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Chinese Chemical Letters 22 (2011) 1017–1020

CHINESE CHEMICAL LETTERS

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Preparation and properties of two new soluble carbazole-containing functional polyacetylenes

Wei Ju Zhu, Zhen Yu Wu, Ji Ming Song, Cun Li *

School of Chemistry and Chemical Engineering, Anhui University, Hefei 230039, China

Received 16 February 2011
Available online 25 June 2011

Abstract

Two new functional polyacetylenes bearing carbazole group as pendant, poly{3-[(4-ethynylstyryl)-*N*-butyl] carbazole}(P1) and poly{3-[4-(prop-2-ynyloxy)phenyl-*N*-butyl]carbazole}(P2), were prepared using $[Rh(nbd)Cl]_2$-Et_3N as catalyst. The polymers were soluble in common organic solvents such as $CHCl_3$ and THF. Their structures and properties were characterized and evaluated with FTIR, ^{1}H NMR, UV, TGA, GPC, and CV, respectively. The results show that the polymers possess high thermal stability and well hole-injection property.

Keywords: Polyacetylene; CV; Hole-injection; Carbazole; Thermal stability

Polymers containing carbazole moieties in the main or side chains have attracted much attention because of their unique properties such as photoconductivity, photorefractivity, and electroluminescence, and used as hole-transport and blue emission materials for photoelectronic devices [1–4]. Much effort has been done to synthesize polymers carrying carbazole in the main and side chains, poly-(carbazole) consisting of carbazolylene main chains exhibit different properties each other according to the position of linkage [5–8]. Namely, 3, 6-linked poly(carbazole) undergoes redox reaction *via* stable cation radical species [9,10]. Polyacetylenes (PAs) possess alternating double bonds along the main chain, and many functional PAs with unique optical-electrical properties and high thermal stability have been reported [11–14]. However, PAs with long π-electron conjugated carbazole pendent were little investigated [6,15].

In this paper, we report the synthesis and polymerization of two novel acetylene monomers, 3-[(4-ethynylstyryl)-*N*-butyl]carbazole (compound **3**) and 3-[4-(prop-2-ynyloxy)phenyl-*N*-butyl] (compound **6**), which are substituted with 4-ethynylstyryl and 4-(prop-2-ynyloxy)phenyl group at 3-position of carbazole, and then their π-bridge is extended to conjugated styryl units. It is expected that incorporation of carbazole moieties into PA leads to the development of novel functional polymers on the basis of synergistic effect of carbazole units and PA main chain conjugation. The thermal stability and electron affinity of two novel soluble carbazole-containing PAs were investigated in detail.

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* Corresponding author.
E-mail address: cunliahu@yahoo.com.cn (C. Li).

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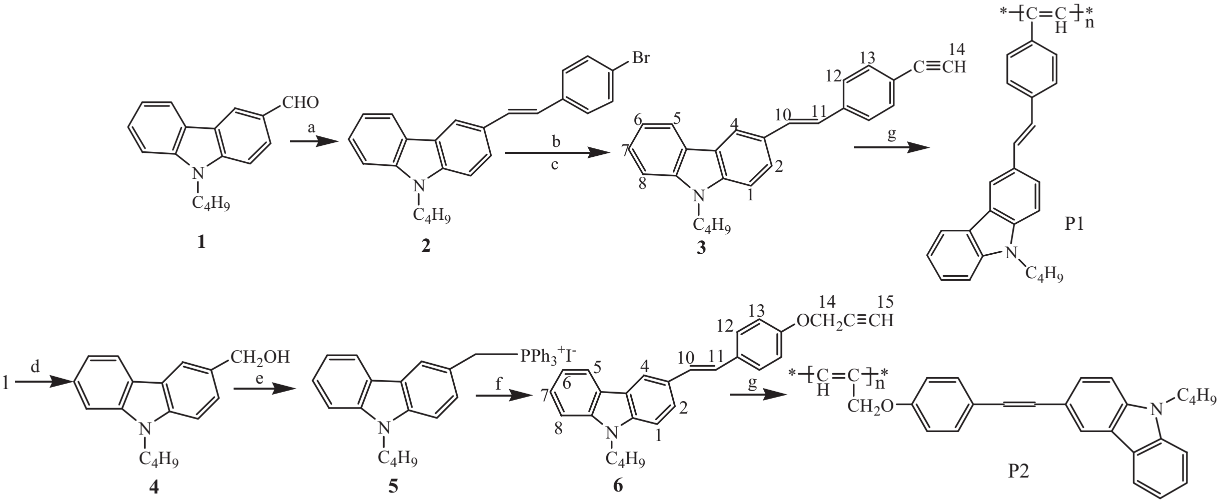
doi:10.1016/j.cclet.2011.05.008

