Organic Nonlinear Optical (NLO) Polymers.[1] A Study of in-Situ Poling and Quaternization/Cross-Linking of Polymers by a NLO-Tweezer

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ABSTRACT: The paper describes the syntheses of a *NLO-tweezer*, α,α′-bis[*N*-ethyl-*N*-{4′-stilbazolyl}-amino]-*m*-xylene (**3**), functionalized copolymers **4a** [poly(2-bromoethyl methacrylate)/polystyrene], **4b** [poly(2-chloroethyl methacrylate)/polystyrene], and **4c** [poly(3-chloropropyl methacrylate)/polystyrene], and NLO-phore **6**, 4′-(*N*-ethyl-*N*-hexylamino)stilbazole. Kinetic analyses were carried out for the cross-linking/quaternization reaction of the NLO-tweezer with copolymers **4a**, **4b**, and **4c**. Energy of activation (E_a) values of 15.3, 18.8, and 18.4 kcal/mol, respectively, were experimentally determined. Films containing 9.1 wt % of the NLO-tweezer and NLO-phore **6** were subjected to corona poling with heating (90–120 °C) for varying lengths of time. The materials displayed improved temporal stability for the second harmonic (SH) signal with an increasing degree of quaternization, and the best temporal stability (at 80 °C) for the SH signal was observed for the side-chain NLO polymer (*i.e.* from NLO-phore **6**), which was not cross-linked. The NLO-tweezer, which did form a cross-linked material, showed an initial rapid loss of SH signal; however, the long term signal decay was similar to the side-chain analog.

Introduction

Second-order nonlinear optical polymers (NLOPs) have demonstrated themselves as lead materials for use in optical switching devices due to their relatively high optical nonlinearity, fast switching speeds, and exceptional ability for processing for device fabrication.[2] Initially, NLO-phores (organic dyes) were doped in glassy material and the dipoles aligned at elevated temperatures by electric field induced poling.[3] The most significant problem associated with these systems is the gradual relaxation of the aligned dipoles at ambient temperatures. In addition, a problem of low solubility of the guest NLO-phores in the host material is often encountered.[4] Numerous design strategies have been used to stabilize the poling-induced order. These include incorporation of the NLO-phore in a heavily cross-linked matrix,[5] attachment of the NLO-phore to a polymer backbone as a pendant group,[6] and placement of the NLO-phore in the polymer backbone.[7]

The concept of poling with concurrent cross-linking has been explored by various research groups.[8] In these systems either the polymer host or the guest NLO-phore contains functional groups which can polymerize photochemically or thermally to create a cross-linked system. Thus cross-linking reduces polymer chain motion and produces a more stable NLO material than the corresponding non-cross-linked guest/host NLO systems.[8] Bifunctional NLO-phores have been prepared and subsequently cross-linked, resulting in immobilization of the poled NLO-phores.[9,10] These systems demonstrated that cross-linking led to stabilization of the aligned NLO-phores and dipolar asymmetry.

NLO chromophores containing the *N*-alkylpyridinium ion as an acceptor group have remarkably large second-order nonlinearity in the powder form.[11] The pyridinium NLO-phores have been aligned by various methods.[12] We have designed a bifunctional molecule containing two pyridyl-based NLO-phores in which the NLO-phores can adopt a geometry resembling a *tweezer*.[13] We hereafter refer to this class of molecules as NLO-tweezer. The shape of the NLO-tweezer (Figure 1) should be enhanced within the poling field (alignment of the dipole moments) and will serve as a cross-linking site after poling/alignment. At the same time we have synthesized a second compound containing a single pyridyl–NLO-phore (**6**) capable of forming a side-chain NLO polymer but unable to produce a cross-linked matrix.

In this paper, we present the syntheses and characterization of a NLO-tweezer and the copolymers hosts. In addition, important kinetic studies for the quaternization reaction of the NLO-tweezer in the absence of an electric field is reported and the study of temporal stability of poled dipolar order is probed using NLO spectroscopy.

Results and Discussion

NLO Tweezer Synthesis. Utilizing chemistry developed by Lindsay and co-workers,[14] NLO-tweezer precursor **2** was synthesized in 85% yield from the reaction of α,α′-dibromo-*m*-xylene with *N*-ethylaniline followed by Vilsmeier formylation. For the synthesis of monomer **3**, condensation of **2** with 4-($LiCH_2$) pyridine produced an alcohol intermediate which was easily dehydrated by heating in the presence of acid catalyst, pyridinium *p*-toluenesulfonate (PPTS) (Scheme 1).

Synthesis of NLO-phore 6. 4′-(*N*-Ethyl-*N*-hexylamino)stilbazole was prepared by utilizing a reaction sequence similar to that discussed above for the synthesis of **3** (Scheme 2). *N*-Ethylaniline was alkylated with iodohexane, then formylated using the Vilsmeier reaction, and treated with 4-($LiCH_2$)pyridine to afford an intermediate alcohol product. The latter was treated with PPTS, which led to dehydration and formation of **6** in 90% yield. It is noteworthy to mention that 4′-(*N*,*N*-dimethylamino)stilbazole was also prepared; however,

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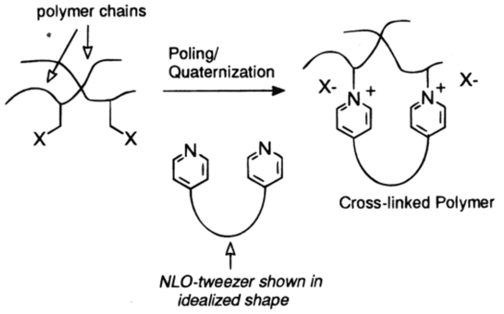
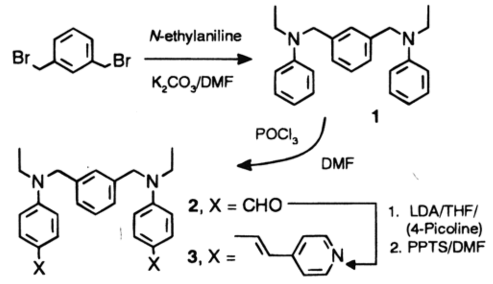
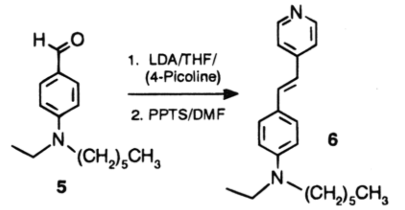


Figure 1. Illustration of quaternization/cross-linking that can occur for a NLO-tweezer in a functionalized copolymer.

