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Dyes and Pigments 75 (2007) 567–573

DYES and PIGMENTS

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Synthesis and characterization of carbazole derived nonlinear optical dyes

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Received 5 January 2006; received in revised form 12 April 2006; accepted 17 July 2006

Abstract

Three kinds of carbazole derived dyes, Caz-MN, Caz-Fu, and Caz-Vm-MN of push–pull molecules were synthesized and their nonlinear optical properties measured. The second harmonic generation (SHG) coefficients, d_{33}, of Caz-Fu/PVK[poly(9-vinylcarbazole)] (0.1:0.9) and Caz-Vm-MN/PVK (0.1:0.9) were 2.06×10^{-9} esu and 7.3×10^{-9} esu, respectively. The electro-optic coefficients (r_{33}) of these PVK blends with dyes were also observed to be 1.23 pm/V, 4.03 pm/V at a wavelength of 632.8 nm. The synthesized novel carbazole based dyes Caz-MN, Caz-Fu, and Caz-Vm-MN were characterized by means of ^{1}H NMR spectroscopy, IR spectroscopy, thermogravimetric analysis, electro-optic coefficients (r_{33}), and their NLO properties were evaluated by Maker fringe method.

Keywords: Second harmonic coefficients (d_{33}/d_{31}); Electro-optic coefficients (r_{33}); Push–pull molecules; Carbazole; Organic dye

1. Introduction

Nonlinear optical (NLO) and electro-optic (EO) properties of organic dyes have been attracting considerable attention because of the potential applications in optical switching, optical telecommunication devices, optical disks, new type of dye lasers, photonic large-scale integration (PLSI), etc. [1–3]. Generally, for successful applications, the nonlinear optical organic dye and polymers should have good processibility, high thermal stability, and low optical loss, in addition to high electro-optic coefficient [4–8]. Carbazole derivatives have important roles of optical material due to their special photorefractive, electrical, and chemical properties. Carbazoles are well known as a conjugated, good hole transporting, electron-donor, planar compound and ease to introduce solubilizing groups to rigid ring structure. Sasabe and coworkers reported that Λ shaped chromophore oriented shoulder-to-shoulder by poling which increased off-diagonal tensor component in nonlinear optical properties [9–12]. The synthesized 2-(9-decyl-9*H*-carbazole-3-ylmethylene)-malononitrile (Caz-MN), 9-decyl-3-[2-(5-nitrofuran-2-yl)-vinyl]-9*H*-carbazole (Caz-Fu), and 2-{3-[2-(9-decyl-9*H*-carbazole-3-yl)-vinyl]-5, 5-dimethylcydohex-2-enylidene}malononitrile (Caz-Vm-MN) were characterized by means of ^{1}H NMR spectroscopy, IR spectroscopy, UV and fluorescent spectroscopy, and thermogravimetric analysis (TGA) (Fig. 1).

2. Experimental part

2.1. Materials

1-Bromohexadecane was used after purification by vacuum distillation. Carbazole (96%) was used after recrystallization.

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doi:10.1016/j.dyepig.2006.07.004