1. Experimental

The synthetic route is described in Scheme 1. The synthesis of compound **2** and **3** are similar to Refs. [14,16]. The crude product of **3** was purified by column chromatography (Al_2O_3, ethyl acetate: petroleum ether = 1:20 as eluent) and pale orange resultant product was obtained in 47.6% yield. FTIR (KBr, cm^{-1}) 3315 (s, $\equiv$C–H), 2954, 2928, 2862 (m, C–H), 2104 (w, C$\equiv$C), 1593, 1504, 1471 (s and vs, Ar), 821 (s, Ar). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (s, 1H, 4-H), 8.15 (d, 1H, 5-H), 7.69 (d, 1H, 1-H), 7.55–7.48 (m, 5H, 6,7,8,13-H), 7.43 (t, 2H, 12-H), 7.36 (d, 1H, J = 16.00 Hz, 10-H), 7.26 (d, 1H, 2-H), 7.14 (d, 1H, J = 16.40 Hz, 11-H), 4.34 (t, 2H, N–CH_2–), 3.15 (s, 1H, $\equiv$C–H), 1.95–1.83 (m, 2H, –CH_2–), 1.43 (m, 2H, –CH_2–), 0.98 (t, 3H, CH_3–). Anal. Calcd. for $C_{26}H_{23}N$: C 89.36, H 6.63, N 4.01. Found: C 89.27, H 6.66, N 3.97.

To obtain intermediate **4**, 1.0 g (4 mmol) compound **1** was dissolved in 20 mL CH_3OH, then 0.12 g (3 mmol) $NaBH_4$ was added slowly under stirring and the mixture was refluxed overnight. After the completion of the reaction, the mixture was washed with distilled water. Ether was added to the mixture, the organic phase was dried over $MgSO_4$. After the removal of the solvent with a rotary evaporator, the residue was purified by recrystallized from ethanol. 0.88 g of white solid **4** was obtained in 86.6% yield. The synthesis of intermediate **5** and resultant monomer **6** are similar to our previous work [16]. The crude product of **6** was purified by column chromatography (Al_2O_3, ethyl acetate: petroleum ether = 1:10 as eluent) and white crystal resultant product was obtained in 65.4% yield. FTIR (KBr, cm^{-1}) 3288 (s, $\equiv$C–H), 2958, 2869 (m, C–H), 2127 (w, C$\equiv$C), 1599, 1508, 1471 (s and vs, Ar), 808 (s, Ar). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (s, 1H, 4-H), 8.15(d, 1H, 5-H), 7.67 (d, 1H, 1-H), 7.54–7.39 (m, 5H, 6,7,8,12-H), 7.27 (d, 1H, 2-H), 7.23 (d, 1H, J = 15.60 Hz, 10-H), 7.13 (d, 1H, J = 16.40 Hz, 11-H), 7.02 (d, 2H, 13-H), 4.75 (s, 2H, –OCH_2–), 4.33 (t, 2H, –NCH_2–), 2.57 (s, 1H, $\equiv$C–H), 1.89 (m, 2H, –CH_2–), 1.42 (m, 2H, –CH_2–), 0.98 (t, 3H, CH_3–). Anal. Calcd. for $C_{27}H_{25}NO$: C 85.45, H 6.64, N 3.69, O 4.22. Found: C 85.43, H 6.68, N 3.65, O 4.24.

