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Development of Carbazole Photorefractive Materials

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Recently a large number of organic photorefractive materials, especially amorphous materials, have been developed based on polymeric composite approach, fully functional polymer approach and multifunctional chromophore approach. Among these organic photorefractive materials, carbazole derivatives exhibit high performance of the photorefractive effects. The carbazole building blocks with a charge transporting function or multifunction play very important role and have been widely used in the molecular design approach to new organic photorefractive materials such as amorphous multifunctional chromophores, amorphous monolithic chromophores and amorphous dendrimers.

1 Introduction

The refractive index change (photorefraction) of the materials can be caused by many mechanisms when light is transmitted through the certain materials. Most of these mechanisms generally lead to irreversible photorefraction process. However, some of them are really reversible processes which are very important for many potential applications.^{[1],[2]} Reversible photorefraction process in the materials is attributable to several microscopic mechanisms such as space charge field induced photorefractive effect, photodimerization, photoisomerization, thermo-optic effects and photoinduced inter- or intramolecular structural change.^{[3],[4]} In the case of the space charge field induced photorefractive effect, the spatial modulation of refractive index occurs uniformly in the material in response to an optically induced charge distribution. Therefore among various mechanisms mentioned above only the space charge field induced process can cause a phase shift between the refractive index grating and the light intensity pattern. This phase shift leads to an energy transfer between the two light beams interfering in a photorefractive medium.

The space charge field induced photorefractive effect was firstly observed by Ashkin et al.^[5] in 1966 in the inorganic electro-optic crystal LiNbO_3 . After this discovery, the photorefractive effect has been found in a large number of inorganic materials^{[1],[2],[6],[7]} such as KNbO_3 , BaTiO_3 , $\text{Bi}_{12}\text{SiO}_{20}$ (BSO), $\text{B}_{12}\text{GeO}_{20}$ (BGO), GaAs, and InP:Fe. Based on these photorefractive crystals, various types of optical devices have been developed for applications including high density optical data storage, optical image processing, dynamic hologram, optical computing, phase conjugated mirrors, etc.^{[8]–[10]}

In 1990, the first observation of the photorefractive effect in an organic doped crystal was reported by Sutter et al.^{[11],[12]} However, the growth of high quality organic single crystals is a very difficult task. In 1991 IBM group reported amorphous polymers based on a guest-host system.^[13] Amorphous organic photorefractive materials can offer many advantages over the photorefractive crystals, such as large optical nonlinearities, low cost, low dielectric constant, structural modification flexibility, ease of fabrication and so forth. Compared with inor-

ganic photorefractive crystals, the low dielectric constant of organic materials is one of the important reasons for pursuing the development of organic photorefractive materials. A useful figure of merit for photorefractive materials can be defined as $Q = n^3 r_e / \epsilon$, where n is the refractive index, r_e the effective electro-optic coefficient, and ϵ the dc relative dielectric constant. Thus Q is approximately measured the ratio of the optical nonlinearity to the screening of the internal space charge distribution caused by the medium polarization. In inorganic materials, the optical nonlinearity is given mainly by the large ionic polarizability. The electro-optic effects due to the space charges in inorganic crystals appear to be limited, because any increase in the electro-optic coefficient of a material is effectively counterbalanced by an increase in the corresponding dielectric constant. Therefore, Q value remains low in most of inorganic crystals. For organic materials, on the other hand, the electro-optic nonlinearity is a molecular property arising from the asymmetric distribution of electronic charges in the molecular ground and excited states.^[14] For this reason, in organic materials large electro-optic coefficients are not accompanied by large dc dielectric constants, thus a potential improvement in the performance of the photorefractive effects can be achieved by a suitable and reasonable molecular design.

It is well known that the single crystal growth is generally an expensive and difficult process. This is really a serious factor to be considered when attempting to engineer the properties of single crystal by the modification of crystal structure and/or constituents 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 be processed into a device structure with large area and useful geometries by the simple coating and other methods.

In this review, the recent progress of organic photorefractive materials with carbazole functional moieties are summarized. Following a brief introduction to necessary functional components for molecular design approaches to organic photorefractive materials, the new molecular design approach based on carbazole building blocks, e.g., carbazole multifunctional conjugated trimers, carbazole monolithic conjugated trimers and carbazole dendrimers will be presented.

