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Carbazole photorefractive materials

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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 multifunctional 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 photorefractive materials. Based on carbazole functional building blocks, amorphous multifunctional chromophores, amorphous monolithic chromophores and amorphous dendrimers have also been developed as new types of organic photorefractive materials. This paper reviews the recent progress of organic photorefractive materials, especially organic photorefractive materials containing carbazole functional components.

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 processes 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] Except for the space charge field induced processes, other processes have local mechanisms which lack the nonlocal property of the photorefractive effect arising from the physical motion of the charges in the materials. Only the space charge field induced reversible process can cause a phase shift between the refractive index grating and the light intensity pattern. An important consequence of this phase shift is energy transfer between the two light beams interfering in a photorefractive medium. This space charge field induced photorefractive effect is defined as the spatial modulation of a material's refractive index in response to an optically induced charge distribution and is a nonlocal physical process. In this paper, the progress of the space charge field induced photorefractive effects in organic materials will be discussed.

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,[1,2,6,7] such as $KNbO_3$, $BaTiO_3$, $Bi_{12}SiO_{20}$ (BSO), $B_{12}GeO_{20}$ (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.[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 difficult. The IBM group reported the first amorphous polymeric photorefractive material based on a guest–host composite system in 1991.[13]

Amorphous organic photorefractive materials 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. A useful figure of merit for photorefractive materials can be defined as $Q = n^3 r_e/\varepsilon$, where n is the refractive index, r_e the effective EO coefficient, and ε the dc relative permittivity. Thus Q is approximately measured as the ratio of the optical nonlinearity to the screening of the internal space charge distribution caused by polarization of the medium. For inorganic materials, the optical nonlinearity is driven chiefly by the large ionic polarizability. The EO effects from the space charge in inorganic crystals appear to be limited, since any increase in a component of the EO coefficient of a material is effectively counterbalanced by an increase in the corresponding ε value. Therefore, Q values remain low in most inorganic crystals.[14] For organic materials, the nonlinear optical (NLO) response is a molecular property arising from the asymmetric distribution of the electronic charges in the molecular ground and excited state.[15] 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.

Necessary functional components for approaches to photorefractive design

To be photorefractive, a material must have photoinduced charge generation, charge transporting and charge trapping properties, as well as an EO response. When 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 EO effect in noncentrosymmetric materials. The mechanism behind the photorefractive effect is summarized from the considerable body of prior work on the inorganic photorefractive crystals.[16] The formative process of the refractive index grating in organic photorefractive materials is similar to that of the inorganic crystals.[14,16,18] According to the requirements and the mechanism of the photorefractive effects, photorefractive materials must have two main functions, photoconductivity for the establishment of a space charge field and the linear EO effect for the formation of a refractive index grating. Photoconductivity in organic materials consists of photocharge generation and charge transporting processes. In amorphous organic photorefractive materials, photocharges can be induced by addition of appropriate sensitizers, such as organic dyes; generated charges can be transported through the hole transporting component, such as carbazole and triphenylamine; the defects in the materials can play a trapping role for these charges. Second-order NLO chromophores can provide the linear EO effect when the dipole orientation of chromophores is achieved by an applied electric field. Thus the multifunctionality of organic photorefractive materials can be achieved by two molecular design approaches: the guest–host composite approach[14,17] and the fully functional polymeric material approach.[18] Most of the reported amorphous photorefractive materials were based on guest–host composite systems using second-order NLO polymers, a charge transporting polymer, or an inert polymer as a host doped with the corresponding necessary functional components.[14,17] Recently, bifunctional chromophores combining both charge transporting function and EO function doped in inert polymers have also been reported.[14,17] The composite materials approach has the advantage of easy optimization of the multifunctionality by independently varying the nature and concentration of each component. However, there are inherent problems in phase separation of these doped systems which limit the concentrations 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 evident advantage of long-term stability and minimized phase separation.[18] However, the time-consuming chemical synthesis and difficulty in rational design are constant 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 supporting photorefractive materials.

Characterization of organic photorefractive materials

Absorption coefficient for the charge generation

In order to observe a photorefractive effect, a material should have a suitable optical absorption coefficient at the operating laser wavelength for the generation of the photocharges. In the optimal case, this absorption coefficient should come from the contribution of the charge generation molecules, such as C_{60} and charge-transfer complex. The absorption coefficient for charge generation from any of the other components, such as second-order NLO chromophores, will increase other competing processes.[22] When we design molecules for photorefractive materials, the absorption coefficient at the operating wavelength from the charge generation molecules should first be confirmed by a spectroscopic measurement. Any absorption due to other functional components should be avoided from the operating laser wavelength for photorefraction.

Photoconductivity for the establishment of the space charge field

Photoconductivity in amorphous organic materials consists of photocharge generation and charge transport processes. The charge generation molecules absorbing photons produce electron–hole pairs which, under the influence of a driven electric field, dissociate to produce electrons and holes.[23] These free carriers then migrate through the material *via* a hopping mechanism by the charge transport components.[24] Measurement of these properties is an important first step for the characterization of a potential organic photorefractive material. The photocharge generation quantum yield and the photoconductivity can be measured using a simple photocurrent technique or a xerographic discharge technique.[25] Charge mobility can be measured by the time-of-flight technique.[26] One detailed study on the photoconductivity of an organic photorefractive material has been presented.[27]

Linear EO effect for formation of a refractive index grating

A number of different methods have been developed to measure the EO coefficient in polymer films. The most widely used methods for thick polymer films are the reflection technique[28] and the Mach–Zehnder interferometric technique.[29,30] These two methods are also widely used for measuring the EO coefficients of amorphous organic photorefractive materials. It should be pointed out that the EO coefficients obtained at low frequencies contain the contribution from the field induced birefringence. More accurate measurements of the EO coefficients should be performed at high modulation ac frequencies at which the birefringence effect is insignificant and only the EO effect of chromophores can respond to these ac frequencies.[31]

Two-beam coupling measurements

In order to unambiguously distinguish between the photorefractive effect and other types of gratings, two-beam coupling measurements must be performed. The phase shift between the refractive index grating and the light interference pattern can be determined by two-beam coupling techniques. 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 the other refractive index change processes. Therefore, the nonlocal character of the photorefractive effect can be directly confirmed by an observation of the phase shift or the asymmetric energy transfer in two-beam coupling experiments. Experimental details of two-beam coupling techniques can be found in the literature.[12,32,33]

Four-wave mixing measurements

The four-wave mixing experiments reveal a large amount of information about photorefractive materials. Using four-wave mixing techniques, grating formation dynamics can be studied. The diffraction efficiency, a key parameter judging from the performance of the photorefractive effects can also be measured by a four-wave mixing technique. Such measurements have been carried out in detail for many organic photorefractive materials.[14,17,18]

Identifying characteristics of nonlocal photorefractive effect

Other local processes as mentioned above can also lead to changes in the refractive index of the materials. How can we distinguish the space charge field induced photorefractive effects from other local photorefraction processes? There are many ways to distinguish photorefraction from competing mechanisms that lead to changes in the refractive index. Here some of the important characteristics for identifying nonlocal photorefractive effects are listed.

Phase shift and energy transfer

When the grating is only produced by the migration of the charge by diffusion away from the illuminated regions (nonlocal process), the phase of the index grating is shifted by 90° with respect to the light intensity grating. An important consequence of this phase shift is asymmetric energy exchange in two-beam coupling.[1,32] Photorefractive effects involving other processes do not show a 90° phase shift. A critical element in this coupling is the nonzero phase shift between the refractive index grating and the light intensity grating. Techniques for measuring the grating phase are reported.[12,32]

Hologram erasability

The traps that lead to the formation of the space charge fields in photorefractive materials must themselves be photoionizable. If so, the photorefractive diffraction grating can be erased simply by bathing the material in a uniform field of the appropriate frequency. The photorefractive index changes can be written and erased repeatedly over a long time without noticeable change in the chemical structure of the material.[34] For photochemical effects, reversibility generally requires heating or other chemical treatment. Most photochromic gratings tend to be only partially erasable under uniform illumination.[4]

EO response and photoconductivity

Most local effects, such as photochromic and photochemical effects, do not depend upon the absence of the linear EO and the photoconductive effects. For photorefractive materials, the photoconductivity and EO nonlinearity of materials must be measurable at the same wavelengths as used for photorefractive measurements. These two functional properties are basic necessary conditions for the nonlocal photorefractive effects.[14,17]

Enhancement by external fields

Drift mobilities in amorphous organic photoconductors generally scale with the square root of the applied electric field.[35] For amorphous organic materials, the linear EO effects can be enhanced by the high orientation degree of second-order NLO chromophores at the high applied electric field. Application of a high external field can enhance photorefractive effects due to the increase of both the EO nonlinearity and the photoconductivity.[14,17]

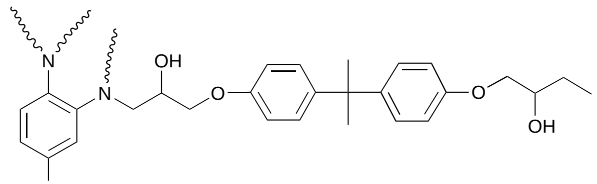
Polarization anisotropy of the grating readout and modulation of refractive index (Δn)

The photorefractive response is dependent upon the polarization of the incident beam. If pure s- or p-polarized light is used in writing the grating, the diffraction efficiency will be different for the s- and p-polarized components of an oblique reading beam.[14] Unlike the two-beam coupling, the four-wave mixing diffraction efficiency is independent of the phase shift of the index grating. In principle, a local grating induced by many other mechanisms such as photochemistry and photochromism can also contribute to the four-wave mixing diffraction efficiency. If the modulation of the refractive index determined from independent experimental results such as from the diffraction efficiency of four-wave mixing and from the two beam coupling gain, are in agreement within experimental error. We can say that the nonlocal index grating is a dominant mechanism.[21]

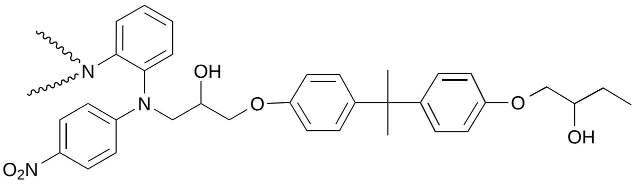
Amorphous organic photorefractive materials without carbazole functional components

Second-order NLO polymers as hosts

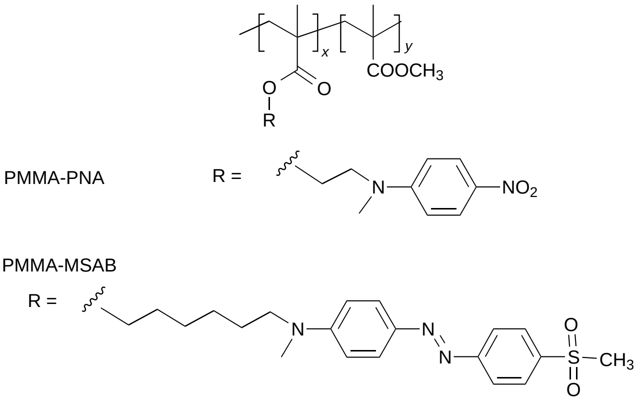
To date, three types of second-order NLO polymers, cross-linkable epoxy polymers,[13,32,36,37] copolymers of methyl methacrylate and acrylate[38–40] and linear epoxy polymers,[41–44] have been used as the host matrix for photorefractive composites.



