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A class of *cis*-polyarylenevinylene: preparation and optical properties of the oligomeric polyarylenevinylene derivative having an 1,2-diphenylmaleimide moiety

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Abstract

A novel π-conjugated polymer, poly(3,4-bisphenyl-*N*-*n*-hexyl-pyrrole-2,5-dione), was synthesized by dehalogenation polycondensation with the zerovalent nickel complexes (the Yamamoto method), of which the chemical architecture was based on the polyarylenevinylene having a fixed *cis*-vinylene group. This polymer showed high solubility in common organic solvents, high spin-castability and high thermal stability up to ca. 400°C and the T_g of 152°C. The dilute polymer solution (THF) showed the greenish yellow photoluminescence with the maximum at 526 nm. © 2001 Published by Elsevier Science Ltd.

Keywords: Poly(arylenevinylene)s; Yamamoto method; Diphenylmaleimide

1. Introduction

Studies on polymers with a highly π-conjugated structure, such as polyacetylene, polyarylene, polyarylenevinylene and their derivatives, are of great interest in polymer science due to their potential applications, such as electrical conductivity, nonlinear optics and electroluminescence [1–3]. Many synthetic methods have been reported and applied to prepare π-conjugated polymers, including transition metal-catalyzed polymerization [1–3]. Dehalogenation carbon–carbon coupling polymerization by zerovalent nickel complexes has been regarded as one of the useful techniques to produce π-conjugated polyarylenes having a well-defined structure [4–7]. Among these polymerization methods, the Yamamoto method using bis(1,5-cyclooctadiene)nickel ($Ni(COD)_2$) as a nickel(0) complex has largely been used due to relatively high yield and mild polymerization temperature [7].

Till date, Yamamoto et al. reported polybiphenylenevinylene-type polymers using the Yamamoto method with stilbene-type monomers, which showed that $Ni(COD)_2$-promoted polycondensation was not affected by the vinyl group in the monomer [8,9]. Recently, we reported alternating π-conjugated copolymers based on 1,2-diphenylmaleimide moieties prepared by the Heck-type [10] and the Sonogashira-type [11] palladium-catalyzed polymerisation [12,13]. 1,2-Diphenylmaleimide moieties can be regarded as *cis*-stilene derivatives, repeating units of polyarylenevinylene, which have been known as fluorescent materials [14]. In line with the development of novel π-conjugated polymers based on a 1,2-diphenylmaleimide moiety, we introduced the Yamamoto method to preparing a polybiphenylenevinylene-type polymer.

In this paper, we report the synthesis of the novel monomer based on a diphenylmaleimide structure and its π-conjugated polymer as well as physical properties of the polymers, such as thermal and optical properties.

2. Experimental

2.1. Materials

All chemical reagents were purchased from Aldrich, Acros, Jassen, Merck and TCI. 2,2′-Bipyridyl (bpy) was used after recrystallization from ethanol. Other reagents were used without further purification.

2.2. Synthesis

2.2.1. Bis(4-bromophenyl)-3-cyclobutene-1,2-dione (**1**)

The catalytic amount of *N*,*N*-dimethylformamide (DMF) was added to a suspension of squaric acid (3.04 g, 26.6 mmol) in thionyl chloride ($SOCl_2$) (6.42 g,

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54.0 mmol) at room temperature. The reaction mixture was heated at 55°C for 12 h and then allowed to cool to 0°C. Bromobenzene (21 ml) and powdered $AlCl_3$ (8.50 g, 63.8 mmol) were added to the mixture. The mixture was stirred overnight at room temperature. The mixture was poured onto ice-cooled water, filtered and extracted with methylene chloride (CH_2Cl_2). The organic layer was dried over $MgSO_4$ and evaporated under reduced pressure. The crude residue was purified by recrystallization from ethanol. Yield: 4.90 g (47%). Mp: 172°C. ^1H NMR ($CDCl_3$): $\delta = 7.95$ and 7.75 (H^8, aromatic CH). IR (KBr): 1780 (sym. C=O) and 1718 cm^{-1} (asym. C=O). $C_{16}H_8Br_2O_2$ (392.04) — calc.: C 49.02, H 2.06; found: C 48.58, H 2.04.

