Synthesis and Nonlinear Optical Properties of a New Syndioregic Main-Chain Hydrazone Polymer

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Received October 17, 2000; Revised Manuscript Received December 29, 2000

ABSTRACT: The synthesis of a syndioregic main-chain hydrazone nonlinear optical polymer is reported. The nonlinearity is thermally stable up to 140 °C and retains 90% of the original value even when stored at 100 °C for 100 h. The polymer has a relatively low nonlinearity ($d_{33} = 3.6$ pm/V) due to the incorporation of a low β chromophore.

Introduction

In high-frequency light-modulating devices requiring the integration of optical and electronic circuits, second-order nonlinear optical (NLO) polymer films are very promising.[1] Polymer films combining low optical loss, large NLO properties, and good thermal stability have advantages over inorganic crystals, such as lithium niobate, due to the ease of processing polymer films on silicon wafers. The US Navy's Research Department at the China Lake Weapons Division has investigated the development of main-chain NLO polymers for many years.[2] For a given chromophore, it has been found that the chemical structure of the polymer chain plays an important role in the degree of polar order that can be imparted to the chromophores by corona poling. For a given glass-transition temperature (T_g) the main-chain configuration of chromophores can give a higher degree of thermal stability than the side-chain configuration (e.g., as measured by ramping the temperature at 1 °C/min and observing the decrease in NLO property).[3] It was found that main-chain NLO polymers having a head-to-head (syndioregic) configuration[4,5] were superior to main-chain NLO polymers having a head-to-tail (isoregic) configuration in corona-poled films.[6]

In this paper, we present the synthesis, linear optical, and NLO properties of a new syndioregic main-chain polymer having low optical loss in the visible wavelengths and a high thermal stability. This NLO polymer may be useful for light modulation in the visible region of the spectrum. However, the main purpose for preparing this polymer was for a study (to be reported elsewhere) comparing the relative relaxation rates of a chromophore in the syndioregic configuration and in the side-chain configuration. Use of the hydrazone chromophore in the NLO polymer of this study was motivated by the results reported by Gulotty's group at the Dow Chemical Company on side-chain hydrazone polymers.[7] The syndioregic polymer of the present study (**3** in Figure 1) exhibits low optical loss and good thermal stability of the NLO properties but has a low absolute nonlinearity.

Experimental Section

Materials. All starting materials were obtained from Aldrich (Milwaukee, WI) and used as received. The synthetic route for polymer **3** is shown in Scheme 1. Throughout this paper we will refer to this polymer generically as AC2729.

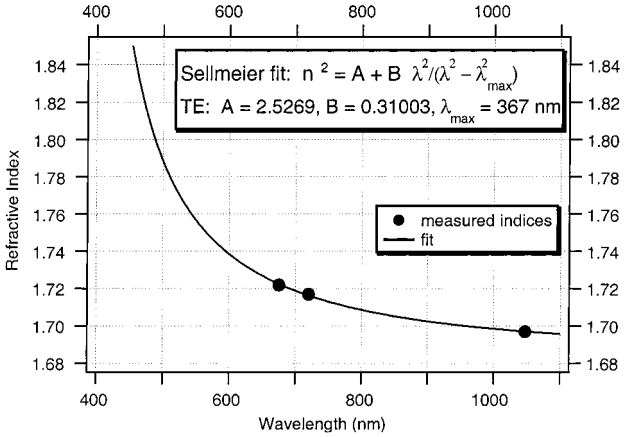
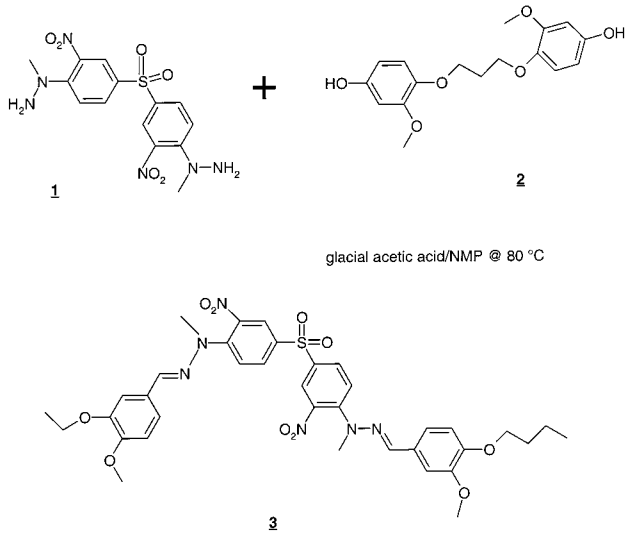


Figure 1. Dispersion of the refractive index in AC2729.

