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MOLECULAR DESIGN OF CARBAZOLE POLYMERS FOR PHOTOREFRACTIVE APPLICATIONS

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Abstract New carbazole photorefractive polymers with net photorefractive gain are reported.

INTRODUCTION

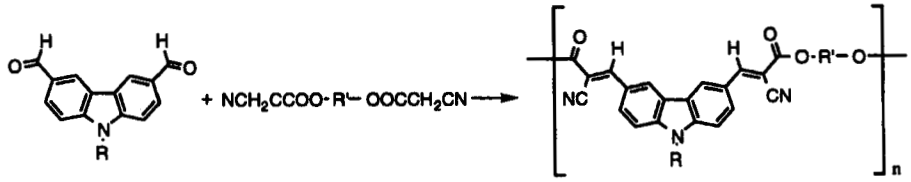
Recently organic photorefractive materials combining both electro-optic effect and photocoductivity have attracted a lot of attention due to their potential applications for holographic memory.[1] In the few years since the first report of organic photorefractive crystals[2] and polymers,[3] much research has been done to improve the materials' characteristics in order to meet the necessary requirement for the photorefractivity.[1] To date most of the organic photorefractive materials reported have been guest-host polymeric systems, using nonlinear optical polymers, charge transporting polymers or inert polymers as a host.[4] In the case of guest-host systems, materials must contain three components: a charge-transporting agent, a second-order chromophore, and a photocharge generation sensitizer for photocarrier generation. However, one of the inherent problems in these doped systems is the limitation of the concentration of each component due to phase separation and crystalization. To avoid these problems, the photorefractive polymers incorporated with all three necessary components have been developed.[4] Recently some new molecular design approaches have been successfully developed for preparation of "monolithic photorefractive materials" in our laboratory. For example, one multifunctional chromophore shows good photorefractive effects.[5]

In order to decrease the number of component moieties while maintaining all necessary properties in photorefractive materials, a multifunctional building block, acceptor-substituted carbazole is used as an important role for material molecular design. It is well know that carbazole compounds have photoconductive properties and internal donor group on 9-position. After the various acceptors are introduced to 3- and 6-positions, carbazole compounds might show both photoconductive and second-order nonlinear optical properties. To achieve our target, new photorefractive polymers

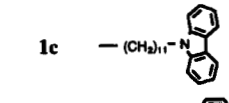
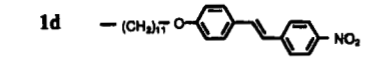
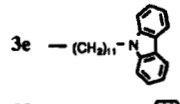
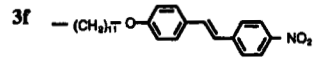
containing single carbazole moirty as a multifunctional chromophore is reported in this paper.

EXPERIMENTAL

The main-chain polymers containing carbazole moiety with two acceptor groups as a multifunctional chrompohore have been synthesized by the Knoevenagel polycondensation using 4-(N,N-dimethyl)pyridine (DMAP) as a base (as shown in **Scheme 1**). It has been found that one stage polycondensation carried out in THF solution afforded the main-chain polymers with low molecular weights in the low yields.[6] In order to obtain the main-chain polymers with high molecular weights in the high yields, a two-stage polycondensation was carried out. The base DMAP, 3,6-diformylcarbazoles **1a-1d** and bis(cyanoacetate)s **2a-2b** were dissolved in THF to obtain good mixing reaction system. After removal of THF and the water yielded by polycondensation, the yellow polymers **3a-3f** could be quickly formed.



1 2 3

	R		R'		R	R'
1a	$-(CH_2)_{15}CH_3$	2a	$-(CH_2)_{10}-$	3a	$-(CH_2)_{15}CH_3$	$-(CH_2)_{10}-$
1b	$-(CH_2)_8CH_3$	2b	$-(CH_2)_8-$	3b	$-(CH_2)_{15}CH_3$	$-(CH_2)_8-$
1c				3c	$-(CH_2)_8CH_3$	$-(CH_2)_{10}-$
1d				3d	$-(CH_2)_8CH_3$	$-(CH_2)_8-$
				3e		$-(CH_2)_8-$
				3f		$-(CH_2)_8-$

SCHEME I Synthesis of carbazole main-chain polymers

RESULTS AND DISCUSSION

In thses polymers, carbazole chromophores lie parallel to each other, "shoulder-to-shoulder" arrangement. In the main chain, the dipole alignment should be more easily

achieved by applying an electric field in a shoulder-to shoulder arrangement than in the other main chain polymers, like head-to-tail polymer, and head-to-head polymer. All the polymers in this study are soluble in common organic solvents, and exhibit absorption maximum (λ_{max}) at about 421 nm in chloroform. Their IR, NMR and elemental analysis are in accordance with their chemical structures.

