

Novel 1,4-Diketo-3,6-diphenyl pyrrolo[3,4-c]pyrrole (DPP)-based Copolymers with Large Stokes Shift

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ABSTRACT: Two novel alternating π -conjugated copolymers, named PDPPDOPV and PDPPDOPE, constituted of 1,4-diketo-3,6-diphenyl pyrrolo[3,4-c]pyrrole (DPP) with 2,5-dioctyloxy-1,4-phenylenevinylene (DOPV) or 2,5-dioctyloxy-1,4-phenyleneethynylene (DOPE), respectively, were synthesized and characterized by UV-vis, FT-IR, and photoluminescence spectroscopy. They are dark red solid readily soluble in various common organic solvents including THF and chloroform. The UV-vis absorption spectra of the polymers show strong absorption bands, which correspond to the π - π^* transition of π -conjugated

segments. Photoluminescence (PL) spectra show that both polymer films and solution have large Stokes shifts. From their fluorescence behavior, Stokes shifts of 173 nm and 199 nm are derived for the films of PDPPDOPV and PDPPDOPE, respectively, which are the largest two values ever reported for DPP-containing polymers. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 1976–1984, 2009

Key words: conjugated polymers; copolymerization; films; fluorescence; photophysics; pyrrole

INTRODUCTION

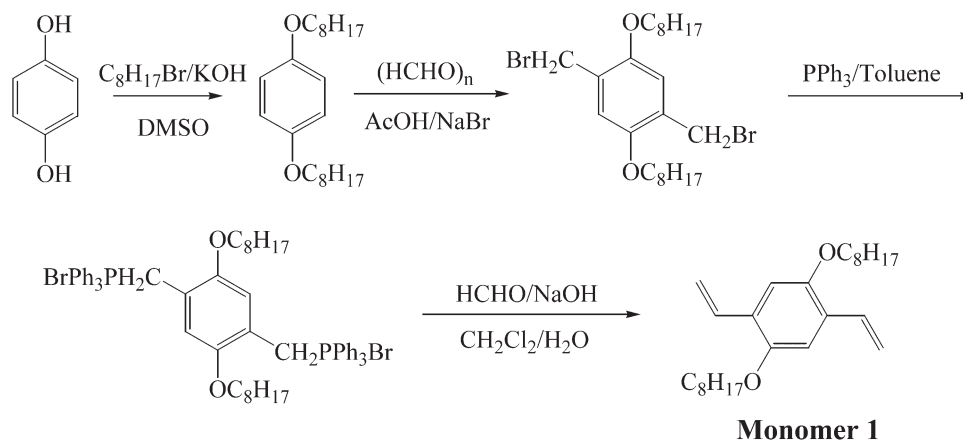
During the past decades, there has been a great deal of interest in the synthesis of novel conjugated polymers because of their excellent optoelectronic properties. They have been actively investigated for a variety of optoelectronic applications, such as field effect transistors (FETs), lasers, light emitting diodes (LEDs), organic solar cells, and photon mode optical storage,^{1–9} moreover, for the application in fluorescence probe.¹⁰ It is known that some conjugated polymers generally have strong fluorescence, superior brightness, and photostability. In particular, some conjugated polymer dyes usually have large Stokes shift, similar to the organic fluorescence dyes. It was reported that large Stokes shift could be utilized to maximize fluorescent signals whereas minimize issues of absorbance, autofluorescence, and light scattering at longer wavelengths, particularly above 600 nm,¹¹ which are very important for their practical applications. Compared with the organic dyes, conjugated polymers exhibited the advantages of easy modification of wavelength of fluorescent emission and Stokes shift by copolymerization with appropriate monomers.¹² As a result, conjugated

polymers with large Stokes shift attracted much attention recently.^{13,14}

1,4-Diketopyrrolo[3,4-c]pyrrole and some of its derivatives are commercialized as high performance pigments with exceptional light, weather, and heat stability.^{15,16} Diketopyrrolopyrroles are industrially important red pigments side by side with phthalocyanine, quinacridone, and perylene pigments. 1,4-Diketo-3,6-diphenyl pyrrolo[3,4-c]pyrroles (DPPs) belong to the class of hydrogen-bonded pigments such as quinacridone and indigo compounds.¹⁷ One of the appealing features of the H-bond pigments is to exhibit vivid red or blue colors in the solid state, although their molecular weights are quite small and they are thus vaguely colored in solution. The H-bond pigments are typically composed of a π -conjugated system as chromophore and of two pairs of NH (donor) and C=O (acceptor) as auxochromes. The molecules are firmly held together in the solid state by means of intermolecular hydrogen bonds based on NH...O, forming a three-dimensional H-bond network.^{18–20}

Although low molecular weight derivatives of DPP have been extensively studied on their optical and photophysical properties, relatively little is known about DPP-containing polymer based materials and their properties. As yet few publications and patents on DPP-polymers were reported.^{21–23} Recently, there have been several reports,^{24–28} which reveal that the incorporation of DPP units into

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Scheme 1 Synthesis of monomer 1.

polymers results in deeply colored, highly photoluminescence and electroluminescent materials. Two of the most well-established classes of conjugated polymers are poly(*p*-phenyleneethynylene)s (PPEs) and poly(*p*-phenylenevinylene)s (PPVs).^{29–34} Both are promising candidates for the molecular wire used as active components in polymer-based electronic and photonic devices. Moreover, phenylenevinylene (PV) and phenyleneethynylene (PE) both have π -conjugated structure and their polymers have been widely used as electroluminescent materials.^{35–43}

In our contribution, two novel alternating π -conjugated copolymers (PDPPDOPV and PDPPDOPE) constituted of DPP with 2,5-dioctyloxy-1,4-phenylenevinylene (DOPV) or 2,5-dioctyloxy-1,4-phenyleneethynylene (DOPE) structure units, respectively, were synthesized and characterized. The DPP unit as underlying chromophore system was incorporated into poly(*p*-phenylenevinylene) (PPV) or poly(*p*-phenyleneethynylene) (PPE) backbone by palladium catalyzed Heck coupling reaction to obtain novel conjugated copolymers. These copolymers, PDPPDOPV and PDPPDOPE, exhibit red emission, which is based on the assumption that DPP units in the copolymer have red fluorescence. In the present article, we designed and synthesized these copolymers PDPPDOPV and PDPPDOPE, hoping to combine the excellent properties of both DPP and PV/PE, and thus obtain potential materials for LED, photovoltaic applications, and especially in fluorescence probe due to their large Stokes shift.

