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Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
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To cite this Article Mizogami, Shigeyoshi and Yoshimura, Susumu(1988) 'A New Class of Polyconjugated Systems: Synthesis and Properties of Polymetacyclophanes', Journal of Macromolecular Science, Part A, 25: 5, 601 — 616
To link to this Article: DOI: 10.1080/00222338808053387
URL: http://dx.doi.org/10.1080/00222338808053387

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J. MACROMOL. SCI.–CHEM., A25(5-7), pp. 601-616 (1988)

A NEW CLASS OF POLYCONJUGATED SYSTEMS: SYNTHESIS AND PROPERTIES OF POLYMETACYCLOPHANES

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ABSTRACT

A unique polyconjugated systems having longitudinal π-electron overlaps was synthesized by using a metacyclophane monomer, 8,16-dihydroxy-[2,2]-metacyclophane. The monomer was synthesized according to Tashiro's method and was converted to two types of polycyclophanes. One was obtained as a quinoid-type polymer from $FeCl_3$-catalyzed oxidative coupling of the 2,5-disubstituted phenols. The polymer obtained was composed of [2,2,]-metacyclophane units polymerized via a diphenoquinone linkage. Amorphous, bright reddish-orange powders were obtained quantitatively under mild reaction condition. Another one was a phenol-type polymer that contained [2,2]-metacyclophane units linked with a 4,4′-dihydroxybiphenyl skeleton. This polymer was obtained by way of a unique polycondensation reaction characteristic of cyclophane compounds. The polymer obtained had a fine whisker form with a golden luster and partial crystallinity. The structures of these polymers were confirmed by various spectroscopic methods and

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elemental analysis. The electrical conductivity of both polymers was of almost the same order of magnitude (10^{-8} S/cm). When doped with sulfuric acid (H_2SO_4) vapor, the phenol-type polymer exhibited a conductivity of 0.25 S/cm, which was much higher than that of the quinoid-type polymer (10^{-4} S/cm).

INTRODUCTION

Conducting polymers have been studied from various viewpoints, such as synthesis, solid-state properties, applied physics, etc. [1]. Most of them have excellent electrical conductivity upon doping of acceptors or donors. For example, the conductivity of polyacetylene has recently gone up to the order of 10^5 S/cm [2], which is higher than that of graphite single crystals. Until very recently, most conductive polymers have been based on transverse π-electron overlaps with their polymer chains. In this sense, cofacially stacked polyphthalocyanines are thought to be the only polymers that have longitudinal overlaps of π-electron in their phthalocyanine π-system [3]. The longitudinal π-electron overlap is an important factor for the charge transport properties of conductive charge-transfer (CT) complexes, such as TTF-TCNQ [4]. These complexes also have excellent electrical conductivity, 10^3 S/cm, and even display superconductivity near or above liquid-He temperature [5].

It is well known that cyclophane compounds have strong transannular π-electron interaction between two aromatic rings separated by a short interplanar distance [6]. Cyclophanes having an intramolecular mixed valence interaction are also known [7], and this interaction is a necessary condition for metallic conductivity in conductive CT complexes. Additionally, Bohm et al. suggested that polycyclophane having an intramolecular quinhydrone interaction along its stacking axis should exhibit intrinsic metallic conductivity if its interfacial distance is as short as that of a superphane [8].

Longone et al. reported the synthesis and properties of a unique polymer having a [3,3]- or [3,2]-paracyclophane skeleton with a pendent group [9]. The electrical conductivity of these polymers was the order of magnitude of 10^{-4} S/cm upon doping with iodine vapor. These polymers can be considered as electrically conducting cyclophane polymers whose electrons transport along the stacks of the pendent groups.

In this paper we report the design, synthesis, and some properties of polymetacyclophanes [10] whose electron delocalization was facilitated by longitudinal π-electron overlaps in their polymer chain.

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EXPERIMENTAL

Materials

The monomer, 8,16-dihydroxy-[2,2]-metacyclophane, was synthesized according to a procedure reported by Tashiro et al. [11]. Its elemental analysis and spectroscopic properties were consistent with those of the authentic sample. Oxidative reagents, such as ferric trichloride, were received from Wako Pure Chemicals Industry and used without further purification. Spectro grade Chloroform was used as received.

Apparatus and Procedures

The catalytic oxidative polymerization reaction was carried out by general procedures of organic synthesis. Heat treatment of synthesized polycyclophanes was carried out at various temperatures from 500 to 1000°C in an inert atmosphere. An infrared image furnace (Synkuu-Rikoh. Co.) was used for the heat treatment. Polarizing microscopy (Nikon Co.) was used for the measurement of the polarization properties of partial crystalline polymer whiskers. Electrical conductivity was measured by the standard four-probe method at room temperature. Doping experiments were carried out by means of a specially made glass cell containing four threads of platinum wire.

