Synthesis of Soluble Polyphenylene Homopolymers as Polar Macromolecules: Complete Dehydrogenation of Poly(1,3-cyclohexadiene) with Controlled Polymer Chain Structure

Itaru Natori,*,† Shizue Natori,‡ and Hisaya Sato†

Chemical and Material Systems, Graduate School of Bio-Applications and Systems Engineering, Tokyo University of Agriculture & Technology, 2-24-16 Naka-chou, Koganei-city, Tokyo 184-8588, Japan, and Department of Materials and Life Science, Faculty of Science and Technology, Seikei University, 3-3-1 Kichijoji Kitamachi, Musashino-city, Tokyo 180-8633, Japan

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ABSTRACT: Soluble polyphenylene (PPH) homopolymers with a controlled polymer chain structure were synthesized for the first time by the complete dehydrogenation of poly(1,3-cyclohexadiene) (PCHD) having a 1,2-addition (1,2-CHD unit) and 1,4-addition (1,4-CHD unit). The reactivity of PCHD for dehydrogenation strongly depends on the polymer chain structure. The rate of dehydrogenation is fast on a long sequence of 1,4-CHD units, while it is considerably impeded by the presence of 1,2-CHD units in the polymer chain. With a reaction temperature higher than 90 °C, complete dehydrogenation of PCHD proceeds successfully to yield soluble PPH homopolymers. The polymers obtained are soluble in polar solvents. Therefore, the soluble PPH homopolymers *appear* to be polar macromolecules, and the conversion *of polarity* occurs during the dehydrogenation process. UV and fluorescence spectra clearly indicate the nature of a conjugated PPH homopolymer.

Introduction

The study of hydrocarbon polymers that possess a cyclic structure in the main chain is one of the most interesting subjects that has both basic and practical aspects of polymer chemistry. Poly(1,3-cyclohexadiene) (PCHD), which has a special structure in that the main chain has six-membered rings directly connected to each other, has been recognized since the 1950s as an attractive precursor for the synthesis of a new class of high performance hydrocarbon polymers.[1−21] From the perspective of molecular structure, the unique cyclic nature of the repeat unit and the presence of a residual double bond in the cyclic unit have presented opportunities for interesting modifications of PCHD.

A variety of modified derivatives of PCHD have been obtained via several chemical modification reactions directed at the residual double bond present in the cyclic unit of PCHDs. For example, dehydrogenation,[1−3,6−11,13,14,16,17,21] halogenation,[2−4] hydrogenation,[5,12,15,18,19,26] and oxidation [20,21] have been achieved to obtain high performance polymers with cyclic units directly connected in the main chain.

However, the difficulty of PCHD polymerization has been a serious problem and has prevented progress in the study of PCHDs. In contrast to conventional diene monomers, such as butadiene (Bd) and isoprene (Ip), the polymerization of 1,3-cyclohexadiene (1,3-CHD) has sometimes been reported to be difficult under various conditions, including cases of ionic polymerization, radical polymerization, and coordination polymerization. The polymers obtained under these conditions were of low molecular weight or in low yield, and the microstructure of the polymer chain could not be controlled.[1−11,22]

Before our discovery of the living anionic polymerization of 1,3-CHD,[23−25] there had been no successful examples for the controlled polymerization method of 1,3-CHD, and it has been very difficult to elucidate the relationship between the microstructure and the properties of PCHDs or their modified derivatives.

In previous papers,[23−26] we reported the first successful example of living anionic polymerization of 1,3-CHD; homopolymers, copolymers, and block copolymers with narrow molecular weight distribution, controlled molecular weight, and a clear polymer chain structure were successfully synthesized. Furthermore, an effective method for controlling the microstructure of the polymer chain of PCHD was reported. PCHD has a structure consisting of a main chain formed by a 1,2-addition (1,2-CHD unit) and a 1,4-addition (1,4-CHD unit). The molar ratio of 1,2-CHD/1,4-CHD units in the polymer chain can be controlled by the type and amount of amine used, and also by the use of alkyllithium as an initiator.[12,25] The influence of the microstructure of PCHD on the physical and chemical properties was also reported.[12,26] Following the discovery of the living anionic polymerization of 1,3-CHD,[23−26] Mays et al. and Williamson et al. also reported examples of the (living) anionic polymerization of 1,3-CHD under various conditions.[20,27−30]

In the case of dehydrogenation of PCHDs, most interest has been concentrated on PCHD and its copolymers having a high content of 1,4-CHD units as a precursor for the preparation of poly(*p*-phenylene) (PPP) and its copolymers. Therefore, regarding the dehydrogenation of PCHDs, only limited information has been reported concerning the 1,4-CHD unit sequences in the uncontrolled polymer chain.[1−3,6−11,13,14,16,17] To date, there has been no study on the effect of the microstructure of the polymer chain on the dehydrogenation of PCHDs.

Recently, we reported the influence of the molar ratio of 1,2-CHD/1,4-CHD units on the dehydrogenation of PCHD with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ).[21] As a result, it was found that the dehydrogenation of PCHD was strongly influenced by the molar ratio of 1,2-CHD/1,4-CHD units in the polymer chain. Subsequently, we attempted to obtain completely dehydrogenated *CHD units* with a controlled polymer chain consisting of 1,2-phenylene (1,2-Ph) and 1,4-phenylene (1,4-

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* Corresponding author. E-mail: itaru_natori@yahoo.co.jp.
† Tokyo University of Agriculture & Technology.
‡ Seikei University.

