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# New soluble unsaturated polyketone derived from diarylidenecycloalketone: synthesis and optical and electrochemical properties of π-conjugated poly(diarylidenecyclohexanone) with long side chains

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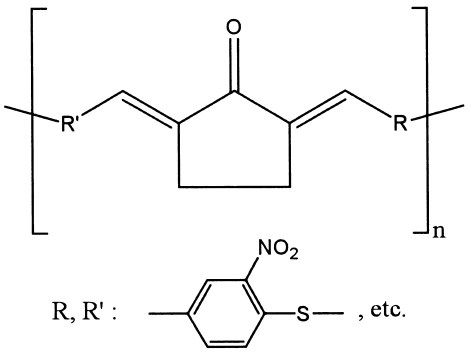
**Abstract**

A new type of unsaturated polyketone having cyclohexanone moiety in a π-conjugated main chain was prepared by polycondensation between 2,6-bis(4-bromobenzylidene)cyclohexanone and 2,5-dihexyloxy-*p*-phenylene diboric ester in the presence of $Pd(PPh_3)_4$. The polymer had good solubility in common organic solvents. Analysis by gel permeation chromatography (GPC; polystyrene standards) showed that the polymer had $M_n$ and $M_w$ values of 7800 and 18 200, respectively. The polymer exhibited a $[\eta]$ value of 0.70 dl $g^{-1}$ in benzene at 30 °C. The chloroform solution of the polymer showed an UV–Vis peak at 392 nm, and the PL spectrum gave a peak at 533 nm. DSC exhibited that the polymer had a $T_g$ of 85 °C. The DSC data, observation with a polarizing microscope, X-ray diffraction data and UV–Vis data of the obtained polymer showed a phase transition above 200 °C. TGA showed that the polymer had good thermal stability with 5 wt% loss temperature of 407 °C under $N_2$. Electrochemical oxidation (or p-doping) of the polymer started at about 0.7 V vs. $Ag/AgNO_3$ and gave a peak at 1.06 V vs. $Ag/AgNO_3$ with a color change of the film from yellow to deep red. The color change was followed by UV–Vis spectroscopy. The corresponding p-dedoping peak appeared at 0.58 V vs. $Ag/AgNO_3$.


*Keywords:* Conjugated polymer; Optical properties; Electrochemical redox reaction

## 1. Introduction

Unsaturated polyketones derived from alkylidenecycloalketones have attracted interest due to their potential applications [1–3]. Compared with conventional polyketones, e.g. poly(ether ether ketone) (PEEK), unsaturated polyketones exhibit unique optical properties and semiconductivity [1–4]. Therefore, in the past 15 years, a series of the polymers, containing the cycloalketone moiety and oxygen or sulfur in the molecular backbone, were prepared and their properties were investigated [1–9].




It was expected that the polymers could be used as a class of new materials in optical and electronic fields [1–3]. Formally, the polymer has neighboring two single bonds along the polymer main chain and the π-conjugation may be cleaved at the alkylidenecycloalketone unit. However, all the carbon atoms at the alkylidenecycloalketone unit have

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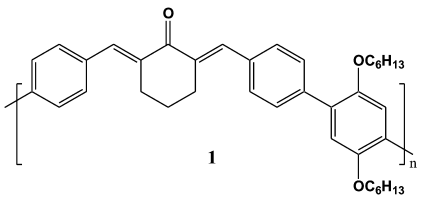


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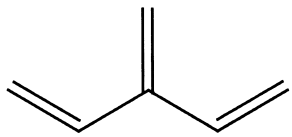
$C_6H_{13}$ = *n*-hexyl

Scheme 1. The structure of the new polymer.

the π-electron and it is known that HOMO and LUMO orbitals of 3-methylene-1,4-pentadiene are expanded over whole of the carbon system [10]. Therefore, formation of an effectively π-conjugated system along the main chain is expected if the R and R′ groups have the π-conjugated system. However, preparation of π-conjugated polymers having the above shown structure has not been reported.



On the other hand, only a few of above shown polymers were soluble in organic solvents [6]; most of them were only soluble in strong acids such as $H_2SO_4$ and $CF_3COOH$ [1–5,7,8]. Consequently, the processibility of polymers was poor, and it limited their usage.

In the field of π-conjugated polymers, it has been established that introducing suitable side-chains to the backbone of the π-conjugated polymers can increase solubility of the polymers [11–13]. These situations promoted us to carry out preparation of the following new π-conjugated polyketone shown in Scheme 1 via polycondensation between 2,6-bis(4-bromobenzylidene)cyclohexanone and *p*-phenylenediboric ester with long side-chains. The polymer showed good solubility and photoluminescence and was electrochemically active. Compared with π-conjugated poly(*p*-phenylenevinylene) (PPV), the π-conjugated polyketone is tunable in chemical structure due to its having functional carbonyl group; transformation of the carbonyl group to various groups (e.g. by Wittig reaction) to construct new π-conjugated polymers will be possible. We here report the synthesis, characterization and optical and electrochemical properties of the polymer.

## 2. Experimental

### 2.1. Materials

The starting chemicals were purchased from Kanto Chemical Co. and used as received unless otherwise stated. $[Bu_4N]BF_4$ (Bu = butyl) was purified by recrystallizing 3 times from ethyl acetate and dried over $P_2O_5$ under vacuum at room temperature for 5 days.

### 2.2. Measurements

FTIR spectra were recorded on a JASCO FT/IR 410 spectrophotometer using KBr pellets. $^1$H NMR spectra were taken with a JEOL P-300 spectrometer (300 MHz). The molecular weight was measured by GPC with a Shimadzu LC-9A liquid chromatograph equipped with a UV detector using chloroform as eluent. The data were relative to polystyrene standards. UV–Vis absorption spectra were measured with a Shimadzu UV-3100 PC spectrophotometer. Photoluminescence and excitation spectra were recorded on a Hitachi Model F4010 spectrophotometer. X-ray diffraction (XRD) patterns were obtained with a Rigaku RINT 2000 Ultima + /PC X-ray diffractometer. The cyclic voltammograms (CV) for the cast films were measured in a 0.10 M $[Bu_4N]BF_4$ acetonitrile solution using Ag/(0.10 M $AgNO_3$) and platinum wire as reference and counter electrodes, respectively. Thermal behavior of the polymer was determined with Shimadzu DSC-50 and TGA-50 analyzers. Polarizing optical microscopy was carried out with an Olympus Polarizing microscope.