EXPERIMENTAL

Measurements

FT-IR spectra were recorded on a Bruker Vector 22 IR spectrometer. ¹H NMR measurements were carried out on Varian 300 MHz spectrometer (solvent: CDCl₃, internal standard: TMS, tetramethylsilane). The elemental analyses were performed on Thermo

Finnigan Instrument Flash EA1112. The UV-vis spectra were recorded on a Varian Cary 100 Bio UV-Vis spectrophotometer. The temperature of onset weight loss was determined with a Delta Series TGA-7 in nitrogen with a heating rate of 10°C/min. The photoluminescence (PL) spectra were recorded on a Perkin-Elmer LS 55 Luminescence Spectrophotometer. Number-average (M_n) and weight-average (M_w) molecular weights were determined by a Waters GPC 2690 in tetrahydrofuran (THF) using a calibration curve of polystyrene standards.

Materials

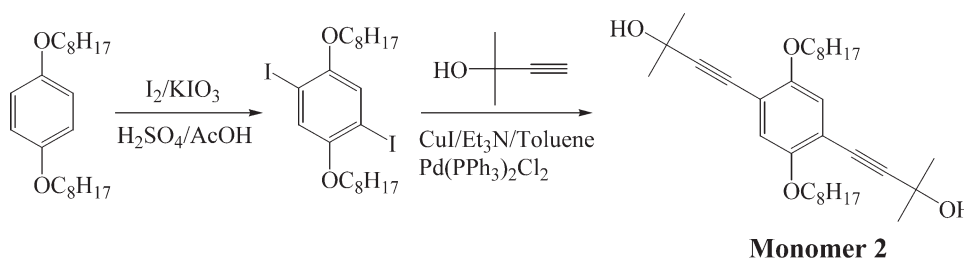
4-Bromo-benzonitrile and potassium *tert*-butoxide were purchased from Alfa Aesar. Hydroquinone, *n*-octyl bromide, and Succinic acid diisopropyl ester were obtained from domestic chemical company. All the chemicals were used as received. *Tert*-Amyl alcohol and triethylamine were distilled over calcium hydride. *N*-Methyl-2-pyrrolidone was purified by reduced pressure distillation.

Monomers' synthesis

1,4-Divinyl-2,5-dioctyloxy benzene (monomer 1)

The synthetic route of the **monomer 1** (1,4-divinyl-2,5-dioctyloxy benzene) is illustrated in Scheme 1. 1,4-Dioctyloxy-benzene,⁴⁴ 1,4-bis(bromomethyl)-2,5-dioctyloxy-benzene,⁴⁵ and 2,5-dioctyloxy-1,4-xylylene-bis(triphenyl phosphonium bromide)⁴⁶ were synthesized according to procedures described in references.

1,4-Divinyl-2,5-dioctyloxy benzene was synthesized as follows: Under argon atmosphere, a mixture of 2,5-dioctyloxy-1,4-xylylene-bis(triphenyl phosphonium bromide) (15.6743 g, 15 mmol) in dichloromethane (200 mL) and formaldehyde aqueous (60 mL) was stirred at 0°C, then an aqueous solution of NaOH (20 wt %, 130 mL) was added by dropwise in



Scheme 2 Synthesis of monomer 2.

1 h. After reaction mixture was stirred for 24 h, the aqueous layer of resulting solution was extracted with dichloromethane three times. The combined organic layer was washed with water and dried with anhydrous sodium sulfate. Subsequently, the solvent was removed by rotary evaporation; the residue obtained was purified by recrystallization from ethanol to give a white crystal. Yield: 3.85 g, 66% (total yield from hydroquinone to monomer 1: 37.5%); m.p 45–46°C; IR (KBr, cm^{-1}): 3081 (m, $\nu(\text{C}=\text{H})$), 2918 (vs, $\nu_{\text{as}}(-\text{CH}_3, -\text{CH}_2-)$), 2850 (vs, $\nu_{\text{s}}(-\text{CH}_3, -\text{CH}_2-)$), 1618–1427 (s, $\nu(\text{Ar}_{\text{C}=\text{C}})$), 1390 (s, $\delta(-\text{CH}_3)$), 1273 (s, $\nu(-\text{CH}_3)$), 1211 (vs, $\nu(\text{C}=\text{O})$), 995, 901 (s, $\gamma(\text{C}=\text{H})$), 721 (w, $\delta(-(\text{CH}_2)_n)$). ^1H NMR (CDCl_3 , ppm) δ : 0.880 (t, 6H, methyl), 1.28–1.82 (m, 24H, methylene), 3.95 (t, 4H, $\text{O}-\text{CH}_2$), 5.23 (d, 2H, vinyl-H(terminal)), 5.70 (d, 2H, vinyl-H(terminal)), 6.98 (s, 2H, Ar-H), 7.00–7.07 (dd, 2H, vinyl-H). Anal. Calcd. for $\text{C}_{26}\text{H}_{42}\text{O}_2$: C, 80.77; H, 10.95. Found: C, 80.74; H, 11.00.

1,4-Bis(3-methyl-3-hydroxybut-1-ynyl)-2,5-dioctyloxy benzene (monomer 2)

The synthetic route of the **monomer 2** (1,4-bis(3-methyl-3-hydroxy but-1-ynyl)-2,5-dioctyloxy benzene) is illustrated in Scheme 2. 1,4-Diiodo-2,5-dioctyloxy-benzene was synthesized according to procedures described in a reference.⁴⁴

