Linear Polymers for Nonlinear Optics. 4.[1] Synthesis and Nonlinear Optical Properties of Side-Chain Poly(methacrylates) with Vinylcyanosulfonyl Groups

Douglas R. Robello,*,† Phat T. Dao,‡ Jay S. Schildkraut,† Michael Scozzafava,§ Edward J. Urankar,⊥ and Craig S. Willand†

Imaging Research and Advanced Development, Eastman Kodak Company, Rochester, New York 14650-2110; Chemical Quality Services Division, Eastman Kodak Company, Rochester, New York 14650-2110; Precision Components Manufacturing Division, Eastman Kodak Company, Rochester, New York 14650-2110; and Department of Chemistry, Cornell University, Ithaca, New York 14853

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Several polymers containing amino–azobenzene–vinylcyanosulfonyl chromophores were synthesized by free-radical polymerization of methacrylate-functionalized monomers. The polymers were soluble and could be spin-coated into somewhat brittle but acceptable quality films. After poling, one sample displayed a large electrooptic coefficient, r_{33}, of 22 pm/V (measured off-resonance at 830 nm). Also, the electrooptic response of this sample was quite stable, retaining approximately 90% of its original r_{33} after storage for 2 months at 80 °C. Light at 1064 nm could be successfully propagated in thin-film waveguides, but polymers containing a high concentration of the chromophore had unacceptable absorption losses at 830 nm. The absorption at 830 nm was attributed to a small amount of chromophore–aggregate in the solid film that led to a broadening of the absorption spectrum of the chromophore. Attempts to suppress the formation of the aggregated species using variations in terminal groups, spacer lengths, and comonomer identity were unsuccessful. Only rather large dilution of the chromophore gave a material capable of waveguiding 830 nm light, with a proportional decrease in nonlinear optical susceptibility.

Introduction

Polymeric materials with large second-order nonlinear optical (NLO) properties have been investigated intensely by many research groups around the world.[2] Such materials may form key elements of integrated components for the efficient manipulation of optical information. A particularly important second-order NLO phenomenon is the electrooptic effect (also known as the Pockels effect), the change of refractive index by a medium with an applied electric field. Devices exploiting this effect may be useful for optical switching, modulation, scanning, printing, and beam control, particularly with diode laser sources in the near-infrared.

The electrooptic coefficient, *r*, describes the magnitude of the refractive index change with voltage and represents a figure of merit for a second-order NLO material. The benchmark for electrooptic coefficient is 31 pm/V, the value for the well-studied inorganic material $LiNbO_3$.[3] Unfortunately, $LiNbO_3$ and related materials suffer from a number of disadvantages in processing and use, which limit their application in optical devices and lead to very high cost. In contrast, organic films offer many potential advantages for NLO devices. For example, their ease and flexibility in processing enables the fabrication of complicated integrated devices. Also, the response time for organic NLO materials is generally much faster than that of inorganic materials.

For organic materials, the macroscopic nonlinear susceptibility, $\chi^{(2)}$, arises almost entirely from contributions of the imbedded NLO-active moieties, known as chromophores. Therefore, it is possible to predict with reasonable accuracy the second-order susceptibility of an organic material from the properties of the constituent molecules, using information about the material structure and other simple measured quantities such as the dielectric constant.[4,5]

For an organic material to exhibit significant NLO susceptibility, its active molecules must be arranged in a noncentrosymmetric manner.[2] One of the most common techniques for establishing this arrangement is by electric field poling.[4] In this technique, a material is held at or above its glass transition temperatures, while

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† Imaging Research and Advanced Development, Eastman Kodak Co.

‡ Chemical Quality Services Division, Eastman Kodak Co.

§ Precision Components Manufacturing Division, Eastman Kodak Co.

⊥ Cornell University.

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applying a strong dc electric field across the sample to orient the molecules. The induced orientation is then stabilized by cooling the sample below the glass transition (T_g) with the poling field still applied, after which point the field can be removed. For an initially amorphous (i.e., glassy) system that is made noncentrosymmetric by electric field poling, the following approximation holds:[2c]

$$r_{33} \propto \frac{N}{V}\beta\frac{E_p\mu}{T} \tag{1}$$

where β is the molecular hyperpolarizability, an intrinsic property of the molecules in the sample, N/V is the concentration of active NLO molecules, E_p is the electric field applied during poling, μ is the ground-state dipole moment, and T is the absolute temperature.

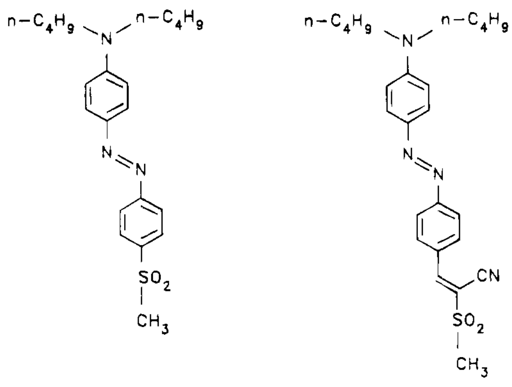
There are practical limitations to many of the quantities in the above expression. For example, the concentration of NLO-active species cannot be made much greater than 10^{22} molecules/cm^3. The poling voltage cannot be higher than about 200 V/μm without the probability of cataclysmic dielectric breakdown in the sample. The temperature during poling must be at or above T_g, which in turn must be well above ambient to prevent subsequent relaxation of the induced order. On the other hand, the poling temperature must be below the decomposition point of the material. Typically, the poling temperature falls between 100 and 250 °C.

Therefore, the principal quantities from which one might hope to gain increased NLO performance are β and μ. The product $\mu\cdot\beta$ is then a figure of merit for a molecule that is to be oriented by poling. This product is conveniently measured by an electric-field-induced second-harmonic generation experiment (EFISH),[6,7] which effectively simulates the orientation that a molecular dipole would experience during poling of a bulk material.

Our previous work[5] dealt with chromophores similar to **1** that contained methylsulfonyl electron acceptors.[7] Katz and co-workers had demonstrated that chromophores bearing *multiple*, *reinforcing* electron accepting groups exhibited enhanced NLO properties.[8] We therefore attempted to extend our earlier work to analogous systems. On the basis of studies of many model compounds, we selected the chromophore **2** (Figure 1) as a candidate for inclusion in polymers for electrooptic modulation. EFISH measurements showed chromophore **2** had a greatly increased nonlinearity over the simpler chromophore **1** (Figure 1). However, it remained to be seen whether polymers containing a high concentration of the chromophore **2** could be prepared.

Results and Discussion

Synthesis and Physical Properties of the NLO Polymers. The model compound **2** and its substituted analogues were synthesized from commerically available 4-aminobenzaldehyde via either of two closely related paths (Scheme 1), differing only by the order in which the reactions were done. Both paths gave about the same overall yields.



1 $\mu\beta$ = 500 × 10^{-48} esu

2 $\mu\beta$ = 1300 × 10^{-48} esu

Figure 1. Donor–acceptor model chromophore structures and EFISH results (1.9 μm fundamental, $CHCl_3$ solution).

