Polym. Bull. (2011) 66:893–903
DOI 10.1007/s00289-010-0322-x

ORIGINAL PAPER

Conjugated opto/electroactive ethynylene-carbazole polymers with TTF as pendant group

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Received: 20 March 2010 / Revised: 4 June 2010 / Accepted: 10 June 2010 /

Abstract Three conjugated ethynylene-carbazole polymers with Tetrathiafulvalene (TTF) as pendant group (P1–P3) were synthesized by using sonogashira coupling reaction and characterized by ^{1}H NMR, GPC, CV, UV–Vis, FL, and TGA. CV and UV–Vis spectra showed that an intramoleular interaction existed between the electron-rich moiety TTF and electron-deficient moiety polyethynylcarbazole of the polymers. A strong fluorescence quench (ca. 99%) could be observed, compared to the polyethynylene-carbazole without TTF units, which could be ascribed to the photo-induced electron transfer (PET) interaction from TTF moiety to the polyethynylene-carbazole backbone. The observed onset decomposition temperatures (T_d) for P1–P3 varied from 256 to 298 °C. The polymers mentioned above exhibited good thermal properties and higher conductivity (neutral conductivity $\sim$7–11 $\times$ 10^{-7} S cm^{-1}; doped conductivity $\sim$6–11 $\times$ 10^{-4} S cm^{-1}).

Keywords Carbazole · TTF · Charge transfer · Electroactive polymer

Introduction

Tetrathiafulvalene (TTF) and its derivatives have been studied extensively since they were strong electron donors and show unique redox feature [1], which make

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them promising candidates for application in field organic metals [2], molecular logic gates [3], and molecular sensors [4, 5]. In recent years, TTF and their derivatives have been widely employed in constructing functional organic polymers either in main chain or in the side chain [6], such as polythiophenes [7, 8], polycarbazole [9], and polysilanes [10]. The concept of incorporating TTF units into organic π-conjugated polymers offers exciting potentialities to develop novel conducting polymers [11]. Considering the particular feature of TTF, such a combination may improve the conductivity of the TTF-polymer based conductors, due to increasing dimensionality of the conductors in their solid state [6, 12].

On the other hand, organic π-conjugated polymers, have been studied extensively for their excellent electrochemical and spectroscopic properties [13]. Among them, polycarbazole is one of the most promising materials [14] for the construction of light-emitting materials [15, 16], conducting polymers [17], and solar cells [18, 19], owning to its superior properties together with its facile substitution at the N site [20]. In our previous research [9], TTF have been attached to the conjugated polycabazole and could be used as a conducting material. Furthermore, the conjugated carbazole polymers with acetylene units in the backbone have drawn our attention since the acetylene linkages can enhance the planarity and induce stronger intermolecular interactions among the chromophore and the π–π stacking between aromatic chromophores can lead to higher charge transportation. We expected, the incorporation of TTF as pendant moieties with a rigid polycarbazole backbone may in principle integrate the advantages of the two moieties to afford a new functional material. The only example in this respect is a homopolymer [9] prepared by using Yamamoto coupling. Relatively speaking, the sonogashira coupling could introduce various groups into the backbone to form copolymers with acetylene group. Thus, we synthesized a series of conjugated ethynylene-carbazole polymers with TTF as pendant group by using sonogashira coupling. The presence of the TTF units with long alkyl chains endued the polyethynylene-carbazole with good solubility and higher conductivity.

Experimental

Materials and instruments

All the reagents and solvents were of commercial quality and were distilled or dried when necessary using the standard procedures.

^{1}H NMR and ^{13}C NMR spectra were obtained on Bruker AVANCE 500 instrument operating at 500 and 100 MHz and chemical shifts were quoted downfield of TMS. Elemental analyses were obtained from an Elementar vario EL III C, H, N analyzer. Mass spectra were recorded using LCQ ADVANTAGE mass spectrometer. Absorption spectra were measured with CARY 100 Conc UV–visible spectrophotometer. Fluorescence spectra were carried out with CARY Eclipse Fluorescence spectrophotometer and were corrected for the spectral response of the machines. Gel permeation chromatography (GPC) was carried out with Water-Breeze GPC apparatus using THF as eluent. All the electrochemical experiments were performed in dried CH_2Cl_2 with n-Bu_4NPF_6 as the supporting electrolyte, platinum as the working and counter electrodes, and Ag/AgCl as the reference electrode. The scan rate was 50 mV s^{-1}. The electric conductivity was measured using a four-probe technique with a SX1934 apparatus. The thermogravimetric analysis (TGA) were carried out under flowing nitrogen conditions at a heating rate of 15 °C/min.

