

A novel π -conjugated polymer : poly(3,4-bis(phenylene)-3-cyclobutene-1,2-dione)

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ABSTRACT: We have investigated a new 1,2-type aromatic dibromide monomer for preparing a modified π -conjugated poly(*p*-phenylenevinylene). A novel π -conjugated poly(*p*-phenylenevinylene) was prepared by dehalogenation polycondensation of a dibromoaromatic compound with a squaric unit as a monomer with zerovalent nickel [Ni(0)] complex. The monomer and the polymer were characterized by FT-IR, ¹H-NMR, Elemental Analysis, TGA, DSC, GPC and UV-Visible. The resultant polymer had good solubility to polar aprotic, solvents, e.g. DMF, DMAc, DMSO and NMP and solvatochromism in DMAc.

INTRODUCTION

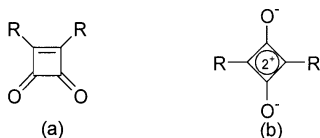
Conjugated polymers such as polyacetylene, polypyrrole, polythiophene, polyphenylene, poly(phenylenevinylene), and polyaniline have been extensively studied because of their interesting electric characteristics such as electrical conductivity, optical properties, optical nonlinearity, photoconductivity, etc.¹⁻⁵ However, in general, the conjugated backbone leads to a rigid chain of the polymeric structure and thus makes the π -conjugated polymers be intractable. These characteristics of the π -conjugated polymer backbone result in the limitation of practical applications. Therefore extensive research efforts have been devoted to improve the processability and solubility of π -conjugated conductive polymers.⁶ To improve the solubility problem, it is effective to introduce the flexible side chains on the aromatic nuclei such as polythiophene, polyphenylene, polypyrrole, poly(*p*-phenylenevinylene), and so forth.⁷⁻⁹ Most of the reported polymers have increased the solubility by introducing long alkyl chains. Without introducing the flexible side chain to the highly conjugated polymers, we propose a novel and solution π -conjugated polymer containing cyclobutenedione.

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Squaric acid (1,2-dihydroxy-cyclobutene-3,4-dione), which has a simple aromatic structure, was synthesized by Cohen *et al.*¹⁰ and West¹¹⁻¹³ suggested that the dianion of squaric acid should be regarded as a novel aromatic compound and explained the aromatic character and the equivalence of the four oxygen atoms in the squaric acid molecule on the basis of resonance. As a consequence, the four-membered ring system of squaric acid has become of interest as a constituent segment in macromolecular compounds such as poly(squaryl amides), polysquaraines, and poly(arylene ether).^{14,15} The resulting polymer shows two types of structure; 1,2-type compounds from reaction of the squaryl esters and 1,3-type compounds from condensation of squaric acid with difunctional amines¹⁶ (Scheme 1).

However, Neuse and Green¹⁷ suggested that the aniline react with squaryl esters to give not exclusively the 1,2-type compound but rather an isomeric mixture of both the 1,2- and 1,3-type derivatives. In the respect of electronic state, the 1,2- and 1,3-type derivatives were highly delocalized electronic systems with a negative charge localized on oxygen and the greater extent of electronic delocalization in 1,3-type polymer should entail the higher stabilization energy in this 1,3-interlinked polymer relative to the 1,2-interlinked polymer.¹⁴ As a result, 1,3-type compounds have been widely employed in the synthesis of derivated squaric acid. Recently, Havinga *et al.*¹⁸ synthesized the 1,3-type selectroactive conducting polymer with squaric acid. However, this polymer exhibited low conductivity. It implies that the factors that counteract the decrease in conductivity are steric hindrance, preventing a completely planar configuration, and the limited conjugation by both the donor (dopant) and ring of squaric acid. Both factors tend to decrease the width of the conduction and valence bands.

In this article, we report the investigation of a novel 1,2-type aromatic dihalide monomer and the formation of a 1,2-type π -conjugated polymer by using Ni-catalyzed dehalogenation polycondensation of the new monomer, expecting the solution in problems of the broken conjugation concerned by a 1,3-type polymer and the enhanced oxidation stability by electron-withdrawing group of diketone in squaric acid.



