Polish J. Chem., **76**, 1495–1503 (2002)

Chromophoric Carbazole Methacrylates as Intermediates for Photorefractive Applications

by K. Diduch and S. Kucharski*

Institute of Organic and Polymer Technology, Wrocław University of Technology,
50-370 Wrocław, Poland

(Received June 21st, 2002; revised manuscript July 16th, 2002)

Methacrylate monomers containing a carbazole fragment and a chromophoric azophenyl sulfonyl group were synthesized, being characterized as definite chemical species and as potential intermediates for photorefractive applications. Quantum chemical calculations were carried out to get values of dipole moments, polarizabilities and hyperpolarizabilities. These values were used to calculate figure of merit (FOM) of the monomers, which indicated a contribution of linear and nonlinear optical effects to photorefractive phenomena. It was found that in the monomers in question the linear optical effect contribution prevailed over nonlinear one.

Key words: methacrylate carbazole polymers, nonlinear optics, photorefractive materials

Photorefractive effect in organic materials results from several phenomena developed at the same time, *i.e.* photoinduced charge generation and charge trapping to create electron rich and electron deficient domains, and nonlinear optical properties (electrooptic response), making thus possible the modulation of refractive index by the electric field [1–3]. To invoke the photorefractive effect it is necessary to combine features, which can hardly be found in a single chemical species. Polymeric materials have been of interests here as they can be easily modified by incorporation of various molecular fragments into the main or side polymer chain or by using polymer blends with functional components in the polymer matrix. According to literature, the carbazole derivatives are important contributors owing to their photoconducting ability. And on the other hand, the molecules with noncentrosymmetric charge distribution with distinct electron donor (D) and electron acceptor (A) groups (D-Π-A) play the role of nonlinear optical chromophores. The symbol Π denotes a system of conjugated double bonds.

The nonlinear response of an isolated molecule in an electric field (such as that associated with light) can be presented as the Taylor series expansion of the dipole moment μ_i induced by the field $E_i(\omega)$:

$$\mu_i = \mu_i^0 + \sum_j \alpha_{ij} E_j + \frac{1}{2}\sum_{j,k} \beta_{ijk} E_j E_k + \frac{1}{6}\sum_{j,k,l} \gamma_{ijkl} E_j E_k E_l + \ldots \qquad (1)$$

---

*Author to whom correspondence should be addressed. E-mail address: kucharski@itots.ch.pwr.wroc.pl where: μ_i^0 is the permanent dipole moment, α_{ij} are the linear polarizability tensor components, β_{ijk} and γ_{ijkl} are the first and second hyperpolarizability tensor components.

$$\beta_i = \beta_{iii} + \frac{1}{3}\sum_{k,i\neq k}(\beta_{ikk} + \beta_{kik} + \beta_{kki}) \qquad (2) \qquad\qquad \beta = \sqrt{\beta_x^2 + \beta_y^2 + \beta_z^2} \qquad (3)$$

where: i, k ∈ (x, y, z).

The refractive index modulation can be achieved by ability of the chromophore group to reorient at room temperature along the external electron field and by electrooptic Pockels effect ascribed to the first hyperpolarizability. Basing on this, the so-called figure of merit (FOM) was defined [4–6] to characterize the chromophore efficiency in terms of photorefractive application. The FOM depends on the molecular parameters of the chromophore and can be written as a sum of two parameters (4). The first term in this equation represents the orientational birefringence contribution FOM (FOM_{OB}), due to the ability of the chromophores to reorient at room temperature along the internal electric field, the second one is due to the electrooptic Pockels effect (FOM_{PEO}):

$$FOM = FOM_{OB} + FOM_{PEO} \quad (4) \qquad FOM_{OB} = \frac{2}{9kT}\mu^2\Delta\alpha \quad (5) \qquad FOM_{PEO} = \mu\beta \quad (6)$$