### 2.3. Synthesis of monomers

#### 2.3.1. Precursor of monomer **2**

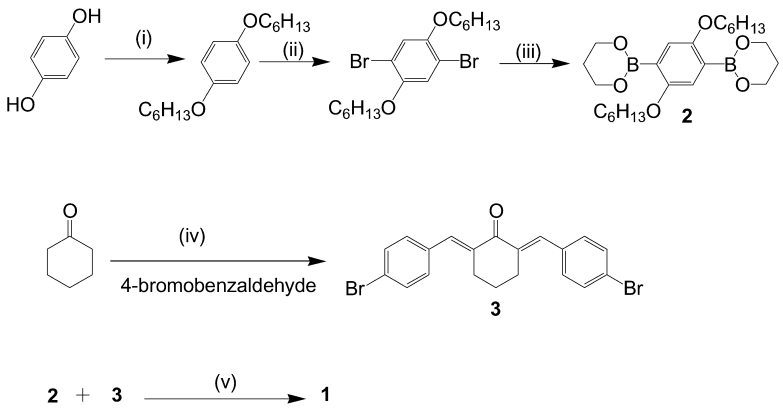
The precursor of monomer **2**, 1,4-dibromo-2,5-bis(hexyloxy)benzene, was prepared by modifying the literature method [14–19].

A $CHCl_3$ (20 ml) solution of $Br_2$ (8 ml, 160 mmol) was added dropwise with stirring to a solution of 1,4-dihexyloxybenzene (14.0 g, 50 mmol, prepared by the reaction between 1,4-hydroquinone and 1-bromohexane in DMF/toluene in the presence of KOH and $K_2CO_3$) in $CHCl_3$ (200 ml) at 0–5 °C. The mixture was stirred for 2 h at room temperature. The resulting deep red solution was washed with 10% $Na_2S_2O_3$, 10% NaOH and water. The organic layer was dried over anhydrous $Na_2SO_4$. After removing the solvent and recrystallizing from methanol, 1,4-dibromo-2,5-bis(hexyloxy)benzene was obtained as crystalline needles. 21 g, 96% yield. $^1$H NMR ($CDCl_3$): δ 7.08 (s, 2H), 3.70 (t, 4H $-OCH_2-$), 1.31–1.84 (m, 16H, alkyl), 0.89 (t, 6H, $-CH_3$). Anal. calcd for $C_{18}H_{28}Br_2O_2$, C 49.56; H 6.47; Br 36.63%. Found 49.79; H 6.66; Br 36.34%.

#### 2.3.2. Bis(propane-1,3-diyl)-1,4-dihexyloxyphenylene-2,5-diborate **2**

This compound was synthesized by modifying a reported procedure [20].

To a stirring solution of 1,4-dibromo-2,5-bis(hexyloxy)-benzene (10.91 g, 25 mmol) in a mixture of diethyl ether (150 ml) and THF (240 ml) was added dropwise a solution of butyllithium in hexane (1.57 M, 64.1 ml, 100 mmol) over 1 h under $N_2$ at −78 °C. The solution was warmed to −5 °C and recooled to −78 °C, followed by dropwise addition of trimethyl borate (26 ml, 250 mmol) during a period of 1 h. After addition, the mixture was warmed to




Scheme 2. The procedure for preparation of the new polymer. Regents and conditions: i) A mixture of KOH and anhydrous $K_2CO_3$ (1:3, molar ratio) in DMF/toluene, reflux for 24 h. ii) $Br_2$ in $CHCl_3$. iii) a) BuLi in hexane (1.6 M), THF/$Et_2O$ at -78 °C for 1.0 h; b) $B(OMe)_3$, stirred for 48h at room temperature (r.t); c) 1,3-propanediol, toluene, reflux for 10 h. iv) EtOH, concentrated HCl, reflux for 2 h. v) aq. $K_2CO_3$, $Pd(PPh_3)_4$, THF/toluene, reflux for 72 h.

room temperature, stirred for 2 days, poured into 1000 ml of 2 M HCl, and stirred for 24 h at room temperature. The white precipitate obtained by filtration was redissolved in acetone, filtered and repoured into deionized water. Filtration and drying under vacuum gave 2,5-dihexyloxy-*p*-phenylenediboric acid, as a white crystalline solid, 6.4 g, 17.5 mmol, 70% yield.

2,5-Dihexyloxy-*p*-phenylenediboric acid thus prepared and 1,3-propanediol (7.6 g, 100 mmol) were mixed in 100 ml of dry toluene, and the mixture was allowed to react under reflux for 10 h. The solvent was removed by evaporation and the residue was dissolved in chloroform. The solution was dried over anhydrous sodium sulfate. A solid was collected after removal of the solvent under vacuum and recrystallized from hexane to obtain **2** (4.4 g, 40% yield) as white crystalline needles. IR ($cm^{-1}$): 2935, 1494. $^1H$ NMR ($CDCl_3$): $\delta$ 7.13 (s, 2H), 4.15 (t, 8H, α-$CH_2$ in boric ester), 3.79 (t, 4H, $-OCH_2-$ attached to the aromatic ring), 2.05 (m, 4H, $-CH_2-CH_2O-$ in boric ester), 1.31–1.90 (m, 16H, $CH_2$ in the alkyl), 0.92 (t, 6H, $-CH_3$). Anal. calcd for $C_{24}H_{40}B_2O_6$, C 64.57; H 8.96%. Found C 64.63; H 9.20%.

### 2.3.3. 2,6-Bis(4-bromobenzylidene)cyclohexanone *3*

This compound was prepared by modifying the literature method [21].