2.2.2. 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*-chloroperbenzoic acid (*m*CPBA) (4.68 g, 19 mmol) was added. The mixture was stirred at room temperature under an N_2 atmosphere. After 18 h, sodium bisulfite (0.52 g) was added, and the mixture was stirred at room temperature for additional 1 h. The resulting greenish fluorescent 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 small amount of ethanol. Yield: 3.84 g (94%). Mp: 169–170°C. ^1H NMR ($CDCl_3$): $\delta = 7.58$ and 7.42 (H^8, aromatic CH). IR (KBr): 3100 and 3033 (aromatic CH), 1825 (sym. C=O) and 1764 cm^{-1} (asym. C=O). $C_{16}H_8Br_2O_3$ (408.04) — calc.: C 47.10, H 1.98; found: C 46.77, H 1.98.

2.2.3. 3,4-Bis(4-bromophenyl)-N-n-hexyl-pyrrole-2,5-dione (**3**)

The mixture of **2** (1.60 g, 5 mmol), *n*-hexylamine (0.53 g, 5.2 mmol) and triethylamine (Et_3N) (catalytic amount) in toluene (40 ml) was refluxed for 24 h. Water was removed using a Dean stark trap. Then, toluene was removed under a reduced pressure. The product was obtained after recrystallization from ethanol. Yield: 1.97 g (95%). Mp: 76°C. ^1H NMR ($CDCl_3$): $\delta = 0.82$ (H^3, CH_3–), 1.25, 1.47, 1.59 (H^8, –$(CH_2)_4$–), 3.56 (H^2, –CH_2N), 7.28 and 7.44 (H^8, aromatic CH). IR (KBr): 2929 and 2857 (aliphatic CH), 1766 and 1702 (C=O) and 1373 cm^{-1} (C–N). $C_{22}H_{21}Br_2NO_2$ (491.22) — calc.: C 53.79, H 4.31, N 2.85; found: C 52.21, H 4.47, N 2.70.

2.2.4. Poly(3,4-bisphenyl-N-n-hexyl-pyrrole-2,5-dione) (**4**)

$Ni(COD)_2$ (0.331 g, 1.2 mmol), bpy (0.187 g, 1.2 mmol) and **3** (0.491 g, 1.0 mmol) under an argon atmosphere were placed in a 20 ml sealed tube. Dry DMF (10 ml) and 1,5-cyclooctadiene (COD) (2.3 mmol, 0.29 ml) were added using a syringe through a rubber septum. The mixture was stirred at 60°C for 45 h under a nitrogen atmosphere. The resultant mixture was poured into the mixture of methanol (200 ml) and concentrated HCl (5 ml). Precipitated yellow polymer **4** was collected, washed with warm methanol, a hot aqueous solution of *N*,*N*,*N*′,*N*′-ethylenediaminetetraacetate (EDTA) (pH = 3.8), a hot aqueous solution of disodium EDTA (pH = 9), warm water and then methanol in order and dried in vacuo. Yield: 0.31 g. ^1H NMR ($CDCl_3$): $\delta = 0.84$ (CH_3–), 1.26, 1.49, 1.61 (– $(CH_2)_4$–), 3.58 (–CH_2N), 7.31 and 7.54 (aromatic CH). IR (KBr): 2929 and 2857 (aliphatic CH), 1766 and 1703 (C=O) and 1356 cm^{-1} (C–N).

2.2.5. 3,4-Bisphenyl-N-n-hexyl-pyrrole-2,5-dione (**5**)

5 was prepared using the same procedure described for **3**. Mp: 74°C. ^1H NMR ($CDCl_3$): $\delta = 0.82$ (CH_3–), 1.26, 1.48, 1.61 (– $(CH_2)_4$–), 3.57 (–CH_2N) and 7.29–7.42 (aromatic CH). IR (KBr): 3060 (aromatic CH), 2939 and 2852 (aliphatic CH), 1766 and 1701 (C=O) and 1375 cm^{-1} (C–N).

2.3. Measurements

^1H NMR spectra were obtained using a Varian VXR-300 and referenced to tetramethylsilane (TMS). IR spectra were recorded on a Nicolet 360 FTIR. Elemental analysis was carried out using an Elementar Analysensysteme GmbH Vario EL. The molecular weight was measured using a Waters gel permeation chromatography (GPC) system with a 410 differential refractometer, Ultrastyragel columns in series (Styragel HR-4, HR-3, HR-1 and HR-5E) and tetrahydrofuran (THF) as an eluent. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were conducted with a TA instruments SDT 2960 Simultaneous DSC-TGA and a TA instruments DSC 2010, respectively, at a heating rate of 10°C min^{-1} under a nitrogen atmosphere. Optical absorption spectra and fluorescence spectra were recorded on a Sinco UVS-2100 and a Shimadzu RF 5301PC Spectrofluorophotometer, respectively, using a quartz cuvette. X-ray diffraction (XRD) pattern of the powdered polymer was recorded on a D/max RINT 2000 wide angle diffractometer using $CuK_{\alpha 1}$ radiation (40 kV, 100 mA).

