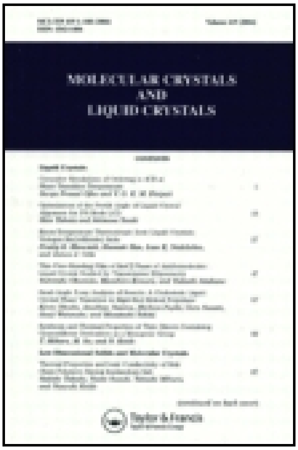

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Tatsuo Wada [a] , Yadong Zhang [a] , Mieko Yamakado [a] & Hiroyuki Sasabe [a]
[a] Frontier Research Program, RIKEN, Hirosawa 2-1, Wako, Saitama, 351-01, JAPAN

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LINEAR AND NONLINEAR OPTICAL PROPERTIES OF CARBAZOLE-CONTAINING POLYMERS

TATSUO WADA, YADONG ZHANG, MIEKO YAMAKADO, AND HIROYUKI SASABE
Frontier Research Program, RIKEN, Hirosawa 2-1, Wako, Saitama 351-01, JAPAN

Abstract Acceptor-substituted carbazole derivatives were newly designed as novel nonlinear optical materials to improve physical properties of poled polymers. Various 3,6- and 9-substituted carbazole derivatives were investigated systematically in terms of second harmonic generation activity in crystalline state and nonlinear optical responses in poled polymers. Enhancement of molecular polarizability was achieved by introducing electron-withdrawing groups in 3 and/or 6-positions. Main chain polymers with head-to-tail configuration of carbazole moieties were designed and the enhancement factor of second-order nonlinear optical susceptibility was elucidated from the studies of monomer and dimer model compounds.

INTRODUCTION

Electric and optical properties of organic charge-transfer (CT) compounds have been attracted a lot of attention from both fundamental science and practical applications. In these decades remarkable progress have been made in development of electroactive CT materials such as organic metals: 7,7,8,8-tetracyanoquinodimethan /tetrathiofulvalene complex (TCNQ/TTF),[1] conducting polymers: doped polyacetylene, and organic photoconductor: poly(vinylcarbazole) /2,4,7-trinitrofluorenone (PVK/TNF).[2] Recently organic intracharge transfer compounds have been experimentally and theoretically elucidated to exhibit anomalously large nonlinear optical effects.[3] Nonlinear optical properties of several CT complex systems have been studied by degenerate four-wave mixing measurement in α-[bis(ethylenedithio) tetrathiofulvalene] triiodide crystal [4] and PVK/TNF thin films.[5] The third-order nonlinear optical susceptibility $\chi^{(3)}$ $(-3\omega;\omega,\omega,\omega)$ of PVK/TNF increased with increase of CT contents.[6] More recently, photorefractive effects has been observed in CT complex crystal such as 2-cyclooctylamino-5-nitropyridine crystal slightly doped with TCNQ[7] and poled polymers.[8]

Electric field poling is widely used to break the centrosymmetry of polymeric systems. Electric field-induced alignment of dye molecules and their stabilization are important issue to develop large and stable nonlinear optical polymers. The head-to-tail polymers with nonlinear active chromophores in main chain are proposed in order to improve the physical properties of poled polymers, especially electric field-induced alignment and their stabilization.[9] Carbazole moiety was selected as a novel chromophore which possesses multi-functional properties and the second-order nonlinear optical responses were examined in crystalline state and in poled polymers.

NONLINEAR OPTICAL RESPONSES OF ACCEPTOR-SUBSTITUTED CARBAZOLE

In searches for multi-functional chromophores we selected carbazole derivatives which possess both photoconductivity and second-order nonlinear optical response. Carbazole compounds are well-known to exhibit good hole transporting properties and their photocarrier generation efficiency can be sensitized by formation of CT complexes.[10] The carbazole molecule has an isoelectronic structure of diphenylamine, that is, electron-donative nature as shown in FIGURE 1. Therefore, the introduction of electron-withdrawing groups in 3 and/or 6-position induces intracharge transfer. Depending on the electron-affinity of acceptor groups, the additional CT band was superimposed in visible region.