2 Necessary Functional Components for Photorefractive Design Approaches

To be photorefractive, a material must have the following necessary processes: a charge generation, a charge transporting and trapping, and an electro-optic response. When a light is incident on a photorefractive material, if the incident light is not uniform in intensity, photogenerated charges will migrate through the transporting component from the illuminated area to the dark area, where these charges get trapped by trapping centers. The resulting charge redistribution creates the space charge fields in the material. These fields produce measurable changes in the refractive index through the linear electro-optic effect in noncentrosymmetric materials. This mechanism of the photorefractive effect is summarized from the considerable body of prior work on the inorganic photorefractive crystals.^[15] The formative process of the refractive index grating in organic photorefractive materials is similar to that of the inorganic crystals.^{[16]–[18]}

According to the requirements and the mechanism of the photorefractive effects, photorefractive materials must have two main functions, i.e., photoconductivity for the establishment of a space charge field and the linear electro-optic effect for the formation of a refractive index grating. Photoconductivity in organic materials con-

sists of photocharge generation and charge transporting processes. In amorphous organic photorefractive materials, photocharges can be induced by addition of appropriate sensitizers, like organic dyes; generated charges can be transported through the hole transporting component, like carbazole and triphenylamine; the defects in the material play a role of traps for these charges. Second-order nonlinear optical chromophores can provide the linear electro-optic effect when the dipole orientation of chromophores is achieved by an applied electric field. Thus the multifunctionality of organic photorefractive materials can be easily achieved by two molecular design approaches: the guest-host composite approach^{[16],[17]} and the fully functional polymeric material approach.^[18] Most of the reported amorphous photorefractive materials were based on guest-host composite system using a second-order nonlinear optical polymers, a charge transporting polymer, or an inert polymer as a host doped with other corresponding necessary functional components.^{[16],[17]} Recently, bifunctional chromophores combined both charge transporting function and electro-optic function doped in inert polymers have also been reported.^{[16],[17]}

The composite materials approach has the advantage of ease optimization for the multifunctionality by independently varying the nature and concentration of each component. However, there are inherent problems of phase separation in these doped systems which limits the concentration of active moieties. In order to overcome this problem, fully functional polymers containing all necessary functional groups either in the polymeric main-chain or in the side-chain have the desirable advantage of long-term stability and minimized phase separation.^[18] However, the time-consuming chemical synthesis and difficulty in rational design are inevitable challenges. More recently, amorphous multifunctional and monolithic chromophore approaches to photorefractive materials have also been developed.^{[19]–[21]} These approaches can result in non-polymeric support-

ing photorefractive materials.

3 Carbazole Photorefractive Composite Materials

Most of organic photorefractive materials reported so far are host-guest polymeric composites. To break the centrosymmetry of the materials and to obtain a macroscopic electro-optic response, the second-order nonlinear optical chromophores are oriented by applying an electric field.^{[16],[17]} The efficiency of the poling process is strongly dependent on the orientational freedom of the second-order nonlinear optical chromophores: At temperatures below T_g , the polymer chains are frozen-in and the orientational mobility of the chromophores is very low. As the temperature is raised close to T_g , the orientational freedom of the chromophores increases, allowing an effective poling. When large amounts of chromophores are doped in PVK, the T_g of PVK (200 °C) is substantially lowered, which is desirable, since then the chromophores can be oriented even at room temperature. Recently a high performance of the photorefractive effects (near 100% diffraction efficiency for the read-out of a hologram as well as more than 200 cm^{-1} net two-beam coupling gain) have been observed in some composite materials based on PVK charge transporting polymers.^{[22],[23]} This was caused by an increase in the orientational mobility of chromophores due to lowering of T_g , resulting in a higher net alignment and hence a larger electro-optic effect. Moreover, in such systems, the chromophores are reoriented under the influence of the space charge field.^[24] In this way, a number of polymeric composites with excellent performance, which approaches or even exceeds that of existing inorganic materials, have been reported.^{[16],[17]}

To date, among organic photorefractive materials, PVK:DMNPAA:ECZ:TNF composite is best photorefractive polymeric material. How-

ever, there are inherent problems of phase separation in this highly doped system of functional components. In order to improve the long-term stability of this high performance photorefractive composite system, two approaches have been tried. First, a racemic ethylhexyl group has been incorporated to azo chromophore.^[25] Second, the eutectic mixture of the two isomeric azo chromophores, DMNPAA and 3,5-dimethyl-4-(p-nitrophenylazo)anisole (3,5DMNPAA), could considerably improve a shelf life time.^[26] Devices using this eutectic mixture composite remained clear for over one year under arbitrary laboratory conditions. The internal performance of these improved materials was found to be comparable to the best materials previously known.