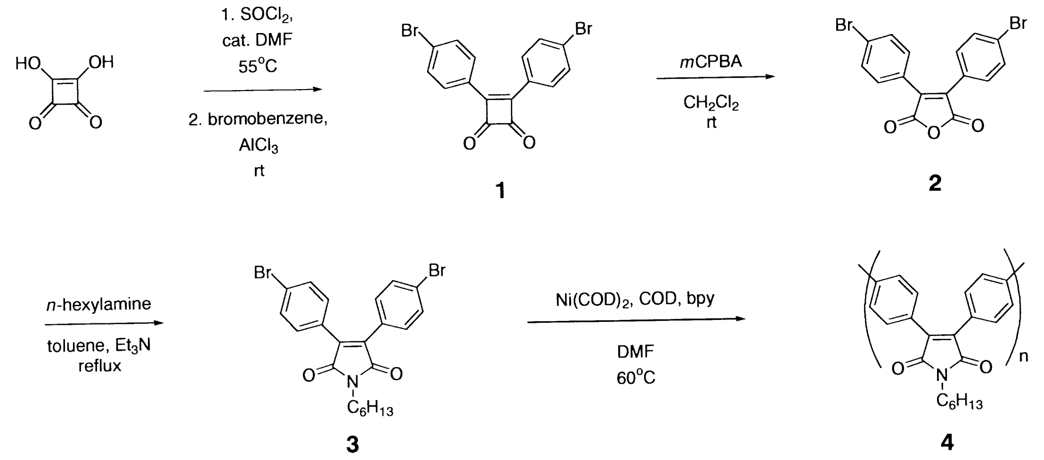
3. Results and discussion

3.1. Monomer synthesis and polymerization

Among several synthetic routes to diphenylmaleic anhydride, a Beayer–Villiger-type mild oxidation reaction [15] of 3,4-diphenylcyclobutene-1,2-dione was reported by Maahs et al. and Blomquist et al. [16,17]. We schemed out the synthetic route to the dibromo-functionalized diphenylmaleimide monomer involving the Beayer–Villiger oxidation of 3,4-disubstituted cyclobutene-1,2-dione as a key step (Scheme 1).

The Friedel–Craft-type acylation of squaryl dichloride, prepared by the chlorination of squaric acid with $SOCl_2$, with bromobenzene provided 3,4-bis(4-bromophenyl)-3-cyclobutene-1,2-dione (**1**) [18].

Maahs et al. and Blomquist et al. used hydrogen peroxide



Scheme 1. Synthesis of the monomer **3** and the polymer **4**.

as an oxidizing reagent to prepare diphenylmaleic anhydride. However, we used *m*CPBA and CH_2Cl_2 as an oxidizing reagent and a solvent, respectively, to prevent hydrolysis of the resulting anhydride product [12,13]. Oxidation of 1,2-diketone **1** by *m*CPBA provided fluorescent 3,4-bis(4-bromophenyl)-2,5-furanedione (**2**) with the yield of 94%, in which the good yield probably was due to the ring strain of cyclobutenedione structure.

The thermal imidization of **2** with *n*-hexylamine in toluene quantitatively provided the 1,2-diphenylmaleimide-based monomer, 3,4-bis(4-bromophenyl)-*N*-*n*-hexylpyrrole-2,5-dione (**3**).

Dehalogenation polycondensation of **3** by the use of a zerovalent nickel complex gave the π-conjugated polymer **4**. Here, we used $Ni(COD)_2$ as a nickel(0) complex, COD and bpy as ligands and DMF as a solvent as described in the Yamamoto coupling method (Scheme 1) [7]. The polymer **4** showed good solubility in most common organic solvents, such as chloroform, THF, toluene and DMF. A pinhole-free transparent film was readily obtained in above solutions by a spin-casting technique.

3.2. Characterization of the monomer and the polymer

3.2.1. Microstructural characterization

As shown in Fig. 1, the IR spectrum of the polymer **4** showed the characteristic imide group vibration bands of symmetric C=O stretching band at 1766 cm^{-1}, asymmetric C=O stretching band at 1703 cm^{-1} and C–N stretching band at 1356 cm^{-1}, which was similar to that of the monomer **3**. The characteristic stretching band of aryl bromide at 1071 cm^{-1}, shown in the IR spectrum of monomer **3**, was apparently diminished in the IR spectrum of the polymer **4**, which implied that the polymerization was carried out to a certain extent. The C–H out-of-plane bending vibration of a *para*-disubstituted benzene in the biphenylene group, formed by the aryl coupling reaction of **3**, at 828 cm^{-1} was observed in the IR spectrum of **4**.