Scheme 1



Scheme 2



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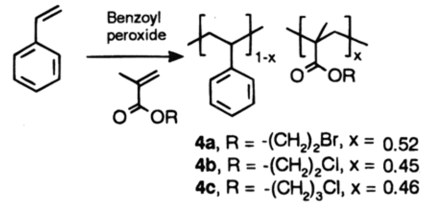
Scheme 3



in our attempts to prepare guest/host films we encountered solubility and phase separation problems at loading values of 9.1 wt %. This problem was effectively resolved by substitution of the hexyl group.

Synthesis of Copolymers 4a, 4b, and 4c. Copolymer **4a** was synthesized from polymerization of 2-bromoethyl methacrylate and styrene (molar ratio 1:1) under bulk conditions with 2 mol % benzoyl peroxide as the initiator (Scheme 3). The copolymer was synthesized in reasonable yield (60%) using free radical initiation. DSC analysis of copolymer **4a** revealed a T_g, but no T_m was observed (Table 1). Synthesis of copolymers **4b** and **4c** was accomplished under conditions similar to those for the synthesis of **4a**. Copolymers **4b** and **4c** were obtained in higher yields but as lower molecular weight materials. The copolymers each contain approximately 3.5 mequiv of $-CH_2X$ (where X is Cl and Br) per gram of copolymer. The T_g of **4b** was not significantly different from that of **4a**; however, introduction of a methylene group in **4c** resulted in a measurable decrease in T_g (Table 1). TGA analysis of copolymers **4a**, **4b**, and **4c** under a nitrogen atmosphere revealed thermal stability (defined as the temperature where a rapid and constant weight loss began to occur) to approximately 310−320 °C.

Table 1. Selected Physical and Spectroscopic Data for Copolymers 4a−c[a]

copolymer	M_n	polydispersity	λ_{max} (nm)	T_g
4a	46 000	2.2	274	81
4b	25 000	1.9	274	79
4c	27 000	2.1	274	70

[a] See Experimental Section for complete analytical, physical, and spectroscopic data.

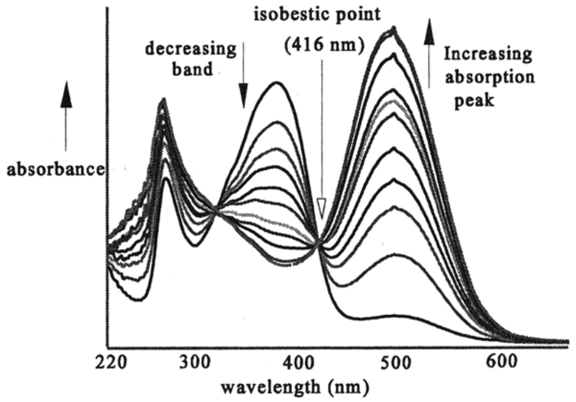


Figure 2. UV−vis spectroscopic data for the quaternization reaction of **3** (9.1 wt %) in **4a** at 90 °C. Peaks at 374 and 486 nm correspond to the absorption band for reactant and product, respectively.

Kinetic Analyses. Films were prepared from CH_2Cl_2 solutions containing 9.1 wt % of the NLO-phore (0.17 mmol of NLO-phore/g of copolymer). The films were prepared using the razor-edge technique, air-dried for 15 min, and then placed under reduced pressure for 4 h. Due to a photoinduced reaction in **4a**, the drying had to be done in the absence of light. The quaternization reaction is characterized by a vivid color change from orange to deep red. During the drying process some color change is noted; however, the guest/host films remain very soluble and UV−vis analysis indicates no more than 3−5% reaction has occurred. TGA analysis of air-dried (15 min) and vacuum-dried (4 h) films shows a weight loss of 6.3% due to residual solvent. Copolymers **4b** and **4c** afford guest/host systems with improved stability. The latter appear by TGA analysis to be free of solvent residue after drying and show no visible signs of color change.

Kinetic analyses were carried out by placing the films on a computer-controlled heating stage with the rate of quaternization/cross-linking monitored by UV−vis spectroscopy in a separate instrument. The λ_{max} for the NLO-tweezer/copolymers before and after the reaction were 374 and 486 nm, respectively. The UV−vis spectroscopic data (Figure 2) show clean conversion of **3**/copolymer **4a** to a cross-linked and quaternized polymeric material. The cross-linking reaction is complete within a 1 h period, and we find the rates of quaternization for copolymer **4a** are much faster when compared to **4b** and **4c** (Table 2). Samples of **4b** and **4c** were reacted at temperatures above T_g. After reaction, the polymer films were not soluble and no T_g's were detected by DSC analysis.[10]

For kinetic analyses, studies were undertaken at various temperatures for each polymer system. Reaction rates were measured from the amount of product formed versus reaction time (Figure 3). The results obtained were used to calculate the rate constants of