Synthesis of Monomer 2

To a solution of TTF 1 (1.443 g, 2.54 mmol) in dried DMF (20 mL), $CsOH{\cdot}H_2O$ (0.448 g, 2.67 mmol) in absolute MeOH (2 mL) was added over a period of 30 min under nitrogen. After stirring for 1 h, a solution of Monomer 1 (0.961 g, 2.54 mmol) in dried DMF (10 mL) was added dropwise over 30 min. The reaction mixture was stirred for another 12 h at room temperature. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (CH_2Cl_2: petroleum ether = 1:4) to give Monomer 2 as dark-red oil (0.930 g, 45.1%). ^{1}HNMR (500 MHz, $CDCl_3$, Me_4Si): δ 8.16 (s, 2H, ph-H), 7.57 (d, 2H, $J = 10$ Hz, ph-H), 7.25 (d, 2H, $J = 10$ Hz, ph-H), 4.19–4.15 (m, 2H, N–CH_2–), 3.10 (s, 2H, –C≡CH), 2.82–2.72 (m, 6H, S–CH_2–), 2.36 (s, 3H, –S–CH_3), 1.82–1.75 (m, 2H, –CH_2–), 1.65–1.52 (m, 6H, –CH_2–), 1.43–1.28 (m, 16H, –CH_2–), 0.91–0.86 (m, 6H, –CH_3). ^{13}CNMR (100 MHz, $CDCl_3$, Me_4Si): δ 140.52, 130.16, 129.71, 127.88, 127.68, 125.38, 124.70, 122.19, 112.79, 110.89, 109.69, 108.93, 84.79, 43.09, 36.32, 36.04, 31.35, 29.75, 29.49, 28.81, 28.23, 28.06, 26.70, 22.59, 19.14, 14.13. MS (70 eV): $m/z = 812.2$ (M^+). Found: C, 60.59; H, 6.11; N, 1.70%. Calcd. for $C_{41}H_{49}NS_8$: C, 60.62; H, 6.08; N, 1.72%.

Synthesis of Polymer 1 (P1)

A mixture of Monomer 2 (225 mg, 0.277 mmol) and 2,5-diiodoxylene (Monomer 4) (99 mg, 0.277 mmol) in diisopropylamine (1.5 mL) and dried toluene (3 mL) was degassed for 30 min. $Pd(PPh_3)_4$ (6.4 mg, 0.0055 mmol) and CuI (2.6 mg, 0.0139 mmol) were added. The mixture was stirred at 70 °C for 48 h and then poured into methanol (200 mL) and filtrated. The solid was extracted with chloroform for 12 h using Soxhlet apparatus. After removing most of the chloroform under reduced pressure, the concentrated liquid was added to methanol (100 mL). The precipitate was filtrated and dried under vacuum at room temperature to give P1 as brown solid (0.193 g, 76.3%). ^{1}HNMR (500 MHz, $CDCl_3$, Me_4Si): δ 8.22–8.20 (m, 2H, ph-H), 7.64–7.59 (m, 2H, ph-H), 7.37–7.30 (m, 4H, ph-H), 4.22 (m, 2H, N–CH_2–), 2.71 (m, 6H, S–CH_2–), 2.49–2.41 (m, 6H, ph-CH_3), 2.31 (s, 3H, S–CH_3), 1.81–1.20 (m, 24H, –CH_2–), 0.80 (m, 6H, –CH_3). ^{13}CNMR (100 MHz, $CDCl_3$, Me_4Si): δ 141.05, 140.24, 139.56, 139.21, 137.72, 133.13, 132.90, 130.42, 128.59, 128.36, 126.13, 124.75, 124.39, 123.75, 123.23, 114.94, 111.69, 110.31, 109.69, 101.23, 96.37, 87.78, 86.90, 43.87, 37.03, 36.75, 31.98, 30.36, 30.13, 29.52, 28.87, 28.73, 28.04, 27.39, 23.21, 20.92, 20.48, 19.86, 14.71. GPC (THF, polystyrene standard): $Mn = 9265$, $Mw/Mn = 2.48$.