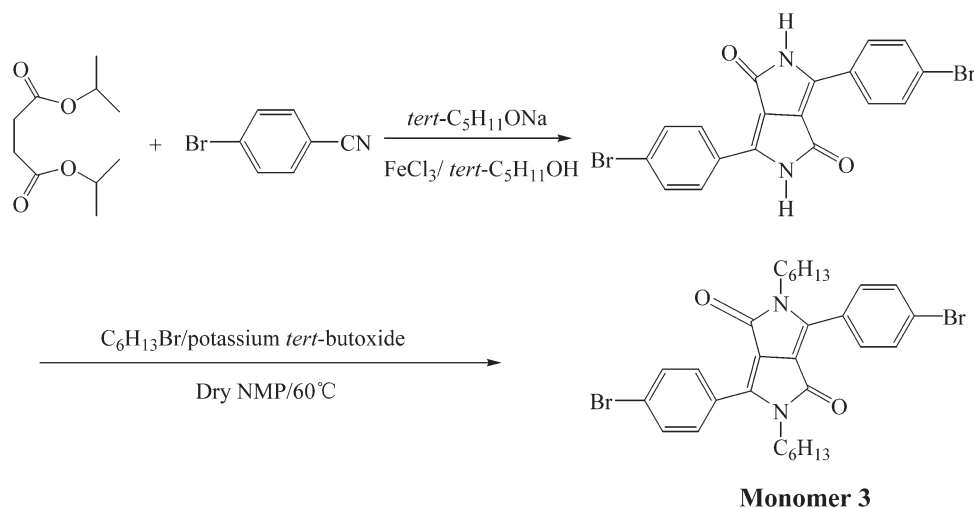
1,4-Bis(3-methyl-3-hydroxy but-1-ynyl)-2,5-dioctyloxy benzene was synthesized as follows: A solution of 1,4-Diiodo-2,5-dioctyloxy-benzene (5.863 g, 10 mmol) and $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.196 g, 0.28 mmol) in dry toluene (40 mL) and dry triethylamine (50 mL) was stirred in three-neck flask for 1 h under argon atmosphere. Then a solution of CuI (0.096 g, 0.5 mmol) in triethylamine (10 mL) and 3-methyl-3-hydroxy-but-1-yne (2.35 mL, 0.024 mol) was added, the reaction was carried out at 55°C for 5.5 h, then the precipitate was removed. After removing the solvent, yellow oil was obtained, the residue was purified by column chromatography on silica using toluene as the eluent and recrystallization from toluene finally to give light-yellow crystal. Yield: 3.64 g, 73%; m.p 107–108°C. IR (KBr, cm^{-1}): 3513, 3399 (s, $\nu(\text{OH})$), 2919 (versus, $\nu_{\text{as}}(-\text{CH}_3, -\text{CH}_2-)$), 2854 (ver-

sus, $\nu_{\text{s}}(-\text{CH}_3, -\text{CH}_2-)$), 2226 (w, $\nu(\text{C}\equiv\text{C})$), 1503–1467 (s, $\nu(\text{Ar}_{\text{C}=\text{C}})$), 1390 (s, $\delta(-\text{CH}_3)$), 1276 (s, $\nu(\text{C}-\text{C})$), 1222 (versus, $\nu(\text{C}-\text{O})$), 1157 (s, $\nu(\text{C}-\text{O})$), 1035, 862, 591 (w, $\delta(\text{Ar}-\text{H})$), 720 (w, $\delta(-(\text{CH}_2)_n)$), $^1\text{HNMR}$ (CDCl_3 , ppm) δ : 0.87 (t, 6H, CH_3-), 1.20–1.40 (m, 24H, $-(\text{CH}_2)_6-$), 1.63 (s, 12H, CH_3- of *t*-butyl), 2.0 (s, 2H, $-\text{OH}$), 3.93 (t, 4H, $-\text{CH}_2\text{O}-$), 6.85 (s, 2H, Ar-H). Anal. Calcd. for $\text{C}_{32}\text{H}_{50}\text{O}_4$: C, 77.06; H, 10.10. Found: C, 77.20; H, 10.13.

1,4-Diketo-2,5-dihexyl-3,6-bis(4-bromophenyl) pyrrolo [3,4-c] pyrrole (monomer 3)

The synthetic route of the **monomer 3** (1,4-Diketo-2,5-dihexyl-3,6-bis(4-bromophenyl) pyrrolo [3,4-c]pyrrole) is illustrated in Scheme 3. At first, 1,4-diketo-3,6-bis(4-bromophenyl) pyrrolo[3,4-c] pyrrole was synthesized. A typical procedure is as follows: Under argon atmosphere, sodium (1.104 g, 48 mmol), FeCl_3 (0.05 g) and dry *tert*-Amyl alcohol (24 mL) were stirred and heated to 90°C until the sodium was dissolved. The mixture was cooled to 50°C and 4-bromo-benzonitrile (4.37 g, 24 mmol) was added, then the mixture was heated to 90°C. A solution of succinic acid diisopropyl ester (1.9392 g, 9.6 mmol) in dry *tert*-amyl alcohol (10 mL) was added by dropwise in 1 h. After standing for 24 h, acetic acid (10 mL) was added, and the mixture was heated to 120°C and maintained for 1 h. Then it was filtered and the precipitate was washed with hot water and methanol repeatedly and dried with P_2O_5 under vacuum. Red solid was obtained. Yield: 3.4428 g (80%).

Monomer 3. (1,4-Diketo-2,5-dihexyl-3,6-bis(4-bromophenyl) pyrrolo [3,4-c]pyrrole) was synthesized by means of the procedure which follows: 1,4-Diketo-3,6-bis(4-bromophenyl) pyrrolo [3,4-c] pyrrole (8.92 g, 20 mmol), potassium *tert*-butoxide (4.94 g, 44 mmol), and NMP(*N*-Methyl-2-pyrrolidone) (150 mL) were mixed and heated to 60°C. 1-Bromohexane (16.9 mL, 120 mmol) was slowly added and the mixture was stirred at 60°C for 24 h. After cooling to room temperature, toluene (250 mL) was added into the reaction mixture and washed with water to remove the NMP. The organic solution was concentrated using a rotary evaporator. Crude product was



Scheme 3 Synthesis of monomer 3.

purified by column chromatography on silica using dichloromethane as eluent to yield an orange-red polycrystalline powder. Yield: 5.1 g (42%). ^1H NMR (CDCl_3 , ppm) δ : 0.70–1.0 (m, 6H, methyl), 1.00–1.25 (m, 12H, methylene), 1.58 (m, 4H, β - CH_2), 3.70 (t, 4H, N - CH_2), 7.65 (d, 4H), 7.66 (d, 4H). Anal. Calcd. for $\text{C}_{30}\text{H}_{34}\text{Br}_2\text{N}_2\text{O}_2$: C, 58.64; H, 5.58; N, 4.56. Found: C, 59.04; H, 5.63; N, 4.53. UV(CHCl_3): 480 nm; photoluminescence (PL): 540 nm.