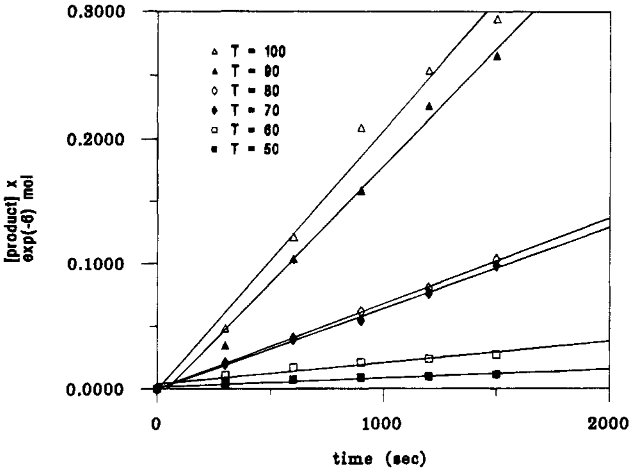


Figure 3. Plot showing the formation of quaternized product versus time at temperatures ranging from 50 to 100 °C for the reaction of **3** (9.1 wt %) in copolymer **4a**.

Table 2. Reaction Rates of Quaternization of NLO-phore 3 and Copolymers 4a, 4b, and 4c at Different Temperatures and the Energy of Activation (E_a) for Each Copolymer

polymer	temp (°C)	rates ($\times 10^{-8}$)[a]	ln *k*	E_a
4a	50	0.1	−2.501	15.3(0.3)
	60	0.18	−1.911	
	70	0.65	−0.629	
	80	0.68	−0.585	
	90	1.86	0.422	
	100	2.07	0.529	
4b	90	0.04	−2.885	18.8(0.4)
	100	0.13	−1.571	
	110	0.24	−0.996	
	120	0.30	−0.751	
	130	0.66	0.100	
4c	90	0.09	−0.1840	18.4(0.4)
	100	0.17	−0.1289	
	110	0.34	−0.602	
	120	0.44	−0.336	
	130	1.32	0.761	

[a] 10 mg (1.82 × 10^{-2} mmol) of **3** was dissolved in 100 mg of copolymers **4a**, **4b**, and **4c**.

the reactions at different temperatures (Table 2) which then enabled us to calculate the energy of activation (E_a)[15] for each system.

Compound **6** has essentially the same NLO-phore as the NLO-tweezer and appears to react with the copolymers **4a** and **4b** in a similar manner and reaction rate. However, the product is a side-chain NLO polymer which is not cross-linked and remains soluble in organic solvents.

Nonlinear Optical Spectroscopy. The relaxation of NLO-phores **3** and **6** after reaction and poling was probed using NLO spectroscopy. The two NLO-phores **3** and **6** have been shown to react with the copolymers to afford cross-linked and side-chain NLO polymers, respectively. The modified polymers have the same NLO-active unit with essentially the same loading (*i.e.* NLO-phore unit/g of copolymer). It is noteworthy to mention that this study was undertaken to investigate the relative temporal stability of the SH signal for the two NLO polymers (side-chain *vs* cross-linked) and not to quantify the $\chi^{(2)}$ observed.

Sample Preparation. A protocol was developed for sample preparation. This involved dissolving 10 mg of the NLO-phore in 100 mg of copolymer using dichloromethane (1.0 mL) as a solvent. The NLO active unit loading is 0.331 and 0.295 mequiv/g for NLO-phore **3** and **6**, respectively, while halogenated units are 3.05, 3.33, and 3.22 mequiv/g for copolymers **4a**, **4b**, and **4c**, respectively. Films of each sample were prepared on clean soda-lime microscope slides using a knife-edge technique.[16] After deposition, the films were dried at ambient temperature for 15 min and then placed under vacuum (30 mmHg) to remove residual solvent. For samples of **4a** drying was done under vacuum at 24 °C for 8 h, and for **4b** samples were first baked under vacuum at 40 °C for 3 h and then held under vacuum at 24 °C for an additional 8 h. The thickness for the resulting films was measured with a digital linear gauge and was found to be 9 ± 2 μm.

Table 3. Poling Conditions for NLO-phores in Copolymers 4a and 4b

entry	copolymer	NLO-phore	temp (°C)	time (min)	temp (°C)	time (min)	% reacn[a]
1	**4a**	**3**	90	30			80
2	**4a**	**3**	90	60			100
3	**4a**	**3**	90	120			100
4	**4b**	**6**	50−55	30	110	60	20
5	**4b**	**6**	50−55	30	110	180	50
6	**4b**	**6**	50−55	30	110	300	90
7	**4b**	**3**	50−55	30	110	300	90

[a] Percent of quaternized product predicted on the basis of kinetic data.

Poling of Film Samples. A protocol was developed for the poling of samples for each polymer system. A non-zero second-order optical susceptibility $\chi^{(2)}$ was imparted to the films via corona poling.[17] The **4a** samples were poled at 90° for varying lengths of time, cooled to 70 °C at 4 °C/min with the poling field on, and then rapidly quenched to room temperature immediately after removal of the poling field. For **4b** systems, the samples were initially poled at 50−55 °C for 30 min, after which the temperature of the films was raised to 110 °C and the poling continued for varying lengths of time (Table 3). The films were then cooled to 90 °C at 4 °C/min and rapidly quenched to ambient temperature immediately following removal of the poling field. All samples containing the NLO-tweezer and NLO-phore **6** displayed approximately the same magnitude of the SH signal. Although calculation of $\chi^{(2)}$ was not performed, the films in this study showed an SH signal ~10% of that observed for DR1/PMMA films (same NLO-phore loading and approximate film thickness).

