새로운 광굴절재료의 제작 및 특성

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Synthesis and Properties of the New Photorefractive Material

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Abstract – Considerable progress has been made in organic photorefractive materials, since the first observation of photorefractive phenomena from organic materials. Within recent years, a large number of organic photorefractive materials, especially amorphous materials, have been developed based on polymeric composites, fully functional polymers and the multi-functional chromophore approach. Among these organic photorefractive materials, some of them containing carbazole components as a charge transporting function have been demonstrated to exhibit high performance photorefractive effects. The carbazole building blocks with charge transporting functionality or multifunctions play a very important role in photorefraction and have been widely used in the molecular design approach to new organic photo- refractive materials.

1. INTRODUCTION

Photorefractive(PR) nonlinear optics has drawn a great deal of attention during the last two decades due to its ability to exhibit a high refractive-index modulation amplitude, high sensitivity, and real-time operation. Devices based on photorefractive nonlinear optics have a potential role in dynamic interferometry and other optical information processing. Polymer materials for these applications have many positive attributes regarding their potential including high figures of merit, easy processing, and material flexibility. A change in refractive index(photorefraction) of a material may have many origins. Most of the mechanisms generally lead to irreversible photorefraction processes. However, some are reversible which is very important for potential applications.[1,2] Reversible photorefraction process can be due to several microscopic mechanisms, such as the space charge field induced photorefractive effect, photodimerization, photoisomerization, thermo-optic effects and photoinduced inter-or intra-molecular structural changes.[3,4] The space charge field induced photorefractive effect was first observed by Ashkin et al.[5] in 1966 in inorganic electro-optic(EO) $LiNbO_3$ crystals. The photorefractive effect has now been observed in a large number of inorganic materials,[1,2] such as $KNbO_3$, $BaTiO_3$, $Bi_{12}SiO_{20}$ (BSO), $B_{12}GeO_2$,(BGO), GaAs, and InP: Fe. Many different devices have been developed for numerous applications, including high density optical data storage, optical image processing, dynamic holography, optical computing and phase conjugated mirrors.[6-7] In 1990, the first observation of the photorefractive effect in

an organic doped crystal was reported by Sutter et al.[8-9]

Amorphous organic photorefractive material can offer many advantages over photorefractive crystals, such as large optical nonlinearities, low cost, low relative permittivity(ε), structural modification flexibility and ease of fabrication. Compared with inorganic photorefractive crystals, the low relative permittivity of organic materials is an important reason for pursuing the development of organic photorefractive materials. For organic materials, the nonlinear optical (NLO) response is molercular property arising from the asymmetric distribution of the electronic charges in the molecular ground and excited state.[10] For this reason, in organic materials large EO coefficients are not accompanied by large dc ε values thus a potential improvement in the performance of the photorefractive effects of organic materials can be achieved by a suitable and reasonable molecular design. It is well known that the growth and preparation of single crystals is generally a time-consuming and difficult processes. This is an even more important factor when attempting to engineer the properties of a single crystal by the modification of the crystal to include desired functionalities for the materials. On the other hand, the photorefractive properties of amorphous organic materials may be improved by both chemical and physical modifications. Amorphous organic materials are generally more amenable to processing into device structures with large areas and useful geometries by coating and other methods. In this review, recent progress in organic photorefractive materials with carbazole moieties is summarized. An introduction to the necessary functional components for molecular design approaches to organic photorefractive materials, characterization of organic photorefractive materials and identifying the nature of nonlocal photorefractive effects are also described.