Synthesis of Polymer 2 (P2)

The synthetic procedure was similar to that of P1 using 4,4′-diiodobiphenyl ether (Monomer 5) instead of Monomer 4. P2 was obtained as brown solid (0.166 g, 57.8%). ^{1}HNMR (500 MHz, $CDCl_3$, Me_4Si): δ 8.28–8.25 (m, 2H, ph-H), 7.64–7.35 (m, 9H, ph-H), 7.05–6.80 (m, 3H, ph-H), 4.30 (m, 2H, N–CH_2–), 2.79 (m, 6H, S–CH_2–), 2.38 (s, 3H, S–CH_3), 1.88–1.27 (m, 24H, –CH_2–), 0.87 (m, 6H, –CH_3). ^{13}CNMR (100 MHz, $CDCl_3$, Me_4Si): δ 139.72, 139.35, 137.79, 132.15, 128.78, 126.91, 126.68, 124.24, 123.08, 121.51, 121.39, 120.26, 117.96, 117.77, 110.01, 108.63, 108.03, 42.20, 35.34, 35.06, 30.29, 28.67, 28.43, 27.83, 27.18, 27.03, 25.70, 21.53, 18.18, 13.03. GPC (THF, polystyrene standard): $Mn = 16518$, $Mw/Mn = 1.60$.

Synthesis of Polymer 3 (P3)

The synthetic procedure was similar to that of P1 using 4,4′-diiodobiphenyl (Monomer 6) instead of Monomer 4. P3 was obtained as dark-brown solid (0.260 g, 74.7%). ^{1}HNMR (500 MHz, $CDCl_3$, Me_4Si): δ 8.21–8.20 (m, 2H, ph-H), 7.70–7.47 (m, 9H, ph-H), 7.30–7.27 (m, 3H, ph-H), 4.20 (m, 2H, N–CH_2–), 2.71 (m, 6H, S–CH_2–), 2.31 (s, 3H, S–CH_3), 1.79–1.19 (m, 24H, –CH_2–), 0.79 (m, 6H, –CH_3). ^{13}CNMR (100 MHz, $CDCl_3$, Me_4Si): δ 141.08, 140.31, 138.61, 132.66, 130.49, 130.41, 129.45, 128.57, 128.34, 127.50, 127.41, 126.07, 124.90, 123.93, 123.71, 123.21, 114.67, 111.65, 110.32, 109.69, 92.31, 88.57, 43.87, 36.98, 36.70, 31.98, 30.37, 30.15, 29.52, 28.86, 28.72, 27.40, 23.21, 19.80, 14.72. GPC (THF, polystyrene standard): $Mn = 16278$, $Mw/Mn = 1.65$.

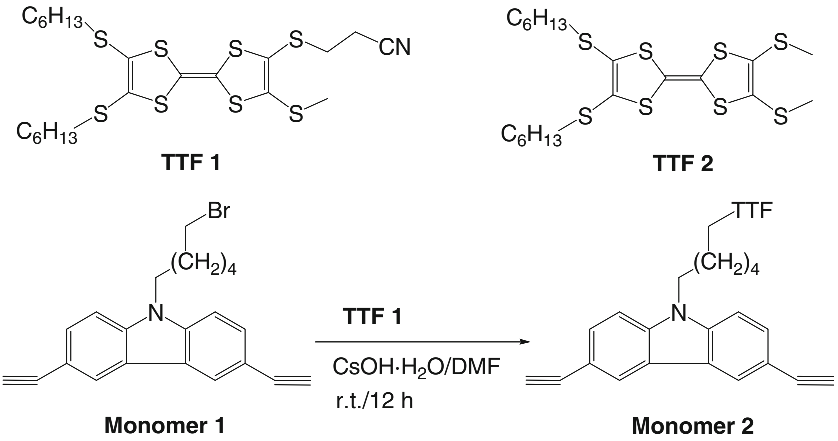
Synthesis of Polymer 4 (P4)

