Synthesis and Characterization of Poly(fluorene vinylene) Copolymers Containing Thienylene–Vinylene Units

Nan Yu,[1] Rui Zhu,[1] Bo Peng,[1] Wei Huang,[2] Wei Wei[1]

[1]*State Key Laboratory for Advanced Photonic Materials and Devices, Department of Optical Science and Engineering, Fudan University, Shanghai 200433, People's Republic of China*
[2]*Institute of Advanced Materials, Nanjing University of Posts and Telecommunications, Nanjing, Jiangsu 210003, People's Republic of China*

ABSTRACT: Narrow-band-gap 2,5-thienylene-divinylene (ThV) units were incorporated into the poly(fluorene vinylene) backbone via a Gilch reaction as an energy trap with various feed ratios; this yielded pronounced changes in the electrochemical and optical properties of the material. The energy levels of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the polymers {poly(9,9-di-*iso*-octylfluorene vinylene) [poly(fluorene vinylene-*co*-thiophene vinylene (FV))], **C1**, and **C2**} were estimated to be −5.53 to −5.10 eV and −2.98 to −2.84 eV, respectively, by cyclic voltammetry measurements. In comparison with poly(FV), the HOMO energy levels of polymers poly(fluorene vinylene-*co*-thiophene vinylene (FV) (90 : 10) (**C1**) and poly(fluorene vinylene-*co*-thiophene vinylene (FV) (80 : 20) (**C2**) were significantly increased, but their LUMO energy levels were slightly decreased. The optical properties were investigated by absorption and emission spectra of the polymers. The good spectral overlap between the emission of poly(FV) and the absorption of polymers **C1** and **C2** revealed a sufficient energy transfer from the majority of 9,9-di-*iso*-octylfluorene vinylene units to the minority of ThV units. The reduction of self-absorption losses of polymers **C1** and **C2** due to spectral separation caused by the incorporation of ThV units could be indirectly confirmed by nonlinear optical (NLO) properties. The result of the NLO properties of the polymers showed that the third-order NLO coefficients of poly(FV), **C1,** and **C2** were 8.1×10^{-10}, 1.35×10^{-9}, and 1.51×10^{-9} esu, respectively. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 2438–2445, 2008

Key words: conjugated polymers; copolymerization; NLO

INTRODUCTION

The development of π-conjugated polymers has been an important research topic in recent years.[1] Compared to classical electronic and photonic materials, such as inorganic molecular and organic oligomers, π-conjugated polymers have evoked considerable interest for further applications, including as light-emitting diodes, plastic lasers, light-emitting electrochemical cells, field effect transistors, polymer photovoltaic cells, and nonlinear optical (NLO) materials.[2–7] One of the most popular π-conjugated polymers, poly(2,7-fluorene) (PF) derivatives, have attracted much interest and are promising materials because of their unique structural features and excellent thermostability and photostability. As a branch of PF derivatives, poly(fluorene vinylene)s, which have similar structures to poly(p-phenylenevinylene) (PPV), exhibit special properties when the dialkylfluorene units are alternated with the vinylene units in the polyfluorene main chain. Normally, poly(fluorene vinylene) homopolymer has been prepared via a Gilch reaction, but there is no insoluble gel formed, as poly(p-phenylenevinylene) (PPV) did, during the polymerization process.[8] The vinylene units in the polymer backbone lead the absorption spectra to broaden and the photoluminescence (PL) emission spectra to redshift in comparison with PFs.[9] The structure is rigid and has a nearly one-dimensional coplanarity, which restrains the distortion of arylic rings. Therefore, the effective conjugation length of poly(fluorene vinylene) is changed.[10]

Thiophene and its derivatives have also been investigated as promising materials for optical devices because of their narrow band gap, high stability, easy design, and advanced NLO properties.[11,12] For copolymers containing fluorene and thiophene units, the process to tune the color across the visible spectrum is well developed.[13] The incorporation of thiophene units in polyfluorene systems changes the band gap and extended absorption area. Additionally, random copolymers have provided the opportunities to bond different contents of functional units so that the electronic and physical properties of the copolymers could be further studied. However, the research work

on polymers consisting of 9,9-di-*iso*-octylfluorene vinylene (FV) units or 2,5-thienylene-divinylene (ThV) units is still insufficient, and only very few studies regarding random copolymers containing FV and ThV units have been reported. We have recognized that the copolymer system containing fluorene, thiophene, and vinylene units is of importance in the development of the optical and electronic characteristics of π-conjugated polymers.

