

Carbazole-based azo group-containing single component polymer exhibiting photorefractive performance

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Photorefractive (PR) polymers have been investigated widely mostly with host–guest polymer composites [1, 2] and fully functionalized polymers [3, 4]. Host–guest polymer composites exhibit poor stability due to phase separation, while fully functionalized polymers are difficult to be synthesized in most cases. Therefore, much effort has been paid in constructing bi-functional polymers with both photoconductivity and electro-optic (EO) effect for photorefractive purpose in recent years. Such bi-functional photorefractive polymers may have good stability against phase separation and be much easier to synthesize; the minor composition of photo-sensitizer may be incorporated in a composite manner.

In constructing the bi-functional photorefractive polymers, carbazole-based polymers have attracted considerable attention, which is because of the fact that polyvinylcarbazole (PVK) based host–guest polymers have been realized to exhibit high EO response and good photorefractive performance. But the high glass transition temperature (T_g) of PVK made it difficult to pole at room temperature to achieve orientational birefringence. Lowering the T_g by adding plasticizer normally resulted in the deduction of photorefractive performance due to the relative lowering of chromophore concentration. On the other hand, the direct polymerization of a functionalized carbazole monomer normally gives a polymer with low molecular weight owing to both the bulkiness of the monomer and the side effect of the functional group, which is not beneficial to the film forming property of the polymer.

In our effort to synthesize carbazole-based azo group-containing bi-functional photorefractive polymer with low T_g through a post-azo-coupling reaction, we surprisingly found that the single component polymer exhibits good PR performance at room temperature without adding any sensitizer and plasticizer. The polymer synthesis is shown in Scheme 1; a precursor polymer bearing carbazole group with a long alkylene chain was prepared through conventional free radical polymerization; then the precursor polymer was allowed to react with diazonium salt in nitrobenzene with the help

of a phase-transfer-catalyst NaDBS yielding the functional polymer bearing both azobenzene and carbazole groups.

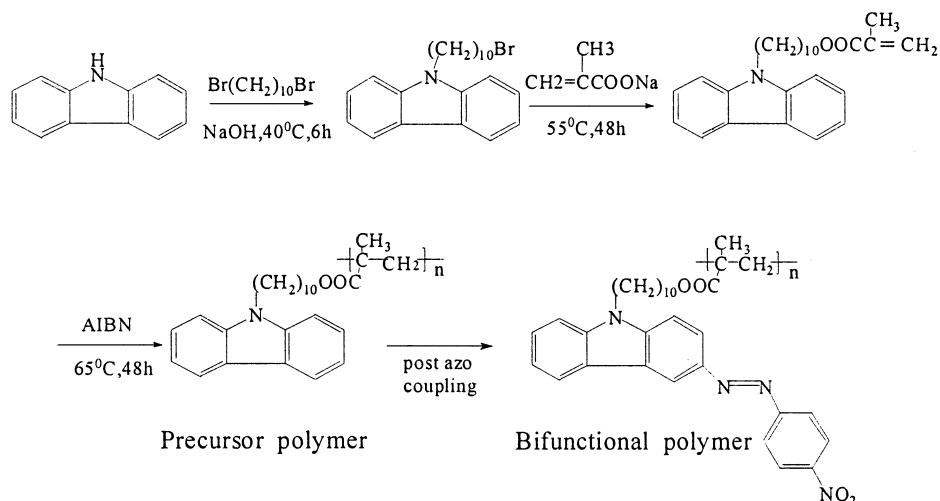
The chemical structure of the resulting polymer was characterized by $^1\text{H-NMR}$ spectrometry (Bruker, DPX-400, 400 MHz) and FTIR spectrometry (Nicolet, 460). $^1\text{H-NMR}$ (CDCl_3 , δ in ppm): 0.2–1.8 (α -methyl and CH_2 in main chain), 3.7–4.9 ($\text{NCH}_2\text{CH}_2\text{O}$), 6.8–9.0 (aromatic protons). The chromophore content (azobenzene group) was calculated as 32% (mol%) from $^1\text{H-NMR}$ spectrum. IR (KBr): 1596 cm^{-1} ($\text{N}=\text{N}$), 1522 and 1341 cm^{-1} ($-\text{NO}_2$), 1726 cm^{-1} (carbonyl group), 2853 and 2926 cm^{-1} ($-(\text{CH}_2)_{10}-$).