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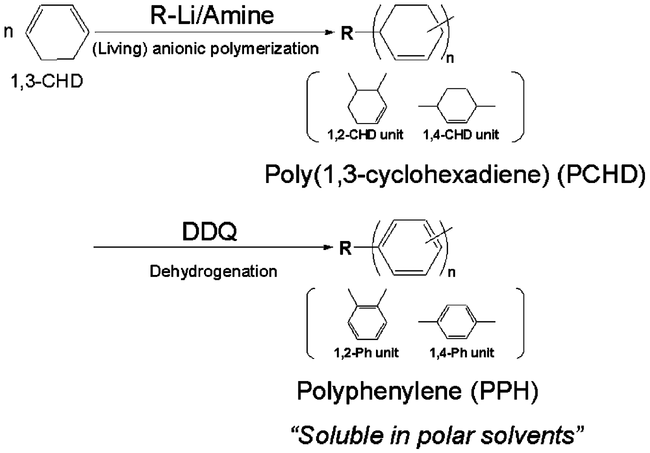
Scheme 1



Ph) units as a new type of polyphenylene (PPH). To determine effective dehydrogenation conditions for PCHD, we examined various dehydrogenation catalysts and quinones. In particular, the dehydrogenation of PCHD with quinone was examined in detail.

When dehydrogenated samples of PCHD, which were reprecipitated from 1,2-dichlorobenzene (DCBz) and 2-propanol-(IPA), were washed with acetone, it was observed that some of the samples began to gradually dissolve in the acetone solution. Accordingly, the solubility of various dehydrogenated PCHDs was examined using many different solvents. Surprisingly, it was discovered that a particular group of dehydrogenated PCHDs were soluble in a polar solvent. In particular, completely dehydrogenated PCHD, that is polyphenylene (PPH), was fully soluble in *N*,*N*-dimethylformamide (DMF) and formed a dark brown transparent solution.

The first successful synthesis of soluble PPH homopolymers obtained by the dehydrogenation of PCHD, as polar macromolecules (Scheme 1) is reported. The conditions for complete hydrogenation of PCHD homopolymers with a controlled polymer chain consisting of 1,2-CHD and 1,4-CHD units, and the characteristics of polyphenylene having 1,2-Ph and 1,4-Ph units are also described.

Experimental Section

Materials. 1,3-Cyclohexadiene (1,3-CHD), cyclohexane, and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) were refluxed over calcium hydride (CaH_2) and then distilled under an argon atmosphere. 1,4-Diazabicyclo[2.2.2]octane (DABCO) was dried under reduced pressure in dry argon. *n*-Butyllithium (*n*-BuLi, 1.60 M in *n*-hexane), *sec*-butyllithium (*s*-BuLi; 1.40 M in cyclohexane), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), 1,2-dichlorobenzene (DCBz), trichlorobenzene (TCBz), methanol (MeOH), ethanol (EtOH), 2-propanol (IPA), chloroform ($CHCl_3$), tetrahydrofuran (THF), *N*,*N*-dimethylformamide (DMF), ethyl acetate (EtOAc), and acetone were used without further purification. All reagents were purchased from Aldrich.

General Procedure for the Anionic Polymerization of 1,3-CHD with Alkyllithium/Amine Systems. A well-dried 50 mL Schlenk tube was purged with dry argon, and cyclohexane and alkyllithium (RLi) were added at room temperature (ca. 25 °C) using hypodermic syringes. Amine was then added to this solution under a dry argon atmosphere and the mixture was stirred for 10 min. 1,3-CHD was then supplied to this solution with a hypodermic syringe, and the reaction mixture was magnetically stirred under an argon atmosphere at room temperature. To terminate the reaction after polymerization, dehydrated MeOH was added to the reaction mixture in an equimolar amount to the amount of lithium atoms present in the reaction mixture. The polymerization mixture was then poured into a large volume of EtOH to precipitate the polymer, which was then separated by filtration. The product was dried under reduced pressure in an argon atmosphere at room temperature for 24 h, resulting in a white powdery polymer.

Table 1. List of Evaluated Poly(1,3-cyclohexadiene)s[a]

polymer no.	initiator system	M_n[b,c]	M_w/M_n[b]	1,2-CHD unit/1,4-CHD unit (%)[d]
PCHD-1	*s*-BuLi	1130[b] (*1090*)[c]	1.38	2/98
PCHD-2	*s*-BuLi/DABCO (4/5)	1680[b] (*1550*)[c]	1.27	6/94
PCHD-3	*n*-BuLi/TMEDA (4/0.5)	1610[b] (*1570*)[c]	1.29	28/72
PCHD-4	*n*-BuLi/TMEDA (4/5)	1650[b] (*1580*)[c]	1.12	52/48

[a] Polymerization was carried out in cyclohexane (20 mL) for 1.0 h (PCHD-1) and 2.0 h (PCHED-2−4). [1,3-CHD)]/[solvent] = 10/90. $[1,3\text{-CHD}]_0/[\text{Li}]_0 = 12.5$ (PCHD-1); 20.0 (PCHD-2−4). [b] M_n and M_w/M_n were estimated by GPC, using polystyrene as standard. [polymer]/[THF] = 0.005 g/5.0 mL. [c] Estimated by ^{1}H NMR. [d] Estimated by ^{1}H NMR.[12,25]