The synthetic procedure was similar to that of P1. P4 was obtained as yellow solid (0.180 g, 80.1%). ^{1}HNMR (500 MHz, $CDCl_3$, Me_4Si): δ 8.33–8.18 (m, 2H, ph-H), 7.62–7.48 (m, 10H, ph-H), 7.34–7.29 (m, 2H, ph-H), 4.24–4.20 (m, 2H, N–CH_2–), 1.47 (s, 2H, –CH_2), 1.25–1.18 (m, 2H, –CH_2), 1.18 (m, 4H, –CH_2), 0.83–0.78 (m, 3H, –CH_3). GPC (THF, polystyrene standard): $Mn = 17211$, $Mw/Mn = 1.85$.

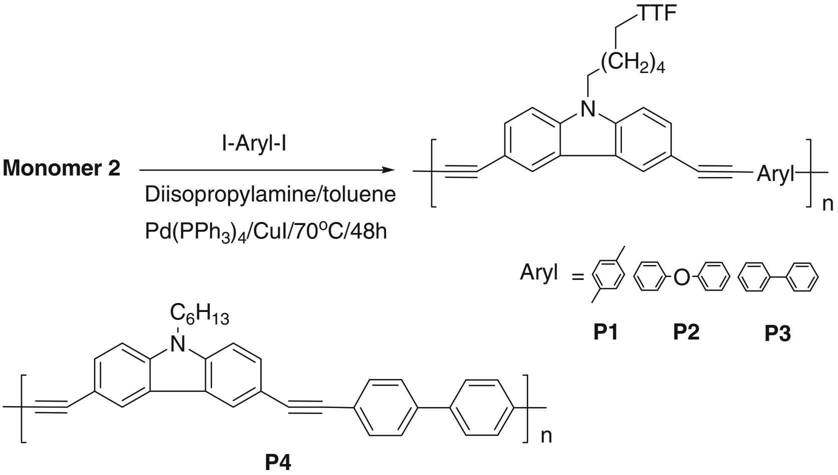
Results and discussion

Design and Synthesis

The TTF 1, TTF 2 [21], and monomers used are shown in Scheme 1. Cyanoethyl groups in TTF 1 was first deprotected by equivalent cesium hydroxide monohydrate ($CsOH{\cdot}H_2O$) to afford TTF thiolates and then trapped by Monomer 1 to form Monomer 2. This carbazole monomer embodying a TTF unit and two terminal acetylene units was the key monomer to constructing TTF functional ethynylene-carbazole copolymers. Sonogashira coupling reaction [22] was conducted to prepare



Scheme 1 Synthesis of Monomer 2 and the structures of TTF 1 and TTF 2



Scheme 2 Synthesis of carbazole-based polymers bearing TTF pendant and the structure of model polymer P4

TTF-bearing conjugated ethynylene-carbazole copolymers. Copolymerization of Monomer 2 and Monomer 4 gave P1 as brown solid (Scheme 2).

Another two polymers (P2 and P3) were obtained by the same methodology, i.e., reaction Monomer 5 and Monomer 6 instead of 2,5-diiodoxylene. For reference, P4 without TTF units was also synthesized by reaction 3,6-diethynyl-9-hexyl-9H-carbazole (Monomer 3) and Monomer 6 in a similar way. These ethynylene-carbazole copolymers were reasonably soluble in normal solvents, such as chloroform, dichloromethane, and THF.

Electrochemistry

The redox properties of P1–P3 and TTF 2 were studied by cyclic voltammetry (CV) in CH_2Cl_2. The CV curves of P1 and P2 were presented in Fig. 1. For reference, the electrochemical data of P3, TTF 2 were listed in Table 1 as well.

