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Synthesis and characterization of polymers for nonlinear optical applications

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ABSTRACT

A difunctional NLO Azo-Dye chromophore has been synthesized and polymerization has been performed with a comonomer bearing a side-chain epoxy group. Deposition of the polymer on glass substrates was performed by spin-coating, resulting in uniform films up to 2 µm thickness. The orientation of the chromophore was performed under a "pin-to-plane" positive corona discharge followed by a heat-treatment in order to obtain reticulation of the films. Molecular orientation has been investigated using UV-Vis. and Raman spectroscopy. Poling of the films results in a decay of absorbency as well as in a blue shift of the spectrum. At the same time, the 1600 cm^{-1} band disappears from the Raman spectra, indicating orientation of the chromophores. Cross-linking has been studied by FTIR and all-optical poling and showed an improved stability of the electro-optic thin films.

Keywords: polymer, chromophore, poling, orientation, cross-linking, electro-optic, thin film, integrated optics

1. INTRODUCTION

The development of thin film organic materials that are suitable for the fabrication of high speed integrated optical devices is presently a major focus of research in nonlinear optics.[1-3] Compared to inorganic materials, polymers have been demonstrated to display large nonlinear optical (NLO) effects. Significant progress in device design with the implementation of polymers has been reported recently,[4,5] and polymer materials have been processed to lay single mode optical wave guides and electro-optic modulators on silica or glass substrates. The orientational distribution of NLO chromophores in the non-poled polymer films is however isotropic. In order to induce the NLO effect, non-centrosymmetry is required. This property originates from the alignment of the chromophores in the polymer matrix that exhibit a strong second order hyperpolarisability. In the present work, orientation of the chromophores has been obtained by the corona poling method. The investigated cross-linkable polymer system as well as the poling and cross-linking procedure are described, the molecular orientation measurements are presented, and the temporal stability of the NLO properties is examined.

2. PREPARATION OF THE POLYMER THIN FILMS

The chemical structure of the electro-optic monomer (PIII) is shown in the Figure 1. Nitro- and tertiary amines were chosen as efficient acceptor and donor groups, respectively, and have been placed at the end of the Π-extended molecule in order to achieve a large electro-optic coefficient. Moreover, a carboxylic group (cross-linking group) is placed on one of the aromatic groups in order to perform anchoring after the poling process. Because of its location and its electronic

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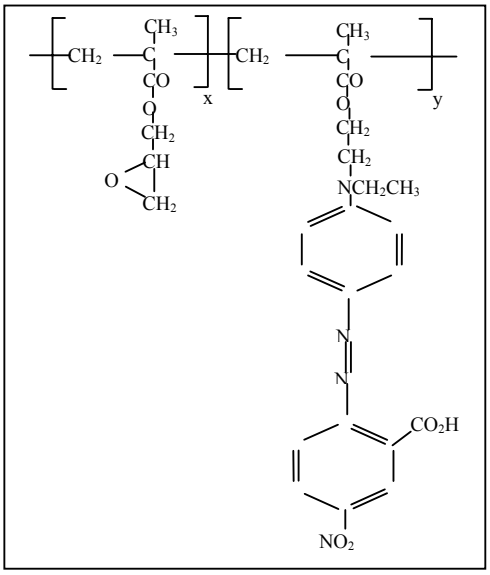

Figure 1: Molecular structure of the cross-linkable monomer PIII

configuration, the anchoring group retains a high level of hyperpolarizability. This monomer can undergo free-radical copolymerization with the methacrylic monomer, bearing a second cross-linking group of epoxy type.

In order to prepare the thin films, the above described polymer powder has been dissolved in 1,2-dichlorethane. The polymer solution has been filtered with a 0.45 μm syringe filter and was deposited on glass substrates by spin-coating, resulting in films of up to 2 μm thickness. The corona poling method uses a "pin-to-plane" geometry and a positive corona discharge. The NLO polymer is heated above its glass transition temperature (T_g = 65°C), an electric field is applied in order to orient the chromophore molecules, and the system is cooled down to room temperature under the electric field. In order to obtain an optimum chromophore orientation in the electric field, the two reacting groups (epoxy and carboxylic acid) must not react at the poling temperature. As a recent study on the cross-linking behavior between the NLO poled molecules and the epoxy group in the copolymer has shown,[6] the reactions involving epoxy and carboxylic groups are achieved at 150°C after 30 minutes. Therefore, in the present experiments, poling of the chromophores has been performed at 70°C (during 30 minutes). The distance between the sample surface and the corona electrode tip has been 20 mm and the poling voltage was 5.8 kV, resulting in a poling current of approximately 1.5 μA. In order to obtain stable NLO properties, the cross-linking process has been performed at 150°C also for 30 minutes.