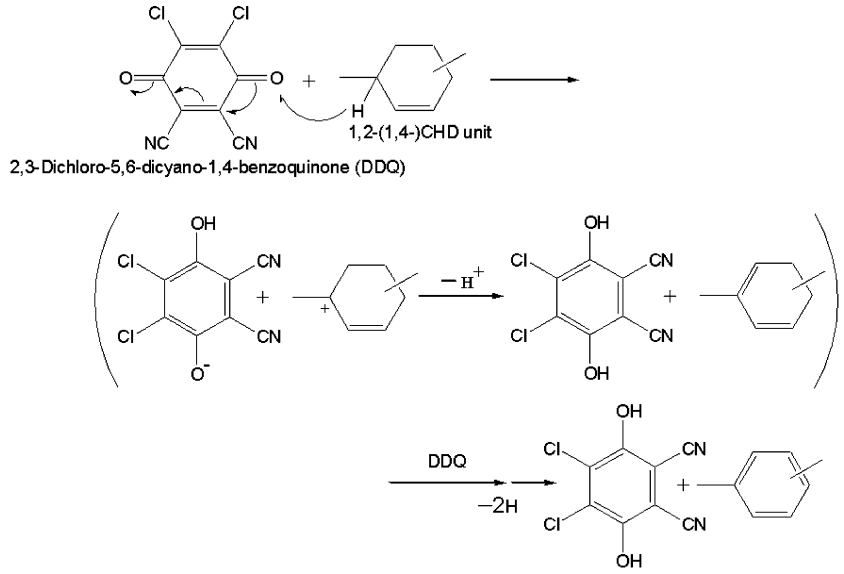
General Procedure for the Dehydrogenation of PCHD with DDQ. PCHD powder (0.20 g, consisting of 2.50 mmol of CHD units) was placed into a 50 mL Schlenk tube and dried under reduced pressure. The Schlenk tube was alternately evacuated and filled with dry argon several times. DCBz (20 mL) was added with a hypodermic syringe, and the mixture was stirred until the polymer was fully dissolved. DDQ (2.27 g, 10 mmol, 400% with respect to CHD units) was added under dry argon atmosphere, and the reaction mixture was magnetically stirred under an argon atmosphere. After dehydrogenation, the reaction mixture was poured into a large volume of IPA to precipitate the polymer, which was then separated by filtration. The product was washed with an excess amount of EtOH and dried under reduced pressure in an argon atmosphere at room temperature for 24 h, resulting in a dark brown powdery polymer.

Measurements. The number-average molecular weight (M_n), weight-average molecular weight (M_w), and molecular weight distribution (M_w/M_n) were determined using gel permeation chromatography (GPC) apparatus equipped with a differential refractometer detector using a Shimadzu Shim-pack GPC-80 M column at 40 °C. THF was used as the eluent, and the flow rate was 1.0 mL/min. A molecular weight calibration curve was obtained using polystyrene *(PSt)* standards. *The Mark−Houwink−Sakurada constants for PSt/THF system were used*. ^{1}H NMR spectra of the polymers were measured in deuterated chloroform ($CDCl_3$), tetrahydrofuran (THF-d_8), or *N*,*N*-dimethylformamide (DMF-d_7) at 500 MHz using a JEOL JNM-LA500 spectrometer. UV/vis spectroscopic measurements were performed in THF using a Shimadzu UV-3101 PC with quartz cells. Fluorescence spectra of the polymers were measured in THF using a Shimadzu RF-5300 PC with quartz cells.

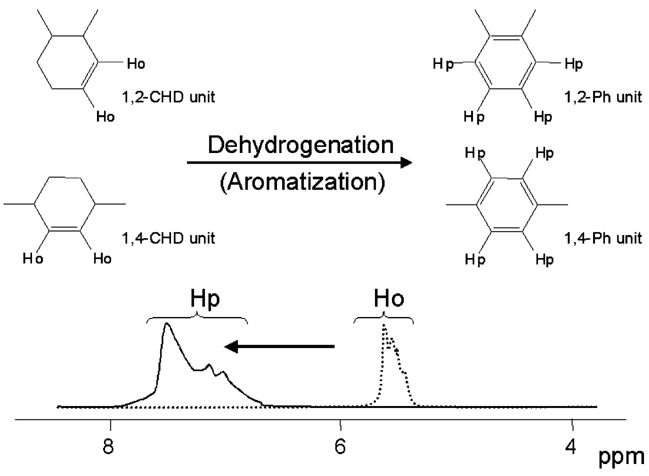
Results and Discussion

Influence of the Microstructure on Dehydrogenation. Samples of PCHD with different 1,2-CHD/1,4-CHD unit ratios and a M_n of approximately 1500 were prepared by (living) anionic polymerization of 1,3-CHD with several different initiators, to reveal the influence of the polymer chain structure of PCHD on the dehydrogenation reaction. The polymer yield (i.e., the conversion from 1,3-CHD to PCHD) for each sample was almost the quantitative yield (>99 wt %). The 1,2-CHD/1,4-CHD unit molar ratios were estimated by ^{1}H NMR.[12,21,25] The PCHD homopolymers that were obtained are listed in Table 1. Subsequently, the dehydrogenation of polymers PCHD-1 to -4 was conducted with DDQ for 72 h at room temperature (ca. 25 °C). A quantitative yield of dehydrogenated polymers was obtained for each sample. In this dehydrogenation reaction, 2 mol of DDQ were reacted with 1 mol of 1,2-CHD or 1,4-CHD units in the polymer chain, and 1 mol of 1,2-Ph or 1,4-Ph units were produced. The diene unit structure in the polymer chain, as an intermediate, is assumed to be more reactive and is