Scheme 1. Synthesis of the Main-Chain Syndioregic Hydrazone Polymer AC2729



Di-(4-(1-methylhydrazino)-5-nitrophenyl)sulfone (1). To 344 mg of 4,4′-difluoro-5,5′-dinitrodiphenyl sulfone (1 mmol) in 5 mL of dry acetonitrile was added 185 mg of methylhydrazine (4 mmol) in 1 mL of dry acetonitrile. The mixture was

10.1021/ma001796p CCC: $20.00
Published on Web 01/31/2001

stirred at room temperature for 24 h and then poured into 100 mL of stirred cold water. The solid precipitate was collected by filtration, washed with methanol, and then air-dried to 390 mg (98.5% yield) of a yellow solid; mp 223−4 °C. ^{1}H NMR (DMSO-d_6): 7.99 (d, 2H, ArH, J = 1.4 Hz), 7.79 (dd, 2H, ArH, J = 1.4 Hz, J = 9.2 Hz), 7.05 (d, 2H, ArH, J = 9.2 Hz), 4.91 (s, 6H, CH3), 3.12 (s, 4H, NH).

Propane-1,3-diol Bis(2-methoxy-5-formylphenyl) Ether (2). To a solution of 0.76 g (33 mmol) of sodium in 150 mL of methanol was added 5.00 g of 2-methoxy-5-formylphenol (39.2 mmol). 1,3-Diiodopropane (1.9 mL, 16.5 mmol) was then added. The mixture was heated to reflux and stirred overnight. The solution was then cooled and concentrated in a vacuum. The residue was taken up in 150 mL of $CHCl_3$ and washed with 4 N aqueous NaOH and water and then dried ($MgSO_4$) and concentrated in a vacuum to give 2.64 g of propane-1,3-diol bis(2-methoxy-5-formylphenyl) ether as a tan solid (46%). ^{1}H NMR (CD_2Cl_2): 9.82 (s, 2H), 7.44 (m, 4H), 7.00 (d, 2H), 4.27 (t, 4H), 3.91 (s, 6H), 2.34 (q, 2H). ^{13}C NMR (CD_2Cl_2): 190.97, 155.37, 149.37, 130.49, 126.79, 65.90, 56.41, 29.47.

Polymer of 3,3′-Dinitro-4,4-bis(1-methylhydrazino)-diphenyl Sulfone and Propane-1,3-diol Bis(2-methoxy-5-formylphenyl) Ether (3). A mixture of 1.264 g of propane-1,3-diol bis(2-methoxy-5-formylphenyl) ether (3.67 mmol), 1.455 g of 3,3′-dinitro-4,4-bis(1-methylhydrazino)diphenyl sulfone (3.67 mmol), and 5 mL of glacial acetic acid in 10 mL of *n*-methylpyrrolidone (NMP) was heated to 80 °C and stirred for 48 h. The mixture was then cooled and poured into methanol. The solids were filtered off and washed with methanol to give 2.48 g of an orange solid. The glass transition temperature of the amorphous polymer was 176 °C by differential scanning calorimetry (TA Instruments 2901 at 10 °C/min in nitrogen). ^{1}H NMR (DMSO-d_6): no aldehyde, 8.29 (s), 8.04 (d), 7.77 (s), 7.47 (d), 7.16 (s), 7.03 (m), 4.17 (br), 3.72 (s), 3.46 (s), 3.32 (s), 2.48 (s), 2.21 (br). ^{13}C NMR (DMSO-d_6): 150.18, 148.17, 143.19, 139.62, 139.18, 130.96, 127.74, 125.27, 121.40, 118.62, 111.68, 109.18, 64.55, 55.55, 33.51.

Molecular Weight. The molecular weight of **3** was determined by gel permeation chromatography using polystyrene standards in dimethylformamide at 60 °C. The number-average molecular weight was 12 800 g/mol while the weight-average was 23 600 g/mol, giving a polydispersity (M_w/M_n) of 1.84.