During poling, charge is deposited onto the samples by corona discharge, the presence of this charge has been shown to affect the rate of chromophore orientation.[18] By measuring the bathochromic shift in the absorption peak of poled DR1/PMMA, prior researchers have reported that greater than 95% of this "trapped" charge had dissipated within 24 h after poling.[19] In addition, other groups[20] have measured the surface voltage of the polymer films due to charge injection during corona poling versus time and temperature. This work also concluded that virtually all trapped charge had dissipated within 24 h after poling. Thus, to ensure that the observed decay in second harmonic (SH) intensity generated by our samples was due to dipolar reorientation associated with NLO-phore motion and not dissipation of trapped charge, we waited 1 day after poling a sample before monitoring the decay of $\chi^{(2)}$. While this procedure allowed some room temperature aging to occur, all samples underwent a similar protocol and experienced the same thermal history. Two different types of SHG measurement were undertaken, temperature ramp studies and isothermal decay of $\chi^{(2)}$.

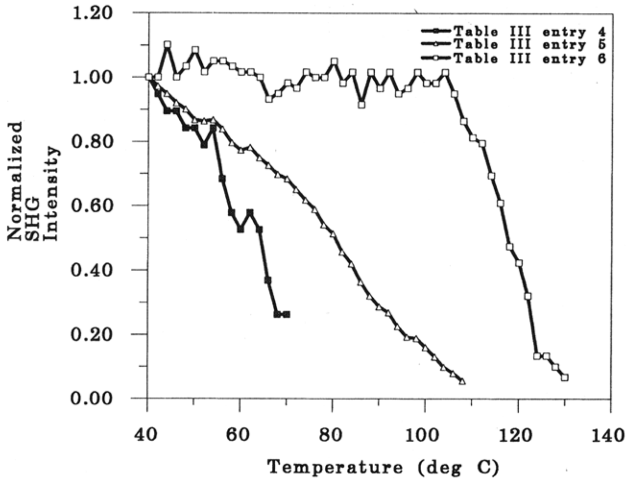


Figure 4. Temporal stability for the normalized SH signal of NLO-phore **6**/copolymer **4b** samples [Table 3; entry 4 (■), entry 5 (△), and entry 6 (□)] as function of increasing temperature. Ramp rate of 7 °C/min.

Ramp Studies. To determine the optimum poling time necessary to achieve the maximum temporal stability of $\chi^{(2)}$, the signal stability as a function of temperature was studied for samples which were poled for different lengths of time (Table 3). For these temperature ramp studies, a sample was placed on an aluminum heating stage initially held at ambient temperature ($\sim$24 °C) and the SH signal was monitored as the temperature of the film was increased at a rate of 7 °C/min.

The results of the temperature ramp study for NLO-phore **6** and **4b** are presented in Figure 4. The data show that the temporal stability of the normalized SH signal depends on the poling period and, hence, percent quaternization. A low percent of quaternization resulted in a signal that rapidly decayed with an increase in temperature; however, a remarkable increase in signal stability is observed with an increase in poling time (Table 3, entry 6; Figure 4). The SH signal shows good stability up to a temperature of 105 °C, after which it rapidly decays. The possibility that the increase in signal stability was due to a change in polymer T_g with polymer modification was investigated by DSC analysis. The analysis showed an absence of a T_g but a rather significant endothermic event at 225 °C. Analysis of a film heated at 225 °C for 20 min by UV–vis spectroscopy showed no change in the absorbance, leading us to believe that decomposition of the NLO-phores does not occur. The significance and cause of the exotherm is still under investigation. It is therefore reasonable to conclude from this data that temporal stability is dependent and enhanced by an increasing concentration of quaternized NLO-phores.[21,22] We attribute the SH signal to quaternized and not unquaternized NLO-phores due to two factors. First, a quaternized NLO-phore has a much larger β value and would therefore contribute more significantly to the SH signal than unquaternized NLO-phores.[11] Secondly, the alignment of unquaternized NLO-phores is not stabilized by attachment to the polymer backbone.

Similar results were observed in ramp studies of the **3**/copolymer **4a** system. However, in this system, cross-linking of the polymer matrix occurs during the quaternization reaction. The bromo copolymer produces a much higher degree of quaternization (Table 3) and is evidenced by modest signal stability (Figure 5). Even though this is a significantly cross-linked polymer matrix, we observe a rapid loss of SH signal at a temperature of 105 °C. The depoling temperature (T_{dp}) of the cross-linked material is similar to that of the side-chain copolymer. Hence, even at a level of $\sim$10% cross-linking, the T_g of the original host copolymer appears to dominate and at approximately this temperature we observe relaxation of the dipolar asymmetry.

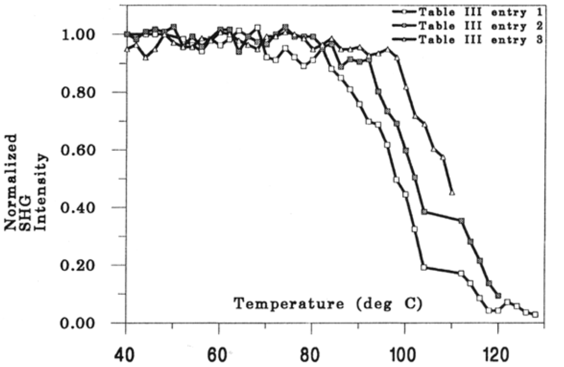


Figure 5. Temporal stability for the normalized SH signal of NLO-tweezer **3**/copolymer **4a** samples [Table 3; entry 1 (□), entry 2 (■), entry 3 (△)] as a function of increasing temperature. Ramp rate of 7 °C/min.