2. Experiment

2.1 Design approaches

Since the first observation of photorefractive effects in amorphous organic polymeric composites, many amorphous organic materials for photorefraction have been developed based on two molecular design approaches: the guest-host composite approach and the fully functional approach. In these two approaches, materials always contain multicomponents to offer multifunction properties. Development of bifunctional

Second-order nonlinear optical moiety
Charge transporting moiety
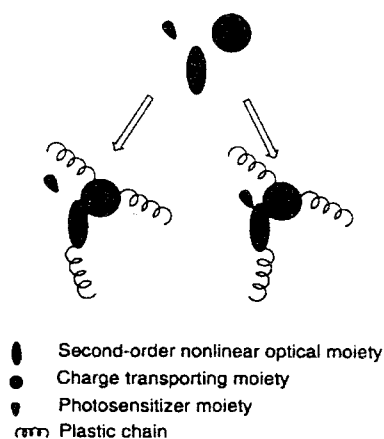**Photosensitizer moiety**
Plastic chain

Fig. 1 Molecular design approach to amorphous non-polymer photorefractive materials.

chromophores is the first approach to try to develop one chromophore with more than one function.[11] High performance of photorefractive effects has been obtained using this design approach. These chromophores provide two main functions, such as EO activity and sufficient charge transport properties for photorefractive behavior; they also provided charge trapping capability which allowed the first demonstration of truly long-lived gratings in a photorefractive polymer, quasi-nondestructive readout.[12] These materials also exhibited improved optical quality due to the reduction in the number of dissimilar constituents. Recently, we developed fully amorphous chromophores for photorefractive materials.[13] These chromophores were synthesized based on carbazole building blocks. The design approach is shown in Fig. 1. The chromophores combining photoconductive and EO functions are plasticized by introducing a suitable flexible alkyl chain. The use of different plastic chains can provide us with a chance to obtain amorphous compounds with controllable Tg. We believe that our carbazole-based design approach has more flexibility for chemical modification, and different types of materials an be obtained. Amorphous carbazole conjugated oligomers and amorphous carbazole dendrimers have been developed for photorefractive materials in this way. A conjugated carbazole structure was used to produce photorefractive materials because of its excel lent charge transporting properties and relatively high carrier mobility of the conjugated carbazole polymers and oligomers. It is well known that photorefractive materials are multifunction. Until this multifunctionality has been limited in molecular design approaches to multicomponent systems for photorefraction. One of our design targets is to develop multifunctional chromophores based on carbazole building blocks by chemical modification. We have tried to find one way of designing photorefractive materials with second-order NLO chromophores. Some successfull examples follow.

2.2 Amorphous carbazole trimers as multifunctonal chromophores.

In carbazole conjugated trimers (X) with acceptor groups for photorefractive materials, three carbazole

rings are linked by ethynyl groups, with the peripheral carbazoles substitutes with electron-withdrawing groups which make the materials EO active. The central carbazole can act as a charge transporting function. In order to obtain amorphous carbazole trimers with a low T_g, the three long aliphatic groups are introduced to the trimers at the 9-position of each of the carbazole moieties.

3. Result and Discussion

3.1 Multifunctional carbazole conjugated trimers

A dicyanovinyl substituted trimer with a T, of 29℃ has been used as a model example for studies of photorefractive effects. A single carbazole trimer with a dicyanovinyl group does not exhibit any absorption coefficient at a wavelength of 633 nm. However, the trimer could be sensitized by addition of a small amount of TNF. The charge transfer complex formed by the central cabazole moiety of the trimer and TNF shows a controllable absorption coefficient at 633 nm. Fig. 2 shows the absorption spectra of the trimer and the trimer doped with different concentrations of TNF. The photoconductive sensitivities were measured on a 10 μm thick sample
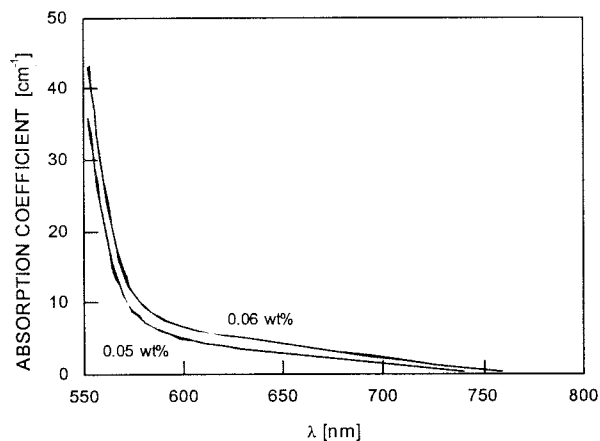