Scheme 1 Structure of 1,2-type (a) and 1,3-type (b) compounds

EXPERIMENTAL PART

All chemicals were purchased from Aldrich, Junsei and Merck chemical company. $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ was dried at 60 °C under vacuum. Triphenylphosphine (PPh_3) was purified by recrystallization from hexane. Powdered zinc was purified by stirring with acetic acid, filtering, washing thoroughly with ethyl ether, and drying at 60 °C under vacuum. All the solvents such as DMAc, DMF were dried over powdered calcium hydride overnight, then distilled under reduced pressure, and stored over 4 Å molecular sieves.

Synthesis of monomer¹³ (3,4-bis(4-bromophenylene)-3-cyclobutene-1,2-dione)

To a one-neck 100ml round bottom flask, equipped with a reflux condenser and stirring arrangement, were added squaric acid (3.04g, 26.6mmol), thionyl chloride (6.42g, 54.0mmol) and DMF as a catalyst. The reaction mixture was heated at 65 °C for 2hr. To the resultant solution,

bromobenzene (20ml) and freshly sublimed aluminum chloride (8.50g, 63.8mmol, 2.4 equivalents) were added and the mixture was stirred (with a calcium chloride tube) for 30hr at room temperature. The mixture was poured on to water (20ml) and extracted with ethyl ether. The ether layer was dried MgSO_4 , and the ether was evaporated. The crude residue was crystallized from ethanol, collected by filtration and dried. The yield was 4.84g (46%). The prepared compound was characterized by $^1\text{H-NMR}$, IR, mass spectroscopy, and elemental analysis; $^1\text{H-NMR}$ (CDCl_3) δ 7.9 (4H, 2-H and 6-H), δ 7.6 (4H, 3-H and 5-H); IR (KBr) 1780cm^{-1} and 1718cm^{-1} (C=O), 1585cm^{-1} and 1489cm^{-1} (aromatic C=C); Mass (M^+) : 392g/mol ; m.p. 172°C

ANAL. Calcd for $\text{C}_{16}\text{H}_8\text{O}_2\text{Br}_2$: C, 48.9; H, 2.04; O, 8.16; Br, 40.77, Found: C, 48.58; H, 2.04

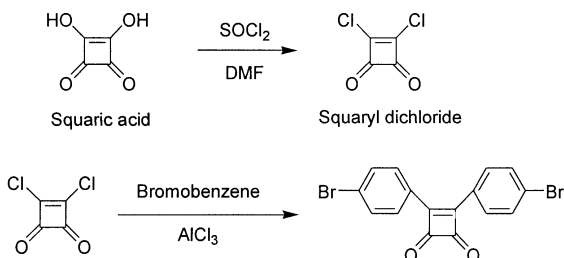
Synthesis of poly(3,4-bis(phenylene)-3-cyclobutene-1,2-dione)

A typical example of the polymerization as follows. To a stirred, deep blue solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (1.18g, 5mmol) and triphenylphosphine (5.2g, 20mmol) in DMF (25ml) under nitrogen at 50°C , zinc powder (0.32g, 5mmol) was added. After 1hr, the color of the mixture was turned into reddish brown. After the red-brown catalyst had formed, 3,4-bis(4-bromophenylene)-3-cyclobutene-1,2-dione (1.96g, 5mmol) was added to the reaction mixture. The reaction was conducted at 80°C for 24hr. The mixture was poured onto a large amount of HCl-methanol (1:9). The resultant polymer was collected, washed with methanol and dried in vacuum at 80°C for 24hr. The yield was 0.68g (60%); $^1\text{H-NMR}$ (DMSO-d_6) δ 7.5-7.6ppm (8H, aromatic C-H); IR (KBr) 1759cm^{-1} and 1724cm^{-1} (C=O) 1604cm^{-1} and 1489cm^{-1} (aromatic C=C)

RESULTS AND DISCUSSION

Synthesis and properties of 3,4-bis(4-bromophenylene)-3-cyclobutene-1,2-dione

A monomer was easily synthesized by a Friedel-Crafts reaction of bromobenzene and squaryl dichloride. Squaryl dichloride (3,4-dichloro-3-cyclobutene-1,2-dione) was an important intermediate in the preparation of mono- and di-arylated cyclobutenediones and treatment of squaric acid with 2 molar equivalents of thionyl chloride, neat or with benzene as a solvent, and catalytic amounts of DMF. In the case of benzene derivatives, which was poor electron donors compared with five-membered heteroaromatics, the Friedel-Crafts reaction was useful in the synthesis of the bisaryl cyclobutene-1,2-dione derivatives.¹³ To demonstrate the Friedel-Crafts reaction of squaryl dichloride and benzene derivatives, a model reaction was carried out using benzene.¹³ For the preparation of a monomer, the Friedel-Crafts reaction of squaryl dichloride and bromobenzene with AlCl_3 were carried out (Scheme 2).