Various kinds of substituent groups were systematically examined in different positions such as R_1, R_2 and/or R_3 in FIGURE 1. Among them the hydrogen bonding in 9-hydroxyethyl substituent plays an important role to generate noncentrosymmetric packing of carbazole molecules. The single crystals of 9-hydroxyethylcarbazole and 3-nitro-9-hydroxyethylcarbazole were determined to have noncentrosymmetric crystallographic structures with tetragonal ($I4_1$) and monoclinic ($P2_1$) crystal systems.[11] In these crystals each carbazole rings are aligned along the same direction through the hydrogen bonding and they show efficient second harmonic generation (SHG) in bulk crystals. Therefore one can expect that second-order nonlinear optical responses of acceptor-substituted carbazole derivatives can be controlled by proper molecular design of substituent groups.

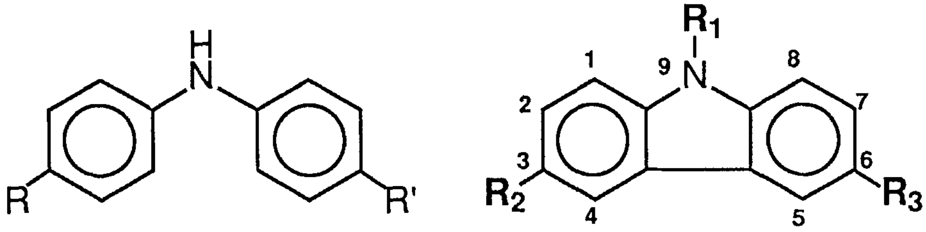

FIGURE 1 Diphenyl amine and substituted carbazole strcutures.

ENHANCEMENT OF OFF-DIAGONAL TENSOR COMPONENT IN POLED POLYMER

Disubstituted carbazoles such as 3,6-dinitrocarbazole derivatives have the similar chemical structure as di-4-nitrophenylamine. Unlike 3-nitro-9-hydroxyethylcarbazole crystal, 3,6-dinitro-9-hydroxyethylcarbazole (DNHEK) has a centrosymmetric unit cell with space group $P\bar{1}$. Although DNHEK crystal shows no SHG activity, one of the interesting feature of this disubstituted carbazole is that the vector direction of net dipole moment is not parallel to that of molecular CT axis. As a consequence, CT contribution to the nonlinear polarizabilities of this molecule has an intrinsic two-dimensional character. Therefore, this dinitrocarbazole molecule can be expected to show different behavior under the electric field-induced alignment of net dipole moment. In poled polymers containing one-dimensional CT molecules such as p-nitroaniline and p-substituted stilbene, the diagonal tensor component d_{33} is three times larger than the other component d_{31} under the low electric field.[12] These components d_{33} and d_{31} can be determined independently by measuring p-polarized second harmonic intensities with s- (▲) and p-polarized fundamental light (●) on poled polymers as shown in FIGURE 2. Poly(methyl methacrylate) doped with 3,6-dinitro-9-heptylcarbazole was determined to possess $d_{33} = d_{31}$ relationship after corona-poling.[13] These two-dimensional CT molecules can be utilized as a nonlinear optically active chromophore to improve the nonlinear optical properties of poled polymers, especially enhancement of off-diagonal tensor component.