Scheme 2



Scheme 3



immediately converted to a Ph unit. Therefore, only 1,2-CHD and/or 1,4-CHD units and 1,2-Ph and/or 1,4-Ph units are supposed to be present in the reacted polymers (Scheme 2).[21]

This dehydrogenation reaction is an aromatization; therefore, the extent of dehydrogenation of PCHD (the conversion of 1,2-CHD and/or 1,4-CHD units to 1,2-Ph and/or 1,4-Ph units) can be estimated by a decrease in the olefinic signals (Ho at ca. 5.7 ppm, 2H per CHD unit) and an increase in the aromatic signals for the Ph units (Hp at ca. 7.5 ppm, 4H per Ph unit), as measured by ^{1}H NMR (Scheme 3).[21] Thus, the conversions of 1,2-CHD and/or 1,4-CHD units to 1,2-Ph and/or 1,4-Ph units (z %) were determined using the following formula, where O is the peak area of olefinic signals (Ho), and P is the peak area of aromatic signals for the Ph units (Hp):

$$z/100 = (P/4)/(O/2 + P/4) = 1/(1 + 2O/P)$$

As shown in Figure 1, the conversion was reduced with an increase in the *content* of 1,2-CHD units in the polymer chain. This suggested that the existence of 1,2-CHD units in the polymer chain significantly impedes the dehydrogenation of PCHD.

To examine the influence of the 1,2-CHD/1,4-CHD molar ratios on dehydrogenation in detail, the dehydrogenation of PCHD-2 (1,2-CHD units/1,4-CHD units = 6/94) and PCHD-4 (1,2-CHD units/1,4-CHD units = 52/48) were performed with DDQ for 504 h (3 weeks) at room temperature (ca. 25 °C). The typical time−conversion curves for the dehydrogenation of PCHD-2 and PCHD-4 are shown in Figure 2.

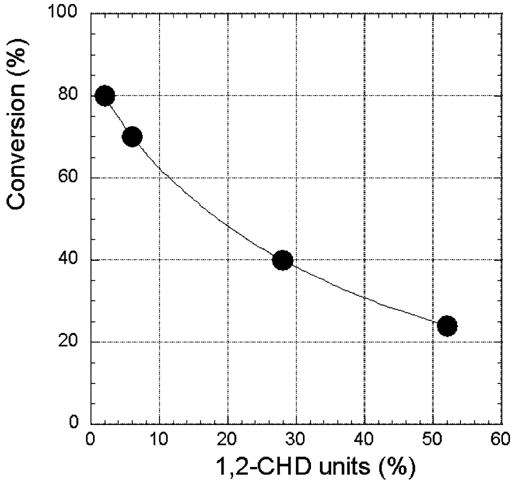


Figure 1. Relationship between 1,2-CHD units (%) in the polymer chain and the conversion (%) for dehydrogenation of PCHD-1 to -4 with DDQ in DCBz at room temperature (ca. 25 °C) for 72 h. [polymer]/[solvent] = 0.2 g/20 mL. [CHD units]$_0$ /[DDQ]$_0$ = 1/4.

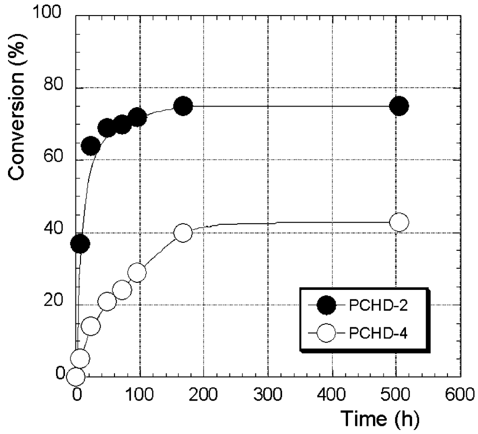
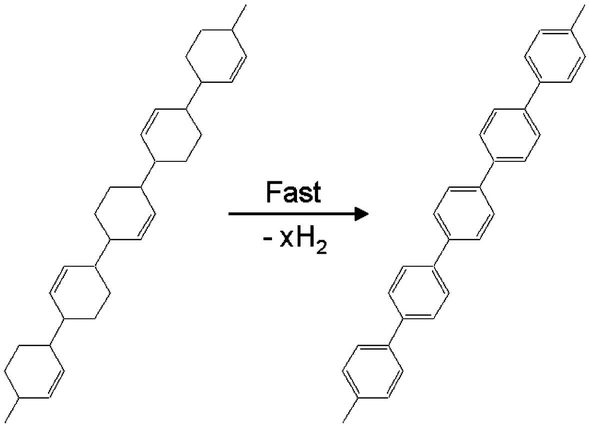


Figure 2. Time−conversion curves for the dehydrogenation of PCHD-2 and -4 with DDQ in DCBz at room temperature (ca. 25 °C). [polymer]/[solvent] = 0.2 g/20 mL. [CHD units]$_0$ /[DDQ]$_0$ = 1/4.