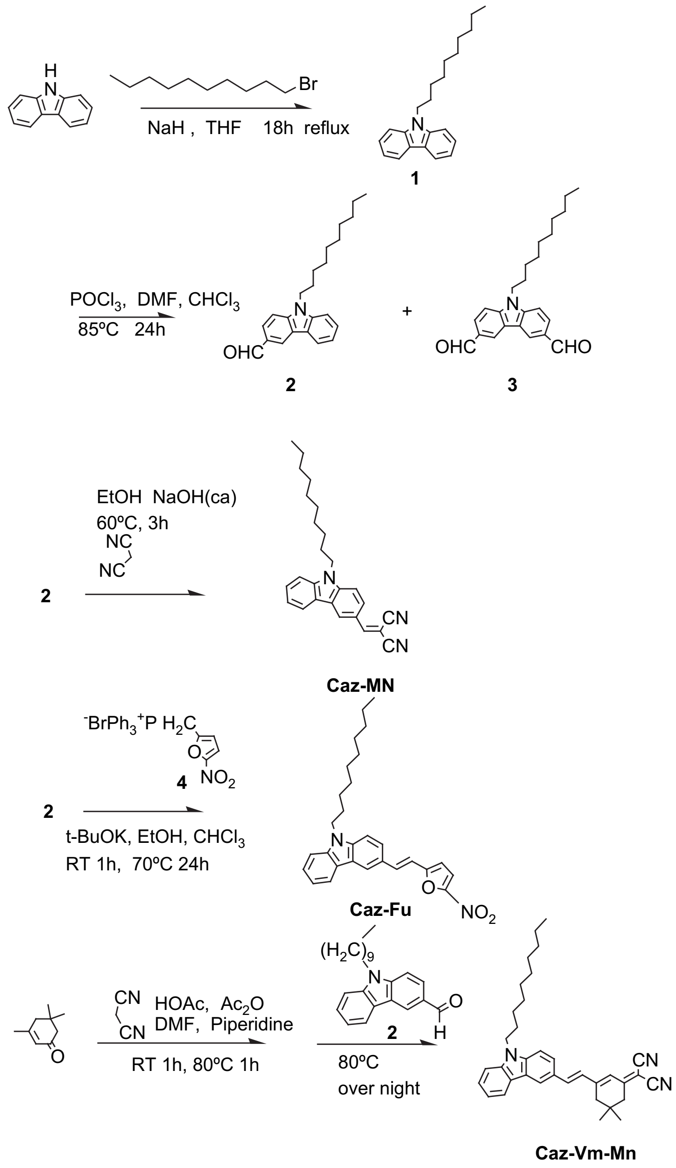

Fig. 1. Schematic representation of the synthesized procedure for Caz-MN, Caz-Fu, and Caz-Vm-MN.

Ethanol (EtOH) (from Aldrich) was used without further purification. Chloroform ($CHCl_3$) and acetone were purified by vacuum distillation over sodium (Na). All other solvents and reagents were analytical grade and used as received, unless otherwise stated.

2.2. Instrumentation

The ^{1}H NMR spectra were obtained with 300-MHz and 500-MHz ^{1}H NMR (Varian Gemini) spectrometers and the IR spectra were recorded using an FT-IR spectrophotometer (Nicolet 205). The thermal properties of the polymers were measured by thermogravimetry (TGA 2050, TA Instruments) and differential scanning calorimetry (DSC 2010, TA Instruments) at a heating rate of 10 °C/min under nitrogen atmosphere. The molecular weights and corresponding polydispersity (PD) indexes were determined by gel permeation chromatograpy (pump: MILTON Roy CM4000, detector: LDC analytical, column: Phenomex) at 40 °C using $CHCl_3$ as eluent at a flow rate of 1 mL/min. UV–vis spectrum (HP, 8452A and 8453) was used to measure chromophore arrangement degree by corona poling. Refractive index was measured at a wavelength 632.8 nm by ellipsometer (Gaertner, model L166C). Electro-optic coefficient, photocurrent degree used 632.8 nm He–Ne laser (LASOS, LGK7672) and 1550 nm diode laser (THORLABS, SIFC1550) to light source in tooth light-wave mixing measure. Oscilloscope (HP, 54602A) and lock-in amp (STANFORD, SR530s) were used. High voltage supply device (Bertan 225) was used in corona poling process.

2.3. Synthesis of 9-decyl-9H-carbazole-3-carbaldehyde

To a three-necked flask, DMF (86 mL, 1.18 mol) and CH_2C1_2 (50 mL) were added and the mixture was stirred at 0 °C and then $POCl_3$ (53.5 mL, 0.57 mol) was slowly added. The reaction mixture was heated at 30 °C for 1 h. To the stirring mixture at 0 °C, 9-decyl-9*H*-carbazole (10 g, 32.5 mmol) was slowly added. The reaction mixture was heated at 80 °C for 20 h and poured into slurry of crushed ice and water (250 mL). The precipitate was washed with water and extracted by $CHCl_3$ and then washed with *n*-hexane. The yellow solids were obtained by column chromatography with a yield of 60%. TLC $R_f = 0.52$ (EA/hexane (2/8)), mp = 66 °C, mol. wt = 335.48; ^{1}H NMR ($CDCl_3$, ppm) δ 10.10 (s, 1H, –CHO), 8.62 (s, 1H, ArH), 8.15 (d, 1H, ArH), 8.00 (d, 1H, ArH), 7.46 (m, 4H, ArH), 4.34 (t, 2H, $-NCH_2-$), 1.89 (m, 2H, $-CH_2-$), 1.24 (m, 16H, $-CH_2-$), 0.87 (t, 3H, $-CH_3$); FT-IR (KBr pellet, cm^{-1}) 2921 (H–C(SP^2)), 2851 (H–C(SP^3), 2716 (H–C=O), 1691 (C=O).