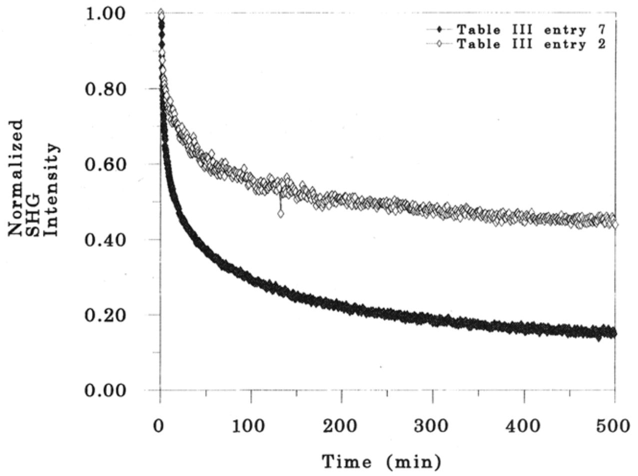


Figure 6. Relative rates for the decay of the normalized SH signal at 80 °C for NLO-tweezer **3**/copolymer **4a** [Table 3; entry 2 (◇)] and NLO-tweezer **3**/copolymer **4b** [Table 3; entry 7 (◆)].

Isothermal Decay of $\chi^{(2)}$. The contribution of the anion to the temporal stability of the signal was probed by comparative isothermal decay of the signals in copolymers **4a** and **4b**. At the same time, similar comparative studies were undertaken for the side-chain and cross-linked NLO polymers. A protocol was developed for the study of the isothermal decay of the samples. The sample was placed on an aluminum heating stage held at 80 °C, and light polarized perpendicular to the plane of incidence (*s*-polarized) was directed onto the sample at 52° from normal incidence. The intensity of the *p*-polarized second harmonic light was measured over time to monitor the isothermal decay of $\chi^{(2)}$.

The temporal stability of the SH signal for the cross-linked NLO-polymer was observed to increase with an increase in the anion size (Figure 6). These data are consistent with results observed in non-cross-linked systems by Prasad and co-workers.[12] The results summarized in Figure 6 show the improved temporal stability by replacing the chloride ion (Table 3, entry 7) with a bromide ion (Table 3, entry 2).

The data showing comparative isothermal decay of the SH signal in the side-chain and cross-linked NLO-

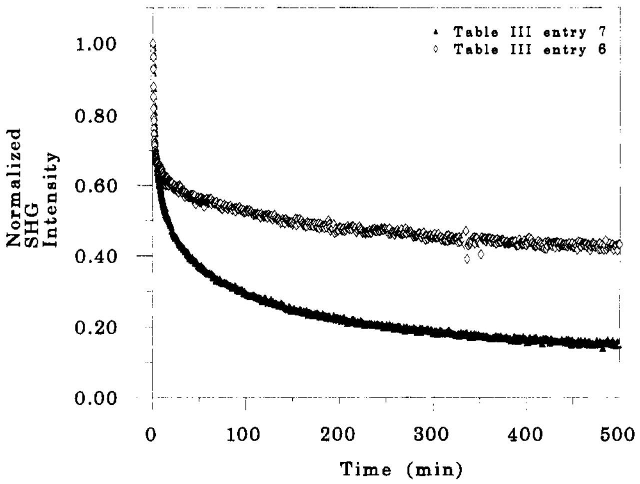


Figure 7. Relative rates for the decay of the normalized SH signal at 80 °C for poled samples of NLO-phore **6** [Table 3; entry 6 (◆)] and NLO-tweezer **3** [Table 3; entry 7 (▲)] in copolymer **4b**.

polymers are summarized in Figure 7. It is apparent and very surprising that cross-linking does not improve the temporal stability of the SH signal. This is an intriguing result since most cross-linked systems have been observed to have enhanced temporal stability.[8] The data of Figure 7 indicate that the cross-linked system may not be fully networked, thus giving rise to the observed relaxation. The broad nature of the decay (as modeled by a stretched exponential) reinforces the likelihood of a wide distribution of cross-linking densities. Another possible explanation for the greater temporal stability of the side-chain system is that the reorientation of the NLO-phore in this system is more restricted due to its longer *N*-alkyl chain. The overall trend of the decays in the side-chain and cross-linked systems are similar in that each has a relatively fast component of about 1–5 min and a longer component of about 80–250 min. However, the amount of short term decay appears greater in the cross-linked system. We suggest that regions of lower density of cross-linked material reorient more quickly than regions of higher density. Therefore, the long term decays of the two systems should be similar since the larger (in length) side-chain NLO-phore will be restricted to the same degree as the more highly cross-linked portions of the tweezer material.

Concluding Remarks

In summary, we have prepared and characterized two NLO-phores **3** and **6** and a series of modified PMMA/PS copolymers. NLO-phores **3** and **6** react with the copolymers through a quaternization reaction to produce cross-linked and side-chain NLO polymers, respectively. The NLO-phore in these polymers is a pyridinium salt, a more potent NLO-phore than **3** and **6**. The *in-situ* quaternization reactions were performed, in the absence of a poling field, to determine kinetic parameters. At the same time, reactions were done in the presence of a poling field to produce SHG films for NLO spectroscopy. The films were utilized in a comparative study of reorientation of the aligned NLO-phores in a polymer matrix. The results showed that the degree of quaternization and, hence, poling time was the determining factor in the temporal stability of the polymers. However, the cross-linked polymers turned out to possess less temporal stability than the side-chain polymers. We believe that the structural difference between the two NLO-phores is a contributing factor to the difference in temporal stability of the two polymer systems, along with the probable inhomogeneous nature of the cross-linking. In areas of low cross-linking density the relaxation of dipolar asymmetry is controlled by the host polymer T_g (before any cross-linking had occurred).