Molecular weight of the functional polymer in THF solution was determined using GPC analysis (Waters, 515 pump, polystyrene standards). The weight average molecular weight was measured as 2.2×10^4 , which is much higher compared to similar polymers by conventional direct polymerization from the corresponding functionalized monomer [5–7]. In the direct polymerization, the nitrobenzene group in the carbazole monomer may act as an inhibitor for free radical polymerization, and the bulkiness of the monomers may also hinder the polymerization to form a polymer with high molecular weight.

The successful attachment of the azo group to the polymer was also evidenced from UV–vis spectra as shown in Fig. 1. The absorption maximum (λ_{max}) in DMF solution was determined using an UV/vis spectrometry (Shimadzu, 3010). The concentration of both samples is 0.1 mmol/m^3 . After the post-azo-coupling reaction, a new broad absorbance with a λ_{max} at 437 nm was observed, which is virtually the same as that of the corresponding monomer bearing both azo and carbazole groups.

The glass transition temperature (T_g) was determined by differential scanning calorimetry (DSC, TA 2920) at a heating rate of $10\text{ }^\circ\text{C/min}$. In designing the polymer, a long alkylene chain was introduced between the polymer backbone and the carbazole group to facilitate the orientation of the electrooptic moiety under the conditions of PR measurements. The longer alkylene chain

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Scheme 1 Synthesis route for functional polymer.

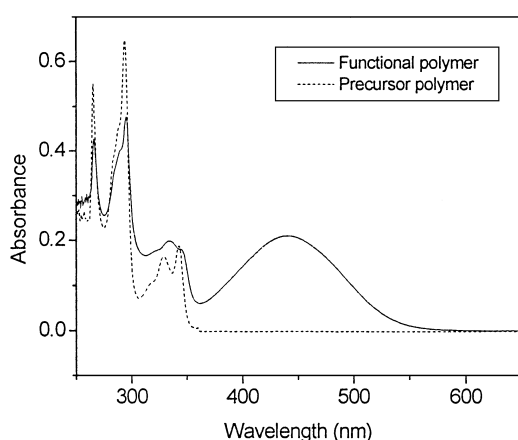


Figure 1 UV-vis spectrum of functional polymer and precursor polymer.

also enables the polymer to have a lower T_g (36°C) and prevented the polymer from crystallization, as evidenced by DSC. This observation indicates that the polymer is capable to form a stable amorphous film with low T_g . The sample for photorefractive measurement was prepared by dipping a THF solution of the polymer onto two indium tin oxide (ITO) glass plates, the dried sample was then sandwiched between two ITO glass plates, and the thickness was controlled to be $80\ \mu\text{m}$ through a Teflon spacer.

The PR performance was characterized by two-beam coupling (TBC) and four-wave-mixing (FWM) experiments. The experimental setup is depicted in Fig. 2. It should be pointed out that there is no poling and external electric field applied on the sample.

In the TBC experiment, the coherent polarized He-Ne laser beams ($\lambda = 632.8\ \text{nm}$) overlapped on the sample. The power of beam 1 and beam 2 was measured to be 18 and 11 mW, respectively. The TBC coefficient Γ can be calculated by the following expression:

$$\Gamma = \frac{1}{d}(\ln(\gamma_0\beta) - \ln(\beta + 1 - \gamma_0)) \quad (1)$$

where d is the optical path length, β is the ratio of the writing beam intensity, and $\gamma_0 = I/I_0$ is the beam-

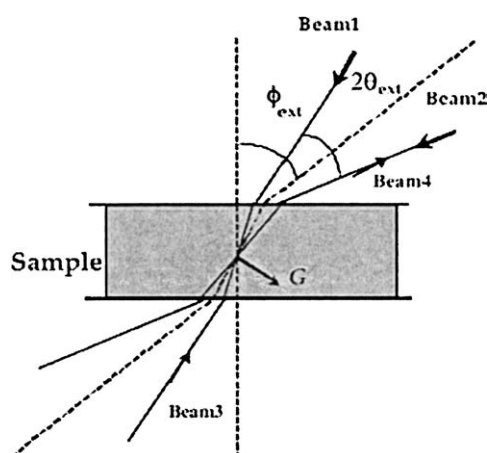


Figure 2 Experimental setup for two-beam coupling and four-wave-mixing. Beam 1 and beam 2 are *P*-polarized He-Ne laser beams, with incidence angles 25° and 45° respectively (in air). Beam 3 is the *S*-polarized probe beam and beam 4 is the diffractive beam. Only beam 1 and beam 2 are present in two-beam coupling experiment.

coupling ratio where I_0 is the signal intensity without the pump beam, and I is the signal intensity with the pump beam.