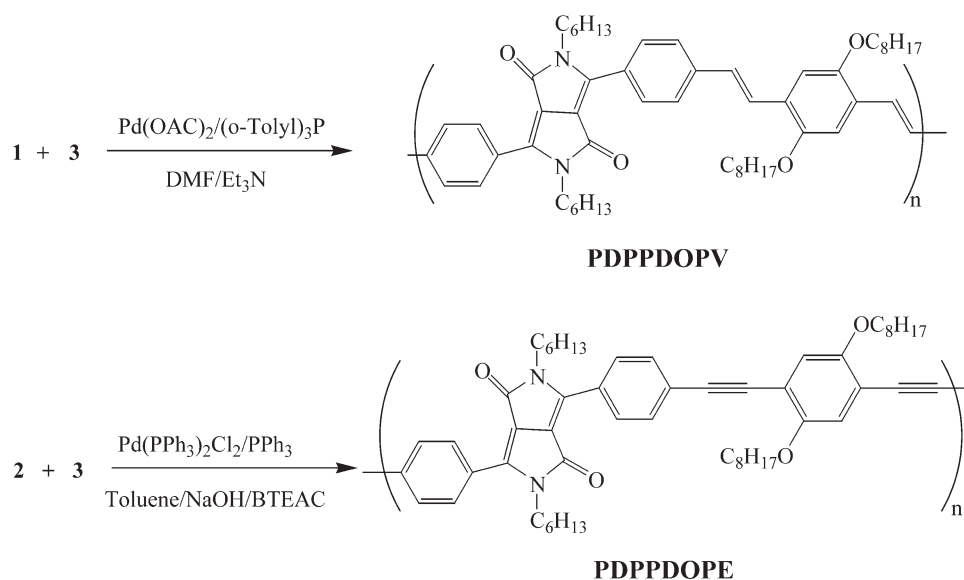
Polymers' synthesis

The synthetic route of the polymers PDPPDOPV and PDPPDOPE is illustrated in Scheme 4.

PDPPDOPV. Under argon atmosphere, monomer 1 (0.3866 g, 1 mmol), monomer 3 (0.6144 g, 1 mmol), $\text{Pd}(\text{OAc})_2$ (0.015 g, 0.06 mmol), and o -(tolyl) $_3\text{P}$

(0.01 g, 0.2 mmol) were dissolved in DMF (10 mL), then triethylamine (5 mL) was added. The solution was stirred at 80°C for 24 h. Cooled reaction mixture was poured into methanol and precipitated dark red solid was filtered and dried under vacuum. Collected powder was purified by Soxhlet extraction with methanol for 72 h and dried under vacuum to yield a dark red solid.

PDPPDOPE. Under argon atmosphere, monomer 2 (0.4987 g, 1 mmol) and monomer 3 (0.6144 g, 1 mmol) were dissolved in 10 mL toluene, and $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.0615 g), BTEAC (benzyltriethylammonium chloride) (0.0143 g), PPh_3 (0.1259 g), and aqueous NaOH (5.5 mol/L, 3 mL) were added into the mixture, the reaction was carried out at 90°C for 24 h. Then the mixture was poured into methanol. After 3 h, the precipitate was filtered and washed



Scheme 4 Synthetic route of the polymers.

TABLE I
Molecular Weights of the Conjugated Polymers

Polymers	M_n	M_w
PDPPDOPV	6824	29,427
PDPPDOPE	4013	12,021

with water and methanol. The dried polymer was redissolved in chloroform and reprecipitated with methanol. Collected powder was purified by Soxhlet extraction with methanol for 72 h and dried under vacuum to yield a dark red solid.

RESULTS AND DISCUSSION

Synthesis of monomer 3 and polymers

To synthesize DPP-containing polymers, a dibrominated DPP derivative, 1,4-Diketo-3,6-bis(4-bromophenyl) pyrrolo[3,4-c] pyrrole was used as the starting material. Because of the hydrogen-bonding of lactam units, it is poorly soluble in common organic solvents except DMF or NMP and is unsuitable to be directly used as a monomer. To overcome the problem, the lactam group in precursor was alkylated upon reaction with 1-bromohexane (Scheme 3) to increase its solubility. The resulting alkylated DPP monomer 3 is a bright orange red polycrystalline material with melting point of 180°C and exhibits high solubility in common organic solvents.

The preparation of DPP-containing polymers was realized by using palladium catalyzed arylation or vinylation of olefins by aryl halides, which is well known as the classic Heck reaction with genuine synthetic utility for C—C bond formation. Compared with Suzuki/Yamamoto coupling reaction,^{26–30} the Heck reaction shows the advantages of simplicity and convenience for incorporation of C=C double bond into a compound. The coupling of DPP derivatives with aromatic units containing vinyl ending group or ethynyl ending group resulted in a new PPV derivative (PDPPDOPV) and a new PPE derivative (PDPPDOPE) (Scheme 4). Common Heck reaction could be completed between the active H atom in the vinyl or ethynyl group with aryl halides, but alternating copolymers could be prepared via cross-coupling polycondensation with bis(triphenylphosphine) dichloropalladium ($\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$) and phase transfer catalyst (BTEAC).^{47,48} In this reaction, deacetonation of the dibutynol intermediate was realized in the presence of alkali.⁴⁹

The PDPPDOPV and PDPPDOPE obtained are dark-red powder and can be readily soluble in conventional organic solvents, such as chloroform, dichloromethane, toluene, and tetrahydrofuran (THF). Both polymers can be spin coated from solution onto glass substrates to provide visually uniform dark-red

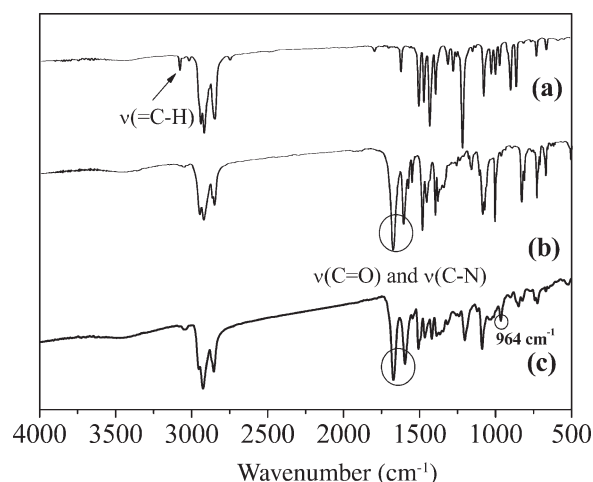


Figure 1 IR spectra of (a) monomer 1, (b) monomer 3, and (c) PDPPDOPV.

films. Their number-average (M_n) and weight-average (M_w) molecular weights are listed in Table I.