RESULTS AND DISCUSSION

Syntheses

Figure 1 shows the synthetic route for polymetacyclophanes that we adopted. 8,16-Dihydroxy-[2,2]-metacyclophane was polymerized via the diphenoquinone linkage by oxidative coupling with a ferric trichloride catalyst which has a strong catalytic ability for C–C coupling of 2,5-disubstituted phenols [12]. Table 1 shows the results of the oxidative polymerization of monomer **1**. Bright reddish-orange powders **2** were quantitatively deposited from stirring of the solution for 1 h at ~0-5°C. The powders neither dissolved in common organic solvents nor melted without decomposition. The structure of the powders obtained was confirmed by elemental analysis, FT-IR spectra, and CP-MAS (cross-polarized magic-angle spectroscopy). The polymerization reaction of **1** with $FeCl_3$ as catalyst proceeded very readily, but if the reaction was carried out under severe conditions, such as at the

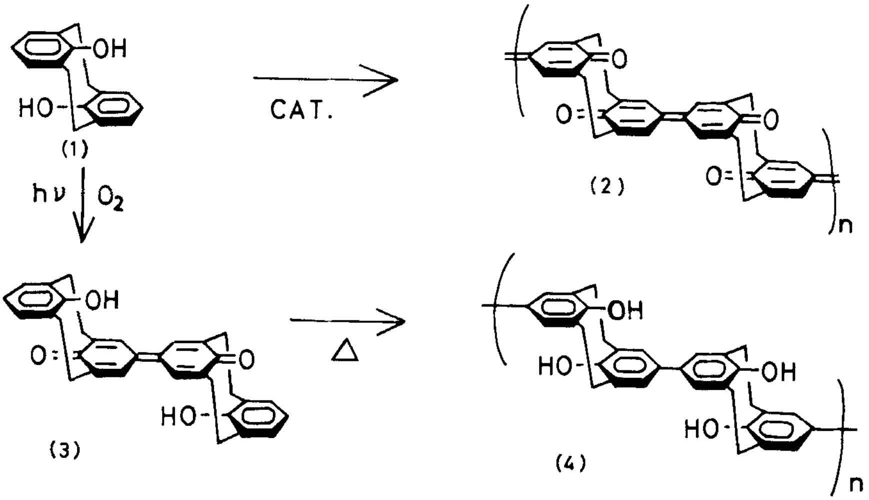

FIG. 1. Synthetic route to cyclophane polymers.

reflux temperature of the solvent, the product assumed a brown-black tint, its IR spectrum suggesting cleavage at the methylene bridges of the cyclophane skeleton. A lutidine-CuCl catalyst, which has been used for the polymerization of poly(phenylene oxide), was also examined, but it did not give any polymerized products. It is noteworthy that Hay at General Electric synthesized a diphenoquinone polymer by means of a similar catalyst with a bifunctional phenol compound as the starting material [13].

Figure 2 shows the FT-IR absorption spectrum of **2** obtained by oxidative polymerization. The spectrum is characterized by a strong and exceptionally low carbonyl band at 1600 cm^{-1}, which offers evidence for the existence of a diphenoquinone structure [14]. In addition, from comparison of the spectrum of **2** with that of **1**, the former retains the stretching bands of methylene bridge at about 2900 cm^{-1} but lacks out-of-bending bands at 700-800 cm^{-1} of three protons adjacent to the aromatic ring. All these data consistently confirm that **1** was polymerized by oxidative C–C coupling to form the desired polymetacyclophane **2** having diphenoquinone linkage.

In controlling the high-order structure of the diphenoquinone-type polycyclophane **2**, we have succeeded in the synthesis of a second polycyclophane **4** polymerized via 4,4′-dihydroxybiphenyl linkages. Although **4** is the com-

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TABLE 1. Electrical Conductivity for Polycyclophanes Obtained from Oxidative Polymerization under Various Conditions