Table 1. Synthesis and Properties of NLO Polymers

polymer code	monomers used[a]	yield (%)	$\bar{M}_n$[b]	$\bar{M}_w$[b]	PD[c]	T_g[d] (°C)
7a	**6a**[e]	90	68 400[f]	173 000[f]	2.53[f]	161
		86	43 000[f]	288 000[f]	5.84[f]	160
			40 000	131 000	3.27	
		94	43 700	130 000	2.98	154
7b	**68a/8** (75/25)	93	35 400	91 300	2.58	139
7c	**6a/MMA** (50/50)	97	43 600	270 000	6.22	127
7d	**6a/MMA** (10/90)	87	35 100	163 000	4.63	121
	6a/S (50/50)	0				
	6a/S (25/75)	0				
	6a/BrS (80/20)	0				
7e	**6a/5b** (50/50)	85	37 200	65 300	1.76	137
7f	**6b**	75	43 700	73 200	1.68	111
7g	**6c**	81	26 500	47 600	1.80	163
			30 400[f]	95 900[f]	3.15[f]	

[a] Code indicates monomer(s) employed and relative weight percentages. MMA = methyl methacrylate, S = styrene, BrS = 4-bromostyrene. For other abbreviations see Scheme 2. [b] Estimated by size exclusion chromatography in DMF, poly(methyl methacrylate) calibration. [c] Polydispersity ($\bar{M}_w/\bar{M}_n$). [d] Determined by differential scanning calorimetry. [e] Three batches were prepared. [f] Absolute molecular weight determination by SEC with viscometric detection, universal calibration.

Three different polymerizable chromophores, **6a–c**, were synthesized by esterification of hydroxy-substituted compounds with methacryloyl chloride (Scheme 2). We were pleased to discover that these dye monomers could be polymerized in solution using conventional free-radical conditions, and moderately high molecular weight polymers could be attained (Table 1). Also, copolymers of the dye monomers could be synthesized with methyl methacrylate (MMA), with the methylsulfonyl-containing monomer **8**[5] (Figure 2, polymer **7b**), and even with each other (polymer **7e**). However, attempts to copolymerize **6a** with the relatively electron-rich comonomers styrene (S) or 4-bromostyrene (BrS) failed completely, and only unreacted monomers were isolated. (Note that the simpler monomer **8** copolymerized well these two comonomers.) An interaction (as yet unexplained) between the electron-rich styrenic monomer or its radical with the very electron-deficient cyano–sulfonyl–vinyl group may prevent chain propagation in these cases.

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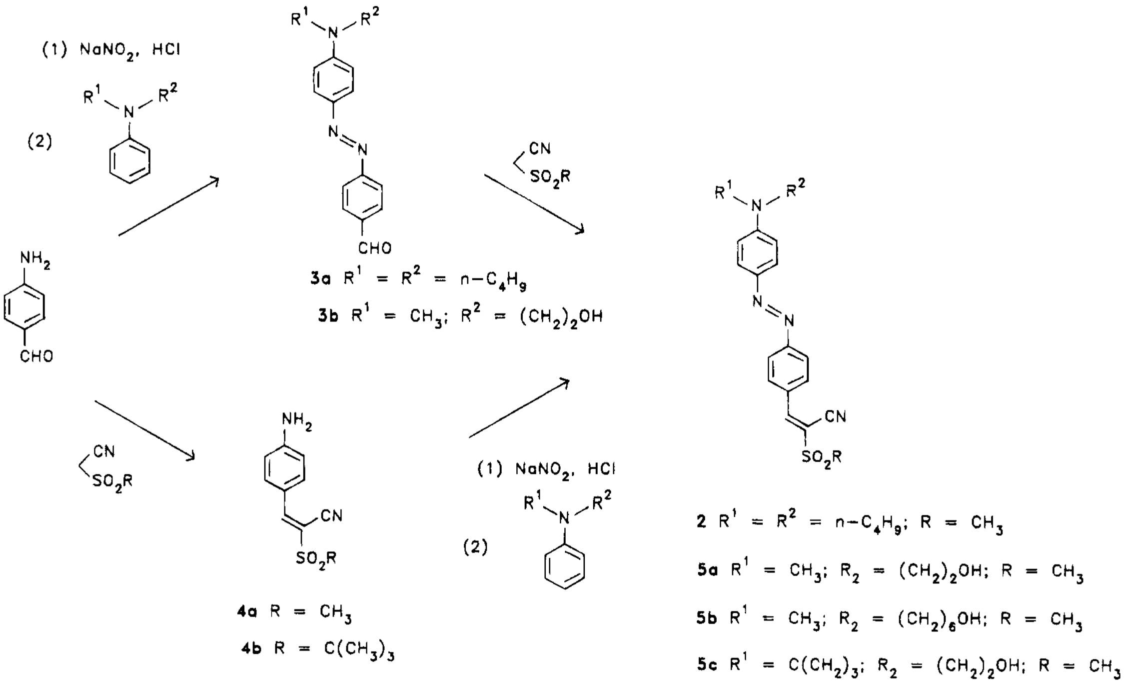
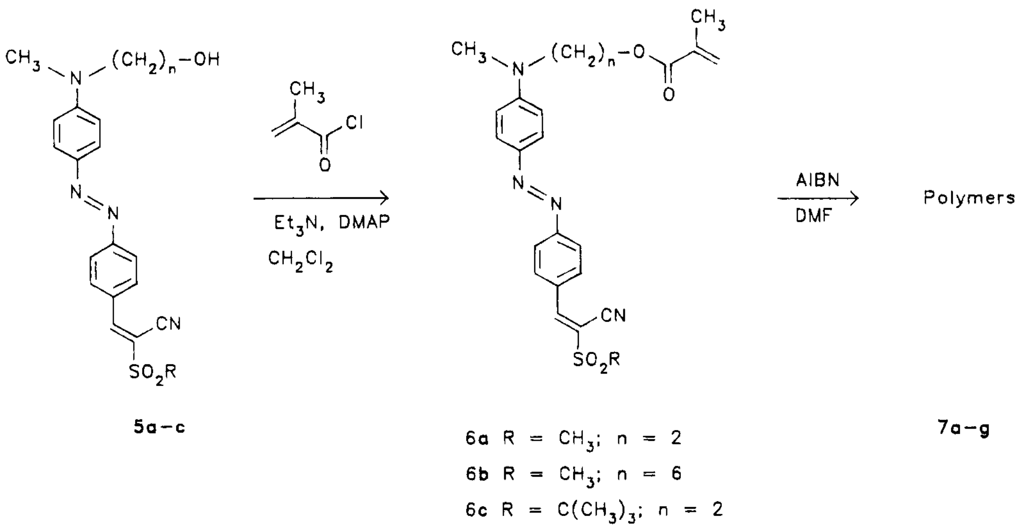
Scheme 1. Syntheses of Nonlinear Optical Chromophores



Scheme 2. Syntheses of Dye-Containing Monomers and Polymers



The molecular weight distributions of polymers containing **6a** are broader than those of the other "double-acceptor" monomers **6b** and **6c**, but the cause of this behavior is also not known.