Experimental Section

Methods. All manipulations of compounds and solvents were carried out using standard Schlenk techniques. Solvents were degassed and purified by distillation under nitrogen from standard drying agents. Spectroscopic measurements utilized the following instrumentation: ^{1}H NMR, ^{13}C NMR, Bruker ARX-400; Infrared, Perkin-Elmer 1750 FT-IR; UV–vis, HP-8452A. NMR chemical shifts are reported in δ versus Me_4Si in ^{1}H NMR and assigning the $CDCl_3$ resonance at 77.00 ppm in the ^{13}C spectra. The compounds α,α'-dibromo-*m*-xylene, 4-picoline, *N*-ethylaniline, diisopropylamine, *n*-BuLi, and iodohexane were purchased from Aldrich Chemical Co. and used as received. Phosphorus oxychloride ($POCl_3$), potassium carbonate (granular), sodium acetate, and sodium bicarbonate were purchased from Mallinckrodt. Synthesis of PPTS was accomplished using a literature procedure.[23] Thermal analysis of the polymers was performed using a Perkin-Elmer TGA7 and DSC7 station. GPC data were collected on a combined system of Beckmann Model 110 A and Perkin-Elmer TriDet employing a PL size-exclusion column (300 × 7.5 nm, 5 μm particle size mixed C). Molecular weight data are referenced relative to polystyrene standards. Elemental analysis were performed at Atlantic Microlab Inc., Norcross, GA.

Preparation of 1. A mixture of α,α'-dibromo-*m*-xylene (26.4 g, 100 mmol), *N*-ethylaniline (24.3 mL, 200 mmol), $NaHCO_3$ (18.0 g), and dimethylformamide (150 mL) was heated to reflux with stirring for 24 h. After cooling, the mixture was poured over K_2CO_3/ice water and the product was extracted into dichloromethane (2 × 150 mL), filtered, and dried over K_2CO_3, and solvents were evaporated under reduced pressure. The white solid was recrystallized from ethanol to give pure **1** (31.0 g, 90%, mp = 83–84 °C): ^{1}H ($CDCl_3$) δ 7.18–7.10 (m, 10 H, Ar), 6.66 (d, J = 8.1 Hz, 4 H, Ar), 4.47 (s, 4 H, NCH_2Ar), 3.42 (q, J = 7.0 Hz, 4 H, NCH_2), 1.15 (t, J = 7.0 Hz, 6 H, CH_3); ^{13}C ($CDCl_3$) δ 148.5, 139.6 (Ar C), 129.1, 128.7, 125.0, 124.8, 116.0, 112.2 (Ar CH), 53.9 ($ArCH_2N$), 45.1 (NCH_2CH_3), 12.1 (CH_3); UV–vis (CH_2Cl_2) 302 nm (ϵ = 1.4 × 10^3). Anal. Calcd for $C_{24}H_{28}N_2$: C, 83.67; H, 8.19. Found: C, 83.58; H, 8.23.

Preparation of 2. A Schlenk flask was charged with $POCl_3$ (6.8 g, 443 mmol) and DMF (14 mL) at 0 °C. After stirring for 2.5 h at 0 °C, compound **1** (6.30 g, 18.3 mmol) was added and stirring was continued for 1 h at 25 °C and then 2 h at 90 °C. The reaction mixture was cooled and poured over a mixture of ice and sodium acetate (15 g). The product was extracted into dichloromethane and dried over K_2CO_3, and the solvents were removed under reduced pressure. Recrystallization from $CHCl_3$/hexanes affords pure **2** (6.4 g, 87%, mp = 49–50 °C): ^{1}H ($CDCl_3$) δ 9.68 (s, 2 H, CHO), 7.62 (d, J = 9.0 Hz, 4 H, Ar), 7.27 (t, J = 7.6 Hz, 2 H, Ar), 7.07 (d, J = 7.6 Hz, 2 H, Ar), 6.90 (s, 1 H, Ar), 6.60 (d, J = 9.0 Hz, 4 H, Ar), 4.56 (s, 4 H, NCH_2Ar), 3.43 (q, J = 7.0 Hz, 4 H, NCH_2), 1.15 (t, J = 7.0 Hz, 6 H, CH_3); ^{13}C ($CDCl_3$) δ 189.8 (CHO), 152.7, 137.9 (Ar C), 131.9, 129.1, 125.2, 125.1 (Ar CH), 123.8 (Ar C), 111.0 (Ar CH), 53.4 ($ArCH_2N$), 45.7 (NCH_2CH_3), 12.0 (CH_3); UV–vis (CH_2Cl_2) 322 nm (ϵ = 9.2 × 10^3); IR $\nu_{C=O}$ 1667 cm^{-1}. Anal. Calcd for $C_{26}H_{28}N_2O_2$: C, 77.97; H, 7.05. Found: C, 78.06; H, 7.07.

Preparation of "NLO-Tweezer" (3). A Schlenk flask was charged with diisopropylamine (4.01 g, 40 mmol) and THF (30 mL) and chilled to −78 °C. The mixture was treated with *n*-BuLi (2.5 M, 16.2 mL, 40 mmol), and after stirring for 1 h at −78 °C, 4-picoline (3.77 g, 40 mmol) was added and allowed to react with stirring for 1 h. The mixture was then transferred by cannula to a flask containing a THF (20 mL) solution of **2** (5.4 g, 14 mmol) and the reaction mixture allowed to warm to ambient temperature with stirring over a period of 18 h. The mixture was diluted with dichloromethane (150 mL) and washed with water (2 × 100 mL), and the organic layer was dried over Na_2SO_4. The solvents were removed under reduced pressure, and the crude product was subjected to column chromatography. A column packed with alumina oxide was first deactivated with MeOH in CH_2Cl_2 (1/20, v/v). Elution with CH_2Cl_2, followed by MeOH in CH_2Cl_2 (1/50, v/v), gave three bands. The third band was collected, and the solvents were removed under reduced pressure to give the product as a dark red solid containing mainly the alcohol product. This mixture was used in the next step without further purification. The product was dissolved in DMF (50 mL), and the solution was treated with PPTS and allowed to react at 50 °C for 2 h. The reaction mixture was cooled, diluted with CH_2Cl_2 (100 mL), washed with water (4 × 150 mL) and 0.01 M NaOAc (30 mL), and dried over K_2CO_3. The solvent was removed under reduced pressure and the product recrystallized from $CHCl_3$/hexanes solution to yield pure **3** as a yellow-brown solid (3.1 g, 40% mp = 69–71 °C): ^1H ($CDCl_3$) δ 8.47 (d, J = 6.0 Hz, 4 H, py), 7.32 (d, J = 9.0 Hz, 4 H, Ar), 7.27 (d, J = 6.0 Hz, 4 H, py), 7.17 (d, J = 16.2 Hz, 2 H, HC=), 7.08 (m, 3 H, Ar), 7.04 (s, 1 H, Ar), 6.72 (d, J = 16.2 Hz, 2 H, HC=), 6.59 (d, J = 9.0 Hz, 4 H, Ar), 4.561 (s, 4 H, NCH_2Ar), 3.44 (q, J = 7.0 Hz, 4 H, NCH_2), 1.16 (t, J = 7.0 Hz, 6 H, CH_3); ^{13}C ($CDCl_3$) δ 149.9 (py CH), 148.7, 145.5 (Ar C), 139.1 (Ar CH), 133.3 (HC=), 128.9 (Ar C), 128.4, 125.0, 124.4 (Ar CH), 124.0 (Ar C), 120.9 (HC=), 120.3 (pyr CH), 112.0 (Ar CH), 53.7 (NCH_2Ar), 45.4 (NCH_2), 12.8 (CH_3); UV–vis (CH_2Cl_2) 374 nm ($\epsilon = 3.1 \times 10^5$). Anal. Calcd for $C_{38}H_{38}N_4$: C, 82.87; H, 6.95. Found: C, 81.66; H, 7.04.