3. OPTICAL PROPERTIES OF THE POLYMER THIN FILMS

The absorbency spectrum of a 1.5 μm thick polymer from the ultraviolet to visible wavelength range is shown in Figure 2, comparing the absorbency of a film as deposited (trace a) and after the poling procedure (trace b). The observed decrease due to the corona poling and cross-linking process gives access to the order parameter $\Phi = 1 - A_1/A_0$, where A_0 and A_1 are the absorbency of the polymer before and after poling, respectively. An isotropic film has an order parameter $\Phi = 0$, and $\Phi = 1$ for a fully oriented film. In the case of the copolymers used in our experiments and with the poling procedure described above, an order parameter of $\Phi = 0.37$ has been obtained. From Figure 2, a slight blue-shift of the absorption maximum for the poled polymer can be seen. This hypsochromic effect is probably due to the anchorage of the chromophore into the copolymer backbone.

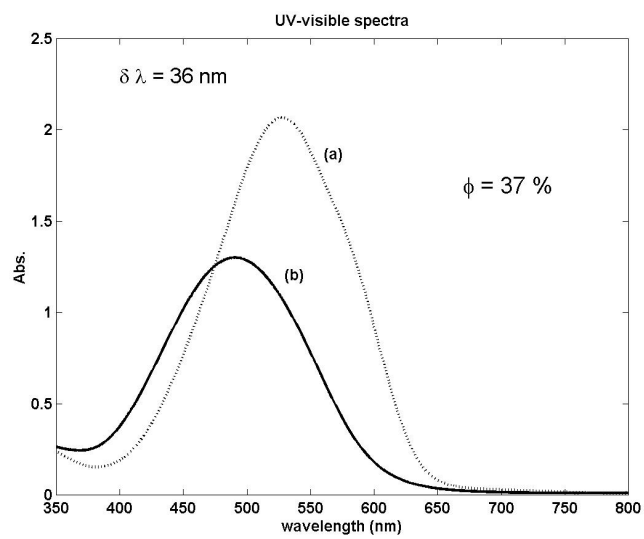

Figure 2: UV-Vis. absorbency spectra of the cross-linkable polymer thin film (a) before poling and (b) after poling

Raman spectroscopy is a particularly useful method to measure a local molecular orientation. Recent studies have shown that upon para-substitution the 'breathing' mode intensity (992 cm^{-1}) of the benzene molecule is distributed on several modes.[7,8] In particular, the 8a mode (C-C stretching) would give a very strong and polarized band in the 1600 cm^{-1} wave number range. This vibration mode is excited when the laser beam polarization is in the plane of the azo-

benzene group and should hence disappear in a poled film, where the chromophores are orthogonal to the beam polarization.

Raman spectra of our polymer thin film ranging from 1300 cm^{-1} to 1650 cm^{-1} before and after poling are presented in Figure 3, curves (a) and (b), respectively. The disappearance of the 1600 cm^{-1} band confirms orientation of the polymer. As the laser beam had a diameter of approximately 10 μm, scanning of the film also provides space-resolved information on the efficiency of the corona poling. In the case of our experimental conditions, no significant difference of the spectrum for the overall film surface of 2.5×2.5 cm^2 could be seen.

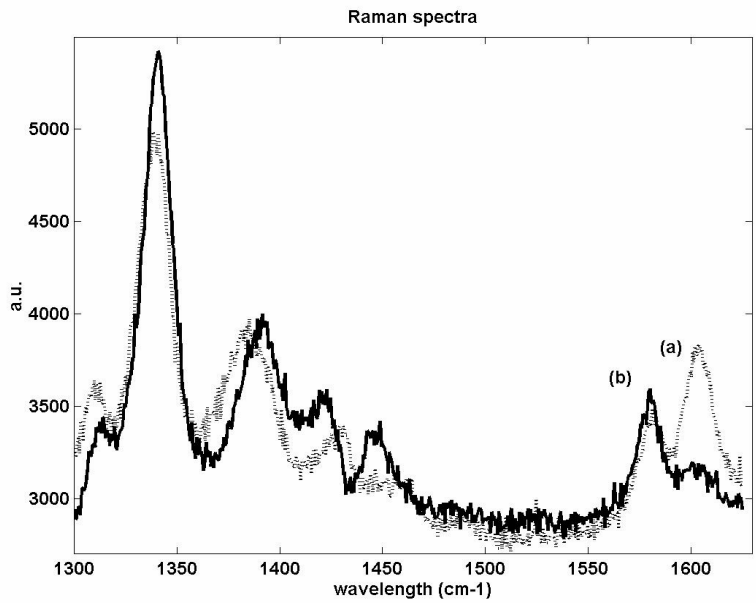

Figure 3: Raman spectra of the cross-linkable polymer thin film (a) before poling and (b) after poling

The cross-linking reaction of the polymer can be probed by studying the intensity of the epoxy-ring vibrational mode at 903 cm^{-1} via FTIR (Fourier Transform Infra Red). FTIR spectra of our polymer thin film before and after reticulation are shown in Figure 4, curves (a) and (b), respectively. Comparison of the intensities at 903 cm^{-1} show that the cross-linking reaction, involving epoxy and carboxylic groups, effectively has been achieved during the heating process.