Catalyst	Solvent	Time, h	Temperature, °C	Color	Conductivity, S/cm
$FeCl_3$	$CHCl_3$	6	RT	Dark brown	7×10^{-9}
,,	,,	12	,,	Grayish brown	9×10^{-9}
,,	,,	6	Reflux	Grayish dark brown	4×10^{-11}
,,	$CHCl_2CHCl_2$	5	,,	Dark gray	10^{-11}
,,	$CHCl_3$	1	0-5	Orange brown	3×10^{-9}
,,	CH_3NO_2	1	0-5	Reddish brown	2×10^{-10}
,,	$CHCl_3$	1	-10	—	—
Lutidine $CuCl/O_2$	$C_6H_5NO_2$	1	Reflux	Reddish orange (trace)	
PbO_2	AcOH	1	RT	Reddish brown (oligomer)	

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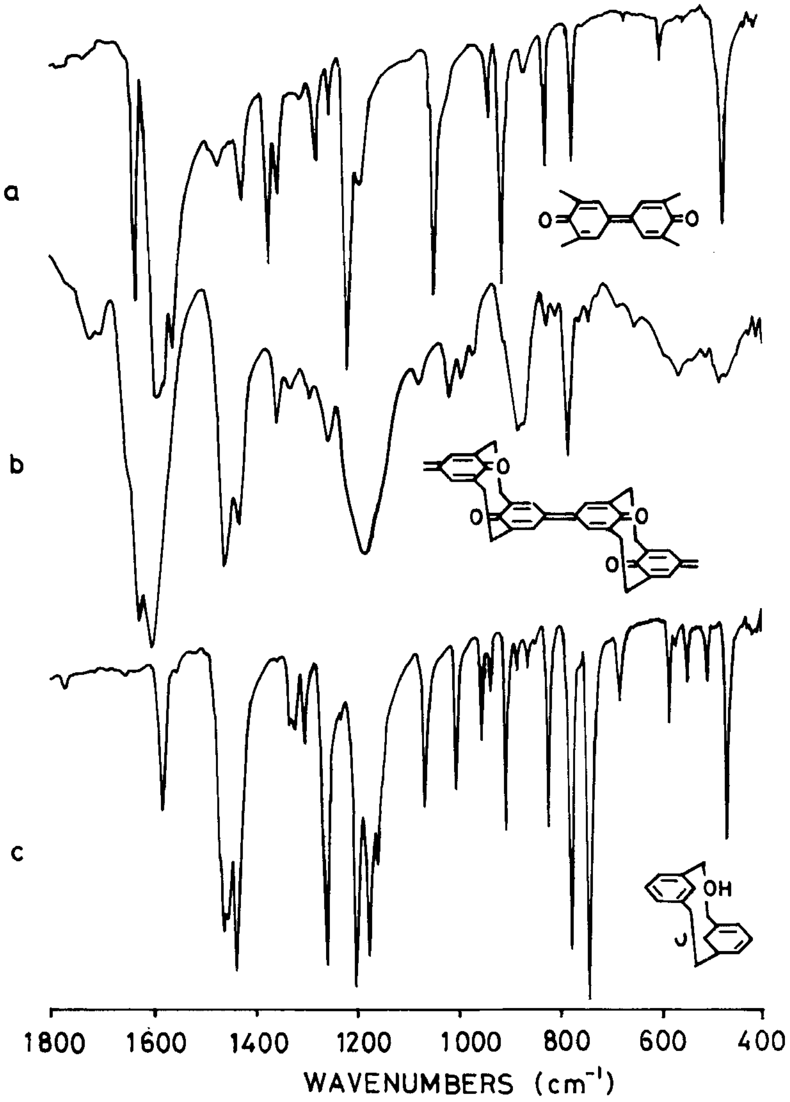

FIG. 2. FT-IR spectra of polycyclophanes obtained by oxidative polymerization.

pletely reduced form of the first polymetacyclophane **2**, it was synthesized by a totally different route.

When **1** was left as a chloroform solution in the absence of catalyst, very fine whiskers were deposited after 2 weeks at room temperature. The whiskers had dimensions of about 2 μm × 2 μm × 1 mm and assumed a bright reddish-orange color characteristic of the diphenoquinone moiety. It was shown by elemental analysis, NMR, FT-IR, and mass spectra that the whiskers obtained had the dimeric structure **3**.

After these whiskers were heated under an inert atmosphere between 300 and 400°C, they converted to another cyclophane polymer **4** containing 4,4′-dihydroxybiphenyl linkages. The polymer obtained preserved the original whiskerlike shape but assumed a bright golden color. A well-formed whisker shape having a rectangular cross-section was recognized in its SEM picture.

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Polymerization Mechanism

The oxidative conversion of **1** into **3** proceeded in the presence of dissolved oxygen and room light, but the detailed reaction mechanism is not clear at the present time. Thermogravimetric analysis of dimer **3** under a nitrogen atmosphere showed that it had very high heat-resistance for a low molecular weight compound. It did not have a melting point but slowly decomposed at about 400°C and had a char yield of about 25% at 1000°C.