Scheme 2 Monomer synthesis

As a result, both 1,2-type and 1,3-type compounds are theoretically possible. The 1,2-type and 1,3-type derivatives were distinguished from IR spectra. Figure 1 shows IR spectra of 1,2- and 1,3-type squaric acid derivatives. In IR spectral analysis, the 1,2-type compound has two carbonyl absorptions in the 1700-1800 cm^{-1} region, and the 1,3-type compound has a band based on a four-membered ring (C_4O_2) in the region of 1600 cm^{-1} . These results are in accordance with a Treibs and Jacob's literature.²⁰ The monomer obtained in this present study exhibits a strong IR-absorption band at 1780 cm^{-1} and 1718 cm^{-1} as shown in Figure 2, thus it is identified as a 1,2-type compound.

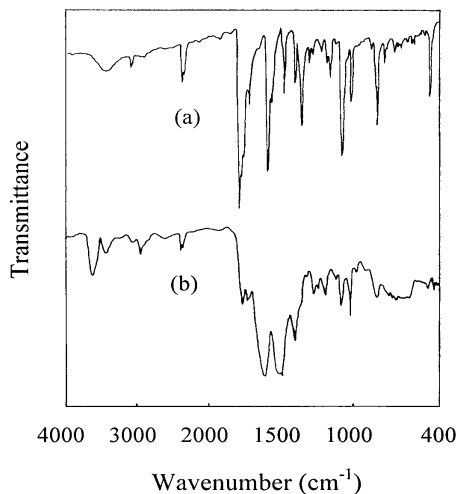
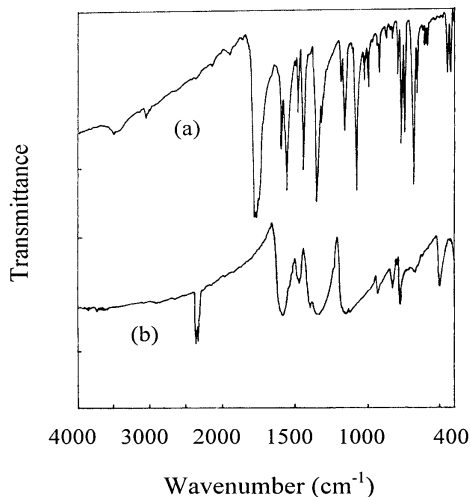


Figure 1 IR spectra of the 1,2-type(a) and 1,3-type compound(b)¹³

Figure 2 IR spectra of the monomer(a) and polymer(b)

Figure 3 shows a $^1\text{H-NMR}$ spectrum of the synthesized monomer. The peaks attributed to the diphenylcyclobutenedione fragment were observed at the expected chemical shifts with correct integration ratios. The aromatic proton ortho to a cyclobutenedione moiety in the monomer had a chemical shift of $\delta 7.9\text{ppm}$, which was as high as that of the proton ortho to a keto group in 4,4-difluorobenzophenone. This implied that the whole of the cyclobutenedione moiety itself provided better electron-withdrawing character than a single keto group.

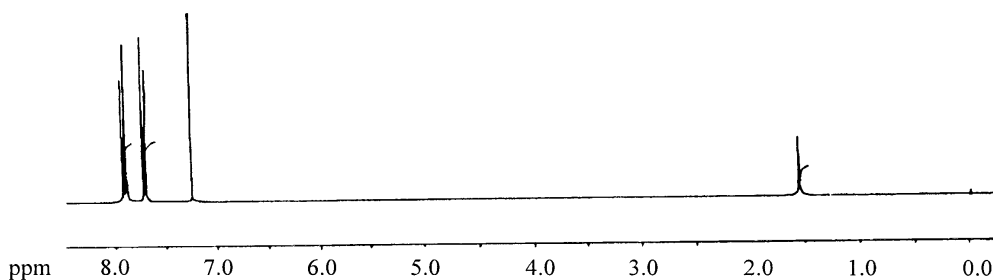


Figure 3 $^1\text{H-NMR}$ spectrum of the monomer

The thermal behavior of the monomer was examined by differentials scanning calorimetry (DSC). As shown in Figure 4, a melting point of the monomer was observed at 172 °C and endothermic peak, shown in the range of 231-320 °C, might indicate the decomposed temperature at which the monomer transformed to bisketene.²¹ In the model compound, a melting point was observed at 93 °C and decomposition occupied at 204-260 °C, thus and it indicated that 1,2-type structure is stable in the air, light and temperature below 170 °C.