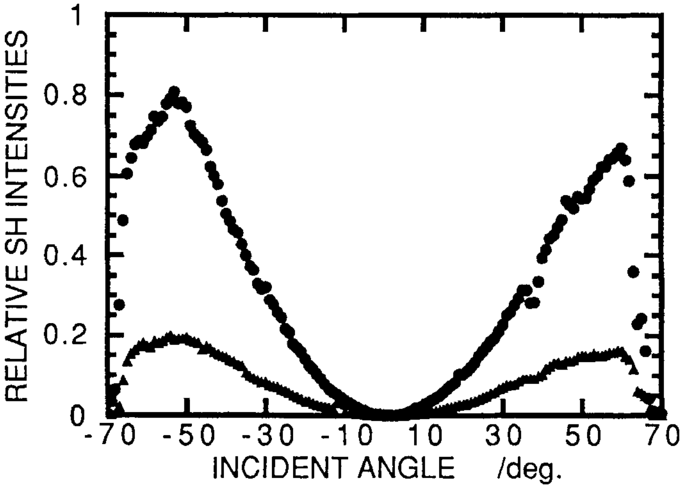

FIGURE 2 Relative second harmonic intensities as a function of incident angle.

MOLECULAR STRUCTURE OF CARBAZOLE HEAD-TO-TAIL DIMER

Acceptor-substituted carbazole moiety was incorporated into the main chain through the cyanocinnamate linkage as shown in FIGURE 3. In order to elucidate the second-order nonlinear optical properties of this head-to-tail polymer we separately synthesized a monomer and a dimer as a model compound (FIGURE 3).

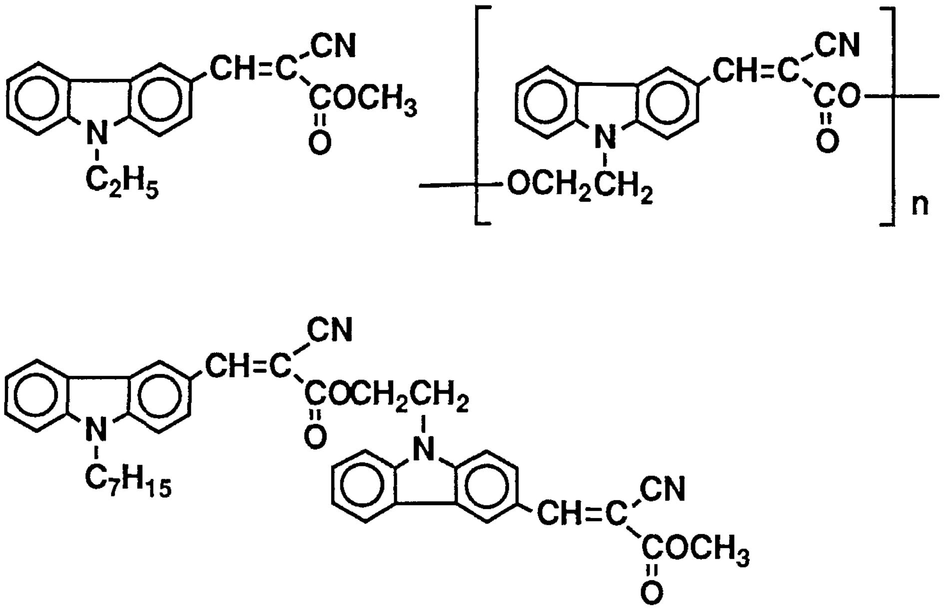

FIGURE 3 Carbazole head-to-tail polymer, monomer and dimer structure.

According to Williams' discussion,[9] macroscopic dipole moment (**M**) and macroscopic polarizability (**B**) for head-to-tail polymer chain with n repeating units can be described by associated vector (**r**) in the chain direction and average directional cosine over the polymer chain:

$$\mathbf{M} = \sum_{i=1}^{n} \mu^{i} = n\mu\langle\cos\phi\rangle\cos\varphi_{\mu} \qquad (1)$$

$$\mathbf{B} = \sum_{i=1}^{n} \beta^{i} = n\beta\langle\cos\phi\rangle\cos\varphi_{\beta} \qquad (2)$$

where the relationship between dipole moment vector (μ), hyperpolarizability vector (β) in a repeating unit, **r** and end-to-end distance vector (**R**) are shown in FIGURE 4. In general μ and β vectors are not parallel to r vector because of a flexible spacer in polymer chain. The angles φ_μ and φ_β are defined with vector pairs (μ, **r**) and (β, **r**). In order to determine φ_μ, φ_β and ϕ values we estimated monomer and dimer structure by semiempirical calculation, and we measured their dipole moment experimentally.