In this study, the motivation for the design of random copolymers was the study of the influence of the incorporation of ThV units into the poly(fluorene vinylene) backbone on the photophysical, electrochemical, and thermal properties and also on the third-order NLO properties. Three polymers with different ratios of FV and ThV units were synthesized and characterized. Poly(9,9-di-*iso*-octylfluorene vinylene) [poly(FV)] was the homopolymer with only FV units. **C1** and **C2** had 10 and 20% molar feed ratios of ThV units, respectively. Additionally, **C1** and **C2** matched the structure of ''chemical defect in a conjugated polymer''.[14]

EXPERIMENTAL

Materials

Fluorene, 2-ethylhexyl bromide, potassium *tert*-butoxide [1*M* solution in tetrahydrofuran (THF)], tetrabutyl-ammonium bromide, and paraformaldehyde were purchased from Aldrich Chemical Co. (Los Angeles, CA) and were used without further purification unless otherwise noted. The solvents were dried and purified by fractional distillation over sodium/benzophenone and handled in a moisture-free atmosphere. Column chromatography was performed with silica gel (200–300 mesh).

Characterization

^{1}H-NMR spectra were recorded with a Varian Mercury Plus 400 spectrometer (Los Angeles, CA) in a deuterated chloroform solution at ambient temperature with tetramethylsilane as the internal standard. Elemental analyses were carried out on a Vario EL III CHNOS elemental analyzer. The molecular masses of 2,7-bis (bromomethyl)-9,9-di-*iso*-octylfluorene (**2**) and 2,5-dibromomethylthiophene (**3**) were determined by matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry (MS). The molecular weights and polydispersities of the polymers were determined by gel permeation chromatography (GPC) analysis relative to polystyrene calibration on a Shimadzu 10A serious (Tokyo, Japan) in THF solution. Thermogravimetric analysis (TGA) was conducted on Shimadzu DTG-60H instrument at a heating rate of 10°C/min in nitrogen

gas. Differential scanning calorimetry (DSC) was performed on Shimadzu DSC-60A instrument at heating and cooling rates of 10°C/min under nitrogen gas. Ultraviolet–visible (UV–vis) absorption spectra were recorded with a Shimadzu UV-2450 UV–vis/near infra-red (NIR) spectrophotometer. PL spectra were obtained with a Shimadzu RF-5301PC luminescence spectrometer. Film samples for the PL spectra were prepared by the casting of the polymer from its THF solution onto a clean quartz substrate. Cyclic voltammetry (CV) was performed on an Autolab PGSTAT30 potentiostat/galvanostat system (Ecochemie, Amsterdam, The Netherlands) with a three-electrode cell in a solution of tetrabutylammonium hexylfluorophosphate (*n*-Bu$_4$NPF$_6$) in nonaqueous acetonitrile (0.1*M*) at a scanning rate of 100 mV/s. The chloroform solution of the polymer was dropcast onto the glass carbon electrode (0.50 cm^2) and then dried in air to form a thin film. A Pt wire was used as the counter electrode, and a Ag/AgNO$_3$ (0.1*M* in acetonitrile) electrode was used as the reference electrode. Before each series of measurements, the cell was deoxygenated with nitrogen. The third-order nonlinear coefficients of the polymers were measured with the Z-scan technique. The excitation source was a Nd:YAG laser with a 12-ns pulse width and a 2-Hz pulse frequency at 532 nm. The energy of the single pulse after amplification was 43 mJ. The precision of Z-scan measurements was controlled with the standard third order nonlinear coefficient ($\chi^{(3)}$) value of carbon bisulfide. The transmission for the sample was simultaneously measured with and without an aperture in the far field of the lens.

Synthesis of the monomers and polymers

The compound 9,9-di-*iso*-octylfluorene (**1**) was synthesized by the reaction of fluorene and *iso*-octyl bromide with *n*-butyllithium in THF according to a literature procedure.[15] Poly(fluorenevinylene) and the polymers were synthesized by the Gilch method;[9] the synthetic routes are shown in Scheme 1.
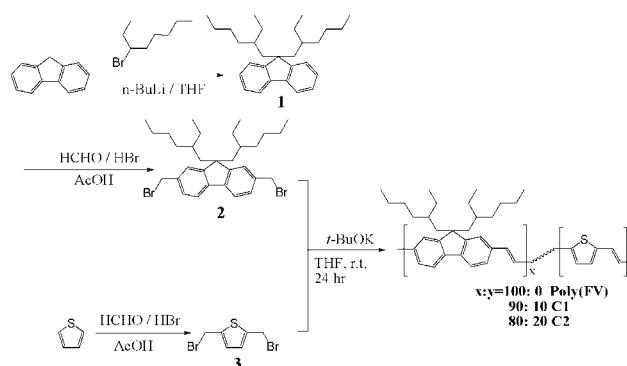
Scheme 1 Synthetic routes and chemical structures of the monomers and polymers.