Polymer orientation by the corona discharge method has been compared with the results from all-optical poling, which allows purely optical orientation of the molecules.[9-11] The experiment consists of two steps, the seeding period (writing) and the readout period. In the seeding phase, two beams, the fundamental (ω) and its second harmonic (SH, 2 ω) illuminate the sample and print the second order $\chi^{(2)}$ susceptibility grating in the medium with a periodicity satisfying the condition of phase matching for SH generation. During the readout phase, only the fundamental beam irradiates the sample and the development in time of the second harmonic generation is observed at the output of the sample. The SHG signal obtained from our corona poled polymer film corresponds to this observed by all-optical poling for 50 minutes of seeding. In order to compare the orientation stability, in Figure 5 the SHG signals of the guest-host polymer DR1-MMA 35/65 and of our cross-likable polymer film are shown. The relaxation behavior can be estimated by fitting the decay curves to a function $f(t) = A \exp(-t/\tau)$. The characteristic decay time τ is about 50 minutes for the

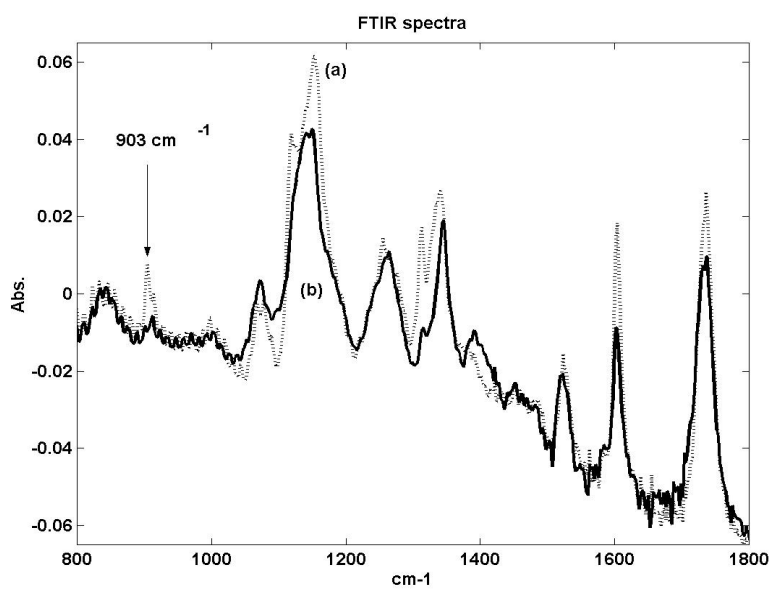

Figure 4: FTIR spectra of the cross-linkable polymer thin film (a) before poling and (b) after poling

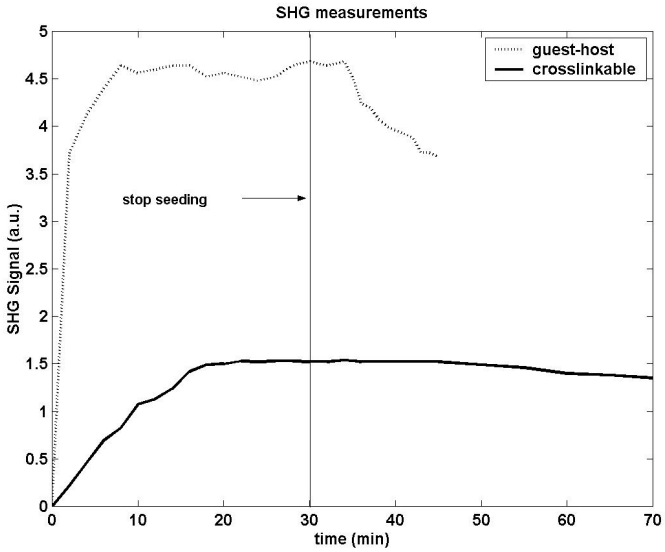

Figure 5: SHG signal relaxation after all-optical poling for the guest-host DR1-MMA 35/65 and in the case of the cross-linkable polymer

guest-host polymer and increases by an factor of approximately six in the case of the cross-linkable polymer (τ = 290 min).

4. CONCLUSIONS

A new difunctional NLO azo-dye chromophore has been synthesized and polymerized with a comonomer, bearing a side-chain epoxy group. Thin film deposition has been obtained by spin-coating, the orientation of chromophores has been performed by corona poling. The optical properties of the polymer films have been characterized by three complementary techniques.

The electronic absorption spectra indicate an order parameter $\Phi = 0.37$ as a result on macroscopic information. Orientation of the benzene cycles perpendicularly to the substrate's surface has been confirmed by Raman spectroscopy. The FTIR measurements indicate that the epoxy group reacts with the carboxylic acid group as expected. The cross-linking of chromophores in the polymer backbone should improve significantly the stability of the electro-optic properties of the material. Preliminary SHG measurements confirm an improvement of the orientation decay time in such a structure as compared to a classical guest-host.[12,13] The results obtained up to now are of qualitative character, and more systematic investigation is needed in order to better conclude on the optical properties of the polymer films used in the experiments. Although research is still in its infancy, the new polymer seems to own a stability which should allow to study the linear Pockels effect for a future application to high bit rate optical modulation in integrated optics.

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