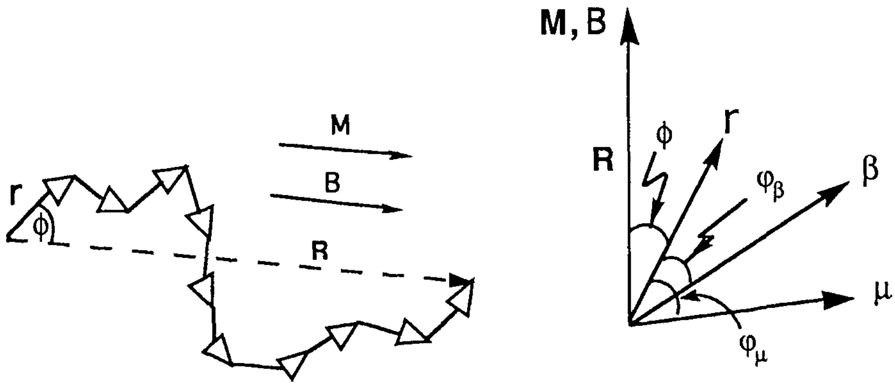

FIGURE 4 Head-to-tail polymer with associated vector (**r**) in the chain direction and the relationship between dipole moment vector (μ), hyperpolarizability vector (β).

Two geometric isomers with similar minimized energy were obtained by AM1. Both geometric isomers have similar values of φ_μ and φ_β. We took E geometric isomer which was usually observed in cyanocinnamate derivatives.[14] In this case the ester group will be trans to the carbazole group. The azimuthal angles φ_μ and φ_β were estimated to be 19° and 16°, respectively, by MOPAC calculation on optimized E geometric isomer.

The structure of a dimer is assumed to be simply composed of two optimized monomer units connected with a flexible spacer such as CH_2-CH_2 linkage neighboring ester group. Although there is no significant minimum or maximum in heat of formation calculated by MOPAC as a function of a dihedral angle, the structures at a dihedral angle of 0° and 90° have maximum and minimum energy. One key feature in these two structures is that the carbazole ring is perpendicular with each other. The net dipole moment of carbazole dimer is sensitive to their conformation. The net dipole moment calculated by vector summation increased with increase of a dihedral angle. Judging from the minimized energy and net dipole moment, the structure at a dihedral angle of around 90° was selected for further consideration. From the concentration dependence of dielectric constants of dioxane solution, the values of diploe moment (μ) for monomer and dimer were determined to be 4.6 D and 6.7 D, respectively. Taking μ and φ_{μ} values the angle (ϕ) between **r** and end-to-end vector (**R**) for dimer was calculated to be 40° which is in good agreement with the value obtained from optimized dimer structure mentioned above.

ELECTRIC FILED-INDUCED ALIGNMENT OF CARBAZOLE DIMER AND ENHANCEMENT FACTOR

Poling dynamics of dimer was examined on the thin films of poly(methyl methacrylate) (PMMA) doped with 1.6×10^{20} carbazole molecules /cm^3. Poling and depoling behavior of carbazole moieties were monitored by transmitted absorption change. Poly(methyl methacrylate) thin films containing carbazole moieties show dichroism after corona-poling, that is, decrease of absorbance at λ_{max}. Similar electric field-induced alignment was obtained in monomer and dimer films under the same poling condition. However, they showed slightly different decay behaviour. FIGURE 5 shows relaxation of alignment of monomer and dimer in PMMA at 40°C with same carbazole concentration monitored the absorbance change at λ_{max} 390 nm. Carbazole head-to-tail dimers can be utilized as a nonlinear optically active chromophore and their thermal relaxation in PMMA was suppressed presumably due to the steric hindrance.