General Procedure for Polymer Syntheses. A Schlenk flask was charged with 2-bromoethyl methacrylate (2.00 g, 10.4 mmol), styrene (1.08 g, 10.4 mmol), and benzoyl peroxide (5.0 mg). The mixture was stirred and heated at 80 °C for 16 h. The solid product was dissolved in dichloromethane and precipitated into hexanes. This process was repeated three times, and then the solution was filtered to give pure copolymer. The following is a summary of spectroscopic and analytical data.

4a: ^1H ($CDCl_3$) δ 7.24–6.58 (m, 5 H, Ar), 4.25–3.80 (m, 2 H, CH_2Br), 3.62–2.98 (m, 2 H, CH_2O), 2.80–2.20 (m, 1 H, CH), 1.52 (m, 4 H, CH_2), 0.58 (m, 3 H, CH_3); ^{13}C ($CDCl_3$) δ 176.4 (CO_2), 145.2 (Ar C), 128.1, 127.9, 126.1 (Ar CH), 63.5 (CH_2O), 50.4 (CCO_2), 44.7, 44.0 (CH_2), 39.9 (CH), 28.6 (CH_2Br), 19.7 (CH_3); UV–vis (CH_2Cl_2) 312 nm; IR $\nu_{C=O}$ 1729 cm^{-1}. Anal. Calcd for $(C_8H_8)_{0.48}/(C_6H_9BrO_2)_{0.52}$: Br, 28.0. Found: Br, 28.0.

4b: ^1H ($CDCl_3$) δ 7.24–6.58 (m, 5 H, Ar), 4.25–3.80 (m, 2 H, CH_2Cl), 3.62–2.98 (m, 2 H, CH_2O), 2.80–2.20 (m, 1 H, CH), 1.52 (m, 4 H, CH_2), 0.58 (m, 3 H, CH_3); ^{13}C ($CDCl_3$) δ 176.4 (CO_2), 145.2 (Ar C), 128.1, 127.9, 126.1 (Ar CH), 63.7 (CH_2O), 50.4 (CCO_2), 44.7, 44.01 (CH_2), 41.1 (CH_2Cl), 39.9 (CH), 19.7 (CH_3); UV–vis (CH_2Cl_2) 312 nm; IR $\nu_{C=O}$ 1729 cm^{-1}. Anal. Calcd for $(C_8H_8)_{0.55}/(C_6H_9ClO_2)_{0.45}$: Cl, 12.6. Found: Cl, 12.6.

4c: ^1H ($CDCl_3$) δ 7.24–6.58 (m, 5 H, Ar), 4.25–3.80 (m, 2 H, CH_2Cl), 3.62–2.98 (m, 2 H, CH_2O), 2.80–2.20 (m, 1 H, CH), 1.52 (m, 4 H, CH_2), 0.58 (m, 3 H, CH_3); ^{13}C ($CDCl_3$) δ 176.4 (CO_2), 145.2 (Ar C), 128.1, 127.9, 126.1 (Ar CH), 63.7 (CH_2O), 60.9 (CH_2), 50.4 (CCO_2), 44.7, 44.01 (CH_2), 41.1 (CH_2Cl), 39.9 (CH), 31.1 (CH_2), 19.7 (CH_3); UV–vis (CH_2Cl_2) 312 nm; IR $\nu_{C=O}$ 1729 cm^{-1}. Anal. Calcd for $(C_8H_8)_{0.54}/(C_7H_{11}ClO_2)_{0.46}$: Cl, 12.3. Found: Cl, 12.3.