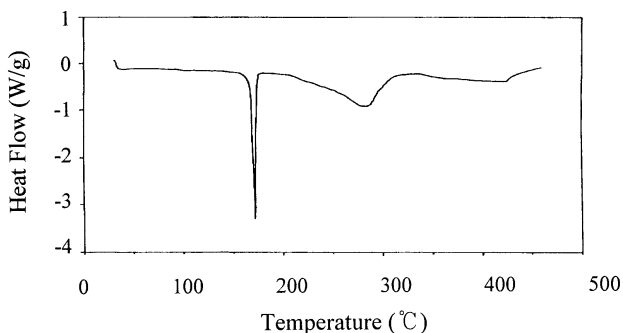
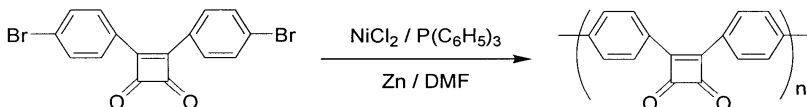


Figure 4 DSC curve of the monomer

Synthesis and properties of poly(3,4-bis(phenylene)-3-cyclobutene-1,2-dione)

The polycondensation was carried out with the monomer in the presence of zinc, triphenylphosphine and nickel(II)chloride. Direct coupling of either aryl bromide or iodide by a zero-valent nickel reagent has been accomplished in high yield under the mild condition. It has been known that this catalyst system is tolerant to aromatic compounds with carbonyl and cyano groups. This catalyst system improved several limitations; that stoichiometric amounts of expensive Ni(0) reagents are necessary, that the air-sensitive reagents require careful handling, and that aryl chloride give poor yields.²³ These results, we have now apply a modification of the method,²² which uses the *in situ* preparation of the nickel(0) complex, Ni(PPh₃)₄, directly from nickel (II) chloridre, triphenylphosphine and zinc, to the synthesis of a polymer (Scheme 3). The polymer was obtained as yellow powder and formed the brittle film from the DMAc solution. On the whole, 1,3-type polymers from squaric acid such as poly(squaryl amides) were insoluble in aprotic solvent,¹⁴ but 1,2-type polymer was soluble in the dipolar aprotic solvents, such as NMP, DMAc, DMF and DMSO. The resulting polymer had a number-average molecular weight of 4,800 by GPC using a μ -styrigel column (standard polystyrene) with DMF as an eluent solvent. The apparent color change from yellow to dark green was immediately observed on dissolving in DMAc indicating the formation of a CT complex of the polymer with DMAc. The UV-Visible spectrum of the polymer-DMAc solution showed strong absorption near 305nm and weak absorption near 720nm. This longer wavelength absorption corresponding to green color implied the interaction between the polymer and the solvent.



Scheme 3 Polymer synthesis

In Figure 2, the FT-IR spectrum of polymer was essentially similar to that of the monomer, and exhibited a FT-IR absorption band at 1700-1800 cm^{-1} region, and a absorption band of C-Br band (428 cm^{-1} for the monomer) disappeared. These results indicated that polymerization was successfully carried out. The $^1\text{H-NMR}$ spectrum of the resulting polymer showed peaks in the range δ 7.5-7.6ppm due to the aromatic protons of the benzene ring (Figure 5).

