Synthesis of Nonlinear Optical Polycarbonates via the Ring-Opening Polymerization of Macrocyclic Prepolymers

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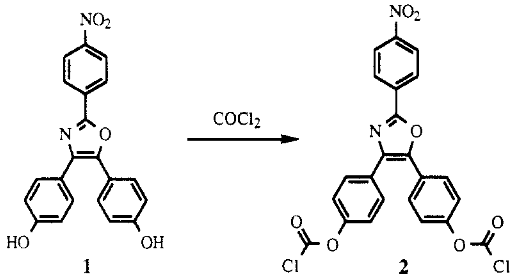
Received April 19, 1994
Revised Manuscript Received June 13, 1994

Polymeric materials with nonlinear optical (NLO) properties have been prepared by different methods including doping polymers with NLO molecules, covalent attachment of NLO chromophores to amorphous and liquid-crystalline polymers, and assembly of NLO chromophores into Langmuir-Blodgett layers.[1] Systems with organic NLO molecules dispersed in a polymer host suffer from limited solubility in the host matrix and loss of NLO chromophore alignment over time.[2] The incorporation of the NLO chromophore into a polymer by covalent attachment as a pendant group or as part of the main chain can give a higher number density of the chromophore. It is imperative that NLO chromophores reside in a noncentrosymmetric environment if the β (first molecular hyperpolarizability) is to lead to an observable $\chi^{(2)}$ (second-order bulk susceptibility). The statistical center of symmetry in polymers can be removed via dipolar alignment by application of an external electric field (poling). Poling is performed by applying a strong electric field and heating the polymer at or preferably below T_g.[3] Lower poling temperatures are preferred in order to minimize complications due to conductivity or thermal stability. Cooling the polymer below the T_g with the field applied leads to a material with noncentric alignment.

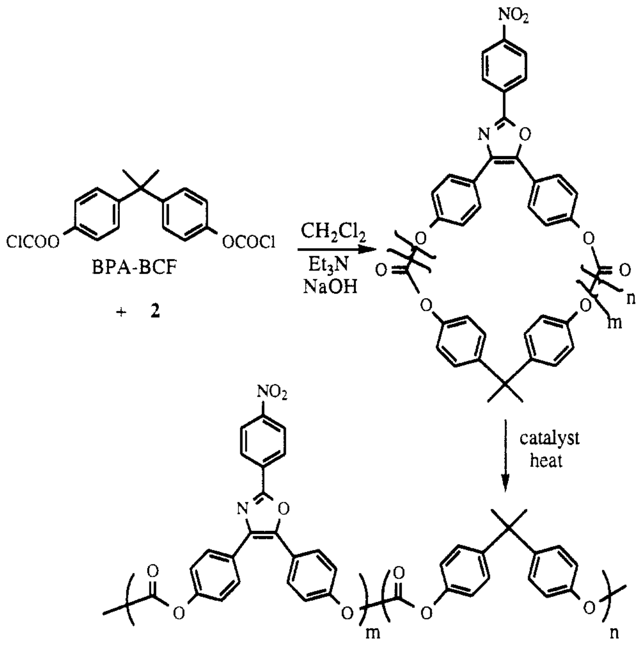
One of the critical problems in the development of second-order NLO polymers is to stabilize the dipolar alignments induced by an electric field.[2] Useful strategies to prepare polymeric NLO materials with good temporal stability include the synthesis of high T_g polymers and *in situ* chemical or photochemical cross-linking.[4] Thus, we have undertaken an investigation of new routes to cross-linkable, high-T_g polymers with covalent incorporation of NLO chromophores.