To a solution of cyclohexanone (2.4 g, 24.5 mmol) and 4-bromobenzaldehyde (10.0 g, 54 mmol) in 100 ml of ethanol was added concentrated hydrochloride acid (37%, 20 ml). This mixture was allowed to react under reflux for 2 h. The resulting yellow crystalline solid was separated by filtration and washed with water and methanol, respectively. After recrystallization from a mixed solvent of chloroform and methanol, **3** was obtained in 75% yield as yellow needles. IR ($cm^{-1}$): 2925, 1665, 1606. $^1H$ NMR ($CDCl_3$): $\delta$ 7.60 (s, 2H, vinylic H), 7.31–7.56 (m, 8H), 2.88 (t, 4H) 1.82 (m, 2H, H at 4-position of cyclohexanone). Anal. calcd for $C_{20}H_{16}Br_2O$, C 55.59; H 3.73; Br 36.98%. Found C 55.32; H 3.73; Br 36.68%.

### 2.3.4. Synthesis of the polymer *1*

The polymer was synthesized in an analogous way given in the literature [16].

To a 200 ml Schlenk tube, **2** (892 mg, 2.0 mmol), **3** (864 mg, 2.0 mmol), $Pd(PPh_3)_4$ (69 mg, 0.06 mmol) and a degassed mixed solvent of 20 ml toluene and 75 ml THF were charged. The mixture was stirred for 20 min at room temperature under $N_2$. Then, 10 ml of a degassed 2 M $K_2CO_3$ aqueous solution (20 mmol) was added to the tube and the reaction mixture was heated to reflux. After maintaining this temperature for 72 h under intensive stirring, the mixture was cooled to room temperature and poured into excess methanol. The precipitate was filtered off and washed with water. The obtained cake was dissolved in chloroform and the polymer solution was concentrated to about 20 ml and poured into 200 ml of methanol to give a polymer precipitate. After filtration and drying under vacuum, polymer **1** was obtained as a yellow powder (820 mg, 75% yield). IR ($cm^{-1}$): 2925, 1666, 1600. $^1H$ NMR ($CDCl_3$): $\delta$ 7.88 (s, 2H, vinylic H), 7.55–7.67 (m, 8H, aromatic ring linked with the cyclohexanone unit), 7.03 (s, 2H, aromatic ring with side-chains), 3.96 (t, 4H, $-OCH_2-$), 3.04 (t, 4H), 1.28–1.86 (m, 18H, 6-H in the cyclohexanone unit and $CH_2$ in the side-chain), 0.86 (t, 6H). Anal. calcd for $Br-(C_{38}H_{44}O_3{\cdot}0.3H_2O)_{14}B(OH)_2$, C 81.14; H 7.96 Br 1.02; $B_2O_3$ 0.95%. Found C 81.11; H 7.97; Br 0.95; ash ($B_2O_3$) 1.40%. $M_n$ = 7800 (GPC, $CHCl_3$), $M_w$ = 18 200.

## 3. Results and discussion

### 3.1. Synthesis and characterization of the polymer

The synthetic procedure of the monomers, bisboric ester **2** and bis(4-bromobenzylidene)cyclohexanone **3**, and that of new polymer **1** are described in Scheme 2. The precursor of **2** was prepared via a somewhat different route from the reported route [15–20] and the new method gave the precursor in a higher yield (70%) than the previously reported methods (40–60%). In standard Aldol reaction

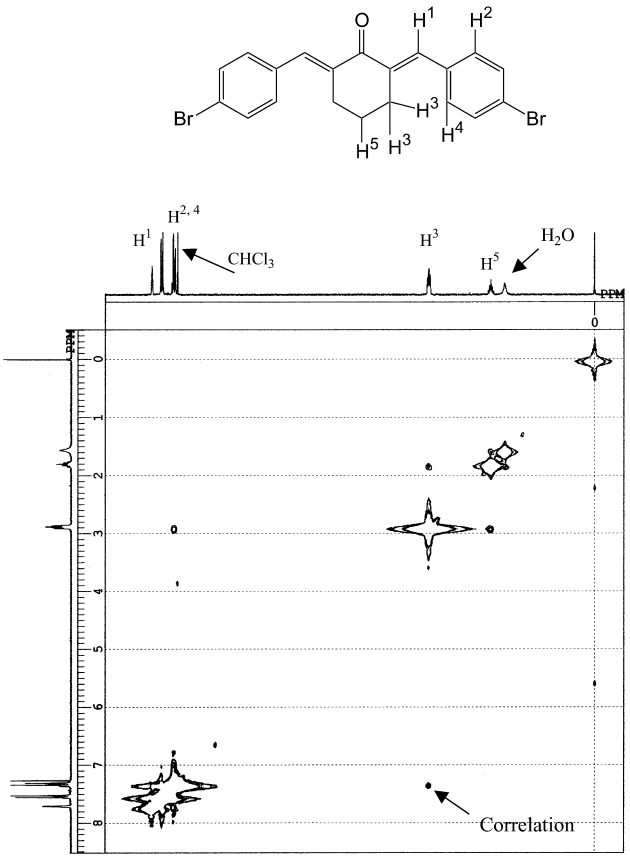



Fig. 1. The NOESY spectrum of monomer **3**.

[21], the analogues of monomer **3** were synthesized by the reaction of ketones and aldehydes in the presence of inorganic bases. Modification of the standard procedure gave **3** in a higher yield (cf. the Section 2).

Organometallic polycondensation are widely used for preparation of π-conjugated polymers [12,13]. Under standard Suzuki conditions [22,23], polymer **1** was prepared using an equimolar mixture of monomers **2** and **3**. Using general purifying procedure, the polymer was obtained in 75% yield as a yellowish powder, which was soluble in common organic solvents such as chloroform, benzene and cyclohexane; however, it was insoluble in DMF and DMSO.

Analysis by GPC (polystyrene standards) showed that the polymer had $M_n$ and $M_w$ values of 7800 and 18 200, respectively. According to number average molecular weight ($M_n$), the number of the repeating unit of the polymer was estimated at about 14, which agreed with the results of elemental analysis (cf. Section 2).

The polymer showed a $[\eta]$ value of 0.70 dl $g^{-1}$ in benzene at 30 °C. As our best knowledge, this $[\eta]$ value is higher than those of the most of the reported unsaturated polyketones [1–9], suggesting the advantages of organometallic polycondensation.

