**Full Paper:** Three carbazole-based copolymers with different long side chains were synthesized using the Wittig reaction. These three copolymers and model compound were characterized by nuclear magnetic resonance (NMR) spectroscopy to determine the *cis/trans* ratio. The *cis/trans* ratios decrease with the side chain length due to the variation in the degree of steric hindrance in the Wittig reaction. They affect the electroluminescence (EL) characteristics of the carbazole-based light emitting polymers. As the length of the side chain increases the wavelength of the emitted light increases proportionally whereas a decrease in the threshold voltages, 5.2, 4.8, 2.5 V was observed. However, EL intensity at same applied voltage increases with the length of the side chain. The energy levels of these three copolymers were also investigated to account for the phenomenon. Key words: carbazole, *cis-trans* ratio and electroluminescence.
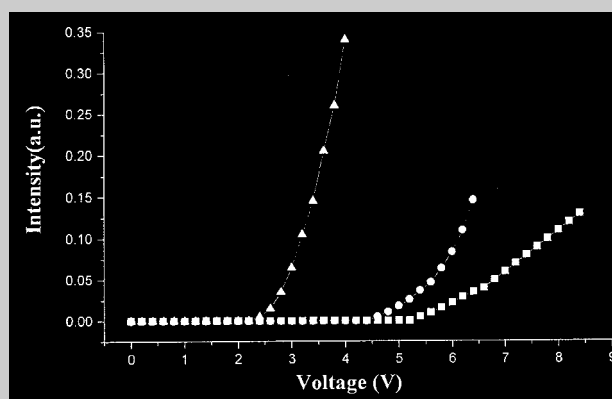
Electroluminescence intensity dependence on voltages in LEDs of (a) CP02 (■), (b) CP08 (●) and (c) CP14 (▲).

Effect of Side Chain Alkyl Length on the Electroluminescence Characteristics of Carbazole-Based Light Emitting Polymers

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Introduction

Polymer light-emitting diodes (PLED) are one of the most promising next-generation large-area flat panel displays.[1, 2] Many scientists have devoted to study PLED. Over the past several years, scientists have explored several options to improve emission characteristics, blending of polymers with different emission and charge transport characteristics,[3, 4] introducing side groups that affect molecular planarity and conjugation,[5, 6] varying lengths of conjugation,[7, 8] using different isomers[9] that lead to variation in the π-π* electronic energy gap[10] or in chain substitution to reduce the molecular packing in solid state to enhance photoluminescence efficiency. The use of side chain to improve photoluminescence efficiency and electroluminescence efficiency is widely practiced.[11] The side chains on polythiophene have significant effect on the electroluminescence characteristics. Carbazole containing conjugated polymers are one of the most attractive materials for use in organic LEDs, owing to their good hole transport properties. The hole mobility of poly(*N*-vinylcarbazole) (PVCz) is 10^{-6} to 10^{-7} cm^2/V · s, as measured by charge decay and time of flight method.[12] However, there is no π-conjugated main chain in PVCz. If used as an electroluminescence light-emitting polymer, it leads to the requirement of high threshold voltages that easily damage the polymeric materials, Romero et al.[13] used carbazole and thiophene to form copolymer as the material for possible applications in light-emitting devices. They observed an increase in the external quantum efficiency in the diodes based on the copolymers with short thiophene segments. Many examples have shown that, the formation of carbon-carbon double bonds in the Wittig reaction leads to a mixture of *cis* and *trans* isomers where geometric isomerism is possible. Further, the bulky groups may interfere with the reaction by virtue of their size. Therefore, the side chain length on the carbazole units may affect the double bond *cis/trans* ratio. In this study, we focus on studying the side chain effect on the *cis/trans* ratio and the electroluminescence characteristics of carbazole-based light emit-

ting polymer. The *cis/trans* ratios may be different from each other due to the different degree of steric factors in the Wittig reaction. The *cis/trans* ratio in turn affects the light emitting characteristics of the light-emitting polymer.

Experimental Part

Materials Preparation

All the chemicals from Tokyo Chemical Industry were used as received. All of the solvents and other chemicals were used after purification according to conventional methods when it required.

Synthesis of N-Octylcarbazole and N-Tetradecylcarbazole

To the mixture of carbazole (3.0 g, 0.018 mol) and potassium carbonate (4.98 g, 0.036 mol) in DMF (50 mL) was added dropwise 1-bromooctane (5.2 g, 0.027 mol) and reaction mixture refluxed for 2 d. The solution was poured into water (100 mL), extracted with dichloromethane (3 × 100 mL). The dichloromethane solution was dried over anhydrous magnesium sulfate and then the solvent was removed under reduced pressure. The residue upon purification by silica gel column chromatography using ethyl acetate/hexane (1:10) as the eluent, yielded the product, yield 85%, melting point 38 °C.

IR (KBr): 1337 (v_{C-N}), 748, 723 (v_{C-H} carbazole ring out of plane) cm^{-1}.

^{1}H NMR (CDCl$_3$): δ = 0.84 (t, J = 6.6 Hz, 3H, CH$_3$); 1.20–1.27 (m, 10H, 5 × CH$_2$); 1.75–1.82 (m, 2H, NCH$_2$CH$_2$); 4.20 (t, J = 7.2 Hz, 2H, NCH$_2$); 7.16–7.21 (m, 2H, Ar—H); 7.33–7.45 (m, 4H, Ar—H); 8.07 (d, J = 7.8 Hz, 2H, Ar—H).