Film Preparation. Thin films were prepared by a blade casting technique onto microscope slides from 10 to 15% solutions of polymer in NMP and diglyme (4:1) solvent mixture. The addition of diglyme tended to improve the wetting of the polymer onto the glass slide. Holes and cracks were minimized by blade casting (>1 μm) onto a thin spin-coated layer (< 1 μm) instead of blade casting onto bare glass. The films were dried at room temperature for 1 h for both layers and then baked after blade casting in the following stages: (i) 70 °C for 1 h, (ii) 90 °C for 1 h, (iii) 120 °C for 1 h, (iv) 150 °C for 1 h, and (iv) 175 °C for 4 h. Multiple stages of baking helped to avoid cracking of the film which resulted from the strain due to volume expansion upon heating.

Corona Poling. To achieve noncentrosymmetry, all samples were corona poled[8] at a voltage ~6 kV and a current of 2 μA, with a positively charged tungsten wire 3 cm above the film at 180 °C for 40−60 min for the films used in the thermal stability study and at 190 °C for 10 min for the *d*-coefficient measurements. To avoid photoinduced chemical modification such as chromophore bond breaking, the film was baked and poled in the dark. To erase any thermal history, the films were annealed for 20−30 min at T_g + 4 °C. The location of the absorption maximum of <1 μm thick films did not show any difference between poled and unpoled films, indicating no significant chromophore decomposition during the poling process.

Thermal Stability Tests. The films were allowed to sit for 2 days at room temperature to dissipate any trapped charge accumulated during poling. This ensures that the observed second harmonic generation (SHG) decay is due to chromophore reorientation associated with polymer motion and not due to dissipation of trapped charge. For the *d*-coefficient measurement, films were tested about 16 h after poling. Film thickness was measured by a stylus profilometer (Tencor instruments, Alpha step 200) and a prism-coupled waveguiding technique[9] with good agreement between the methods. The dispersion of the refractive index was measured using the prism coupling technique at wavelengths of 1047, 720, and 675 nm and fit to the Sellmeier equation shown in Figure 2 where λ_{max} was obtained from UV−vis spectroscopy using a Perkin-Elmer Lambda 3B. SHG measurements employed a Nd:YAG laser (Continuum Minilite; 6 ns pulse duration; 25 mJ/pulse; 10 Hz) with a 1064 nm fundamental beam. The detailed experimental setup is described elsewhere.[10]

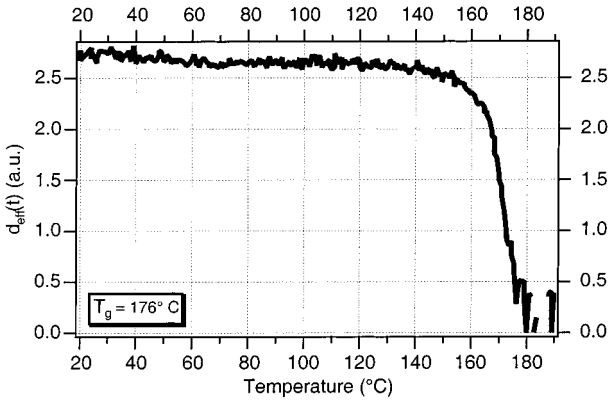


Figure 2. Temporal stability of the second-order optical susceptibility in AC2729.