The polymers **7a–g** were isolated as strongly purple-colored solids. All of the polymers were freely soluble in polar, aprotic solvents such as *N,N*-dimethylformamide and methyl sulfoxide. The copolymers containing MMA were also soluble in chlorinated solvents and in tetrahydrofuran. The materials appeared to be amorphous; no crystalline melting transitions were detected by differential scannning calorimetry (DSC) for any of the samples. In addition, **7a** was examined by wide-angle X-ray powder diffraction, and no peaks indicative of crystallinity were found.

The glass transition temperatures were increased in polymers **7** compared to those containing chromophore **1**, presumably because of the increased size and dipole moment of the chromophore **2** versus **1** (Table 3). Furthermore, the two homopolymers **7a** and **7g** with short alkyl chains between the polymer backbone and chromophore exhibit glass transitions above 160 °C, a very desirable range for preservation of poled orientation (see below). One minor discrepancy in T_g was noted for the copolymer of **6a** and methyl methacrylate MMA

Table 2. Elemental Analyses of NLO Polymers[a]

polymer	%C	%H	%N	%S
7a	61.05	5.25	12.38	7.09
	60.44	5.31	12.22	6.72
7b	61.53	5.35	11.59	7.07
	60.66	5.64	11.46	6.48
7c	60.52	6.70	6.19	3.54
	60.21	6.71	6.03	3.73
7d	60.09	7.78	1.24	0.71
	54.01	6.97	0.89	0.23
7e	62.40	5.84	11.70	6.69
	61.69	5.74	11.60	6.33
7f	63.76	6.34	11.02	6.30
	63.32	6.27	10.90	5.96

[a] Reported as calcd/found. For copolymers, the calculated compositions are based on the monomer feed ratios.

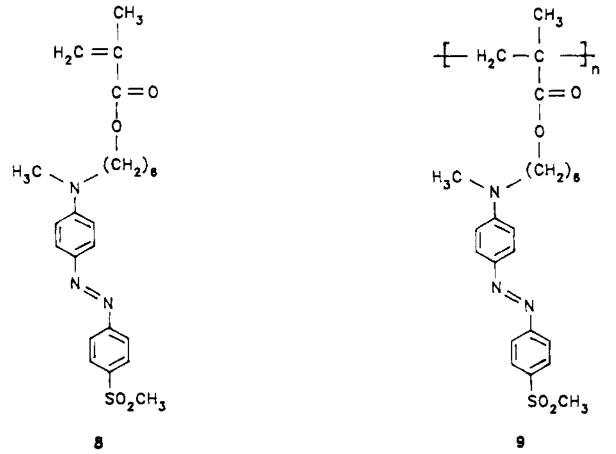
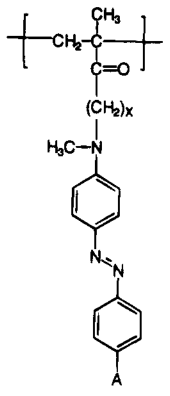


Figure 2. Control monomer **8** and homopolymer **9**.

Table 3. Comparison of Glass Transition Temperatures of NLO Polymers



A	x	$T_g{}^a$ (°C)
SO_2CH_3	2	140^b
$CH{=}C(CN)SO_2CH_3$ (**7a**)	2	160
SO_2CH_3 (**9**)	6	99^b
$CH{=}C(CN)SO_2CH_3$ (**7f**)	6	111

[a] Determined by differential scanning calorimetry. [b] Data taken from ref 5.

(polymer **7c**). On the basis of the properties of homopolymers of its constituent repeat units, one would predict a T_g near 140 °C for **7c**, but the actual value measured by DSC was approximately 127 °C. However, studies of the rate of poling at various temperatures (Figure 3) and dynamic mechanical analysis (Figure 4) were consistent with the expected T_g of 140 °C. The origin of this discrepancy is not understood. Possible factors include unusual effects of molecular sequence, tacticity, or molecular weight distribution. The electrooptic coefficient of **7c** did agree reasonably well with the predicted value (see below).

Thin-Film Preparation and Nonlinear Optical Properties. Good-quality thin films could be prepared by spin-coating from *N,N*-dimethylacetamide (DMAc) solutions of the polymers with high chromophore concentrations. Blanketing the coating apparatus with inert gas markedly improved the quality of the films spun from DMAc, presumably by excluding moisture from this hygroscopic solvent. The copolymers with methyl methacrylate could be coated from 1,2,3-trichloropropane. The homopolymer **7a** was studied most closely. Films of this polymer had a tendency to crack if the sample was not handled carefully. Qualitative inspection of thicker (ca. 100 μm) films of **7a** demonstrated the brittle nature of this material, typical behavior for comblike polymers.

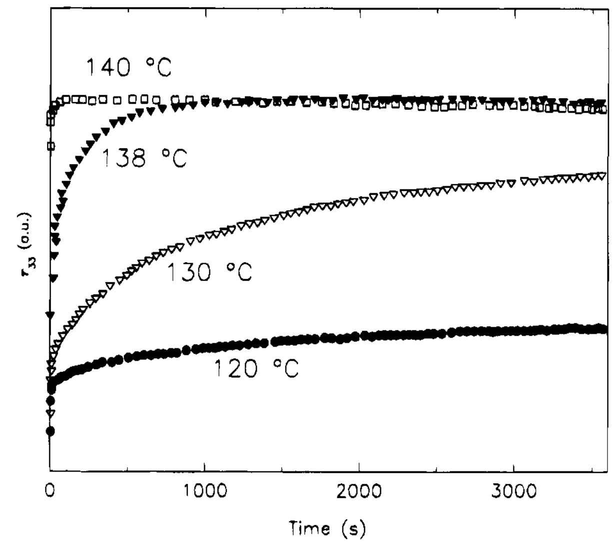


Figure 3. Apparent electrooptic coefficient r_{33} of polymer **7c** as a function of time from the onset of the poling field at various temperatures.

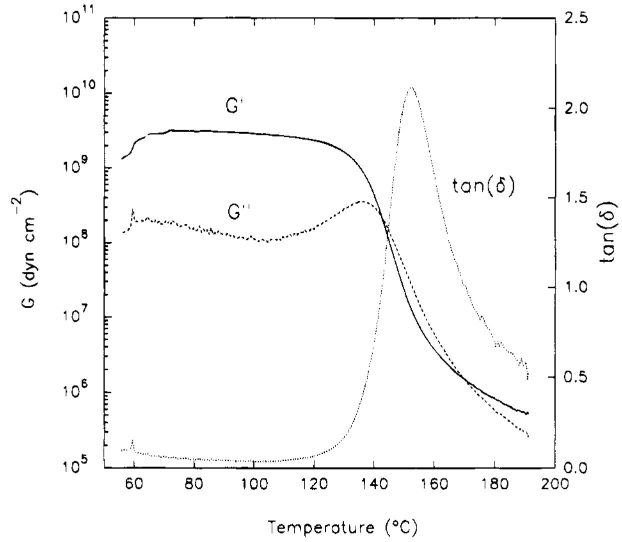


Figure 4. Dynamic mechanical analysis of polymer **7c**.