The chemical structure of the monomers and the polymer were characterized by FTIR and $^1$H NMR spectroscopy and elemental analysis. In some cases, the Aldol reaction gives a *trans*-geometric structure for the products [21]. To reveal the geometric structure of **3**, the NOESY $^1$H NMR spectrum of **3** was taken and it is given in Fig. 1. It is seen that there is a correlation between $H^3$ and one of aromatic-H (presumably $H^4$ in Fig. 1), supporting a view that **3** has a *trans*-configuration, concerned with the carbonyl group and the *p*-phenylene group. Molecular model indicated that taking a *cis*-configuration caused steric repulsion. $H^4$ in **3** can penetrate between two $H^3$ hydrogens. The $^1$H NMR spectrum is simple and no sign for contamination with the *cis* isomer was observed. Fig. 2 gives the IR spectra of polymer **1** and the corresponding monomers **2** and **3**. For the polymer, a characteristic $\nu$ (C=O) peak appeared at 1666 $cm^{-1}$. The peak at 966 $cm^{-1}$ is characteristic of the *trans*-vinylene group. According to the IR data, the carbonyl group is considered to be not reduced during the

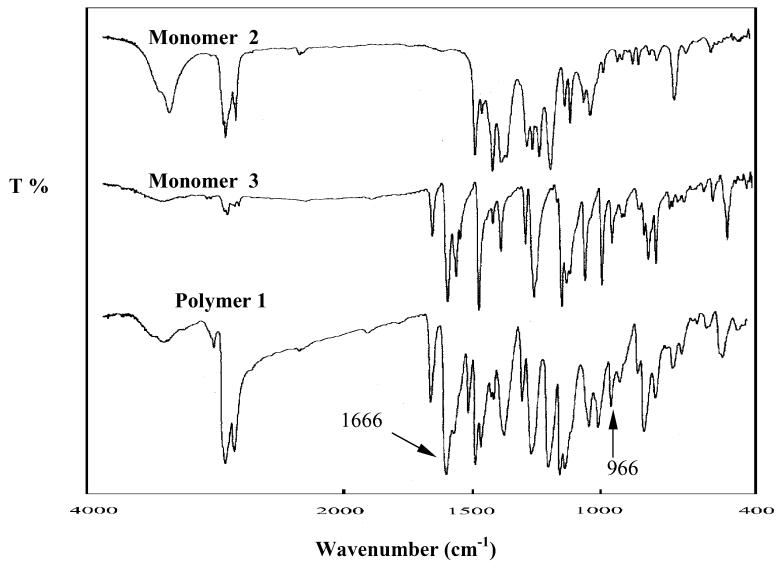



Fig. 2. FTIR spectra of polymer **1** and monomers **2** and **3**.

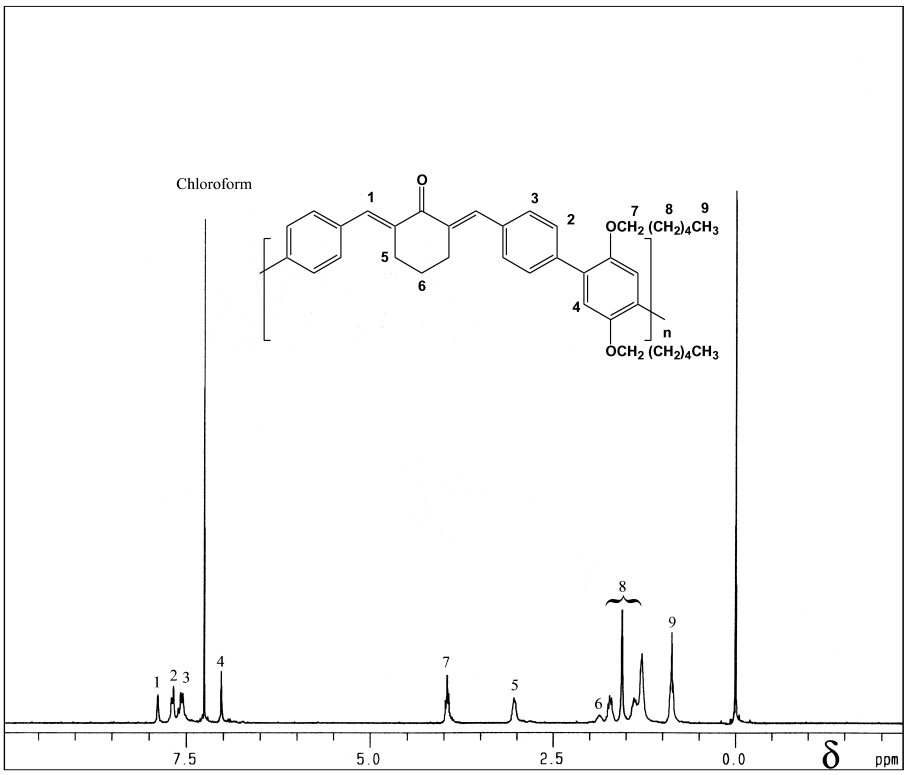



Fig. 3. $^1$H NMR spectrum of polymer **1**.

polymerization. Moreover, the geometric configuration of the double bond is considered to be maintained. $^1$H NMR spectrum of the polymer is shown in Fig. 3. All of the detected peaks were consistent with the proposed structure. Comparing with the peaks of the monomers, those of the polymer are broadened and shift to a lower magnetic field. For example, aromatic-H of **3** at $\delta$ 7.31–7.56 are shifted to 7.55–7.67. This lower magnetic field shift displays the environmental changes of the protons in the π-conjugated system.