Results and Discussion

The dispersion of the refractive index of the polymer is shown in Figure 1. The thermal stability of the second-order optical susceptibility was measured by recording the SHG signal as the sample was heated at 10 °C/min (Figure 2). The effective *d*-coefficient is nearly constant up to 160 °C and then falls off rapidly. This flat response up to the sharp transition is in contrast to that seen in guest−host systems[11,12] and some side-chain systems[13] where β motion contributes significantly to the sub-T_g relaxation of d_{eff}. In AC2729, the chromophore is incorporated directly in the main chain; hence, the relaxation of d_{eff} is affected mostly by α motion, and sub-T_g induced relaxation of d_{eff} is suppressed. Similar sharp transitions are also seen in highly cross-linked nonlinear optical (NLO) polymers[14] and in high-T_g NLO polyimides[15] since these systems also have fewer modes available for sub-T_g relaxation. The depoling temperature (T_d = 171 °C), which we define as the inflection point of the transition, was found to be very close to the T_g measured by DSC (176 °C). The temporal stability of d_{eff} was measured at 125 and 150 °C. The temperature was controlled within ±1 °C for each experiment. The sample stage was heated to the experimental temperature prior to housing the sample, and the data were taken starting 2 min after placing the sample into the sample holder. As shown in Figure 3, d_{eff} only decays by about 10% after 125 h at 125 °C. About a day was required for d_{eff} to decay by half when stored at 150 °C, which is ~20 °C below T_g. To measure the NLO *d*-coefficients, the sample was mounted on a computer-controlled rotation stage in a standard Maker fringe arrangement. Since the polymer was slightly absorbing at the second harmonic wavelength, our fits to the data in Figure 4 used an analysis that accounted for absorption of the second harmonic and dispersion in the refractive indices of the polymer.[16] X-cut quartz (d_{11} = 0.5 pm/V) was used as the reference.

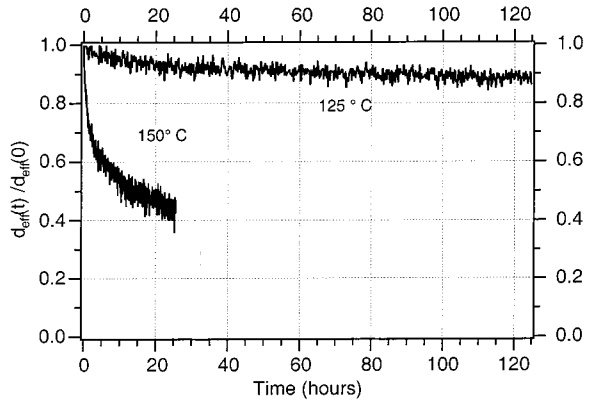


Figure 3. Temporal stability of AC2729 at 125 and 150 °C.

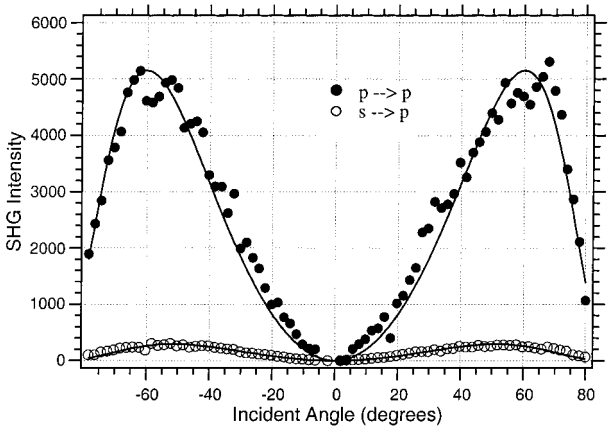


Figure 4. Maker fringe SHG data from a 1.95 mm thick film of AC2729.

The second harmonic data from both p- and s-polarized fundamental light are shown in Figure 4 along with the fits. The d_{31} value was first determined from the s → p data. Then d_{33} was determined from the p → p data, employing the Kleinman symmetry assumption. Using these assumptions, we obtained a $d_{33} = 3.6$ pm/V. This low value is not surprising since the molecular hyperpolarizability, as estimated by MOPAC93, is only 5×10^{-30} esu.[17] Although the thermal and temporal stability of AC2729 is acceptable for device requirements, the relatively low value of d_{eff} needs to be improved.

It is notable that poling at a slightly lower temperature ($T \sim T_g + 3$ °C) results in a considerably smaller SHG signal using the same poling field strength and even a longer poling time (~1 h). For guest−host or side-chain NLO polymer systems, chromophores can be aligned due to side-chain motion as well as small-amplitude motions of torsional oscillations of backbone bonds within a torsional energy well. However, chromophore alignment in a main-chain NLO polymer requires rotational transitions of backbone bonds for appreciable dipole alignment of the chromophores. This type of conformational change requires a longer range of cooperative motion since both of the chromophore ends are chemically connected. Therefore, relatively higher poling temperatures are needed to overcome the torsional energy barrier for the backbone bonds.

Acknowledgment. L.M.H. thanks the National Science Foundation (Grant DMR-9705800) for its support of this work. We also thank Steve Fallis for determining the molecular weight of the polymer.

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