C$_{20}$H$_{25}$N: Calcd. C 85.97 H 9.02 N 5.01; Found C 86.43 H 8.81 N 4.76

N-Tetradecylcarbazole was prepared following the procedure used for *N*-octylcarbazole except that 1-bromotetradecane was used instead of 1-bromooctane. *N*-Tetradecylcarbazole, yield 83%, melting point 39 °C.

IR (KBr): 1336 (v_{C-N}), 748, 723 (v_{C-H} carbazole ring out of plane) cm^{-1}.

^{1}H NMR (CDCl$_3$): δ = 0.84 (t, J = 6.6 Hz, 3H, CH$_3$); 1.23–1.34 (m, 22H, 11 × CH$_2$); 1.84–1.89 (m, 2H, NCH$_2$CH$_2$); 4.29 (t, J = 7.2 Hz, 2H, NCH$_2$); 7.19–7.25 (m, 2H, Ar—H); 7.38–7.49 (m, 4H, Ar—H); 8.10 (d, J = 7.9 Hz, 2H, Ar—H).

C$_{26}$H$_{37}$N: Calcd. C 85.89 H 10.26 N 3.85; Found C 86.24 H 10.33 N 3.43.

Synthesis of N-Ethyl-3,6-diformylcarbazole

Three *N*-alkyl-3,6-diformylcarbazoles were synthesized under similar reaction conditions except the starting material *N*-alkylcarbazole. To 25.0 g (0.34 mol) of *N,N*-dimethylformamide in 20 mL of 1,2-dichloroethane was added dropwise 43.9 g (0.29 mol) of phosphoryl choride at 0 °C. After the reaction mixture attained 35 °C, 4.0 g of *N*-ethylcarbazole (0.02 mol) was added. After stirring for 48 h at 90 °C the mixture was poured into 300 mL of water, extracted with chloroform, and the organic layer was washed with water,

dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (ethyl acetate/hexane, 1:3 as an eluent). *N*-Ethyl-3,6-diformylcarbazole was obtained in 36% yield, melting point 158 °C.

IR (KBr): 2802, 2720 (v_{C-H} stretching), 1679 ($v_{C=O}$ aromatic aldehyde), 1591, 1479 ($v_{C=C}$ aromatic stretching) cm^{-1}.

^{1}H NMR (CDCl$_3$): δ = 1.35 (t, J = 7.3 Hz, 3H, CH$_3$); 4.25 (q, J = 7.2 Hz, 2H, NCH$_2$); 7.36 (d, J = 8.5 Hz, 2H, Ar—H); 7.89 (d, J = 7.2 Hz, 2H, Ar—H); 8.39 (s, 2H, Ar—H); 9.95 (s, 2H, CHO).

C$_{16}$H$_{13}$NO$_2$: Calcd. C 76.48 H 5.21 N 5.57 O12.73; Found C 76.23 H 5.26 N 5.61 O 12.90.

N-Octyl-3,6-diformylcarbazole, yield 35%, melting point 119 °C.

^{1}H NMR (CDCl$_3$): δ = 0.85 (t, J = 7 Hz, 3H, CH$_3$), 1.20–1.35 (m, 10H, 6 × CH$_2$), 1.89–1.95 (m, 2H, NCH$_2$CH$_2$), 4.39 (t, J = 7.3 Hz, 2H, NCH$_2$), 7.56 (d, J = 5.6 Hz 2H, Ar—H), 8.09 (dd, J = 8.5 and 1.6 Hz, 2H, Ar—H), 8.68 (d, J = 1.2 Hz, 2H, Ar—H), 10.14 (s, 2H, CHO).

C$_{22}$H$_{25}$NO$_2$: Calcd. C 78.77 H 7.51 N 4.18 O 9.54; Found C 78.40 H 7.52 N 4.35 O 9.73.

N-Tetradeyl-3,6-diformylcarbazole, yield 37%, melting point 121 °C.

^{1}H NMR (CDCl$_3$): δ = 0.87 (t, J = 6.6 Hz, 3H, CH$_3$); 1.23–1.40 (m, 22H, 11 × CH$_2$); 1.89–1.94 (m, 2H, NCH$_2$CH$_2$); 4.39 (t, J = 7.3 Hz, 2H, NCH$_2$); 7.56 (d, J = 8.6 Hz, 2H, Ar—H); 8.09 (dd, J = 8.5 and 1.6 Hz, 2H, Ar—H); 8.68 (d, J = 1.3 Hz, 2H, Ar—H); 10.14 (s. 2H, CHO).

C$_{28}$H$_{37}$NO$_2$: Calcd. C 80.15 H 8.89 N 3.34 O 7.63; Found C 79.89 H 8.87 N 3.46 O 7.78.