2

A two-necked flask containing a mixture of **1** (10.0 g, 25.6 mmol) and paraformaldehyde (7.68 g, 128 mmol) was placed in an ice bath. A 30% HBr solution (35 mL) in acetic acid was then added carefully to this flask, and the mixture was heated to 70°C and stirred for 24 h under nitrogen until the HBr was consumed. The hot reaction mixture was cooled to room temperature before it was poured into 200 mL of cold water. The resulting mixture was then extracted with methylene chloride, and the combined organic layer was collected and washed with brine. After drying over anhydrous $MgSO_4$, evaporation *in vacuo* afforded the crude product, which was subjected to purification by column chromatography on silica gel (with hexane as an eluent) to yield a slight yellow transparent liquid (8.40 g, 57%).

^{1}H-NMR ($CDCl_3$, δ, ppm): 7.64 (d, 2H, J = 7.4 Hz, Ar—H), 7.36 (m, 4H, Ar—H), 4.62 (s, 4H, —CH_2Br), 1.96 (m, 4H; α-CH_2 of the hexyl group at the 9-position of fluorene), 1.29 (t, 2H, β-CH), 1.06 (m, 16H, γ ~ ζ-CH_2), 0.92–0.88 (t, 12H, —CH_3). MALDI-TOF MS (m/z): ANAL. Calcd for $C_{31}H_{44}Br_2$: 576.2. Found: 576.4.

3

Thiophene (5 mL, 62 mmol), paraformaldehyde (6.0 g, 200 mmol), and acetic acid (20 mL) were mixed in a 250-mL, two-necked flask. A 30% HBr solution (30 mL) in acetic acid was added to the flask in dropwise form at 0°C with stirring. The mixture was then allowed to warm slowly to room temperature and stirring continued for about 3 h under nitrogen protection. After transforming into dark brown mixture, the crude product was poured into cold water and then obtained as a dark brown mud. The mud was separated and then washed with 2M sodium hydroxide and water to remove excess HBr. The remaining mud was added to 100 mL of hexane and stirring continued at room temperature for 1 h. Then, the organic solution phase was collected, and the residual mud was discarded. Evaporation *in vacuo* afforded the crude product, which was further purified by recrystallization from hexane to afford **3** (4.84 g, 29%).

^{1}H-NMR ($CDCl_3$, δ, ppm): 6.95 (s, 2H); 4.68 (s, 4H, —CH_2Br). MALDI-TOF MS (m/z): ANAL. Calcd for $C_6H_6Br_2S$: 269.8. Found: 269.8.

Preparation of the polymers [poly(FV), **C1,** and **C2**]

For the preparation of **C2**, potassium *tert*-butoxide (0.56 g, 5 mmol) in 10 mL of distilled THF was added drop by drop over 30 min to a stirred mixture of **2** (0.460 g, 0.80 mmol) and **3** (0.054 g, 0.20 mmol) in 20 mL of distilled THF. After refluxing was con-

ducted for 48 h under nitrogen, the reaction mixture was cooled to room temperature and precipitated into a mixture of MeOH and H_2O. The crude polymer was collected, washed with excess MeOH, dissolved in chloroform, and then reprecipitated into MeOH. Finally, the polymer was washed with acetone for 48 h with a Soxhlet apparatus and then dried *in vacuo* to yield **C2** (0.185 g, 52%).

The preparations of **C1** and poly(FV) were similar to that of **C2** but only with different molar feed ratios of **2** and **3**, where the ratio of **C1** was 90 : 10 and that of poly(FV) was 100 : 0.

Poly(FV). Yield: 66%. ^{1}H-NMR ($CDCl_3$, δ, ppm): 7.8–6.8 (8H, aromatic and vinylic protons), 2.1–1.9 (s, 4H), 1.5–0.9 (m, 30H). ANAL. Calcd for $(C_{31}H_{42})_n$: C, 89.85%; H, 10.15%. Found: C, 89.67%; H, 10.28%.

C1. Yield: 46%. ^{1}H-NMR ($CDCl_3$, δ, ppm): 7.8–6.8 (12H, aromatic and vinylic protons), 2.1–1.9 (s, 4H), 1.5–0.9 (m, 30H). ANAL. Calcd for $(C_{285}H_{382}S)_n$: C, 89.20%; H, 9.96%; S, 0.84%. Found: C, 89.02%; H, 9.39%; S, 1.16%. Content of ThV units: 12.9%.

C2. Yield: 52%. ^{1}H-NMR ($CDCl_3$, δ, ppm): 7.8–6.8 (12H, aromatic and vinylic protons), 2.1–1.9 (s, 4H), 1.5–0.9 (m, 30H). ANAL. Calcd for $(C_{130}H_{172}S)_n$: C, 88.43%; H, 9.75%; S, 1.81%. Found: C, 87.54%; H, 9.98%; S, 2.28%. Content of ThV units: 24.6%.

