Polymer Bulletin 46, 29–35 (2001)

Polymer Bulletin

Synthesis of a new polyarylenvinylene derivative based on a terstyryl group linked by a maleimide group

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Received: 19 September 2000/Revised version: 4 December 2000/Accepted: 11 December 2000

Summary

The new polyarylenevinylene, structurally based on a terstyryl group linked by a maleimide group, was prepared from a new dibrominated diphenylmaleimide monomer and *p*-divinylbenzene by Heck-type Pd catalyzed polycondensation. The polymer was soluble in common organic solvents and had M_w and the polydispersity index of 73,600 g/mol and 5.0, respectively. Analysis with IR and NMR indicated that the polymer had a stereoregular vinylene sequence in the backbone of *Z*, *E*, *E*-configurations in series. The polymer showed optical absorption maximums at 353 nm and 444 nm and the bright orange red-colored photoluminescence at 570 nm in a solution and 590 nm in a film.

Introduction

π-Conjugated polyarylenevinylene (PAV) derivatives have been attracted many interests in the field of organic electronics and optics such as light emitting devices (LEDs) and nonlinear optics [1,2].

Many synthetic methods, used to prepare stilbenoid compounds, have been introduced to prepare PAVs [1,2]. Among these methods, Pd-catalyzed carbon-carbon coupling reaction such as the Heck and the Stille reaction was a useful technique to synthesize the soluble PAV derivatives [2-7].

Up to date, to prepare soluble PAVs, alkyl and alkoxy groups attached to the aryl or the vinyl group in a polymer backbone have been generally used as solubilizing groups that showed the electron-donor character. In the field of polymer LEDs, better electron-accepting character of polymers has been required to improve the device efficiency [8]. In efforts to improve the electron-accepting ability of PAVs, many researches have been carried out to introduce electron-withdrawing substituents to the polymers [9-11].

In addition, to control optical properties of PAVs, the regulation of π-conjugation length has been conducted by introducing non-conjugated spacers [12] or twisted structures such as a *m*-phenylene linkage [13] and a *cis*-vinylene linkage [14].

We designed the new monomer based on diphenylmaleimide that was expected to have following characteristics: (i) an electron-withdrawing characteristic of an imide moiety attached to a vinylene group to increase the electron affinity of the resulting polymer and (ii) an analogous of a structurally fixed *cis*-stilbene [15] to construct the stereoregular *cis* and *trans* - vinylene sequence in the main chain and, as a result, control the π-conjugation length.

We synthesized the diphenylmaleimide-type monomer and its fully π-conjugated PAV by Heck-type Pd-catalyzed polycondensation. To our knowledge, there has been no report about π-conjugated polymers having diphenylmaleimide moieties in the main chain. This novel diphenylmaleimide-based PAV having the backbone structurally based on a terstyryl group linked by a maleimide group is expected to be applicable to polymer LEDs and laser diodes.

Experimental

Materials

Bromobenzene, 4-bromotoluene, triethylamine (Et_3N) and CH_2Cl_2 were distilled over CaH_2. *N,N*-Dimethylformamide (DMF) was dried over 4A molecular sieves. *m*-Chloroperbenzoic acid (*m*-CPBA), *n*-dodecylamine, toluene, palladium(II) acetate ($Pd(OAc)_2$), tributylamine (BU_3N) and tri-*o*-tolylphosphine ($P(o\text{-Tolyl})_3$) were used as received without further purification. 1,4-Divinylbenzene (*p*-DVB) [16] and the compound **1** [17] were prepared according to the literature.

Instruments

Melting points were measured on an Electrothermal IA9100 digital melting point apparatus. ^{1}H NMR spectra and IR spectra were obtained using a Varian VXR-300 and a Nicolet 360 FT-IR, respectively. The molecular weight of the polymer was determined by gel permeation chromatography (GPC) using a Waters GPC system, Ultrastyragel columns (Styragel HR-4, HR-3, HR-1 and HR-5E) in series and tetrahydrofuran as an eluent. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) was conducted with a TA instruments SDT 2960 and a TA instruments DSC 2010, respectively, at a heating rate of 10 °C/min under a N_2 atmosphere. Optical absorption spectra and photoluminescence spectra were recorded on a Sinco UVS-2100 and Shimadzu RF 5301PC Spectrofluorophotometer, respectively.