CV curves of P1 and P2 showed three single-electron quasi-reversible redox processes, which could be assigned to the successive generation of the radical monocation $TTF^{+\bullet}$, dication TTF^{2+}, and free cation of carbazole$^{+\bullet}$ ($E_{ox1}^{1/2}$, $E_{ox2}^{1/2}$, and E_{ox}^{car}), respectively [9]. The TTF moiety of P1 exhibited 40 and 20 mV anodic shift related to the first and second redox potential compared with TTF 2, suggesting that the TTF units were more difficult to be oxidized than TTF 2. As the injection of the electrons from TTF moiety to the polyethynylene-carbazole backbone caused a lower energy location of HOMO orbital [23], making P1 more difficult to be oxidized than TTF 2. On the other hand, it was found that the electrons injection caused another 50 mV cathodic shift of the polyethynylene-carbazole backbone and the oxidation potential decreased with respect to P4.

The electrochemical behaviors of P2 and P3 were similar to that of P1 and the oxidation potentials of polycarbazole backbone were nearly the same. Nevertheless, the oxidation potentials of the TTF units were lower than that of P1. This phenomenon probably indicated that the oxidation of TTF moiety was influenced by polyethynylene-carbazole moiety [9].

UV–vis spectra

The UV–Vis absorption spectra of P1–P3 in CH_2Cl_2 were given in Fig. 2 and the absorption data of P4 and TTF2 were also given in Table 1 as the reference.

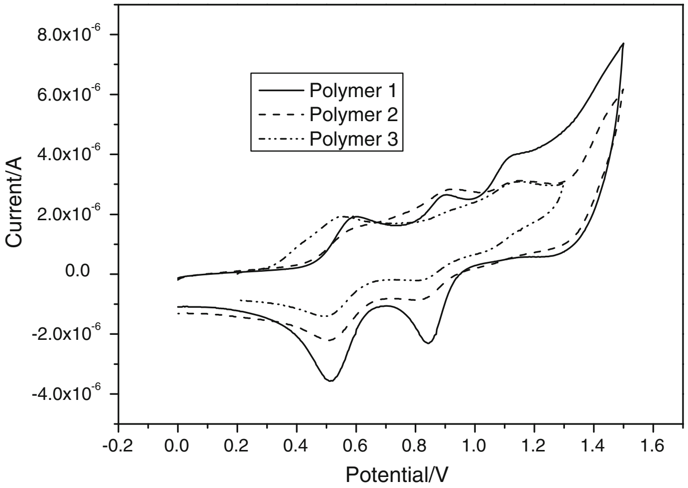


Fig. 1 CV of P1 and P2 (1×10^{-3} M) in CH_2Cl_2 (scanning rate 50 mV/S); platinum as the working and counter electrodes, Ag/AgCl as the reference electrode, n-Bu_4NPF_6 (0.1 M) as the supporting electrolyte

Table 1 CV and UV–Vis absorption data of P1–P4 and TTF2 in CH_2Cl_2

Compound	CV($E^{1/2}_{ox1}$, $E^{1/2}_{ox2}$, E^{car}_{ox}/V)	UV–Vis λ_{max} (nm)
P1	0.55, 0.88, 1.15	227, 248, 318
P2	0.55, 0.86, 1.16	227, 262, 312
P3	0.53, 0.86, 1.15	227, 256, 322, 359
P4	1.20	227, 248, 319, 358
TTF 2	0.51, 0.86	227, 263