RESULTS AND DISCUSSION

Scheme 1 illustrates the synthetic routes of the polymers. Compound **1** was prepared according to the literature.[15] Compound **2** was obtained by the refluxing of compound **1,** paraformaldehyde, and 30% HBr solution in acetic acid in a yield of about 57%. Thin-layer chromatography was used to monitor the reaction to avoid byproducts. The unsubstituted fluorene unit of compound **1** was region-selectively bromomethylated at the 2'- and 7'-positions with bromomethyl in acetic acid.[9] This reaction proceeded at 0°C and was followed by warming to 70°C. A reaction temperature above 80°C would result in the undesirable bromomethylation at other positions of compound **1,** which would be difficult to separate from the target molecule.[16] The *iso*-octyl branches in the monomeric units were perpendicular to the polymer backbone; this structure minimized the close packing of the polymer chains in the solid state. Thiophene was converted into compound **3** in a yield of about 29% via the same bromomethylation reaction as used for compound **1**. However, this reaction started at 0°C and slowly warmed up to room temperature and was refluxed for 3 h to avoid side reactions. All of the compounds were identified by ^{1}H-NMR spectroscopy because the appearance of the characteristic peak at 4.6 ppm was ascribed to the H atoms at bromomethyl. In addition, the results of MALDI-TOF MS of compounds **2** and **3** were 576.4

TABLE I
Polymerization Results and Thermal Data
of the Polymers

Polymer	M_n $(\times 10^{-4})^a$	M_w $(\times 10^{-4})^a$	PDI[a]	TGA (5%)[b]	T_g[c]
Poly(FV)	1.41	1.89	1.34	312	165
C1 (90 : 10)[d]	1.68	2.53	1.51	302	157
C2 (80 : 20)[d]	1.56	3.06	1.96	296	153

M_w = weight-average molecular weight.
[a] Determined by GPC in THF on the basis of polystyrene standards.
[b] Temperature at 5% weight loss under nitrogen.
[c] Determined by DSC at a heating rate of 10°C/min under nitrogen.
[d] The composition was determined from the initial monomer molar ratio of **2** to **3**.

and 269.8, respectively, which were consistent with the proposed structures. The polymers were then prepared by the Gilch reaction between compounds **2** and **3** with various feed ratios. The structures of the polymers obtained were confirmed by ^{1}H-NMR spectroscopy and elemental analysis. In the ^{1}H-NMR spectra of the polymers, the signal at 6.9 ppm was ascribed to the protons at the 3′- and 4′-positions of the thiophene ring, and the signal at 7.1 ppm was ascribed to the protons at the vinylene units. The polymer compositions of **C1** and **C2** were calculated by comparison of the peak areas at 6.9 ppm (from protons on the thiophene ring in the ThV units) and 1.9–2.0 ppm (from the methylene protons in the iso-octyl groups in the FV units), where the ThV unit contents of **C1** and **C2** were 12.9 and 24.6%, respectively. The result revealed that the molar ratio of two monomeric units in copolymers **C1** and **C2** was not equal to the initial feed ratio. This was probably because **3** was more active and connected more easily with other dibromomethyl-aryl units than **2** during the Gilch polymerization. Therefore, the contents of ThV units in **C1** and **C2** were more than 10 and 20%, respectively. Furthermore, the two monomers in the polymerization were added to the reaction bulb at the same time and then stirred sufficiently before potassium *tert*-butoxide was added. Thus, the ThV units were randomly distributed in the copolymers.

Table I summarizes the polymerization results, molecular weights, and thermal characteristics of **C1,** **C2,** and poly(FV). The polymers were soluble in common organic solvents, such as chloroform, toluene, and THF. GPC analysis indicated that **C1** and **C2** had number-average molecular weights (M_n's) of 1.68×10^4 and 1.56×10^4 g/mol, respectively, with polydispersity indices (PDIs) of 1.51 and 1.96, respectively. The thermal properties of polymers **C1** and **C2** were investigated by TGA and DSC. Weight losses of 5% occurred at 302 and 296°C, respectively. In the DSC measurements of **C1** and **C2,** distinct

transition signals at 155 and 152°C, respectively, were observed upon the first heating. No distinct signal was observed on cooling, even at a rate of 5°C/min. For the second heating, transition signals were detected at 157 and 153°C, respectively. Hence, the transitions were attributed to the glass-transition temperatures (T_g's) of **C1** and **C2,** which were slightly lower than that of poly(FV) but much higher than that of poly(9,9-dioctyl-fluorene-2,7-diyl).[17] This result was attributed to the major content of FV units in the polymer backbone, which restricted the segmental mobility and increased the T_g and thermal stability.[9] Such a relatively high T_g and stable structure is desirable for polymer optical materials.