Differential scanning calorimetry (DSC) for the dimer **3** revealed an exothermic peak at about 300°C, as shown in Fig. 3, indicating a thermal polycondensation reaction of **3**. This reaction was directly confirmed by FT-IR spectra of **3** heat-treated at various temperatures, as shown in Fig. 4. The pristine dimer (Fig. 4) has an exceptionally low carbonyl stretching band at about 1600 $\mathrm{cm^{-1}}$, which suggests the existence of the diphenoquinone skeleton, as already pointed out. On heating at ~300-400°C, this carbonyl band disappears, and the absorption bands of a phenolic hydroxy group at 3400 and 1200 $\mathrm{cm^{-1}}$ become considerably stronger than those of the pristine dimer. The cyclophane skeleton is not thought to be broken in this temperature region because the absorption bands of the methylene group are still retained. At higher temperatures, however, the skeleton started to decompose, as is seen in Fig. 4.

From these results we propose the polymerization mechanism depicted in Fig. 5. When the oxidative dimer **3** is thermally polymerized, the hydrogen atoms eliminated from the end benzene ring reduce the quinone carbonyl

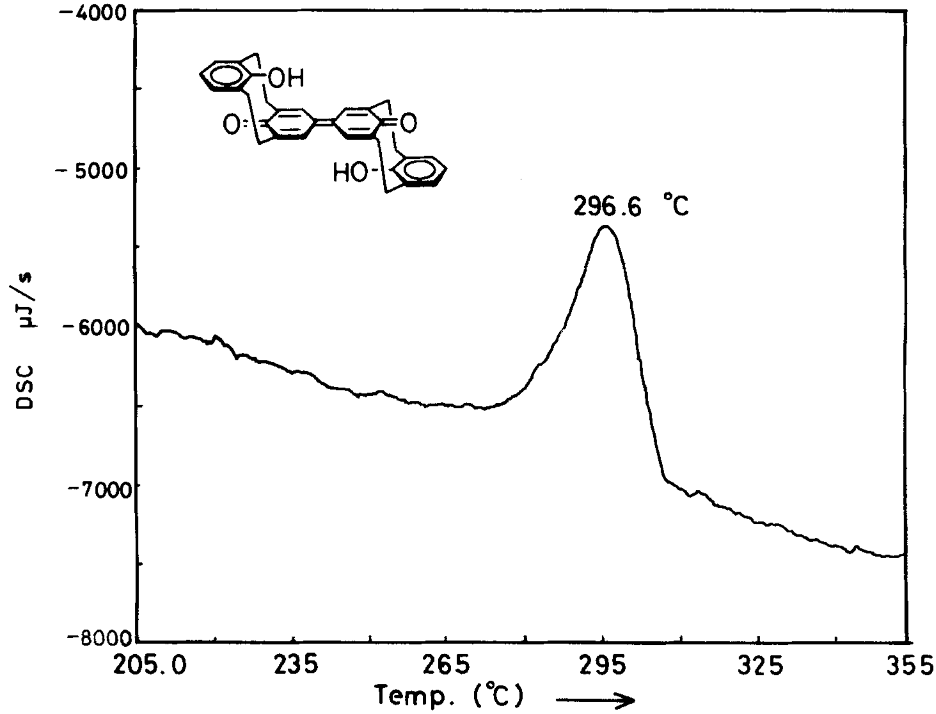

FIG. 3. DSC curve for oxidative dimer.

groups which are located quite close to the hydrogen atoms. The polymer obtained, **4**, is a wholly aromatic-type cyclophane polymer whose structure was directly confirmed by solid-state NMR (CP-MAS) described below. The reaction, which includes intramolecular hydrogen transfer, is unique and may be specific to the cyclophane compounds.

Structure Determination

Figure 6 shows the CP-MAS spectra of the cyclophane polymers **2** and **4** together with that of the dihydroxy-[2,2]-metacyclophane **1** as a reference compound. Monomer **1** has an aliphatic carbon peak at about 30 ppm, a benzenenoid carbon peak at 120 ppm, and the peak of benzenoid carbon substituted by a hydroxy group at 150 ppm, corresponding to the monomer