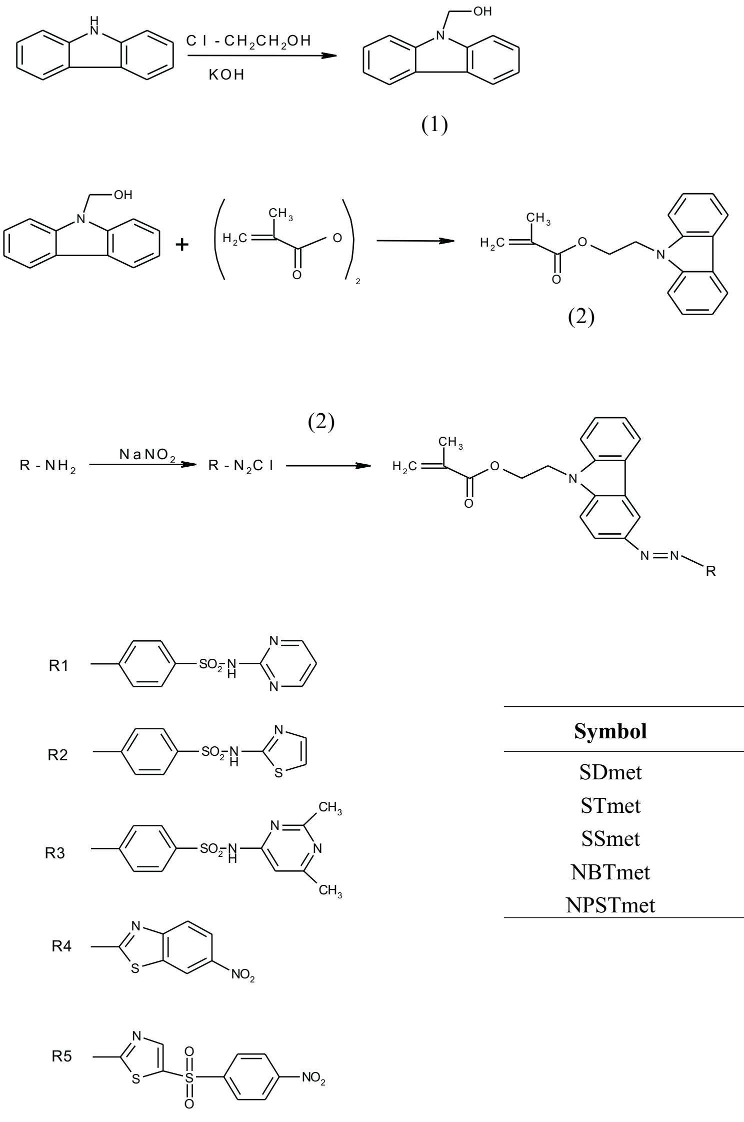
where: μ is the molecular dipole moment, $\Delta\alpha$ is the linear molecular anisotropy polarizability, β is the hyperpolarizability in the Taylor series convention, T is the temperature and k is the Boltzmann constant. The linear polarizability anisotropy $\Delta\alpha$ is defined as:

$$\Delta\alpha = \alpha_{\parallel} - \alpha_{\perp} \qquad (7)$$

where the symbols || and ⊥ are relative to the orientation, respectively, parallel and perpendicular to the molecular *z-axis*.

Several fully functionalized polymers, which have the NLO chromophore, charge generator and charge transporting molecule attached to the same polymer backbone have been reported [7–11]. This kind of polymer systems could have several advantages over those in which components are present as quest molecules. The potential advantage is the stability of such single component systems against phase separation or stability of the electrooptic coefficient. In copolymers, the charge transport could be disturbed if functional molecular groups are attached to the chain in random locations. And, thus, the material containing all functional groups in one chemical compound seem to be a good solution [12–14].

Our aim was to obtain bifunctional methacrylate monomers, which had carbazole fragment responsible for charge transfer and a nonlinear optical chromophore of the azobenzene type with heterocyclic rings as shown in Scheme 1. The monomers in question were not described in available literature. The syntheses and characterization of the monomers were preceded by quantum chemical calculation, which made it possible to evaluate the polarizability and hyperpolarizability to get data for calculations figure of merit (FOM) of the monomers.



Symbol	R
SDmet	R_1
STmet	R_2
SSmet	R_3
NBTmet	R_4
NPSTmet	R_5

Scheme 1. Scheme of the synthesis methacrylate monomers.

EXPERIMENTAL

Materials: 2-Amino-5-(4-nitrophenylsulfonyl) thiazole, 2-amino-6-nitrobenzothiazole, sulfisomidine, sulfadiazine and sulfathiazole were purchased from Merck or Aldrich. 2(9H-Carbazol-9-yl) ethanol was obtained according procedure described in [15]. The naming of the monomers according to IUPAC ACD/Labs (Toronto) computer programs [16].

