

Synthesis and Physical Measurements of a Photorefractive Polymer

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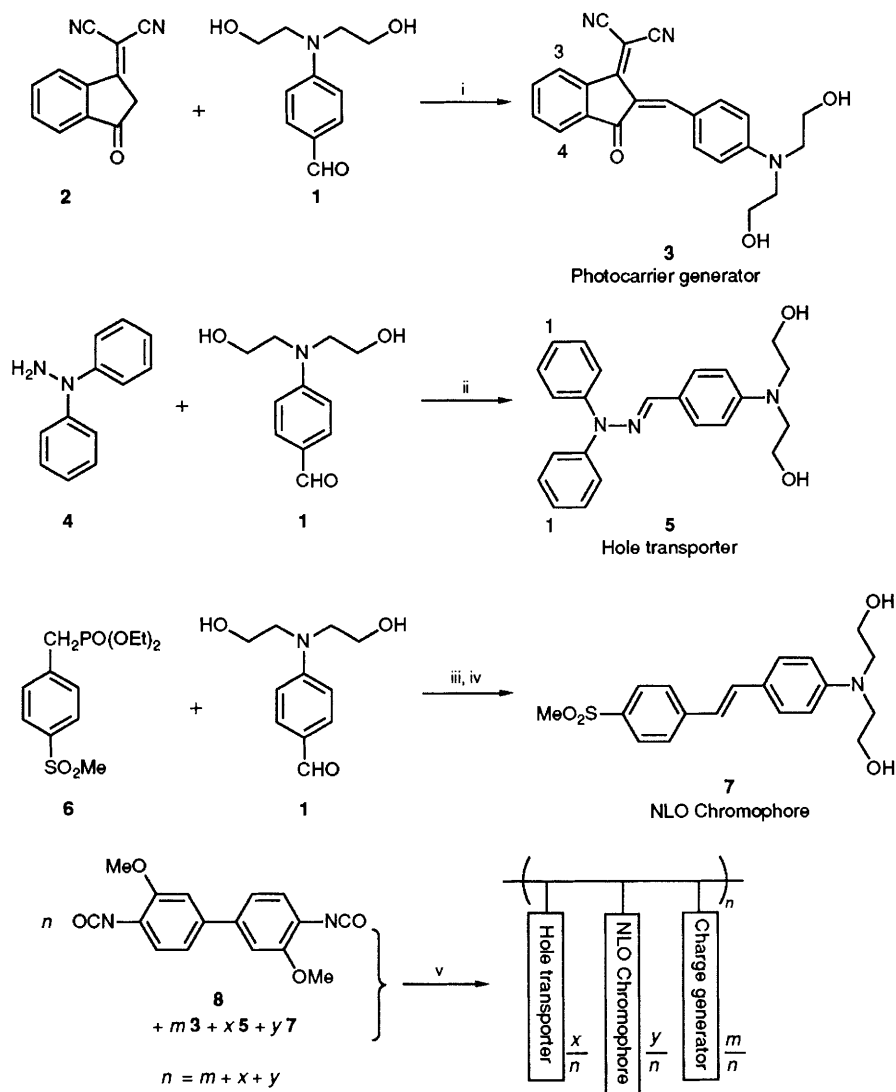
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A novel photorefractive polymer has been synthesized and its photorefractivity has been demonstrated by two-beam coupling.

The photorefractive (PR) effect, a nonlinear optical (NLO) process, involves a photoinduced change in the index of refraction.¹⁻⁴ This effect allows three-dimensional holographic light processing and enables the handling of large quantities of information in real time. In order to manifest the photorefractive effect, the materials must be non-centrosymmetric and photoconductive. Therefore, extensive studies have been focused on inorganic single crystals with non-centrosymmetric structures, such as ferroelectric crystals

(LiNbO₃, LiTaO₃, BaTiO₃) and semiconductors (GaAs, InP, CdF₂).¹⁻⁴ Recently, organic materials with photorefractive effects have been reported, which are very interesting and stimulating.⁵ Organic photorefractive materials have very attractive features, including their low dielectric constant, their versatility in choosing photocarrier generators and trappers for different frequency requirements, and their good processability for device fabrication. Here, we report the synthesis of new photorefractive polymer with an NLO



Scheme 1 Synthetic scheme of photorefractive polymer. The comonomer structure is not explicitly shown in the polymer schematic structure. It is implied that each species is connected to other by a comonomer unit. *Reagents and conditions:* i, EtOH, room temp.; ii, EtOH-NaAc, reflux; iii, NaH-ethylene glycol dimethyl ether; iv, H₂O; v, DMF, 80 °C

chromophore, a photocarrier generator and a transporting compound covalently linked to its backbone, in contrast to the doped systems reported in the literature.⁵

