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Communications to the Editor

Processable Main-Chain Nonlinear Optical Polymer with a New Acceptor Group from Melt Polycondensation

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Organic materials for nonlinear optics (NLO) have interested many researchers due mainly to the flexibility of organic syntheses allowing numerous molecules with desirable properties to be designed and synthesized. In the area of crystalline organics, this approach has been advantageously utilized to synthesize a large number of related small molecules.[1] Unfortunately, the macroscopic polar order needed for a second-order effect ($\chi^{(2)}$) is neither tailorable to any great extent nor predictable.[2,3] Also, the irreproducibility in both crystal quality and crystal size makes this area of research very challenging.[3] As a result, many researchers have focused on polymers.[4] Even though polymers solve many of the problems encountered with crystals, the new problem of dipolar orientation and stability, especially at elevated temperatures over extended periods of time, now emerges. Guest–host, side-chain, cross-linked, and, to a lesser extent, main-chain polymer systems, partially aligned by electric field poling, have been examined as possible solutions.[5–7]

The first main-chain NLO polymers were reported by Hall and co-workers.[5,8,9] These polymers had very polar groups, necessary for high nonlinearity, but were not readily processable. Subsequent polymers by Hall and co-workers based on *p*-oxy-α-cyanocinnamate were more processable, but the nonlinearity was not reported.[9] Lindsay and co-workers extended this work to make soluble polymers, but one would not expect the nonlinearity to be high because the cyanoester is not a very strong electron-withdrawing group.[10,11] Robello and co-workers, and later Dalton and co-workers, synthesized extended conjugated molecules with a sulfone acceptor group as a method of obtaining processable main-chain polymers with high nonlinearity.[12,13] In this paper we present the synthesis and characterization of a novel, processable, main-chain homopolymer with a strong electron-withdrawing group. This low molecular weight homopolymer can be poled and subsequently converted to a high molecular weight insoluble material by heating while still subjected to the electric field to maintain the polar alignment.

The monomer, 3-[(methyoxycarbonyl)methyl]-5-[4′-[*N*-ethyl-*N*-(2″-hydroxyethyl)amino]benzylidene]rhodanine (**3**) was synthesized according to Scheme I. Melt polymerization of **3** under nitrogen produced polymer **4**. Using DSC, a T_g of 63 °C (midpoint) was measured. This correlated well with a T_g of 60 °C measured by the second-harmonic generation technique. The number-average molecular weight of **4** as determined by GPC, relative to polystyrene, was very dependent on the reaction conditions employed as shown in Table I. Higher polymerization temperatures yielded a higher molecular weight polymer, until the decomposition temperature of the monomer was reached. Longer polymerization times at a given temperature also resulted in lower polydispersity. In the synthesis of polymer sample 6, tetraisopropyltitanium catalyst was added to the melt. This resulted in a significantly higher molecular weight material. The T_g of this sample also increased to 110 °C. Like the other polymer samples, this sample displayed only a slight loss in weight (0.6% in air and 0.3% in nitrogen) when heated in a TGA instrument at 10 °C/min from 25 to 200 °C. For the soluble samples, a decrease in the UV–vis absorption maximum was observed when a film was kept at 170 °C in a nitrogen atmosphere for extended periods of time; this indicated decomposition. A lower decomposition temperature would be expected in air.

Scheme I. Synthesis of Main-Chain Polymer

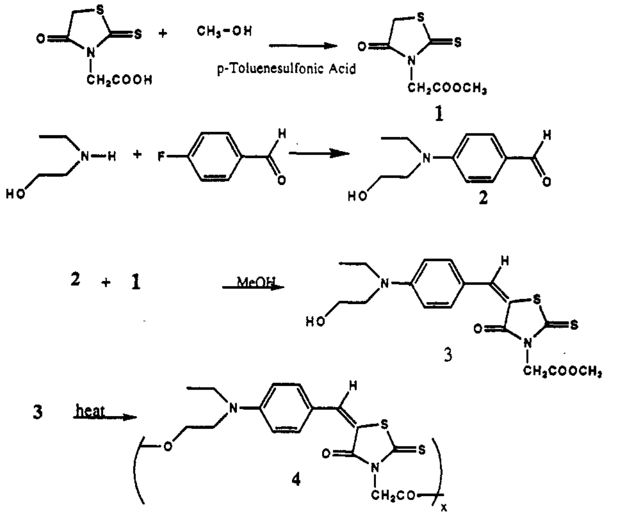

Table I. Molecular Weight and Polydispersity as a Function of Polymerization Temperature

temp/°C	time/h	M_n	M_w/M_n
135	18	4200	1.53
140	8	6200	2.12
150	16	6200	1.43
160	16	6800	1.42
170	3	dec	
140 (catalyst)	6	1400[a]	

[a] Molecular weight for the soluble portion of a polymer calculated from NMR analysis.

The proton spectrum of monomer **3** in dimethyl sulfoxide (DMSO) is assigned as follows: δ 7.69 (s, CH=), 7.43 (d, 9.2, CH ortho to CH=), 6.82 (d, 9.2, CH ortho to N), 4.79 (s, NCH_2CO), 3.68 (s, OCH_3), 3.56 (t, 6.1, CH_2O), 3.47 (t, 6.1, $HOCH_2CH_2N$), 3.47 (q, 7.0, CH_3CH_2N), 1.10 (t, 7.0, CH_3C). The OH is a broad absorption at 4.8 ppm. The carbon-13 spectrum is assigned as follows: δ 192.32 (C=S), 166.76 (CO_2), 166.29 (C=O), 150.56 (ipso C-N), 135.63 (olefinic CH=C), 133.76 (CH ortho to CH=), 119.26 (ipso CCH), 112.48 (*C*=CH of rhodanine ring), 112.07 (CH ortho to N), 58.39 (CH_2OH), 52.65 (OCH_3), 52.02 (NCH_2CH_2O), 45.12 (NCH_2CH_3), 44.75 (NCH_2CO_2), 12.00 (CH_3).