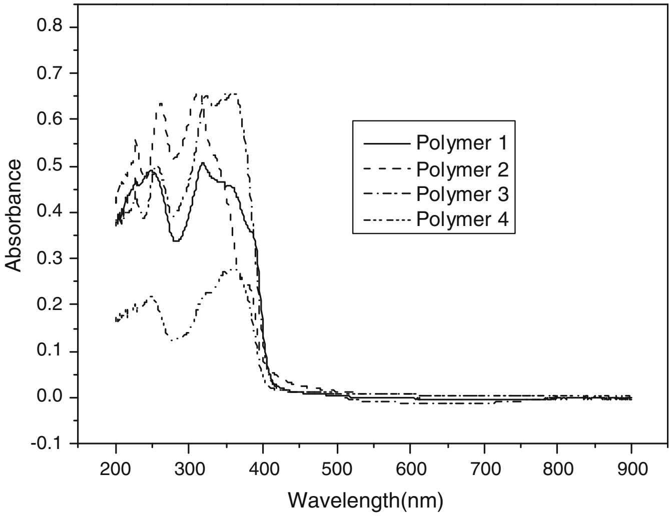


Fig. 2 The absorption spectra of P1–P3 (1×10^{-5} M) in CH_2Cl_2

The absorption curve of P1, P2, and P3 exhibited three absorption peaks at 214, 227, and 318 nm, respectively. The maximum varied from 312 to 322 nm. The absorption peak at 227 nm in the ultraviolet region could be assigned to the absorption of the TTF units with long alkyl chains [24]. The maximum absorption might be to the effect of the π–π* transitions of the conjugated polyethynylene-carbazole backbone [25]. 4 and 10 nm shifts (Table 1) of the backbone absorption band of P3 respect to P1 and P2 could be ascribed to a more planar conformation of the former. In comparison with the absorption spectrum of the reference polymer P4, the maximum absorb band of P3 with TTF pendant was red-shifted by 3 nm (P3 322 nm, P4 319 nm). Clearly the intramolecular charge transfer between the polyethynylene-carbazole moiety and the TTF moiety exerted bathochromic effect on the electronic transitions [26] (also see the CV curves above). As a consequence of the electron injection, the π–π* transitions of the conjugated polyethynylene-carbazole made the main contribution to the absorption spectrum of P3.

Fluorescence spectra

The fluorescence spectra of P1–P3 containing pendant TTF groups were excited at $\lambda_{ex} = 322$ nm, as shown in Fig. 3. For comparison, the fluorescent spectrum of P4 is also given in Fig. 3.

The fluorescence spectra of P4 showed a strong emission peak at 414 nm, which could be ascribed to the polyethynylene-carbazole backbone. This band was not observable in P1 and a strong fluorescence quench (ca. 99%) exhibited. The reason for such fluorescence quench could be considered as the photo-induced electron transfer (PET) interaction from TTF moiety to the polyethynylene-carbazole backbone in the excited state [27]. Moreover, the fluorescence spectra of P2 and P3 were similar to that of P1 and the strong fluorescence quench (ca. 99%) were also occurred, which indicating that the PET interaction between the polyethynylene-carbazole moiety and pendant TTF moiety were slightly influenced by the backbone of the polymers.

Thermal properties

The thermal properties of the polymers were determined by TGA under flowing nitrogen conditions at a heating rate of 15 °C/min. Figure 4 showed the thermogravimetric curve of the polymers. TGA revealed good thermal stability of these polymers. The observed onset decomposition temperatures (T_d) for P1, P2, and P3 were 260, 256, and 298 °C, respectively. These T_d values were lower than that of typical ethynylene-carbazole polymers (~320–330 °C) [28] and P4 (367 °C), indicating that the thermal stability of the ethynylene-carbazole polymers decreased with the incorporation of TTF.

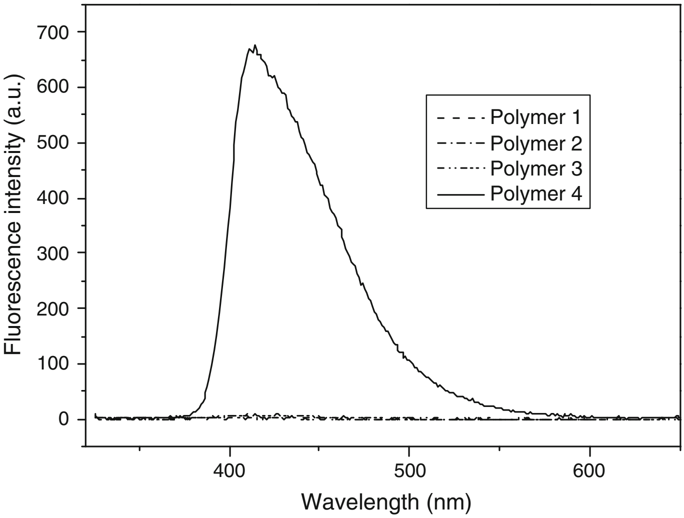


Fig. 3 The fluorescence spectra of P1–P4 (1×10^{-5} M) in CH_2Cl_2. $\lambda_{ex} = 322$ nm