4 Carbazole Multifunctional Photorefractive Polymers

Many types of multifunctional functional polymers have been developed for photorefractive materials in an effort to further minimize phase segregation. Among these polymers, polymers containing carbazole moiety as a charge transporting agent, bifunctional chromophores or monolithic multifunctional chromophores have been reported.^{[27]–[31]} Some of multifunctional polymers with both electro-optic and charge transporting moieties must be doped with suitable sensitizer. However, phase separation can not be observed owing to very low concentration of the dopants.

The first fully functional photorefractive polymer was developed based on carbazole moieties (as shown in Fig.1a)^[27] in 1992. In this polymer, some of the carbazole groups were tri-cyanovinylated. Carbazole substituted with tri-cyanovinyl group acted as two functions: second-order nonlinearity and photocharge generation. Carbazoles without acceptor group could offer a charge transporting function. Its photoconductivity of $9.8 \times 10^{-10} \Omega^{-1} \text{cm}^{-1}$ and electro-optic coefficient of 6.1 pm/V were obtained. Absorptive and photorefractive gratings have been evidenced by four-wave-mixing experiments and electro-optic measurements.^[28] The photorefractive gratings are studied by the electric-field dependence of the diffraction efficiency. The absorptive effect due to permanent photobleaching is dominant in the absence of any external electric effect for this polymer. The dynamics of the erase-write behavior of gratings was also studied on this polymer. Due to low mobilities, the material has a slow speed. However, it is believed that the mobilities can be increased and absorptive grating can be avoided by using some suitable sensitizers and more long wavelength of a laser.

PMMA-like polymer (as shown in Fig.1b)

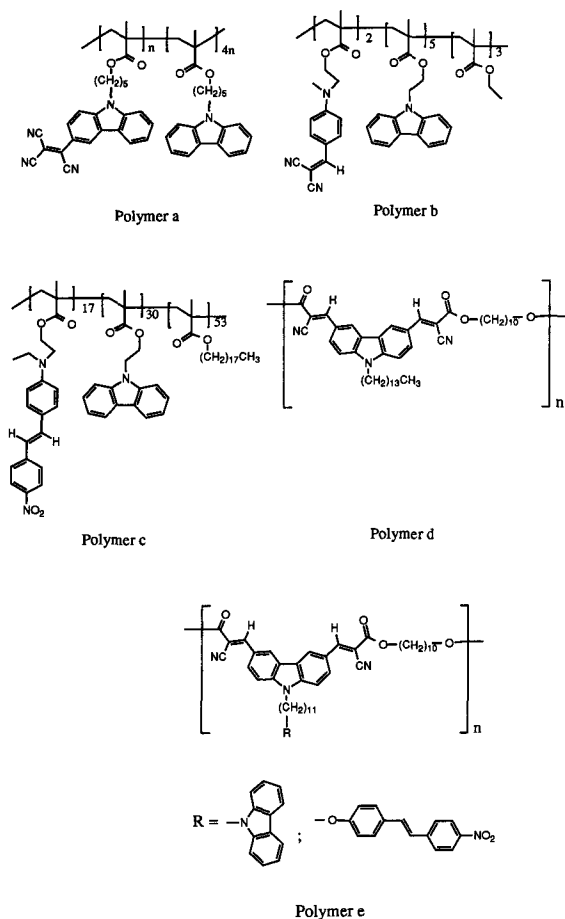


Fig.1 Chemical structures of multifunctional polymers with carbazole functional moieties for photorefractive materials.

DCVANMA:CzEtMA:EA (2:5:3)^[29] doped with 2.3 wt% of TNF for photorefractive materials has also been reported. In this system, carbazole can form charge transfer complex with TNF. This complex shows a photogeneration function at a wavelength of 633 nm due to its optical absorption. Diffraction efficiency was on the order of 10^{-6} , and the change of the refractive index was reversible in this polymer system. It was found that the observed photorefraction was mainly due to the molar refraction change of carbazole moiety caused by photoinduced ionization. This is an evidence that trapped ion radicals formed the gratings in the polymer, which is necessary for the real photorefractivities.