Characteristic properties of the monomers and the polymers

As shown in Scheme 4, the copolymer PDPPDOPV was prepared by coupling reaction of monomer 1 and monomer 3. Figure 1 shows the FT-IR spectra of monomer 1 (a), monomer 3 (b), and PDPPDOPV (c). The absorption peak at 3081 cm^{-1} in Figure 1(a) is attributed to the C—H vibration of the C=C double bond in monomer 1,⁵⁰ whereas the absorption peaks at 1681 cm^{-1} and 1611 cm^{-1} in Figure 1(b) are due to the typical C=O and C—N stretching modes of alkylated lactam groups of DPP unit in monomer 3.¹⁷ The IR examination results of PDPPDOPV copolymer [Fig. 1(c)] indicated a characteristic absorption at 964 cm^{-1} , which confirms the all-trans configuration of the vinylene double bonds.⁵⁰

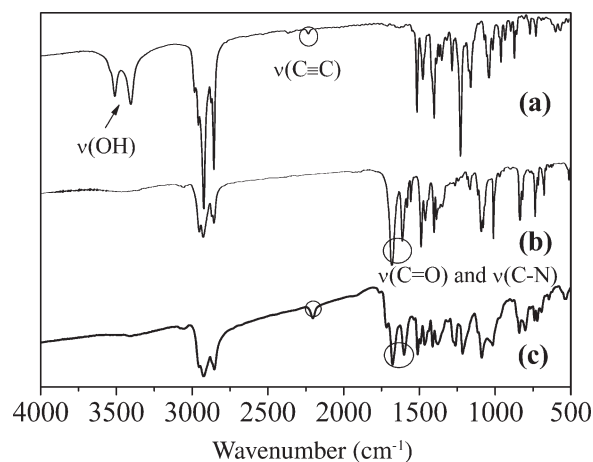


Figure 2 IR spectra of (a) monomer 2, (b) monomer 3, and (c) PDPPDOPE.

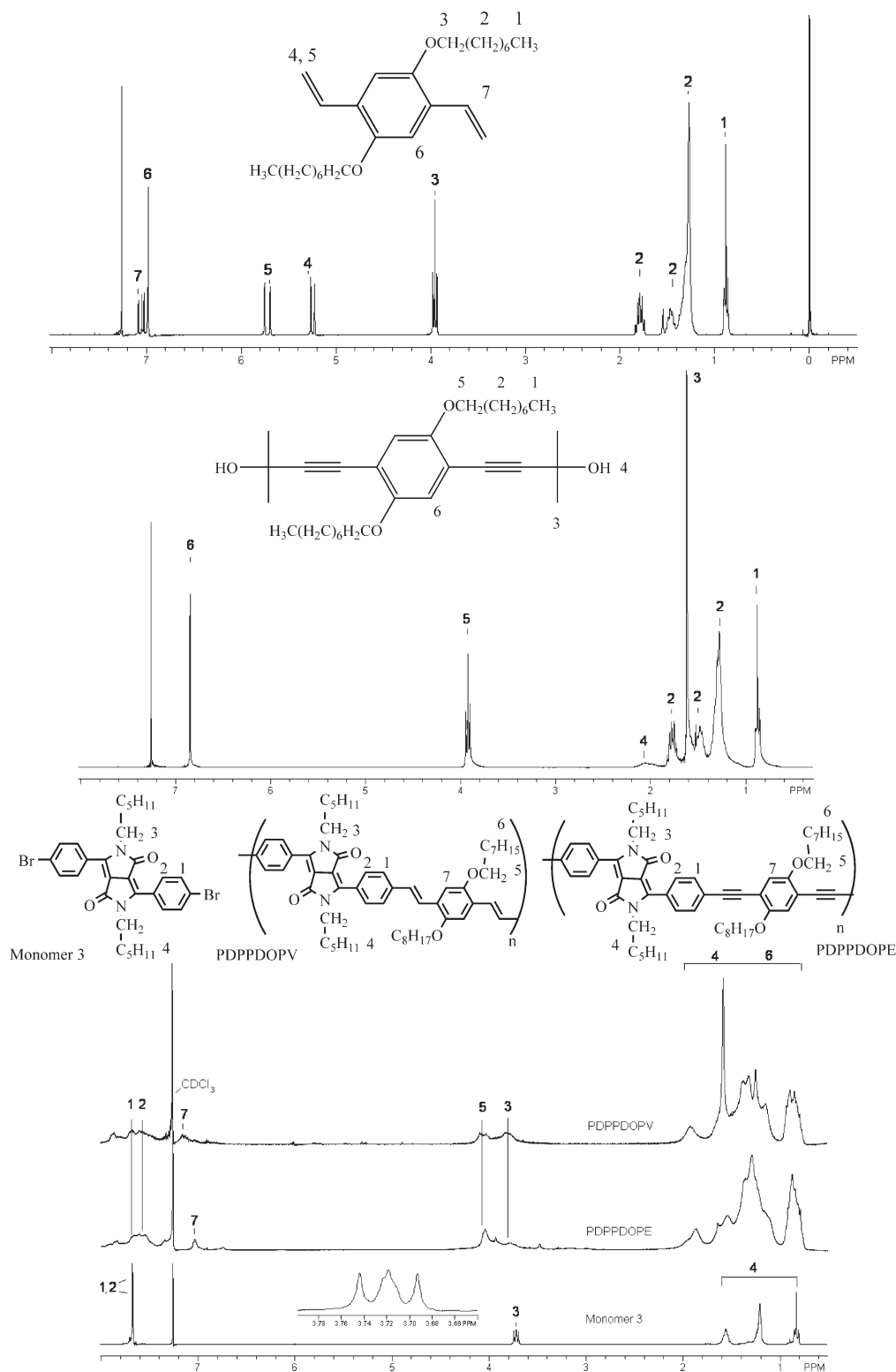


Figure 3 ^1H NMR spectra of (a) monomer 1, (b) monomer 2, and (c) monomer 3, PDPPDOPV and PDPPDOPE.

Similarly, the coupling reaction of monomer 2 and monomer 3 gives another DPP-containing copolymer PDPPDOPE. Figure 2 shows FT-IR spectra of monomer 2 (a), monomer 3 (b), and the polymer (c). The spectrum of monomer 2 shows the O—H stretching

vibration at 3513 and 3399 cm^{-1} . In the spectrum of the polymer, the absorption peaks at 1677 and 1601 cm^{-1} are attributed to the typical C=O and C—N stretching modes of the alkylated lactam groups of DPP.²⁴ Furthermore, the IR spectrum of

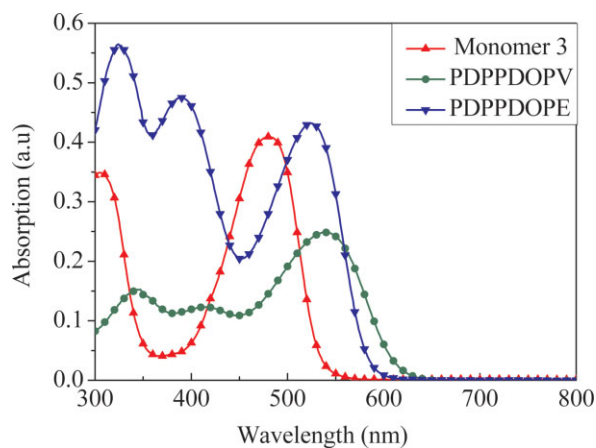


Figure 4 UV-vis spectra of monomer 3, PDPPDOPV, and PDPPDOPE in chloroform. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the PDPPDOPE copolymer shows an absorption peak at around 2226 cm^{-1} due to $\text{C}\equiv\text{C}$ vibration, but no peaks relating to terminal hydroxy group are observed.⁴⁸ The IR analysis suggests that we have successfully obtained the copolymer.