Fig. 2 Absorption spectra of trimer doped with different TNF concentrations.

sandwiched between Al and indium-tin oxide (ITO) electrodes. It was found that the TNF concentration has a significant influence on photoconductivity, and the maximized photoconductivity sensitivity value was observed in a 0.06 wt% TNF doped trimer in Fig. 3. The density of charge transfer complex units which act as the charge generation functions increased with the doping concentration of TNF. Uncomplexed TNF can also act as the hole trap. The density of free carbazole units, which are responsible for hole -transport decreased simultaneously, and sensitively influenced the magnitude of charge drift mobility.[14] Therefore, there is a balance between the charge generation and charge transporting components, which results in the observation of an optimized TNF concentration of 0.06 wt% in photoconductivity. Due to the low Tg of the timer, the chromophores could

be effectively aligned at room temperature by applying a dc electric field across the sample. The EO coefficient was measured on the same sample (134 μm) for the photorefractive measurements using a transmission technique.[15]
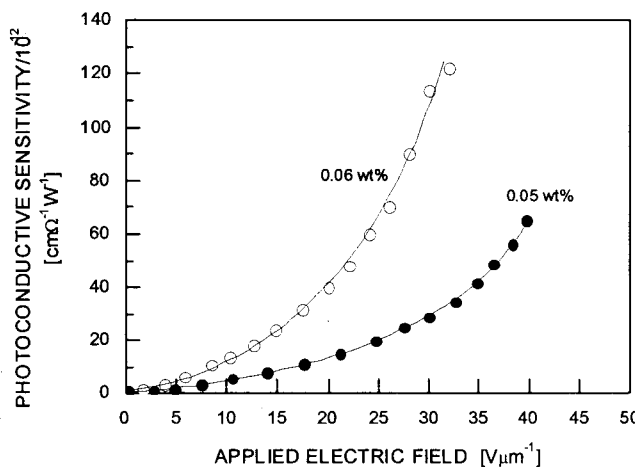

Fig. 3 Photoconductive sensitivity as a function of the applied electric field for dicyanovinyi-substituted carbazole trimer doped with different TNF concentrations.
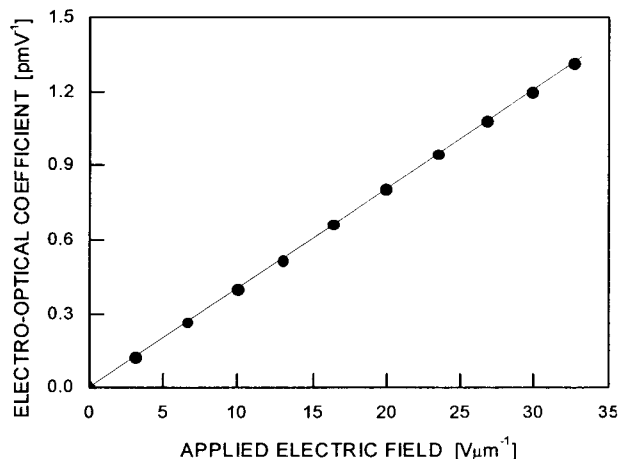

Fig. 4 The electro-optic coefficient of dicyanovinyi-substituted carbazole trimer as a function of the applied electric field at an ac frequency of 6 KHz.

In order to avoid the birefringence contributed from.orientation of second-order NLO chromophores, more accurate measurements of EO coefficients have been performed at high modulation ac frequencies at which the birefringence effect is insignificant and only the EO effect of chromophores can respond to the applied ac frequencies.[16] Fig. 4 shows the electric field dependence of the EO coefficient. These values are comparable with those obtained from other photorefractive materials systems.[17] The photorefractive nature of the trimer was confirmed by a two-beam coupling experiment. Two important photorefractive effects were observed.