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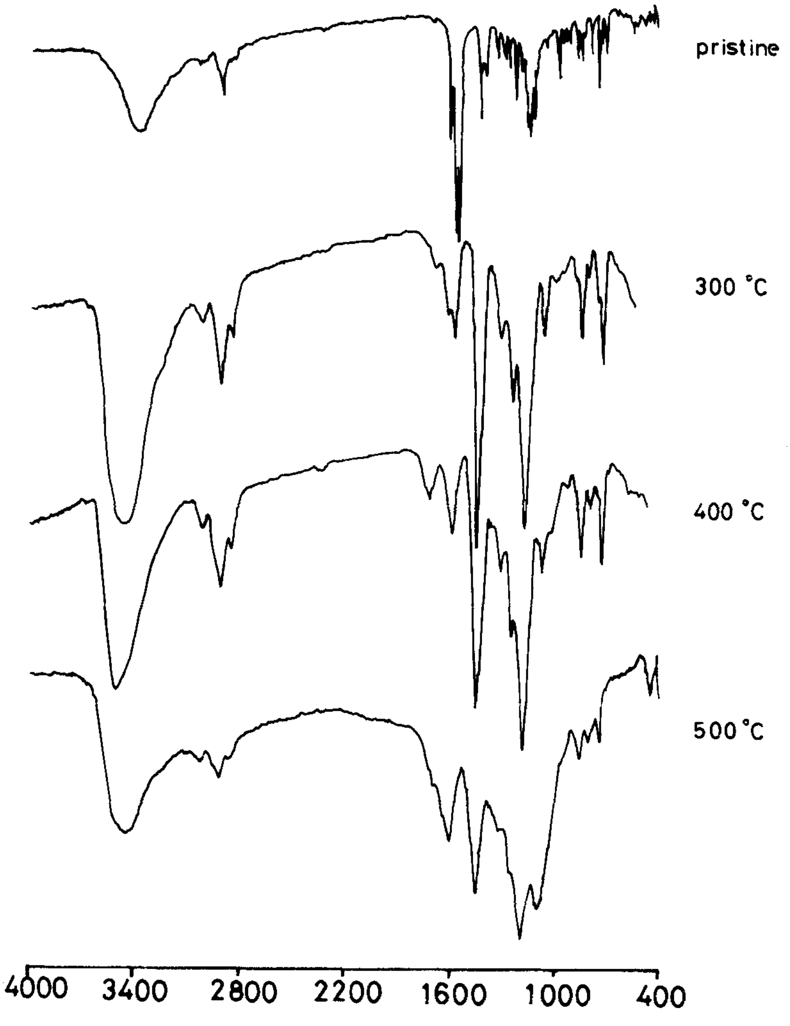

FIG. 4. FT-IR spectra of polycyclophanes heat-treated at various temperatures.

structure. Polymer 2 shows the same pattern as that of the monomer, except for a quinoid carbon peak at about 180 ppm instead of the benzenoid carbon peak at 150 ppm, supporting the desired quinoid structure. Polymer 4 does

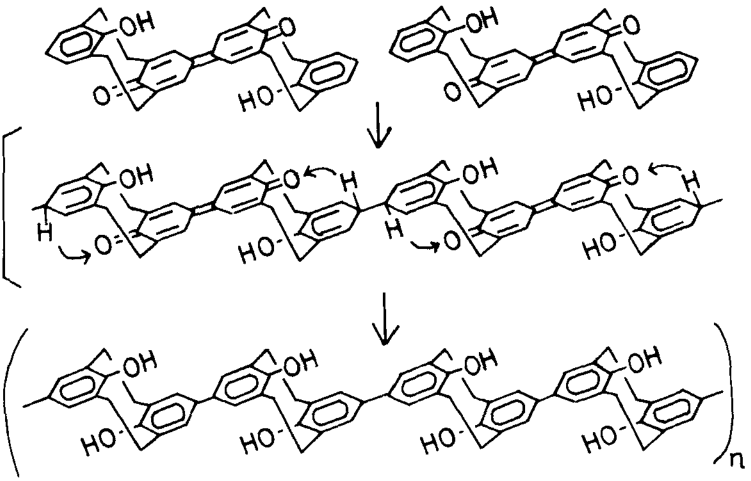

FIG. 5. Proposed polymerization mechanism.

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not exhibit the quinoid carbon peaks, and the positions of the other peaks are the same as those of Monomer **1**. These spectra confirm the structure of the respective polymers shown in Fig. 1.

The optical absorption spectra of Polymers **2** and **4** obtained in the solid state are shown in Fig. 7 together with that of oxidative dimer **3**. The spectrum of Polymer **2** is remarkably similar to that of the dimer **3** but red-shifted by about 70 nm. Polymer **4** has a benzenoid absorption band at about 300 nm which is not observed in the spectrum of the quinoid polymer **2**. Accordingly, it is strongly supported that Polymer **4** has a phenol-type structure with little diphenoquinone skeleton, though the diphenoquinone band is still retained weakly in its spectrum. The long-wavelength tail of the spectra of **2** and **4** is thought to be attributable to the longitudinal π-electron overlaps.

