

Structural Design and Property Characterization of Bi-functional Photorefractive Polymer

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Abstracts: A novel bi-functional photorefractive acrylate polymer with pendant carbazolyl groups and azo derivatives as side chains was synthesized. Photorefractive experiments showed a high two-beam coupling gain coefficient of 93 cm^{-1} , diffraction efficiency of 12% and electro-optic coefficient of 26 pm/V were obtained.

Keywords: Acrylate polymer, bi-functional polymer, photorefractive material.

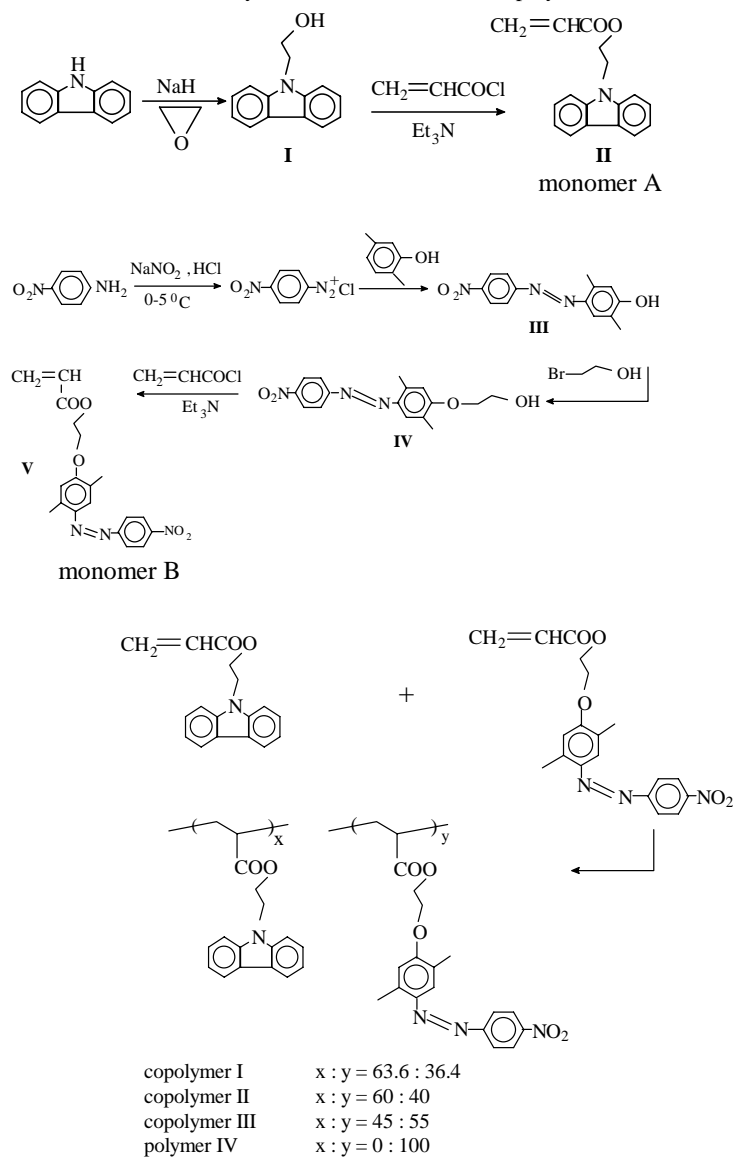
Introduction

The driving force to pursue research on photorefractive polymers comes from both fundamental interests and practical expectations. It has been known that photorefractive materials are multifunctional materials which combine the electro-optic (EO) effect and photoconductivity to manifest a new property: photorefractivity¹. Since 1990, photorefractive studies have been extended into organic materials: both doped organic crystals and polymeric materials²⁻⁵. Organic photorefractive materials exhibit reasonably large electro-optic response and a lower dielectric constant than inorganic materials; they are versatile in structural design and have very good processibility for device fabrications. In the past six years, Yu *et al* have developed different approaches to synthesize multi-functional photorefractive polymers^{4,5} including novel photorefractive polymers with a nonlinear optical (NLO) chromophore, a charge generator and a transporting compound, all covalently linked to a single polymer backbone.

More recently, we have designed new polymers with the structure shown in **Scheme 1**. We expected this kind of polymer to be photorefractive (PR) and to exhibit improved performances. Designing this kind of PR system is based on the facts that alkoxy azo dyes / poly(N-vinyl carbazole) / 2,4,7-trinitrofluorenone (TNF) composite systems are well-known photorefractive systems and exhibit high electro-optic response and large asymmetric optical energy exchange, as verified by Peyghambarian's group⁶ and our research group⁷⁻⁹. In this letter, we report the results on the synthesis and characterization of this new photorefractive

polymer system. A azo derivative as the EO chromophore and carbazolyl as photoconductive moieties are covalently linked on a acrylate backbone.