### 3.2. Optical properties

A chloroform solution of **1** was light yellow and fluoresced green under the irradiation with UV light (336 nm). Figs. 4 and 5 show the UV–Vis and photoluminescent (PL) spectra of **1**, respectively. The polymer shows $\lambda_{max}$ at a longer wavelength (392 nm, log $\varepsilon$ = 4.36; molarity is based on the repeating unit) than those of the corresponding monomers (**2**: $\lambda_{max}$ = 321 nm and **3**: $\lambda_{max}$ = 338 nm), indicating that the polymer has an expanded π-conjugated system. The peak position is located at a longer wavelength than those of *p*-terphenyl ($\lambda_{max}$ = 276 nm) and *p*-quaterphenyl ($\lambda_{max}$ = 294 nm), indicating that the π-conjugation is expanded through the quinone unit. As described above, HOMO and LUMO of 3-methylene-1,4-pentadiene are expanded over whole of the carbon system, and participation of the carbonyl group to form a π-conjugated system due to the resonance between the conjugated C=C double bond and C=O in cyclohexanone moiety has been proposed [24]. The $\lambda_{max}$ position of **1** is comparable to those of π-conjugated poly(2,5-dialkyoxy-*p*-phenylene)s ($\lambda_{max}$ = ca. 340 nm) [25] and poly(*p*-phenylenevinylene) with alkoxy substituents ($\lambda_{max}$ = ca. 410 nm) [26]. The steric repulsion occurred in poly(2,5-dialkyoxy-*p*-phenylene)s seems to be released in **1** due to insertion of the =CH– group.

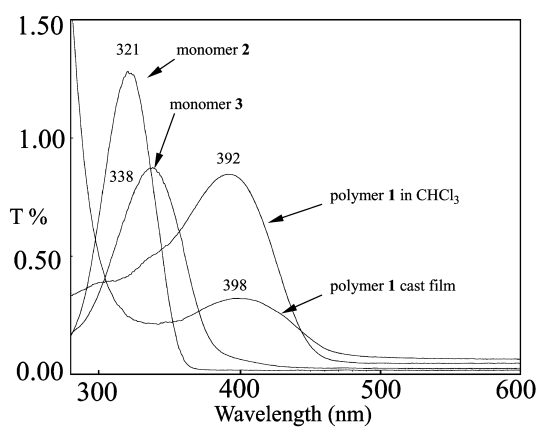



Fig. 4. UV–Vis spectra of the monomers and polymer **1**.

Film of the polymer showed the UV–Vis peak at a somewhat longer wavelength (398 nm), suggesting the presence of certain intermolecular electronic interaction. However, the degree of the red shift is considerably smaller than those observed with polymers that take face-to-face stacking [27–29]. The PL spectrum of the chloroform

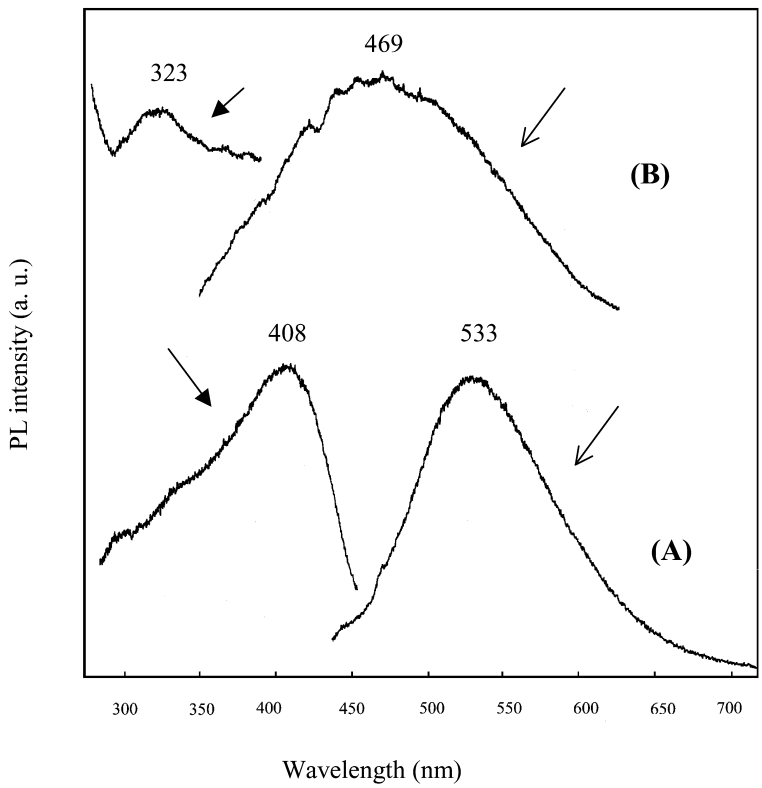



Fig. 5. Excision (–►) and emission ( → ) spectra of polymer **1** (A) in $CHCl_3$ and (B) in solid state.

solution shows a peak at 533 nm. Usually the PL peak appears near the onset position of the UV–Vis absorption band of aromatic compounds and polymers. However, for the $CHCl_3$ solution of **1**, the PL peak appears at a considerably longer wavelength compared with the onset position (about 470 nm; cf. Fig. 4), suggesting formation of an excimer-like adduct between photoexcited **1** and **1** in the ground state. The photoluminescence peak in film is shifted by 64 nm to a shorter wavelength and appears near the onset position of the UV–Vis absorption band, which implies that formation of the excimer-like adduct is prevented due to loss of mobility of the polymer molecule in the solid.

### *3.3. The structure of the polymer in the solid state*

XRD patterns of powder and cast film of **1** are shown in Fig. 6. As shown in Fig. 6(A), **1** has certain crystallinity. π-Conjugated polymers with long side-chains often give an XRD peak in a low angle region below $2\theta = 10°$ (Cu Kα), and the $d$ spacing calculated form the peak often corresponds to the distance between the π-conjugated main chains separated by the long side-chains [12,13, 27–31]. When flat plane of the π-conjugated polymer forms a face-to-face stacked assembly, it usually gives another XRD peak corresponding to an interplane distance at about $d = 3.8$ Å [12,13,27–31]. All-aromatic polyesters with long side-chains also form similar layered structure [32]. For better understanding of the structure of **1** in the solid state, a HGS molecular model was constructed and the

