Optical-Limiting Properties of Poly(arylene ethynylenes) Containing Thiophene Ring

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ABSTRACT: Poly(arylene ethynylenes) containing thiophene ring were synthesized in good yield. In synthesis, pyridine was added to accelerate reaction owing to its phase transfer effect on CuI. The optical-limiting properties of the prepared polymers were investigated with a Q-switched Nd : YAG laser at 532 nm with 10-ns pulse width. The experiments showed that the order of the optical-limiting response of the polymers is poly(3-hexyl-2,5-thienyleneethylene) (P3) > poly(2,5-dihexyloxy-1,4-benzyleneethylene-3-hexyl-2,5-thienyleneethylene) (P2) > poly(9-hexyl-3,6-carbazoleethylene-3-hexyl-2,5-thienyleneethylene) (P1). It can be understood well by the comparison of their conjugation length and D-A structure. In addition, the results indicated that introducing the electron-rich aromatic ring into the polymer backbone to enhance the D-A structure would be an effective way to improve its optical-limiting property. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 131–135, 2004

Key words: conjugated polymers; NLO; charge transfer

INTRODUCTION

The need for passive optical limiters to protect human eyes and optical sensors exposed to sudden intense laser beams has generated much interest in the development of optical-limiting materials. For the time being, the development of optical-limiting materials is mainly focused on small molecules, such as mentallophthalocyanines,[1–3] fullerenes,[4,5] metalloporphyrin,[6,7] carbon nanotubes,[8] and their derivatives. However, the poor processing and the difficulties in device fabrication have become the main problem for further investigation. For conjugated polymers, their opt-electrical properties can be easily tuned through copolymerization and their good film-forming properties will facilitate their practical application. Recently, conjugation polymers show the potential value of practical application.[9] Therefore, in this article, the optical-limiting properties of poly(arylene ethynylene) containing thiophene ring are reported. This might be helpful in designing the polymeric optical-limiting materials.

EXPERIMENTAL

Materials

Triethylamine, pyridine, and toluene were purchased from Beijing Chemical Co. (Beijing, China) and refluxed over sodium for 5 h and distilled prior to use. PPh_3, carbazole, and CuI (Beijing Chemical Co.) were used as received. Trimethylsilylaceylene was obtained from Acros. Other starting materials, catalysts, and reactive intermediates, such as $Pd(PPh_3)_2Cl_2$[10] and $Pd(PPh_3)_4$,[11] 2,5-dibromo-3-hexylthiophene,[12] 2,5-diiodo-3-hexylthiophene,[13] 1,4-diiodo-2,5-dihexyloxybenzene,[14] 2,5-bis[(trimethylsilyl)ethynyl]-3-hexylthiophene,[15] 2,5-diethynyl-3-hexylthiophene,[15] 9-hexylcarbazole,[16] and 3,6-diiodo-9-hexylcarbazole,[16] were synthesized following the methods described in the literature, respectively.

Characterization

FTIR spectra were recorded on a Perkin–Elmer 1600 Series spectrophotometer. ^{1}H-NMR spectra were obtained on a Bruker AC300P spectrometer. The UV–Vis properties were characterized with a Shimadzu UV-160PC system. The molecular weights of the polymers were measured on a PL-GPC model 210.

Measurement of optical limiting

The optical-limiting properties were performed with a Q-switched Nd : YAG laser at the repetition rate of 10 Hz. The laser frequency was doubled to 532 nm with 10-ns pulse width for Gaussian mode. The laser beam

was split into two beams. One was for measuring and another one was for reference. The measuring beam was focused by a lens to change the incident energy radiated on the sample. The solution sample was contained in a 1-mm quartz cell. By moving the sample in the Z-direction, the incident and transmitted energy were detected simultaneously by two power meters (LPE-1A).[3]