Synthesis of 2-(9H-carbazol-9-yl) ethyl 2-methacrylate ***(1)***. 2-(9H-Carbazol-9-yl) ethanol (0.067 mole; 14.2 g), 4-(dimethylamino) pyridine (0.0055 mole; 0.673 g) and 4-methoxyphenol (0.047 g) were dissolved in anhydrous pyridine (35 ml) and methacrylic acid anhydride (0.079 mole; 12.11 g) was gradually added. The mixture was heated under reflux for 10 minutes. The solvent was removed with a rotary evaporator and a residue was dissolved in ethyl acetate. The solution was washed with 0.1 M aqueous $NaHCO_3$ solution and with water several time and dried over anhydrous Na_2SO_4. The solvent was then removed using a rotary evaporator and the solid was recrystallized from methanol to yield 11.5 g of 2(9H-carbazol-9-yl) ethyl 2-methacrylate (61%). M.p. 82°C, ^{1}H NMR (300 Hz, DMSO-d_6, TMS) ppm: 1.63 (s, 3H, $-CH_3$); 4.44–4.74 (m, 4H, $-CH_2-CH_2-$); 5.49 (s, 1H, $=CH_2$ *trans*); 5.72 (s, 1H, $=CH_2$ *cis*); 7.16–7.65 (m, 6H, carbazole ring protons 1,2,3,6,7,8); 8.12–8.14 (m, 2H, carbazole ring protons 4,5).

Synthesis of 2{3-((E)[4-{4-[(2,6-dimethylpyridin-4-yl) amino] sulfonyl} phenyl] diazenyl)-9H-carbazol-9-yl} ethyl methacrylate (SSmet) ***(2)***. Sulfisomidine (0.02 mole; 5.57 g) was dissolved in a hot mixture of concentrated HCl (6 ml), water (40 ml) and glacial acetic acid (60 ml). The mixture was cooled down to 0–4°C and the solution of $NaNO_2$ (1.6 g) in water (4 ml) was dropped slowly in. After 20 minutes the excess of nitric acid was removed with solution of sulfamic acid. Then solution of (**1**) (0.03 mole; 6.4 g) in 50 ml of 2-methoxyethan-1-ol cooled down to 0–4°C was added under stirring into diazonium salt (obtained previously). Sodium acetate was then added (10 g) and the mixture was kept 24 h in fridge while stirring it occasionally. The reaction mixture was diluted with water (three time as much, by volume). The precipitation was then filtered, washed with water and air-dried. The product was purified by crystallization from dimethylformamide yield 81%. M.p. 199–204°C, ^{1}H NMR (300 Hz, DMSO-d_6, TMS) ppm: 2.09 (s, 3H, $-CH_3$); 2.74 (s, 3H, $-CH_3$); 2.90 (s, 3H, $-CH_3$); 4.48–4.76 (m, 4H, $-CH_2-CH_2$); 5.53 (s, 1H, $=CH_2$, *trans*); 5.75 (s, $=CH_2$, *cis*); 7.02 (m, 1H, pyrimidine ring proton); 7.19 (m, 1H, -NH); 7.22–8.17 (m, 4H, phenyl ring protons and 7H carbazole ring protons).

Synthesis of 2{3-((E)[4-{4-[(pyrimidin-2-yl) amino] sulfonyl} phenyl] diazenyl)-9H-carbazol-9-yl} ethyl methacrylate (SDmet) ***(3)***. It was prepared by the same procedure as (**2**) using sulfadiazine in place of sulfisomidine. Yield 67%. M.p. 159–164°C, ^{1}H NMR (300 Hz, DMSO-d_6, TMS) ppm: 2.09 (s, 3H, $-CH_3$); 4.48–4.77 (m, 4H, $-CH_2-CH_2-$); 5.53 (s, 1H, $=CH_2$, *trans*); 5.75 (s, 1H, $=CH_2$, *cis*); 7.06 (m, 1H, -NH); 7.19 (m, 1H, pyrimidine ring proton); 7.22–7.78 (m, 6H, carbazole ring protons 1,2,4,5,6,7); 7.96 (m, 2H, phenyl ring protons 2,3); 8.17 (m, 2H, phenyl ring protons 1,4); 8.48–8.52 (m, 2H pyrimidine ring protons); 8.49 (m, 1H, carbazole ring proton 3).