Scheme 4



(a) All 1,4-CHD units sequence (b) All 1,4-Ph units sequence

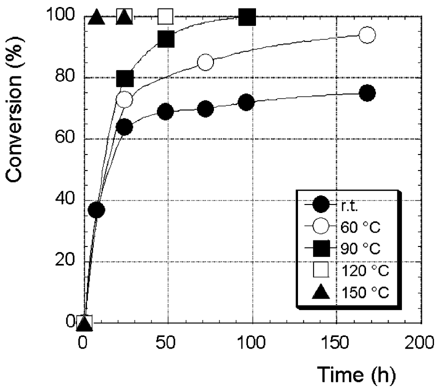


Figure 3. Effect of the reaction temperature on the dehydrogenation of PCHD-2 (1,2-CHD/1,4-CHD units = 6/94) with DDQ in DCBz. [polymer]/[solvent] = 0.2 g/20 mL. [CHD units]$_0$ /[DDQ]$_0$ = 1/4.

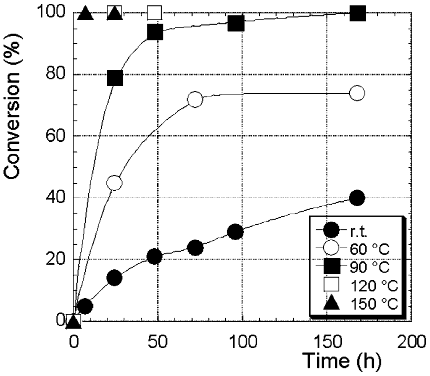


Figure 4. Effect of the reaction temperature on the dehydrogenation of PCHD-4 (1,2-CHD/1,4-CHD units = 52/48) with DDQ in DCBz. [polymer]/[solvent] = 0.2 g/20 mL. [CHD units]$_0$ /[DDQ]$_0$ = 1/4.

The dehydrogenation of PCHD-2 proceeded relatively easily compared with that of PCHD-4. However, the dehydrogenation of PCHD-2 and PCHD-4 appear to be suspended after 168 h. The conversion of PCHD-2 remained at below 80% after 504 h, and was below 50% for PCHD-4.[31] These results show that the rate of dehydrogenation depends on the polymer chain structure. Specifically, the rate of dehydrogenation is fast on a long sequence of 1,4-CHD units (e.g., Scheme 4), while the rate is relatively slow in the case of a 1,2-CHD/1,4-CHD (≈1/1) unit sequence (e.g., Scheme 5).

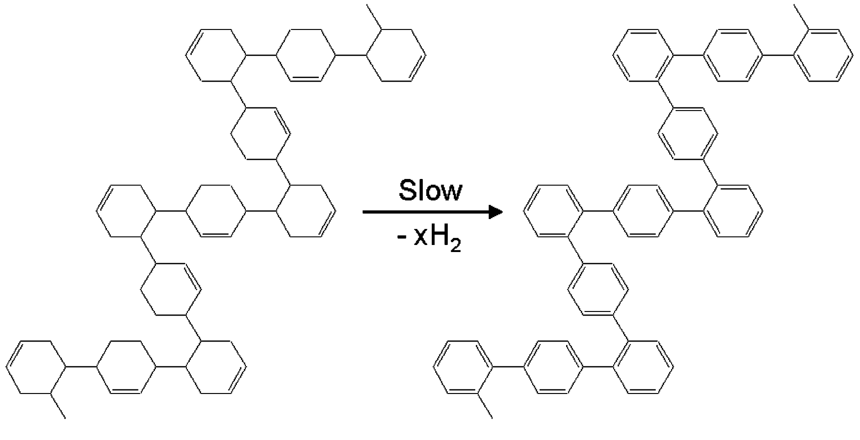
For PCHD polymer chains, the insetion of 1,2-CHD units seems to prevent the movement of the polymer chain by producing large steric hindrances. The steric hindrance effect in the molecular structure of PCHD should be considered as an explanation for these results. Steric hindrance effects for a long sequence of 1,4-CHD units, such as PCHD-2, do not seem to be so severe (Scheme 4a). On the other hand, the polymer chain is crowded between 1,2-CHD/1,4-CHD (≈1/1) units (Scheme 5a), and for this reason, the approach of DDQ molecules to the PCHD-4 polymer chain would be difficult.

Therefore, it was strongly suggested that an improvement of the reaction conditions would be required to obtain completely dehydrogenated PCHD.

Effect of the Reaction Temperature on Dehydrogenation. As shown in Figure 2, the dehydrogenation of PCHD-2 and PCHD-4 by DDQ did not progress completely at room temperature. From those results, it was determined that the low reactivity of DDQ for PCHD, and/or low solubility of the dehydrogenated polymers, prevented the complete dehydrogenation of the PCHDs. The dehydrogenation of PCHD-2 and PCHD-4 was then performed under various reaction temperatures, and the results are shown in Figures 3 and 4.