Film samples of polymers **7a** and **7c** were prepared on indium tin oxide (ITO) coated glass slides. After the films were dried in a vacuum oven, gold electrodes were evaporated onto the surface. The kinetics of the poling process were determined by observing the electrooptic coefficient[9] of the films in real time after applying the poling field. Figure 3 shows representative results for **7c**. In this way, optimized poling conditions could be found. Interestingly, all polymer samples tested exhibited an apparently instantaneous electrooptic response (ca. 15% of the total apparent r_{33}) when the poling field was first applied near T_g, followed by a slower increase of r_{33} to the equilibrium value under the field. The rapid response was observed even at room temperature, far below T_g, but the subsequent rise was absent.

The second relatively slow process can be attributed to actual poling. The initial rapid process may be short-

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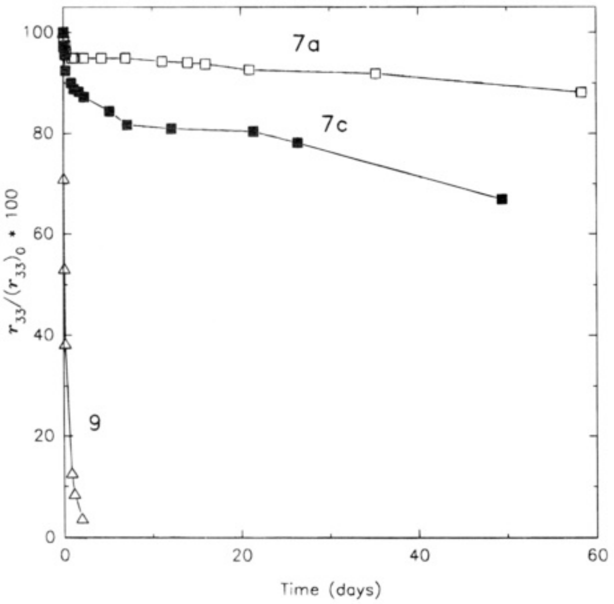

Figure 5. Decay of the electrooptic coefficient r_{33} at 80 °C under nitrogen for NLO polymers **7a** (open squares), **7c** (filled squares), and **9** (open triangles).

Table 4. Electrooptic Coefficients of NLO Polymers

polymer	T[a] (°C)	r_{33}[b] (calcd)	r_{33}[c] (exp)
7a	180	28	22
7c	150	14	11
9	89[d]	11.9[d]	12.5[d]

[a] Poling temperature. Note that the poling field in all cases was ca. 10^6 V/cm. [b] Calculated electrooptic coefficients using EFISH data for $\mu \cdot \beta$, dielectric data, and measured concentrations.[5] [c] Experimental electrooptic coefficients at 830 nm using a reflection technique.[9] [d] Data taken from ref 5.

range orientation (libration) of the chromophores within their local free volume, or a third-order NLO effect, or a combination of both processes. Preliminary investigation of this phenomenon indicated that the magnitude of the rapid electrooptic response begins to fall off at very high frequencies, indicating that a librational orientation is a contributing factor.

A film sample of **7a** was poled at 100 V/μm, and an electrooptic coefficient r_{33} of 22 pm/V was measured (at 830 nm), a high value approaching that of $LiNbO_3$ (Table 4). (Note: at 1064 nm, see below, r_{33} is estimated to be 20 pm/V, according to the two-level model.[2c]) The possibility exists of achieving even larger values of r_{33} by poling at higher fields. The r_{33} of **7c** poled under similar conditions was 11 pm/V, a value consistent with the halved concentration of chromophore in this material.

The stability of the electrooptic response of **7a** was excellent; a sample aged at 80 °C for 35 days exhibited *90% of its original* r_{33} (Figure 5). Most of the decay in r_{33} occurred in the first few days, after which time the decrease became very slow. For comparison, r_{33} of the homopolymer **9** (T_g = 99 °C)[5] decayed to zero within 1 day of storage under these aggressive conditions. Therefore, **7a** represents a significant improvement over earlier linear polymers in both the magnitude and the stability of electrooptic response. As expected, **7c** showed poorer temporal stability compared to **7a**, consistent with its lowered T_g. As is by now widely recognized, slow cooling (physical aging) of the films from the poling temperature with the field still applied led to the best temporal stability.

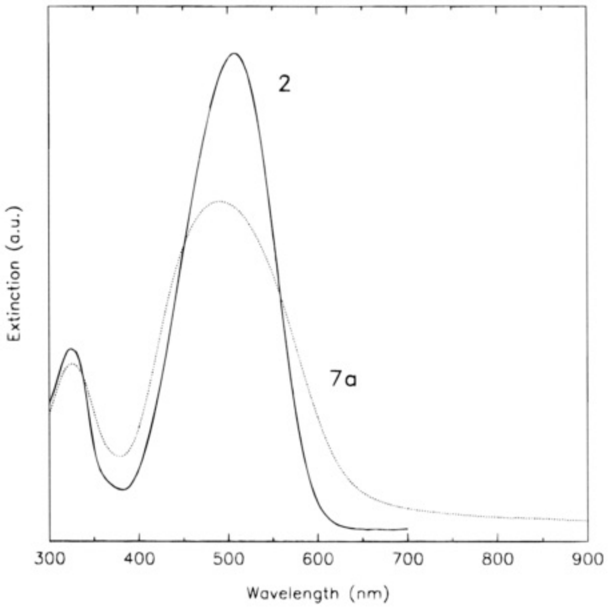

Figure 6. Comparison of absorption spectra of solid polymer **7a** (dotted line) and a dilute solution of model compound **2** in $CHCl_3$ (solid line). The extinction of the polymer is shown in arbitrary units.

Light at 1064 nm was introduced into a thin-film waveguide of **7a** by prism-coupling, and a streak of several centimeters was noted. Therefore, optical losses at this wavelength were, at most, a few dB/cm. However, light at 830 nm failed to propagate at all in the film of **7a**, although **9** had been shown to guide this wavelength with relatively low loss.[5] Physical defects in the film of **7a**, either intrinsic or from damage caused by contact with the prism, could be eliminated as possible causes of the failure to waveguide 830 nm light because 1064 nm light propagated well. Therefore, some light absorption by the polymer must be occurring at 830 nm, an unanticipated problem.