Synthesis

1,4-Bis[(trimethylsilyl)ethynyl]-2,5-dihexyloxybenzene

Under N_2 atmosphere, 1,4-diiodo-2,5-dihexyloxybenzene (0.6 g, 1.2 mmol), PPh_3 (3 mg), CuI (1.5 mg), and $(PPh_3)_2PdCl_2$ (1.5 mg) were added to a mixture of dry triethylamine (15 mL) and pyridine (5 mL) at room temperature. Then, trimethylsilylacetylene (0.26 g, 2.65 mmol) was added to the mixture dropwise with a syringe. After being stirred at room temperature for 1 h, the reaction mixture was kept at 80°C for 5 h under stirring. After cooling to room temperature, the same amount of PPh_3, CuI, $(PPh_3)_2PdCl_2$, and trimethylsilylacetylene was added to the reaction mixture again. The reaction was allowed to proceed for 6 h at 80°C. The solution was cooled to room temperature and filtered to remove the precipitated salts and then diluted with chloroform (30 mL) and washed with water. The organic phase was dried over $MgSO_4$, filtered, and concentrated at reduced pressure to give a brown oil, which was purified by a silica gel chromatograph with petroleum ether as eluant. A yellow solid (0.54 g, 95%) was obtained.
^{1}H-NMR (CDCl$_3$, ppm): δ 6.93 (s, 2H, aromatic), 3.98 (t, 4H, —O—CH$_2$—), 1.82 (m, 4H, —CH$_2$—), 1.54 (m, 4H, —CH$_2$—), 1.38 (m, 8H, —CH$_2$—), 0.94 (t, 6H, —CH$_3$), 0.29 (s, 18H, —Si—CH$_3$); EI m/e: 470 (M$^+$).

Poly(9-hexyl-3,6-carbazoleethylene-3-hexyl-2,5-thienyleneethylene) (P1)

Dry toluene (15 mL), triethylamine (3 mL), and pyridine (1.5 mL) were added to a dry flask. Then, it was flashed with N_2. 2,5-Diiodo-3-hexylthiophene (0.793 g, 1.88 mmol), 3,6-diethynyl-9-hexylcarbazole (0.560 g, 1.88 mmol), CuI (7.06 mg), and Pd(PPh$_3$)$_4$ (20.25 mg) were charged to the flask. The reaction mixture was heated to 110°C and kept at this temperature for 6 h. Then, the solution was cooled to room temperature and filtered to remove the salts formed. The filtrate was poured into the methanol (50 mL). An orange precipitate (0.77 g, 90%) was obtained.
^{1}H-NMR (CDCl$_3$, ppm): δ 8.29–7.13 (m, 7H, aromatic), 4.30 (t, 2H,)N—CH$_2$—), 2.80 (t, 2H, —S—C≡C—CH$_2$—), 1.84–1.10 (m, 16H, —CH$_2$—), 0.93–0.89 (b, 6H, —CH$_3$); FTIR (KBr, cm^{-1}): ν 2952, 2925, 2853 (C—H), 2194 (—C≡C—), 1624, 1595, 1482 (aromatic ring); M_w = 21,000, PDI = 2.30.

Poly(2,5-dihexyloxy-1,4-benzyleneethylene-3-hexyl-2,5-thienyleneethylene) (P2)

^{1}H-NMR (CDCl$_3$, ppm): δ 7.13–6.89 (m, 3H, aromatic), 3.99 (t, 4H, —O—CH$_2$—), 2.76 (t, 2H, —S—C≡C—CH$_2$—), 1.84–1.25 (m, 24H, —CH$_2$—), 0.91–0.88 (b, 9H, —CH$_3$); FTIR (KBr, cm^{-1}): ν 2955, 2928, 2853 (C—H), 2196 (—C≡C—), 1601, 1536, 1498,1464 (aromatic ring). M_w = 29,000, PDI = 2.20 was prepared with the similar method described above.

Poly(3-hexyl-2,5-thienyleneethylene) (P3)

^{1}H-NMR (CDCl$_3$, ppm): δ 7.03 (s, 1H, aromatic), 2.65 (t, 2H, —S—C≡C—CH$_2$—), 1.70–1.02 (m, 8H, —CH$_2$—), 0.89 (b, 3H, —CH$_3$); FTIR (KBr, cm^{-1}): ν 2953, 2926, 2855 (C—H), 2180 (—C≡C—), 1679, 1538, 1459 (aromatic ring); M_w = 25,000, PDI = 2.70 was prepared with the similar method described above.