Polymer Morphology and Crystallinity

The thermal polycondensation of the oxidative dimer **3** proceeded in the solid state with retention of its shape. Additionally, the Polymer **4** obtained assumed a bright golden color, suggestive of a highly oriented polymer. Few conducting polymers are known as oriented or crystalline polymers. In this sense, diacetylenic polymer is exceptional, having high crystallinity [15].

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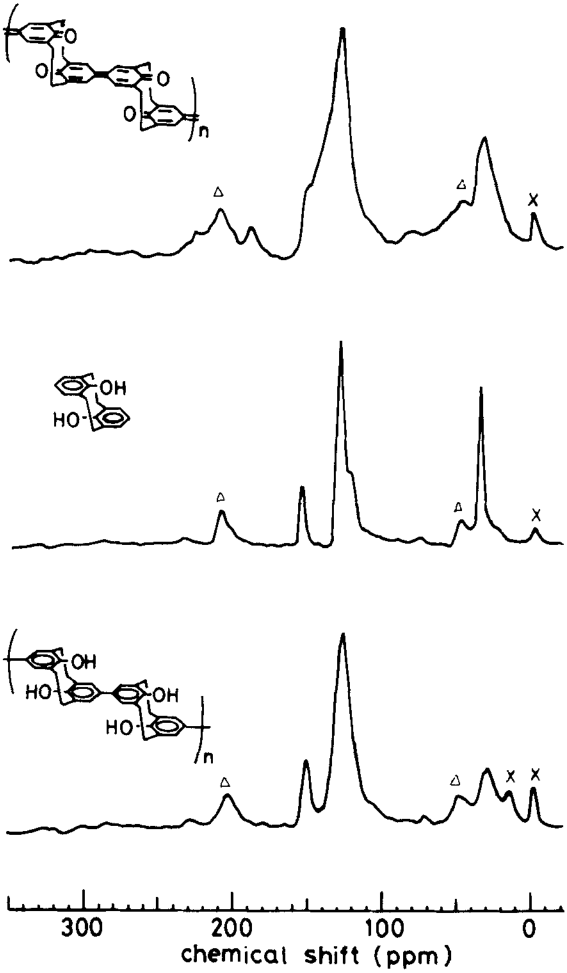

FIG. 6. CP-MAS spectra of polycyclophanes together with that of the monomer, dihydroxy-[2,2]-metacyclophane.

Polarizing microscopy can be applied to the measurement of the degree of crystallinity [16]. As shown in Fig. 8, Polymer **4** had a fine whisker form and showed strong birefringence along the whisker axis. The color with a 530-nm test plate was blue when the whisker axis was set along the *Z*′-axis