The absorption maximum of chromophore **2**, present in polymers **7**, is red-shifted somewhat from that of chromophore **1**, present in polymer **9** (508 vs 450 nm, respectively). However, the main portion of the absorption band of **2** is still very far from 830 nm, so it is unlikely that the observed attenuation is inherent to the chromophore. In agreement with this supposition, 830 nm light was successfully guided in the copolymer **7c**. The only difference between **7a** and **7c** is a factor of 2 in chromophore concentration, an insufficient reason for the observed large improvement in absorption. The cause for the attenuation at 830 nm in **7a** became apparent on examination of the visible spectra of relatively thick (ca. 20 μm) films of the polymers. Severe broadening including a small but significant tailing of the absorbance band of **7a** was observed in the bulk film at and even above 830 nm (Figure 6), when compared to the spectrum of model compound **2** in dilute solution. A close examination of the region of interest (Figure 7) demonstrated that the absorbance at 830 nm for **7a** was 5−10 times greater than that of **7c**, despite a factor of only 2 in chromophore density. This nonideal behavior indicates that interaction among the chromophores occurs in **7a**, leading to an aggregated species that has a longer absorption wavelength. The aggregation is disrupted by dilution in **7c**. Unfortunately, the methyl methacrylate units have negligible NLO activity,

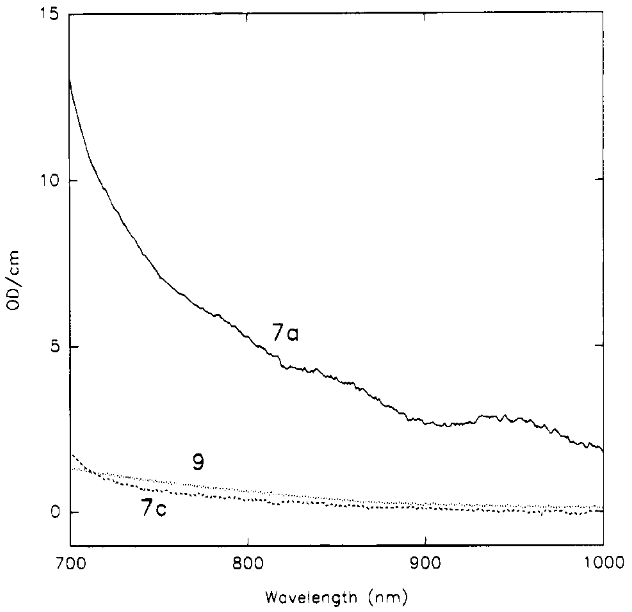

Figure 7. Absorption spectra of solid films of polymers **7a** (solid line), **7c** (dashed line), and **9** (dotted line).

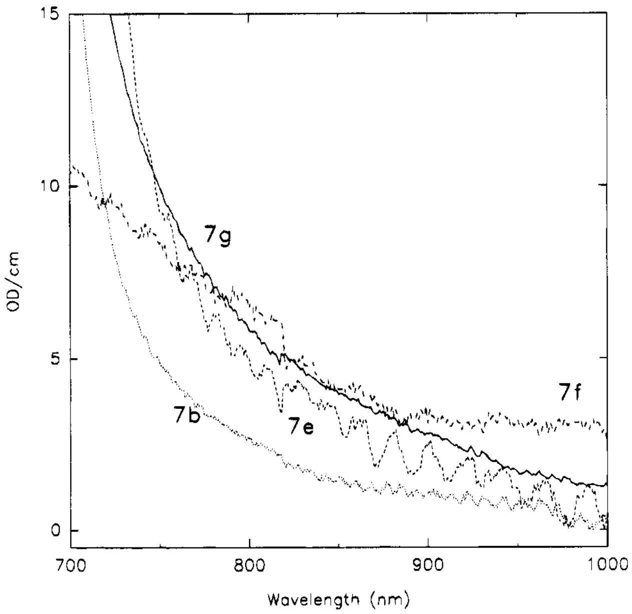

Figure 8. Absorption spectra of solid films of polymers **7g** (solid line), **7b** (dotted line), **7e** (short dashed line), and **7f** (long dashed line).

so the dilution by 2 decreases the susceptibility proportionately (Table 4).

We then made several attempts to disrupt the putative aggregate and thereby improve the optical transparency of this class of polymer without significantly reducing the nonlinearity, but without success. For example, we synthesized monomer **6c**, which is identical to **6a** except for a bulky *tert*-butyl group at the terminus of the side-chain, which we hoped would inhibit close approach of the chromophores. Similarly, we synthesized monomer **6b**, which has an extended (six carbon) spacer, in case close attachment to the polymer backbone was promoting aggregation. However, neither of the homopolymers of these two monomer (polymers **7f** and **7g**) exhibited improved transparency at 830 nm (Figure 8).

We also examined a random copolymer of **6a** and **6b** (polymer **7e**) in hopes that mixing the spacer lengths might inhibit chromophore aggregation, but the absorption spectrum was virtually identical to the corresponding homopolymers (Figure 8). Similarly, we synthesized 75/25 (wt %) copolymer (polymer **7b**) containing randomly placed, dissimilar repeat units **6a** and **8**, respectively (i.e., a mixture of chromophores **1** and **2**), but again the absorption at 830 nm remained unacceptably high (Figure 8).

The accumulated structure–property data suggest that the aggregation may be nonspecific, and therefore all materials of this structure containing a high concentration of the chromophore **2** may tend to exhibit undesirable broadening of the absorption band.

Conclusions

The amino–azobenzene–vinylcyanosulfone NLO chromophore is compatible with standard free-radical methacrylate polymerization. Side-chain homopolymers bearing this chromophore in every repeat unit could be readily synthesized, with high molecular weights. Consistent with their structure, a strong and stable electrooptic response could be obtained with these polymers. The temporal stability at 80 °C of polymer **7a** (with a T_g of 162 °C) *was as good as that of many cross-linked NLO systems described in the literature.*[12] Therefore, the preservation of poling-induced order does not necessarily require in situ cross-linking with its accompanying complications. Linear polymers with high glass transitions may be sufficient to achieve thermally stable NLO properties.

We have successfully prepared materials containing very high concentrations of NLO-active chromophores, a desirable feature for achieving the maximum NLO response. However, our data suggest that, at high concentrations, a small amount of aggregated species may be formed. These aggregates, if present, are responsible for a tailing of the absorption band that leads to undesirable attenuation of guided light below 1000 nm. However, these materials may be useful for electrooptic applications at longer wavelengths, especially those used for optical communications applications.

Experimental Section

General Techniques. NMR spectra were recorded on a General Electric QE-300 instrument operating at 300 MHz for ^{1}H and at 75.5 MHz for ^{13}C. All coupling constants are given in hertz. Field desorption mass spectrometry (FD-MS), size-exclusion chromatography (SEC), and differential scanning calorimetry (DSC) were performed by Eastman Kodak Co., Analytical Technology Division. *N*-(2-Hydroxyethyl)-*N*-methylaniline (Pfaltz and Bauer), (methylsulfonyl)acetonitrile and (*tert*-butylsulfonyl)acetonitrile (Lancaster), and 4-aminobenzaldehyde ("monomer", American Tokyo Kasei) were used as received. *N*-(6-Hydroxyhexyl)-*N*-methylaniline was prepared as previously reported.[10] Irganox 1010 (inhibitor) was obtained from Ciba-Geigy Co.

4,4-(Dibutylamino)-4′-(β-cyano-β-(*tert*-butylsulfonyl)-vinyl)azobenzene (2). A mixture of 0.50 g (1.5 mmol) of 4-(dibutylamino)azobenzene-4′-carboxaldehyde (**3a**), 0.25 g (2.1 mmol) of (methylsulfonyl)acetonitrile, and 0.15 g (1.9 mmol) of ammonium acetate was stirred at reflux in ethanol solution

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for 4 h. The reaction mixture was cooled to 0 °C, and the precipitated product was collected and dried in vacuo. Yield 0.20 g (31%).

