New Random Main-Chain, Second-Order Nonlinear Optical Polymers

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The design and synthesis of polymers containing second-order nonlinear optical (NLO) chromophores have been a subject of continuing interest. Three types of polymer materials have been developed for this purpose: guest–host systems, side-chain polymers, and main-chain polymers. These materials demonstrate second-order NLO effects after heating above the polymer glass transition temperature (T_g), electric field poling, and stabilization of poling-induced order.

While many guest–host and side-chain NLO polymers have been developed, relatively few main-chain polymers have been prepared.[1-7] Most of the main-chain, second-order NLO polymers reported are head-to-tail; namely, all the chromophore dipole moments point in the same direction along the polymer backbone. The head-to-tail assembly of chromosphores was expected to increase greatly the effective dipole moment.[2,3] The results published so far, however, have not realized these expectations.[3,6,7] In fact, reorienting the entire polymer main chain to align with the electric field is quite difficult. Lindsay and co-workers have recently reported the synthesis of new syndioregic main-chain polymers in which the dipoles are arranged head-to-head or tail-to-tail in the polymer main chain.[7] For these polymers, the dipole alignment upon electric poling can be effected by wrinkling the polymer backbone.

For any poled NLO polymer materials, one of the major problems encountered in developing electrooptics devices is the temporal relaxation of the dipole orientation after the poling field is removed. Cross-linking reactions have proven to be effective in stabilizing electric-field-induced dipole alignment.[8-12] It is expected that after cross-linking the main-chain polymers will provide improved temporal, thermal, and photo NLO stability because of their potential for high cross-linking density and locking-in of both ends of the chromophore dipoles. In this paper, we demonstrate that polymers incorporating NLO chromophores into the main chain can be effectively poled, yielding macroscopic second-order optical nonlinearities comparable to polymers containing virtually the same chromophore as a pendant. We also present our preliminary result that poling-induced order can be stabilized for the main-chain NLO polymers by cross-linking.

In the polymers discussed in this paper, the chromophore dipoles are expected to be randomly arranged in the polymer backbone (i.e., the dipoles can be head-to-tail, tail-to-tail, or head-to-head), as shown in Figure 1a, because of the similarity of the chemical environments of the two hydroxy groups in monomer 1 (see Figure 2). We assume that, for amorphous polymers, the chromophore arrangements in the backbone should not be a problem for dipole alignment upon electric field poling, because the polymer chains are random-coil conformations (Figure 1b) instead of extended chains (Figure 1a). When an electric field is

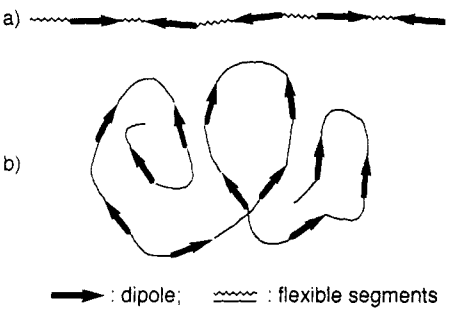
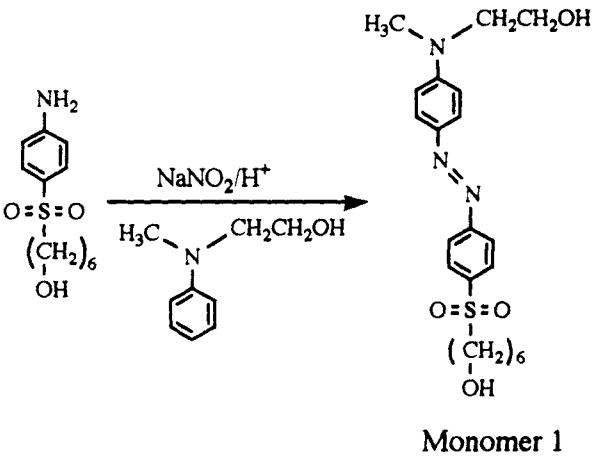
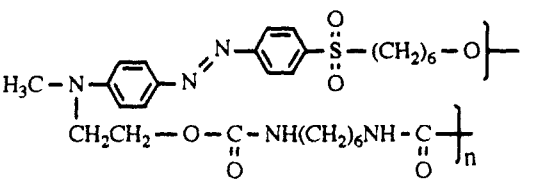


Figure 1. Dipole arrangements in the polymer backbone; (a) extended random chain; (b) poling-induced dipole alignment in a random chain.