Another low T_g polymer PENHCOM^[30] based on PMMA structure doped with 0.2 wt% of TNF has also been developed. In this polymer, 4-(N-ethyl-N-(hydroxyethyl)amino-4'-nitrostilbene was used as a second-order nonlinear optical chromophore, whereas a carbazole moiety as a charge transporting agent. In order to obtain copolymer with a low T_g , the long aliphatic octyl group was attached as a side chain plasticizer. The ratio of the function X:Y:Z is 17:30:53 (Fig.1c). This material showed an absorption coefficient of 25 cm^{-1} at a wavelength of 633 nm. A four-wave mixing diffraction efficiency of 0.9% and a two-beam coupling gain coefficient of 7.5 cm^{-1} have been obtained at an electric field of $100 \text{ V}/\mu\text{m}$.

More recently, polymers containing a single multifunctional carbazole chromophore (e.g., as shown in Fig.1d) have been obtained in our laboratory.^[31] In the polymer 1d, the carbazole substituted with two acceptor groups exhibited multifunctional properties. The carbazole chromophores lie parallel to each other, "shoulder-to-shoulder". In this arrangement the dipole alignment is easier to be achieved by applying electric fields than in structures where dipole moments are pointing along the polymeric main chain. 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. It could be controlled in the range from 35 to 87°C . Among these carbazole main-chain polymers, the polymer with a relatively low T_g enables photorefractive measurements at room temperature. These carbazole main-chain polymers were proved to be both photoconductive and electro-optic active.^[32] The photorefractive properties of the carbazole main-chain polymers were studied by four-wave mixing and two-beam coupling techniques. The two-beam coupling gain of 14 cm^{-1} was obtained at an applied electric field of $23 \text{ V}/\mu\text{m}$, with an absorption coefficient of 8 cm^{-1} . The photorefractive gain at this electric field was larger than the absorption coefficient. A net gain of 6 cm^{-1} was obtained from the carbazole main-chain polymer. A diffraction efficiency of about 1.5% was also obtained at same electric field.

Carbazole main-chain polymers with side functional moieties (as shown in Fig.1e) exhibit more efficient photorefractive effects^[33] compared with corresponding carbazole main-chain polymer.^[31] It was found that the polymer with carbazole moiety as a charge transporting functional side group showed net two-beam coupling gain of about 45 cm^{-1} and diffraction efficiency of 2.5% at an applied electric field of $23 \text{ V}/\mu\text{m}$.

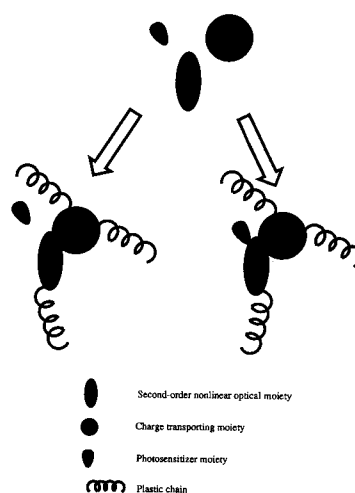


Fig.2 Molecular design approach to amorphous non-polymer photorefractive materials.

Carbazole main-chain polymer with second-order nonlinear optical chromophore as an electro-optic functional side group exhibited photorefractive effects without poling electric field due to the thermal induced orientation of second-order nonlinear optical chromophore. The film prepared by thermal casting has been demonstrated to exhibit second-order nonlinear optical response.

5 Carbazole Photorefractive Chromophores

5.1 Design approach

Since the carbazole molecule has an isoelectronic structure with diphenylamine, the introduction of electron-withdrawing groups in the 3- and/or 6-position induces an intracharge-transfer and a mesomeric dipole moment. Depending on the electron-affinity of acceptor groups, polarizabilities of carbazole derivatives can be tuned by the proper molecular design of the substituent groups.^[34] Acceptor-introduced carbazoles have been considered to be very promising for the second-order nonlinear optical chromophores.^{[35],[36]} Besides the 3- and 6- position substitution, N-substitution (9-position) offers various function to chemical modifications: solubilization and amorphism by different length of alkyl chain,^{[37],[38]} control of noncentrosymmetric packing in the crystalline state through hydrogen bonding.^[39]

Development of bifunctional chromophores is the first approach to try to develop one chromophore with more than one functions.^{[40],[41]} High performance of photorefractive effects has obtained from this design approach. These chromophores provide two main functions, such as electro-optic activity and sufficient charge transport properties for photorefractive behavior. They also provided a charge trapping capability which allowed the first demonstration of truly long-lived gratings in a photorefractive polymer, quasi-nondestructive readout.^[42]