^{1}H NMR (CDCl$_3$) δ 0.99 (t, *J* = 7.3, 6 H, CH$_2$**CH**$_3$), 1.4 (m, 4 H, **CH**$_2$CH$_3$), 1.6 (m, 4 H, **CH**$_2$CH$_2$CH$_3$), 3.23 (s, 3 H, SO$_2$**CH**$_3$), 3.39 (t, *J* = 7.8, 4 H, SO$_2$**CH**$_3$), 6.70 (d, *J* = 9.2, 2 H, arom **CH** ortho to NBu$_2$), 7.88 (d, *J* = 9.2, 2 H, arom **CH** meta to NBu$_2$), 7.92 (d, *J* = 8.6, 2 H, arom **CH** ortho to N=N), 8.06 (d, *J* = 8.6, 2 H, arom **CH** meta to N=N), 8.14 (s, 1 H, vinyl **CH**).

4-(Dibutylamino)azobenzene-4′-carboxaldehyde (3a). 4-Aminobenzaldehyde (4.0 g, 33 mmol) was suspended in 20% aqueous HCl and diazotized at 0−5 °C with a solution of 2.8 g (40 mmol) of sodium nitrite in a minimum amount of water. (Dibutylamino)aniline (7.2 g, 35 mmol) and 16.3 g of sodium acetate were added, and the resulting mixture was stirred mechanically for 18 h and allowed to warm slowly to 23 °C. The crude product was extracted into dichloromethane and was purified by chromatography on silica gel (eluting with dichloromethane). The product was recrystallized from isopropyl alcohol to provide 3.5 g (31%) as a red powder.

^{1}H NMR (CDCl$_3$) δ 0.98 (t, *J* = 7.3, 6 H, CH$_2$**CH**$_3$), 1.4 (m, 4 H, **CH**$_2$CH$_3$), 1.6 (m, 4 H, **CH**$_2$CH$_2$CH$_3$), 3.38 (t, *J* = 7.7, 4 H, N**CH**$_2$), 6.72 (d, *J* = 9.1, 2 H, arom **CH** ortho to NBu$_2$), 7.84 (d, *J* = 9.0, 2 H, arom **CH** meta to NBu$_2$), 7.94 (AB, *J* = 8.5, Δν = 12.0, 4 H, arom **CH** on same ring as CHO), 10.05 (s, 1 H, **CH**O).

4-[(2-Hydroxyethyl)methylamino]azobenzene-4′-carboxaldehyde (3b). A suspension of 12.1 g (0.10 mol) of 4-aminobenzaldehyde in 170 mL of 10% aqueous ethanol was stirred for 30 min at 23 °C and then cooled to 0 °C. A solution of 6.9 g (0.10 mol) of sodium nitrite in 20 mL of water was added dropwise, maintaining the temperature of the reaction mixture between 0 and 5 °C. The reaction mixture was stirred for 30 min, and then a solution of 15.1 g (0.10 mol) of *N*-(2-hydroxyethyl)-*N*-methylaniline in 30 mL of ethanol was added. The reaction mixture was stirred and gradually warmed to 23 °C over 4 h and then poured into excess aqueous sodium carbonate. The red precipitate was filtered and air dried. The crude product was dissolved in dichloromethane and passed through a short column of silica gel, eluting with additional dichloromethane. The eluate was concentrated, and the residue was recrystallized from isopropyl alcohol. Yield 14.0 g (49%).

^{1}H NMR ((CD$_3$)$_2$SO) δ 3.06 (s, 3 H, N**CH**$_3$), 3.56 (m, 4 H, N**CH**$_2$ + O**CH**$_2$), 4.78 (t, *J* = 5.3, 1 H, O**H**), 6.83 (d, *J* = 9.2, 2 H, arom **CH** ortho to NR$_2$), 7.78 (d, *J* = 9.1, 2 H, arom **CH** meta to NBu$_2$), 7.88 (d, *J* = 8.3, 2 H, arom **CH** ortho to N=N), 8.00 (d, *J* = 8.4, 2 H, arom **CH** meta to N=N), 10.02 (s, 1 H, **CH**O). ^{13}C{^{1}H} NMR ((CD$_3$)$_2$SO) δ 38.9 (N**C**H$_3$), 54.0 (N**C**H$_2$), 58.2 (O**C**H$_2$), 111.5 (arom **C**H ortho to NR$_2$), 122.2, 125.5, 130.9, 135.9, 142.6, 152.5, 156.0, 192.4 (**C**HO).

4-Amino-β-cyano-β-(methylsulfonyl)styrene (4a). A mixture of 100.0 g (0.825 mol) of 4-aminobenzaldehyde, 98.4 g (0.826 mol) of (methylsulfonyl)acetonitrile, 3.1 g (0.04 mol) of ammonium acetate (catalyst), and 500 mL of absolute ethanol was stirred mechanically at reflux for 24 h. The reaction mixture was cooled to 23 °C, and the precipitated product was filtered, washed successively with cold ethanol and with pentane, and dried at 40 °C in vacuo. Yield 124.2 g (68%).

^{1}H NMR ((CD$_3$)$_2$SO) δ 3.20 (s, 3 H, SO$_2$**CH**$_3$), 6.62 (d, *J* = 8.6, 2 H, arom **CH** ortho to NH$_2$), 6.78 (s, 2 H, N**H**$_2$), 7.74 (d, *J* = 8.5, 2 H, arom **CH** meta to NH$_2$), 7.81 (s, 1 H, vinyl **CH**).

4-Amino-β-cyano-β-(*tert*-butylsulfonyl)styrene (4b). A mixture of 30 g (0.25 mol) of 4-aminobenzaldehyde, 40 g (0.25 mol) of (*tert*-butylsulfonyl)acetonitrile, and 19.3 g (0.25 mol) of ammonium acetate was stirred in refluxing ethanol for 16 h under nitrogen. The solution was hot-filtered and then cooled to 5 °C. The precipitated product was collected, providing 21.6 g. The mother liquor was concentrated to dryness, and the residue was recrystallized from tetrahydrofuran (THF)/isopropyl alcohol to provide an additional 49.2 g of product. Total yield 75%; mp 210−212 °C.

^{1}H NMR ((CD$_3$)$_2$SO) δ 1.33 (s, 9 H, C(**CH**$_3$)$_3$), 6.88 (s, 2 H, N**H**$_2$), 7.23 (AB, *J* = 8.7, Δν = 353, 4 H, arom **CH**), 7.74 (s, 1 H, vinyl **CH**). FD-MS *m/e* 264 (M$^+$).