Monomer 1



Polymer 2

Figure 2. Structures of the monomer and polymer.

applied above T_g, the dipoles will align with the field through segmental motions of the polymer chains, as illustrated in Figure 1b. To assist the segmental motion, and hence the electric-field-induced alignment, appropriate flexible chains, which can bend through bond rotations, are introduced between the rigid chromophores. These polymers can be simply synthesized by common condensation polymerization methods. Well-developed polymerization techniques together with a vast array of available monomers not only will increase the size of the main-chain NLO polymer family but also will permit the synthesis of a great many main-chain NLO polymers and the study of the relationship between structure and properties. For example, by introduction of cross-linking units from the comonomers, cross-linkable main-chain, second-order NLO polymers can be synthesized. Indeed, we have succeeded in preparing such materials, and the preliminary results of using this approach to stabilize poling-induced order will be briefly discussed.

In our experiment, we used 4-aminophenyl 6-hydroxyhexyl sulfone, which was prepared by published literature methods,[5] and *N*-(2-hydroxyethyl)-*N*-methylaniline to synthesize the chromophore monomer by the diazonium coupling reaction. The chromophore monomer obtained was purified using column chromatography and recrys-

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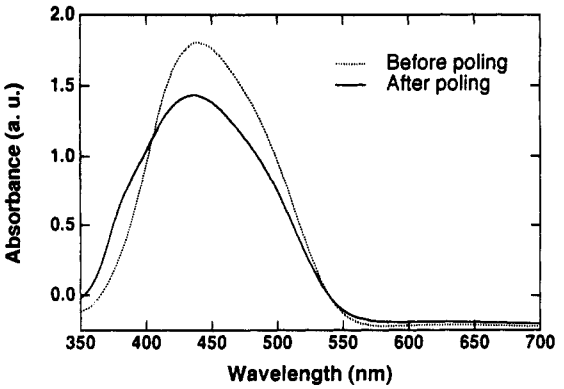

Figure 3. Ultraviolet–visible spectra of a polymer film on a ITO glass slide before and after poling.

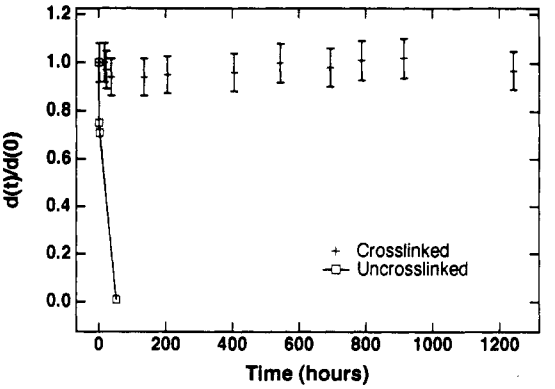

Figure 4. Comparison of the temporal NLO stability between the cross-linked and un-cross-linked films. $d(0)$ is the SHG coefficient measured at $^1/_2$ h after poling.

tallization methods. The monomer was polymerized with 1,6-diisocyanatohexane in dioxane by refluxing overnight. The polymer solid was obtained by pouring the reaction solution into excess methanol. Then it was further purified by dissolving in dioxane and precipitating in methanol again. The monomer synthesis and polymer structure are shown in Figure 2.

