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Synthesis and Photorefractive Property of a Polymer Containing Azobenzene Group in the Side Chain

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The polyurethane (DR-PU) containing azobenzene group in the side chain was synthesized by the polycondensation reaction of Disperse Red 19 (DR19) and toluene-2,6-diisocyanate. A device consisting of the (DR-PU, PVK and C₆₀) mixture between ITO glasses was fabricated. E4, a liquid crystal, was sandwiched between the two polymer mixture films with 20- μ m-thick beads as a spacer. In order to distinguish the photorefractive effect, two-beam coupling (2BC) measurement was performed. The asymmetric change of intensities of two writing beams was observed by the 2BC measurement.

Keywords Polyurethane; Azobenzene; Photorefractive effect; Two-beam coupling; Polycondensation reaction

INTRODUCTION

Photorefractive materials have many potential applications, including high-density holographic data storage, optical image processing, pattern recognition, and phase conjugated mirror, etc. [1-2] The photorefractive gratings appear in materials that exhibit both an electric-field-

dependent refractive index change and an optical induced charge distribution. The refractive index modulation is out of phase with the optical interference pattern, and this phase shift can induce an energy exchange between two beams, which leads to a variety of useful applications.

Since Sutter *et al.* did the first demonstration of the photorefractive effect in an organic crystal in 1990^[3], photorefractive studies have been extended into organic materials. In 1991, the photorefractive effect was first demonstrated in a polymer system by Ducharme *et al.*^[4] and the photorefractive polymer composites have drawn much attention due to their advantages including low cost, ease of fabrication, and the ability to fabricate complex structure.^[5-6] Some of the most promising results have been obtained for the compositional guest-host approach of doping photorefractive polymers with nonlinear optical chromophores.

The objective of this research is to prepare a DR-PU containing azobenzene unit in the side chain by the polycondensation reaction and to investigate photorefractive property of the DR-PU by two beam coupling (2BC) method.

EXPERIMENTAL

A solution of 6.6g of DR 19 (0.02 mol) and 3.48g of toluene-2,4-diisocyanate (0.02 mol) in 40 ml of DMF was heated to 80°C with vigorous stirring under nitrogen purge for 24h. The reaction mixture was cooled to room temperature, and then poured into methanol. The resulting precipitates were filtered out, washed with methanol and acetone thoroughly, and dried in a vacuum oven for 24h. The DR-PU was obtained as a dark red powder. The reaction path of the formation of DR-PU is illustrated in FIGURE 1. The structure of the DR-PU was identified using FT-IR spectroscopy and ¹H-NMR spectroscopy. The thermal property of the DR-PU was measured by means of differential scanning calorimetry (DSC). The photorefractive property of the DR-PU was measured by 2BC method.

In order to fabricate an orientational device, DR-PU, Poly(*N*-vinyl carbazole) (PVK) and C₆₀ were dissolved in CHCl₃. The solution was filtered by 0.45 μm syringe filter and then spun on ITO glass at 2500 rpm and then a device consisting of liquid crystals (LCs) E4

sandwiched with polymer films was fabricated. FIGURE 2 shows the structure of the device.

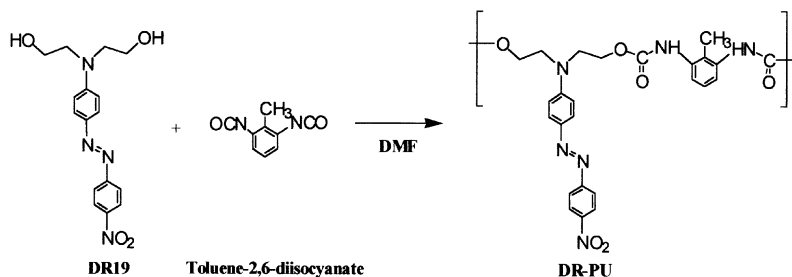


FIGURE 1. The synthetic route of DR-PU.

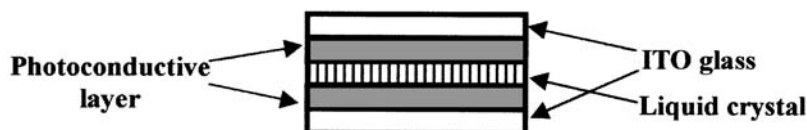


FIGURE 2. The structure of the device.

RESULTS AND DISCUSSION

We have synthesized the polyurethane (DR-PU) containing azobenzene group in the side chain by the polycondensation reaction of Disperse Red 19 (DR19) and toluene-2,6-diisocyanate. The structure of DR-PU was characterized by FT-IR spectra and ^1H -NMR spectra. The detailed structural data can be summarized as follows.

Spectra data for DR-PU: FT-IR (KBr pellet, cm^{-1}), 2917 (CH aromatic), 2893 (CH aliphatic), 1710 ($-\text{COO}-$), 1599 ($-\text{NH}-$); ^1H -NMR(DMSO- d_6 , ppm), δ 8.59 (2H, $-\text{NH}-$), 8.36-8.33, 7.93-7.90 (4H, NO_2 -aromatic- $\text{N}=\text{N}-$), 7.83-7.81, 7.32-7.31 (4H, $-\text{N}=\text{N}$ -aromatic- $\text{N}-$), 7.06-6.95 (8H, -aromatic- CH_2 -aromatic-), 4.27 (4H, $(-\text{NCH}_2\text{CH}_2\text{O}-)$), 3.85-3.73 (4H, $-\text{NCH}_2\text{CH}_2\text{O}-$), 3.60-3.64 (2H, -aromatic- CH_2 -aromatic-). DR-PU had the average molecular weight (M_w) of 10,200. From DSC, the glass transition temperature (T_g) of DR-PU was found to be 136.4°C . In the 2BC experiment the change in the transmitted intensity of either

of the write beams is recorded as the other write beam is switched on and a grating is formed. A He-Ne laser beam at 633 nm with $E_0=3$ V/ μm and β (beam ratio)=1 was used as the write beam. The experimental results are shown in FIGURE 3. The asymmetric change of intensities of two writing beams was observed by the 2BC measurement. 2BC gain coefficient was calculated as $\Gamma = 40.2$ cm⁻¹.

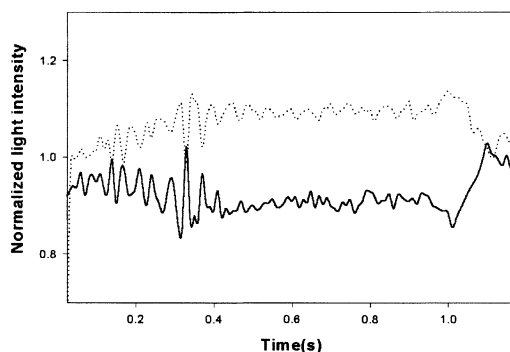


FIGURE 3. Two beam coupling (2BC) experiment for the PVK:DR-PU:C₆₀ device at 633 nm with $E_0=3$ V/ μm and $\beta=1$.

ACKNOWLEDGMENTS

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