One goal of our work is to prepare NLO polycarbonates by the ring-opening polymerization of macrocyclic oligomers. Aromatic polycarbonates are glassy, amorphous polymers with good mechanical and optical properties.[5] Brunelle and co-workers[6] have optimized an alternative route to the preparation of Bisphenol A (BPA) polycarbonates. Starting from bis(chloroformates), an interfacial process is used to selectively produce macrocyclic carbonate oligomers in yields up to 90%. Ring-opening polymerization of the macrocycles in the presence of catalyst affords high molecular weight polycarbonate; molecular weights 6-10 times higher than the conventional process have been obtained.[7] Preparation of NLO polycarbonates via macrocyclic prepolymers has the advantage that the low viscosity oligomer mixtures make reactive processing possible. The conversion of macrocycles to polymer occurs with no volatile byproducts or any change in volume. It is this feature of the macrocyclic carbonates that makes them especially promising as prepolymers for the fabrication of polymeric NLO materials.

Scheme 1



Scheme 2



Our long-term goal is to perform the polymerization simultaneously with electric field poling and, if desired, chemical cross-linking to produce high-T_g, NLO polymers with predictable sample dimensions, good dipole alignment, and good thermal stability. The ring-opening polymerization is a solvent-free process that proceeds via a low-viscosity stage which will facilitate electric-field-induced dipolar alignment. Wnek and co-workers observed higher SHG (second-harmonic generation) responses in polyurethanes when the poling was performed at the same time as melt polymerization.[8] In this paper, we report results for the first phase of our program where we have demonstrated the polymerization chemistry and determined that the polymers produced by this synthetic route have a reasonable NLO response.

We have prepared polycarbonates based on a triphenyloxazole monomer (**1**). This monomer fulfills the following requirements: (1) a π-conjugated system with electron-donating and accepting groups leading to a finite value of β,[9] (2) good thermal stability to withstand ring-opening polymerization condition (15-30-min cycle at 250 °C), and (3) structural similarity to BPA.

The conversion of monomer **1** to NLO polycarbonates via macrocyclic intermediates starts from the corresponding bis(chloroformates) (**2**) which are prepared by the reaction of the bisphenol monomer with phosgene (Scheme 1). Attempts to prepare the homopolymer produced intractable materials. Therefore, subsequent efforts were focused on the BPA copolymers (Scheme 2). The bis(chloroformate) of BPA (BPA-BCF) is prepared independently and used in a mixed monomer feed with bis(chloroformate) (**2**). The T_g of the final polymer can be controlled by the ratio of monomers; the incorporation

Table 1. Glass Transition Temperatures for Polycarbonate Copolymers

compsn, mole fraction of 1 (m)[a]	polycarbonate T_g, °C	compsn, mole fraction of 1 (m)[a]	polycarbonate T_g, °C
1.0	[b]	0.15	166
0.31	214	0.0[c]	148

of 1 increases the T_g. Table 1 displays thermal data for several polycarbonate compositions. Changes in the monomer composition of the macrocycles can be used to alter the melting point of cyclics which sets a lower limit for a practical polymerization temperature. The molecular weights of the polycarbonate copolymers obtained via ring-opening polymerization vary with the level of catalyst used. To date, we have obtained M_w values up to 69 000 (relative to polystyrene standards). The decomposition temperature of the copolymer containing 15% 1 was examined using thermal gravimetric analysis; T_{dec} (2% wt loss) = 360 °C. The UV–vis spectrum of the 15% copolymer has an absorption maximum at 370 nm with a cutoff at 560 nm. The amount of 1 incorporated into the copolymer is always less than the amount of 1 in the monomer feed. We speculate that this may reflect differences in the pK_a values of the phenol hydrogens which are intermediates in the macrocyclization.[6] Current work is exploring the relationship between monomer feed and copolymer composition and the upper limit for incorporation of 1.