bisA-NPDA

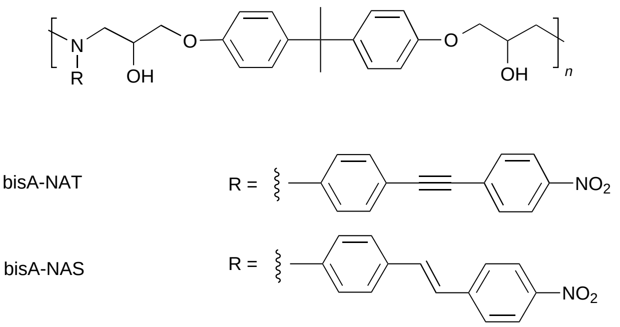


NNDN-NAN



PMMA-PNA

PMMA-MSAB



bisA-NAT

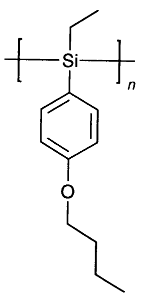
bisA-NAS

In this material system, benzaldehyde diphenylhydrazone (DEH) was used as a charge transporting agent and the second-order NLO chromophores played two roles: as the EO function and the charge generation function. The first photorefractive effect was found in this system based on a second-order NLO cross-linkable epoxy polymer doped with DEH as a hole transporting agent.[13] The photorefractive nature of this material was demonstrated by two-beam coupling.[13,36] It was found that the photorefractive grating was dependent on the applied electric field: at low electric fields a weak in-phase grating and the low EO coefficient prevent observation of a phase shifted photorefractive grating and at high electric fields a much stronger photorefractive index grating with a phase shift approaching 90° could be observed,[32,36] New phenomena, electric field stabilization of photorefractivity and grating revelation which cannot be observed in inorganic photorefractive crystals, was observed from the second-order polymer bisA-NAT doped with 40 wt% of DEH.[37]

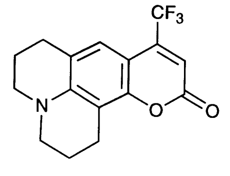
Some photosensitizers, such as borondiketonate and C_{60}, as a charge generation functional component were also used as dopants in second-order NLO polymers. The performance of various sensitizers used to generate mobile charges at suitable long wavelengths were studied.[39–41] In order to improved photorefractive effects, other charge transporting components, such as *p*-(diethylamino)benzaldehyde *N*-(1-naphthyl)-*N*-phenylhydrazone, *N*-{[(4-diethylamino)phenyl]methylene}-9*H*-carbazol-9-amine and tritolylamine have also been used.[36,40] The results indicate low photorefractive performance with the two-beam coupling gains of $<2.2\ \mathrm{cm}^{-1}$ and diffraction efficiencies of $<0.11\%$ for the photorefractive system using second-order NLO polymers as a functional matrix. Recently linear epoxy polymers with 4,4′-nitroaminostilbene (bisA-NAS) as a second-order NLO chromophore containing 29 wt% of DEH were reported, with the stilbene dye substitutent NAS also serving as a charge generation function.[42] This composite material exhibited good photorefractive performance with two-beam coupling gains as large as $50\ \mathrm{cm}^{-1}$ at an applied electric field of $70\ \mathrm{V}\ \mu\mathrm{m}^{-1}$. However, no net gain was obtained due to the large absorption coefficient ($\alpha > 200\ \mathrm{cm}^{-1}$) at the wavelength of the laser beam ($\lambda = 650$ nm) used.

Non-carbazole charge transporting polymer as a host

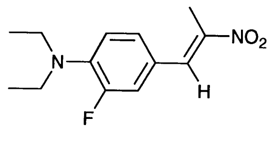
Only one non-carbazole charge transporting polymer, poly(4-*n*-butoxyphenylethylsilane) (PBPES), was used for photorefractive composites.[45] In this polymer, either 20 wt% of the laser dye coumarin-153 (C-153) or 40 wt% of (*E*)-*β*-nitro-(*Z*)-*β*-methyl-3-fluoro-4-*N*,*N*-diethylaminostyrene (FDEAMNST) as a second-order NLO chromophore, and 0.2 wt% of either trinitrofluorenone (TNF) or the fullerene C_{60} as a sensitizer were doped.



PBPES



C-153

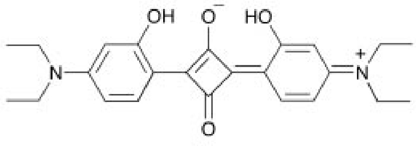


FDEAMNST

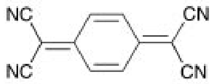
The photorefractive properties of these guest–host polymeric composites were characterized by both four-wave mixing and two-beam coupling. Steady-state diffraction efficiencies as high as 10^{-4} and rise times as short as 39 ms were obtained by four-wave mixing. This is one of the fastest responses in organic photorefractive polymers. Net two-beam coupling gains were also observed in this system.

Inert polymers as hosts

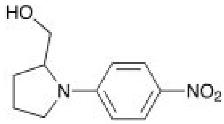
Two inert polymers, poly(methyl methacrylate) (PMMA) and polycarbonate (PC) were used as hosts for photorefractive composites, in which each of three components exhibits one necessary function.[46–49]



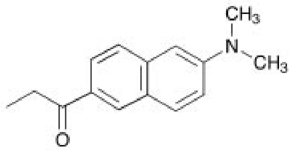
SQ



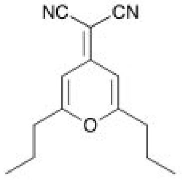
TCNQ



NPP



PRODAN

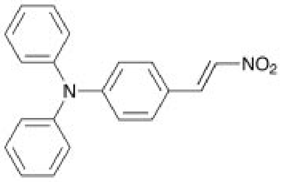


DPDCP

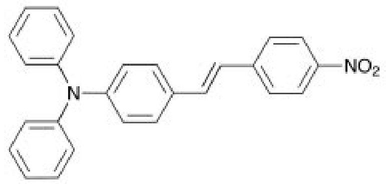
PMMA composites doped with 30 wt% of DEH (a charge transporting moiety), 30 wt% of NPP (a second-order NLO chromophore) and less than 0.1 wt% of a squarylium dye (SQ) or 0.2 wt% of tetracyanoquinodimethane (TCNQ) (a charge generation moiety) showed lower glass transition temperature (T_g) due to the high doping level of DEH and NPP. The photorefractive nature of these inert composites was confirmed by the two-beam coupling. A phase shift of 90° between a refraction grating and a fringe pattern with applied electric fields was obtained.[46] A diffraction efficiency of 1.1% and a beam-coupling gain coefficient of $10\ \mathrm{cm}^{-1}$ were achieved at a dc electric field of $34.9\ \mathrm{V}\ \mu\mathrm{m}^{-1}$.[47] Burzynski *et al.*[48] used PC as a host for a charge transporting agent, TTA (30 wt%), a second-order NLO chromophore, either NPP (20 wt%) or 6-propionyl-2-dimethylaminonaphthalene (PRODAN) (20 wt%), and a charge generation sensitizer, C_{60} (0.25 wt%). Photoconductivity and the EO effect were observed in both composites along with their electric field dependence. In the case of composites containing PRODAN as a second-order NLO chromophore, the chromophore showed absorption at short wavelength. This enabled the authors to demonstrate photorefractivity at a wavelength as short as 488 nm. A maximum diffraction efficiency of 3.2% (at $75\ \mathrm{V}\ \mu\mathrm{m}^{-1}$) and a net two-beam coupling gain coefficient of $20\ \mathrm{cm}^{-1}$ (at $42.5\ \mathrm{V}\ \mu\mathrm{m}^{-1}$) have been obtained for a PC–TTA–NPP–C_{60} composite at a wavelength of 633 nm. More recently, a novel photorefractive polymeric composite using PMMA as a host was reported.[49] In this material, 2,6-di-*n*-propyl-4*H*-pyran-4-ylidenemalonoitrile (DPDCP), a transparent, highly dipolar chromophore with large anisotropy of the optical polarizability and negligible second-order nonlinearity was chosen as a functional dye. *N*,*N*′-Bis(3-methylphenyl)-*N*,*N*′-bis(phenyl)-benzidine (TPD) was employed as an efficient charge transport agent.[50] The fullerene C_{60} was used as a sensitizer. The photorefractive measurements were carried out on a doped polymer material consisting of 30 wt% DPDCP, 15 wt% TPD, 55 wt% PMMA, and 0.3 wt% C_{60}. A 100 μm thick film of this material exhibits a steady-state diffraction efficiency of 25% and net two-beam coupling gain of $50\ \mathrm{cm}^{-1}$ at a bias field of $100\ \mathrm{V}\ \mu\mathrm{m}^{-1}$. It was found that the microscopic mechanism of the photorefractive effect in this material involves the formation of a refractive index grating through a space-charge field-modulated Kerr effect.

Bifunctional chromophores doped in inert polymers

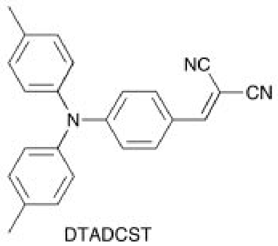
Usually multicomponent composite photorefractive systems, in which each component exhibits one functional process



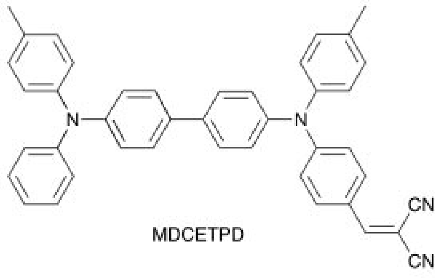
DPANST



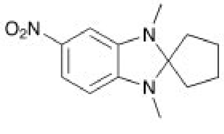
DPANS



DTADCST



MDCETPD



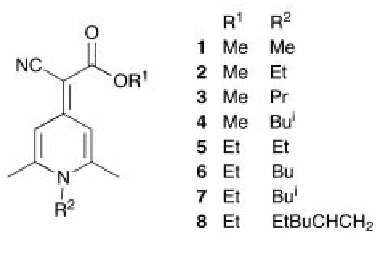
DTNBI

mentioned above, are inherently unstable and have a tendency towards phase separation which results in loss of the optical quality.

Among these functional components, the linear EO and photoconductive moieties play the main roles in photorefractive process. However, phase separation limits the concentration of EO and charge transporting functional components. In order to obtain a high degree of loading for these two functional components, one chromophore combining several functions might be desirable. This multifunctional design approach might circumvent the problem of phase separation which limits the concentrations of main components. The bifunctional molecules combining both second-order NLO and charge transporting properties[51–57] have already been developed based on charge transporting molecule building blocks, such as triphenylamine (TPA)[24] and N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1,1′-biphenyl-4,4′-diamine (TPD).[58] Therefore, by increasing the concentration of a bifunctional chromophore in a supporting matrix, a higher photorefractive figure-of-merit (large EO coefficient and photoconductive effect) and faster response (higher charge mobility) can be simultaneously obtained. Several examples of using bifunctional chromophores in photorefractive composites have been reported by Stankus *et al.*,[53] Zhang *et al.*[56] and Bolink *et al.*[57] In all studies, C_{60} was used as a photocharge generation sensitizer to extend the photoconductivity to longer suitable wavelengths. Inert polymers poly(methyl methacrylate) (PMMA) for 4′-(N,N'-di-p-tolylamino)-β,β-dicyanostyrene (DTADCST), poly(n-butyl methacrylate) (PBMA) for 4-(N,N'-diphenylamino)-β-nitrostyrene (DPANST) as well as 4-(N,N'-diphenylamino)-4′-nitrostilbene (DPANS) and polystyrene (PS) for monodicyanoethene–TPD (MDCETPD) were used as host matrices, respectively. Among these bifunctional chromophores, chromophore MDCETPD is found to be fully amorphous, with a T_g of 110 °C. In order to enhance the orientational degree of MDCETPD at room temperature, the plasticizer dioctyl phthalate (DOP) was added to decrease T_g.[57] All composites with a certain component ratio show low T_g. These low T_g materials allow the measurements of the photorefractive effects to be carried out at room temperature. Results indicate that the photorefractive effects (the two-beam coupling gains, the four-wave mixing diffraction efficiencies and their response times) increase with the increase in the chromophore concentration.[54] The relation between the photorefractive effects and trap density also has been studied. It is found that the gain coefficient and diffraction efficiency can be enhanced by adding small amounts of the trap molecule, 1,4-bis(N,N-dimethylamino)benzene (BDB).[57] Simultaneously the phase-shift between the illumination pattern and the refractive index grating decrease with increasing BDB concentration. The trap molecules have an effect on the creation of the space charge field. Chromophore concentration dependence of the EO coefficients, photoconductivity, four-wave mixing diffraction efficiency and the two-beam coupling gain coefficients indicates the great potential of this bifunctional design approach.[53,56]

Glass molecules for photorefractive materials

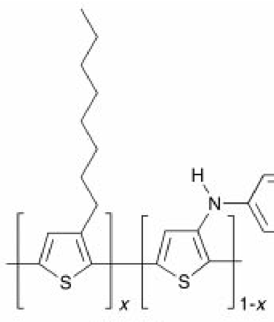
Recently the IBM group reported on a family of dihydropyridines **1**–**8**.