To determine the energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), CV, with an Ag/Ag$^+$ reference electrode, was carried out to investigate the redox behavior of polymers **C1** and **C2** in thin film with ferrocene as the internal standard.[18] The redox behavior of poly(FV) was also examined for comparison. It is well known that the energy level of the ferrocene reference is 4.8 eV (below the vacuum level), and the HOMO or LUMO level can be estimated according to the following equation:

$$E_{\text{HOMO/LUMO}}(\text{eV}) = (-4.8 - E_{\text{ref}} - E_{\text{OX/RED}}) \quad (1)$$

where $E_{\text{HOMO/LUMO}}$ is HOMO energy level or LUMO energy level, E_{ref} is the potential of the ferrocene reference and $E_{\text{OX/RED}}$ is the onset potential for the oxidation or reduction of the film.[18] The onset potential for the oxidation and reduction of poly(FV), **C1,** and **C2** are outlined in Table II for comparison. As shown in Figure 1, upon the anodic sweep, the onset potential of poly(FV) was 0.83 V (vs Ag/Ag$^+$), which was different from the values of 0.45 V for **C1** and 0.40 V for **C2**. During the cathodic scan, two reversible reduction processes were observed for poly(FV), **C1,** and **C2** with the onset potential at -1.76, -1.93, and -1.94 V, respectively. We estimated that the HOMO and LUMO energy levels of poly(FV) were -5.53 and -2.98 eV, respectively, which were nearly identical to those reported in the literature.[9] On the basis of the onset potentials of **C1** and **C2**, we evaluated that the HOMO and LUMO energy levels of **C1** were -5.15 and -2.83 eV, respectively, and that the HOMO and LUMO energy levels of **C2** were -5.10 and -2.84 eV, respectively. The result implies that the HOMO energy level was significantly increased by the incorporation of ThV units into the poly(fluorene vinylene) backbone. However, the HOMO energy level was only slightly decreased in comparison with that of poly(FV). From the onset potentials of the oxidation and reduction processes, we estimated that the band gaps of **C1** and **C2** in the solid state film were 2.32 and 2.26 eV, respectively.

TABLE II
Electrochemical Data of the Polymers

Polymer	n-Doping (V)[a]			p-Doping (V)[a]			Energy level (eV)		
	E_{onset}	E_{pc}	E_{pa}	E_{onset}	E_{pc}	E_{pa}	E_{HOMO}[b]	E_{LUMO}[b]	E_g[c]
Poly(FV)	−1.76	−1.91	−1.71	0.83	0.91	0.86	−5.53	−2.98	2.55
C1	−1.93	−2.27	−1.98	0.45	—	0.57	−5.15	−2.83	2.32
C2	−1.94	−2.22	−1.85	0.40	0.78	0.54	−5.10	−2.84	2.26

[a] E_{pa} and E_{pc} stand for the anodic peak potential and the cathodic potential, respectively. E_{onset} is onset potential energy of cyclic voltammogram curve.
[b] HOMO and LUMO energy level values calculated from the sum of the CV data and 4.8 eV (reference to ferrocene).
[c] E_g stands for the bandgap energy.

The optical properties of **C1, C2,** and poly(FV) were investigated by UV–vis absorption and PL spectra in both dilute solution and thin film, as shown in Figures 2 and 3. Compared with poly(9,9-dioctyl-fluorene-2,7-diyl), all three of the polymers exhibited broad and redshifted absorption peaks, which indicated a wider distribution of conjugation length of chain conformation in the ground state.[17] The absorption maxima of the three polymers were nearly uniform. This was ascribed to the absorption by the fluorene vinylene units. In comparison with the spectrum of poly(FV), both **C1** and **C2** showed the broadened absorption bands and redshifted emission maxima in different circumstances, which indicated that the influence of ThV units of the main chain on the conjugation length was distinct for both solution and thin film. In Figure 3, the PL spectra of the poly(FV) film displays two sharp peaks at 465 and 492 nm, which are nearly identical to those in literature.[9] However, the PL spectra of **C1** and **C2** films presented single peaks at 532 and 541 nm, respectively. Compared with the PL spectra of the three polymers in dilute solution, all of the PL spectra of the films had a bathochromic shift of about 20–40 nm. It was reported that this bathochromic shift is the result of the different dielectric constants of the environment.[19] However,

branches that are nearly perpendicular to the polymer backbone might lead to conformational changes in the main chain in the solid state, that is, variations in the twist angle between neighboring aryl rings, which will thus give rise to the shift.[20] In addition, the branches on the polymer backbone will reduce the interchain interaction and restrict the formation of aggregates or excimers between polymer chains.[17]