The ^1H NMR spectra of the monomers and polymers PDPPDOPV and PDPPDOPE are shown in Figure 3(a–c). In the ^1H NMR spectrum of monomer 3 [Fig. 3(c)], the signal of the *R*-methylene unit directly attached to the N atom of the lactam unit appears in the region from 3.73 to 3.79 ppm.^{24,26} The two shoulders in the central peak could be attributed to the two doublets for the 2H of CH_2 , because the rotation is not free and consequently the 2H of $\text{N}-\text{CH}_2-\text{CH}_2$ have different coupling constants in these long hydrocarbon chains. The spectrum shows strong signals in the δ -region from 0.68 to 1.74 ppm originating from the alkyl protons in DPP units.²⁴ The ^1H NMR spectrum of monomer 3, its UV-vis/Photoluminescence spectrum, and elemental analyses are all in accordance with the results of same monomer as outlined by Tieke and coworkers.²⁶ Therefore, it is concluded that we have successfully obtained the monomer 3.^{24,26} The small signal at 1.91 ppm is proposed to relate to the alkyloxy units protons in PV unit or PE unit. The signals of the phenylene (vinylphenyl) protons occur between 7.16 and 7.70 ppm (the strong peak at 7.27 ppm originates from protons in the solvent CDCl_3).

In the ^1H NMR spectrum of PDPPDOPV copolymer, the terminal vinyl peak of monomer 1 [Fig. 3(a)] at 5.23 and 5.70 ppm⁵⁰ is absent, while a weak new peak centered at 7.32 ppm, which is due to vinylene protons in PDPPDOPV copolymer, can be observed.

In the ^1H NMR spectrum of PDPPDOPE copolymer, the terminal hydroxyl peak of monomer 2 [Fig. 3(b)] at 2.0 ppm⁴⁸ is absent, while two new

multiple peaks centered at 7.04 and 7.60 ppm, which are due to the aromatic proton in DPP units and phenylene rings, can be observed.

Figure 4 shows the UV-vis spectra of the polymers PDPPDOPV, PDPPDOPE, and monomer 3 in chloroform. Compared with monomer 3, the absorption maxima of PDPPDOPV and PDPPDOPE exhibit a large red shift from 480 to 540 nm and from 480 to 524 nm, respectively. The phenomenon is assumed to originate from the extension of the π -conjugated system. For PDPPDOPV, the peak centered at around 364 nm is associated with the absorption of 1,4-phenylenevinylene segments.⁵⁰ For PDPPDOPE, the peak centered at around 324 nm is associated with the absorption of 1,4-phenyleneethynylene segments.⁴⁸

Figure 5 shows the photoluminescence (PL) spectra of the polymers PDPPDOPV, PDPPDOPE, and monomer 3 in chloroform. Monomer 3 is highly fluorescent with maximum emission at 540 nm, and the polymer solutions exhibit a bordeaux-red emission color.^{25–27} PDPPDOPV shows fluorescence maximum at 623 nm which is red-shifted by 83 nm compared with monomer 3. Although PDPPDOPE exhibits fluorescence maximum at 592 nm which is red-shifted by 52 nm compared with monomer 3.

Figure 6 shows the UV-vis and photoluminescence (PL) spectra of the polymer films cast from the chloroform solution [PDPPDOPV (a), PDPPDOPE (b)]. The UV-vis spectra of polymer films are very similar to that of the solutions, except for a red-shift by 13 and 6 nm in the absorption maxima for PDPPDOPV and PDPPDOPE, respectively. The red-shift might be explained in terms of interactions between transition moments of nearest neighbor molecules in the solid-state.^{48,50} But fluorescence spectra of polymer films exhibit an unusually large red-shift relative to the solutions by 103 and 128 nm for PDPPDOPV

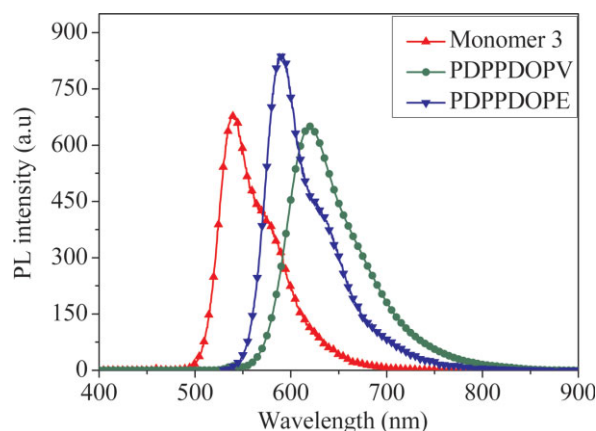


Figure 5 PL spectra of monomer 3, PDPPDOPV and PDPPDOPE in chloroform. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

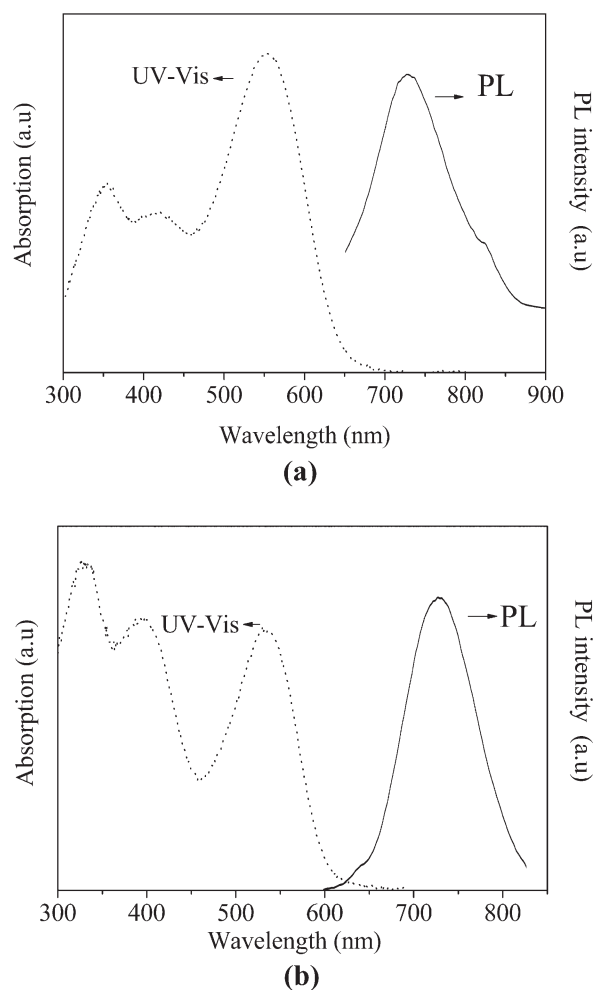


Figure 6 UV visible and photoluminescence spectra of (a) PDPPDOPV and (b) PDPPDOPE as solid film.