2.4. 2-(9-Decyl-9H-carbazole-3-ylmethylene)-malononitrile (Caz-MN)

To a three-necked flask, 9-decyl-9*H*-carbazole-3-carbaldehyde (**3**) (2 g, 5.96 mmol) and malononitrile (0.4 g, 6.05 mmol) were stirred in 30 mL EtOH and then NaOH/EtOH (about 0.1 M) 4–5 drops was slowly added. The precipitate was washed with water and extracted by $CHCl_3$ and then washed with *n*-hexane. The yellow solids were obtained by column chromatography with a yield of 60%. TLC $R_f = 0.64$ ($CHCl_3$), mp = 75 °C, mol. wt = 383.53; ^{1}H NMR ($CDCl_3$, ppm) δ 8.62 (s, 1H, ArH), 8.11 (m, 2H, ArH), 7.85 (s, 1H, $-CH{=}C(CN)_2$), 7.5 (m), 4.33 (t, 2H, $-NCH_2-$), 1.89 (m, 2H, $-CH_2-$), 1.24 (m, 16H, $-CH_2-$), 0.87 (t, 3H, $-CH_3$); FT-IR (KBr pellet, cm^{-1}) 2917 (H–C(SP^2)), 2843 (H–C(SP^3)), 2213 (CN). Anal. Calcd. for

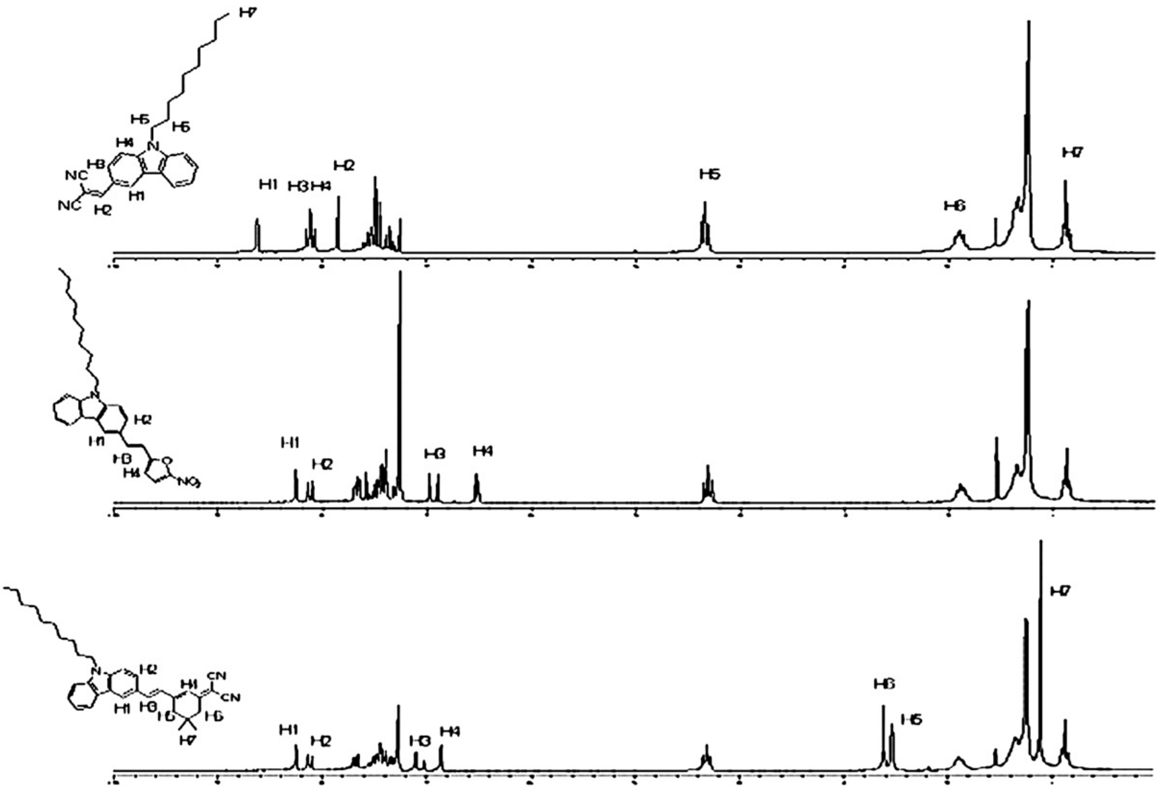

Fig. 2. NMR spectrum of Caz-MN, Caz-Fu, and Caz-Vm-MN.