4-[*N*-Methyl-*N*-(2-hydroxyethyl)amino]-4′-(β-cyano-β-(methylsulfonyl)vinyl)azobenzene (5a). A mixture of 10.0 g (35.3 mmol) of 4-[(2-hydroxyethyl)methylamino]azobenzene-4′-carboxaldehyde (**3**), 4.21 g (35.3 mmol) of (methylsulfonyl)-acetonitrile, and 2.72 g (35.3 mmol) of ammonium acetate in 100 mL of absolute ethanol was stirred at reflux for 18 h. The reaction mixture was cooled to 23 °C, and the precipitated product was filtered, washed with cold ethanol, and air-dried. The product was recrystallized from THF/toluene (~70/30 v/v) to provide 8.8 g (65%) of purple powder.

^{1}H NMR ((CD$_3$)$_2$SO) δ 3.10 (s, 3 H, N**H**$_3$), 3.42 (s, 3 H, SO$_2$**CH**$_3$), 3.57 (m, 4 H, N**CH**$_2$ + O**CH**$_2$), 4.80 (t, *J* = 5.1, 1 H, O**H**), 6.87 (d, *J* = 9.2, 2 H, arom **CH** ortho to NR$_2$), 7.82 (d, *J* = 9.1, 2 H, arom **CH** meta to NR$_2$), 7.93 (d, *J* = 8.4, 2 H, arom **CH** ortho to N=N), 8.19 (d, *J* = 8.6, 2 H, arom **CH** meta to N=N), 8.33 (s, 1 H, vinyl **CH**). ^{13}C{^{1}H} NMR ((CD$_3$)$_2$SO) δ 39.1 (N**C**H$_3$), 42.1 (SO$_2$**C**H$_3$), 54.1 (N**C**H$_2$), 58.1 (O**C**H$_2$), 111.6 (arom **C**H ortho to NR$_2$), 112.6, 113.7 (**C**≡N), 122.4, 125.8, 130.3, 132.3, 142.7, 152.6, 155.5. FD-MS *m/e* 384 (M$^+$). Anal. Calcd for $C_{19}H_{20}N_4O_3S$: C, 59.36; H, 5.24; N, 14.57; S, 8.34. Found: C, 59.44; H, 5.29; N, 14.22; S, 7.98.

4-[*N*-Methyl-*N*-(6-hydroxyhexyl)amino]-4′-(β-cyano-β-(methylsulfonyl)vinyl)azobenzene (5b). A suspension of 55.5 g (0.25 mol) of 4-amino-β-cyano-β-(methylsulfonyl)styrene (**4a**) in 550 mL of 10% aqueous HCl was stirred and cooled to −5 °C. A solution of 19.3 g (0.28 mol) of sodium nitrite in 100 mL of water was added dropwise, and the reaction mixture was stirred for 45 min. *N*-6-(Hydroxyhexyl)-*N*-methylaniline (51.75 g, 0.25 mol) was added, and a red color formed immediately. The mixture was stirred for 2 h at −5 °C, and then 40 g of sodium nitrite was added. The reaction mixture was stirred and gradually warmed to 23 °C overnight. The supernatant liquid was decanted, and the solid residue was recrystallized from isopropyl alcohol and dried in vacuo to provide 43 g (39%) of **5b** as a red powder.

4-[*N*-Methyl-*N*-(2-hydroxyethyl)amino]-4′-(β-cyano-β-(*tert*-butylsulfonyl)vinyl)azobenzene (5c). A suspension of 4-amino-β-cyano-β-(*tert*-butylsulfonyl)styrene (**4b**, 46.1 g, 0.17 mol) in 200 mL of 30% aqueous HCl was stirred mechanically and cooled to 5 °C. A solution of sodium nitrite (13.8 g, 0.2 mol) dissolved in a minimum amount of water was added to the suspension of 1 h. *N*-(2-Hydroxyethyl)-*N*-methylaniline (30.2 g, 0.20 mol) was added slowly, and stirring was continued for 2 h until the reaction mixture warmed to 23 °C. The mixture was neutralized with sodium acetate and was stirred at 23 °C overnight. The product was extracted into dichloromethane, and the extract was washed well with water, dried (Na$_2$SO$_4$), and concentrated at reduced pressure. The residue was recrystallized from isopropyl alcohol to provide 47.0 g (65%) of **5c** as a purple solid; mp 169−171 °C.

^{1}H NMR (CDCl$_3$) δ 1.53 (s, 9 H, C(**CH**$_3$)$_3$), 3.16 (s, 3 H, N**CH**$_3$), 3.65 (t, *J* = 5.6, 2 H, N**CH**$_2$), 3.90 (t, *J* = 5.6, 2 H, O**CH**$_2$), 6.82 (d, *J* = 9.1, 2 H, arom **CH** ortho to NR$_2$), 7.79 (m, 4 H, arom **CH**), 8.00 (s, 1 H, acceptor vinyl **CH**), 8.07 (d, *J* = 8.6, 2 H, arom **CH** meta to N=N). FD-MS *m/e* 426 (M$^+$).

4-[*N*-Methyl-*N*-(2-(methacryloyloxy)ethyl)amino]-4′-(β-cyano-β-(methylsulfonyl)vinyl)azobenzene (6a). A stirred solution of 24.7 g (64.2 mmol) of 4-[*N*-methyl-*N*-(2-hydroxyethyl)amino]-4′-β-cyano-β-(methylsulfonyl)vinyl)azobenzene (**5a**), 6.50 g (64.2 mmol) of triethylamine, and 1.57 g (12.8 mmol) of 4-(dimethylamino)pyridine in 150 mL of dichloromethane was treated with a solution of 8.06 g (77.1 mmol) of freshly distilled methacryloyl chloride at 23 °C under nitrogen. The reaction mixture was heated at reflux for 3 h under nitrogen, cooled to 23 °C, and then passed through a short column of silica gel, eluting with 25% ether/75% dichloromethane. The eluate was washed with water and then with saturated aqueous NaHCO$_3$. The organic layer was dried (MgSO$_4$) and concentrated at reduced pressure. The residue was twice recrystallized from toluene to provide 17.6 g (60%) of a purple powder.

^{1}H NMR (CDCl$_3$) δ 1.92 (s, 3 H, allyl **CH**$_3$), 3.16 (s, 3 H, N**CH**$_3$), 3.23 (s, 3 H, SO$_2$**CH**$_3$), 3.80 (t, *J* = 5.7, 2 H, N**CH**$_2$), 4.39 (t, *J* = 5.7, 2 H, O**CH**$_2$), 5.57 (s, 1 H, methacryloyl vinyl **CH**), 6.08 (s, 1 H, methacryloyl vinyl **CH**), 6.82 (d, *J* = 9.0, 2 H, arom **CH** ortho to NR$_2$), 7.91 (d, *J* = 9.2, 2 H, arom **CH** meta to NR$_2$), 7.94 (d, *J* = 8.7, 2 H, arom **CH** ortho to N=N), 8.07 (d, *J* = 8.5, 2 H, arom **CH** meta to N=N), 8.14 (s, 1 H, acceptor vinyl **CH**). ^{13}C{^{1}H} NMR (CDCl$_3$) δ 18.3 (allyl **C**H$_3$), 39.0 (N**C**H$_3$), 41.9 (SO$_2$**C**H$_3$), 50.9 (N**C**H$_2$), 61.7 (O**C**H$_2$), 111.7 (arom **C**H ortho to NR$_2$), 112.2, 113.4 (**C**≡N), 123.2, 126.1, 126.2, 130.0, 132.4, 135.9, 144.2, 152.1 (acceptor vinyl **C**H), 152.3, 156.5, 167.2 (**C**=O). FD-MS *m/e* 452 (M$^+$). Anal. Calcd for $C_{23}H_{24}N_4O_4S$: C, 61.05; H, 5.35; N, 12.38; S, 7.09. Found: C, 61.00; H, 5.40; N, 12.26; S, 7.78.