and PDPPDOPE, respectively. Furthermore, the absorption and emission bands of the polymer films become broad and shift toward the longer wavelength region compared with the bands of the solutions. This is due to the ground state energy increasing with increasing intermolecular interaction as a result of closer packing of the molecules in the film state.⁵¹

Table II summarizes the Stokes shifts derived from the polymer films and solutions. It is clearly seen that the Stokes shifts of the polymer films are

as large as 173 and 199 nm for PDPPDOPV and PDPPDOPE, respectively, which are the largest values ever reported for a DPP-containing polymer film (110 nm of PDPP,²⁶ 98 nm of PF-DPP,²⁷ 133 nm of PDPPP²⁵). In comparison, the polymer solutions show much smaller Stokes shift of only 83 (PDPPDOPV) and 67 nm (PDPPDOPE). Compared with the previously reported DPP-containing polymers, i.e., the homopolymer of DPP²⁶ and copolymers of DPP with aryl (fluorene,²⁷ phenyl²⁵), PDPPDOPV and PDPPDOPE would have a higher conjugation degree as a result of introduction of C=C double bond or C≡C triple bond in the main chain. And the difference in the structure of main chain may relate to their different photophysical properties as outlined in Table II.

It is known that Stokes shift reflects the energy difference between the π - π^* transitions in the absorption and emission spectra. In our contribution, the large Stokes shifts derived from emission spectra of the DPP-containing polymers are indicative of a polar excited state, which is presumably due to the electron-withdrawing nature of the lactam groups and the energy transfer process of DOPV-DPP self-forming donor-acceptor systems.⁵² Furthermore, it is proposed that C≡C triple bonds enhance the rigidity of polymer backbone, and intensify the mutual effect between molecules. Thus PDPPDOPE with 1,4-phenyleneethynylene segments exhibited a larger Stokes shift than PDPPDOPV.

Apart from the photophysical properties, we also investigated thermal properties of the two polymers by thermogravimetric analysis (TGA). As indicated in Figure 7, PDPPDOPV exhibits good thermal stability with the onset decomposition temperature at $\sim 250^\circ\text{C}$, followed by a 5% weight loss occurring at 267°C . PDPPDOPE also exhibits good thermal stability with the onset decomposition temperature at $\sim 250^\circ\text{C}$ followed by a 5% weight loss occurring at 284°C .

CONCLUSIONS

Two novel DPP-based copolymers PDPPDOPV and PDPPDOPE have been synthesized by palladium catalyzed Heck coupling reaction, which contain DPP and 1,4-phenylenevinylene or 1,4-

TABLE II
Optical Properties of PDPPDOPV/PDPPDOPE and Some DPP-Containing Polymers Reported in References

Polymers	Solution			Film		
	UV (nm)	PL (nm)	Stokes shift (nm)	UV (nm)	PL (nm)	Stokes shift (nm)
PDPP ^[26]	523	627	104	533	643	110
PF-DPP ^[27]	512	578	66	511	609	98
PDPPP ^[25]	503	570	67	509	640	133
PDPPDOPV	540	623	83	553	726	173
PDPPDOPE	524	591	67	530	729	199

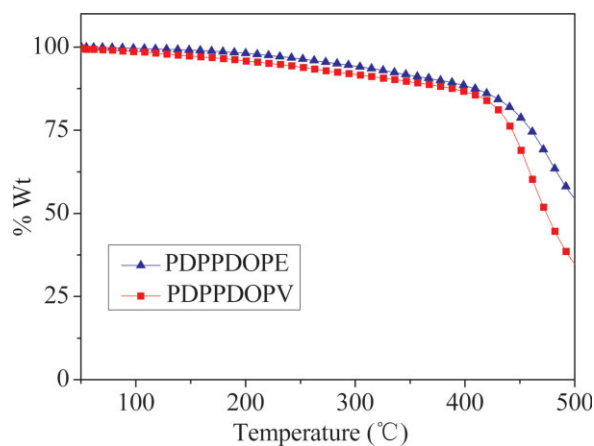


Figure 7 TGA trace of the polymers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

phenyleneethynylene structure units. The polymers exhibit good solubility in common organic solvents. Their solutions exhibit a bordeaux-red emission color and show large Stokes shifts of 80 and 67 nm for PDPPDOPV and PDPPDOPE, respectively. The polymer films are deep red color and exhibit the largest Stokes shifts ever reported for a DPP-containing polymer, reaching 173 and 199 nm for PDPPDOPV and PDPPDOPE, respectively. Good solubility and processability into thin films, and interesting photophysical properties render the polymers great potentials in optical and electronic applications.