Scheme 1. Synthesis of monomers and copolymers.



Experimental

As shown in **Scheme1**, the key steps are the synthesis of compound **IV** and N-hydroxyethyl carbazole (compound **I**). Compound **IV** was synthesized from azo coupling between p-nitroaniline and 2,5-dimethylphenol followed by the etherization of azophenol with bromoethanol. N-hydroxyethyl carbazole was synthesized by the approach developed in our laboratory by reaction of sodium carbazole and ethylene oxide. All of these monomers were carefully purified by column chromatography with dichloromethane as eluent.

The polymerizations were carried out in purified toluene in sealed vacuum tube. The polymers were precipitated out in methanol and were purified by redissolving in chloroform and re-precipitation in methanol.

Results and Discussion

The structural information of these polymers are provided by FTIR spectra, elemental analysis and UV/VIS spectra. The compositions ([NLO]/[T]) were deduced from the elemental analysis, where NLO and T stand for the NLO chromophore and the charge transporting compound, respectively. The average molecular weight (M_w), the decomposition temperature (T_d) and the glass transition temperature (T_g) of the four polymers were presented in **Table 1**.

Table1. The composition and physical properties of polymers

polymer	[NLO]/[T]mole ratio [§]	$\overline{M_w} \times 10^{-3}$ [#]	T_d (°C)*	T_g (°C)*
copolymer I	36.4 / 63.6	6.53	360	227
copolymer II	40 / 60	4.71	345	231
copolymer III	55 / 45	3.30	357	250
polymer IV	100 / 0	2.87	327	252

[§] The compositions of polymers are calculated from Elemental analysis.

[#] The average molecular weights are obtained from GPC.

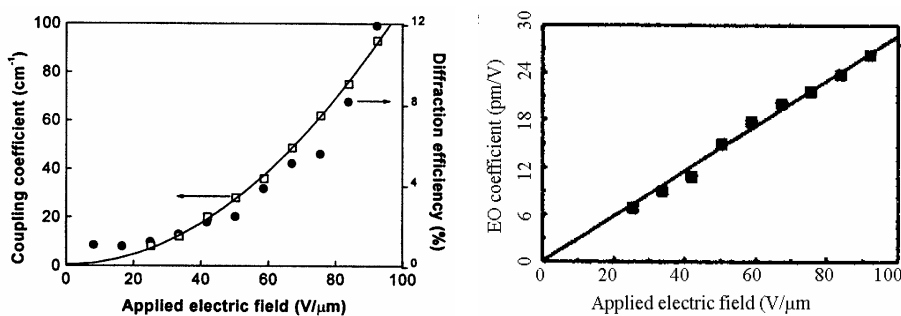
* The T_g and T_d are measured by using DSC.

In order to make the poling of thicker samples (100 μm) possible and obtain the contribution of large birefringence, we modified the polymer to have lower glass transition temperature T_g by changing the backbone from methacrylate to acrylate and by adding a plasticizer (9-ethyl carbazole). The photorefractive composite containing 65%wt copolymer **III**, 34%wt ECZ and 1%wt TNF is sandwiched between two slides of ITO glass to fill a window cut in a Teflon film as a spacer. In such samples, poling at room temperature can be achieved with lower fields. To detect the photorefractive effect in our low T_g thick samples, we performed two-beam coupling (2BC) experiments, four-wave mixing (FWM) experiments, in addition to electro-optic measurements. The description of all physical experiments were presented elsewhere⁹. **Figure 1** shows the measured 2BC

coefficient, diffraction efficiency and effective EO coefficient as function of the applied electric field. The highest diffraction efficiency, the 2BC gain coefficient, and the effective EO coefficient measured in our sample were $\eta = 12\%$, $\Gamma = 93 \text{ cm}^{-1}$, and $\gamma_{\text{eff}} = 26 \text{ pm/V}$, respectively, at an applied field of $92.4 \text{ V}/\mu\text{m}$.

In summary, we have demonstrated a new idea to synthesize novel photorefractive polymer systems by utilizing the principles for the design of NLO chromophore. Larger asymmetric optical energy exchange was observed, indicating the photorefractive nature of the polymer.

Figure 1. Applied electric field dependence of two-beam coupling coefficient and diffraction efficiency (insert: The effective EO coefficient as a function of applied electric field). The solid lines are theoretical fits.



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