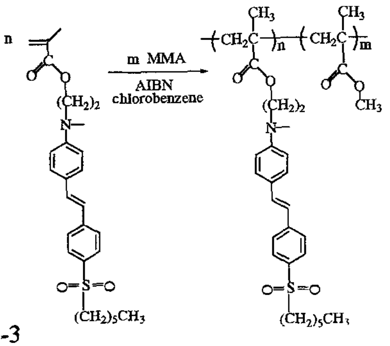


Figure 1. Dielectric constant (ε) of the P-3 samples before and after poling according to frequencies.

Scheme 2



However, a methacrylate monomer bearing hexyl sulfonyl stilbene chromophore was isolated as stable crystalline solid. Free radical polymerization was carried out in a chlorobenzene solution at 70 °C using AIBN initiator as shown in scheme 2. Synthetic and characterization data for the polymers are presented in Table 1. It is known that, in the polymerization of stilbene based monomers, increasing the portion of stilbenyl chromophore results in an intractable materials due to the crosslinking reaction of stilbenyl double bond. Recently, it was reported that the practical concentration limit of methyl sulfonyl stilbene-containing monomer is approximately 25 mol % (10). However, we have synthesized the soluble polymers up to 64 mol % of hexyl sulfonyl stilbene chromophore monomers with good yield above 95 %. The weight average molecular weights (Mw) and polymer dispersity values of the resulting polymers were estimated to be in the range (6.87 - 16.12) x 10^4 and 2.2 - 3.7, respectively. All of the polymers were fully characterized by ^{1}H, ^{13}C NMR, FTIR, and UV-visible spectroscopies. The composition of copolymers (determined by integration of ^{1}H NMR signals) closely matched the composition of the monomer feed mixture. Polymers were appeared to be amorphous when examined by polarized optical microscopy and by DSC. In contrast, polymers containing a nitro group in place of the sulfonyl group exhibited crystalline and liquid crystalline morphologies. The relatively bulky hexyl sulfonyl group may prevent the efficient packing of the aromatic groups and inhibit the formation of an ordered phase. Glass transition temperatures of the resulting polymers were ranged from 105 to 116 °C determined by DSC.

Table 2. Linear and Nonlinear Optical Data for Polymers

polym.	Dye conc. (mol %)	n_{TE}	n_{TM}	V_p[b]	T_p[c]	r_{33}, pm/V[d]
		(1.3 μm)[a]		(V/μm)	^{0}C	(1.3 μm)
P-1	19	1.5495	1.5451	98	110	1.1
P-2	37	1.5812	1.5796	130	125	4.7
P-3	64	1.6183	1.5997	156	123	6.4

[a] Indices of refraction were determined from waveguiding experiments. [b] Electric field during poling. [c] Temperature during poling. [d] Electro-optic coefficient.

Electro-optical properties. Electronic absorptions of the polymers show the characteristic broad peak at 390 nm due to the $\pi - \pi^*$ transition of the conjugated NLO chromophores as shown in Figure 3. The refractive indices, n, (measured at 1.3 μm), for unpoled polymer samples were shown in Table 2. Refractive indices increase with the content of the NLO chromophore. Optical losses were found to be ca. 1.5 dB/cm at 1.3

μm for waveguide samples of P-2. Figure 1 shows the dielectric constants (ε) of the P-3 samples before and after poling at various frequencies. The dielectric constants of all polymers are appreciably higher than n^2, indicating that there is a significant amount of polarization occurring at these frequencies (10). And also, the values of ε increased after poling due to the highly oriented NLO chromophores along the electric field direction.

Table 2 summarized the poling conditions and measured electrooptic coefficient (r_{33}) of the polymer films at 1.3 μm. As expected, the electrooptic coefficient (r_{33}) is enhanced with increasing the amount of chromophores and the poling field strength. The electrooptic coefficient (r_{33}) of the P-3 in present study was 6.4 pm/V for the poled at the 156 V/μm at the wavelength of 1.3 μm. To evaluate the temperature stability of the polymers, we studied the temporal stability of a electrooptic coefficient. It was found that the EO coefficient of P-3 was maintained about 80 % of original signal after two months at room temperature.

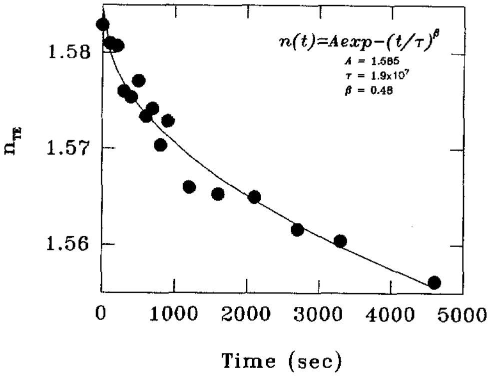


Figure 2. Effect of exposure dose of large area illuminator (40 mW/cm^2, λ=350~450 nm) on refractive index of P-2. Measured on glass substrate at 1.3 μm by prism coupling.

Photobleaching of NLO polymers have been widely used for the lateral confinement of the light in polymer channel waveguid (13, 14). We also measured the refractive index and the electronic absorption change during photobleaching. The experiments were carried out using the near-UV lines (350~450 nm). The refractive index change are shown in Figure 2 as a function of irradiation dose (time) for a thin film of P-2. The refractive index data indicate that even at wavelength far from resonance (1.3 μm), a substantial index reduction can be obtained by irradiation.

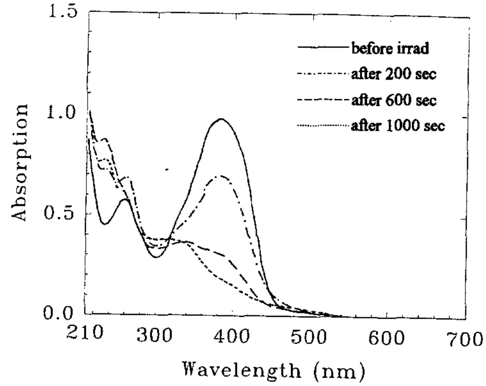


Figure 3. Absorption spectra of a thin film of P-2 before irradiation using the large area illuminator (40 mW/cm^2, λ=350~450 nm) and then at intervals after irradiation.

The reduction of refractive index could be fitted by a streched exponential equation as shown inset of Figure 2. Figure 3 shows the electronic absorption spectra at time intervals after irradiation. Initially, the main absorption peak is at 389 nm, corresponding to the transition between ground and excited states of the complete chromophore. It can be seen that, immediately after irradiation, the absorption maximum at 389 nm has been substantially reduced. It is believed to be due to the photo-oxidation of the stilbene double bond (CH=CH) excited by exposed photon (15). We are presently investigating the Mach-Zehnder modulator using the titled polymers.

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