Unexpectedly, complete dehydrogenation was somewhat difficult for not only PCHD-4 having a 1,2-CHD/1,4-CHD (≈1/1) unit sequence (Scheme 5a), but also for PCHD-2 having a long 1,4-CHD unit sequence (Scheme 4a). Some portion of undehydrogenated CHD units remained in the polymer chain for each PCHD when the reaction temperature was lower than 60 °C. Accordingly, the dehydrogenation of PCHD was carried out at a higher reaction temperature. When the reaction temperature was higher than 90 °C, complete dehydrogenation

Scheme 5



(a) An 1,2-CHD/1,4-CHD units sequence (b) An 1,2-Ph/1,4-Ph units sequence

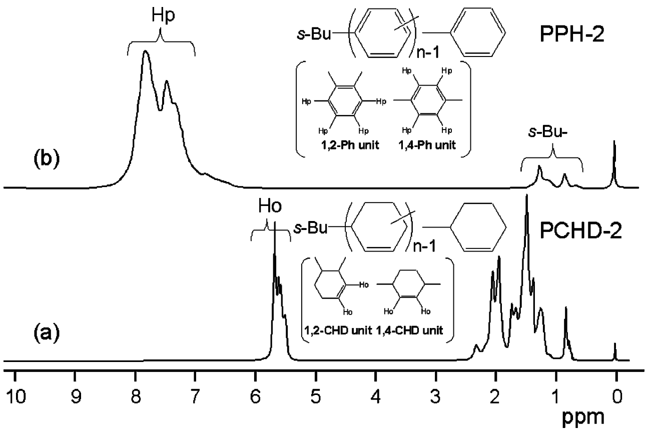


Figure 5. ^{1}H NMR spectra of PCHD homopolymer and its completely dehydrogenated polymer (PPH homopolymer): (a) PCHD-2 (1,2-CHD/1,4-CHD units = 6/94) in a 3.0 wt % solution of $CDCl_3$ at 50 °C; (b) PPH-2 (1,2-Ph/1,4-Ph units = 6/94) in a 3.0 wt % solution of DMF-d_7 at 50 °C.

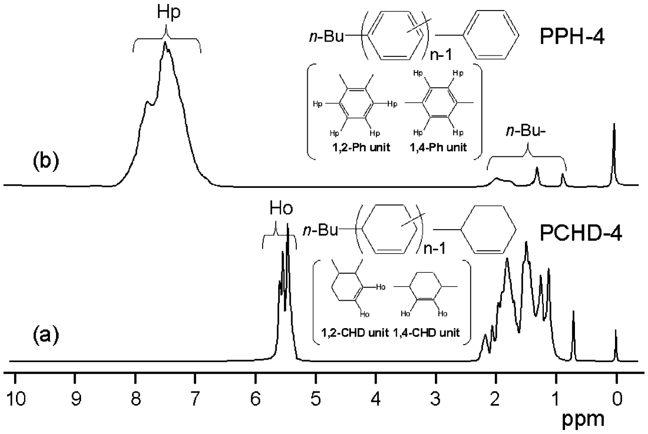


Figure 6. ^{1}H NMR spectra of PCHD homopolymer and its completely dehydrogenated polymer (PPH homopolymer): (a) PCHD-4 (1,2-CHD/1,4-CHD units = 52/48) in a 3.0 wt % solution of $CDCl_3$ at 50 °C; (b) PPH-2 (1,2-Ph/1,4-Ph units = 52/48) in a 3.0 wt % solution of DMF-d_7 at 50 °C.

Table 2. List of Obtained Polyphenylens[a]

polymer no.	original polymer	conversion (%)[b]	M_n[c,d]	M_w/M_n[c]	1,2-Ph unit/1,4-Ph unit (%)[e]
PPH-1	PCHD-1	100	1010[c] (*1390*)[d]	1.63	2/98
PPH-2	PCHD-2	100	1410[c] (2210)[d]	1.25	6/94
PPH-3	PCHD-3	100	1550[c] (1710)[d]	1.29	28/72
PPH-4	PCHD-4	100	1310[c] (2090)[d]	1.20	52/48

[a] Dehydrogenation was carried out in 1,2-dichlorobenzene (20 mL) at 90 °C for 96 h (PPH-1 and -2) and 168 h (PPH-3 and -4). [polymer]/[solvent] = 0.2 g/20 mL. $[\text{CHD units}]_0/[\text{2,3-dichloro-5,6-dicyano-1,4-benzoquinone}]_0 = 1/4$. [b] Estimated by ^{1}H NMR. [c] Estimated by GPC, using polystyrene as standard. [polymer]/[THF] = 0.005 g/5.0 mL. [d] Estimated by ^{1}H NMR. [e] Estimated from ^{1}H NMR spectra of original polymers.

Table 3. Difference of Solubility between Poly(1,3-cyclohexadiene) and Polyphenylene[a]

polymer no. [original polymer/ obtained polymer]	TCBz	$CHCl_3$	THF	DMF	acetone	EtOAc	MeOH
PCHD-1	A	A	A	C	C	C	C
PPH-1	C	B	B	B	B	C	C
PCHD-2	A	A	A	C	C	C	C
PPH-2	C	B	B	A	B	C	C
PCHD-3	A	A	A	C	C	C	C
PPH-3	C	B	A	A	B	B	C
PCHD-4	A	A	A	C	C	C	C
PPH-4	C	B	A	A	B	B	C

[a] [polymer]/[solvent] = 0.03 g/1.0 g. Key: A, soluble; B, partially soluble; C, insoluble.

of PCHD-2 and PCHD-4 proceeded and successfully yielded soluble PPH homopolymers for the first time.