Preparation of 5. A Schlenk flask was charged with $POCl_3$ (9.75 g, 44.3 mmol) and 21 mL of DMF at 0 °C. After stirring for 2.5 h at 0 °C, (*N*-ethyl-*N*-hexylamino)benzene (5.6 g, 27 mmol) was added and stirring was continued for 1 h at 25 °C and then 2 h at 90 °C. The reaction mixture was cooled and poured over a mixture of ice and sodium acetate (15 g). The product was extracted into dichloromethane and dried over K_2CO_3, and the solvents were removed under reduced pressure. Recrystallization from $CHCl_3$/hexanes afforded pure **5** (4.7 g, 73%): ^1H ($CDCl_3$) δ 9.63 (s, 1 H, CHO), 7.63 (d, J = 9.0 Hz, 2 H, Ar), 6.59 (d, J = 9.0 Hz, 2 H, Ar), 3.38 (q, J = 7.0 Hz, 2 H, NCH_2), 3.27 (t, J = 7.6 Hz, 2 H, NCH_2), 1.56 (m, 2 H, CH_2), 1.27 (m, 6 H, CH_2), 1.14 (t, J = 7.0 Hz, 3 H, CH_3), 0.84 (t, J = 6.8 Hz, 3 H, CH_3); ^{13}C ($CDCl_3$) δ 189.2 (CHO), 152.1 (Ar C), 131.8 (Ar CH), 124.3 (Ar C), 110.3 (Ar CH), 50.1, 44.8 (NCH_2), 31.3, 27.0, 26.3, 22.2 (CH_2), 13.6, 11.9 (CH_3); UV–vis (CH_2Cl_2) 322 nm ($\epsilon = 9.2 \times 10^3$); IR $\nu_{C=O}$ 1667 cm^{-1}.

Preparation of Compound 6. A Schlenk flask was charged with diisopropylamine (2.6 g, 26 mmol) and THF (30 mL), chilled to −78 °C, and treated with *n*-BuLi (2.5 M, 10.3 mL, 26 mmol). After stirring for 1 h at −78 °C, 4-picoline (2.4 g, 26 mmol) was added and the stirring was continued for 1 h. The mixture was transferred by cannula to a flask containing a THF (20 mL) solution of **5** (4.0 g, 17 mmol) and the reaction mixture allowed to warm to ambient temperature with stirring over a period of 18 h. The mixture was diluted with dichloromethane (150 mL) and washed with water (2 × 100 mL), and the organic layer was dried over Na_2SO_4. The solvents were removed under reduced pressure, and the crude product was subjected to column chromatography. A column packed with alumina oxide was first deactivated with MeOH in CH_2Cl_2 (1/20, v/v). Elution with CH_2Cl_2, followed by MeOH in CH_2Cl_2 (1/50, v/v) gave three bands. The third band was collected and the solvents were removed under reduced pressure to give the product as a dark red solid containing mainly the alcohol product. This mixture was used in the next step without further purification. The product was dissolved in DMF (50 mL) and treated with PPTS and allowed to react at 50 °C for 2 h. The reaction mixture was cooled, diluted with CH_2Cl_2 (100 mL), washed with water (4 × 150 mL) and 0.01 M NaOAc (30 mL), and dried over K_2CO_3. The solvent was removed under reduced pressure and the product recrystallized from $CHCl_3$/hexanes solution to yield pure **6** as a yellow-brown crystalline solid (4.73 g, 90%, mp = 65–67 °C): ^1H ($CDCl_3$) δ 8.48 (d, J = 6.0 Hz, 2 H, py), 7.38 (d, J = 9.0 Hz, 2 H, Ar), 7.28 (d, J = 6.0 Hz, 2 H, py), 7.20 (d, J = 16.2 Hz, 1 H, HC=), 6.74 (d, J = 16.2 Hz, 1 H, HC=), 6.62 (d, J = 9.0 Hz, 2 H, Ar), 3.39 (q, J = 7.0 Hz, 2 H, NCH_2), 3.27 (t, J = 7.6 Hz, 2 H, NCH_2), 1.59 (m, 2 H, CH_2), 1.30 (m, 6 H, CH_2), 1.16 (t, J = 7.0 Hz, 3 H, CH_3), 0.89 (t, J = 6.8 Hz, 3 H, CH_3); ^{13}C ($CDCl_3$) δ 149.9 (py CH), 148.5, 145.7 (Ar C), 133.4 (HC=), 128.5 (Ar CH), 123.3, (Ar C), 120.5 (HC=), 120.3 (py CH), 111.6 (Ar CH), 50.5, 45.0 (NCH_2), 31.7, 27.5, 26.8, 22.6 (CH_2), 14.0, 12.4 (CH_3); UV–vis (CH_2Cl_2) 374 nm ($\epsilon = 3.1 \times 10^5$). Anal. Calcd for $C_{21}H_{28}N_2$: C, 81.77; H, 9.15. Found: C, 81.79; H, 9.17.

Preparation of Samples for SHG Studies. A 100 mg sample of the copolymer and 10 mg (0.0182 mmol) of NLO-tweezer were dissolved dichloromethane (1 mL) to give an orange solution. Using a knife-edge technique, the solution was coated on clean soda-lime microscope slides.[16] After deposition, the films were dried at ambient temperature for 15 min and then placed under vacuum (30 mmHg) to remove residual solvent. For samples of **4a** drying was done under vacuum at 24 °C for 8 h, and for **4b** samples were first baked under vacuum at 40 °C for 3 h and then held under vacuum at 24 °C for an additional 8 h.

Poling of Films. A non-zero second-order optical susceptibility $\chi^{(2)}$ was imparted to the films via corona poling. The **4a** samples were poled at 90 °C for varying lengths of time, cooled to 70 °C at 4 °C/min with the poling field on, and then rapidly quenched to room temperature immediately after removal of the poling field. For **4b** systems, the samples were initially poled at 50–55 °C for 30 min, after which the temperature of the films was raised to 110 °C and the poling continued for varying lengths of time. The films were then cooled to 90 °C at 4 °C/min and rapidly quenched to ambient temperature immediately following removal of the poling field.

Temperature Ramp Studies. A film sample was placed on an aluminum heating stage initially held at ambient temperature (~24 °C), and the SH signal was monitored as the temperature of the film was increased at rate of 7 °C/min.

Isothermal Decay Studies of $\chi^{(2)}$. A film sample was placed on an aluminum heating stage held at 80 °C, and light polarized perpendicular to the plane of incidence (*s*-polarized) was directed onto the sample at 52° from normal incidence. The intensity of the *p*-polarized second harmonic light was measured over time to monitor the isothermal decay of $\chi^{(2)}$.

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