Recently we have developed fully amorphous chromophores for photorefractive materials.^{[20],[43]} These chromophores were synthesized based on carbazole building blocks. The design approach is shown in Fig.2. The chromophores combining photoconductive and electro-optic functions are plasticized by introducing some suitable flexible alkyl chain. The introduction of different alkyl chains can provide us amorphous compounds with a controllable T_g . According to this design idea, amorphous carbazole conjugated oligomers and amorphous carbazole dendrimers have been developed for photorefractive materials. Conjugated carbazole structure was used to design the photorefractive materials owing to excellent charge transporting properties and relatively high carrier mobility in the conjugated carbazole polymers and oligomers.^[44]

One of our design targets is to develop multifunctional chromophores and monolithic chromophores based on carbazole building block by chemical modifications. We try to find the way to design photorefractive materials like design of second-order nonlinear optical chromophores. Some successful examples from our design idea will be demonstrated hereafter.

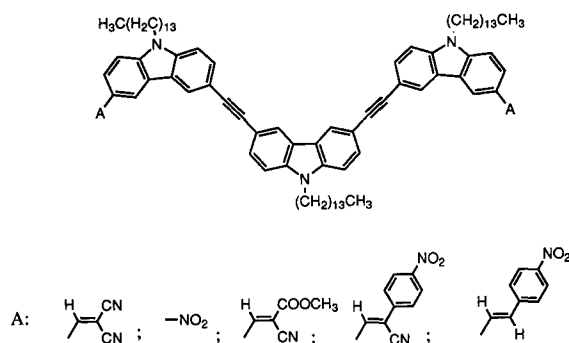


Fig.3 Chemical structures of conjugated carbazole trimers.

5.2 Amorphous carbazole trimer as a monolithic photorefractive chromophore

A novel multifunctional conjugated carbazole trimer with nitro acceptor groups (as shown in Fig.3) is a first monolithic photorefractive chromophore. It was found that this trimer doped without any other functional components showed an efficient photorefractive effect.^[45] In this trimer, three carbazole rings are linked each other by acetylene bond and both side carbazoles are substituted with nitro group. A nitro substituted carbazole trimer displays suitable absorption coefficient of 8.2 cm^{-1} at a wavelength of 532 nm. This trimer was demonstrated to be both photoconductive and second-order nonlinear optically active. The orientation of the chromophores can be achieved by an electric poling and proved by means of a second harmonic generation (SHG) technique at room temperature due to its low T_g of 20°C . SHG experiment was carried out on the same sample for the photorefractive measurements at the fundamental wavelength of 1064 nm in a transmission mode. With no electric field applied, the SH intensity could not be observed as a result of the centrosymmetric random arrangement of chromophores. Fig.4 shows the angular dependence of the SH intensity at a poling electric field of $23 \text{ V}/\mu\text{m}$. The photoconductive properties were studied on a sample sandwiched between an ITO and a gold coated glass substrates at a wavelength of 532 nm. The photocurrent was almost independent of the laser intensity, but strongly dependent on the applied electric field. The photoconductive sensitivity of the carbazole trimer with nitro group was measured to be $1.2 \times 10^{-11} \text{ cm}/\Omega\text{W}$ at an external field of $39 \text{ V}/\mu\text{m}$. No detectable dark conductivity was observed. It was found that upon the exposure to the light the photocurrent increased rapidly with a time constant $< 0.1\text{s}$ due to large carrier mobility of the carbazole trimer.

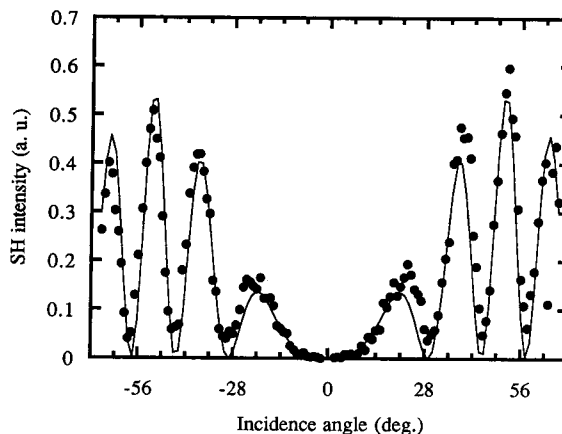


Fig.4 The SH intensity of carbazole trimer with nitro group as a function of incidence angle at an applied electric field of $23 \text{ V}/\mu\text{m}$.