The polymerization reaction was performed as following: a baked 20-mL Schlenk tube with a side arm was added 1.0 mmol of the monomer. The tube was evacuated under vacuum and then flushed with dry nitrogen three times through the side arm. 3 mL of dioxane was injected into the tube to dissolve the monomer. The catalyst solution was prepared in another tube by dissolving 4.6 mg (0.01 mmol) $[Rh(nbd)Cl]_2$ and 2.02 mg (0.02 mmol) Et_3N in 2 mL of dioxane, which was transferred to the monomer solution using a hypodermic syringe. The reaction mixture was stirred at 60 °C under nitrogen for 6 h. The mixture was then diluted with 5 mL of dioxane and added dropwise to 200 mL of methanol under stirring. The precipitate was centrifuged and redissolved in THF. The THF solution was added dropwise into 200 mL of methanol to precipitate the polymer. The dissolution–precipitation process was repeated three times, and the finally isolated precipitant was dried under vacuum to a constant weight. P1: Brown red powder, yield: 65.2%. GPC: $M_w = 1.86 \times 10^4$, $M_w/M_n = 1.23$. FTIR (KBr, cm^{-1}) 3023 (w, =C–H), 2927, 2872 (m, C–H), 1596,



Scheme 1. The synthesis routes of monomer and polymerization: (a) 4-Bromobenzyl(triphenyl)phosphonium bromide, NaOH, CH_2Cl_2; (b) CuI, $PdCl_2(PPh_3)_2$, riethylamine, DMF; (c) toluene, KOH; (d) $NaBH_4$, methanol; (e) KI, HAc, PPh_3, $CHCl_3$; (f) 4-(prop-2-ynyloxy)benzaldehyde, NaOH, CH_2Cl_2; (g) $[Rh(nbd)Cl]_2$, triethylamine, 1, 4-dioxane.

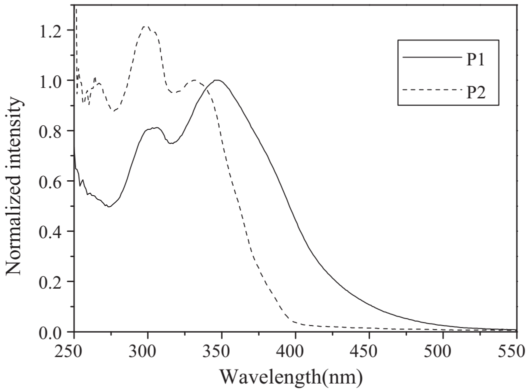


Fig. 1. UV–vis absorption spectra of P1 and P2 in THF solution.

1471 (s and vs, Ar), 818(s, Ar). ^{1}H NMR(400 MHz, $CDCl_3$): δ 0.99 (br., 3H, CH_3), 1.44 (br., 2H, CH_2CH_3), 1.90 (br., 2H, CH_2CH_2), 4.37 (br., 2H, NCH_2), 6.22, 6.94 (br., Ar–H and *trans* C–H), 7.36–8.18 (br., Ar–H). P2: Gray solid, yield: 72%. GPC: $M_w = 2.05 \times 10^4$, $M_w/M_n = 1.18$. FTIR (KBr, cm^{-1}): 3022 (w, C–H), 2926, 2869 (m, C–H), 1600, 1507 (s and vs, Ar), 816 (s, Ar). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.97 (br., 3H, CH_3), 1.42 (br., 2H, CH_2CH_3), 1.87 (br., 2H, CH_2CH_2), 4.31 (br., 2H, NCH_2), 5.15 (br., 2H, OCH_2), 6.54, 6.75 (br., Ar–H and *trans* C–H), 7.01–8.21 (br., Ar–H).

2. Results and discussion

The electronic absorption spectra of polymers in THF are shown in Fig. 1. P1 has two absorption peaks at 304 and 346 nm, corresponding the π–π* transitions of the phenyl and carbazole chromophore, respectively. Compared with P1, P2 exhibits the absorption peak at 300 and 332 nm, which significantly blue-shifts when the pendant of the carbazole-chromophoric segment varies, hinting that P1 has larger π electron delocalization effect than P2. This fact means the extension of conjugation length upon transformation from the P2 to P1.