	R^1	R^2
1	Me	Me
2	Me	Et
3	Me	Pr
4	Me	Bu^i
5	Et	Et
6	Et	Bu
7	Et	Bu^i
8	Et	$EtBuCHCH_2$

4 2BNCM

These molecules can be used to formulate organic photorefractive materials in which the chromophore serves as a charge transporting function and the optical birefringence species, and additionally acts as the amorphous host.[19,59] Most of the work reported here was done on methyl N-isobutyl-2,6-dimethyl-4H-pyridin-4-ylidene(cyano)acetate **4** (2BNCM) which exhibits a T_g at 25 °C and, at room temperature, persists without crystallization. When a small amount (< 1 wt%) of a photosensitizer, TNF, was added to these glassy monomers, the resulting material exhibited outstanding photorefractive effects such as high diffraction efficiencies and two-beam coupling gain.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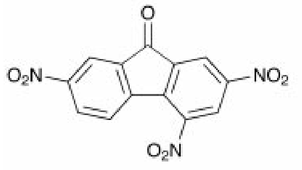
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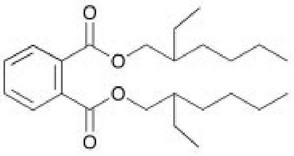
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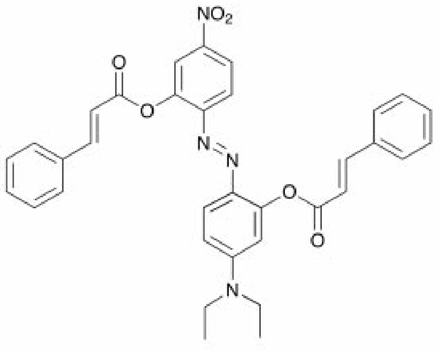

CNNB-R

It was found that significant increases in the hologram growth rate can be obtained by doping the chromophore with a small amount of inert polymers, such as 10 wt% of PMMA and polysiloxane, or polyvinylcarbazole. 2BNCM–PMMA–TNF (90 : 9.7 : 0.3 wt%) was selected for a more detailed study on photorefractivity. High diffraction efficiency of 80% and two-beam coupling gain of 69 cm^{-1} were obtained from this system at an external field of 40 V μm^{-1}. High density holographic digital data storage has also been studied in this system.

Fully functional polymers

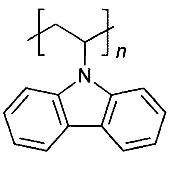
In the last few years fully functionlized polyurethanes,[60] conjugated polymers[61] and polyimides[62] with relatively high T_g have been developed by Yu *et al.* for photorefractive applications.[18] Photoconductive, EO and photorefractive studies have been done on these polymers. Two-beam coupling gains without applied electric fields were obtained from one high T_g polymer.[62] Recently a new conjugated polymer with an ionic tris(bipyridyl)ruthenium complex as the charge generating species has been synthesized. A very large net optical gain of 200 cm^{-1} was obtained at a zero external electric field. However, four-wave mixing diffraction efficiency was still low.[63]

Bifunctional polymers

It is well known that conjugated polymers, due to their delocalized π-electron distribution, have much large carrier mobilities.[64] Thus, conjugated polymer-based photorefractive materials are expected to exhibit a faster response. Thiophene copolymer, poly[3-octylthiophene-co-*N*-(3-thienyl)-4-amino-2-nitrophenol] (POMDT) with second-order NLO chromophores used as a bifunctional host for photorefractive materials has been reported.[65] To 61 wt% of POMDT was added 30 wt% of diisooctyl phthalate (DOP) as a plasticizer, 7.6 wt% of 3-cinnamoyloxy-4-[4-(*N*,*N*-diethylamino)-2-cinnamoyloxyphenylazo]nitrobenzene (CNNB-R) as a chromophore to enhance the linear EO effect and 1.4 wt% of TNF as a sensitizer. The linear and second-order NLO properties, photoconductivity and photorefractivity for this material were investigated; a relatively large two-beam coupling gain coefficient of 24.5 cm^{-1} was obtained.

Carbazole photorefractive composite materials

It is well known that organic photorefractive materials consist of two main functional components: a charge transporting agent and a linear EO agent. Carbazole polymers, such as poly-*n*-vinylcarbazole (PVK), are well known as exhibiting good charge transport properties and their photocharge generation efficiency can be sensitized by the formation of a charge transfer complex between the carbazole moiety and acceptor molecules, such as TNF.[66–68]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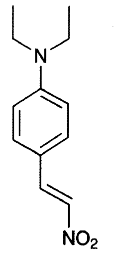
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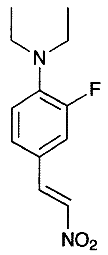
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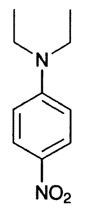
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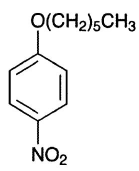
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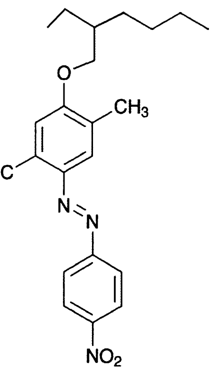
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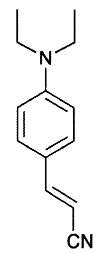
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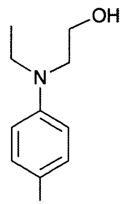
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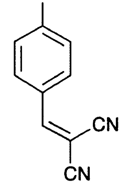
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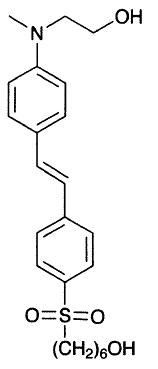
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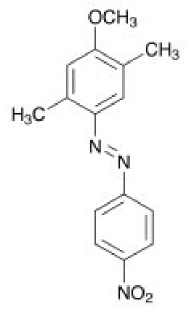
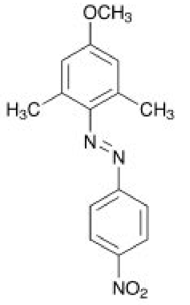


DMNPAA



3,5DMNPAA

PVK with charge transporting functionality has been widely used as the charge transporting host component for organic photorefractive materials.[14,17] An initial report of photorefractivity in a carbazole system was based on a PVK polymer composites in 1992.[69] There has since been increasing interest in such systems owing to the native charge transporting ability of PVK. The high performance of the photorefractive effects (near 100% diffraction efficiency for the readout 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.[70,71] To date, many photorefractive composites based on carbazole polymers, multifunctional polymers with carbazole functional components, carbazole sol–gel systems, amorphous carbazole oligomers and carbazole dendrimers for photorefractivity have been developed.

PVK as a charge transporting host

Zhang *et al.*[69] reported the first carbazole organic composite system for photorefractive materials. C_{60} (0.48 wt%) as a photosensitizing molecule and 4-*N*,*N*-diethylamino-*β*-nitrostyrene (DEANST) (32 wt%) as a second-order NLO chromophore were doped into PVK. Silence *et al.*[39] also used C_{60} as a sensitizer due to the presence of multiple stable reduced state[72] and high triplet yield.[73] C_{60} can form charge-transfer complexes with PVK. For PVK doped with C_{60}, field dependent photocarrier generation followed the Onsager model[74] with very large generation efficiency above 10^6 V cm^{-1}. The high solubility of the C_{60} and the presence of absorption extending throughout the visible led to the evaluation of C_{60} as a sensitizer for photorefractive materials. The photorefractive properties as a function of C_{60} concentration have been studied.[39] The EO coefficient and the photoconductivity of this PVK-based material were determined. Four-wave mixing signal from a 100 μm thick film was measured. It was found that when no electric field was applied, no diffracted signal was detected. When an external field was applied, a diffracted signal was built up. The strong field dependence of the four-wave mixing diffraction efficiency can be explained by the photorefractive effect. This dependence was due to the enhancement of photoconductivity and linear EO coefficient by the applied electric fields. A maximum diffraction efficiency of 2×10^{-5} was obtained at an external field of 50 V μm^{-1}.

Thiopyrylium dye (TPY) as a new photosensitizer was also used in PVK–DEANST systems.[75,76] The composite contained 79 wt% of PVK, 20.8 wt% of DEANST and 0.2 wt% of TPY. Due to the high concentration of DEANST, the composite showed a T_g of 53 °C. The DEANST chromophore can be electrically poled at room temperature in this low T_g composite. This could be confirmed by the observation of EO modulation at room temperature, when a dc electric field was applied. The EO coefficient was measured as a function of the poling electric field and a linear dependence was obtained up to 100 V μm^{-1}, with $r_{33} = 4.2$ pm V^{-1} at 62.5 V μm^{-1}. The photoconductivity sensitivity was measured as 5.4×10^{-11} (Ω cm)$^{-1}$/W cm^{-2}) with 703 nm illumination at 62.5 V μm^{-1}. Photorefractive gratings are written at a wavelength of 703 nm and four-wave mixing diffraction efficiencies as high as 2% have been achieved in films less than 200 μm thick. Asymmetric energy exchange was also observed and a two-beam coupling gain of 7 cm^{-1} was obtained. The application of this material to information storage and image processing has been explored with demonstrations of holographic image recording and retrieval.[76]

Two-beam coupling net gain of organic photorefractive materials was first obtained from a PVK-based composite material.[77] The photoconducting polymer PVK was doped with the optically nonlinear chromophore 3-fluoro-4-*N*,*N*-diethylamino-*β*-nitrosyrene (F-DEANST) (33 wt%) and sensitized for charge generation with TNF (1.3 wt%). The fluoro-substituted second-order NLO chromophore was used due to its absorption at relatively short wavelength. This composite exhibited T_g at about 40 °C, considerably below the T_g of pure PVK (212 °C), owing to the plasticization by the NLO chromophore and residual solvent. A small amount of TNF was added, which forms a charge transfer complex with PVK,[66,78] to provide long wavelength photosensitization. The PVK–F-DEANST–TNF system exhibits diffraction efficiencies as high as 1%, at least two orders of magnitude larger than previously reported values for any organic photorefractive polymer, and more importantly, this material is the first organic to show net internal two-beam coupling gain (>10 cm^{-1}). Grating growth times of the order of 100 ms were observed. These photorefractive values make PVK–F-DEANST–TNF comparable with some of the inorganic photorefractive materials,[79] such as $Bi_{12}SiO_{20}$ and $BaTiO_3$. After this observation, various different second-order NLO chromophores were examined as a functional dopant in a PVK–TNF matrix.[80] It was found that doped PVK composite exhibits enhanced performance of photorefractive effects compared with the previously reported photorefractive polymers. This improvement in performance is partly due to the formation of larger space charge fields and the higher nonlinearity that results from the application of larger poling electric fields. However, the large photoinduced refractive index changes in these new materials cannot be explained by the simple models based on the EO photorefractive effect which have worked so well for previously known photorefractive materials.