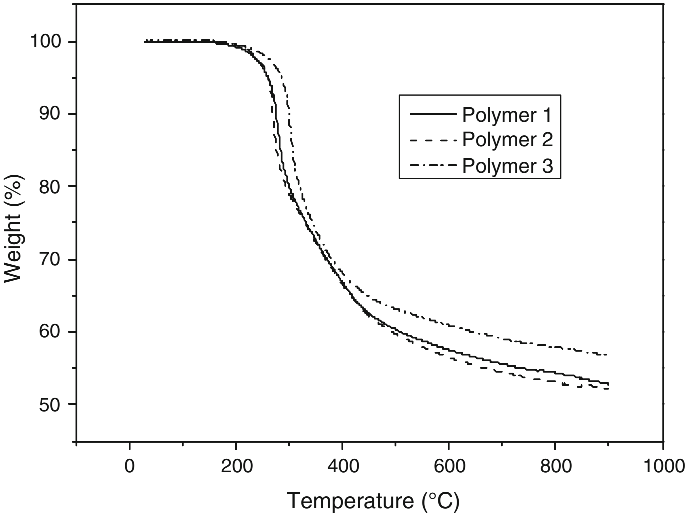


Fig. 4 TGA of P1, P2, and P3 in N_2 at a heating rate of 15 °C/min

Conductivity

P1, P2, and P3 were treated with electron acceptor tetracyanoquinodimethane (TCNQ) in THF and the doped films were obtained from a drop of cast solution of polymer/TCNQ (1:2 M ratio) onto ITO glass plates [29] and then dried in vacuum at 35 °C for 10 h. The conductivities of these polymers in neutral and doped state were measured by four-probe conductivity measurements with a SX1934 apparatus and the values were shown in Table 2.

As shown in Table 2, the electrical conductivity measurements of P1, P2, and P3 showed that oxidation caused the transition from a low-conductivity to a conductive state as generally found in conjugated polymers [30]. The doping of the polymers led to significant increase by three orders of magnitude of the electrical conductivity, when compared to the neutral state. In the doped state, the acetylene linkages allowed the conjugated polyethynylene-carbazole backbone to adopt a more planar structure. This increasing planarity and rigidity optimized the overlap of π-orbital thus enhancing the electron delocalization between the $TTF^{+\bullet}$ moiety and the polyethynylene-carbazole backbone and resulted in a considerable increase in conductivity. Meanwhile, the π–π interactions between neighboring $TTF^{+\bullet}$ units [9, 31] might be another reason for the increasing conductivity. Moreover, the

Table 2 The conductivity of neutral and doped P1, P2, and P3

Polymer	Neutral conductivity/S cm^{-1}	Doped conductivity/S cm^{-1}
P1	1.1×10^{-6}	1.7×10^{-3}
P2	7.3×10^{-7}	6.6×10^{-4}
P3	8.7×10^{-7}	1.2×10^{-3}

doped polymers were stable in air and their conductivities were almost changeless just like other TTF-based polymers [31]. Notably, the conductivities of P2 and P3 were similar to that of P1 indicating that the conductivity was slightly influenced by the backbone of the polymers.

Conclusions

Three conjugated ethynylene-carbazole polymers with electro-donating TTF as pendant groups (P1–P3) were synthesized and characterized. These polymers exhibited intramolecular interaction between the TTF moiety and the polyethynylcarbazole backbone. The strong fluorescence quench occurred in the fluorescence spectra with respect to the polyethynyl-carbazole without TTF units could be ascribed to the PET interaction. The observed onset decomposition temperatures (T_d) for P1–P3 varied from 256 to 298 °C. Their conductivity measurements showed higher conductivity.

Acknowledgments This work was supported by National Natural Science Foundation of China (No. 20676036, 20872035), Specialized Research Fund for the Doctoral Program of Higher Education (No. 20070251018).

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