Fig. 5 shows the two-beam coupling gain as a function of the applied electric field for the trimer doped with different concentrations of TNF. The diffraction efficiency was measured with a four-wave mixing experiment.
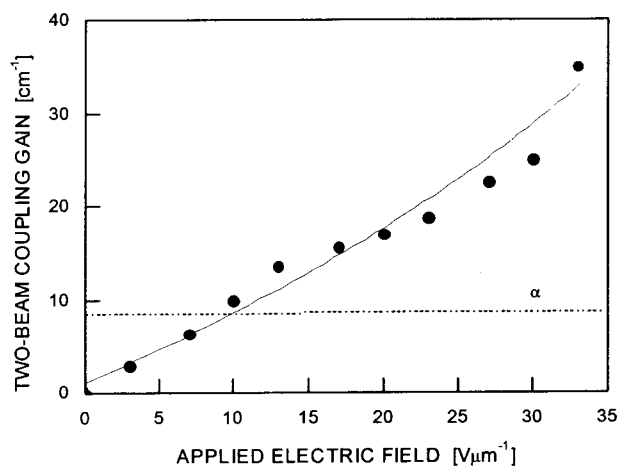

Fig. 5 The photorefractive gain coefficient as a function of the applied electric field for dicyanovinyi-substituted carbazole trimer doped with different TNF concentrations: (●) 0.06 wt%.
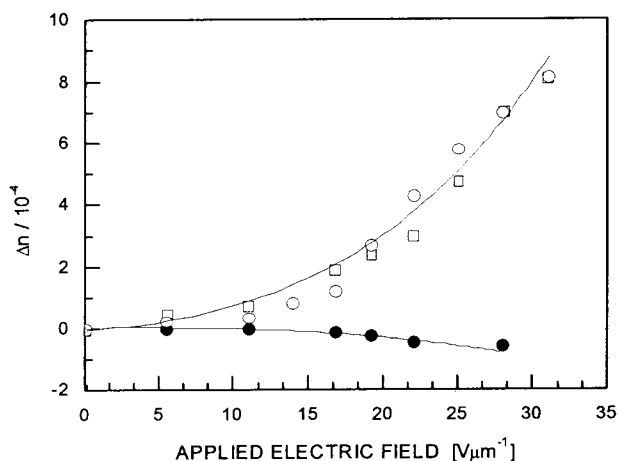

Fig. 6 Magnitude of index modulation of dicyanovinyl-substituted carbazole trimer doped with 0.06 wt% of TNF versus applied electric field: calculated from (O) p-polarized two-beam coupling gain, (●) s-polarized two-beam coupling gain and (□) p-polarized diffractionefficiency

The modulation of the refractive index from both measurements is in good agreement within experimental error as shown in Fig. 6. This result indicates that the nonlocal index grating is the dominant mechanism of the holographic gratings.

The amorphous trimer as the first multifunctional chromophore has been demonstrated to exhibit good photorefractive effects. This trimer approach has several advantages: (1) high concentration of carrier transporting agent and second-order NLO moieties, (2) large carrier mobility arising from the conjugated structure, (3) good film-forming properties without any amorphous supporting matrix, (4) flexibility in optimizing the photorefractivity by adjusting the concentration of TNF, and (5) phase-separation-free due to very low concentration of the dopant.
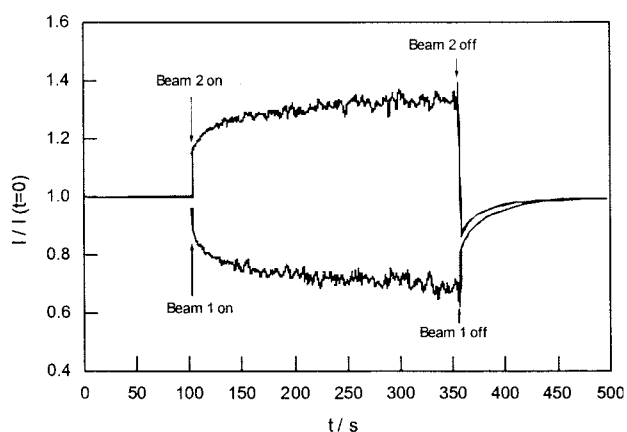
Fig. 7 The intensity of beam I (upper trace) monitored as beam 2 (lower trace) is switched on at time t = 0 s and off at t = 255 s, and the intensity of beam 2 monitored as beam I is turned on and off. The applied electric field was 33Vμm-1.
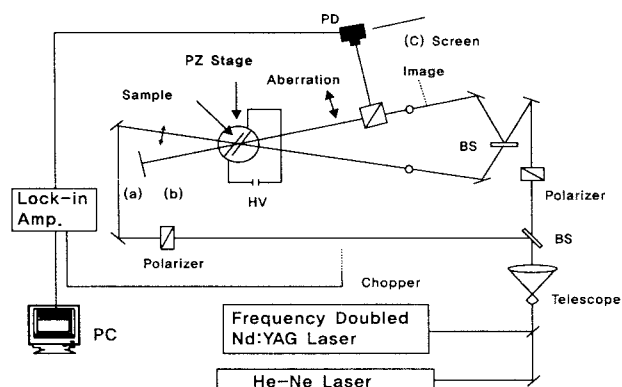