Fig. 2 showed the ^1H NMR spectrum of the monomer **3**, which was well in accordance with the expected chemical structure of **3**. The protons in the aliphatic chain were found between δ 0.82 and δ 3.56 ppm. The methylene proton peak

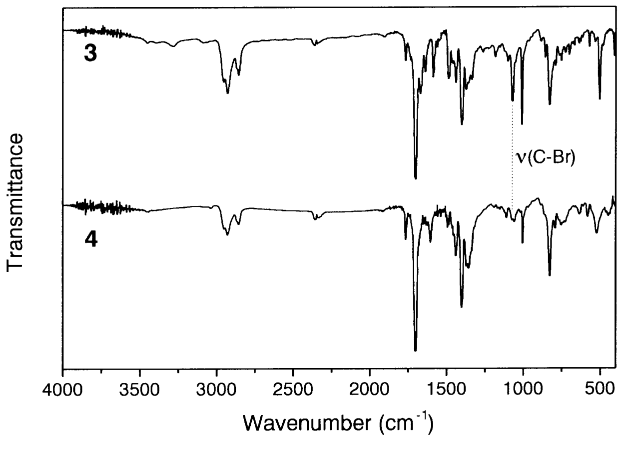


Fig. 1. IR spectra of **3** and **4**.

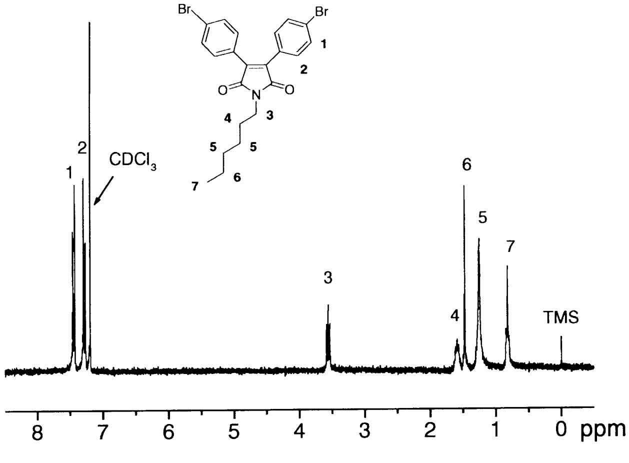


Fig. 2. ^1H NMR spectrum of **3**.

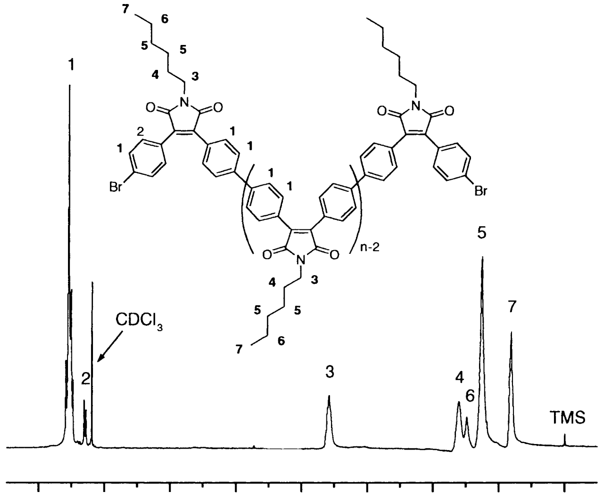
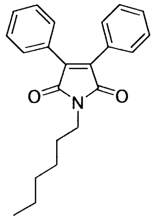


Fig. 3. ^{1}H NMR spectrum of **4**.



Scheme 2. The model compound: 3,4-bisphenyl-*N*-*n*-hexyl-pyrrole-2,5-dione (**5**).

adjacent to the nitrogen was shifted downfield to 3.56 ppm due to the electron withdrawing effect of the nitrogen. Aromatic protons in the *ortho*- and *meta*-position to the bromide were found at δ 7.28 and δ 7.44, respectively.