Synthesis of Poly(N-alkylcarbazolylvinylene-1,4-phenylenevinylene)

The Wittig polymerization was carried out under similar conditions for preparing three poly(*N*-alkylcarbazolylvinylene-1,4-phenylenevinylene)s. For the synthesis of poly(*N*-ethylcarbazolylvinylene-1,4-phenylenevinylene), sodium (0.112 g, 0.0048 mol) in ethanol (5 mL) was added dropwise to the solution of 0.51 g (0.002 mol) of 3,6-diformyl-*N*-ethyl-carbazole and 1.398 g (0.002 mol) *p*-xylylene bis(triphenylphosphonium chloride) in 40 mL of ethanol/chloroform (1:1) co-solvent. After the mixture was stirred overnight at room temperature, dilute HCl (0.78 g, 0.0048 mol, 2%) was added and a tanning precipitate was obtained. The precipitate was first washed with ethanol/D.I. water (3:1, 400 mL), and then with D.I. water (500 mL). The precipitate was dissolved in chloroform and re-precipitated from cyclohexane twice, followed by vacuum drying for two days, yield 48%. The product was denoted as CP02.

IR (KBr): 1605 ($v_{C=C}$ vinyl stretching), 1475 ($v_{C=C}$ aromatic stretching), 810 (v_{C-H} aromatic ring out of plane) cm^{-1}.

$\bar{M}_n$ = 3053; $\bar{M}_w$ = 3173; polydispersity index = 1.04.

Poly(*N*-octylcarbazolylvinylene-1,4-phenylenevinylene) was denoted as CP08 with 46% yield from *p*-xylylene bis(triphenylphosphonium chloride) (1.398 g, 2 mmol) and 3,6-diformyl-*N*-octylcarbazole (0.67 g, 2 mmol).

IR (KBr): 1605 ($v_{C=C}$ vinyl stretching), 1479 ($v_{C=C}$ aromatic stretching), 810 (v_{C-H} aromatic ring out of plane) cm^{-1}.

$\overline{M}_n = 3\,273$; $\overline{M}_w = 3\,475$; polydispersity index = 1.1.

Poly(N-tetradecylcarbazolylvinylene-1,4-phenylenevinylene) was denoted as CP14 with 46% yield from p-xylylene bis(triphenylphosphonium chloride) (1.38 g, 2 mmol) and 3,6-diformyl-N-tetradecylcarbazole (0.84 g, 2 mmol).

IR (KBr): 1604 ($v_{C=C}$ vinyl stretching), 1478 ($v_{C=C}$ aromatic stretching), 811 (v_{C-H} aromatic ring out of plane) cm^{-1}.

$\overline{M}_n = 3\,871$; $\overline{M}_w = 5\,029$; polydispersity index = 1.4.

Normally, polymer containing cis-olefinic links can be isomerized to the all-$trans$ form by refluxing in toluene for 4 h in the presence of a catalytic amount of iodine.[14–19] This procedure was applied to the $cis/trans$ mixture of CP02, CP08 and CP14 and black precipitates were obtained. They became insoluble and of no fluorescence.

Synthesis of Model Compound Bis(3-N-ethylcarbazolyl)-terephthalidene of a cis-trans Mixture and All-trans Form

The Wittig reaction was carried out for preparing the bis(3-N-ethylcarbazolyl)terephthalidene. For bis(3-N-ethylcarbazolyl)terephthalidene, sodium (0.112 g, 0.0048 mol) in ethanol (5 mL) was added dropwise to the solution of 0.45 g (0.002 mol) of N-ethylcarbazole-3-carboxaldehyde and 1.398 g (0.002 mol) of p-xylylene bis(triphenylphosphonium chloride) in 40 mL of ethanol/chloroform (1 : 1) co-solvent. After the mixture was stirred overnight at room temperature, an aqueous solution of HCl (0.78 g, 0.0048 mol, 2%) was added and a tanning precipitate was obtained. The product at this step was a cis-$trans$ mixture. Using silica gel column chromatography with hexane as eluent, the product was purified. The product was dissolved in chloroform and re-precipitated from cyclohexane, then vacuum-dried for two days. The product was found to be all-$trans$ form, yield 74%, melting point 268 °C.

IR (KBr): 1604 ($v_{C=C}$ vinyl stretching), 1475 ($v_{C=C}$ aromatic stretching), 961 (out-of-plane bending of $trans$-vinylene), 809 (v_{C-H} aromatic ring out of plane) cm^{-1}.

$C_{38}H_{32}N_2$: Calcd. C 88.34 H 6.24 N 5.42; Found C 88.22 H 6.16 N 5.45.

Diode Preparation

ITO glass was cleaned by following standard procedure: The substrates were washed ultrasonically (NEY200 ultrasonic bath) in a solution of Al conox surfactant (Al-conox) in deionized water for 0.5 h, then rinsed with deionized water, washed in ultrasonic bath for 0.5 h in acetone, then rinsed again in deionized water, and finally dried in a vacuum oven at 100 °C for several hours. Thin polymer films for PL and EL studies were obtained by spin casting the polymer chloroform solutions on ITO glass at 2000 rpm and then dried at 80 °C under vacuum. The metal Al was then thermally evaporated onto the surface of the carbazole-based polymer. The ITO was used as an anode material and vacuum evaporated aluminium as cathode.