RESULTS AND DISCUSSION

Synthesis

All the monomers and the polymers were synthesized in good yield (Scheme 1), but the synthesis of the intermediate 1,4-bis[(trimethylsilyl)ethynyl]-2,5-dihexyloxybenzene should be paid attention to. Although the mole ratio of 1 : 2.3 (1,4-diiodo-2,5-dihexyloxybenzene/trimethylsilylacetylene) was employed, the yield of the target product was only about 50% and a substantial amount of monosubstituted compound was formed that even lengthened the reaction time. It is considered that the electron-withdrawing group on the aromatic ring would facilitate the reaction of displacement of halogen atom on the aromatic ring with the trimethylsilylethynyl group.[17] The two electron-donating hexyloxy groups on the benzene would be detrimental to the reaction[17] and a large amount of monosubstituted compound was obtained (yield ca. 50%). It was found that the catalyst and the trimethylsilylacetylene were added to the reaction mixture once again during the reaction to benefit the formation of the target product with good yield (95%). Different from most of literatures, in which only triethylamine acted as solvent and the acid absorber, the mixture of triethylamine and pyridine was employed to replace triethylamine in this work. Owing to the good solubility of CuI in it, pyridine might act as the role of phase-transfer agent for CuI. Consequently, the reaction was accelerated.

Optical-limiting properties

Figure 1 shows the UV–Vis absorption spectra of the polymers in chloroform at room temperature, indicating that the λ_{max} of P1 is 370 nm and that of P2 and P3 are 438 nm. There is a high transmission zone around 532 nm, which is very important for studying their optical-limiting properties at this wavelength.
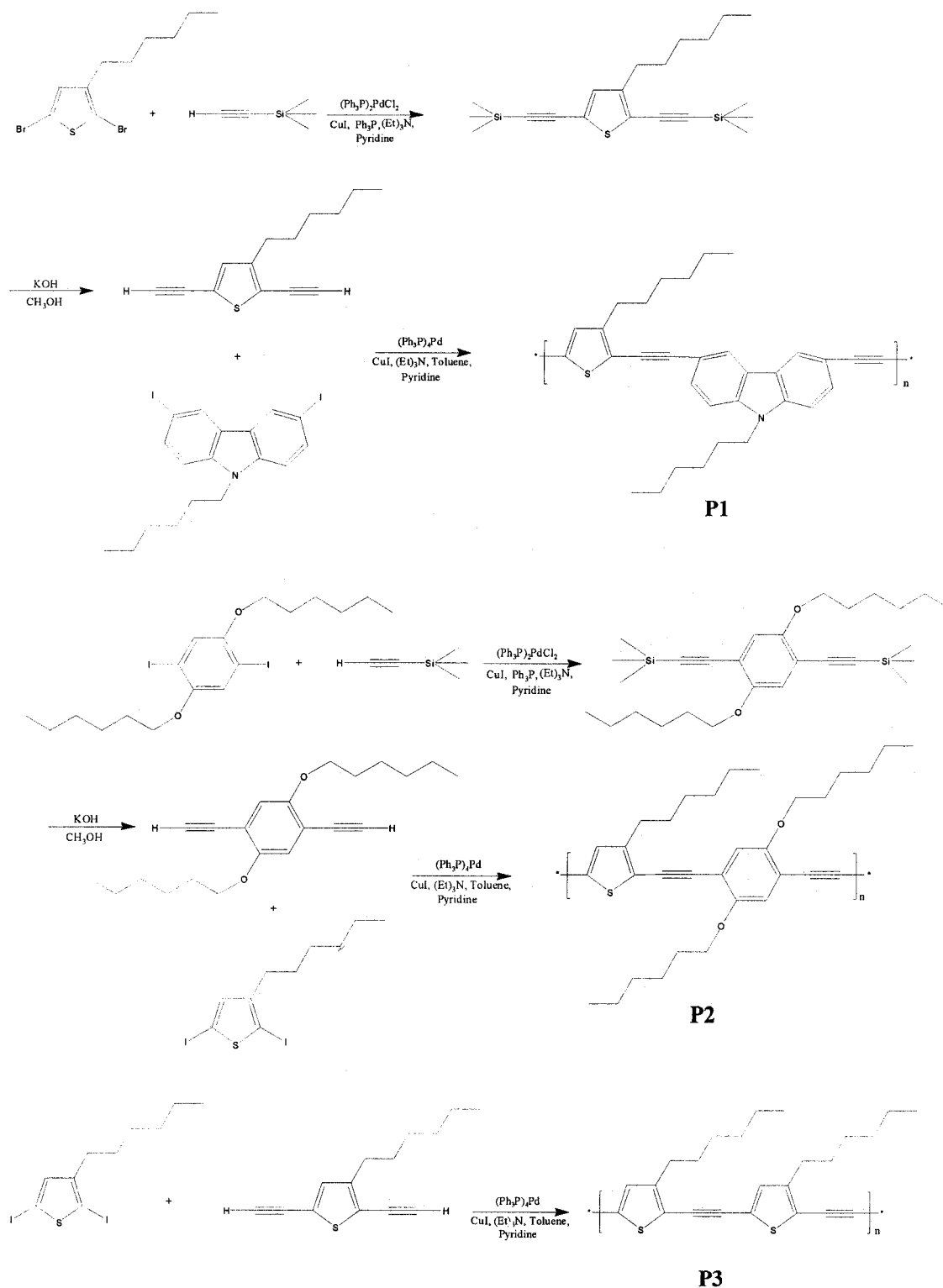
Scheme 1 Synthesis of the P1, P2, and P3.