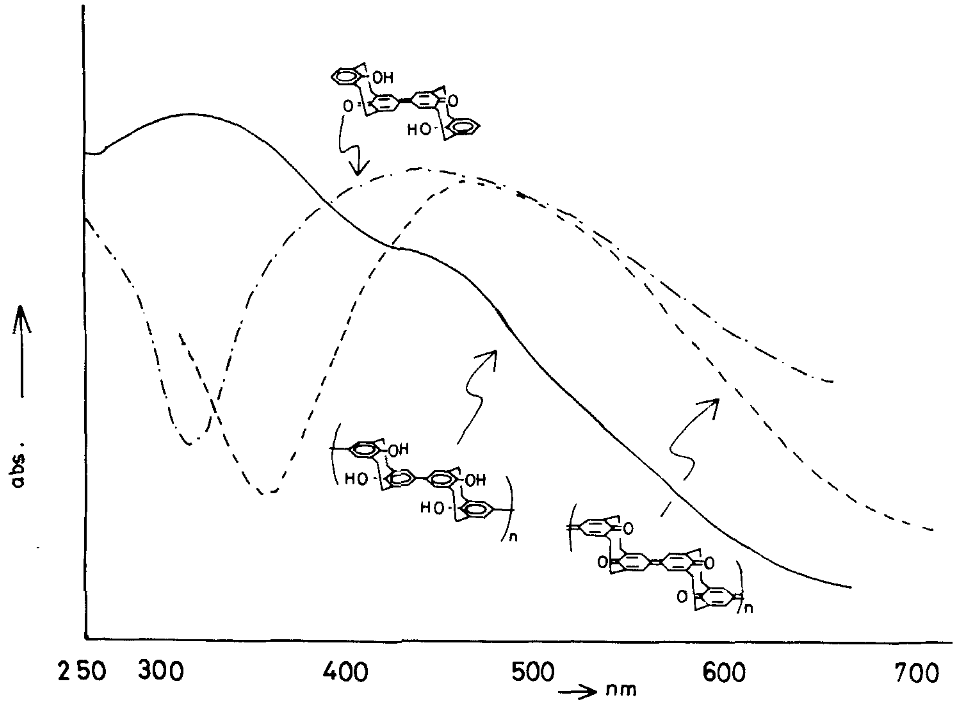

FIG. 7. UV-VIS spectra of polycyclophanes in the solid state.

and yellow along the X'-axis. This indicates that the molecular orientation in the polymer whisker is parallel to the whisker axis. The electron diffraction measurement of **4** showed that strong diffraction spots existed along the whisker axis and at a right angle to the whisker axis. Particularly, the diffraction spots at a right angle to the whisker axis (with a lattice spacing of 2.8 Å) were much denser than those along the whisker axis. This agrees very well with the results of polarizing microscopy. However, there were strong halos in the electron diffraction pattern, indicating the presence of a noncrystalline phase. Hence, the polymer whiskers are composed of highly oriented polycyclophane macromolecules embedded in an amorphous phase. No crystalline phase was observed in the quinoid-type polymer powders **2** by polarizing microscopy and electron diffraction measurements.

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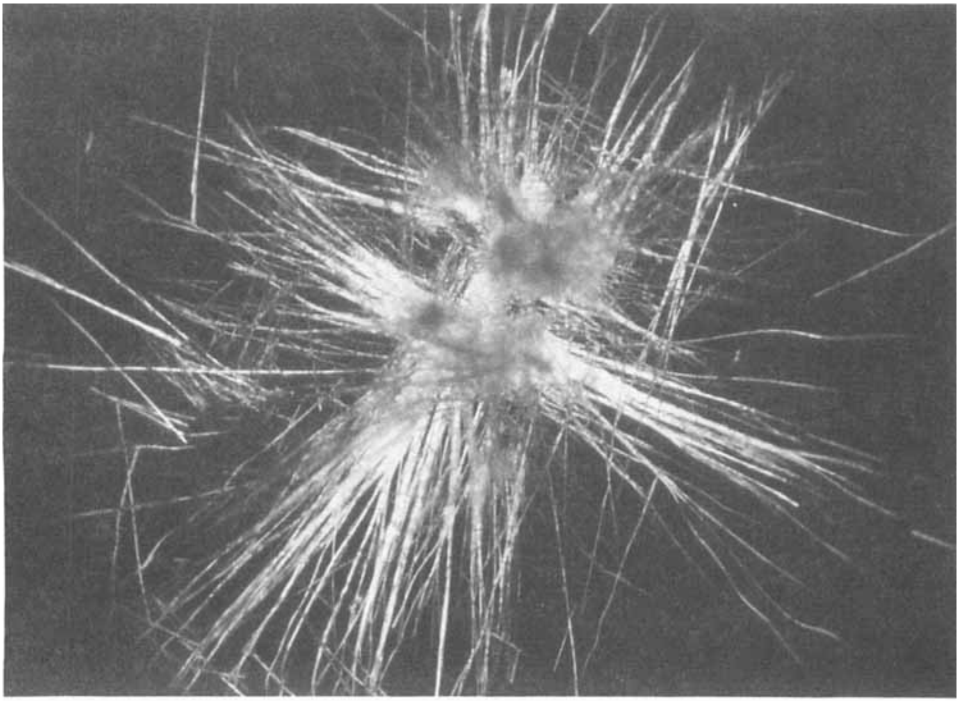

FIG. 8. Photograph of Polymer **4** by polarizing microscopy.

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Solid-State Properties

The thermal properties of the polycyclophanes obtained together with that of the dimer **3** are depicted in Fig. 9. The wholly aromatic-type polymer **4** has the highest thermal stability of these compounds, even though the difference between quinoid polymer **2** and aromatic polymer **4** is not very large. This behavior can be explained on the basis of the difference in thermal stability between the aromatic ring of **4** and the quinoid ring of **2**. The oxidative dimer **3** has the lowest stability of these compounds because it thermally decomposes on heating before it completes the conversion into the wholly aromatic polymer **4**.