The ^{1}H NMR spectra of the polymers were remarkably changed after dehydrogenation, as shown in Figures 5 and 6. These spectra clearly confirmed the complete dehydrogenation of PCHD (PCHD-2 and PCHD-4), and the polymer chain structure of the obtained PPH (PPH-2 and PPH-4). The olefinic signals of PCHD (Ho at ca. 5.7 ppm) completely disappeared and the aromatic signals of PPH (Hp at ca. 7.5 ppm) definitively appeared for each polymer. At the same time, the methylene (CH_2) and methine (CH) signals of PCHD (from 1.0 to 2.5 ppm) completely disappeared, exclusive of those on *sec*- and *n*-butyl groups that were residual from the *sec*- and *n*-butyllithium initiators used for anionic polymerization of 1,3-CHD. In addition, as shown in Figures 5b and 6b, the observed Hp signals for each PPH are not simple signals; some torsions and/or bends seem to exist in the PPH-2 and PPH-4 polymer chains.

The reaction temperature was therefore regarded as one of the dominating factors for the dehydrogenation of PCHD containing 1,2-CHD units and 1,4-CHD units in the main chain. Subsequently, the dehydrogenation of PCHD-1 and PCHD-3 was performed with DDQ at 90 °C in order to compare the properties of PPH having various 1,2-Ph/1,4-Ph molar ratios. The CHD units in PCHD-1 and PCHD-3 were completely converted to Ph units under these reaction conditions. Surprisingly, all of the completely dehydrogenated polymers obtained, even the polymer containing a high content of 1,4-Ph units (e.g., PPH-1 and PPH-2), were soluble in THF or DMF. Accordingly, accurate ^{1}H NMR and GPC analyses were possible for each of the PPH homopolymers. The results obtained are summarized in Table 2.

For the dehydrogenation reactions shown in Table 2, each PCHD homopolymer produced the corresponding PPH homopolymer with a quantitative yield. 100% conversion from CHD units to Ph units was observed for each polymer. In addition, the M_n and M_w/M_n for PPH-1 to -4 are not so different from the original polymers (PCHD-1 to -4). This suggested that unfavorable side reactions (e.g., decomposition of the polymer chain, or cross-linking) did not occur during the dehydrogenation reaction.

Solubility of PPH Homopolymers. It is well-known that PPHs such as PPP are believed to be insoluble or have extremely low solubility in organic solvents, due to the rigid crystalline polymer chain. *PPP (poly(1,4-Ph))becomes insoluble, infusible, and intractable at more than 6 repeat units.*[32,33] *Although various attempts to obtain processable PPHs have been studied,*[34] *to date,* this is the major problem in preventing the application of PP*H* consisting only of 1,4-Ph units. Therefore, the most important challenge in the improvement of PPP is the synthesis of soluble PPH homopolymers.

In contrast, PPH-1 to -4 are soluble in THF, DMF, and acetone. Therefore, 1,2-Ph units in the polymer chain are regarded as the key molecular structure imparting solubility to PPH homopolymers. Although PPH-1 and PPH-2 contain only small amounts of 1,2-Ph units, these polymers can be soluble in polar solvents such as THF, DMF, and acetone. This is an unusual property for PHH homopolymers. Accordingly, the solubility of PPH-1 to -4 at room temperature was examined not only for nonpolar solvents, but also for polar solvents ([polymer]/[solvent] = 0.03 g/1.0 g). The results obtained are summarized in Table 3.

Of particular note, is that the solubility of each polymer is dramatically changed after dehydrogenation. The original

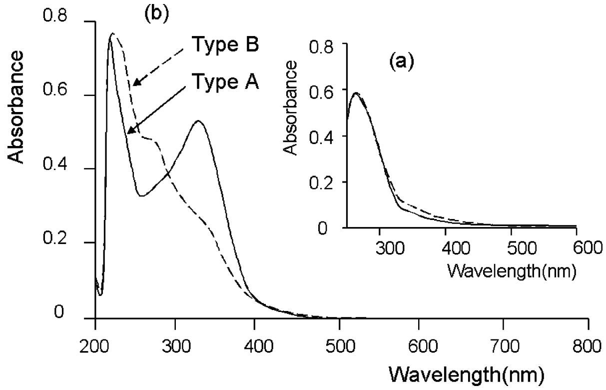


Figure 7. UV/vis spectra of original polymers and completely dehydrogenated polymers: (a) PCHD-2 (solid line) and PCHD-4 (broken line) in THF. [polymer]/[solvent] = 0.1 mg/10 mL. (b) PPH-2 (Type A, solid line) and PPH-4 (Type B, broken line) in THF. [polymer]/[solvent] = 0.1 mg/10 mL.

polymers (PCHD-1 to -4) are mainly soluble in nonpolar solvents such as TCBz and CHCl$_3$. Thus, PCHDs are regarded as nonpolar macromolecules. THF is a common solvent for both groups of polymers (i.e., PCHD-1 to -4 and PPH-1 to -4). On the other hand, the completely dehydrogenated polymers (PPH-1 to -4) are soluble in polar solvents such as DMF and acetone. Therefore, the PPH homopolymers composed of 1,2-Ph units and 1,4-Ph units *appear* to be polar macromolecules, and the conversion *of polarity* occurs during the dehydrogenation process.