$C_{26}H_{29}N_3$: C, 81.42; H, 7.62; N, 10.96. Found: C, 81.38; H, 7.67; N, 11.00.

2.5. *9-Decyl-3-[2-(5-nitrofuran-2-yl)-vinyl]-9H-carbazole (Caz-Fu)*

To a three-necked flask, 2-bromomethyl-5-nitrofuran (3.13 g, 15.2 mmol) and PPh3 (4.9 g, 18.7 mmol) were added and the mixture was stirred in 20 mL toluene and refluxed for 12 h and compound **4** was obtained.

The mixture of compounds **3** (7.67 g, 16.4 mmol) and **4** (5.5 g, 16.3 mmol) in $CHCl_3$ (20 mL) and EtOH (10 mL) was stirred at room temperature and then *t*-BuOK (1.5 equiv)/EtOH was slowly added at normal temperature. The reaction mixture was heated at 70 °C for 24 h. The precipitate was washed with water and extracted by $CHCl_3$ and then washed with *n*-hexane. The yellow solids were obtained by column chromatography with a yield of 70%.

The precipitate was recrystallized from *n*-hexane. Caz-Fu was obtained as reddish crystal. TLC $R_f = 0.79$ ($CHCl_3$), mp = 104 °C, mol. wt = 444.57; ^1H NMR ($CDCl_3$, ppm) δ 8.25 (s, 1H, ArH), 8.11 (d, 1H, ArH), 7.58 (m), 6.90 (d, 1H, −CH=CH−), 6.51 (d, 1H, ArH), 4.30 (t, 2H, −NCH2−), 1.88 (m, 2H, −CH2−), 1.23 (m, 16H, $-CH_2-$), 0.87 (t, 3H, $-CH_3$); FT-IR (KBr pellet, cm^{-1}) 2925 (H−C(SP^2)), 2850 (H−C(SP^3)), 1355 (NO). Anal. Calcd. for $C_{28}H_{32}N_2O_3$: C, 75.65; H, 7.26; N, 6.30. Found: C, 75.65; H, 7.24; N, 6.06.

2.6. *2-{3-[2-(9-Decyl-9H-carbazole-3-yl)-vinyl]-5,5-dimethylcydohex-2-enylidene}malononitrile-(Caz-Vm-MN)*

To a three-necked flask, malononitrile (0.66 g, 10 mmol) was dissolved in DMF (25 mL) and the mixture was stirred at room temperature. To the reaction mixture were added slowly isophorone (1.52 g, 11 mmol), piperidine (0.15 g, 1.82 mmol), and acetic anhydride (41 mg, 0.2 mmol) through a syringe following the procedure. The reaction mixture was heated at 80 °C for 1 h and cooled to room temperature and then compound **2** was added slowly, stirring the mixture at 80 °C for 16 h. The resulting mixture was extracted by $CHCl_3$. The resulting mixture was poured into *n*-hexane (250 mL). Viscous liquid product was obtained by column chromatography with a yield of 70%. The precipitate was recrystallized from *n*-hexane. Caz-Vm-MN was obtained as reddish shaped needles. TLC $R_f = 0.69$ ($CHCl_3$), mp = 119 °C, mol. wt = 503.72; ^1H NMR ($CDCl_3$, ppm) δ 8.25 (s, 1H, ArH), 8.11 (d, 1H, ArH), 7.5 (m), 7.05 (d, 1H, −CH=CH−), 6.86 (s, 1H, $>$C=CH−), 4.31 (t, 2H, $-NCH_2-$), 2.61 (s, 2H, $-CH_2-$), 2.53 (s, 2H, $-CH_2-$), 1.88 (m, 2H, $-CH_2-$), 1.24 (m, 16H, $-CH_2-$), 1.10 (s, 6H, $(CH_3)_2C$), 0.87 (t, 3H, $-CH_3$); FT-IR (KBr pellet, cm^{-1})