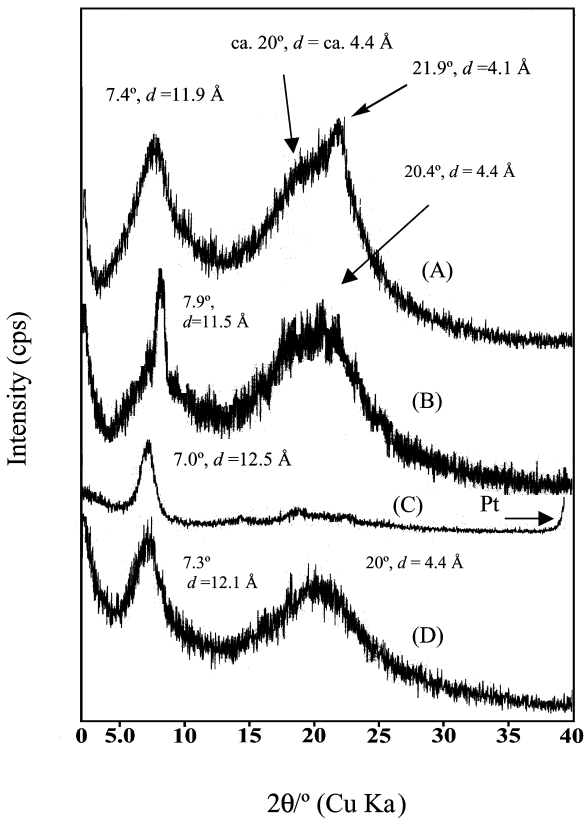



Fig. 6. XRD pattern of polymer **1** in the powder state and in the film. (A): powder; (B): the powder was heated at 220 °C for 1 h and then cooled to room temperature (C): film on a platinum plate; (D): crushed film after peeled from the platinum plate. The XRD pattern was taken at a reflection mode.

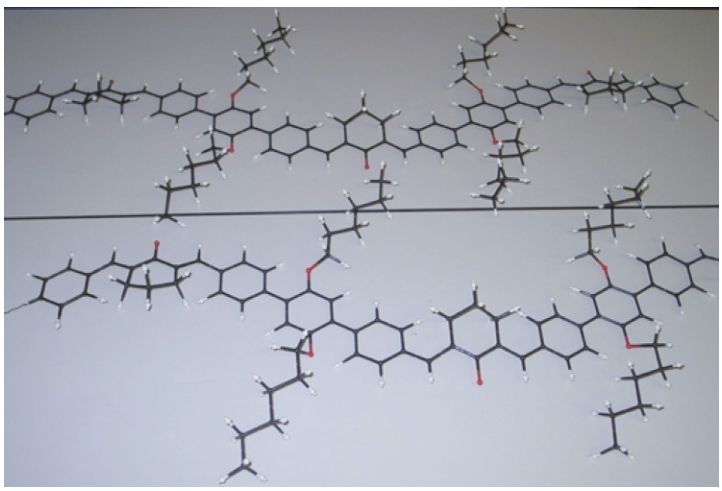


Fig. 7. The molecular model image of polymer **1** (partly).

image is depicted in Fig. 7. As a whole, the polymer chain is considered to assume a ⁀╲_╱⁀╲_ type liner structure. The cyclohexanone unit contains the non-planar 4-$CH_2$ unit. However, as a whole, **1** is considered as a flat-like molecule. According to Fig. 7, the schematic packing structure of **1** is shown in Fig. 8. Thus, the two XRD peaks in Fig. 6 at $2\theta = 7.4°$ ($d_1 = 11.9$ Å) and $2\theta = 21.9°$ ($d_2 = 4.1$ Å) may be assigned to distance $d_1$ and the interlayer distance $d_2$, respectively, shown in Fig. 8. A broad shoulder peak at about 20° ($d =$ ca. 4.4 Å) is usually assigned to a side-to-side distance between the alkyl chains which has a packing dimension of about 4.5 Å [33].

In order to investigate further the structure of the polymer in the solid state, the density of the polymer was calculated using the XRD data and a Chem 3D software (Cambridge Company). According to the Chem 3D model, the length of a repeating unit of the polymer was estimated at 16.2 Å as depicted in Fig. 8.

These data give a calculated density of $\{(548/(6.02 \times 10^{23})\}/(16.2 \times 11.9 \times 4.1 \times 10^{-24}) = 1.15$ g $cm^{-3}$ for **1**. This value is consistent with an observed density of 1.18 g $cm^{-3}$. Thermal treatment of the polymer powder seems to cause certain phase transition at 220 °C. After thermal treatment at 220 °C, **1** gives rise to an XRD pattern exhibited in Fig. 6(B). The peak at $2\theta = 7.4°$ ($d = 11.9$ Å, Fig. 6(A)) is changed to a sharper peak at 7.9° ($d = 11.5$ Å, Fig. 6(B)) and the peak at $2\theta = 21.9°$ in Fig. 6(A) becomes obscure, suggesting occurrence of a