The structures of both monomer 1 and polymer 2 are characterized by ^{1}H-NMR and FTIR. ^{1}H-NMR chemical shifts (δ): for the monomer ($CDCl_3$ solvent), 7.94 (q, 4 H), 7.86 (d, J = 9.1 Hz, 2 H), 6.83 (d, J = 9.2 Hz, 2 H), 3.88 (t, J = 5.4 Hz, 2 H), 3.63 (t, J = 5.8 Hz, 2 H), 3.58 (t, J = 6.4 Hz, 3 H), 3.14 (s, 3 H), 3.08 (t, J = 5.2 Hz, 2 H), 1.76–1.32 (m, br, 8 H); for the polymer ($CDCl_3$), 7.94 (br, 6 H), 6.81 (d, J = 8.9 Hz, 2 H), 4.70 (vb), 4.26 (t, br, 2 H), 3.98 (t, br, 2 H), 3.70 (br, 2 H), 3.18–2.94 (m, br, 9 H), 1.71–1.23 (m, br, 16 H). The NMR analysis permits observation of the disappearance of the monomers and formation of the polymer. FTIR spectra also showed the disappearance of both the hydroxy group (3346 cm^{-1}) and isocyanate group (2268 cm^{-1}) and the formation of the urethane group (1697 cm^{-1}). The weight-average molecular weight, measured by size-exclusion chromatography (SEC) with polystyrene as a reference, is 7720 (M_w/M_n = 1.6).

The polymer obtained is an orange powder and is readily soluble in common organic solvents. The transparent and optical quality thin films were made by spin casting onto indium–tin oxide (ITO) coated glass slides from a 10% polymer solution in chloroform. The NLO properties of the film were subsequently studied by second-harmonic generation (SHG). The film was poled at 115 °C for 15 min using a corona-discharge setup. The poling voltage was around 6 kV with a tip-to-plane distance of about 1.5 cm. The film thickness of 1.5 μm was measured by a Dektak II profiler. A Q-switched Nd:YAG laser (λ = 1.064 μm) with a pulse width of <10 ns was used as the fundamental beam, and a quartz crystal (d_{11} = 0.5 pm/V) was used as the reference. The SHG coefficient (d_{33}) of the polymer film of 40 pm/V was obtained by published literature methods.[13,14] The SHG coefficient depends on the electric poling procedure, i.e., the poling temperature, time, and voltage. The d_{33} value reported here may not be optimized. The electric poling alignment was also confirmed by the absorbance change from the spectrophotometer scan in the ultraviolet and visible range, as shown in Figure 3.

The poled and cross-linked polymer films were obtained by heating and poling the films containing the polymer synthesized and cross-linker, 3,3′-dimethoxy-4,4′-biphenylene diisocyanate, at 120 °C through a known allophanate-linking reaction.[15] Figure 4 illustrates the comparison of the temporal stability between the cross-linked and un-cross-linked polymer films. As can be seen, the SHG coefficient of the cross-linked film has not shown, within the experimental errors, any significant change for more than 1000 h, while the un-cross-linked film exhibits a fast decay of the SHG signal.

As an initial report on the randomly polymerized main-chain, second-order NLO polymers, the result to be emphasized is that a random polymer can be effectively poled by an electric field, its poled polymer film shows a second-order nonlinearity comparable to that of the side-chain polymer with virtually the same NLO moiety,[16] and its second-order optical nonlinearity can be stabilized by a cross-linking reaction. This opens the way to a new class of second-order NLO polymers.

In summary, a random main-chain, second-order NLO polymer has been synthesized. Optical-quality thin films can be obtained by spin casting. This polymer film can be effectively poled by an electric field and exhibits a sizable nonlinearity, $\chi^{(2)}$ = 80 pm/V, at a 1.064 μm fundamental wavelength. The NLO stability of the polymers can be enhanced by cross-linking the main chains. Our simple synthesis scheme can be extended to prepare many cross-linkable main-chain NLO polymers for stabilizing poling-induced order.

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Registry No. 1, 144042-95-5; 2, 144042-96-6; *p*-$H_2NC_6H_4SO_2(CH_2)_6OH$, 131110-20-8; $PhN(CH_3)CH_2CH_2OH$, 93-90-3.