To fabricate poled thick films, polymer with low glass transition temperature (T_g) has been selected as a "monolithic" photorefractive polymer research. The T_g of the polymers (as shown in **Table 1**) could be controlled by introducing alkyl spacer groups between two carbazole moieties and alkyl chains on 9-position with a different length. Differential scanning calormetry (DSC) measurments demonstrated the amorphous character of the polymers. Molecular weights of the carbazole main-chain polymers were obtained by gel permeation chromatography (GPC). The determined weight-average molecular weights versus polystyrene for the polymers **3a-3f** are in the range of 32,000-820,000 g/mol. From GPC data, it was found that the polydispersities of molecular weights are very large. This might be due to slight imbalances in stoichiometry and the solid state polycondensation.

TABLE I The T_g of the polymers **3a-3f**

Polymer	**3a**	**3b**	**3c**	**3d**	**3e**	**3f**
T_g (°C)	35	53	59	87	63	87

T_g was measured by PERKIN ELMER DSC 7 at a scanning rate of 10°C/min.

The second-order nonlinear optical properties of this type of polymers have been confirmed by second harmonic generation.[6] Photoconductivity measurements were performed on a 3 μm thick film of the polymer **3a** by the xerographic discharge method. The photoconductive sensitivity to 534 nm light and at an electric field of 50 V/μm was 1.2×10^{-12} $(Scm^{-1})/(Wcm^{-2})$.

The preliminary research work of photorefraction was done on the polymer **3a** which has lowest T_g by the two beam coupling (TBC) and four-wave mixing (FWM) techniques. A laser with λ = 532 nm was used for photorefractive measurements. Because of the low T_g of the polymer, no poling was performed prior to photorefractive measurements which were carried out at room temperature. In TBC experiment, holographic gratings were written by two p-polarized laser beams with equal intensity of

142 mW/cm. The normal of the sample surface was tilted 60° to yield a projection of the grating wave vector along the poling axis. An asymmetric optical energy exchange in TBC measurements could be obtained when an external electric field was applied. From this energy transfer, the photorefractive optical gain could be estimated. The TBC gain monotonously increases with an applied electric field as shown in Figure 1. FWM experiment was carried out with two s-polarized writing beams ($2x142mW/cm^2$) and a weak (12 mW/cm^2) p-polarized reading beam propagated in the direction opposite to one of writing beams. The diffraction efficiency is about 1.7% at electric field of 23 V/μm.

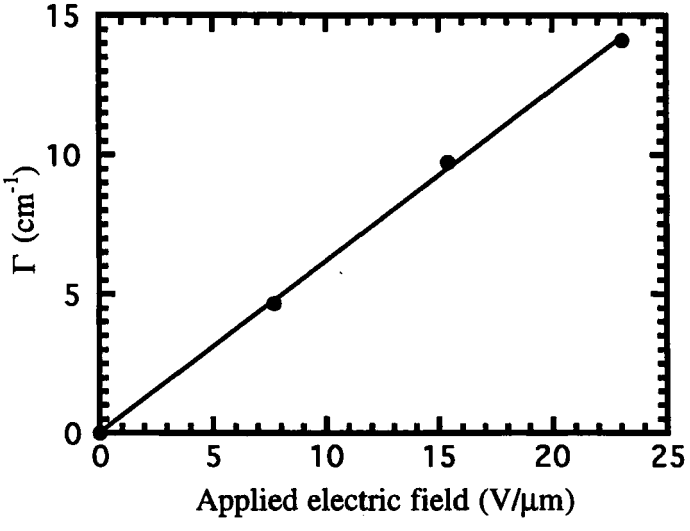


FIGURE 1 External electric field dependence of the photorefractive gain for polymer **3a**

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