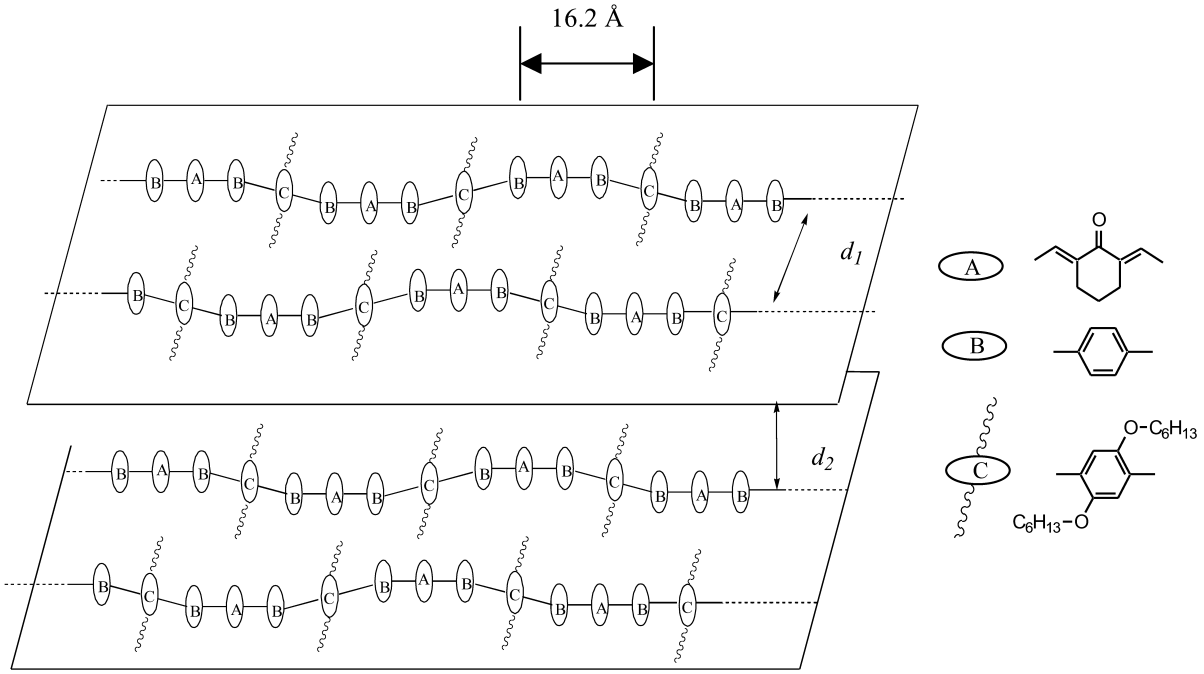



Fig. 8. The postulated solid structure of **1**.

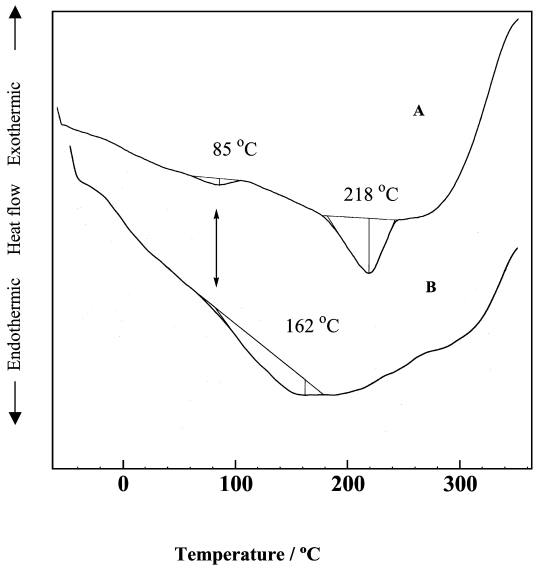



Fig. 9. DSC curve of **1** at a heating rate of 5 °C $min^{-1}$ (A, first scanning; B, second scanning).

crystallographic change by the thermal treatment. Compound **1** is considered to form a quasi-stable packing structure during reprecipitation (cf. Section 2) and assume a stable packing structure after the thermal treatment. Due to the crystallographic change, density of **1** somewhat increased to 1.24 g $cm^{-3}$. Changes of crystallographic data by thermal treatment were also found in phenylene–ethynylene oligomers, which behave liquid crystals, by J. Le Moigne group [34].

On the other hand, for a cast film of **1** on a Pt plate, no evident peak in the range of 25–40° was observed as depicted in Fig. 6(C). However, when the film was crushed after peeling from the Pt plate, it gave an XRD pattern similar to that of the powder of **1** as depicted in Fig. 6(D). Similar phenomena have been reported for regioregular head-to-tail poly(3-hexylthiophene) and another π-conjugated polymer [31,35], and they are considered to indicate a parallel alignment of the π-conjugated polymer with the alkyl chain oriented to the surface of the substrate. The driving force of such alignment has not been revealed, and details of the alignment will be investigated in our further work.

### 3.4. Thermal properties of *1*

DSC traces of **1** are shown in Fig. 9. The curve A represents the DSC trace in the first scanning from − 100 to 350 °C. The peaks appeared at 85 and 218 °C are assigned to a glass transition temperature ($T_g$) and a phase transition temperature of **1**, respectively.

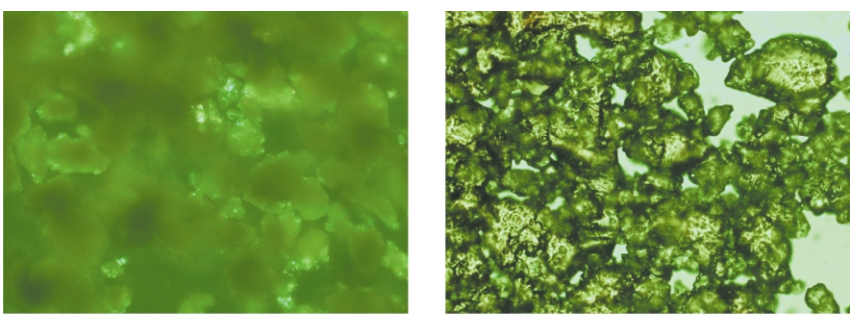
In order to reveal the thermal phase transition, investigation using polarizing microscope (POM) has been carried out for a range of 80–230 °C. Fig. 10 shows POM images of the polymer solid at 80 and 220 °C, respectively; they were taken under cross Nichols conditions. At 80 °C, no bright area was observed. After raising the temperature, the POM image became somewhat bright. When the temperature was raised to 220 °C, bright areas are clearly observed, indicating that the polymer molecules can move above 220 °C to form a new solid phase where the polymer molecules form an aligned structure with a higher order of alignment.

After heating higher than 220 °C, **1** forms the more stable phase as discussed in the Section 3.3, and the DSC curve B becomes different from the DSC curve A. Similar irreversibility of DSC curve was also found in some polymers containing acetylenic units [36]. After forming the more stable solid, the polymer was still soluble in chloroform, however, it became only partly soluble in benzene. After thermal treatment, IR spectrum of **1** showed no obvious changes. However, UV–Vis spectrum of **1** exhibited a blue shift of ca. 20 nm as shown in Fig. 11.

Compound **1** showed 5 wt% loss temperature at 406 °C in TGA.