^{1}H NMR spectrum of the polymer **4** showed that the polymer had the well-defined structure, which also provided the applicability of the end-group analysis to estimate the molecular weight (Fig. 3). Aliphatic C–H peaks at the side chain appeared between δ 0.89 and δ 3.63 ppm. Aromatic proton peaks near 7.54 ppm came under the protons at biphenyl groups in the main chain, formed by the carbon–carbon coupling reaction, and the *ortho*-protons to the bromide at terminal phenylene groups of the polymer chain. The *meta*-protons to the bromide at terminal phenylene groups appeared at 7.31 ppm. From the analysis of the integration of the proton peaks, 2:1:3 = 0.33:3.56:1 (Fig. 3), we could estimate the degree of polymerization was ca. 6 conformed with an oligomeric weight of ca. 2100. The GPC result of **4** showed M_n and M_w of 2500 and 5100, respectively. This result matched well with that of NMR analysis.

3.2.2. Thermal properties

TGA thermogram of the polymer **4** indicated that the polymer showed very good thermal stability up to ca. 400°C under an N_2 atmosphere in spite of the low molecular weight (Fig. 4). The thermal stability of **4** was better than those of polybiphenylenevinylene derivatives reported by Yamamoto et al. (ca. 300°C) [9] and alkoxy-substituted soluble poly(*p*-phenylenevinylene)s reported by Vanderzande et al. and Shim et al. (ca. 330°C) [19,20]. The temperature at 5% weight loss of **4** was 465°C and the residue at 900°C was 37.6%. As shown in Fig. 4, the glass-transition temperature (T_g) of **4** was 152°C, which was higher than those of alkoxy-substituted soluble poly(*p*-phenylenevinylene)s reported by Chan and Yu (90 ∽ 125°C) [21].

3.2.3. Optical properties

The model compound **5** (Scheme 2), having the same structure of the repeating unit of the polymer **4**, was prepared to compare their photophysical properties with those of **4**. Both **4** and **5** showed the photoluminescence property. As shown in Fig. 5, the maximum absorption wavelength (399 nm) of **4** was red-shifted relative to that (371 nm) of **5** due to the extension of π-conjugation. The

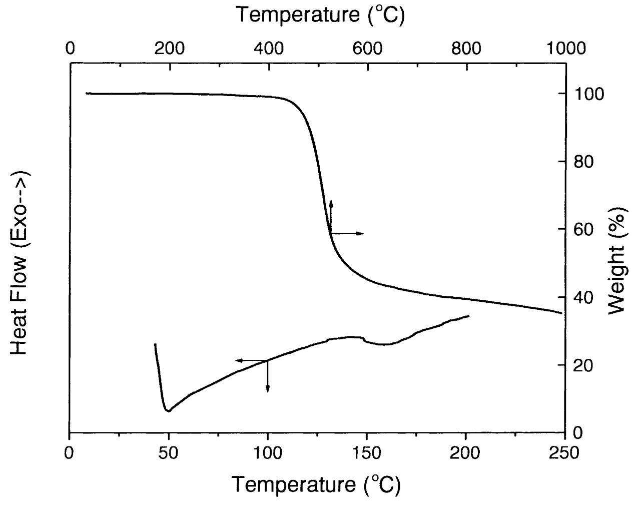


Fig. 4. TGA and DSC thermograms of **4**.

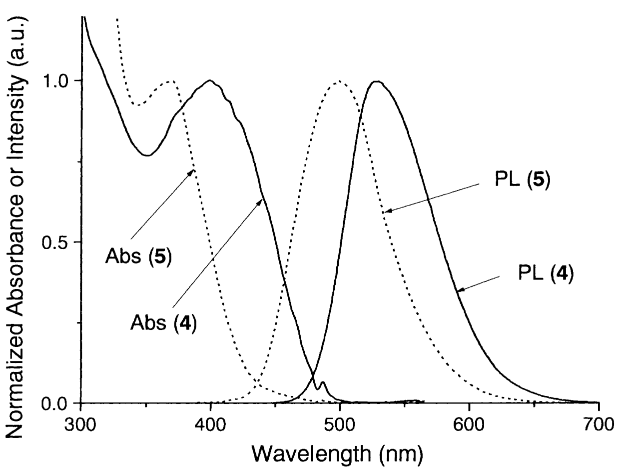


Fig. 5. Optical absorption (Abs) and photoluminescence (PL) spectra of the polymer **4** and the model compound **5** in THF solutions (ca. 1×10^{-5} M).