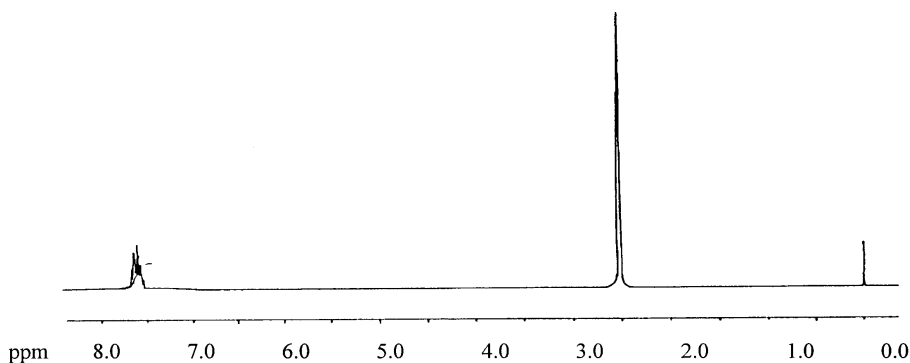
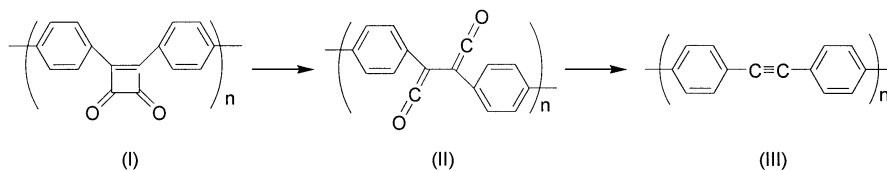


Figure 5 $^1\text{H-NMR}$ spectrum of the polymer

The glass transition temperature of the polymer was not detected by differential scanning calorimetry (DSC). Instead, a clear exothermic peak was observed at 350 °C. The thermal stability of the polymer was examined by thermogravimetry analysis (TGA). The weight loss of the polymer began to start at 200 °C in accordance with the onset ring-opening temperature of the cyclobutenedione, as assessed by TGA (Figure 6). These phenomena are not unusual and have been explained in many papers as follows. The cyclobutenedione ring might open to form a highly reactive bisketene upon thermolysis and further yielded the acetylene by ejecting two molecules of carbon monoxide at an elevated temperature.²¹ A few ring cleavage reactions of cyclobutenedione derivatives were reported,^{24,25} in which bisketene derivatives were only postulated as an intermediate. In our research, the temperature range of transformation to bisketene in the DSC curve was similar to that of ring-opening of the cyclobutenedione in the TGA curve. The loss of carbon monoxide from the cyclobutenedione unit in the polymer was confirmed by the combined TGA and IR technique. An absorption band of aromatic C=C and carbonyl C=O appears at 1600 cm^{-1} and 1780 cm^{-1} region respectively, but, after raising temperature, an absorption band of C=O at 1780 cm^{-1} region disappeared, while that of aromatic C=C at 1600 cm^{-1} region remained unchanged. These results indicates that the polymer gradually released carbon monoxide, starting at 200 °C and continuing until the decomposition temperature of 580 °C. Therefore, it may be proposed that the polymer(I) transforms to the diphenylacetylene(III) *via* bis-phenylketene(II) (Scheme 4). The polymer showed a 45% residual weight at 1000 °C in nitrogen.



Scheme 4 Mechanism of thermal transformation in the related polymer

In summary, our result indicates that a polymer with 1,2-type π -conjugated system can readily be prepared and characterized by nickel-catalyzed coupling polymerization of aromatic dibromides containing a charged 2π -aromatic carbocyclic zwitterion structure. The polymer has the new π -conjugated structure with good solubility in polar aprotic solvents. The research of thermolysis will be progressed in detail.

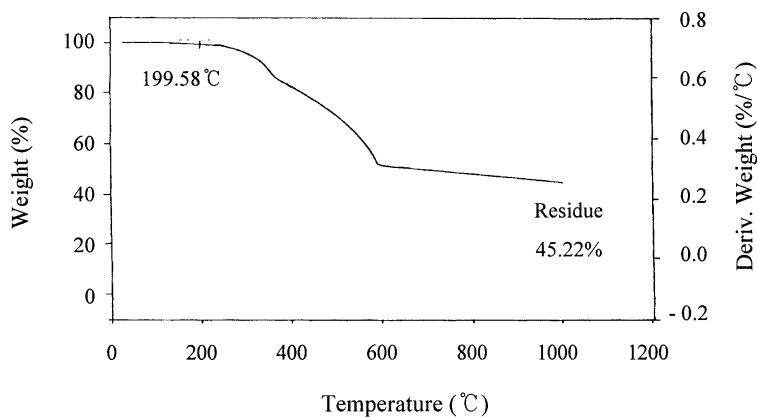


Figure 6 TGA curve of the polymer in nitrogen.

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