Synthesis of 2{3-((E)[4-{4-[(1,3-thiazol-2-yl) amino] sulfonyl} phenyl] diazenyl)-9H-carbazol-9-yl} ethyl methacrylate (STmet) ***(4)***. It was prepared by the same procedure as (**2**) using sulfathiazole in place of sulfisomidine. Yield 71%. M.p. 158–167°C, ^{1}H NMR (300 Hz, DMSO-d_6, TMS) ppm: 1.64 (s, 3H, $-CH_3$); 4.45–4.76 (m, 4H, $-CH_2-CH_2-$); 5.53 (s, 1H, $=CH_2$, *trans*); 5.74 (s, 1H, $=CH_2$, *cis*); 7.18–8.01 (m, 6H, carbazole ring protons 1,2,4,5,6,7); 7.42–7.67 (m, 4H, phenyl ring protons); 7.52–7.85 (m, 2H, thiazole ring protons); 8.44 (m, 1H, carbazole ring proton 3); 9.10 (m, 1H, -NH).

Synthesis of 2{3-((E)-{5-[(4-nitrophenyl) sulfonyl]-1,3-thiazol-2-yl} diazenyl)-9H-carbazol-9-yl} ethyl methacrylate (NPSTmet) ***(5)***. It was prepared by the same procedure as (**2**) using 2-amino-5 (4-nitrophenylsulfonyl) thiazole in place of sulfisomidine. Yield 89%. M.p. 79–80°C, ^{1}H NMR (300 Hz, DMSO-d_6, TMS) ppm: 1.63 (s, 3H, $-CH_3$); 4.44–4.74 (m, 4H, $-CH_2-CH_2-$); 5.49 (s, 1H, $=CH_2$ *trans*); 5.72 (s, 1H, $=CH_3$ *cis*); 7.16–7.65 (m, 6H, carbazole ring protons 1,2,4,5,6,7); 8.12–8.15 (m, 4H, phenyl ring protons 1,2,3,4); 8.23 (s, 1H, carbazole ring proton 3); 8.37–8.40 (m, 1H, thiazole ring proton).

Synthesis of 2{3-[(E)-(6-nitro-1, 3-benzothiazol-2-yl) diazenyl]-9H-carbazol-9-yl} ethyl methacrylate (NBTmet) ***(6)***. It was prepared by the same procedure as (**2**) using 2-amino-6-nitrobenzothiazole in place of sulfisomidine. Yield 91%. M.p. 78–79°C, ^{1}H NMR (300 Hz, DMSO-d_6, TMS) ppm: 1.63 (s, 3H, $-CH_3$); 4.43–4.74 (m, 4H, $-CH_2-CH_2-$); 5.49 (s, 1H, $=CH_2$ *trans*); 5.72 (s, 1H, $=CH_2$ *cis*); 7.16–7.64 (m, 6H, carbazole ring protons 1,2,4,5,6,7); 8.11-8.17 (m, 2H, benzothiazole ring protons 1,2); 8.32-8.40 (m, 1H, carbazole ring proton 3); 9.16 (m, 1H, benzothiazole ring proton 3).

Characterization: ^{1}H NMR spectra of the monomers were recorded in DMSO in the presence of TMS as a standard in a Bruker AMX 300 MHz apparatus. The purity of the monomer was determined by thin layer chromatography using Merck silica gel aluminium foils. Melting points of products were measured using Digital Melting Point Apparatus Electrothermal IA 9100.

Quantum chemical calculations: Quantum chemical calculations were carried out at Wrocław Supercomputer Center using GAUSSIAN 98 program. The calculation comprised geometry optimization and calculation of NLO response with GAUSSIAN 98 at the restricted Hartree-Fock (RHF) *ab initio* with a split-valence 3-21G basis set.

RESULTS AND DISCUSSION

Synthetic approach: The monomers were synthesized as described in Scheme 1 in three-step reaction. 2-(9H-Carbazol-9-yl) ethanol were obtained by alkylation of carbazole with 2-chloroethanol in the presence of powdered potassium hydroxide according to procedure described by Ho *et al.* [15]. Esterification of the 2-(9H-carbazol-9-yl) ethanol with methacrylic acid anhydride gave the monomer, which then was coupled with proper (prepared before) diazonium salts. The final products were obtained with sufficient yields as a orange-brown or yellow powders. The melting temperatures of the monomers were between 432–477 K for sulphonamides derivatives (SSmet, SDmet, STmet), and between 351–353 K for 2-amino-6-nitrobenzothiazole and 2-amino-5 (4-nitrophenylsulfonyl) thiazole derivatives (NPSTmet, NBTmet). All the monomers were crystallized from dimethylformamide.