*Synthesis of 3,4-bis(4-bromophenyl)-2,5-furanedione (**2**)*

To a solution of **1** (3.92 g, 10 mmol) in CH_2Cl_2 (10 mL), *m*-CPBA (4.68 g, 19 mmol, 70%) was added. The mixture was stirred at room temperature under a N_2 atmosphere. After 14 h sodium bisulfite (1.0 g) was added and the mixture was stirred at room temperature for additional 1 h. The resulting greenish yellow solution was filtered using a short column of silica gel (CH_2Cl_2) to remove *m*-chlorobenzoic acid. The greenish yellow crystalline product was obtained after recrystallization from ethanol. Yield 3.84 g (94 %); mp 169 - 170 °C; IR (KBr, cm^{-1}): 3100, 3033, 1825, 1764, 1629, 1586, 1484, 1397, 1353, 1266, 1191, 1068, 1009, 929, 827, 740, 565, 508; ^{1}H NMR ($CDCl_3$, ppm): δ 7.42 and 7.58 (8H, aromatic); Anal Calcd. for $C_{16}H_8Br_2O_3$ (408.04): C, 47.10; H, 1.98. Found: C, 46.77; H, 1.98.

*Synthesis of 1,2-di(4-bromophenyl)-N-n-dodecyl maleimide (**3**)*

The mixture of **2** (2.27 g, 5.6 mmol), *n*-dodecylamine (1.1 g, 5.9 mmol, Aldrich) and toluene (20 mL) was stirred at room temperature for 1 h. Et_3N (catalytic amount) and toluene (20 mL were added to the mixture, witch was refluxed for 14 h. Water was removed using a Dean stark trap. Then, toluene was removed under reduced pressure. The fluorescent residue was purified by a silica gel column chromatography (eluent: CH_2Cl_2). Yield 2.88 g (89 %); mp 63 °C; IR (KBr, cm^{-1}): 3084, 2922, 2852, 1768, 1701, 1586, 1485, 1438, 1406, 1374, 1337, 1183, 1068, 1009, 859, 829, 791, 753, 506; ^{1}H NMR ($CDCl_3$, ppm): δ 0.88 (3H, CH_3-), 1.25, 132, 1.57, 1.65 (20H, $-(CH_2)_{10}-$), 3.62 (2H, $-CH_2N$), 7.35 and 7.51 (8H, phenyl); Anal Calcd. for $C_{28}H_{33}Br_2NO_2$ (575.38): C, 58.45; H, 5.78; N, 2.43. Found: C, 58.32; H, 5.84; N, 2.50.

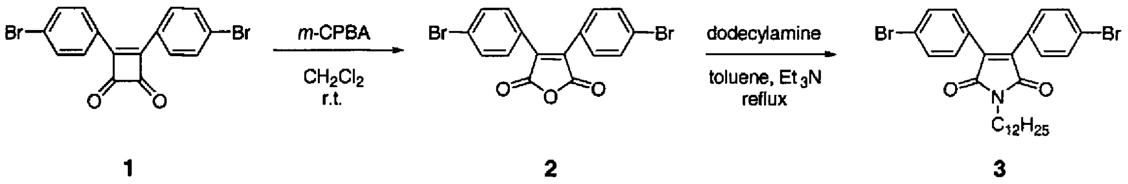
Polymerization of Polymer (4)

BU_3N (0.7 mL, 3 mmol) was added to a homogeneous solution of *p*-DVB (0.13 g, 1 mmol), **3** (0.58 g, 1 mmol), $Pd(OAc)_2$ (9.2 mg, 0.04 mmol), and P(*o*-Tolyl)$_3$ (63 mg, 0.2 mmol) in 10 mL of dry DMF. The reaction mixture was stirred at 100 °C for 20 h under a N_2 atmosphere. The reaction mixture was poured onto 200 mL of methanol. The precipitated polymer was collected by filtration and further purified by dissolving in 3 mL of chloroform and then precipitating from 150 mL of acetone. Yield 0.52 g (96 %); IR (KBr, cm^{-1}): 3021, 2923, 2852, 1764, 1701, 1599, 1509, 1438, 1401, 1354, 1185, 962, 838, 755, 577, 549; ^1H NMR ($CDCl_3$, ppm): δ 0.88 (3H, CH_3-), 1.26, 1.61 (20H, -$(CH_2)_{10}$-), 3.64 (2H, -CH_2N), 7.14 (4H, vinyl), 7.52 (12H, phenyl); Anal Calcd. for $(C_{28}H_{33}Br_2NO_2)_n$ $(575.38)_n$: C, 83.94; H, 7.60; N, 2.58. Found: C, 80.21; H, 7.53; N, 2.63.