The host–guest system is an active topic in the field of optical materials, and the method of blends of conjugated polymers invokes considerable interest. However, Martin et al.[14] suggested a new type of host–guest system called *chemical defect in a conjugated polymer,* which contains major wide-band-gap components (that absorb the light) as the host and a limited amount of small energy-gap "defects" (that emit the light) as the guest. This type of system, because the major host components and the minor guest components are both located in a polymer, eliminates the undesirable phase separation that is commonly observed in polymer blends; meanwhile, the energy transfer from the host to guest is proved to be complete.[14] Interestingly, in our study, polymers **C1** and **C2** matched this type of system because the content of ThV units was minor and the energy transfer from the wide-band-gap components
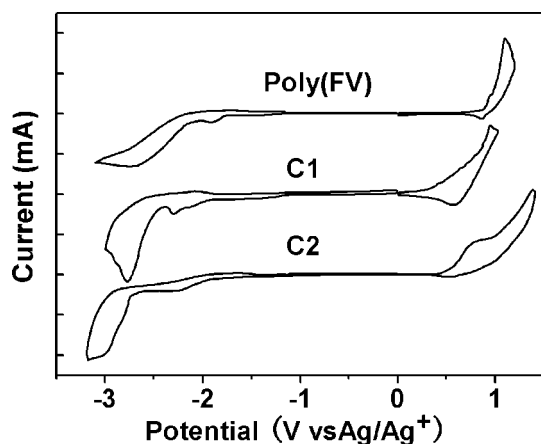

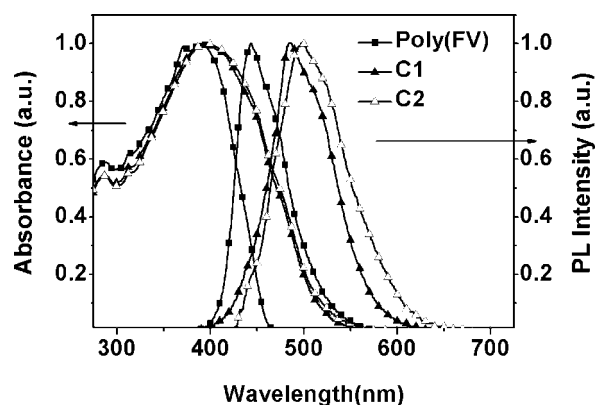**Figure 1** Cyclic voltammograms of the polymers.

Figure 2 Normalized UV–vis absorption and PL spectra of the polymers in dilute THF solutions.

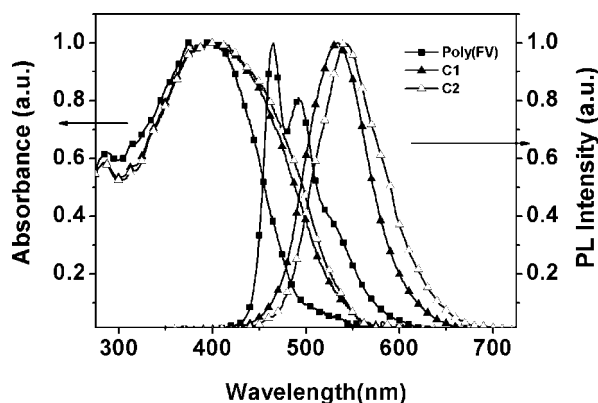**Figure 3** Normalized UV–vis absorption and PL spectra of the polymers as thin films spin-coated from THF solutions onto a quartz substrate.

Figure 5 PL spectrum of the poly(FV) film and absorption spectra of the **C1** and **C2** films.

(FV) to narrow-band-gap components (ThV) was sufficiently efficient. A minor content of ThV units, which affected as a small number of potential disturbing on a one-dimensional periodic potential, led to a localized state within the band gap.[14] Thus, ThV units could be considered an energy trap on the one-dimensional polymer chain. Consequently, fluorene vinylene units predominantly absorbed the light, and ThV units emitted the light. The mechanism of this process is sketched in Figure 4, and we expected it to be effective when the energy transfer from host to guest was efficient. The simplest equation to calculate the energy-transfer rate (k_{HG}) can be presented as