References

- Zhang, C.; Choi, S. B.; Haliburton, J.; Cleveland, T.; Li, R.; Sun, S. S.; Ledbetter, A.; Bonner, C. E. *Macromolecules* 2006, 39, 4317.
- Tan, Z. A.; Hou, J. H.; He, Y. J.; Zhou, E. J.; Yang, C. H.; Li, Y. F. *Macromolecules* 2007, 40, 1868.
- Kumar, A.; Buyukmumcu, Z.; Sotzing, G. A. *Macromolecules* 2006, 39, 2723.
- Thompson, B. C.; Kim, Y. G.; McCarley, T. D.; Reynolds, J. R. *J Am Chem Soc* 2006, 128, 12714.
- Roquet, S.; Cravino, A.; Leriche, P.; Alévêque, O.; Frère, P.; Roncali, J. *J Am Chem Soc* 2006, 128, 3459.
- Wang, S.; Hong, J. W.; Bazan, G. C. *Org Lett* 1907 2005, 7.
- Hou, J. H.; Tan, Z. A.; Yan, Y.; He, Y. J.; Yang, C. H.; Li, Y. F. *J Am Chem Soc* 2006, 128, 4911.
- Choi, H. B.; Lee, H. W.; Kang, Y. J.; Kim, E. Y.; Kang, S. O.; Ko, J. *J Org Chem* 2005, 70, 8291.
- Corredor, C. C.; Huang, Z. L.; Belfield, K. D.; Morales, A. R.; Bondar, M. V. *Chem Mater* 2007, 19, 5165.
- Smith, R. C.; Tennyson, A. G.; Lim, M. H.; Lippard, S. *J Org Lett* 2005, 163, 573.
- Stefani, F. D.; Kohl, C.; Avlasevich, Y. S.; Horn, N.; Vogt, A. K.; Mullen, K.; Kreiter, M. *Chem Mater* 2006, 18, 6115.
- Zhang, Z. B.; Fujiki, M.; Tang, H. Z.; Motonaga, M.; Torimitsu, K. *Macromolecules* 2002, 35, 1988.
- Kim, Y.; Whitten, J. E.; Swager, T. M. *J Am Chem Soc* 2005, 127, 12122.
- Yang, C.; Jacob, J.; Mullen, K. *Macromolecules* 2006, 39, 5696.
- Hao, Z.; Iqbal, A. *Chem Soc ReV* 1997, 26, 203.
- Iqbal, A.; Jost, M.; Kirchmayr, R.; Pfenniger, J.; Rochart, A.; Wallquist, O. *Bull Soc Chim Belg* 1998, 97, 615.
- Herbst, W.; Hunger, K. *Industrial Organic Pigments*; VCH: Weinheim, 1993.
- Mizuguchi, J. *J Phys Chem A* 2000, 104, 1817.
- Mizuguchi, J.; Wooden, G.; Ber, B. *Phys Chem* 1991, 95, 1264.
- Mizuguchi, J.; Rihs, G.; Ber, B. *Phys Chem* 1992, 96, 597.
- Chan, W. K.; Chen, Y.; Peng, Z.; Yu, L. *J Am Chem Soc* 1993, 115, 11735.
- Lange, G.; Tieke, B. *Macromol Chem Phys* 1999, 200, 106.
- Hofkens, J.; Verheijen, W.; Shukla, R.; Dehaen, W.; Schryver, F. D. *Macromolecules* 1998, 31, 4493.
- Beyerlein, T.; Tieke, B. *Macromol Rapid Commun* 2000, 211, 82.
- Beyerlein, T.; Tieke, B.; Lengerb, S. F.; Brutting, W. *Synth Metals* 2002, 130, 115.
- Rabindranath, A. R.; Zhu, Y.; Heim, I.; Tieke, B. *Macromolecules* 2006, 39, 8250.
- Cao, D.; Liu, Q. L.; Zeng, W. J.; Han, S. H.; Peng, J. B.; Liu, S. P. *Macromolecules* 2006, 39, 8347.
- Cao, D.; Liu, Q. L.; Zeng, W. J.; Han, S. H.; Peng, J. B.; Liu, S. P. *J Polym Sci Part A: Polym Chem* 2006, 44, 2395.
- Xiao, Y.; Yu, W. L.; Pei, J.; Chen, Z.; Huang, W.; Heeger, A. J. *Synth Met* 1999, 106, 165.
- Park, L. S.; Han, Y. S.; Kim, S. D.; Kim, D. U. *Synth Met* 2001, 117, 237.
- Ram, M. K.; Sarkar, N.; Bertocello, P.; Sarkar, A.; Narizzano, R.; Nicolini, C. *Synth Met* 2001, 122, 369.
- Liu, Y.; Lahti, P. M.; La, F. *Polymer* 1998, 39, 5241.
- Jeong, H. Y.; Lee, Y. K.; Talaie, A.; Kim, K. M.; Kwon, Y. D.; Jang, Y. R.; Yoo, K. H.; Choo, D. J.; Jang, J. *Thin Solid Films* 2002, 417, 171.
- Wang, L. H.; Kang, E. T.; Huang, W. *Thin Solid Films* 2002, 417, 151.
- Jin, S. H.; Jang, M. S.; Suh, H. S.; Cho, H. N.; Lee, J. H.; Gal, Y. S. *Chem Mater* 2002, 14, 643.
- Lee, J. I.; Han, J. Y.; Shim, H. K.; Jeoung, S. C.; Kim, D. *Synth Met* 1997, 84, 261.
- Detert, H.; Sugiono, E. *Synth Met* 2000, 115, 89.
- Winkler, B.; Dai, L.; Mau, A. W. H. *Chem Mater* 1999, 11, 704.
- Beljonne, D.; Hennebicq, E.; Daniel, C.; Herz, L. M.; Silva, C.; Scholes, G. D.; Hoeben, F. J. M.; Jonkheijm, P.; Schenning, A. P. H. J.; Meskers, S. C. J.; Phillips, R. T.; Friend, R. H.; Meijer, E. W. *J Phys Chem B* 2005, 109, 10594.
- Vijila, C.; Pivrikas, A.; Chun, H.; Kuan, C. Z.; Osterbacka, R.; Jin, C. S. *Org Electron* 2007, 8, 8.
- Li, J.; Pang, Y. *Synthetic Metals* 2004, 140, 43.
- Egbe, D. A. M.; Cornelia, B.; Nowotny, J.; GuInther, W.; Klemm, E. *Macromolecules* 2003, 36, 5459.
- Egbe, D. A. M.; Bader, C.; Nowotny, J.; Klemm, E. In the Proceedings of SPIE; 2004; 5215, p 79.
- Weder, C.; Wrighton, M. S. *Macromolecules* 1996, 29, 5157.
- Egbe, D. A. M.; Tillmann, H.; Birckner, E.; Klemm, E. *Macromol Chem Phys* 2001, 202, 2712.
- Xiao, S. X.; Wang, S.; Fang, H. J.; Li, Y. L.; Shi, Z. Q.; Du, C. M.; Zhu, D. B. *Macromol Rapid Commun* 2001, 22, 1313.
- Yang, M. J.; Niu, J. F.; Markus, H.; Liu, X.; Ye, H.; Fan, X. Z.; Chen, J. *Chem Res Chinese U* 2002, 18, 65.
- Lu, S. L.; Yang, M. J.; Luo, J.; Cao, Y.; Bai, F. L. *Synth Metals* 2004, 146, 175.
- Chi, J. H.; Lee, C. L.; Kim, J. J.; Jung, J. C. *J Appl Polym Sci* 2008, 108, 914.
- Lu, S. L.; Yang, M. J.; Luo, J.; Cao, Y.; Bai, F. L. *Macromol Chem Phys* 2005, 206, 664.
- Iijima, T.; Lee, C. H.; Fujiwara, Y.; Shimokawa, M.; Suzuki, H.; Yamane, K.; Yamamoto, T. *Opt Mater* 2007, 29, 1782.
- Pu, K. Y.; Zhang, B.; Ma, Z.; Wang, P.; Qi, X. Y.; Chen, R. F.; Wang, L. H.; Fan, Q. L.; Huang, W. *Polymer* 2006, 47, 1970.