Polarizability, hyperpolarizability and figure of merit (FOM): For calculation of the first hyperpolarizability by quantum chemical methods the GAUSSIAN program was chosen at RHF (restricted Hartree-Fock) *ab initio* level of theory with the 3-21 G split-valence basis set. As the first step of our calculation, we carried out the geometry optimization using the GAUSSIAN followed by CPHF (coupled perturbed Hartree-Fock) procedure for calculation of polarizability and hyperpolarizability. As a result of calculation the program gave six tensor components of polarizability α and ten tensor components of first hyperpolarizability β^0; the calculation was carried out to obtain static hyperpolarizability (without external field; $\lambda = \infty$ nm). With help of (2) and (3), and taking into account the Kleinmann symmetry [18], the β^0 values were obtained. The anisotropy of the optical polarizability $\Delta\alpha$ was calculated using (7).

The aim of our calculation was to propose the bifunctional monomers containing both charge-transporting and chromophore moiety as the promising NLO materials. Basing on literature [12–15,19–21] the carbazole as a charge-transporting group was chosen. As chromophores, attached at C atom in the 3-positions of the carbazole ring thought an azo-conjugated bridge, the sulfonamides of different types were chosen. They differed from each other by heterocyclic group as shown in Scheme 1: sulfadiazine (SD), sulfathiazole (ST), sulfisomidine (SS) and 2-amino-5 (4-nitrophenylsulfonyl) thiazole (NPST) derivatives were chosen. 2-Amino-6-nitrobenzothiazole (NBT) was no sulphonamide type. The nonlinear optical properties of two first, *i.e.* derivatives of sulfadiazine and sulfathiazole, were confirmed before [22–24].

The results of our calculation of dipole moments, anisotropy of polarizability and first hyperpolarizability are given in Table 1. The values of the dipole moments calculated for the monomers were in the range of 31.34–37.35 10^{-30} C m. That results were about 20–40% higher than the values obtained for *p*-nitroaniline (PNA) [22]. Only for SSmet the μ value was closed to PNA and amounted to 26.27 10^{-30} C m. For an isolated molecule, the values of β^0 (static) for NPSTmet and NBTmet were about two times higher than for sulfonamide derivatives and above seven times exceeded first hyperpolarizability of *p*-nitroaniline. The values of β^0 for SSmet, SDmet, STmet were between 9.4 and 9.8 10^{-50} C^3 m^3 J^{-2} (Tab. 1).

The μ and β^0 values have a direct influence on the magnitude of figure of merit, in particular for the second term FOM_{PEO} due to electrooptic Pockels effect. It is to mention that using β values to determine FOM_{PEO} seemed to be justified approach as there is a correlation between nonlinear optical coefficient and electrooptical coefficient. The results of Table 1 show that the contribution of FOM_{PEO} to total FOM is rather small and only for two monomers (NBTmet and NPSTmet) having higher values of the first hyperpolarizability it reaches *ca*. 3%. In light of the common requirements for the photorefractive materials to show nonlinear optical properties manifested by first hyperpolarizability, the contribution of this term to total FOM seems to be rather small. In fact, the photorefractive experiments are carried out under illumination of the material with laser beams (two beam coupling or four wave mixing) mostly of 672 nm wavelength. This means that the external field will have influence on both values of linear polarizability and first hyperpolarizability. Both parameters will increase with external field and β will grow faster.

The monomers in question have a structure of push-pull molecules and they may be subjected to a two level model formalism of calculation of first hyperpolarizability [22,27]

$$\beta^0_{CT} = \frac{3(\mu_e - \mu_g)\mu^2_{eg}}{2\varepsilon_0 \hbar^2 \nu^2_{eg}} \tag{8}$$

where μ_e, μ_g are dipole moments in excited and ground state, respectively, μ_{eg} is the transition moment between the excited and ground state, ε_0 is vacuum permittivity, $\hbar$ is Planck constant and ν_{eg} is the transition frequency from ground state to first excited state. When the photorefractive experiments are carried with red laser beam, say at λ = 672 nm, the values of $\Delta\alpha$ and β_{PEO} at the frequency corresponding to this wavelength can be recalculated using following equations

$$\alpha(\omega) = \frac{\omega^2_{eg}}{\omega^2_{eg} - \omega^2}\alpha(0) \tag{9}$$

$$\beta^{(-\omega,\omega,0)} = \frac{\omega^2_{eg}(3\omega^2_{eg} - \omega)}{3(\omega^2_{eg} - \omega^2)^2}\beta^0_{CT} \tag{10}$$

Table 1. Figure of merit (FOM) calculated using values of polarizabilities and first hyperpolarizabilities obtained from Gaussian *ab initio* 3-21 g.