$$k_{HG} = \frac{1}{\tau_0} \left(\frac{R_0}{R_{HG}} \right)^6 \qquad (2)$$

which indicates that k_{HG} depends strongly on R_0 and R_{HG}. In this equation, θ_0 is the exciton lifetime in the pristine polymer, which consists of host units and can be treated as a constant parameter in this equation; R_0 is the FÖster radius and is maximized when the host emission and the guest absorption had good spectra overlap; and R_{HG} is the average host–guest distance. Usually, a large average separa-
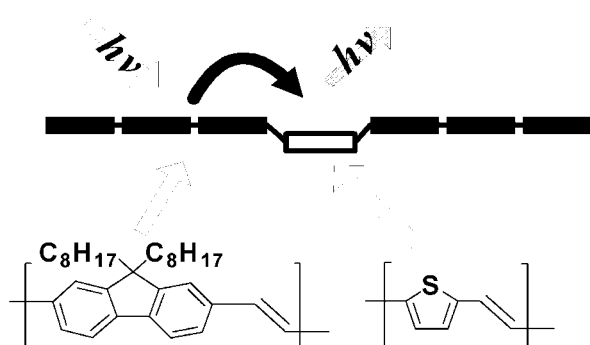
tion of different polymer chains is the cause of incomplete energy transfer in the blend.[21] However, both **C1** and **C2** eliminated this effect. As shown in Figure 5, the emission spectrum of poly(FV), which ranged between 420 and 560 nm, exhibited good overlap with the UV–vis absorption spectra of **C1** and **C2,** respectively. This overlap indicated that the energy transfer probably had a high rate, which may have occurred from the excited fluorene vinylene units to the ThV units. Also, as shown in Figure 3, the absorption spectra of the three polymer films were similar, and the absorption maxima were identical, whereas the PL spectra of **C1** and **C2** were quite different from that of poly(FV). Importantly, no residual peak was observed between 460 and 500 nm of the PL spectra of **C1** and **C2**, which indicated that the energy transfer from fluorene vinylene units to ThV units was complete. Moreover, the PL maxima of **C1** and **C2** were redshifted 70–80 nm in comparison with that of poly(FV). As shown in Figure 6, the spectral separation of the emission of **C1** and **C2** and the absorption of poly(FV) is significant. Hence, this separation may have led to a pronounced reduction of self-absorption losses. The effect of the reduc-
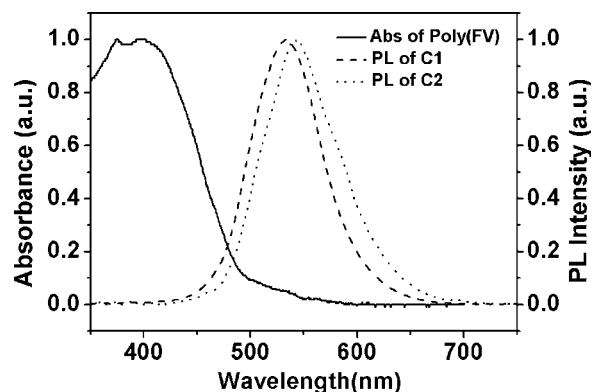

Figure 4 Hypothesized energy-transfer mechanism of **C1** and **C2**. *hv* is the energy of light.

Figure 6 Absorption spectrum of the poly(FV) film and the PL spectra of the **C1** and **C2** films.

tion of optical losses was investigated indirectly by the NLO properties of the three polymers. In a one-dimensional, π-conjugated polymer system (aryl ring and —C=C— alternating with each other), the optical losses caused by increasing conjugation length importantly influence the third-order nonlinear coefficients of polymers, especially homopolymers such as poly(FV), and the incorporation of a minor content of the narrow-band-gap ThV units was expected to improve the NLO properties.[22] Therefore, the Z-scan technique was carried out to research the third-order nonlinear properties of the polymers. The closed-aperture Z-scan spectra of the polymers are
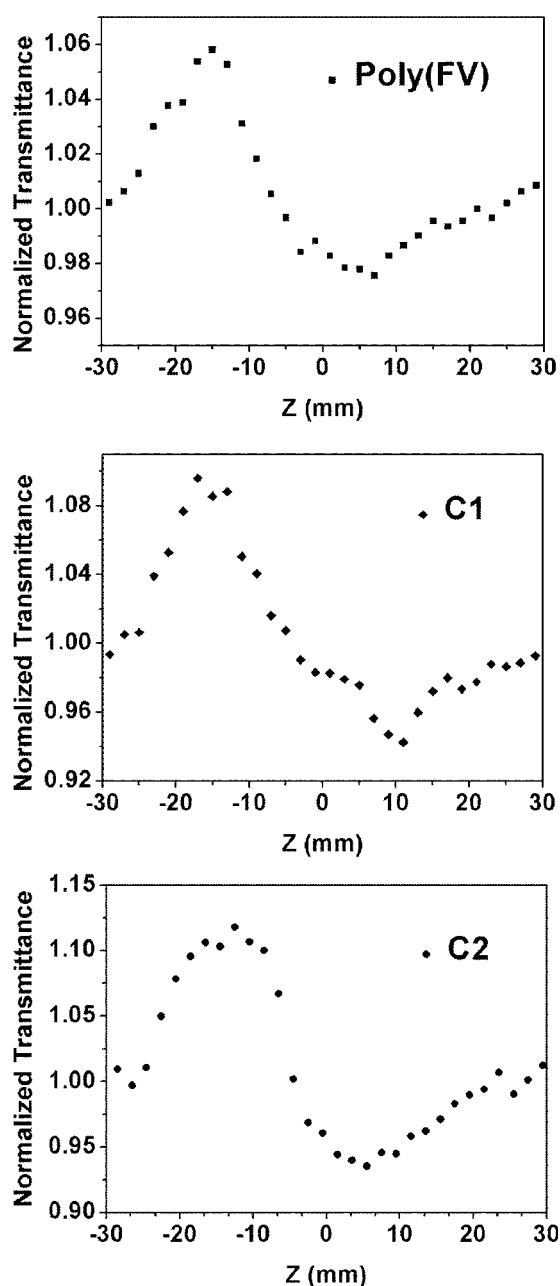