Characterization

These new compounds were characterized by ^{1}H NMR using a Bruker AM 300 spectrometer. Infrared spectra were measured with Nicolet Protégé 460. Molecular weights and poly-

dispersities of polymers were determined by gel permeation chromatography (GPC) analysis with polystyrene as the standard (High-pressure GPC assembly Model M590 Pump, μ-stryragel columns of 10^5, 10^4, 10^3, 500 and 100 Å, refractive index detectors, solvent THF). The mobile phase was THF flowing at 1.0 mL/min. Absorption, photoluminescence (PL) spectra were studied with solution or thin films. The absorption spectra were taken with HP8453 UV-VIS spectrometer. The PL spectra were taken with Shimadzu RF-5301 PC Spectrofluorophotometer. The energy level of electronic structure of the polymers is determined from UV-VIS absorption spectra and the data of cyclic voltammetry using CHI600A Electrochemical Analyzer. The cyclic voltammetry was carried out using Pt counter electrode and a Ag/Ag$^+$ reference at scan rate of 10 mV/s. The electrolyte was 0.1 M $tetra$-BuNClO$_4$ in acetonitrile. Film thickness was measured using Alpha Step Dektak ST surface profiler. The electroluminescence (EL) spectra were measured with a Jasco FR-770 spectrometer. The light emitting polymers were sandwiched between Al and ITO glass to form light emitting diodes. The current-voltage characteristics were measured with a Keithley 237 electrometer. The intensity-voltage characteristics were measured with a Keithley 237 electrometer and a photodiode detector connected with a New Port power meter (Model 1815-c). All measurements were carried out at room temperature.

Results and Discussion

The polymerization was proceeded with the Wittig reaction, which easily led to a mixture of cis- and $trans$-isomers. In order to determine the $cis/trans$ ratio, the model compound bis(3-N-ethylcarbazolyl)terephthaldiene of all-$trans$ form and cis-$trans$ mixture were prepared. The ^{1}H-^{1}H correlated spectrum (^{1}H-^{1}H-COSY) in Figure 1 is used to determine the correlated protons of the all-$trans$ form. We assign the signal $\delta = 8.41$ ppm to H(8) because of its chemical shift, and the Figure 1 also shows the H(5) correlated with H(7), H(7) correlated with H(6), and H(6) correlated with H(5). Similarly, we assign the signal $\delta = 8.18$ ppm to H(1), $\delta = 7.6$ ppm (2H) to H(16) and H(20) H(17) and H(19) are symmetrical to them) and $\delta = 7.31$ ppm to H(4) due to spin-spin splitting and chemical shift, so we can observe the H(2), H(13), and H(14) at chemical shift $\delta = 7.23, 7.25, 7.45$ ppm, respectively. As shown in Figure 2, the ^{1}H NMR spectra of the model compound bis(3-N-ethylcarbazolyl)terephthalidene of all-$trans$ form and the cis-$trans$ mixture are very similar except the chemical shift due to different —CH=CH— configuration. The peak of $\delta = 6.53$–6.74 ppm exists only in the spectrum of the cis-$trans$ mixture. We use ACD/Dictionary Version 1.0 software of Advanced Chemistry Development Inc. to calculate the chemical shift of the bis(3-N-ethylcarbazolyl)terephthalidene of all-cis form chemical shift of —CH=CH— located at 6.6–6.8 ppm, and the Aldrich Library of NMR Spectra also show that the cis-CH=CH chemical shift of the cis-stilbene is 6.58 ppm
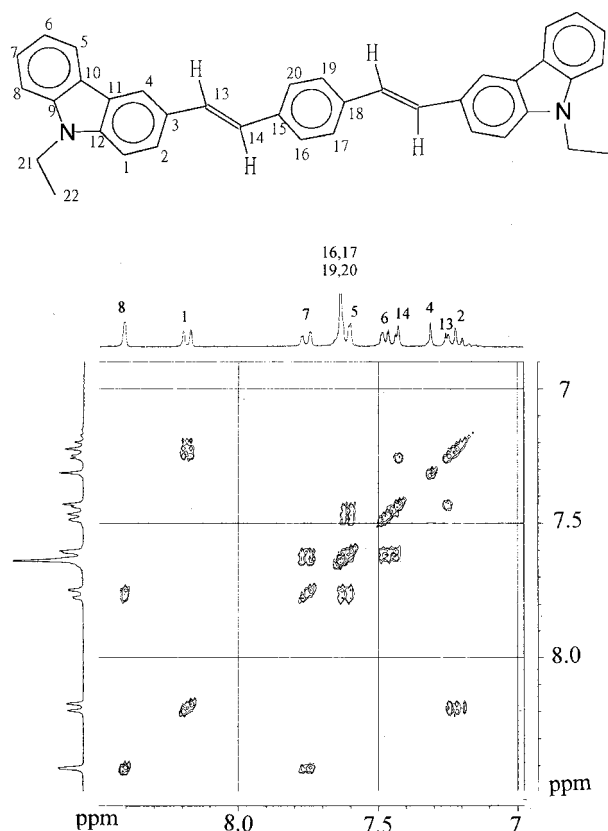
Figure 1. ^{1}H-^{1}H COSY of the all-*trans* model compound in DMSO-d_6 and the atomic numbering scheme.