The optical-limiting performance of the polymers was investigated with 532 nm laser pulse of 10-ns duration in chloroform solution. Figure 2 gives out the optical-limiting behavior of the polymers at the same linear transmittance of 75%. From the curves, it can be seen that all the polymers show obvious optical-limiting response. At low input fluency, the transmittance of the polymer solution remains constant, obeying Beer's law, whereas at high input fluency the transmittance of the solution decreases and a nonlinear
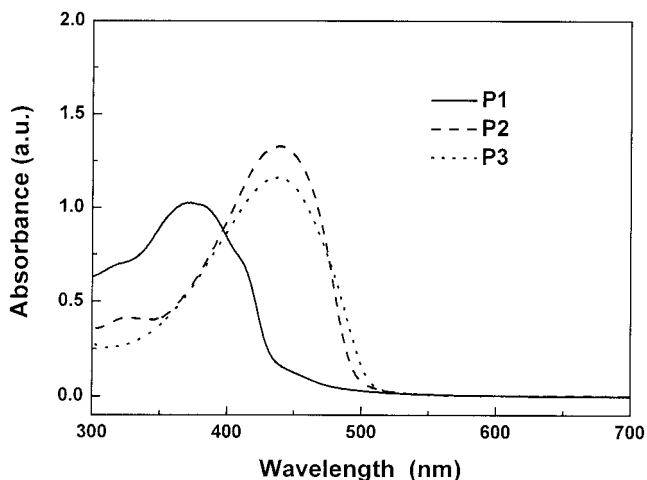
Figure 1 UV–Vis spectra of P1, P2, and P3 in chloroform at room temperature.

relationship is observed. In Ref. 18, the ratio of effective excited-state to the ground-state absorption section δ_{eff}/δ_0 was employed for a figure of merit for optical-limiting based on reverse saturable absorption, which was defined as

$$\delta_{eff}/\delta_0 = \ln T_{sat}/\ln T_L \qquad (1)$$

with

$$T_{sat} = \exp(-\delta_{eff}N_0l) \qquad (2)$$

where T_{sat} is the saturated transmittance for high degrees of excitation, T_L is the linear transmittance of the
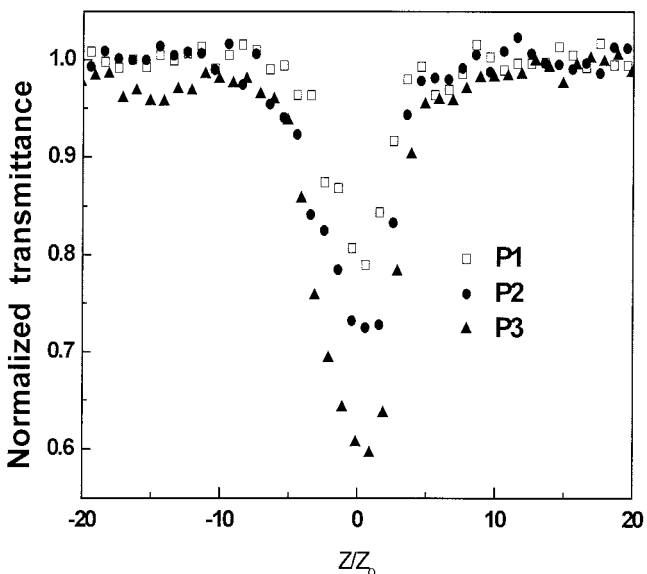

Figure 2 The open aperture Z-scan results for the polymers at the same linear transmittance (T_L = 75%).