### 3.5. Electrochemical redox properties

Fig. 12 gives CV of cast film of **1** on a platinum plate. It is seen that electrochemical oxidation (or p-doping) starts at about 0.7 V vs. $Ag/AgNO_3$ and gives p-doping peak at 1.06 V vs. $Ag/AgNO_3$. The corresponding p-dedoping peak appears at 0.58 V vs. $Ag/AgNO_3$. The color of the film changed from yellow to deep red on oxidation. The film revealed stable upon repeat scanning of CV, giving same CV curves. Sweeping to higher



80 °C 220 °C

Fig. 10. The polarizing microscope images of 1 at 80 and 220 °C measured under crossed polarizers.

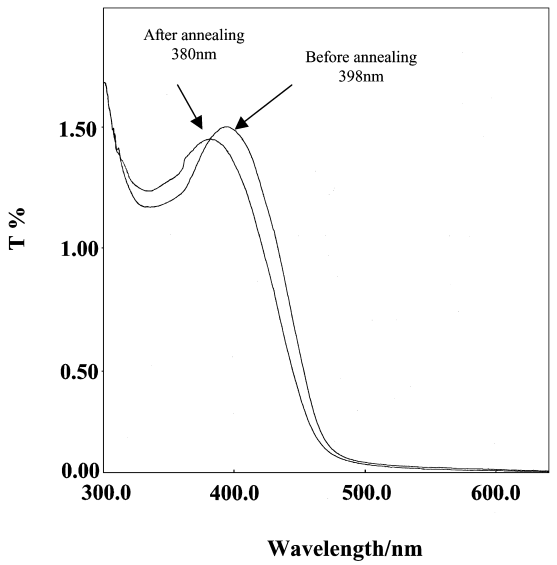



Fig. 11. The change of the film of **1** after annealing.

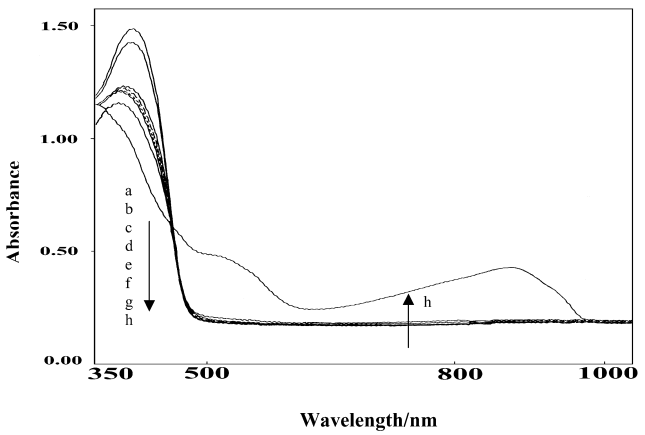



Fig. 13. Changes in the UV–Vis spectrum of a film of **1** on an ITO glass electrode at various applied potentials vs. $Ag/AgNO_3$. The curve a shows the UV–Vis spectrum of the cast film of **1**. Applied potential ($V$) : 0.0 → b (−1.94) → c (−2.3) → d (−1.8) → e (−1.5) → f (0.0) → g (0.9) → h (1.5). In a $CH_3CN$ solution of $[Bu_4N][BF_4]$ (0.10 M).

potential 1.5–2.0 V vs. $Ag/AgNO_3$ gave no peak, revealing high stability of the polymer in this oxidative region. Compound **1** gives a reducing (or n-doping) in −1.92 V, however, no color change is observed and its corresponding n-dedoping peak is not observable near the n-doping potential.

Optoelectrochemical data of the cast film of **1** on an ITO glass plate in a 0.10 M $[Bu_4N]BF_4$ acetonitrile solution are shown in Fig. 13. At an applied potential of −1.94 V, the UV–Vis spectrum does not show a large change (Fig. 13, chart b). On application of a higher negative potential of −2.3 V, the absorption band is somewhat changed with a shift of UV–Vis peak from 398 to 386 nm (Fig. 13, chart c). Charts d–g represent the absorption spectra of the polymer film at applied potentials of −1.8, −1.5, 0, and 0.9 V, respectively. Compared with chart a, the intensity of the absorbance at about 400 nm is gradually decreased for the charts d–g. When the applied potential becomes 1.5 V (chart h), the absorption peak at 386 nm almost disappears and two new absorption bands appears at about 550 and 870 nm. The yellow color of the film turned to red as show in Fig. 12. Many papers reported that oxidized state of π-conjugated polymer gave new absorption peak(s) in the wavelength range of 500–1500 nm [12,13].

## 4. Conclusion

A new unsaturated conjugated polyketone was for the first time prepared. It was soluble in common organic solvents. The polymer was photoluminescent and electrochemically active. The polymer is considered to form an order structure, similar to previously reported π-conjugated polymers.

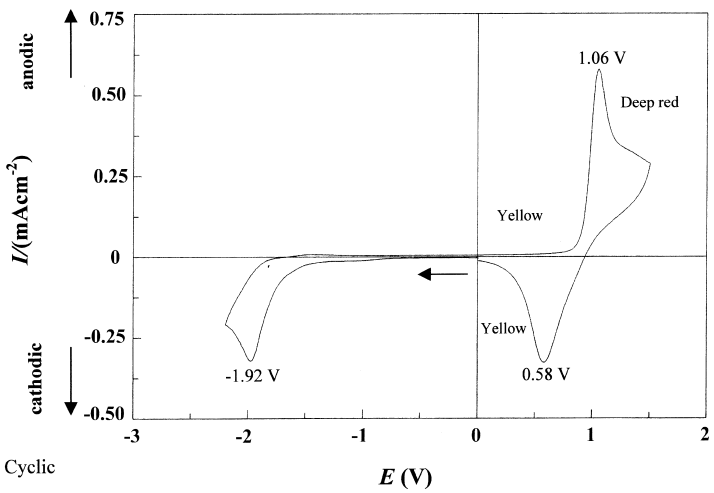



Fig. 12. CV chart for **1** cast on a Pt plate. In a $CH_3CN$ solution of $[Bu_4N][BF_4]$ (0.10 M) at 50 mV $s^{-1}$.

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