Photorefractive polymers containing a single multifunctional chromophore

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Main-chain polymers containing carbazole substituted with two acceptor groups as a multifunctional moiety are synthesized and exhibit photorefractive net gain.

Since its discovery in organic materials in 1990,[1] the photorefractive effect has been observed in both organic crystals and polymeric materials.[2,3] The necessary elements of photorefractive materials are photoinduced charge generation, charge transport, trapping, and electrooptical non-linearity. Therefore photorefractive materials should combine these functional properties to be multifunctional materials. To date, there are two design approaches to synthesize photorefractive polymer materials.[4] The first approach is *via* host–guest composite materials. In this case, the non-linear optical polymers, charge transporting polymers or inert polymers are doped with the corresponding necessary functional moieties.[5–13] The second approach is *via* fully functional polymers. In this type of the polymer, all of the necessary functional moieties have been attached as the side-chain.[14–16] To date, several potential materials of this type have been reported. However, the performance has been inferior to that for the composite materials, and also photorefractive net gain has not been observed from this type of material.

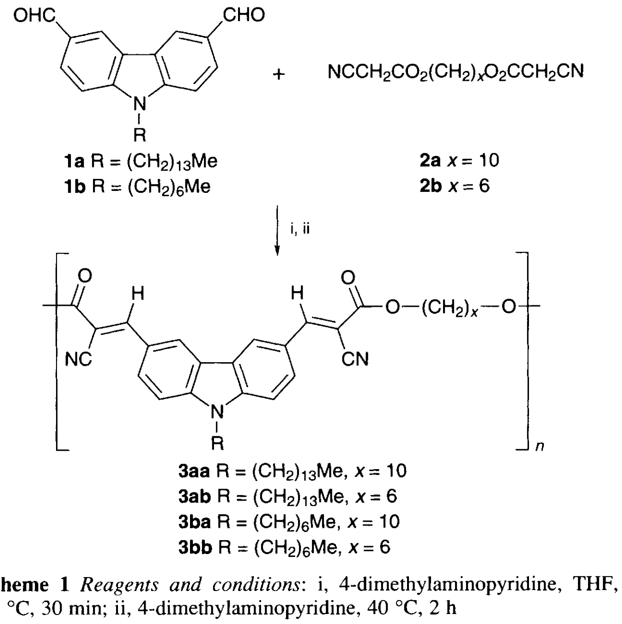
In our laboratory, carbazole derivatives as basic building blocks were selected for molecular design and synthesis of photorefractive materials. It is well known that carbazole compounds with multifunctional properties, such as second-order NLO and photoconductive properties, have already played an important role in photorefractive materials. Based on the carbazole rings, new photorefractive materials, carbazole oligomers[17,18] and dendrimers,[19] have been developed in our laboratory. These carbazole materials showed good photorefractive effects. Here, we report the synthesis and photorefractive properties of new photorefractive main-chain polymers which contain carbazole substituted with two acceptor groups as a single multifunctional chromophore. In these polymers, the carbazole chromophores lie parallel to each other, 'shoulder-to-shoulder'. In this arrangement dipole alignment should be easier to achieve by applying an electric field than in structures where dipole moments are pointing along the polymer main-chain.[20] The glass transition temperatures of the polymers could be controlled by introducing different spacers.

The syntheses of the polymers were performed as shown in Scheme 1. Two-stage Knoevenagel polycondensation of 3,6-diformyl-9-alkylcarbazole **1** and bis(cyanoacetate)s **2** yields carbazole main-chain polymers **3** in high yields. All compounds and polymers have been characterized by ^{1}H NMR, IR and elemental analysis.

The molecular masses of the polymers were estimated in chloroform by gel permeation chromatography (GPC) using polystyrene as a standard to give mass and number average molecular masses shown in Table 1. All the polymers had high molecular masses with wide distributions. Differential scanning calorimetric (DSC) analysis showed no crystalline transitions for the polymers. It was found that the glass transition temperature (T_g) was strongly dependent on the length of the alkyl spacer between the carbazole chromophores and of the alkyl group on the 9-position of the carbazole ring and the results are summarized in Table 1. It should be noted that the alkyl chain attached to the 9-position of carbazole has a greater effect on T_g than alkyl spacer length in the main chain. This behaviour may be explained by the side-chain effect. Among these four carbazole main-chain polymers, polymer **3aa** with relatively low T_g can enable a photorefractive measurement to be made at room temperature.