Figure 2. ^{1}H NMR spectra of (a) the all-*trans* model compound bis(3-*N*-ethylcarbazolyl)terephthalidene and (b) the *cis-trans* mixture in DMSO-d_6.

but the *trans*-stilbene does not show any peak in the range of 6–7 ppm.[20] As a result, we assign the chemical shift of δ = 6.53–6.74 ppm in Figure 2 due to *cis*-CH=CH configuration. The peaks at δ = 4.45 and 1.25 ppm are assigned to H(21) and H(22), respectively. The peaks at 2.45 and 3.35 ppm are due to DMSO and H$_2$O, respectively. Table 1 shows the ^{1}H chemical shifts of bis(3-*N*-ethylcarbazolyl)terephthalidene of all-*trans* form and of the *cis-trans* mixture. The *cis-trans* percentage can be determined from dividing the integration of the peak at δ = 6.53–6.74 ppm by that at δ = 4.45 ppm in the *cis-trans* mixture. The results showed in Table 2, revealing a high *cis/trans* ratio in bis(3-*N*-ethylcarbazolyl)terephthaldiene indicates that small ethyl side chain provides a greater tendency of *cis*-formation in the Wittig reaction. As the side chain length increases, the *cis/trans* ratio of the carbazole-based polymers decreases. It unveils that long side chain length on the carbazole groups impedes the formation of *cis*-form. Figure 3 is proposed to show the possible mechanism of the Wittig reaction to form *cis*- and *trans*-conformations, and their relative potential energies of the intermediate states are surmised and sketched in Figure 4. Due to the lower steric hindrance, the *trans*-conformation has a lower energy barrier, activation energy of the reaction. The energy barrier difference
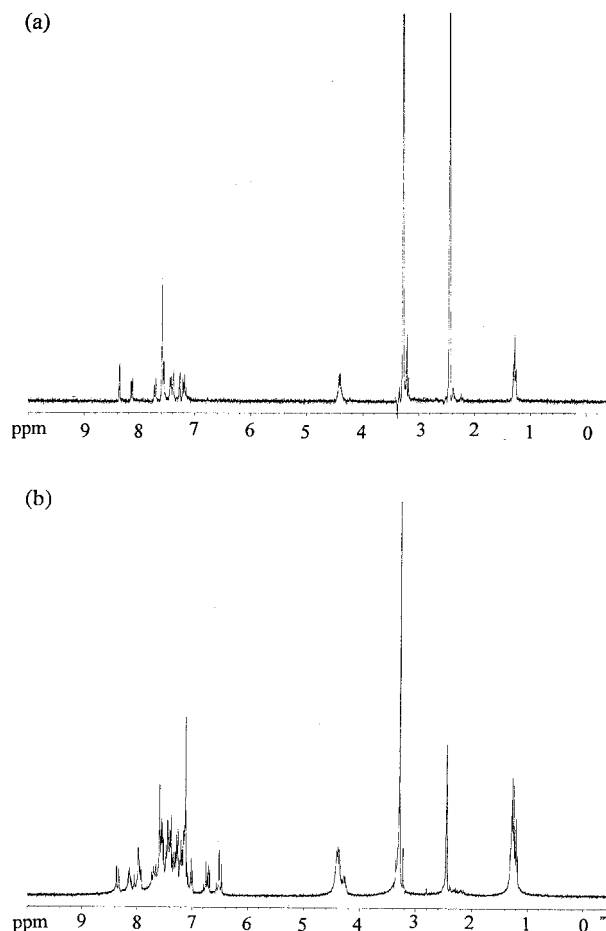
of the double bond formation between *cis*- and *trans*-conformation becomes more prominent, as the side chain group becomes longer. Therefore, the *N*-ethylcarbazole-based polymer has high *cis/trans* ratio, 46/54 because of its small side chain ethyl group with nearly equal but not equal activation energy. And the *N*-tetradecylcarbazole-based polymer has almost exclusively *trans* conformation due to its large side chain tetradecyl group leading to great difference in the activation energy. Figure 5 shows the typical FT-IR spectra of 3,6-diformyl-*N*-ethylcarbazole and the model compound bis(3-*N*-ethylcarbazolyl)-terephthalidene of all-*trans* form. The former shows an aldehyde carbonyl band at 1687 cm^{-1}, but it disappears in the latter. However, a medium and sharp absorption peak at 961 cm^{-1} appears in the latter. It corresponds to the out-of-plane bending mode of the *trans*-vinylene.[21, 22]

Figure 6 shows the UV-VIS spectra of the polymers and a model compound of a *cis-trans* mixture and all-*trans* form in chloroform. In the range of the wavelength below 350 nm, the absorbance decreases with the side chain length. But in the range of the wavelength higher

Table 1. ^{1}H NMR chemical shifts (in ppm relative to TMS) of bis(3-*N*-ethylcarbazolyl)terephthalidene of all-*trans* form and *cis-trans* mixture in DMSO-d_6.

Proton[a]	all-*trans* isomer	*cis-trans* mixture
Carbazole ring		
H(1)	8.18 (1H)	Complicated[b]
H(2)	7.23 (1H)	
H(4)	7.31 (1H)	
H(5)	7.60 (1H)	
H(6)	7.48 (1H)	
H(7)	7.76 (1H)	
H(8)	8.40 (1H)	
Olefinic link		
H(13)	7.25 (1H)	7.25
H(14)	–	6.53
	7.45 (1H)	7.45
	–	6.74
Central ring		
H(16), (20)	7.63 (2H)	7.63
Side chain		
H(21)	4.45 (2H)	4.45
H(22)	1.25 (3H)	1.25

[a] The protons are numbered in Figure 1.