Figure 7 Spectra of the Z-scan measurements of the polymers: (a) poly(FV), (b) **C1,** and (c) **C2**.

TABLE III
Third-Order Nonlinear Coefficients of Poly(FV), C1, and C2

Polymer	n_2 ($\times 10^{-15}$ m^2/W)	$\chi^{(3)}$ ($\times 10^{-9}$ esu)
Poly(FV)	1.127	0.81
C1	2.191	1.35
C2	2.432	1.51

shown in Figure 7(a–c); all of the polymers exhibited peak-to-valley characteristics, presenting negative nonlinear refractive indices (n_2's). The third-order nonlinear coefficients of the polymers were calculated according to the following equations:[23]

$$n_2 = (T_P - T_V)/(0.405 \times K \times L_{\text{eff}} \times I_0) \quad (3)$$

$$\chi_R^{(3)} = \frac{n_0^2 \varepsilon_0 c n_2}{32\pi} \quad (4)$$

$$\chi_I^{(3)} = \frac{n_0^2 \varepsilon_0 c \beta \lambda}{32\pi} \quad (5)$$

$$\chi^{(3)} = \sqrt{\left[\chi_R^{(3)}\right]^2 + \left[\chi_I^{(3)}\right]^2} \quad (6)$$

where T_P and T_V are the normalized peak and valley transmittances, respectively; K equals 2π/wavelength of incident light (λ); L_{eff} is the effective thickness of the sample; L_0 is the intensity of incident light and $\chi_R^{(3)}$ are third order nonlinear refraction coefficient and $\chi_I^{(3)}$ are third order nonlinear absorption coefficient, respectively. Then, n_2 was calculated by Eq. (3). n_0 represents the linear refractive index and approximately equals the refractive index of the solvent of the sample. ε_0 and c in both eqs. (4) and (5) are the Faraday coefficient and velocity of light, respectively. β is the nonlinear absorption coefficient of sample. The results of n_2 and $\chi^{(3)}$ of poly(FV), **C1,** and **C2** are summarized in Table III. The homopolymer poly(FV) exhibited a lower $\chi^{(3)}$, which was 8.1×10^{-10} esu, whereas the $\chi^{(3)}$ values of **C1** and **C2** were 1.35×10^{-9} and 1.51×10^{-9} esu, respectively; these values increased about 66.7 and 86.4%, respectively, in comparison with that of poly(FV). The reduction of optical losses caused by the incorporation of smaller numbers of narrow-band-gap ThV units was proven to be effective. Furthermore, instead of simply increasing the polymer conjugation length, the addition of a minor content of lower energy units to the homopolymer main chain can be an effective way to develop promising NLO materials.

CONCLUSIONS

Three polymers [poly(FV), **C1,** and **C2**], whose main chains were introduced by a minor content of ThV units, were prepared by the Gilch reaction of two

bromomethylated monomers with various feed ratios. Accompanying large numbers of wide-band-gap units (fluorene vinylene), the smaller band-gap units (ThV) acted as energy traps on the one-dimensional polymer chain, and consequently, the fluorene vinylene units predominantly absorbed the light, and the ThV units emitted the light. Complete energy transfer from wide-band-gap units to smaller band-gap units was demonstrated by the absorption and PL spectra of poly(FV), **C1,** and **C2**. The reduction of self-absorption losses was investigated by the third-order nonlinear coefficients of the polymers; these studies were carried out with the Z-scan technique. In addition, broadened absorption bands and redshifted emission maxima indicated the distinct influence of the ThV units on the conjugation lengths for both the solution and thin film. All of the polymers could be dissolved in common solvents and possessed good thermal stability, which was determined by DSC and TGA. In comparison with poly(FV), the significant change in the HOMO energy level along with a slight change in the LUMO energy level of polymers **C1** and **C2** was determined by CV measurements. The results imply that this type of material is promising for polymer optical device applications.

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