Table 2 shows the electrical conductivity at room temperature for pristine

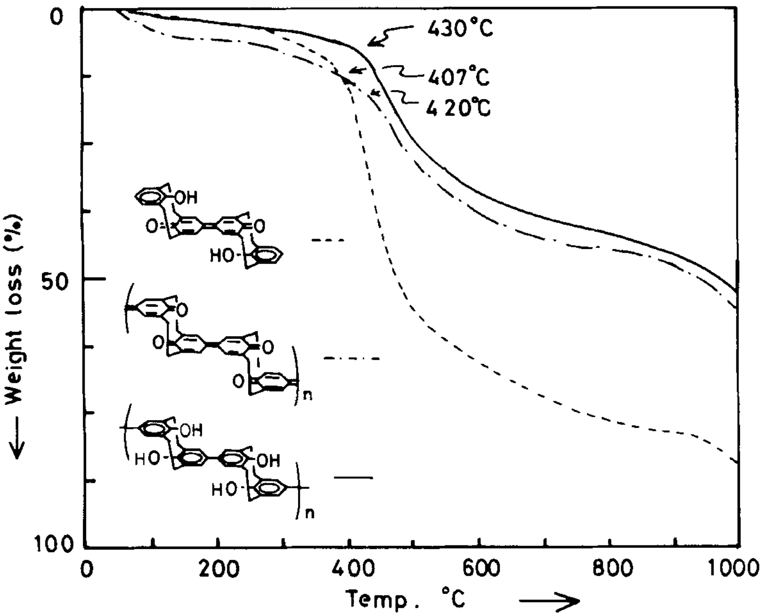

FIG. 9. TGA curves of polycyclophanes.

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polycyclophanes and those doped with H_2SO_4 vapor, **4** exhibited a conductivity enhanced by 7 orders of magnitude. The maximum conductivity of 0.25 S/cm was attained within 10 min upon doping, which is of the same order of magnitude as that of cofacially stacked phthalocyanine polymers. The conductivity enhancement of **2** upon doping with the same dopant was only 3 orders of magnitude. These results suggest that the phenol-type polymer **4** has a low ionization potential and a more ordered structure than those of the quinoid-type polymer **2**.

The effects of heat-treatment on the electrical conductivity for the polycyclophanes obtained are summarized in Table 3. The quinoid-type polymer **2** had a higher conductivity than the aromatic-type polymer **4**. This contrasts with the case of chemical doping. This phenomenon is also thought to reflect the higher stability toward thermal decomposition of the aromatic ring of **4** than that of the quinoid ring of **2**. The crystalline phase of Polymer **4**, developed at about 300°C, was so stable that the graphitization of **4** was not likely to proceed at higher temperatures. These properties are thought

TABLE 2. Chemical Doping Effect for Electrical Conductivity[a] of Polycyclophanes

		Doped	
	Undoped	H_2SO_4	I_2
Quinoid-type	9×10^{-9}	5×10^{-5}	–
Phenol-type	5×10^{-8}	0.25	1.9×10^{-5}

[a] In S/cm.

to be very abnormal for an organic compound. The detailed properties are under study and will be published elsewhere.

CONCLUSION

We have succeeded in synthesizing two new polymetacyclophanes, quinoid- and phenol-types, having longitudinal π-electron overlaps. A unique solid-state polycondensation reaction characteristic of a cyclophane compound was found. Particularly, the wholly aromatic-type polymer had relatively high crystallinity and electrical conductivity. The higher electron-donating ability and thermal stability of the wholly aromatic-type polymer than those of the quinoid-type polymer were reflected in their electrical and thermal properties. On heating from 500 to 1000°C, the graphitization of **4** hardly occurred because its stable crystalline phase developed at about 300°C.

TABLE 3. Heat-Treatment Effect on Electrical Conductivity[a] of Polycyclophanes

	Quinoid-type	Phenol-type
Pristine	9.0×10^{-9}	5.0 X 10-8
500°C	1.3×10^{-9}	1.0 X 10-8
700°C	15	1.4 X 10-4
1000°C	83	1.5

[a] In S/cm.

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ACKNOWLEDGMENTS

This work was supported by the Research Development Corporation of Japan as a part of Exploratory Research on Advanced Technology (ERATO). We heartily thank Prof N. Ogata of Sophia University as the project manager. We especially express our thanks to our colleagues Dr Y. Yumoto, Mr H. Yasujima, Mr S. Naitoh, Mr K. Watanabe, and Dr M. Murakami for their helpful discussions on our research. We are deeply indebted to Prof M. Tashiro of Kyushu University and Prof S. Misumi of Osaka University for their encouragement and helpful discussions.

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