[b] Due to the mixture structure there are too many singles in the range of 7–8.4 ppm. Therefore, we can not characterize the carbazole ring peak of *cis-trans* mixtures.

Table 2. Chemical shifts (δ in ppm) of ^{1}H NMR and *cis*-isomer percentages of the model compounds and the polymers in DMSO-d_6.

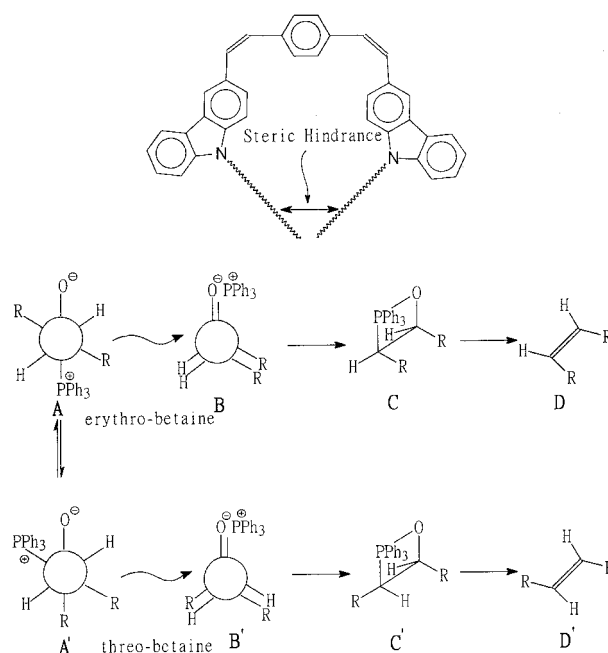| Proton	all-*trans* model	*cis-trans* model	CP02	CP08	CP14
Olefinic link					
H(13)	7.25	7.25	7.25	7.25	7.25
		6.53	6.53	6.53	–
H(14)	7.45	7.45	7.45	7.45	7.45
		6.74	6.74	6.74	–
Side chains					
H(21)	4.45	4.45	4.45	4.45	4.45
cis/trans ratio	0	0.72	0.67	0.41	–

Figure 3. Part of the Wittig reaction mechanism, emphasizing the stereochemical course, erythro- and threo-betaine are shown in their presumably lowest energy conformation.

than 350 nm, the absorbance increases with the side chain length. We compared the all-*trans* form with the *cis-trans* mixture and found a significant red shift in the former due to the *trans* form having better effective π-conjugation. The longer side chain leads to a longer onset UV-VIS absorption wavelength and a lower energy gap of the polymers. The latter corresponds to 2.71, 2.67 and 2.65 eV for CP02, CP08, and CP14, respectively.

Figure 7 shows the PL spectra of CP02, CP08 and CP14. The PL spectrum of CP02 displays a major maximum at 440 nm and a minor maximum 470 nm. The PL spectrum of CP08 shows a doublet maximum with almost equal intensity at 450 and 470 nm. The CP14 show a relatively narrow peak at 480 nm. A red shift and narrowing