In order to explain the large photoinduced refractive changes, a new orientational enhancement mechanism[81,82] was applied to doped PVK[77,80] and other systems.[83] The enhancement relies on the ability of the NLO chromophores to be aligned not only by the externally applied electric field but also *in situ* by the space charge field itself during grating formation. The resulting periodic poling of the sample leads to a modulation of the birefringence of the materials and to a modulation of EO response, the combination of which contributes favorably to the diffraction efficiency fields in the appropriate polarization. A nonlocal photorefractive effect was also observed in a low T_g non-EO PVK-based composite.[84] It was shown that the effects of orientation birefringence and modulation of EO coefficient resulting from the periodic local field induced by the orientation of dipolar chromophores have to be properly taken into account to describe the formation of the refractive index grating.

N,*N*-Diethyl-substituted *para*-nitroaniline (EPNA) (39 wt%) as a second-order NLO chromophore was used to dope the well known photoconductor PVK sensitized with 0.1 wt% of TNF.[85] For the alignment of the EPNA molecules, which is essential for the activation of the EO effect, corona poling with a tungsten needle is used. This poling technique offers the advantage of easier sample preparation compared with using a sandwich cell. The two-beam coupling experiments provided undoubted evidence of photorefractivity for this PVK–EPNA–TNF. A phase shift of 90° was obtained from the modulation of the transmitted power of the two beams when the voltage across the sample increased. Asymmetric energy transfer between the two beams was observed when the corona voltage was switched on. The two-beam coupling net gain of 18 cm^{-1} and response time were measured on a 65 μm thick film at an electric field of about 10 kV.

Control of charge trapping has great technological importance: optimization of charge trapping might be the route toward the longer storage times and high diffraction efficiencies required for optical data storage applications. Based on the PVK–EPNA–TNF system, studies of the modification of the trap density have been carried out by Malliaras.[86,87] The response time and the phase shift of the photorefractive grating as a function of doping with various amounts of DEH have been studied. Measurements indicate that at low concentrations, DEH acts as a trap due to its lower ionization potential, while at higher concentrations a new charge transport pathway through hopping between DEH molecules is established. This behavior has also been observed in the case of PVK doped with TPD.[88] Due to this photoconductive behavior, the response time and the phase shift of photorefractive gratings decrease with a small amount of DEH and increase at relatively higher concentrations of DEH. A small amount of DEH acts as a trap, decreasing the mobility of holes in PVK. As the response time is proportional to the mobility, photorefractive response time follows the same trend. When the concentration of DEH exceeds 1 per 100 carbazole units, DEH begins to contribute to dominant charge transport and the response time increases. The dependence of the phase shift on the DEH concentration can be understood according to the standard theory of photorefractivity.[89]

The transient behavior of the photorefractive grating in the PVK–EPNA–TNF system doped with various amounts of DEH has also been studied.[90,91] The influence of the trap density induced by DEH on the hole drift mobility was directly measured. Study of the transient behavior of the photorefractive gratings in polymers is very interesting, because charge transport in these materials is very different from that in inorganic crystals, displaying a highly dispersive character, and strong temperature and electric field dependence.[92] The holographic time-of-flight technique was applied in a photorefractive polymer composite system.[93,94] In this composite, PVK as a charge transporting host was doped with 40 wt% of 4-(hexyloxy)nitrobenzene (HONB) as a second-order NLO chromophore and 0.1 wt% of TNF as a sensitizer. Two-beam coupling experiments on a 100 μm thick film at 633 nm have shown the PVK–HONB–TNF composite to be purely photorefractive, giving rise to asymmetric energy exchange with a gain coefficient of 3 cm^{-1} at 70 V $\mu\mathrm{m}^{-1}$. The measured electric field, temperature and drift length dependencies of the hole-drift mobility in this composite are in agreement with literature data for PVK.[95]

Based on PVK–EPNA and PVK–HONB, much detailed research work on the space charge field formation[96] and design of functional components such as the role of absorbing NLO chromophores[22,97] has been done also by Malliaras *et al.* Recently they summarized their research work on the mechanism of photorefractivity and unique photorefractivity in PVK-based composite materials.[98]

An azo derivative 1-(2′-ethylhexyloxy)-2,5-dimethyl-4-(4′-nitrophenylazo)benzene (EHDNPB) has been used to provide an EO response in PVK–TNT polymer composite.[98] This type of azo chromophore was first used by Kippelen *et al.*[100] In this case, the chromophore has been modified to incorporate a racemic ethylhexyl group. This nonpolar functionality has two important roles. First, it renders the dye a plasticizer and as such activates the orientation enhancement mechanism.[81] Secondly, it increases the solubility of the dye in PVK inhibiting crystallization. The resulting composite can reproducibly form stable, optically transparent films with good reorientation mobility. No separate plasticizing agent is required. The photorefractive composite consisted of PVK–EHDNPB–TNF in a mass ratio of 44 : 55 : 1. This materials exhibited a 60% device steady-state diffraction efficiency and 120 cm^{-1} two-beam coupling gain, well in excess of its absorption coefficient of 3.5 cm^{-1}, at a wavelength of 676 nm.

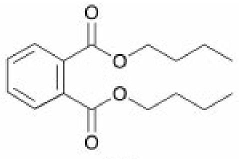
Sandalphon *et al.*[101] reported dual-grating formation through photorefractivity and photoisomerization in azo-dye-doped PVK–TNF polymeric composite. TNF as a sensitizer and disperse red I (DR1) as a second-order NLO chromophore were doped in the PVK host. Photorefractivity and photoisomerization in polymer composites have been studied. Both types of hologram were observed and reversible. The photorefractive diffraction efficiency is strongly dependent on the external applied field, as expected for other photorefractive polymers. High diffraction efficiencies and storage times of several minutes have been demonstrated. The photoisomerization diffraction efficiency was highest in the absence of an applied field and showed some reduction as an external field was applied. Photoisomerization may turn out to be a useful way to enhance the photorefractive properties of these azo-dye-doped polymeric composites for erasable optical storage applications.

Multiple-grating formation was reported in photorefractive composite polymers.[102] In this material, PVK–TNF was doped with two second-order NLO chromophores, (*E*)-4-*N*,*N*-diethylaminocinnamonitrile (DEACST) and DR 1. DR 1 has been proven to show strong photoisomerization grating formation. It was present in the composite at a very low concentration, so that it contributed negligibly to the formation of photorefractive gratings. The composition of the mixture by mass was in the ratio 100:40:0.5:0.5 (PVK–DEACST–DR 1–TNF). Similar results to those observed by Sandalphon *et al.*[101] could be obtained; photorefractive gratings, and photoisomerization intensity and polarization gratings were observed in this material system, essentially a photorefractive polymer ‘seeded’ with an azo-dye to allow the formation and separate optimization of photoinduced gratings.

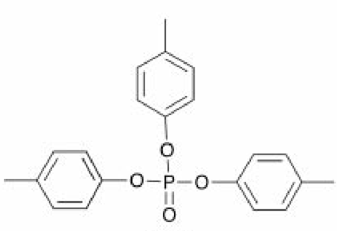
PVK as a charge transporting host with the plasticizers

Most organic photorefractive materials reported so far are host–guest polymeric composites. To break the centrosymmetry of the materials and to obtain a macroscopic EO response, the second-order NLO chromophores have to be aligned by an applied electric field (poled).[14,17] The efficiency of the poling process is strongly dependent on the orientational freedom of the second-order NLO chromophores. At temperatures below the T_g, the polymer chains are frozen and the orientational mobility of the chromophores is very low. As the temperature is raised close to the T_g, the orientational freedom of the chromophores increases, allowing efficient poling. When large amounts of second-order NLO chromophores are doped in PVK, the T_g of PVK (200 °C) is substantially lowered and the chromophores can be oriented even at room temperature. Recently a large increase in the photorefractive performance of a PVK-based polymer composite was observed after the incorporation of additional plasticizer molecules.[70,71] This was caused by an increase in the orientational mobility of second-order NLO chromophores, due to the additional lowing of the T_g, resulting in a higher net alignment and hence a larger EO effect. Moreover, in such systems, the chromophores are reoriented under the influence of the space charge field.[81] In this way, a number of polymeric composites with excellent performance, which approaches or even exceeds that of existing inorganic materials, have been reported.[14,17] Two kinds of plasticizers, inert plasticizers and a charge transporting functional plasticizer, have been used.

Inert plasticizer. Since an electric field is always applied to facilitate photocharge generation, efficient photorefractive effects in low T_g PVK-based polymeric composites should be reasonable. The efficient electric field-induced alignment of the chromophore can be obtained in these low T_g polymer composites. In order to obtain low T_g composite, the material containing PVK and about 0.56 wt% of C_{60} was doped with 25 wt% of DEANST and 20 wt% of a chemically inert plasticizer, dibutyl phthalate (DBP).[103]



DBP



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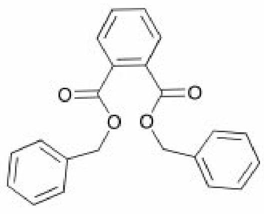
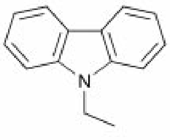


BBP



ECZ

In situ electrical poling experiments on low T_g PVK–DEANST–C_{60} doped with DBP demonstrated that at room temperature the SHG signal strongly increases with the DBP concentration. Moreover, the response time of the NLO active DEANST molecules to the poling field was observed to decrease into the subsecond regime in the PVK–DBP matrix. The composite shows a relatively high field-dependent EO coefficient and quantum yield of photocarrier generation. The photorefractive diffraction efficiencies obtained from this plasticized composite compare well with those of well-known inorganic materials and reached 1.5% at a applied electric field of about 40 V μm^{-1}. The four-wave mixing diffraction efficiency was found to be strongly electric field dependent. This behavior originates in the field dependence of EO activity of the material and the space charge field formation. The photorefractive nonlocal character of the observed effect in the sample was finally confirmed by performing a two-beam coupling experiment. A two-beam coupling gain of 4 cm^{-1} was also obtained at electric field of 40 V μm^{-1}. The composite shows very fast kinetics of photorefractive grating formation and erasure, occurring in the millisecond time scale.

A liquid inert plasticizer, tricresyl phosphate (TCP),[104] was also used in the PVK–C_{60}–DEANST composite system for enhancement of photorefractive performance. This composite contains PVK, 36 wt% of TCP, 3.75 wt% of DEANST and 0.22 wt% of C_{60}. The T_g of PVK–TCP–DEANST–C_{60} was determined to be lower than 14 °C. Due to the low T_g of the composite, the chromophore with a large dipole moment could be perfectly aligned at room temperature. A large EO coefficient was obtained due to efficient plasticization of the host polymeric matrix and a large dipole moment of the NLO chromophore. At a field of 140 V μm^{-1}, the EO coefficient is 37.6 pm V^{-1}, which represents a major increase of the EO activity compared to the related higher T_g composite without plasticizer, PKV–C_{60}–DEANST.[69] Both the diffraction efficiency and the two-beam coupling gain in low T_g polymeric materials are highly dependent on the applied electric field. The electric field plays a crucial and multifunctional role: it forces a noncentrosymmetric alignment of second-order NLO chromophores,[105] it enhances the quantum yield of photocarrier generation,[106] and it assists in transport of the photogenerated carriers.[107] Diffraction efficiency as high as 40% and asymmetric net two-beam coupling gain coefficients in excess of 130 cm^{-1}, surpassing those of known inorganic single crystalline photorefractive media, were obtained from this composite at an applied electric field of 110 V μm^{-1}.