Fig. 8 Experimental geometry for optical image reconstruction.

3.2 The amorphous carbazole trimer as a monolithic photorefractive chromophore

A novel multifunctional conjugated carbazole trimer X with nitro acceptor groups has been found to be the first monolithic photorefractive material. It was found that this trimer doped with no other functional components showed an efficient photorefractive effect. [18] In this trimer, carbazole ings were also linked by the ethynyl group and peripheral carbazoles were substituted with nitro groups. The nitro-substituted carbazole trimer displays a suitable absorption coefficient of 8.2 cm^{-1} at a wavelength of 532 nm. This absorption coefficient can allow observation of the photorefractive properties of this trimer at an operating wavelength of 532nm. This trimer was demonstrated to be both photoconductive and to have second-order NLO activity. The noncentrosymmetric alignment of the chromophores can be achieved by an electric poling field at room temperature due to its low Tg of 20℃ and this can be confirmed by a second harmonic generation(SHG) measurement. The SHG experiment was carried out on the same sample for the photorefractive measurements at a fundamental wavelength of 1064 nm in transmission mode. With no electric field applied, the SH intensity could not be

observed, as a result of the centrosymmetric random arrangement of the chromophores. After switching on the electric field, repeatable orientation of the chromophores was realized, reaching a stable plateau value within a few seconds. This partial orientation of the chromophores at room temperature came as a result of the low Tg of the carbazole trimer. The SH intensity is strongly dependent on the applied electric field.

Fig. 7 shows typical asymmetric behavior for the monolithic carbazole trimer at an applied electric field of 33 Vμm^{-1}. The two-beam coupling gain coefficient could be estimated from the asymmetric energy transfer.

Films for NLO and photorefractive measurements were made by spin-coating and casting from chloroform solution, revpectively. In Fig. 8, the second-harmonic generation (SHG) measurements were Performed using a Q-switched ND-YAG laser beam (1064 nm) as a fundamental beam. In the two beam coupling experiment. two p-polarized laser beams at a wavelength of 532 nm from ND-YAG laser were used for writing holographic gratings,

4. CONCULSION

Considerable progress has been made in understanding both the photorefractive origins as well as the molecular design of amorphous organic photorefractive materials. Many organic amorphous materials with low cost and case of fabrication exhibiting better photorefractive performance than inorganic crystals have been developed. However, before amorphous organic photorefractive materials can be considered for practical applications, many important issues have to be addressed. Development of new material systems with optimized photorefractive properties and fabrication abilities remains a major challenge for chemical research work.

Almost all amorphous organic photorefractive materials reported must be induced to exhibit photorefractive effects by a high applied electric field. Therefore, this high electric field must limit practical device applications of these materials. New high performance materials that do not require an applied electric field or with low driven electric field should be developed for practical applications.

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