the bandwidth with increasing the chain length is observed in the photoluminescence spectra. After refluxing these polymers in toluene for 4 h in the presence of catalytic iodine, the fluorescence character of the polymer disappears. We have not been able to get a pure *trans* form of these from the above procedure. Karasz et al. reported that the transformation from *cis* to *trans* is effective for the soft segment-containing polymers, but it does not work for the rigid main chain polymers.[14–19] Our single layer EL devices (ITO/CPs/Al) show a broad electroluminescence with a maximum at (λ_{max} = 460 nm) for CP02, a doublet maximum at 460 and 485 nm for CP08, and a major maximum at 495 nm and a minor maximum at 460 nm for CP14 as shown in Figure 8. The EL bandwidth also decreases with the side chain length. The bandwidth of the EL spectrum is greater than that of the PL spectrum for the same polymer. The wavelength of the EL peak also showed a red shift relative to the corresponding PL peak wavelength. It may be due to the condensed phase effect on the cross-interaction between energy levels. The current density versus voltage from an LED fabricated with CP02, CP08, and CP14 is shown in Figure 9. The onset of driving voltage decreases with the chain length. It corresponds to 2.5, 4.8, and 5.2 V, for CP14, CP08, and CP02, respectively. The molecular orbital level diagram of HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) of these polymers in Figure 10 may account for the situation. All these three polymers have comparable oxidation potential (HOMO level close to each other), but
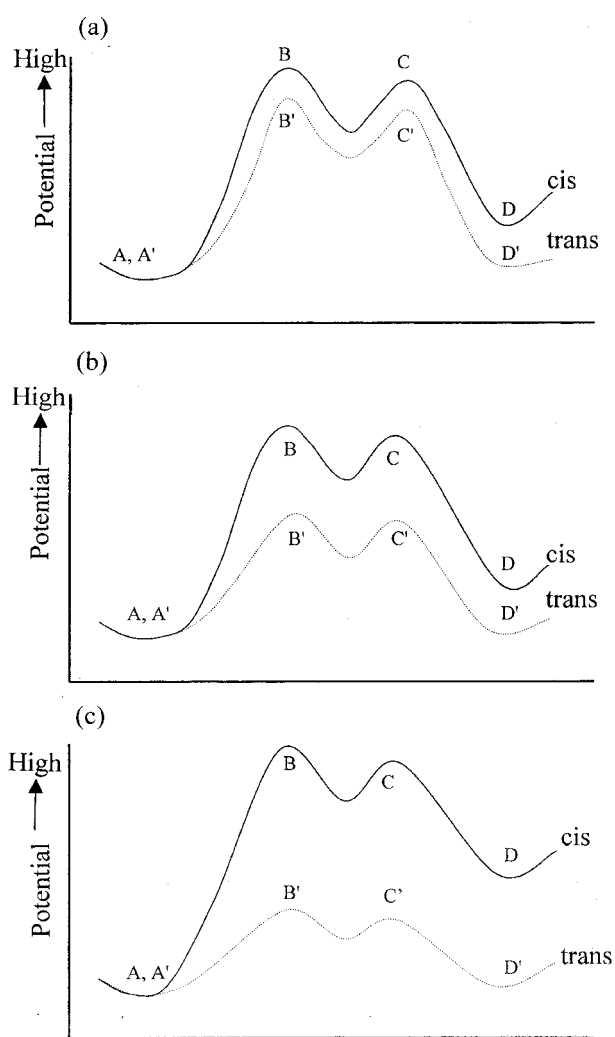
Figure 4. Relative potential of the intermediates in the Wittig reaction. (a) *N*-ethyl, (b) *N*-octyl, (c) *N*-tetradecyl.
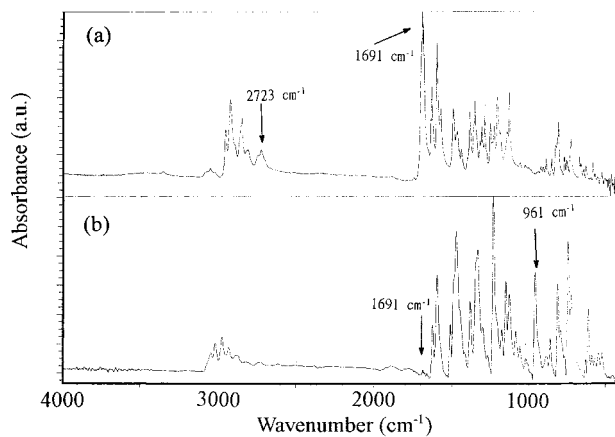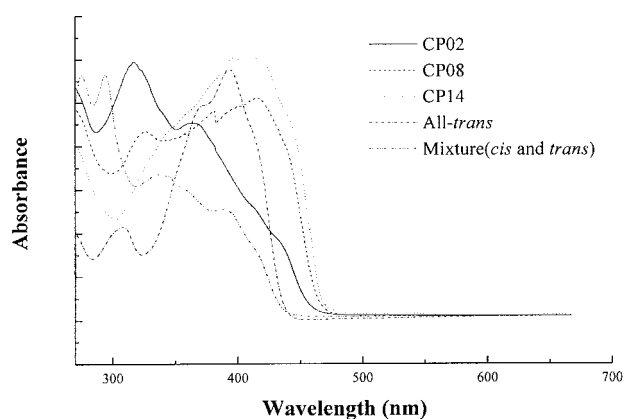

Figure 6. UV-VIS absorption of the CP02, CP08, CP14, all-*trans* form and a *cis-trans* mixture in chloroform (1 mg/1 ml) at ambient temperature.
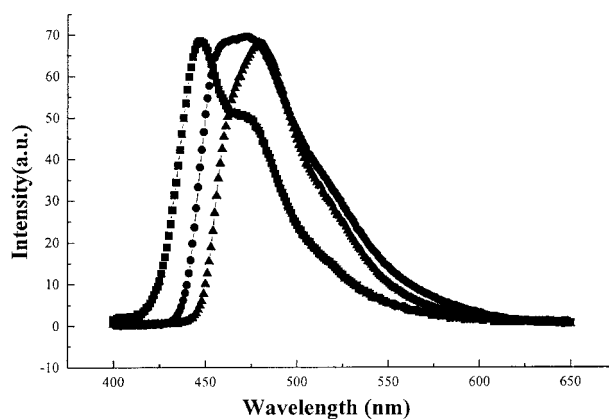

Figure 7. Photoluminescence spectra of (a) CP02 (■), (b) CP08 (●) and (c) CP14 (▲) at ambient temperature.