Electro-optic measurements have been performed on the copolymer containing 15% 1 using a modulated ellipsometric technique.[10,11] The electro-optic coefficient was r_{33} = 0.6 pm/V as measured at 820 nm. Moylan and co-workers[12] reported r_{33} = 2.5 pm/V at 1300 nm for a lophine derivative (20% in a poly(ether imide)) which had been poled at 300 V/μm. After scaling for the different loading and poling conditions, our results are consistent; however, direct comparison is not possible because the EO coefficients were measured at different wavelengths. Gulotty and Bales[13] prepared NLO polycarbonates in the conventional manner (phosgenation of bisphenol monomers) using BPA derivatives substituted with nitro in the *ortho* position relative to the phenolic oxygens. However, they measured nonlinear optical coefficients (d_{33}) which makes comparison to our results difficult.

We have demonstrated that ring-opening polymerization of macrocyclic carbonate oligomers containing triphenyloxazole chromophores can be used to prepare NLO polymers. EO measurements of the triphenyloxazole copolymer gave results comparable to similar systems in the literature. The significant feature of this work is that it represents the first phase in a feasibility study of a new reactive processing approach to NLO polymers. Currently, we are studying the advantages of poling simultaneously with ring-opening polymerization. In addition, we are making systems with a higher number density of NLO chromophores and using different NLO chromophores which have higher values of β. Temporal stability studies are also underway.

Experimental Section. ^{1}H NMR spectra were recorded with a Varian Gemini 200 spectrometer. IR spectra were recorded with a Nicolet System 730 spectrometer. Gel permeation chromatography was performed with a Waters system using two PL gel 5-μm MIXED-D columns with THF eluent at a flow rate of 1 mL/min. Thermal gravimetric analysis was performed using a DuPont Model 951, and thermal analysis was performed using a DuPont Model 910 differential scanning calorimeter. Unless noted otherwise, all other reagents were used as received. The synthesis of 4,5-bis(p-hydroxyphenyl)-2-(p-nitrophenyl)oxazole (1) and its conversion to the bis(chloroformate) (2) have been described previously.[9,14]

Mixed Macrocycles Synthesis. A Morton flask was charged with 670 mL of CH_2Cl_2, 100 mL of water, 1.98 mg of NaOH, and 7.8 mL of triethylamine. To this refluxing mixture was added at a rate of 6.1 mL/min a solution of 2 (10.0 g, 21 mmol) and Bisphenol A bis(chloroformate) (21.43 g, 60.5 mmol) in 75 mL of CH_2Cl_2. Simultaneously, 3.19 g of NaOH and 2.1 mL of triethylamine were added over the course of the reaction. The reaction mixture was washed with 1 N HCl, 0.1 N HCl, and twice with water. Solvent was removed *in vacuo*, and the cyclics were extracted with 120 mL of acetone. The byproduct polycarbonate was removed by filtration and the solvent removed *in vacuo* to afford 9.5 g of macrocycles (43% yield); M_n = 890 (based on polystyrene standards). ^{1}H NMR ($CDCl_3$, TMS, 200 MHz): δ 8.45, 7.9, 7.5 (m, 12H, oxazole aromatic), 7.2 (m, 8H, BPA aromatic), 1.7 (s, 6H, isopropylidine). Based on NMR, the macrocycles contained 15% of monomer 1. Yields of macrocycles for the other compositions given in Table 1 ranged from 25 to 60%.

Ring-Opening Polymerization. The mixed macrocycles containing 15 mol % 1 (0.256 g) and 180 μg of Tyzor AA (0.01 mol %, titanium diisopropoxide bis(2,4-pentanedionate)) were dissolved in 5 mL of CH_2Cl_2. The solvent was removed, and the solids were heated at 275 °C for 60 min. GPC analysis was consistent with conversion to polymer: M_w = 69 000 (based on polystyrene standards).

Film Preparation. The copolymer obtained from ring-opening polymerization was dissolved in toluene (10%, w/w) and was spin-cast onto an indium–tin oxide coated substrate to give a 1-μm film. Following solvent bakeout and vapor deposition of a gold overlayer, electrode poling was performed at 170 °C using a poling field of 100 V/μm.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. The authors acknowledge helpful discussions with R. J. Twieg (IBM) and D. H. Reneker (The University of Akron).

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