Symbol of monomer	μ [Cm/10^{-30}]	β [C^3 m^3 J^2/10^{-50}]	$\Delta\alpha$ [C^2 m^2 J^1/10^{-40}]	FOM$_{OB}$ [C^4 m^4 J^2/10^{-78}]	FOM$_{PEO}$ [C^4 m^4 J^2/10^{-78}]	FOM [C^4 m^4 J^2/10^{-78}]	% FOM$_{PEO}$ in FOM [%]
SDmet	37.37	9.4	42.9	321.8	3.5	325.3	1.08
STmet	32.56	9.2	48.2	274.2	3.0	277.2	1.08
SSmet	26.27	9.8	45.8	169.8	2.6	172.4	1.49
NBTmet	31.34	22.6	21.8	266.5	7.1	273.6	2.66
NPSTmet	34.83	19.8	35.1	228.5	6.9	236.4	2.93

Table 2. Figure of merit (FOM) calculated basing on ZINDO yielded two-level approach of first hyperpolarizability (Eq. 8,9 and 10).

Symbol of monomer	β^0_{CT} [C^3 m^3 J^2/10^{-50}]	β^{672}_{EOPE} [C^3 m^3 J^2/10^{-50}]	λ_{eg} [nm]	$\Delta\alpha^{672}$ [C^2 m^2 J^1/10^{-40}]	FOM$^{672}_{OB}$ [C^4 m^4 J^2/10^{-78}]	FOM$^{672}_{PEO}$ [C^4 m^4 J^2/10^{-78}]	FOM^{672} [C^4 m^4 J^2/10^{-78}]	% FOM$^{672}_{PEO}$ in FOM^{672} [%]
SSmet	9.7	17.2	360	64.33	238.2	4.5	242.7	1.86
SDmet	8.9	16.0	362	60.26	451.5	6.0	457.5	1.31
STmet	9.5	17.0	361	67.64	458.9	6.0	464.9	1.30

where ω is applied field frequency. Application of this procedure is recommended for the molecules, where the β_x component contributes predominantly to the first hyperpolarizability. The parameters of the ground state and the first excited state (usually) are then used to determine the charge transfer hyperpolarizability, β_{CT} in the two-level model according to (8). The values of β^0_{CT}, shown in Tab. 2, calculated with help of ZINDO parameters from Gaussian, are very close to those obtained by *ab-initio* CPHF option. The figure of merit values obtained for SSmet, SDmet and STmet, recalculated with use of (9) and (10) for laser light frequency corresponding to $\lambda = 672$ nm, are higher than those obtained from static polarizability and hyperpolarizability. This statement is valid if one takes into account absolute values of FOM but considering relative contribution of the FOM part attributed to the hyperpolarizability effect one comes to the conclusion that it is still rather low.

This purely computational conclusion is valid only for polymeric materials with low glass transition temperature [25,26], where the chromophores are able to orient at room temperature under the influence of total internal modulated field and externally applied field. The compounds synthesized by us are, therefore, recommended to be used for syntheses of this kind of polymeric photorefractive materials.

CONCLUSIONS

The methacrylate monomers containing carbazole fragments connected *via* –N=N- bridge with heterocyclic sulphonamide can be easily obtained, as those which contain charge transport carbazole fragment and showing nonlinear optical properties owing to the presence of electron donor and electron acceptor groups separated by conjugated double bond system. The calculation of polarizability and hyperpolarizability by quantum chemical method indicated the possibility for manifesting a photorefractive effect due to linear polarizability anisotropy. The contribution of this effect to figure of merit (FOM) was found prevailing over the contribution ascribed to the first hyperpolarizability. This is an indication that the monomers obtained can be used for syntheses of low T_g photorefractive materials.

Acknowledgment

This research was supported by the Polish State Committee for Scientific Research, Grant No. 3 T09B 047 17.