More recently, the IBM group reported a high performance photorefractive polymer based on PVK doped with the second-order NLO chromophore, 4-piperidin-4-ylbenzylidene-malononitrile (PDCST), the liquid plasticizer butyl benzyl phthalate (BBP) and C_{60} for increased charge generation at longer wavelengths.[71] In comparison to the use of the crystal plasticizer, BBP showed dramatic suppression in crystallization. This photorefractive composite, PVK–PDCST–BBP–C_{60}, with a mixing ratio of 49.5 : 35 : 15 : 0.5 wt% showed T_g at 28 °C. The electric field dependence of photorefractive effects was measured. This photorefractive polymer composite with improved material stability exhibited a high two-beam coupling gain coefficient of 200 cm^{-1}, and a fast response time of 50 ms at 100 V μm^{-1} and at 1 W cm^{-2}. Overmodulation of the diffraction efficiency and a high sensitivity of about 3 cm^3 kJ^{-1} were also obtained from this photorefractive material. All the photorefractive properties of this material compare with those of the faster inorganic crystals.[14]

Temperature dependence studies of the photorefractive effect in PVK–TCP–DEANST–C_{60} prepared in the mixtures in the mass ratio 60.03 : 36 : 3.75 : 0.22% have been carried out in the temperature range 20–75 °C.[108] It was found that as the temperature of the sample increases, an increase in the photorefractive figures of merit, such as diffraction efficiency, two-beam coupling gain coefficients and speed of grating formation and erasure, are seen. At elevated temperatures, decreased rigidity of the host matrix leading to increased orientational mobility of the second-order NLO chromophores results in enhanced photorefractive performance. When the applied electric field was fixed at 90 V μm^{-1}, the diffraction efficiency increased with temperature. For temperatures above 37 °C, the diffraction efficiency approached 100%. Also an increase in the two-beam coupling gain coefficient from 55 cm^{-1} at 25 °C to 95 cm^{-1} at 40 °C was obtained. The observed increase in the speed of erasure with temperature is consistent with the results of measurements of the quantum yield of photocarrier generation and the carrier mobility for the polymeric composite discussed. At a poling field of 9 V μm^{-1} and temperature of 20 °C, the quantum yield of photocarrier generation was of the order of 10^{-6}, and the carriers' mobility was found to be 10 cm^2 V^{-1} s^{-1}. When the sample was heated to 58 °C, the quantum yield of photocarrier generation increased fourfold and the hole mobility increased by more than one order of magnitude. In order to achieve a broad spectral response, a new second-order NLO chromophore, 4-[*N*-(2-hydroxyethyl)-*N*-methylaminophenyl]-4′-(6-hydroxyhexylsulfonyl)stilbene (APSS) with high transparency over a broad wavelength was used together with a PVK–TCP–C_{60} matrix.[108] The composite PVK–TCP–APSS–C_{60} was prepared with a mass ratio of 47.7 : 47.6 : 4.5 : 0.2%. This composite with low T_g shows high photorefractive figures of merit at 488, 514.5 and 632.8 nm. Diffraction efficiencies up to 40%, as well as net two-beam coupling of 60 cm^{-1} have been achieved at these operating wavelengths.

N-Ethylcarbazole as a charge transporting plasticizer. According to charge transporting functional requirements of photorefractive materials, Kippelen *et al.* first used N-ethylcarbazole (ECz) as a charge transporting functional plasticizer.[100] In comparison to the use of inert materials as plasticizers, ECz shows important charge transporting for photorefraction and allows one to keep charge transporting functional moieties at a high ratio. We believe that further improvements in stability will be achieved when suitable liquid or amorphous functional plasticizers are developed. Based on carbazole polymer PVK, one composite system containing ECz as a functional plasticizer has been reported to exhibit high photorefractive effects by Meerholz *et al.*[70] Much research work on photorefractive materials followed this report using the same type of second-order NLO chromophores[99,109,110] or the same carbazole functional plasticizer.[103,109,111]

ECz plasticized PVK-based photorefractive system doped with 2,5-dimethyl-4-(p-nitrophenylazo)anisole (DMNPAA) as an EO chromophore was first reported by Kippelen *el al.*[100] As the dipoles of the second-order NLO molecules are randomly oriented, there is *a priori* no overall EO effect in these materials. Second-order NLO properties of the bulk material can only be induced by poling the chromophores by an external electric field. Azo-dye-doped PVK composites exhibited rather low T_g, because the chromophores act as a plasticizer for the PVK matrix, *i.e.* with increasing dye concentration the glass transition temperature decreases. However, the concentration of the dye is limited due to crystallization. In order to overcome this problem and further decrease T_g at around room temperature, ECz was added as a charge transporting plasticizer. The chromophores were then aligned by the dc electric field that is applied for photorefractive and photoconductive recording. The charge transfer complex between PVK and TNF provides photosensitivity in the visible spectrum. Compared with other azo dyes, such as DR 1, the best results were obtained for PVK–ECz–TNF doped with DMNPAA.[112] A suitable second-order NLO chromophore azo dye DMNPAA with an absorption band at relatively short wavelength was selected. The performance of PVK–DMNPAA–ECz–TNF was improved considerably by Meerholz *el al.*[70] to 86% diffraction efficiency and a net two-beam coupling gain of more than 200 cm^{-1}. This performance by far surpasses that of the other organic photorefractive materials reported to date. High performance in photorefractive effects was obtained from this material due to the usage of an appropriate second-order NLO chromophore, plasticizer and component ratio. PVK–DMNPAA–ECz system doped with C_{60} as a photosensitizer was also demonstrated to exhibit high performance photorefractive effects.[113]

The birefringence, the linear EO and Kerr properties of low T_g PVK–DMNPAA–ECz–TNF photorefractive polymers have been measured by a simple frequency-dependent ellipsometric technique.[114,115] The birefringence induced by the orientation of chromophores in this low T_g composite polymer plays a major role in the overall field-induced refractive index change. For the first time, Kerr contributions in photorefractive polymers were identified. This study clearly shows that modulated birefringence is responsible for the high steady-state diffraction efficiencies measured in four-wave mixing experiments in PVK–DMNPAA–ECz–TNF due to the orientation of DMNPAA. In order to compare the contribution from the birefringence with other second-order NLO chromophores, F-DEANST was used.[114] It was found that the DMNPAA–PVK–ECz–TNF composite has a much higher orientational birefringence contribution to the total refractive-index modulation at low ac frequencies compared with that of the F-DEANST–PVK–ECz–TNF composite. The difference in orientational birefringence can explain the higher four-wave mixing diffraction efficiency observed for the DMNPAA composite over that of the F-DEANST composite. Because the local poling field in the photorefractive material is essentially dc for four-wave mixing, the large contribution from the poling birefringence to the total refractive index modulation in the DMNPAA doped composite more than compensates for the smaller contributions arising from the linear EO and the Kerr effects. This technique should be very useful for the screening of many candidate materials in the search for those with optimized performance. In traditional photorefractive materials, the refractive index modulation arises solely from the space charge field acting on the EO effect of the materials.[1] Thus, the photorefraction in high T_g polymers is related purely to EO effects. In contrast, photorefractive polymers with a low T_g exhibit an orientational contribution to the refractive index modulation. The chromophore design approach to orientational enhancement of photorefractive has recently become an interesting research topic.[49,116]

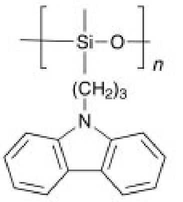
To date, among organic photorefractive materials, the PVK–DMNPAA–ECz–TNF composite is the best photorefractive polymeric material. However, there are inherent problems of phase separation with such a high density of functional components in the multi-component system. In order to improve long-term stability of this high performance photorefractive composite system, two approaches have been tried. First, a racemic ethylhexyl group has been incorporated into the azo chromophore.[99] Secondly, the eutectic mixture of the two isomeric azo second-order NLO chromophores, DMNPAA and 3,5-dimethyl-4-(p-nitrophenylazo)anisole (3,5DMNPAA) could considerably lengthen shelf-life.[117] Devices using this eutectic composite remain clear for over one year under ambient laboratory conditions. The internal performance of these improved materials was found to be comparable to that of the best materials known previously.

The photorefractive polymeric composite DMNPAA–PVK–ECz–TNF shows diffraction efficiencies as high as 86%, two-beam coupling gain coefficients of more than 200 cm^{-1}, refractive index modulations up to 7×10^{-3}, good sensitivity, and reasonably fast response times (about 0.5 s) and is useful as a recording medium for dynamic holographic interferometry and pattern recognition.[70,118–121] Devices can be operated with inexpensive low-power laser diodes, unlike many other holographic recording materials that require expensive high-power laser systems. The device performance can be easily adjusted by means of an external voltage. Information is reversibly stored in this polymer. Thus, storage, readout, and erasure can be carried out such that one device can be used for real-time monitoring with no additional intermediate developing steps. This photorefractive polymeric material has been successfully demonstrated in efficient optical image processing applications.[120] Furthermore, the use of such high performance photorefractive polymers in an optical pattern recognition system for security verification has also been demonstrated recently.[123] Good quality interferograms of the mode patterns of a vibrating membrane with good fringe contrast were obtained by using inexpensive laser sources, such as laser diodes or HeNe lasers.[120]

A systematic study of the effect of plasticization on the photorefractive performance of PVK based polymeric composites was also reported.[124] It is shown that ECz can be used as an efficient plasticizer, leading to a large increase in the gain coefficient and the diffraction efficiency, which arises solely due to an improvement in the orientational mobility of the NLO chromophores and was not caused by the alteration of the space charge field. Phase separation was observed in samples with a high ECz concentration.

Carbazole polysiloxanes as charge transporting hosts

Zobel *et al.*[110] first reported photorefractive materials based on carbazole polysiloxane (PSX).



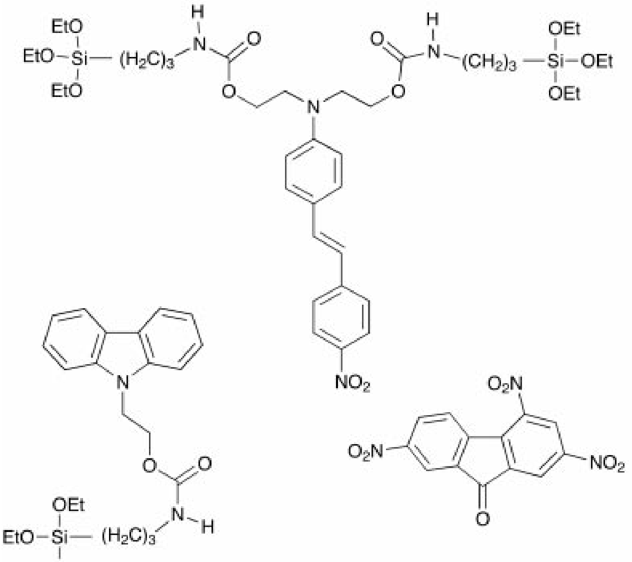
PSX

A large number of carbazole-containing polymers have been prepared.[125–127] Among these carbazole polymers, PSX shows relatively low T_g, and the T_g could be controlled in a very wide range from -45 to 51 °C by introducing different spacer lengths. PSX with a T_g at 51 °C was selected as a host for photorefractive materials due to the relatively high ratio of charge transporting function. A composite was obtained from a mixture of PSX (56 wt%), the second-order NLO chromophore DMNPAA (43 wt%) and TNF (1 wt%). Due to the low T_g of this PSX composite, no plasticizers were necessary in this case. A laser beam of wavelength 650 nm was used for four-wave mixing and two-beam coupling measurements. A large diffraction efficiency of 60% and net optical gain of 220 cm^{-1} were obtained from this composite. According to the behavior of both the phase and amplitude of the resulting refractive index grating, the photoisomerization and the photorefractive grating are competitive. However, at electric fields larger than about 10 V μm^{-1}, the refractive index change due to the photorefractive grating exceeds that of the photoisomerization grating. It can be shown that with this composite material the orientational effects of the DMNPAA dominate the photorefractive effect. The authors pointed out that in order to obtain pure electronic photorefractive effects, the photoconductive and the second-order NLO properties of this material must be further improved.