The photorefractive properties of the trimer were characterized by a two-beam coupling and a four-wave mixing. In two-beam coupling experiment, an asymmetric energy transfer between the two beams was observed when an electric field applied. This provided a proof that a true photorefractive effects is present.^[16] Figure 5 shows a typical asymmetric behavior for monolithic carbazole trimer at an applied electric field of $33 \text{ V}/\mu\text{m}$. The two-beam coupling gain coefficient could be estimated from the asymmetric energy transfer. It increases monotonously with the applied electric field as shown in Fig.6. At the applied electric field of $33 \text{ V}/\mu\text{m}$, the photorefractive gain of 35.0 cm^{-1} was obtained. Since the absorption coefficient for this trimer was 8.2 cm^{-1} , the net gain coefficient became 26.8 cm^{-1} . An applying electric field plays an important role to enhance the photorefractive effects because of a better alignment of second-order nonlinear optical chromophores and higher photoconductivity at higher electric fields. If the external electric field is not applied during ‘writing’, no detectable gratings are observed due to the centrosymmetric random alignment of second order nonlinear optical chromophores. Four-wave-mixing was used to determine the steady-state diffraction efficiency

of the carbazole trimer. Figure 7 shows the applied field dependence of the diffraction efficiency. At $33.3 \text{ V}/\mu\text{m}$, the diffraction efficiency reached 13.2%. Optical image reconstruction of distorted images using phase conjugated was demonstrated in this monolithic photorefractive material.

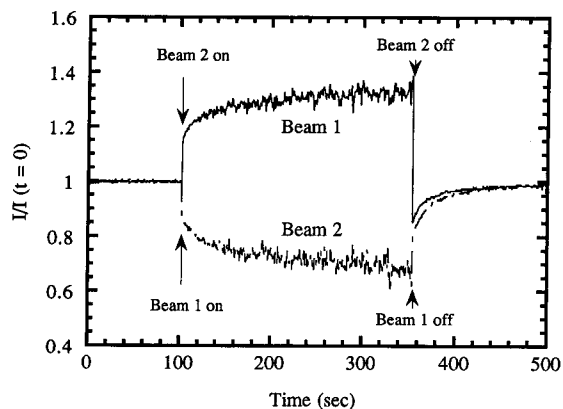


Fig.5 The intensity of beam 1 (upper trace) monitored as beam 2 (lower trace) is switched on at time $t = 0 \text{ s}$ and off at $t = 255 \text{ s}$, the intensity of beam 2 monitored as beam 1 is turned on and off. The applied electric field was $33 \text{ V}/\mu\text{m}$.

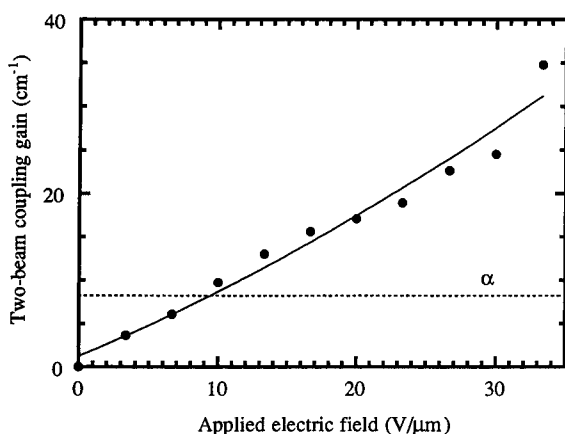


Fig.6 The two-beam coupling gain of nitro-substituted carbazole conjugated trimer as a function of the applied electric field. The dashed line is the absorption coefficient at a wavelength of 532 nm .