REFERENCES

1. Nalva H.S. and Miyata S., (Editors), Nonlinear Optical Properties of Organic Molecules and Polymers, CRC Press, 1997.
2. Moerner W.E. and Silence S.M., *Chem. Rev.*, **94**, 127 (1994).
3. Zhang Y., Wada T. and Sasabe H., *J. Mater. Chem.*, **8**, 809 (1998).
4. Barzoukas M. and Blanchard-Desce M., *J. Chem. Phys.*, **112**, 2036 (2000).

5. Wortmann R., Poga C., Twieg R.J., Geletneky C., Moylan C.R., Lundquist P.M., DeVoe R.G., Cotts P.M., Horn H., Rice J.E. and Burland D.M., *J. Chem. Phys*., **105**, 10637 (1996).
6. Moylan C.R., Wortmann R., Twieg R.J. and McComb I.H., *J. Opt. Soc. Am. B*, **15**, 929 (1998).
7. Yu L., Chan W., Bao Z. and Cao S., *Macromol*., **26**, 2216 (1993).
8. Wang F., Chen Z., Gong Q., Chen Y. and Chen H., *Solid State Comm*., **108**, 295 (1998).
9. Meng H., Yu W.L. and Huang W., *Macromol*., **32**, 8841 (1999).
10. Chang C.J., Whang W.T., Hsu C.C., Ding Z.Y., Hsu K.Y. and Lin S.H., *Macromol*., **32**, 5637 (1999).
11. Chen Y., He Y., Chen H., Wang F., Chen Z. and Gong Q., *J. Modern Opt*., **46**, 1003 (1999).
12. Thelakkat M., Schmitz C., Hohle C., Strohriegl P., Schmidt H.W., Hofmann U., Schloter S. and Haarer D., *Phys. Chem. Chem. Phys*., **1**, 1693 (1999).
13. Hohle C., Hofmann U., Schloter S., Thelakkat M., Strohriegl P., Haarer D. and Zilker S.J., *J. Mater. Chem*., **9**, 2205 (1999).
14. Sohn J., Park S.Y., Moon H., Mun J. and Yoon C.S., *Reactive & Functional Polymers*, **45**, 109 (2000).
15. Ho M.S. Barrett C., Peterson J., Esteghamatian M., Natansohn A. and Rochon P., *Macromol*., **29**, 4613 (1996).
16. *ACDLabs ILAB Program (Toronto)*.
17. Frisch M.J., Trucks G.W., Schlegel H.B., Gill P.M.W., Johnsom B.G., Robb M.A., Cheeseman J.R., Keith T., Peterson G.A., Montgomery J.A., Raghvachari K., Al.-Laham M.A., Zakrzewski V.G., Ortiz J.V., Foresman J.B., Cioslowski J., Stefanov B.B., Nanayakkara A., Challacombe M., Peng C.Y., Ayala P.Y., Chen W., Wong M.W., Andres J.L., Replogle E.S., Gonperts R., Martin R.L., Fox D.J., Binkley J.S., Defrees D.J., Baker J., Stewart J.P., Head-Gordon M., Gozalez C. and Pople J.A., **Gaussian 98**, Gaussian, Inc., Pittsburgh PA, 1998.
18. Kleinman D.A., *Phys. Rev*., **126**, 1977 (1962).
19. Barrett C., Choudhury B., Natansohn A. and Rochon P., *Macromol*., **31**, 4845 (1998).
20. Bogda D., *Polimery*, **44**, 555 (1999).
21. Bogda D., Warzała M., Pielichowski J. and Sanetra J., *Polimery*, **44**, 146 (1999).
22. Kucharski S., Janik R. and Kaatz P., *J. Mater. Chem*., **9**, 395 (1999).
23. Kucharski S., Janik R., Hodge P., West D. and Khand K., *J. Mater. Chem*., **12**, 449 (2002).
24. Kułakowska J. and Kucharski S., *European Polym. J*., **36**, 1805 (2000).
25. Kippelen B., Meyers F., Peyghambarian N. and Marder S.R., *J. Am. Chem. Soc*., **119**, 4559 (1997).
26. Kippelen B., Sandalphon, Volodin B.L., Meerholz K. and Peyghambarian N., ACS SYMP. Ser., 672, Photonic and Optoelectronic Polymers, Washington, DC, 1977.
27. Fort A., Muller J. and Mager L., *Chem. Phys*., **243**, 115 (1999).