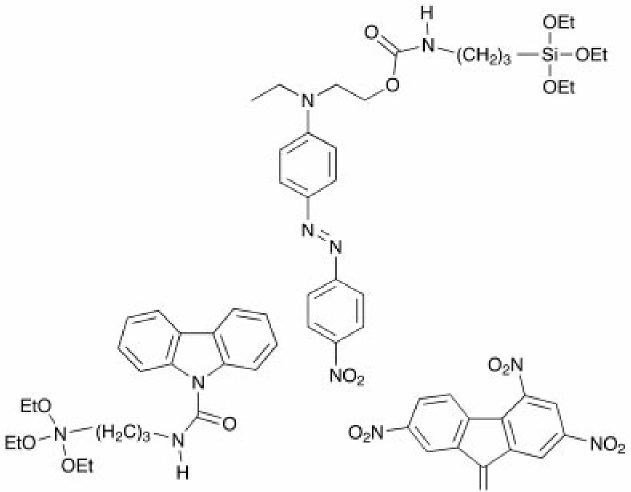
The same carbazole PSX and electron acceptor molecule TNF have also been used in photorefractive composites by the IBM group.[128] In this case, 33 wt% of F-DEANST was used as a second-order NLO chromphore. Photorefractive and optical data storage measurements were carried out on this composite. High photorefractive performance was also demonstrated. PSX composites exhibit excellent optical clarity and low optical scattering characteristics. These optical properties are necessary in high density holographic digital data storage applications. The utility of PSX based photorefractive polymers for storage applications was demonstrated by recording digital data at a density of 0.52 Mbit cm^{-2} and reading it back without error up to 5 min after recording.[128]

Carbazole sol–gel photorefractive materials

Sol–gel processed optically transparent silica based materials are a new generation of multifunctional molecular composites used in the design of optical devices.[129,130] Sol–gel technology provides an attractive route to the preparation of rigid amorphous inorganic oxide glass matrices at ambient temperatures, in which dopants such as inorganic and organic functional moieties can be successfully incorporated. A wide variety of unique functional composites can be formed using sol–gel inorganic–organic processing techniques. In the last few years, studies have also focused on NLO sol–gel systems.[131,132] Two sol–gel processed composites exhibiting photorefractive effects have recently been reported by Burzynski *et al.*[133] and Chaput *et al.*[134] In both cases, a carbazole derivative (Cz) was used as a charge transporting agent and formed a charge transfer complex with TNF to facilitate photocarrier generation at the visible wavelengths. 4-[*N*,*N*-Bis(β-hydroxyethyl)amino]-4′-nitrostilbene derivatives (DHD) and DR 1 were used as second-order NLO chromophores by Burzynski *et al.* and Chaput *et al.*, respectively. In Burzynski's case, EO effects and photoconductivity have been observed. Holographic four-wave mixing and two-beam coupling experiments proved the photorefractive nature of the sol–gel composite DHD–Cz–TNF.



DHD:CZ:TNF



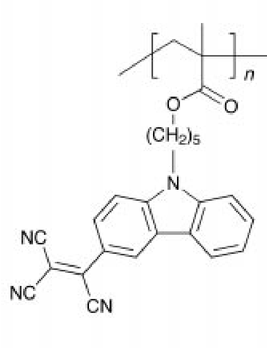
DR1:CZ:TNF

The materials show a low diffraction efficiency (0.01%) and a small two-beam coupling gain coefficient (0.3 cm^{-1}). In Chaput's case (DR 1–Cz–TNF), noncentrosymmetric chromophore orientation and a large stable EO response (15 pm V^{-1}) were obtained. A large two-beam coupling gain of 110 cm^{-1} was obtained at a wavelength of 633 nm. However, comparison with the absorption coefficient of 450 cm^{-1} means that a net gain cannot yet be achieved. Such a two-beam coupling gain has been obtained without applying external electric fields during the two-beam coupling measurements. Although these materials show a low diffraction efficiency and non-net two-beam coupling gain coefficient, the sol–gel processing of composite, seems to be a promising approach towards the preparation of photorefractive materials. Sol–gel processing offers materials with excellent optical qualities and the potential for retaining the orientation of chromophores during the formation of the sol–gel by applying an electric poling field.

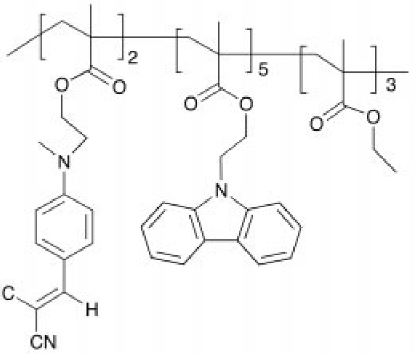
Carbazole multifunctional photorefractive polymers

Many types of multifunctional functional polymers have been developed for photorefractive materials to suppress further phase separation. Among these polymers, polymers containing the carbazole moiety as a charge transporting agent, bifunctional chromophores or multifunctional chromophores have been reported.[135–139] Some multifunctional polymers with both EO and charge transporting moieties must be doped with a suitable sensitizer. However, phase separation cannot observed owing to the very low concentration of the dopants.

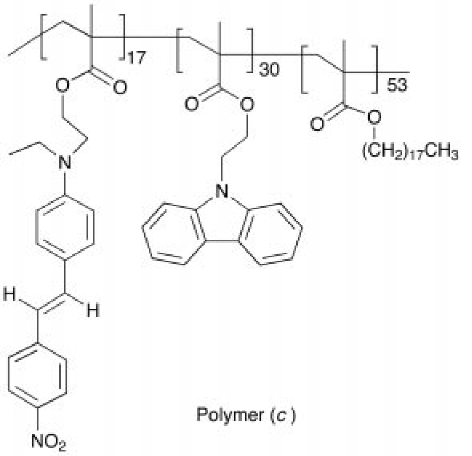
The first fully functional photorefractive polymer was developed based on carbazole moieties [polymer (*a*)][135] in 1992.



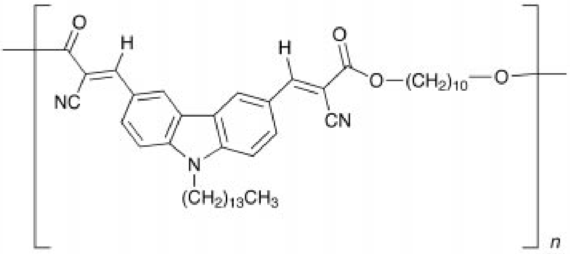
Polymer (*a*)



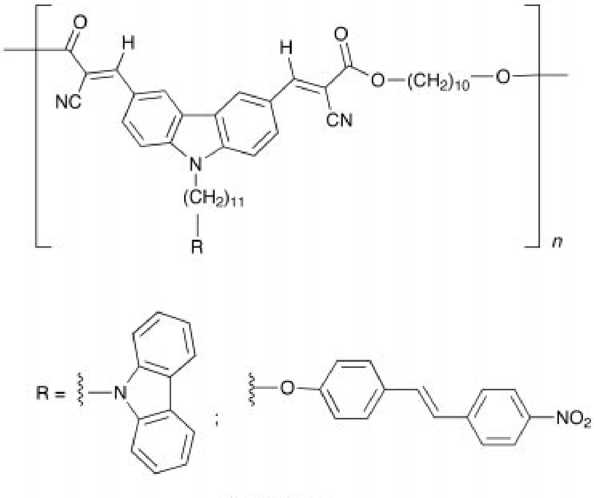
Polymer (*b*)



Polymer (*c*)



Polymer (*d*)



Polymer (*e*)

In this polymer, some of the carbazole groups were tricyanovinylated. Carbazole substituted with tricyanovinyl group had two functions: second-order nonlinearity and photocharge generation. Carbazoles with no acceptor groups could offer a charge transporting function. A photoconductivity of 9.8×10^{-10} $\Omega^{-1}\,\mathrm{cm}^{-1}$ and EO coefficient of 6.1 pm V^{-1} were measured. Evidence for absorptive and photorefractive gratings has been obtained by four-wave mixing experiments and EO measurements.[136] The photorefractive grating was studied by investigating the electric-field dependence of the diffraction efficiency. The absorption changes due to permanent photobleaching are dominant in the absence of any external electric effect for this polymer. The dynamics of the erase–write behavior of gratings was also studied in these polymers. Due to low mobilities, the material has a slow response. However, it is believed that mobilities can be increased and the absorption grating can be avoided by using suitable sensitizers and a longer wavelength of a laser.

PMMA-like polymer (*b*), DCVANMA–CzEtMA–EA (2 : 5:3)[137] doped with 2.3 wt% of TNF for photorefractive materials has also been reported. In this system, carbazole can form charge transfer complexes with TNF. This complex acts as a photocarrier generation function at a wavelength of 633 nm due to its absorption coefficient at the same wavelength. Diffraction efficiency was of the order of 10^{-6}; the change in the refractive index was reversible in this polymer system. It was found that the observed photorefraction was mainly due to the molar refraction change in the carbazole moiety caused by photoinduced ionization. This provides evidence that trapped ion radicals exist in the polymer forming grating, which is necessary for real photorefractivities.

Another low T_g polymer PENHCOM[138] [polymer (*c*)] based on the PMMA structure doped with 0.2 wt% of TNF has also been developed. In this polymer, 4-[*N*-ethyl-*N*-(2-hydroxyethyl)amino-4′-nitrostilbene] was used as a second-order NLO chromophore and the carbazole moiety was used as a charge transporting agent. In order to obtain a copolymer with a low T_g, long aliphatic octyl chains were attached to the side chain as a plasticizer. The ratio of the functions X : Y : Z is 17 : 30 : 53. 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 V μm^{-1}.

More recently, polymers containing a single multifunctional carbazole chromophore [polymer (*d*)] have been obtained in our laboratory.[139] In this polymer, carbazole substituted with two acceptor groups exhibited multifunctional properties. The carbazole chromophores lie parallel to each other, in a 'shoulder-to-shoulder' arrangement. In this arrangement, alignment of dipole moment is more readily achievable by applying an electric field than in the structures where dipole moments are pointing along the polymer main chain. The T_g was strongly dependent on the length of the alkyl spacer between the carbazole chromophores and of the alkyl group at the 9-position of the carbazole ring. The T_g could be controlled in the range from 35–87 °C. Among these carbazole main-chain polymers, polymers with a relatively low T_g enable photorefractive measurements to be made at room temperature. These carbazole main-chain polymers have proved to have both photoconductivity and EO activity.[140] 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 V μm^{-1}, 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 with the same electric field.

Carbazole main-chain polymers with additional functional moieties [polymer (*e*)] exhibit more efficient photorefractive effects[141] compared with pristine polymer.[139] It was found that the polymer with a carbazole moiety as a charge transporting functional side group showed a net two-beam coupling gain of about 45 cm^{-1} and a diffraction efficiency of 2.5% at an applied electric field of 23 V μm^{-1}. Carbazole main-chain polymers with an additional second-order NLO chromophore in the side chain exhibited enhanced second harmonic coefficients.

Carbazole photorefractive chromophores

Design approach

Since the carbazole molecule has a structure isoelectronic with diphenylamine, the introduction of electron-withdrawing groups in the 3- and/or 6-position induces intracharge-transfer and a mesomeric dipole moment. Depending on the electron-affinity of acceptor groups, polarizabilities of carbazole derivatives can be tuned by appropriate molecular design of the substituent groups.[142] Acceptor-introduced carbazoles have been shown to be very promising as second-order NLO chromophores.[143,144] Besides the 3- and 6-substitution positions, *N*-substitution (9-position) allows various chemical modifications: solubilization and amorphism of substituted carbazole by different length of alkyl chain on the 9-position,[145,146] and control of noncentrosymmetric packing in the crystalline state through hydrogen bonding.[147]

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 chromophores is the first approach to try to develop one chromophore with more than one function.[53,55] 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.[57] These materials also exhibited improved optical quality due to the reduction in the number of dissimilar constituents. Recently, the IBM group reported that a family of related dihydropyridines can be used to formulate organic photorefractive materials which represent significant advances in many respects.[19] The most novel aspect of these chromophores is that in high concentrations they form stable organic glasses instead of microcrystallites. In this case, there is no need to devote sample volume to a host polymer or to plasticizing constituents because the chromophores form optical quality films even at 100% chromophore concentration. These chromophores show three functions: second-order NLO properties, charge transporting properties and glass state formation properties. High performance photorefractive effects have been obtained from these so-called photorefractive glass molecules doped with small amounts of a sensitizing agent, such as C_{60} or TNF.