Energy transfer in TBC and FWM experiments is illustrated in Figs 3 and 4, respectively. Energy transfer occurs in the non-polarized sample and the coupling gain Γ was measured to be $140\ \text{cm}^{-1}$. This unique phenomenon can be explained by photo-induced poling when the azo group was illuminated by polarized light [8, 9]. In the FWM experiment, a much weaker *S*-polarized beam 3 counter propagating with beam 1 and the diffracted beam intensity was measured in the reverse direction of writing beam 2. The FWM efficiency was measured to be 8.3% when the power of beams 1 and 2 were both controlled to be 11 mW.

The present polymer shows better PR performance compared to a bi-functional polymer with a short spacer between the functional group and polymer backbone as reported earlier [10]. This may be attributed to the enhanced free rotation of the second-order chromophore through the more flexible spacer, and the higher chromophore concentration being without any added plasticizer. In addition, its low T_g made it easy to achieve

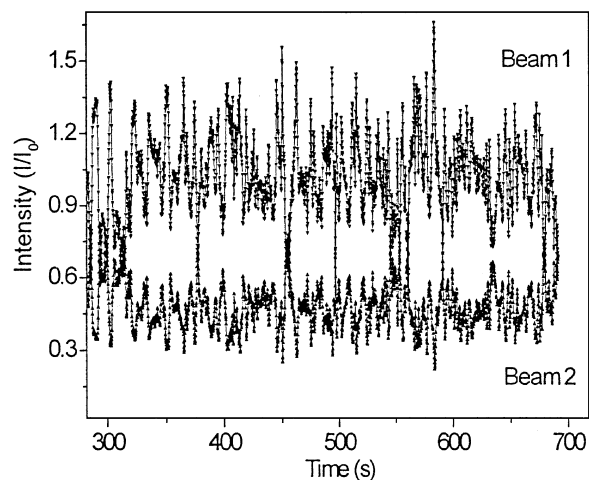


Figure 3 Energy transfer in two-beam coupling experiment of functional polymer.

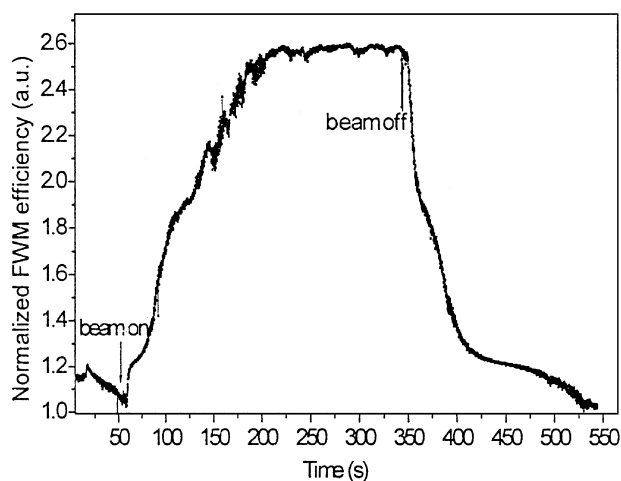


Figure 4 Energy transfer in four-wave mixing experiment of functional polymer (beam on and beam off refers to beam 2 turn on and turn off, respectively).

photo-induced poling when the azo group was illuminated by polarized light.

In conclusion, the single component functional polymer reported in this paper is composed of a hole-transporting carbazole group and an azobenzene chromophore attached via post-azo-coupling reaction. The polymer is amorphous with a low T_g (36°C). 2BC measurement indicated a gain coefficient of 140 cm^{-1} at zero applied electric field while the FWM efficiency was measured to be 8.3%.

Acknowledgment

This project was supported by the National Natural Science Foundation of China (No. 20274042).

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Received 17 December 2003
and accepted 10 February 2004