The synthetic scheme and the polymer structure are shown in Scheme 1. Compound **3** was prepared by condensing aldehyde **1** with 3-dicyanovinylindan-1-one **2**.^{6†} Condensation of 1,1-diphenylhydrazine with aldehyde **1** yielded the hole transporting compound **5**. The NLO chromophore was prepared according to the literature.^{6,7} The comonomer chosen is compound **8**, which is not very sensitive to the moisture in air. The polymerization was carried out in the purified dimethylformamide (DMF) under a nitrogen atmosphere. The polymer is a red-purple powder and is soluble in a variety of solvents. The gel-permeation chromatography (GPC) measurements in tetrahydrofuran (THF) indicated a weight averaged molecular weight of about 5000–20 000 using polystyrene as the standard samples. The polymer solution can be cast into optical quality films. Since the polymer has a polyurethane structure, hydrogen bonds exist among the imide groups. This is reflected in the high *T_g* (glass transition temperature) value, around 146 °C, which helped to stabilize the NLO effect.

† All of the compounds gave satisfactory NMR and mass spectroscopic results.

The structural information of this polymer was provided by both a ¹H NMR spectrum and a UV-VIS spectrum. The NMR results clearly indicate that all of the three species were indeed incorporated into the polymer chain. The UV-VIS spectrum shows the typical absorption of the generator at 550 nm. The absorptions of the NLO chromophore and the transporting compound appear at 375 nm, which does not exist in the spectrum of the charge generator.

Photoconductivity measurements were performed by monitoring the photocurrent response to a laser beam at 514.5 nm with an intensity of 0.4 W cm⁻². A maximum photocurrent of 10.9 μA was observed with an applied electric field of 100 V, while the dark current is very small and barely detectable. The quantum yield of the photocharge generation was calculated to be ca. 2.6 × 10⁻³ C photon⁻¹. The electrooptic (EO) effect in the polymer was studied by following the literature method using a HeNe laser beam;⁸ an electrooptic coefficient, *r*₃₃, of 14.5 pm V⁻¹ was detected after electrical poling in a waveguide structure (poling field, 70 V μm⁻¹). The EO coefficient in this polymer was found to be quite stable; a value of 13.3 pm V⁻¹ was detected three months after poling.

In order to confirm the photorefractive effect, a distinctive experiment is the two-beam coupling experiment. This involves the 'writing' of a hologram by the two beams intersected at the polymer sample and the coupling of the

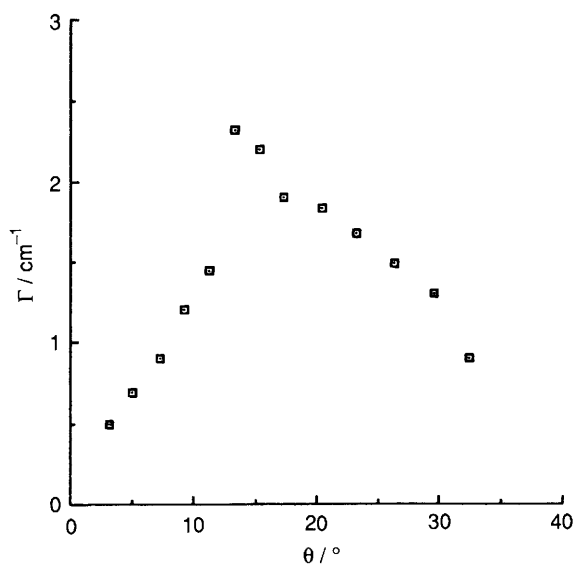


Fig. 1 Two-beam coupling gain (Γ) vs. intersection angle (θ)

same beams by the hologram formed, resulting in optical energy exchange between the two beams. By monitoring this optical energy exchange, one can deduce the optical gain coefficient which is proportional to the internal field (E^{sc}) induced by the separated charges. We performed this experiment in a waveguide structure using a HeNe laser; Fig. 1 shows the two-beam coupling gain as a function of the intersection angles (θ). The result indicated multiple contributions from different mechanisms. More detailed experiments involving measurements of diffraction efficiencies at various

conditions revealed three types of contributions: photoconductive contribution with a phase shift of 90° (accounting for 65% gain), a photovoltaic contribution with phase shift of 0° (accounting for 24% gain) and a photochromic absorption grating with phase shift of 0° (accounting for 11% gain).⁹

In conclusion, we have synthesized the first polymeric photorefractive material, which contains a photocarrier generator, a hole transporting compound and an NLO optical chromophore, covalently linked to a polymer backbone; and the two-beam coupling experiment in a waveguide structure unambiguously demonstrated the photorefractive effect.

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