Results and discussion

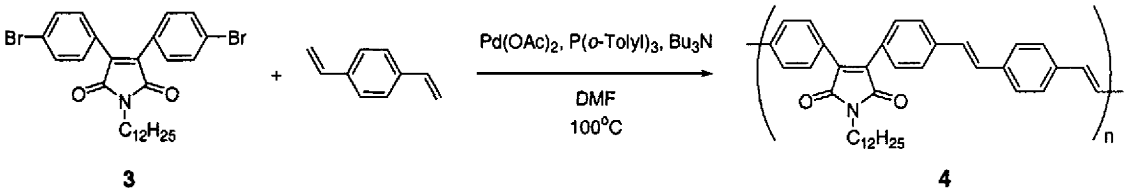
Scheme 1 showed the synthetic route to the monomer, 1,2-di(4-bromophenyl)-*N*-*n*-dodecyl maleimide (**3**). The anhydride compound **2** was prepared from 3,4-bis(4-bromophenyl)-3-cyclobutene-1,2-dione (**1**) [17] by a Beayer-Villiger oxidation reaction [18] using *m*-CPBA as an oxidizing agent. The insertion of oxygen atom into the 1,2-diketone compound **1** by this reaction was processed efficiently due to the ring strain of a cyclobutenedione group. The compound **3** was prepared from the compound **2** with dodecylamine by a conventional thermal imidization process. *p*-DVB was easily prepared from terephthalaldehyde by a Wittig reaction according to the literature [16].

As shown in Scheme 2, Heck polycondesation polymerization of the dibrominated compound **3** with *p*-DVB yielded the PAV **4** having the weight average molecular weight (M_w) of 73,600 g/mol and the polydispersity index (M_w/M_n) of 5.0. In this polymerization system, palladium(II) acetate (4 mol %) and tri-*o*-tolylphosphine (20 mol %) were used as a Pd catalyst and a ligand, respectively.



Scheme 1. Synthetic route to the monomer **3**.

The polymer was soluble in common organic solvents such as tetrahydrofuran, chloroform, toluene and DMF. Spin coating from a chlorobenzene solution of the resulting polymer could produce a homogeneous and transparent film.



Scheme 2. Synthetic scheme of the polymer **4**.

In IR studies, characteristic symmetric and asymmetric C=O stretching bands at 1764 cm^{-1} and 1701 cm^{-1}, respectively, of an imide group were shown in the IR spectrum of the polymer **4** (Figure 1). A typical out-of-plane bending absorption band of the C-H bond in a *para*-disubstituted benzene and in a *trans*-ethylene group at 838 cm^{-1} and 962 cm^{-1}, respectively, indicated that the polymer had the *E*-configuration in its vinylene units derived from *p*-DVB [5,6].

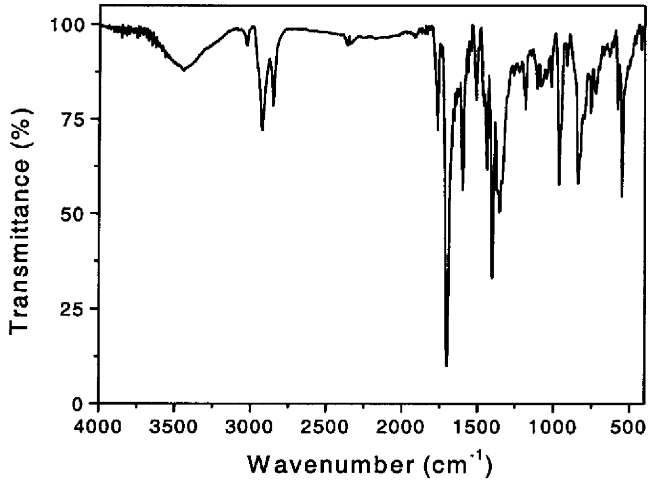


Figure 1. IR spectrum of the polymer **4**.

As shown in Figure 2, the result from a ^{1}H NMR spectrum was in good agreement with the proposed structure of **4**. The proton peaks at phenyl groups and a *trans*-vinyl group appeared at 7.52 and 7.14 ppm, respectively. There were no *cis*-vinylene and terminal vinylene proton peaks near 6.5 ppm and 5 - 6 ppm, respectively. Aliphatic proton peaks in the side chain were between 0.88 and 3.64 ppm. The methylene proton peak adjacent to the nitrogen in an imide moiety was shifted downfield to 3.64 ppm.

Judged from IR and ^{1}H NMR spectra, the π-conjugated polymer **4**, based on a terstyryl group linked by a maleimide group, had a stereoregular C=C sequence of *Z, E, E*-configurations in series in the main chain. In case of the *cis*-vinylene derived from a maleimide moiety, the *Z*-configuration was structurally fixed so that the *cis-trans* isomerization could not occur [15]. In the Heck-type reaction, it is well known that the thermodynamically more stable *E*-configured alkene products are generally obtained [19]. Therefore, *E, E*-configurations in vinylenes derived from *p*-DVB in the resulting polymer were typical characteristics of a Heck coupling reaction performed with a terminal alkene [3-7]

As shown in Figure 3, the polymer **4** was relatively stable up to ca. 395 °C under an inert atmosphere, which was similar to the thermal stability observed in substituted poly(*p*-phenylenevinylene)s [5]. Determined by DSC, the glass transition temperature (T_g) of **4** was 145 °C.