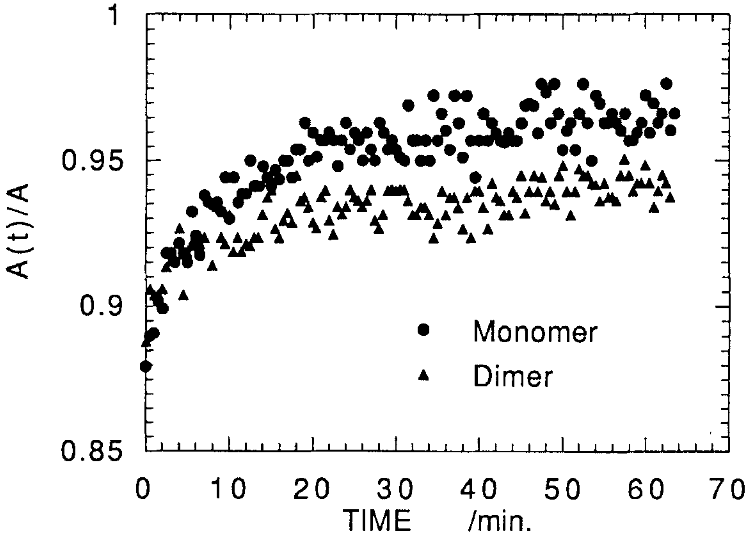

FIGURE 5 Absorbance change as a function of time after poling.

The enhancement factor of susceptibility per repeating unit can be defined using equation (1) and (2):

$$\frac{\chi^{(2)}_{zzz}(\text{polymer})}{\chi^{(2)}_{zzz}(\text{monomer})} = \frac{\left(\frac{\text{MB}}{\text{n}}\right)}{\mu\beta} = \text{n}\left(\langle\cos\phi\rangle\right)^2 \cos\varphi_\mu \cos\varphi_\beta \qquad (3).$$

Taking ϕ, μ, φ_μ and φ_β values the enhancement factor was calculated to be 0.53 n, where n is number of repeating units. Namely, $\chi^{(2)}$ for head-to-tail polymer was enhanced with the degree of polymerization. Although carbazole head-to-tail polymers were obtained by conventional high-temperature polyesterification procedure, these homopolymer did not dissolve in usual organic solvents. In order to improve the polymer solubility, copolymers were obtained with 12-hydroxydodecanoate. There mean square dipole moments of processable (3:7) copolyesters increased with increase of molecular weight. Further electric induced-alignment of copolymers is underway to elucidate nonlinear optical responses.

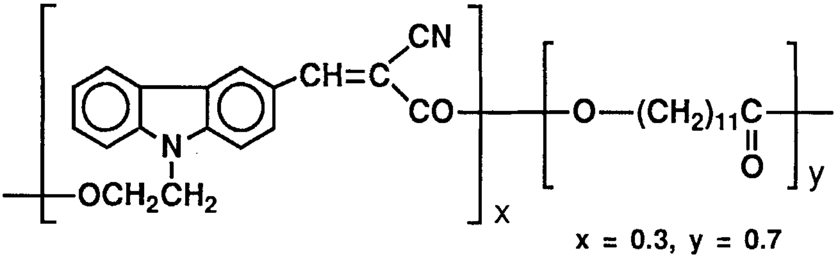

FIGURE 6 Carbazole head-to-tail copolymer.

CONCLUSIONS

We have successfully developed acceptor-substituted carbazole derivatives as a multifunctional chromophore for nonlinear optical applications. Second-order polarizability of carbazole can be tuned by introduction of electron-withdrawing groups in 3 and/or 6-position. The hydroxyethyl group in 9-position is effective to break centrosymmetric packing of carbazole molecules in crystalline state. Disubstituted carbazole can be utilized to improve the off-diagonal tensor components of poled polymers. Head-to-tail sequence of carbazole moieties can enhance the macroscopic susceptibility with an additive way by factor of 0.53.

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