TABLE I
Dihedral Angle Between the Aromatic Moieties in the Polymer Backbone

Polymer	Dihedral *angle* (°)
P1	26
P2	19
P3	11

sample (T_L = 75%), N_0 is the total molecular population, and l is the thickness of the sample (l = 1 mm). As shown in Figure 2, the T_{sat} for P1, P2, and P3 are estimated to be 59, 55, and 44%, respectively, at the input fluency ∼ 1 J/cm². With the T_L = 75% for all samples, the corresponding values δ_{eff}/δ_0 for P1, P2, and P3 are 1.83, 2.08, and 2.85 according to eq. (1). P3 with the δ_{eff}/δ_0 value of 2.85 shows better optical-limiting property than that of P1 and P2 (with the δ_{eff}/δ_0 value of 1.83 and 2.08, respectively). The optical-limiting merit of the polymers thus is in the order of P3 > P2 > P1. Compared with that reported for the leading optical-limiting material C_{60} (δ_{eff}/δ_0 ∼ 3), P3 shows good optical-limiting property.

It is well known that optical-limiting properties have a relationship to the conjugation structure of the materials.[19,20] It has been established that the bulk third-order nonlinear optical (NLO) susceptibility χ^3 can generally be related exponentially to conjugation length N in the form $\chi^3 \propto N^n$.[20,21] Theoretical predictions have usually afforded exponents, n, in the range from 3 to 5.4. Compared with those of the P2 and P3, the λ_{max} and the absorption onset of the P1 are obviously hypsochromic, which indicates that it possesses much shorter conjugation length than that of P2 and P3. From the theoretical computation results about the dihedral angle between the aromatic moieties in the polymer backbone (Table I),[22] it can be seen that the dihedral angle between the thiophene moiety and carbazole moiety of P1 is about 26°, which is larger than that of the P2 (19°) and P3 (11°). Furthermore, the theoretical optimization results show that the molecular configuration of P1 is spiral in shape and that of P2 and P3 is linear in shape. The molecular configuration of P1 is not beneficial to extending its conjugation length. Consequently, it is not difficult to understand the shorter conjugation length and the hypsochromic shift of λ_{max} of P1. As a result, the optical-limiting response of the P1 is weaker than that of the P2 and P3.

For P2 and P3, they show almost the same λ_{max}. However, according to the molecular engineer principle, donor–acceptor (D-A) structure of one-dimensional conjugated material will enhance the third-order nonlinear optical properties of the material and the strength of the donor will play a more important

role in the D-A structure.[20] In P3 and P2, there are D-A structures along the polymer backbone in which the aromatic rings act as the donor and the triple bond will play the role of acceptor, owing to its electron-withdrawing properties.[23] However, the ability to donate electron of the electron-rich thiophene is stronger than that of the benzene ring.[24] This means that the intramolecular charge transfer of P3 is larger than that of P2. Therefore, P3 shows stronger optical-limiting response than P2, so it can be concluded that introducing the electron-rich aromatic ring to the polymer backbone of this kind to enhance the D-A structure along the backbone will be a workable way to improve its optical-limiting property.

CONCLUSION

In summary, three poly(arylene ethynylenes) containing thiophene ring were synthesized with good yield. Their optical-limiting properties at 532 nm were investigated on a Q-switched Nd : YAG laser at the repetition rate of 10 Hz with 10-ns pulse width for Gaussian mode. The results show that, because of its shorter conjugation length, P1 shows weaker optical-limiting response than that of P2 and P3. The P3 with stronger D-A structure shows much better optical-limiting behavior than that of P2. In brief, introducing the electron-rich aromatic ring to the polymer backbone of this kind to enhance the D-A structure will be an effective way to enhance its optical-limiting property.

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