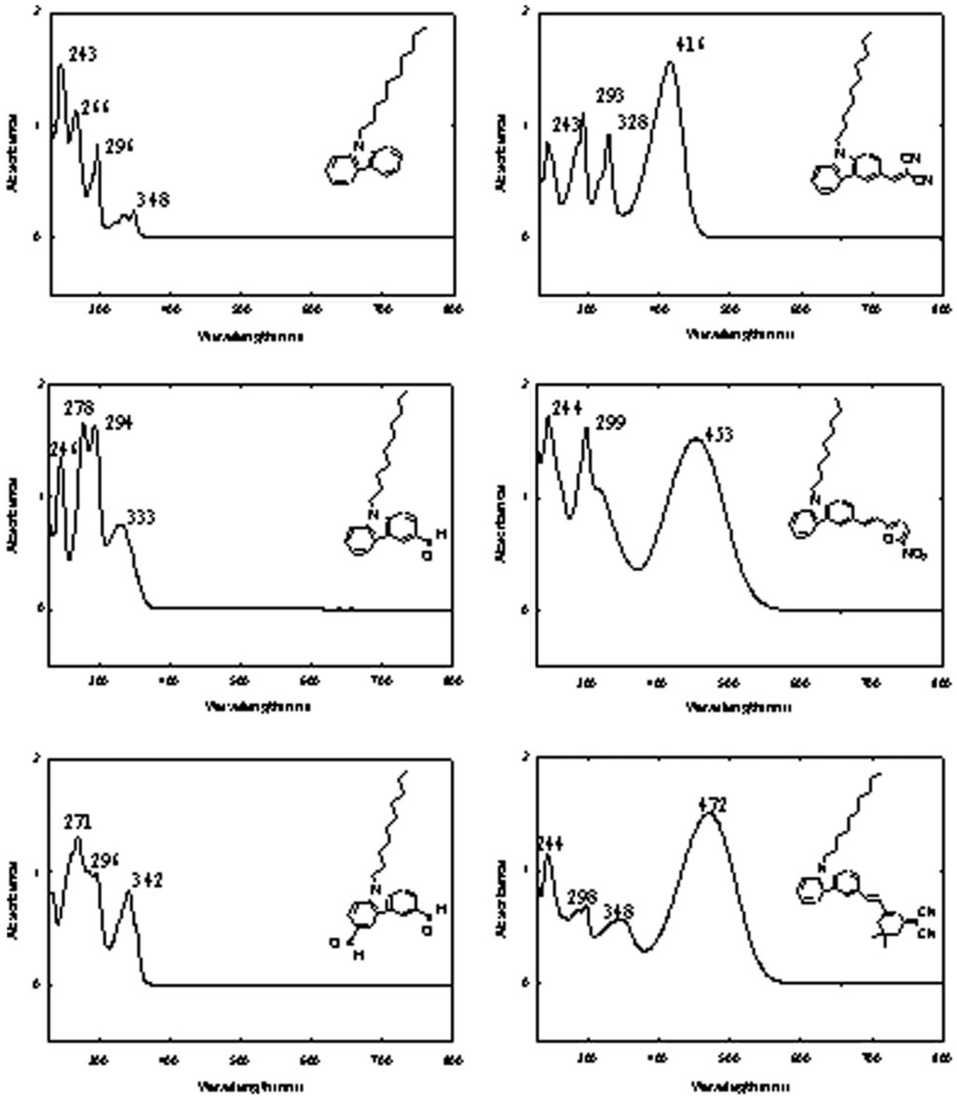

Fig. 3. UV and fluorescent spectra of Caz-MN, Caz-Fu, and Caz-Vm-MN.

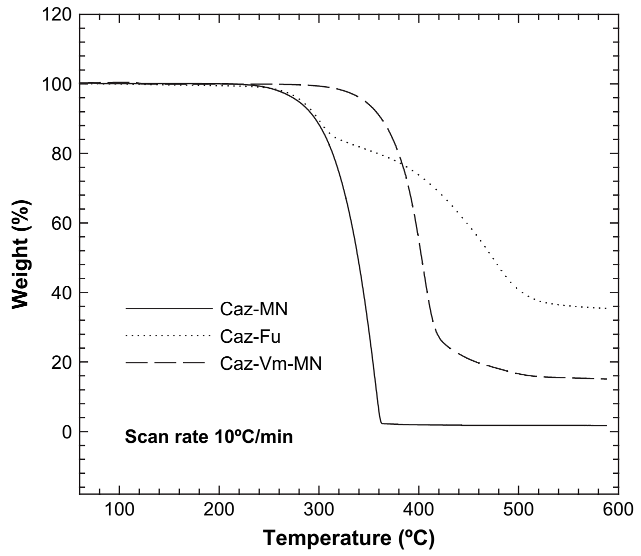

Fig. 4. Thermogravimetry analysis of Caz-MN, Caz-Fu, and Caz-Vm-MN.