Recently, we developed fully amorphous chromophores for photorefractive materials.[20,148] 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 T_g. We believe that our carbazole-based design approach has more flexibility for chemical modification, and different types of materials can 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 excellent charge transporting properties and relatively high carrier mobility of the conjugated carbazole polymers and oligomers.[149]

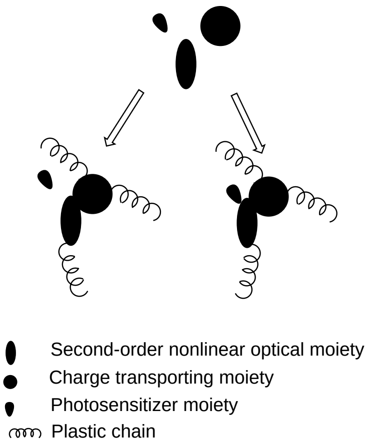
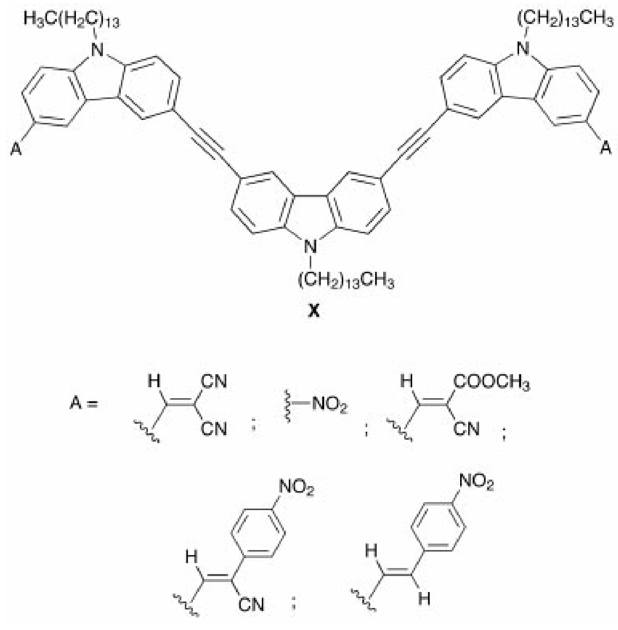


Fig. 1 Molecular design approach to amorphous non-polymer photorefractive materials

It is well known that photorefractive materials are multifunctional. Until now, 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.[150,151] Some successful examples follow.

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 substituted 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.



X

Multifunctional carbazole conjugated trimers

A dicyanovinyl substituted trimer with a T_g of 29 °C has been used as a model example for studies of photorefractive effects.[21] 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 sandwiched between Al and indium-tin oxide (ITO) electrodes.[25] 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 (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.[66] 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 T_g of the trimer, 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.[28] 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.[31] Fig. 4 shows the electric field dependence of the EO coefficient. These values are comparable with those obtained from other photorefractive materials systems.[16,99] The photorefractive nature of the trimer

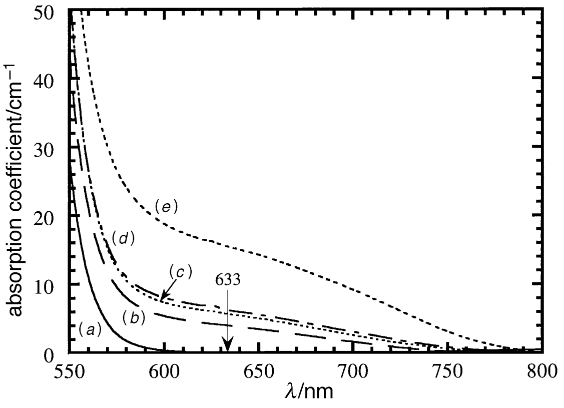


Fig. 2 Absorption spectra of trimer doped with different TNF concentrations: (*a*) 0, (*b*) 0.055, (*c*) 0.06, (*d*) 0.0625 and (*e*) 0.125 wt%

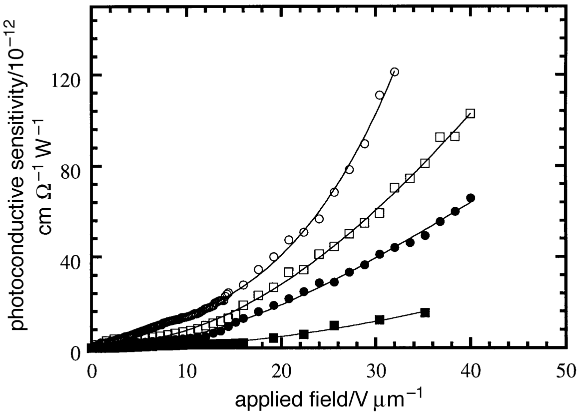


Fig. 3 Photoconductive sensitivity as a function of the applied electric field for dicyanovinyl-substituted carbazole trimer doped with different TNF concentrations: (●) 0.05, (○) 0.06, (□) 0.125 and (■) 0.5 wt%

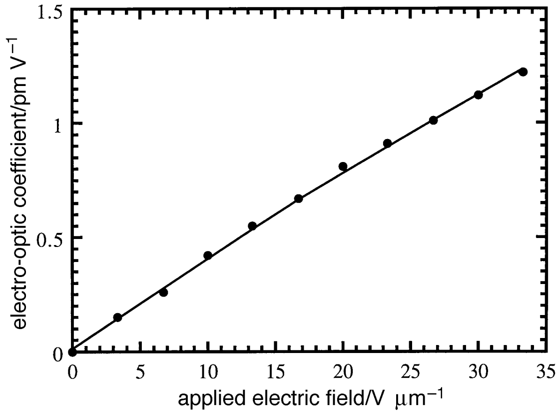


Fig. 4 The electro-optic coefficient of dicyanovinyl-substituted carbazole trimer as a function of the applied electric field at an ac frequency of 6 KHz

was confirmed by a two-beam coupling experiment. Two important photorefractive effects were observed. According to the standard model of photorefractivity,[89] the phase shift between the illumination pattern and the refractive index grating increased with the applied electric field (Fig. 5:). It was found that the phase shift at low electric fields is non-zero between 0 and 90°. At relatively high electric field, the phase shift approaches 90°. Asymmetric energy transfer between the two beams caused by the non-zero phase shift was also observed from a trimer sample when an electric field was applied. The nonlocal nature of the index grating arises from an applied electric field which makes the sample photoconductive and EO active.[14] Fig. 6 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. It was found that the diffraction efficiency depended strongly on the applied electric field (Fig. 7) and reaches 18.3% at a field of 30.6 V μm^{-1} in a 0.06 wt% TNF doping sample. The effect of optimized TNF concentration was also found in the photorefractive two-beam coupling and four-wave mixing experiments.

Unlike the two-beam coupling experiment, the four-wave mixing diffraction efficiency is not dependent only on the phase shift of the grating. In principle, local gratings induced by many other mechanisms such as photochromism, thermochromism and photochemical effects, can also contribute to the diffraction efficiency. In order to confirm the diffraction efficiency of the trimer arising from pure space charge field induced effects, the modulation of the refractive index can be determined from the diffraction efficiency and the two-beam coupling gain, independently. The modulation of the refractive index from both measurements is in good agreement within experimental error (as shown in Fig. 8) This result indicates that the nonlocal index grating is the dominant mechanism of the holographic gratings.

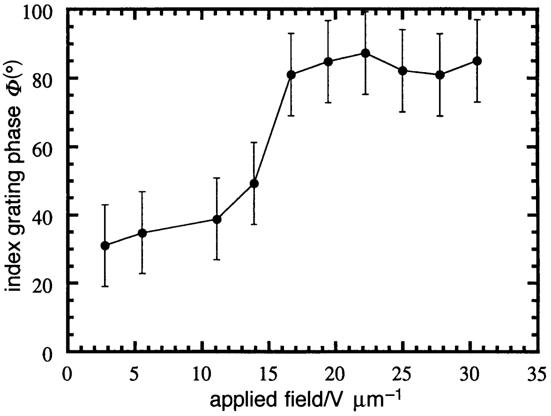


Fig. 5 The phase shift of index grating of dicyanovinyl-substituted carbazole trimer doped with 0.06 wt% TNF as a function of the applied electric field

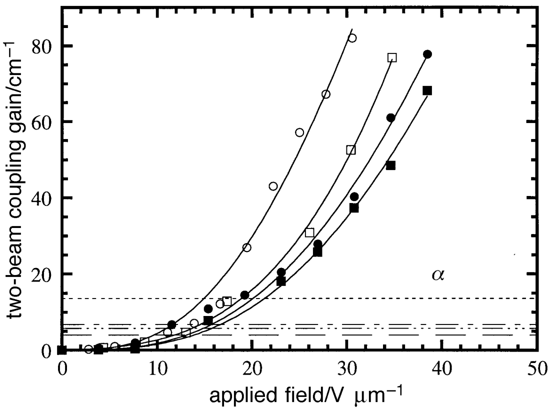


Fig. 6 The photorefractive gain coefficient as a function of the applied electric field for dicyanovinyl-substituted carbazole trimer doped with different TNF concentrations: (□) 0.055, (○) 0.06, (●) 0.0625 and (■) 0.125 wt%

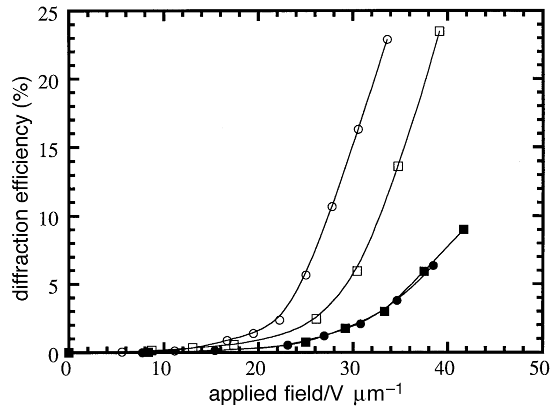


Fig. 7 The diffraction efficiency as a function of the applied electric field for dicyanovinyl-substituted carbazole trimer doped with different TNF concentrations: (■) 0.05, (□) 0.055, (○) 0.06 and (●) 0.0625 wt%

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.

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.[152] In this trimer, carbazole rings 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 532 nm. This trimer was demonstrated to be both photoconductive

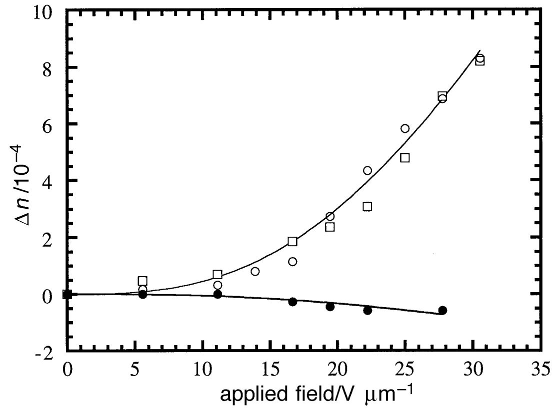


Fig. 8 Magnitude of index modulation of dicyanovinyl-substituted carbazole trimer doped with 0.06 wt% of TNF *versus* applied electric field: calculated from (○) p-polarized two-beam coupling gain, (●) s-polarized two-beam coupling gain and (□) p-polarized diffraction efficiency

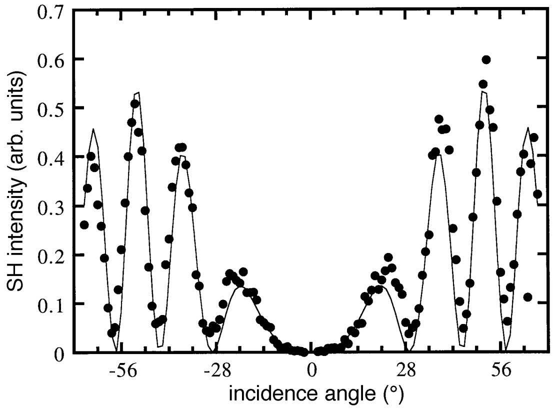


Fig. 9 The SH intensity of carbazole trimer with a nitro group as a function of incidence angle at an applied electric field of 23 V μm^{-1}