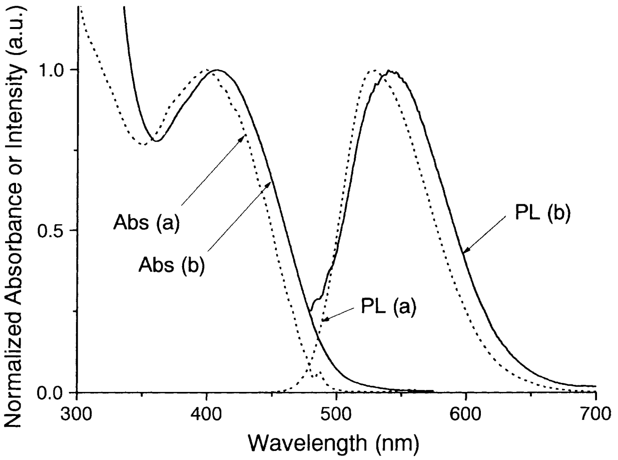


Fig. 6. Optical absorption (Abs) and photoluminescence (PL) spectra of the polymer **4**: (a) ca. 1×10^{-5} M THF solution; (b) a film onto a glass plate.

photoluminescence spectrum of **4** with the maximum intensity of 526 nm was also red-shifted by 29 nm relative to that (497 nm) of **5**, in which the Stokes shift of **4** was similar to that of **5** (ca. 126 nm) (Fig. 5). From the analysis of optical absorbance and integration of luminescence [22], the luminescence efficiency of **4** was 9% of that of **5**.

As shown in Fig. 6, a spin-cast film of **4** onto a glass plate also showed the greenish yellow photoluminescence (the maximum at 539 nm) when it was excited at the absorption maximum of 410 nm. In general, soluble polyarylenevinylene derivatives show the significantly large red-shifted emission in a solid state compared to that in a solution due to high packing density in a solid state [9,20,21]. The small deviation of the optical absorption and photoluminescence spectra between the one in a solution and that in a film (13 nm) of **4** may be due to the low packing density in solid state, contributed to by the polymer structure, such as the aliphatic side chain, the *cis*-stilbenoid structure [23] and the biphenyl twist [24].

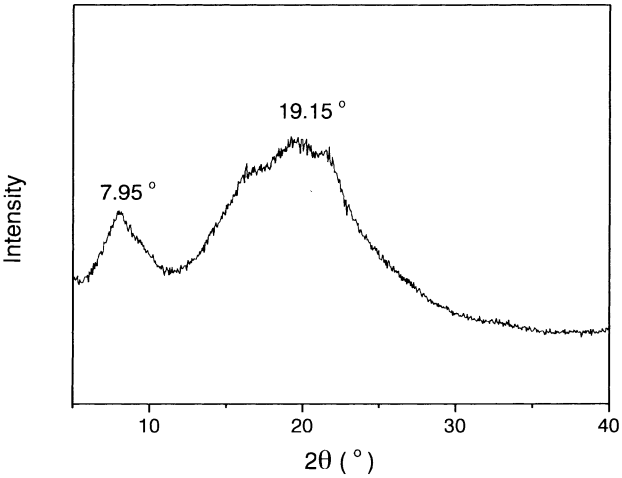


Fig. 7. Powder XRD pattern of the polymer **4**.

3.2.4. Powder XRD pattern

As shown in Fig. 7, powder XRD pattern of the polymer **4** showed broad peaks at $2\theta = 7.95$ and 19.15°. The peak at $2\theta = 7.95°$ (11.1 Å) and peaks near $2\theta = 19.15°$ (4.6 Å) may be caused by the distance between the polymer main chain and the organization of *n*-hexyl side chains, respectively. This XRD result is similar to that of dialkyl-substituted poly(biphenylenevinylene) reported by Yamamoto et al. [9]. In spite of the relatively short length and small number of the solubilizing side chain, the degree of crystallinity of **4** was determined to be fairly low in comparison with polybiphenylenevinylene derivatives reported by Yamamoto et al. [9].

4. Conclusions

1,2-Diphenylmaleimide-type monomer **3** with a fixed *cis*-stilbenoid structure was synthesized in four steps using squaric acid as a starting material and its π-conjugated polymer was prepared by a zerovalent Ni complex-mediated dehalogenation polycondensation. The resultant polymer showed high solubility in common organic solvents and spin-castability from a solution. In spite of the oligomeric molecular weight of the polymer, it showed higher thermal stability up to 400°C than other reported polyarylenevinylene derivatives. The polymer showed greenish yellow photoluminescence with the maximum at 526 and 539 nm in a THF solution (ca. 10^{-5} M, based on a repeating unit) and in a film, respectively.

Acknowledgements

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