2921 (H−C(SP^2)), 2851 (H−C(SP^3)), 2213 (CN). Anal. Calcd. for $C_{35}H_{41}N_3$: C, 83.45; H, 8.20; N, 8.34. Found: C, 83.45; H, 8.32; N, 8.42.

3. Results and discussion

Carbazole derivatives, which have various electron acceptors at positions 3 and 6, are well known to exhibit photoconductivity and second order nonlinear optical properties. The carbazole derivatives were synthesized by Knovenagel condensation and Wittig reactions and characterized by ^{1}H NMR, FT-IR, and UV–vis spectroscopy (Fig. 1).

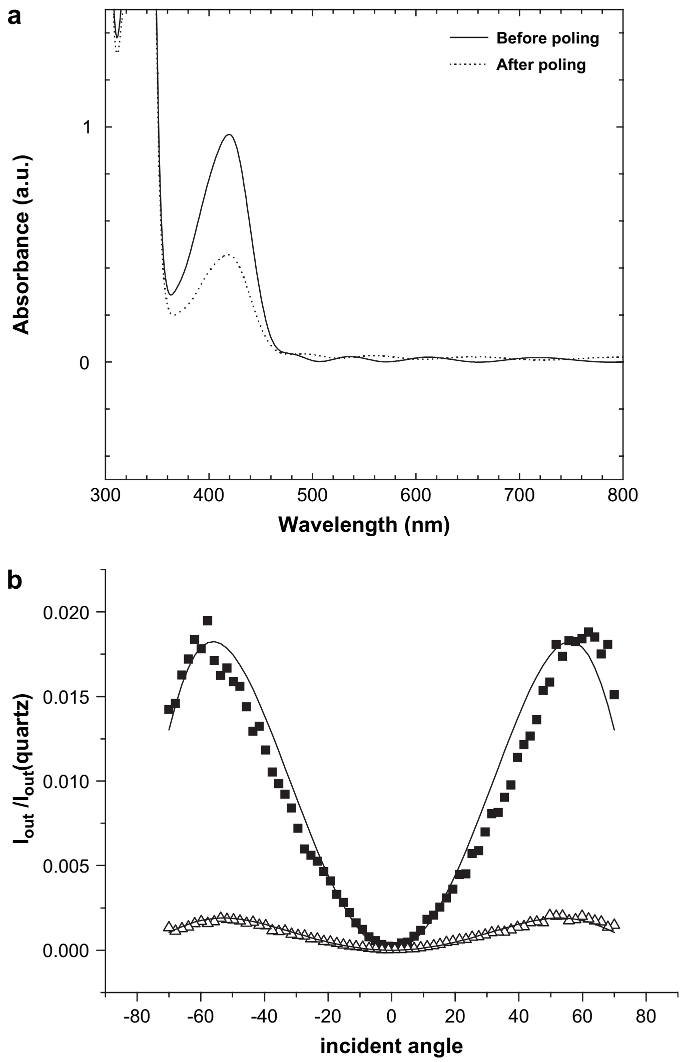

Fig. 5. (a) UV–vis absorption spectrum of Caz-MN/PVK film coated on glass substrate before and after poling (poled at 7 kV and 210 °C for 1 h). (b) Angular dependence of SHG signal in Caz-MN/PVK film.