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Carbon-13 and proton NMR were used to confirm the structure of the polymer. Condensation polymerization of **3** proceeded with loss of methanol to give polyester **4**. The proton spectrum of the polymer shows broad absorptions with chemical shifts similar to those observed in the monomer, except for the loss of the terminal methyl resonance and the downfield shift of the α protons of the alcohol group from 3.60 to 4.35 ppm, as expected for an ester methylene. End groups are not observable in the proton spectrum due to overlap with the NCH_2 absorptions. The carbon-13 spectrum showed similar changes, with the downfield shift of the CH_2OH from 58.39 ppm to a typical CH_2OCO methylene at 63.2 ppm. Other major changes in the appearance of the carbon spectrum include the upfield shift of the $HOCH_2CH_2$ from 52.02 to 47.7 ppm (a γ steric effect of the carbonyl) and the loss of the 52.65 CH_3O absorption.

Quantitative integration (on a nuclear Overhauser effect (NOE) suppressed ^{13}C spectrum) of the carbon polyester CH_2OCO absorption at 63.2 ppm relative to the monomer absorptions at 58.39, 52.65, and 52.02 ppm was used to calculate a number-average molecular weight of the soluble portion of the polymer. A polymer/CH_2OH end group ratio of 3/1 was found. This implies a number-average molecular weight of 1400.

Determination of the second-harmonic generation (SHG) coefficient, d_{33}, of a spin-coated film of polymer **4** was made at 1580-nm fundamental wavelength during poling. Refractive indices of the polymer, obtained by analysis of the interference observed in a spectrophotometric trace of a film on fused silica, were 1.678 at 1580 nm and 1.760 at 790 nm. The polymer film was poled under an effective field of 43 V/μm and the temperature ramped up to 65 °C. The onset of SHG occurred at 60 °C, and the off-resonance (λ_{max} for polymer = 473 nm) d_{33} value measured at 65 °C was 7.3 pm/V relative to a quartz reference ($d_{11} = 0.5$ pm/V).

A spin-coated film of polymer **4** was heated under dry nitrogen at 150 °C for 4 h. This resulted in an insoluble film, indicating an increase in the molecular weight of the material. Work continues on polymerizing poled films of polymer **4** under the electric field and examining the stability of the aligned dipoles.

Experimental Section. Synthesis. Rhodanine-3-acetic acid and 4-fluorobenzaldehyde were obtained from Aldrich Chemical Co. and used without further purification. NMR spectra were obtained on Varian XL-400 or UNITY 500 spectrometers operating at 400 and 500 MHz, respectively, for ^1H, on samples in DMSO-d_6. Chemical shifts are reported relative to tetramethylsilane. Approximate relaxation times, determined using a 180°–τ–90° inversion–recovery pulse sequence, were under 0.2 s. Integrals were determined from a quantitative NOE suppressed ^{13}C run overnight with a 0.5-s relaxation delay (with the decoupler off). The carbon spectrum of the monomer was assigned using proton–carbon one-bond and multiple-bond heteronuclear correlation (HMQC and HMBC) 2D spectra and comparison to a reference spectrum of *N*,*N*-diethylaniline.

Synthesis of 4-[*N*-ethyl-*N*-(2′-hydroxyethyl)amino]benzaldehyde. A general procedure for the preparation of amino-substituted benzaldehydes was adapted from Tournilhac.[14] The modified procedure is reported in ref 6.

Synthesis of 3-[(Methyoxycarbonyl)methyl]-5-[4′-[*N*-ethyl-*N*-(2″-hydroxyethyl)amino]benzylidene]rhodanine (3).[6,15] Methyl rhodanine-3-acetate (3.07 g, 0.0207 mol) was dissolved in methanol (30 mL), 4-[(2′-hydroxyethyl)ethylamino]benzaldehyde (4.00 g, 0.0207 mol) dissolved in methanol (10 mL) was added, and the resultant mixture was refluxed for 2 h before it was cooled to room temperature. The red crystals that formed were filtered to yield 6.5 g (97%) of product. Mp = 140–141 °C.

Polymer Synthesis. A typical polymer synthesis involves heating 0.5 g of **3** at a temperature slightly below or above its melting point under a stream of dry nitrogen for a period of time. The resulting polymer is recovered when the sample is cooled to room temperature under dry nitrogen.

Electric Field Poling. Polymer **4** was dissolved in pyridine to make a 15% solution by weight. This solution was filtered and used to spin-coat films approximately 1 μm thick onto glass substrates coated with indium–tin oxide (ITO) electrodes. After drying for 2 h at 75 °C, ITO was sputtered onto the films to serve as the other poling electrode.

The fundamental wavelength employed in the SHG measurements was 1580 nm, generated by Raman-shifting the frequency-doubled output (532 nm) of a pulsed Nd^{3+}:YAG laser by means of a high-pressure hydrogen cell. The incident radiation and the second harmonic detected at 790 nm were *p*-polarized with the beam direction oriented at 45° from the normal of the poled film. The sample was contained in a temperature-controlled oven which permitted passage of the laser beam and application of the poling voltage.

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