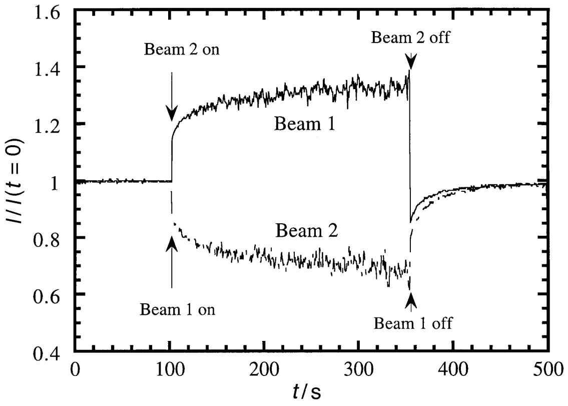


Fig. 10 The intensity of beam 1 (upper trace) monitored as beam 2 (lower trace) is switched on at time $t=0$ s and off at $t=255$ s, and the intensity of beam 2 monitored as beam 1 is turned on and off. The applied electric field was 33 V μm^{-1}

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 T_g of 20 °C 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 T_g of the carbazole trimer. The SH intensity is strongly dependent on the applied electric field. Fig. 9 shows the angular dependence of the SH intensity at a poling electric field of 23 V μm^{-1}. The photoconductive properties were studied on a sample sandwiched between an ITO and a gold coated glass substrate at a wavelength of 532 nm.[25] 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 groups was measured to be 1.2×10^{-11} cm S W^{-1} at an external field of 39 V μm^{-1}. No detectable dark conductivity was observed. It was found that the photocurrent increased rapidly with a time constant <0.1 s upon exposure to light as a result of the large carrier mobility of the carbazole trimer.

The photorefractive properties of the trimer were characterized by a two-beam coupling and a four-wave mixing. In the two-beam coupling experiment, an asymmetric energy transfer between the two beams was observed when an electric field was applied. This provided proof that an electronic photorefractive effect is present.[14] Fig. 10 shows typical asymmetric behavior for the monolithic carbazole trimer at an applied electric field of 33 V μm^{-1}. The two-beam coupling gain coefficient could be estimated from the asymmetric energy

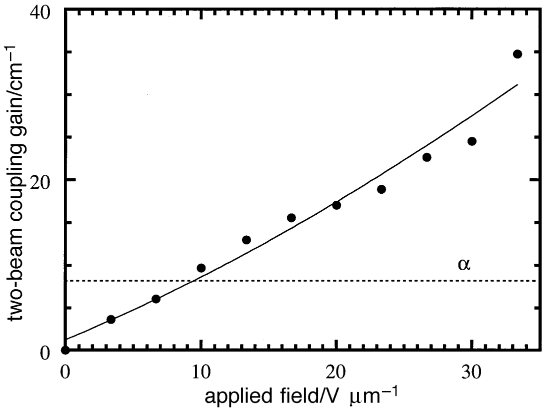


Fig. 11 The two-beam coupling gain of a nitro-substituted carbazole conjugated trimer as a function of the applied electric field. The dashed line is the absorption coefficient at a wavelength of 532 nm.

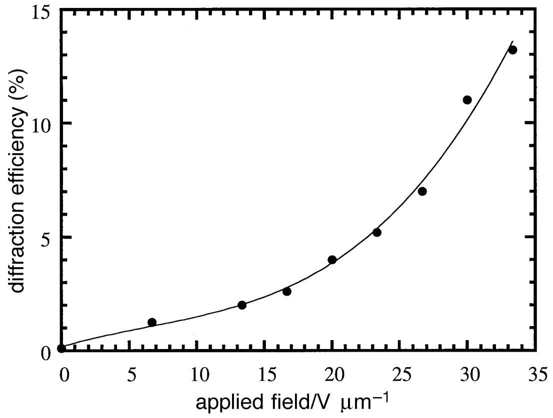


Fig. 12 The diffraction efficiency of a nitro-substituted carbazole conjugated trimer as a function of the applied electric field

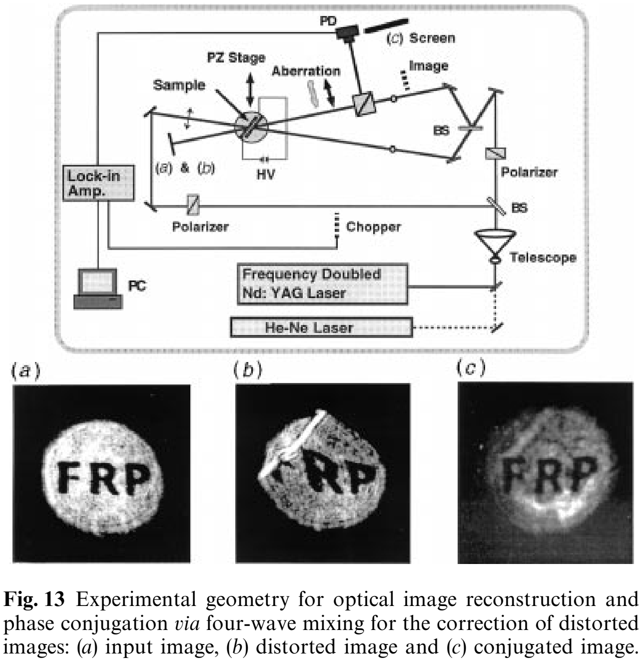


Fig. 13 Experimental geometry for optical image reconstruction and phase conjugation *via* four-wave mixing for the correction of distorted images: (*a*) input image, (*b*) distorted image and (*c*) conjugated image. Reproduced by permission from ref. 153.

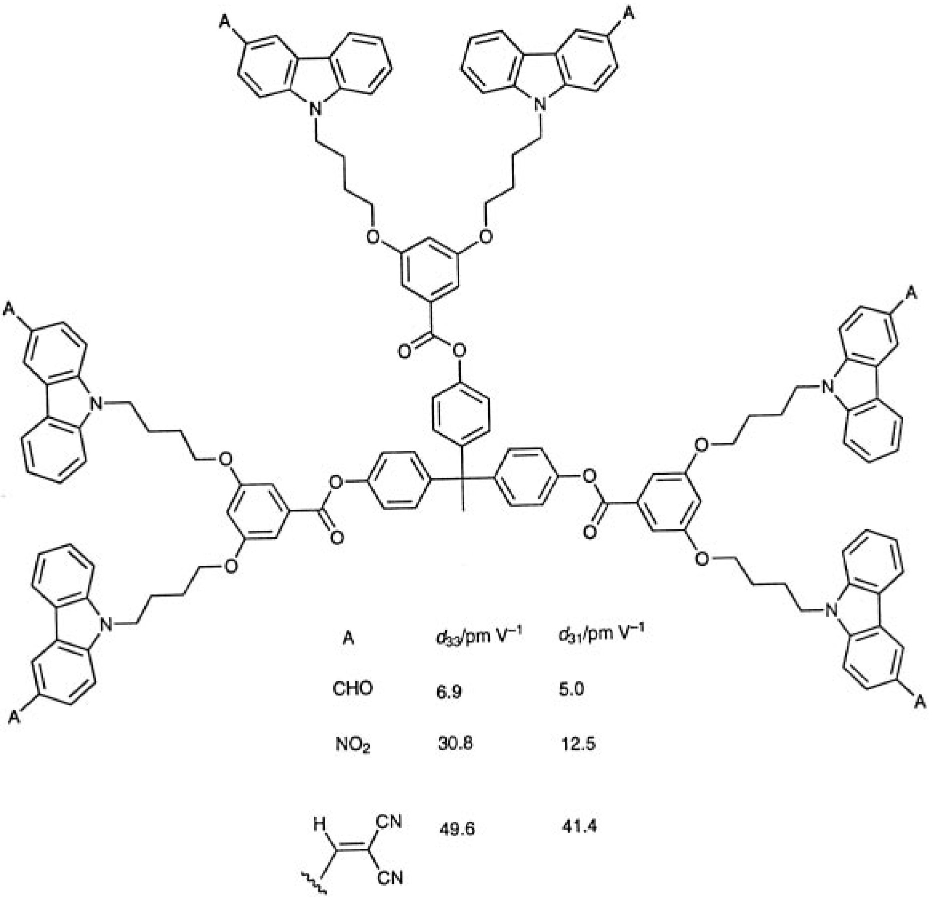


Fig. 14 Chemical structures and d_{ij} values of carbazole dendrimers

transfer. The two-beam coupling gain increases monotonically with the applied electric field as shown in Fig. 11. At an applied electric field of 33 V μm^{-1}, a photorefractive gain of 35.0 cm^{-1} was obtained. The absorption coefficient for this trimer was 8.2 cm^{-1}, leading to a net two-beam coupling gain coefficient of 26.8 cm^{-1}. The applied electric field plays an important role in enhancing the photorefractive effects because of improved alignment of the second-order NLO chromophores and higher photoconductivity at a higher electric field. If an external electric field is not applied during writing, no detectable gratings are observed due to the centrosymmetric random alignment of second order NLO chromophores. Four-wave mixing was used to determine the steady-state diffraction efficiency of the carbazole trimer. Fig. 12 shows the dependence of the diffraction efficiency on the applied electric fields. At an electric field of 33.3 V μm^{-1}, a diffraction efficiency of 13.2% was reached. Optical image reconstruction of distorted images (as shown in Fig. 13) using phase conjugation was demonstrated in this monolithic photorefractive material.[153]

Carbazole dendrimers. The development of materials with new chemical structures for photorefractivity is an extremely active field.[14,17] In order to develop new amorphous molecules with good modification flexibility, dendrimers have been selected as a molecular design approach to photorefractive materials. Dendrimeric structures have several advantage for design of photorefractive materials: (1) they are amorphous, (2) the core and different generation can be modified with different functions for meeting the multifunctional requirements of photorefractive materials, (3) different dendrons with different functions can also meet the multifunctional requirements. Their spherical structure is expected to impart unusual properties.

Several dendrimers with mono-acceptor substituted carbazoles as the multifunctional chromophores have been synthesized in our laboratory.[153] These carbazole dendrimeric oligomers have film-forming properties and show glass transition behavior. Values of T_g could be controlled by the length of spacer, and the number of carbazole rings or acceptor groups. Amorphous molecular solid films could be prepared without a supporting matrix by spin-coating. These thin films could be poled above T_g to achieve noncentrosymmetric alignment of the molecular dipoles required for an EO response. Second-order NLO responses were examined on thin films by SHG. The values of the second-order NLO coefficients (d_{ij}) were strongly dependent on the acceptor groups. The chemical structures and d_{ij} values are summarized in Fig. 14. Photoconductive properties of this dendrimer system have been examined by means of a xerographic discharge technique. It is clear that these molecular systems have multifunctional properties, *i.e.* both photoconductiveity and second-order NLO responses. Two-beam coupling experiments on dendrimers with carbazole substituted with dicyanovinyl groups indicated that the induced index grating is shifted by 90° with respect to the light intensity grating. 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 with a zero applied electric field.

Summary and outlook

Considerable progress has been made in understanding both the photorefractive origins as well as the molecular design of amorphous organic photorefractive materials. For example, many interesting new phenomena which do not occur in crystalline materials have been observed. The material design approach based on a single chromophore has been developed.

Many organic amorphous materials with low cost and ease 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. Several successful examples of photorefractive materials, such as high T_g polymers,[69,141] sol–gel composite materials,[134] and amorphous dendrimers,[153] have been reported and demonstrated to display photorefractive effects with a driven applied electric field.

For low T_g photorefractive materials, the high performance of photorefractive effects reported mainly comes from the contribution of orientation induced birefringence. According to the application requirements, materials with photorefractive effects contributed by EO effects should be promising candidates for practical applications.

Due to the limitation of space, this paper did not include photorefractive liquid crystals[154–156] and only summarizes amorphous organic photorefractive materials based on materials chemistry.

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