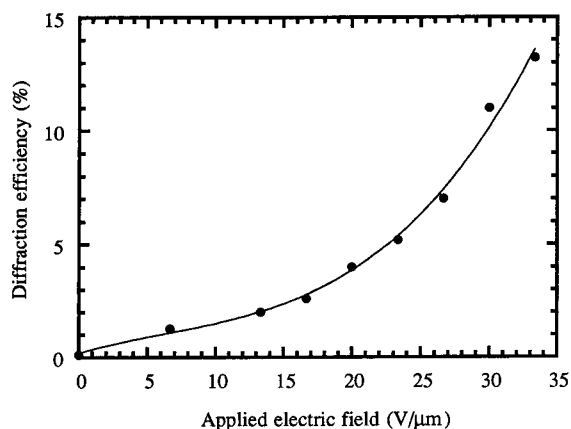


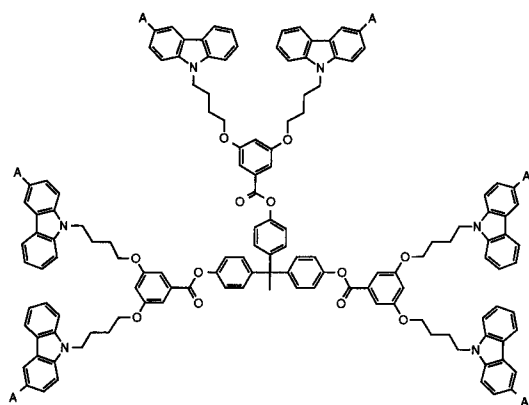
Fig.7 The diffraction efficiency of nitro-substituted carbazole conjugated trimer as a function of the applied electric field.

5.3 Carbazole dendrimers

The development of the materials with new chemical structures for photorefractivity is an extremely active field.^{[16],[17]} In order to develop new amorphous molecules with good modification flexibility, dendrimer structure has been selected as a molecular design approach to photorefractive materials. Dendrimer structures has several advantage for design of photorefractive materials: 1) dendrimers are amorphous, 2) core and different generation can be modified as different functions for meeting the multifunctional requirement of photorefractive materials, 3) different dendron with different functions can also meet the multifunctional requirements. Such dendrimers are expected that their unique spherical structure will impart unusual properties.

Several dendrimers with mono-acceptor substituted carbazoles as the multifunctional chromophores have been synthesized in our laboratory.^[46] These carbazole starburst oligomers have a film-forming property and show a glass transition behavior. Values of T_g could be controlled by the length of spacer, the number of carbazole rings or acceptor groups. Amorphous molecular solid films could be prepared without supporting matrix by spin-coating. These thin films could be poled at above T_g to achieve

the noncentrosymmetric alignment of molecular dipoles required for an electro-optic response. Second-order nonlinear optical responses were examined on the thin films by SHG. The values of the second-order nonlinear optical coefficients (d_{ij}) were strongly dependence on the acceptor groups. The chemical structures and d_{ij} values are summarized in Fig.8. Photoconductive properties of this dendrimer system have been examined by means of a xerographic discharge technique. It is clearly confirmed that these molecular systems have multifunctional properties, i.e., both photoconductiveity and second-order nonlinear optical responses. Two-beam coupling experiment on dendrimer with carbazole substituted with dicyanovinyl indicated that the induced index grating is shifted by 90° with respect to the interference pattern. This phase shift, or nonlocal nature of the photorefractive effect, gives rise to an asymmetric energy transfer between the two writing beams, which does not occur in any of other processes. The two-beam coupling gain of 11.8 cm^{-1} was obtained for this dendrimer at a applied electric field of zero.



A	d_{33} (pm/V)	d_{31} (pm/V)
-CHO	6.9	5.0
-NO ₂	30.8	12.5
	49.6	41.4

Fig.8 Chemical structures and d_{ij} values of carbazole dendrimers.

6 Summary and Outlook

Considerable progress has been made in both the understanding of photorefractive origins and the molecular design of amorphous organic photorefractive materials. Many organic amorphous materials with low cost and ease of fabrication exhibiting larger figure-of-merit than inorganic crystals have been developed. However, before amorphous organic photorefractive materials can be considered for practical applications, many of the limitation issues should be solved. Developments of new material systems with optimized photorefractive properties and fabrication feasibilities remain as a major challenge for chemical research work.

Almost all amorphous organic photorefractive materials reported must be treated with a poling procedure to induce photorefractive effects. Therefore, this high electric field must limit practical device applications of these materials. Novel high performance materials without applied electric field or with low driven electric field are needed for applications. Several successful examples of photorefractive materials, such as high T_g polymers^[33] sol-gel composite material,^[47] and amorphous dendrimer,^[46] have been reported and demonstrated to display the photorefractive effects at a driven electric field of zero.

In low T_g photorefractive materials reported, the high performance of photorefractive effects mainly come from the contribution of orientation-induced birefringence. Following the application requirements, the materials with photorefractive effects contributed by electro-optic effects might be a promising candidate for applications.

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