The thermal stability of the resulting polymers was evaluated by thermogravimetric analysis (TGA) under nitrogen atmosphere. As shown in Fig. 2, the carbazole-containing polyacetylenes exhibit high thermal stability. When 3-position of carbazole was substituted by different groups, the resulting polymers showed T_d (defined as the temperature of 5% weight loss) at 266 and 242 °C for P1 and P2, which are much higher than that for PPA (225 °C). Thus, the incorporation of the carbazole groups to polyacetylenes endowed the polymers with better thermal stability. It may be due to the ‘‘jacket effect’’ of the carbazole pendants. Similar phenomenon is also found by our previous work [11–14].

Cyclic voltammetry (CV) was employed to investigate the redox potentials, and then to estimate the HOMO and LUMO energy levels of polymers according to the well-known semi-empirical method [17,18]. CV measurements

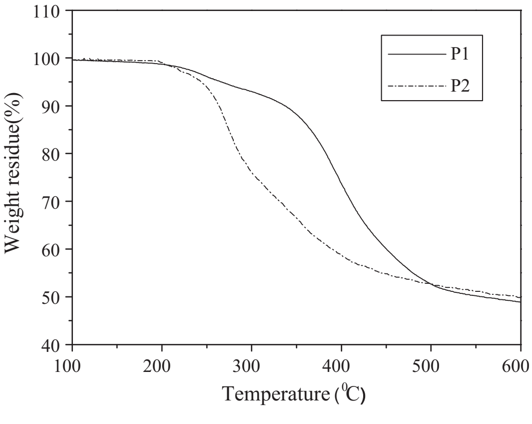


Fig. 2. TGA thermograms of polymers measured under nitrogen.

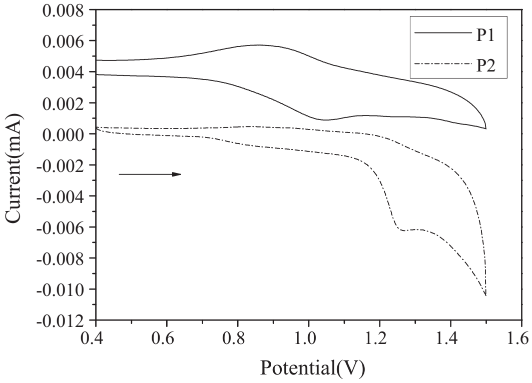


Fig. 3. Cyclic voltammogram of P1 and P2 in a 0.1 mol/L (n-Bu)$_4$NClO$_4$/acetonitrile solution. Scan rate: 50 mV/s.

were carried out at a scan rate of 50 mV/s on a LK98C electrochemical analyzer with a three electrode system (platinum was used as working electrode and as counter electrode, and Ag/AgCl reference electrode) (in a 0.1 mol/L (n-Bu)$_4$NClO$_4$/acetonitrile solution). The HOMO and LUMO energy levels of P1 and P2 obtained by CV analysis are shown in Fig. 3. The onset potentials of P1 and P2 appear at −0.71 and −1.07 V, respectively. The onset potentials can be utilized to estimate the HOMO energy levels. The HOMO energy levels of P1 and P2 are −5.11 and −5.47 eV, respectively. This attributes to the fact that P1 has larger π-electron conjugation owing to the direct linkage of carbazole into PA main chain. The HOMO of P1 is higher than P2, meaning that the hole can be better injected into P1. The high-lying HOMO energy level suggests that the polymers may find potential application for hole injection in organic light-emitting diode (OLED).

In conclusion, two new functional PAs bearing different carbazole group as pendant were successfully synthesized and their CV properties and thermal stability were evaluated. The results show that the polymers possess high thermal stability and well hole injection properties. This work provides a new method for preparing soluble functional PA with good hole injection performance and high thermal stability.

Acknowledgments

This research was financially supported by the National Natural Science Fund of China (No. 21071002/B0111) and the Natural Science Fund of Anhui Province (No. 11040606M33).

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