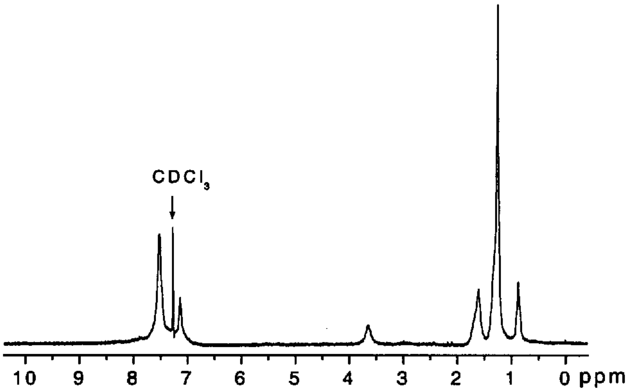


Figure 2. ^{1}H NMR spectrum of the polymer **4**.

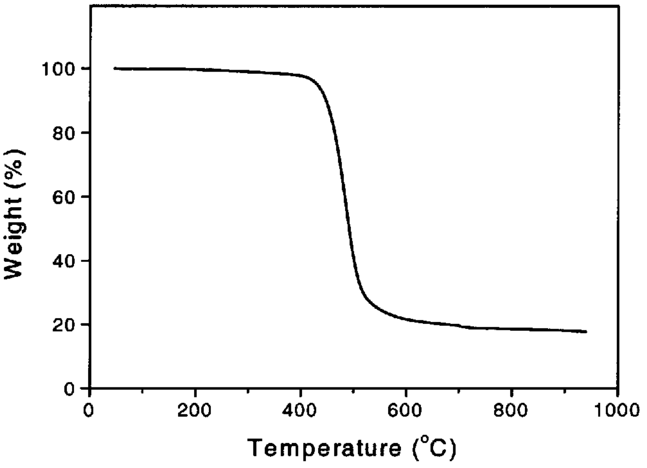


Figure 3. TGA thermogram of the polymer **4**.

Figure 4 showed the optical absorption and photoluminescence spectra of the PAV **4**. The concentration of a polymer solution was 1.7X10^{-4} M in benzene, estimated by a repeating unit. A polymer film was obtained by a spin-cast technique from a chlorobenzene solution onto a glass plate. Optical absorption maximums of **4** appeared at 353 nm and 444 nm in both a solution and a film. Evaluated from the absorption edge at 524 nm in a solution, the band gap of **4** was 2.37 eV. The polymer showed bright orange red-colored emission at 570 nm and 590 nm in a benzene solution and in a film, respectively, when it was excited at absorption maximums.

More detailed studies of the polymer **4** such as cyclic voltammetry and electroluminescence are in progress.

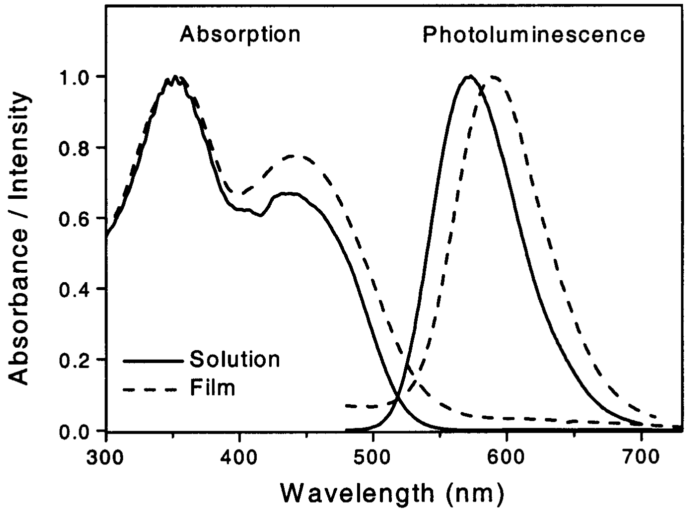


Figure 4. Optical absorption and photoluminescence spectra of the polymer **4**.

Conclusions

We synthesized and characterized a new soluble fully π-conjugated PAV having maleimide moieties in the main chain *via* the standard Heck polymerization. Estimated by IR and NMR spectra, the PAV-type polymer had a stereoregular vinylene sequence in the main chain of *Z, E, E*-configurations in series. The polymer film showed strong orange red-colored photoluminescence at 590 nm, which probably provides its applicability to polymer LEDs and laser diodes.

Acknowledgements

The authors are grateful to National Research Laboratory (NRL) 2000 program (Plastic Optical Fiber) by Korea Institute of Science and Technology Evaluation and Planning (KISTEP) for the financial support.

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