4-[*N*-Methyl-*N*-(6-(methacryloyloxy)hexyl)amino]-4′-(β-cyano-β-(methylsulfonyl)vinyl)azobenzene (6b). A stirred solution of 43 g (0.10 mol) of 4-[*N*-methyl-*N*-9-(6-hydroxyhexyl)amino]-4′-β-cyano-β-(methylsulfonyl)vinyl)azobenzene (**5b**) and 16.8 mL (0.12 mol) of triethylamine, and 1.2 g (0.01 mol) of 4-dimethylaminopyridine, and a small amount of Irganox 1010 (inhibitor) in 600 mL of dry dichloromethane was cooled to −5 °C under nitrogen. A solution of 12.54 g (0.12 mol) of freshly distilled methacryloyl chloride in 50 mL of dichloromethane was added over 10 min. The resulting solution was stirred, gradually warmed to 23 °C overnight, and then washed twice with cold water. The organic layer was separated, dried (MgSO$_4$), and passed through a short silica gel column, eluting with additional dichloromethane. The eluate was concentrated to approximately 200 mL, and ligroin was added slowly to precipitate the product. The product was collected, washed with excess ligroin, and dried in vacuo at 45 °C. Yield 31.5 g (65%). Further purification could be accomplished by recrystallization from THF/hexanes.

^{1}H NMR (CDCl$_3$) δ 1.4 (m, 4 H, NCH$_2$CH$_2$**CH**$_2$**CH**$_2$CH$_2$-CH$_2$O), 1.65 (m, 4 H, NCH$_2$**CH**$_2$CH$_2$CH$_2$**CH**$_2$CH$_2$O), 1.94 (s, 3 H, allyl **CH**$_3$), 3.10 (s, 3 H, N**CH**$_3$), 3.22 (s, 3 H, SO$_2$**CH**$_3$), 3.46 (t, *J* = 7.4, 2 H, N**CH**$_2$), 4.15 (t, *J* = 6.6, 2 H, O**CH**$_2$), 5.55 (s, 1 H, methacryloyl vinyl **CH**), 6.10 (s, 1 H, methacryloyl vinyl **CH**), 6.74 (d, *J* = 9.2, 2 H, arom **CH** ortho to NR$_2$), 7.90 (d, *J* = 9.1, 2 H, arom **CH** meta to NR$_2$), 7.93 (d, *J* = 8.7, 2 H, arom **CH** ortho to N=N), 8.06 (d, *J* = 8.6, 2 H, arom **CH** meta to N=N), 8.14 (s, 1 H, acceptor vinyl **CH**). Anal. Calcd for $C_{26}H_{30}N_4O_4S$: C, 63.14; H, 6.11; N, 11.33; S, 6.48. Found: C, 62.90; H, 6.06; N, 11.03; S, 6.80.

4-[*N*-Methyl-*N*-(2-(methacryloyloxy)ethyl)amino]-4′-(β-cyano-β-(*tert*-butylsulfonyl)vinyl)azobenzene (6c). A mixture of 45 g (0.11 mol) of 4-[*N*-methyl-*N*-(2-hydroxyethyl)-amino]-4′-β-cyano-β-(*tert*-butylsulfonyl)viyl)azobenzene (**5c**), 13.1 g (0.13 mol) of triethylamine, and a catalytic amount of 4-(dimethylamino)pyridine in 300 mL of dry dichloromethane under nitrogen was cooled to 5 °C. Freshly distilled methacryloyl chloride (13.8 g, 0.13 mol) was added slowly with stirring, and then the mixture was heated at reflux for 2 h. The reaction mixture was cooled to 23 °C, filtered, and then concentrated at reduced pressure. The residue was twice recrystallized from ethanol/toluene to give 36.0 g (66%) of purple crystals; mp 146−148 °C.

^{1}H NMR (CDCl$_3$) δ 1.54 (s, 9 H, C(**CH**$_3$)$_3$), 1.91 (s, 3 H, allyl **CH**$_3$), 3.16 (s, 3 H, N**CH**$_3$), 3.79 (t, 2 H, *J* = 5.6, N**CH**$_2$), 4.39 (t, 2 H, *J* = 5.6, O**CH**$_2$), 5.56 (d, *J* = 1.3, 1 H, methacryloyl vinyl **CH**), 6.07 (s, 1 H, methacryloyl vinyl **CH**), 6.82 (d, *J* = 9.2, 2 H, arom **CH** ortho to NR$_2$), 7.93 (m, 4 H, arom **CH**), 8.05 (s, 1 H, acceptor vinyl **CH**), 8.10 (d, *J* = 8.6, 2 H, arom **CH** meta to N=N).

Polymerization Procedure. The following description of the synthesis of polymer **7c** typifies the procedure employed for all polymers described herein.

A flask was charged with 30.0 g (66.3 mmol) of 4-[*N*-methyl-*N*-(2-(methacryloyloxy)ethyl)amino]-4′-(β-cyano-β-(methylsulfonyl)vinyl)azobenzene (**6a**), 30.0 g (299 mol) of methyl methacrylate (MMA, freshly vacuum-distilled from CaH$_2$), 0.65 g of azobisisobutyronitrile (AIBN, 3.9 mmol, recrystallized from methanol), and 200 mL of *N*,*N*-dimethylformamide (DMF, freshly vacuum-distilled). The resulting solution was degassed by bubbling nitrogen through for 10 min. The reaction mixture was heated at 60 °C under nitrogen for 72 h and then cooled to 23 °C. The polymer was precipitated into excess vigorously stirred methanol, filtered, washed with methanol, and dried. The polymer was purified successive reprecipitations from DMF into methanol, from chloroform into methanol, and then finally from THF into deionized water. The polymer was dried to constant mass in a vacuum oven, gradually raising the temperature to 100 °C over 4 days. Yield 58.4 g (97%).

Yields and characterization data for all of the polymers are given in Tables 1 and 2.

Film Preparation and Electrooptic Measurements. Thin (ca. 1 μm) films of the polymers were spun onto indium tin oxide (ITO)-coated glass substrates from *N*,*N*-dimethylacetamide (DMAc) solution (15−20% w/v) under a dry nitrogen atmosphere. Dumbbell-shaped gold electrodes were deposited as previously reported.[11] The electrooptic coefficient, r_{33}, was determined by a reflection technique[9] in an apparatus that allowed for simultaneous heating. Samples for aging studies were stored at 80 ± 1 °C under nitrogen.

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