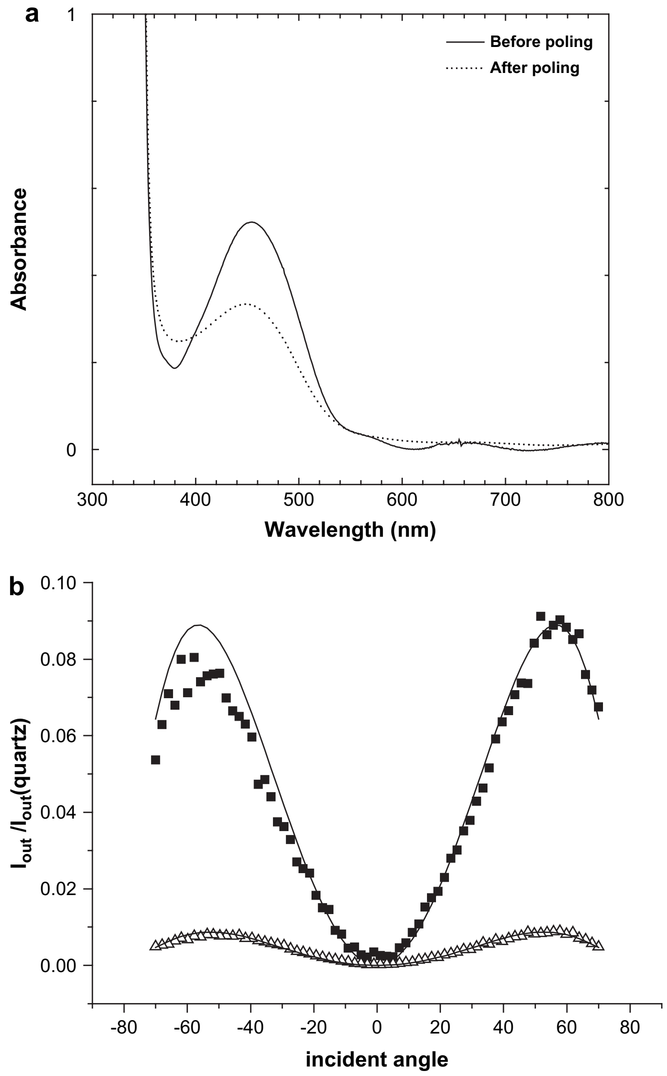

Fig. 6. (a) UV–vis absorption spectrum of Caz-Fu/PVK film coated on glass substrate before and after poling (poled at 7 kV and 210 °C for 1 h). (b) Angular dependence of SHG signal in Caz-Fu/PVK film.

Optical properties and EO relaxation processes were investigated by Maker fringe and simple reflection methods. Extensive studies have been done to put optical properties on polymers by introducing novel synthesized NLO chromophores. The ^{1}H NMR peaks were assigned based on the structure of carbazole: 8.25 (s, 1H, ArH), 8.11 (d, 1H, ArH), 7.5 (m), 7.05 (d, 1H, $-CH{=}CH-$), 6.86 (s, 1H, $>C{=}CH-$) (Fig. 2). The absorption λ_{max} of Caz-MN, Caz-Fu, and Caz-Vm-MN in chloroform appeared at 416 nm, 453 nm and 472 nm, respectively. The λ_{max} of Caz-Vm-MN was red shifted by 56 nm compared to that of Caz-MN due to extended π-conjugation. UV–vis absorption and photoluminescence spectra of the synthesized chromophores in chloroform solution showed the maximum absorptions corresponding to the π–π* transition (Fig. 3).

The alignment order parameters of the dyes were calculated from

$$\Phi = 1 - A_p/A_0,$$

where A_0 and A_p are the absorbance at the maximum of the spin coating film before and after poling, respectively.

In the TGA thermograms (Fig. 4) of these dyes, the point of initiated-weight-loss occurred in the range of 279–346 °C. The initiated-weight-loss temperatures (T_i) of the Caz-Vm-MN, Caz-Fu and Caz-MN were 346, 283 and 279 °C, respectively. Judging from the TGA thermograms, the dyes are stable above 250 °C.

The largest EO coefficient ($r_{33} = 4.03$ pm/V) and SH coefficient ($d_{33} = 3.06$ pm/V) were observed in the Caz-Vm-MN/PVK system (Figs. 5–7). The photorefractive properties of these carbazolyl dyes were demonstrated by two-beam coupling experiment at 632.8 nm. The physical properties of the PVK/dyes are summarized in Table 1.