Fundamentally, the benzene (phenylene) ring is thought to be a slightly polar molecule (benzene is somewhat soluble in H$_2$O). For PPH-1 to -4, the 1,2-Ph units seem to impart some torsions and/or bends to the polymer chain, and prevents the crystallization of PPH consisting of *slightly* polar monomer units. This is considered to be the reason PPH-1 to -4 are soluble in polar solvents.

UV/Vis Absorption and Fluorescence Properties of PPH Homopolymers. To determine the optical properties of PPH-1 to -4 as conjugated polymers, UV/vis spectroscopic measurements were performed for the original polymers (PCHD-1 to -4) and the completely dehydrogenated polymers (PPH-1 to -4).

As expected, PCHD-1 to -4 showed almost the same UV/vis spectra, with an absorption band appearing in the region at approximately 270 nm. Representative UV spectra (PCHD-2 and PCHD-4) are given in Figure 7a. In contrast, PPH-1 to -4 showed two interesting types of UV/vis spectra, as shown in Figure 7b. PPH-1 and PPH-2 exhibited similar UV/vis spectra (type A in Figure 7b), and PPH-3 and PPH-4 showed similar UV/vis spectra (type B in Figure 7b). However, there was a remarkable difference between the type A and type B spectra.

The type A spectra exhibits a new absorption band in the region from 260 to 400 nm, and the maximum point ($\lambda^{ab}{}_{max}$) on each new absorption was at approximately 330 nm. On the other hand, the type B spectrum shows two inflection points at approximately 280 and 350 nm. The absorption at 330 nm in the type A spectrum was stronger than that of the type B spectrum. Consequently, the absorption in the region from 310 to 380 nm can be considered to be caused by the 1,4-Ph unit in the polymer chain of PPH homopolymer. In addition, the intensity of the absorption seems to depend on the amount and length of the 1,4-Ph unit sequences. That is, a strong absorption is considered to be caused by a long sequences of 1,4-Ph units (Scheme 4b). A weak absorption is considered to be caused by small amounts of short 1,4-Ph unit sequences (Scheme 5b).

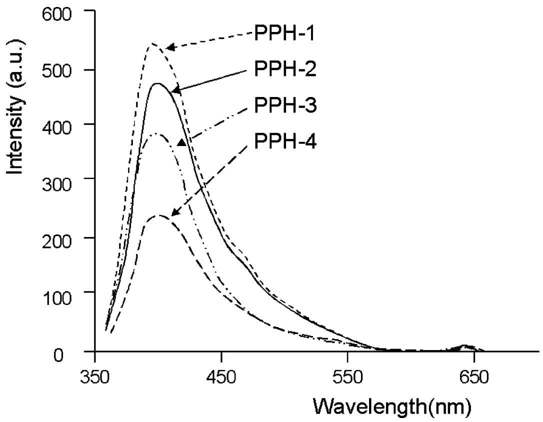


Figure 8. Fluorescence spectra of complete dehydrogenated PCHD homopolymers (PPH homopolymers) in THF. [polymer]/[solvent] = 0.1 mg/10 mL. Excitation wavelength is 330 nm.

Subsequently, to clarify the fluorescence properties of PPH homopolymers, fluorescence analysis was performed for PPH-1 to -4 at an excitation wavelength of 330 nm. The fluorescence spectra obtained are provided in Figure 8.

The emission maximum ($\lambda^{em}{}_{max}$) for each spectrum was observed in the region from 390 to 410 nm, and the emission maximum of the fluorescence spectra was found to decrease as the molar ratio of 1,2-Ph units in the polymer chain increased. Therefore, each PPH homopolymer has fluorescence properties, and the resultant fluorescence spectra corresponds to the emission caused by 1,4-Ph units in the polymer chain. In addition, the molar ratio of the 1,2-Ph/1,4-Ph units is reflected in the emission intensity of the fluorescence spectra.

Conclusion

Soluble PPH homopolymers with controlled polymer chain structure were synthesized for the first time by complete dehydrogenation of PCHD homopolymers with a structure consisting of a main chain formed by 1,2-CHD and 1,4-CHD units. The PPH homopolymers obtained were composed of 1,2-Ph and 1,4-Ph units. The reactivity for dehydrogenation of PCHD with DDQ strongly depends on the polymer chain structure. The rate of dehydrogenation is fast on a long sequence of 1,4-CHD units, while it is considerably impeded by the presence of 1,2-CHD units in the polymer chain. Complete dehydrogenation is somewhat difficult to achieve, not only for a 1,2-CHD/1,4-CHD ($\approx$1/1) unit sequence, but also for a long sequence of 1,4-CHD units. When the reaction temperature was higher than 90 °C, complete dehydrogenation of PCHD proceeded successfully and yielded soluble PPH homopolymers. These polymers are soluble in polar solvents such as THF, DMF, and acetone. PPH homopolymers composed of 1,2-Ph units and 1,4-Ph units *appear* to be polar macromolecules, and the conversion *of polarity* occurs during the dehydrogenation process. The UV/vis and fluorescence spectra clearly indicate the nature of a conjugated PPH homopolymer. The information that has been obtained concerning soluble PPH homopolymers should accelerate the development of new high performance materials containing six-membered hydrocarbon rings as a key molecular structure.

References and Notes

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