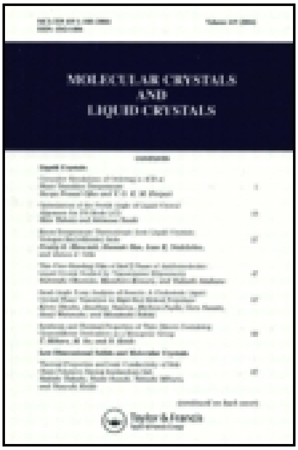

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Spontaneous Ordering of Nonlinear Optical Groups in a Polymer Thin Film Through Cross-Linking

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Polymer thin films with nonlinear optical groups were prepared by spin-coating poly-DR1-(anthranilic acid) on glass substrates. These films were then heated to different temperatures and cooled down to obtain samples with various degrees of cross-linking. The visible absorption decreased for samples annealed at high temperatures. Strong second-harmonic signal generated from the polymer film indicated the nonlinear side chains of the polymer were aligned macroscopically through the heat treatment without external field.

INTRODUCTION

Polymers containing groups with large optical nonlinearity have been actively investigated as a new material for optoelectronic device [1]. To utilize its second-order optical nonlinearity, the polar chromophores of the polymer should be oriented macroscopically. Common method was to apply an electric field at temperatures where the polymer chains can move or reorient easily [2], so the techniques such as electronic, corona [3], electron-beam, and photothermal [4] polings. In this paper, we report the observation of the spontaneous ordering of the nonlinear optical groups in the polymer thin film without external field.

EXPERIMENTS AND RESULTS

The monomer solution was prepared by dissolving 30g (0.22 mol) of anthranilic acid in 400 mL of 0.3 M HCl solution. The oxidant solution was prepared by dissolving 23g (0.1 mol) of ammonium persulfate $((NH_4)_2S_2O_8)$ in 600 mL of 0.3 M HCl solution. The oxidant solution was added to the monomer solution dropwisely for 1.5 hours and stirred afterwards for 24 hours. After separation of the precipitate by filtration followed by rinse with water and methanol, the final product PAA [poly(anthranilic acid)] was obtained. A 0.5g (3.6 mmol) portion of PAA and 1.15g (3.6 mmol) of Disperse Red 1 (DR1) were dissolved in 10 mL of dry dimethylformamide (DMF). To this solution, 0.75g (3.6 mmol) of dycyclohexylcarbodiimide (DCC) was added and stirred for 24 hours. The precipitate obtained from the above solution by adding the methanol was recrystallized with ethyl acetate to yield PDR1AA (poly-DR1-(anthranilic acid)).

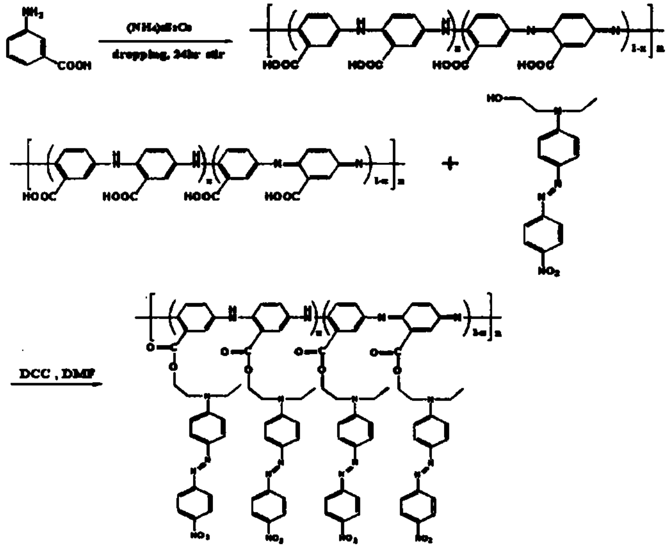
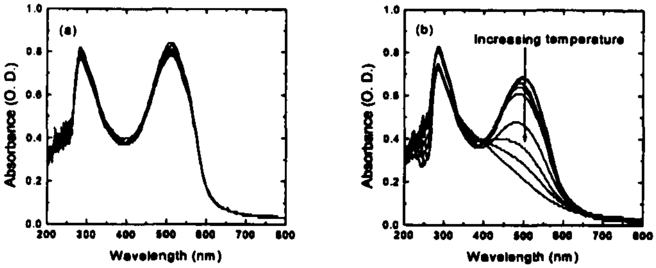


FIGURE 1 The synthesis of PDR1AA (poly-DR1-(anthranilic acid)).



FUGURE 2 UV-visible absorption spectra, (a) before, and (b) after annealing.

The 5 wt%- solution of PDR1AA in chloroform was spin-coated on a glass substrate and annealed at various temperatures ranging from 50°C to 250°C with a 25°C-interval. The UV-visible absorption spectra before and after annealing are shown in Fig. 2. About the two peaks in the spectra, the peak around 290 nm is due to the backbone of the polymer, and the other in the visible range is mainly due to DR-1. The spectra for the various conditions of annealing show the decrease of the chromophore peak height with increasing temperature, while the peak due to the backbone of the polymer remains essentially the same, suggesting the chromophores tend to align close to the normal to the substrate after annealing [3].

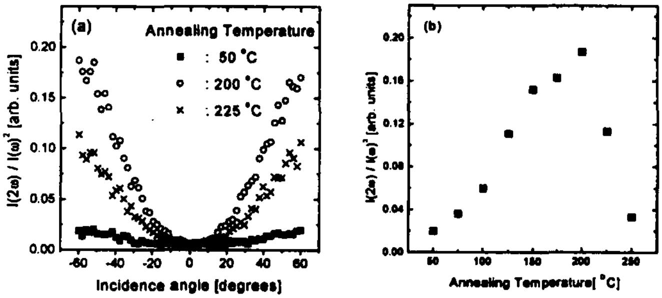


FIGURE 3 (a) SH signal from the polymer films. (b) SH signal (at 60° incidence angle) vs. annealing temperature.

These macroscopic ordering of the DR1 group suggested was probed further with second-harmonic (SH) generation. The 1.06 μm output from Q-switched Nd:YAG laser illuminated the sample (p-polarized) and the transmitted SH was measured as a function of the incidence angle. Figure 3(a) shows the SH signals from the samples with different annealing temperatures. The increase in the signal with incidence angle indicates macroscopic ordering of the chromophores in the film normal to the substrate through annealing. In Fig. 3(b) the SH signals (at 60° incidence angle) are compared for the same set of films as in Fig. 2. The signal increased and reached its maximum around 200°C, afterwards it decreased rapidly, presumably due to the disintegration of the chromophores in the polymer.

Because the bulk of the polymer does not have any preferred direction, the observed spontaneous ordering should only be an interfacial phenomenon. To confirm our idea, we prepared the films with thicknesses varying from 60 nm to 360 nm and annealed them all at the same temperatures. If the macroscopic ordering happened through the volume of these samples, the SH signal should increase as the square of the film thickness. The strength of the observed signals for the samples were all similar, suggesting the chromophore ordering occurred either at the air-polymer or at the polymer-glass interfaces.

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References

[1] See, for example, *J. Opt. Soc.Am. B* **15** (1998).
[2] S. Bauer, *J. Appl. Phys.* **80**, 5531 (1996).
[3] M. A. Mortazavi et al., *J. Opt.Soc.Am. B* **6**, 733 (1989).
[4] F. Charra, F. Kajzar, J. M. Nunzi, P. Raimond, and E. Idiart, *Opt. Lett.* **18**, 941 (1993).