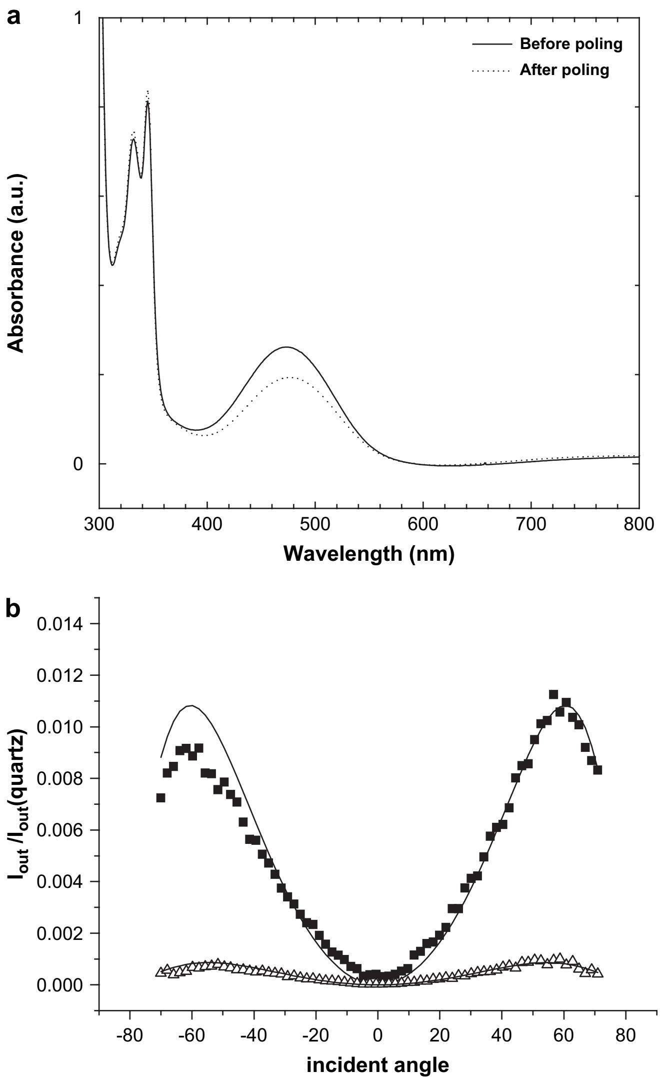

Fig. 7. (a) UV–vis absorption spectrum of Caz-Vm-MN/PVK film coated on glass substrate before and after poling (poled at 7 kV and 210 °C for 1 h). (b) Angular dependence of SHG signal in Caz-Vm-MN/PVK film.

4. Conclusion

We demonstrated that carbazole derived NLO chromophores of Caz-MN, Caz-Fu, and Caz-Vm-MN were thermally stable and had good optical properties. The absorption λ_{max} of Caz-MN, Caz-Fu, and Caz-Vm-MN in chloroform appeared at 416 nm, 453 nm and 472 nm, respectively. The λ_{max} of Caz-Vm-MN was red shifted by 56 nm compared to that of Caz-MN due to extended π-conjugation. The largest EO coefficient ($r_{33} = 4.03$ pm/V) and SH coefficient ($d_{33} = 3.06$ pm/V) were observed in the Caz-Vm-MN/PVK system. The photorefractive properties of these carbazolyl chromophores were demonstrated by two-beam coupling experiment at 632.8 nm. Asymmetric energy transfer between the two beams was observed.

Table 1
Physical properties of the polymers

	r_{33} (pm/V)	[a]d_{33} (esu)/(pm/V)	d_{31} (esu)	λ_{max} (nm)	[b]Φ	n^x		
						532 (nm)	632.8 (nm)	1064 (nm)
Caz-Vm-MN/PVK (0.1:0.9)	4.03	$7.3 \times 10^{-9}/3.06$	1.9×10^{-9}	473	0.26	1.70^t	1.693^p	1.49^t
Caz-Fu/PVK (0.1:0.9)	1.23	$2.06 \times 10^{-9}/0.86$	1.86×10^{-9}	454	0.36	1.71^t	1.691^p	1.65^t
Caz-MN/PVK (0.1:0.9)	0.06	$0.81 \times 10^{-9}/0.34$	0.74×10^{-9}	419	0.53	1.69^t	1.684^p	1.61^t

A_p: Absorbance at λ_{max} after poling; A_o: absorbance at λ_{max} before poling; n^x of x is measured methods: $x = t$ (transmittance), $x = p$ (prism coupling); $x = e$ (ellipsometery).

[a] $d_{33} = \chi^{(2)}/2$, 1 pm/V $= 2.386 \times 10^{-9}$ esu.

[b] $\Phi = 1 - (A_p/A_o)$.

Acknowledgment

This work was supported by BK21 and Hannam University.

Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.dyepig.2006.07.004.

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