The second-order non-linear optical properties of this type of polymer have been demonstrated by second harmonic generation.[20] Polymer **3aa** with the lowest T_g at 35 °C was used for the photorefractive studies. Photoconductivity measurements were performed on a 3 μm thick film of the polymer **3aa** by the xerographic discharge method.[21] The photoconductive sensitivity in the polymer **3aa** to 534 nm light and at an electric field of 33 V μm^{-1} was 2×10^{-12} Ω^{-1} cm^{-1} (W cm^{-2})$^{-1}$. These measurements indicate that the photoconductivity of the carbazole main-chain polymers is significant enough to account for the observation of photorefraction in these main-chain polymers.[21]

The photorefractive properties of the polymer **3aa** were studied by the four-wave mixing and the two-beam coupling techniques.[4] The solid polymer was sandwiched between two ITO-covered glass substrates at an elevated temperature at which the polymer softens. The film thickness was controlled to



Scheme 1 *Reagents and conditions*: i, 4-dimethylaminopyridine, THF, 40 °C, 30 min; ii, 4-dimethylaminopyridine, 40 °C, 2 h

Table 1 Properties of the carbazole main-chain polymers **3**

Polymer	M_w	M_n	Polydispersity	T_g/°C
3aa	62000	22000	2.8	35
3ab	820000	81000	10.1	53
3ba	32000	9700	3.3	59
3bb	83000	16000	5.2	87

130 μm with a Teflon spacer. The films prepared in this manner were of good optical quality.

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 the two-beam coupling experiment, holographic gratings were written by two laser beams from a COHERENT DPSS 532 laser operating at 532 nm. Two p-polarized mutually coherent incident beams with an equal intensity of 142 mW cm^{-2} intersected in the sample to write the holographic grating. The normal of the sample surface was tilted 60° to yield a projection of the grating wave vector along the poling axis. The intensities of transmitted beams were detected with two identical large-area photodiodes (Hamamatsu Photonics S2386) and recorded by a digital oscilloscope (LeCroy 9310). Asymmetric energy transfer between the p-polarized writing beams was observed when an external electric field was applied providing evidence for a phase shifted grating. Each of the two beams was in turn diffracted by the index grating after its formation and one beam was amplified and another attenuated as a result of the non-local nature of the index grating and asymmetry of the applied electric field. From this energy transfer, the beam-coupling ratio, defined as the ratio between the power of this beam in the presence or absence of the other beam, could be obtained as shown in Fig. 1. The photorefractive gain could be estimated from the beam-coupling ratio.[22]

The two-beam coupling gain monotonously increases with the applied electric field and a gain of 14 cm^{-1} was obtained at an applied electric field of 23 V μm^{-1}, with an absorption coefficient of 8 cm^{-1} at 532 nm. The photorefractive gain at this electric field was larger than the absorption coefficient. A net gain of 6 cm^{-1} was obtained from our carbazole main-chain polymer **3aa**. This is the first report that fully functional polymers exhibit photorefractive net gain.

In the four-wave mixing experiments, the two writing beams were s-polarized with an equal intensity of 142 mW cm^{-2}, and a weak (12 mW cm^{-2}) p-polarized beam propagated in the direction opposite to one of the writing beams and read the written grating. A polarizing beam splitter was used to separate the diffracted light from the counter-propagating writing beam. The diffracted light was then detected by a photodiode. The diffraction efficiency was strongly dependent on the applied electric field. A diffraction efficiency of about 1.5% was obtained at an applied electric field of 23 V μm^{-1}.

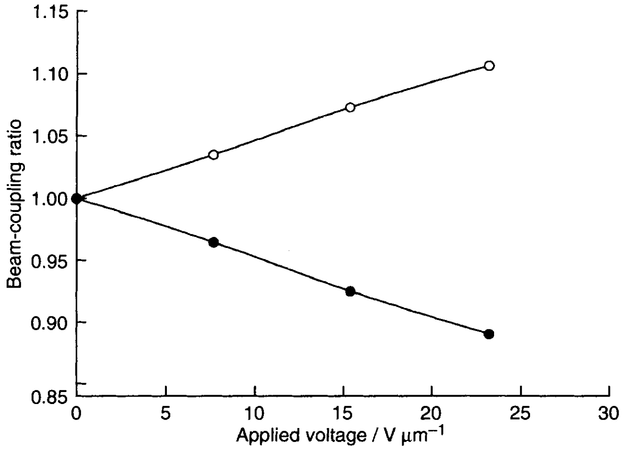


Fig. 1 Beam-coupling ratio *vs.* applied voltage shown for the beam which gains (○) or loses intensity (●)

New low T_g main-chain polymers have been synthesized and characterized for photorefractive applications, which contain single multifunctional chromophores, carbazole substituted with two acceptor groups. The photorefractive properties of these polymers have been determined by two-beam coupling and four-wave mixing experiments. Detailed research work on synthetic modification and photorefraction of this type of carbazole main-chain polymers is now under way.

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