Figure 5. Infrared spectra of (a) 3,6-diformyl-*N*-ethylcarbazole and (b) the model compound (all-*trans*).
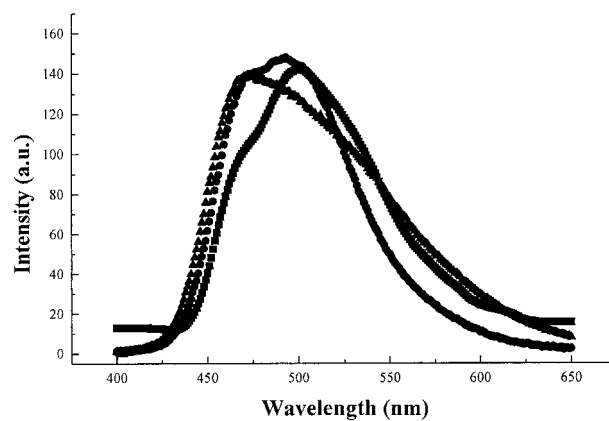

Figure 8. Electroluminescence spectra of (a) CP02 (■), (b) CP08 (●) and (c) CP14 (▲) at ambient temperature.
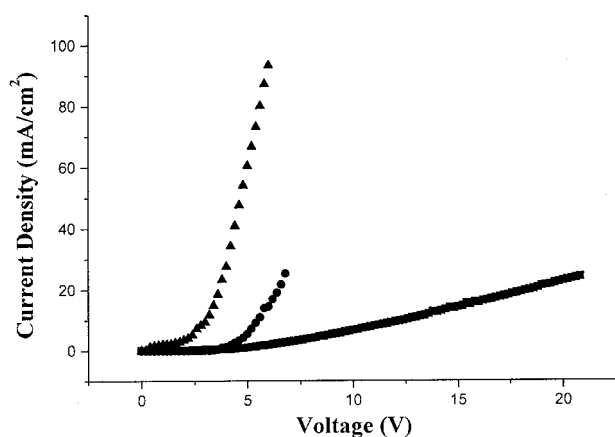
Figure 9. Current density dependence on voltages in LEDs of (a) CP02 (■), (b) CP08 (●) and (c) CP14 (▲).
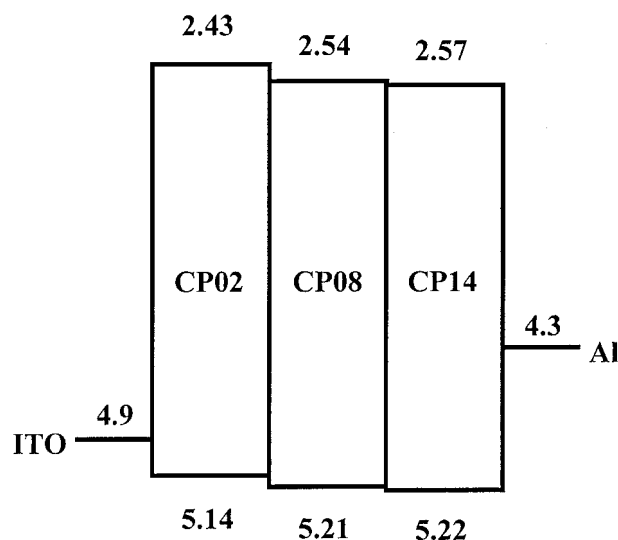

Figure 10. The energy level diagram of CP02, CP08 and CP14.
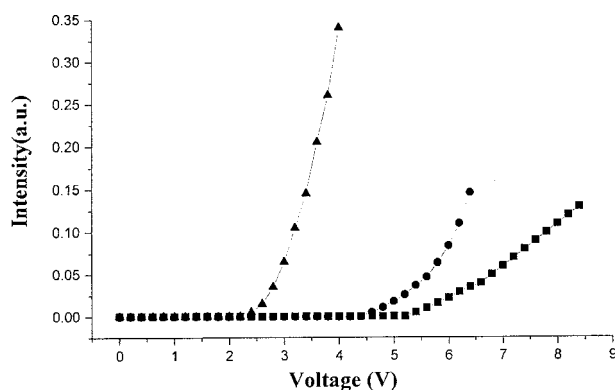

Figure 11. Electroluminescence intensity dependence on voltages in LEDs of (a) CP02 (■), (b) CP08 (●) and (c) CP14 (▲).

have different reduction potential. The LUMO level follows the order: CP02 higher than CP08, which in turn, higher than CP14. Thus CP14 has the lowest electron injection barrier. Therefore, it has a lowest onset of the driving voltage. The current EL intensity versus voltage is shown in Figure 11. The lowest threshold voltage of CP14 leads to the best EL intensity in all these three polymers and CP02 exhibits the poor EL characteristics. The *cis/trans* ratio in the light-emitting polymer practically changes the molecular level and affects the PL and EL characteristics.

Conclusions

We have synthesized a series of carbazole-based copolymers by Wittig reaction as light emitting polymers. The resulting polymers are highly soluble in common organic solvents. They can be spin-cast onto various substrates to give highly transparent homogenous thin films. Different side chains on the carbazole unit lead to different degree of steric hindrance in the Wittig reaction. The *cis/trans* ratio decreases with increasing side chain length. The bulky groups interfere with the reaction by virtue of their energy barrier in CH=CH formation much higher for the *trans* form. The side chain length controls the *cis/trans* ratio of the polymers. With a longer side chain, the PL and EL spectra show a slight red shift in comparison with the spectra of the polymer with a shorter side chain. The carbazole-based polymer has a lower threshold voltage and higher electroluminescence intensity due to the lower LUMO energy level. These three polymers have a comparable HOMO energy level. Apparently, the device performance is promoted when the *trans*-CH=CH composition increases. The side chain groups affect the *cis/trans* ratio and in turn, affecting the photoluminescence and electroluminescence characteristics of polymer.

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