Soluble High Molecular Weight Poly(*p*-phenylene) as a Charge-Transfer Complex

Itaru Natori,* Shizue Natori, and Kenji Ogino

Department of Organic and Polymer Materials Chemistry, Tokyo University of Agriculture and Technology, 2-24-16 Naka-chou, Koganei-city, Tokyo 184-8588, Japan

Received November 14, 2008; Revised Manuscript Received January 21, 2009

ABSTRACT: Soluble high molecular weight poly(*p*-phenylene) (PPP), in the form of a charge-transfer complex, was synthesized by complete dehydrogenation of poly(1,3-cyclohexadiene) (PCHD) with excess tetrachloro-1,2-(*o*)-benzoquinone (TOQ). The yield of the PPP-TOQ complex increased as the molecular weight of the original PCHD increased. The addition of TOQ to the PPP polymer chain occurred mainly at the 1,4-phenylene (Ph) units. The PPP-TOQ complex showed good solubility in tetrahydrofuran; the solubility was not limited by the length of the 1,4-Ph sequence. The formation of the PPP-TOQ complex effectively suppressed crystallization of PPP due to the decrease in $\pi-\pi$ intermolecular interactions in the PPP molecules, and had a significant effect on π-orbital conjugation in PPP.

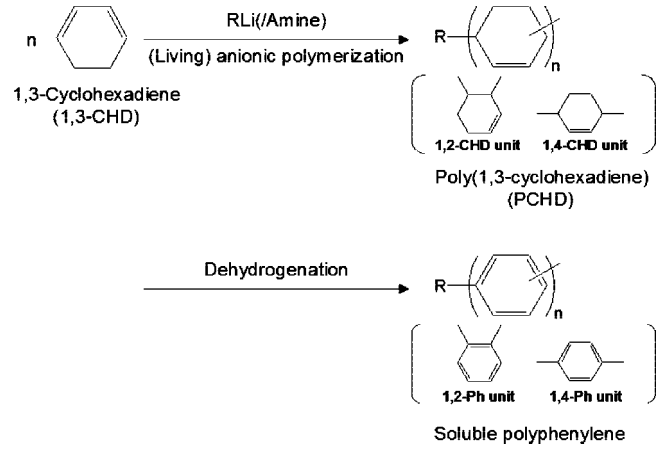
Introduction

Poly(*p*-phenylene) (PPP), also known as poly(1,4-phenylene), is recognized as a useful high-performance polymer due to its thermal[1] and chemical[2] stability and its electrical and optoelectronic properties.[3−5] The source of these properties is thought to be π-orbital conjugation in the polymer chain structure based on regioregular repetition of the 1,4-phenylene (Ph) unit. However, the degree of crystallization of the polymer chain increases with the length of the sequence of 1,4-Ph units, with the polymer becoming insoluble, infusible, and intractable at more than 6 repeat units.[1,6] This serious problem has been an obstacle to further study on the application of PPP.

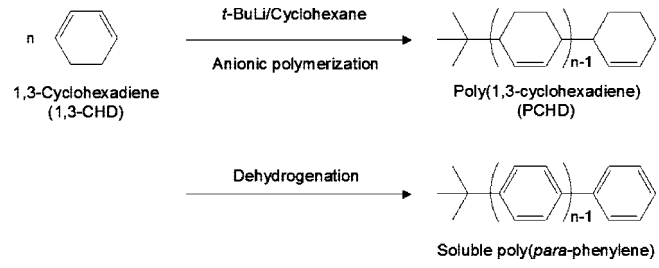
A variety of approaches have been attempted in the challenge to improve the solubility of PPP. In particular, dehydrogenation of poly(1,3-cyclohexadiene) (PCHD) and its derivatives, which are obtained by anionic polymerization, is considered the most promising route to the synthesis of soluble PPP. François et al. synthesized polystyrene (PSt)-PCHD block copolymers and subjected them to dehydrogenation with tetrachloro-1,4-(*p*)-benzoquinone (TCQ) to give PSt-PPP block copolymers, which are soluble in organic solvents due to bonding of the PSt block.[7−11] Subsequently, we demonstrated through complete dehydrogenation of PCHD with a well-controlled polymer chain structure that the introduction of 1,2-Ph units into the 1,4-Ph sequences dramatically improved the solubility of PPP (Scheme 1).[12,13] We further reported that the addition of a *tert*-butyl group to the polymer chain-end effectively improved the solubility of PPP obtained by complete dehydrogenation of PCHD consisting of only 1,4-cyclohexadiene (CHD) units, with the result that PPP with up to 16 repeat units became soluble in organic solvents (Scheme 2).[14] All of these studies concerning soluble PPP have been based on same concept; that is, suppression of crystallization of the polymer chain.[7−14] Although the concept is thought to be correct, the methods reported have been insufficient in terms of obtaining soluble high molecular weight PPP.

We recently tried to find a new method for suppressing crystallization in PPP, and we noticed that the formation of a charge-transfer complex consisting of PPP and an electron acceptor had potential as an effective method for preventing crystallization of PPP. In this paper, we report the first successful example of soluble high molecular weight PPP, in the form of a charge-transfer complex consisting of PPP (an electron donor) and tetrachloro-1,2-(*o*)-benzoquinone (TOQ, an electron acceptor).

Scheme 1. Synthesis of PCHD, Consisting of 1,2-CHD and 1,4-CHD Units, and the Corresponding Dehydrogenated Polymers



Scheme 2. Synthesis of PCHD Containing only 1,4-CHD Units, and the Corresponding Dehydrogenated Polymers



Experimental Section

Materials. 1,3-Cyclohexadiene (1,3-CHD, 97%), cyclohexane (≥99.5%), and toluene (≥99.8%) were refluxed over calcium hydride (CaH_2) and then distilled under dry argon. TOQ was dried under reduced pressure in dry argon. *tert*-Butyllithium (*t*-BuLi; 1.70 mol/L in *n*-pentane), *p*-quaterphenyl (≥99.0%), 1,2-dichlorobenzene (DCBz), methanol (MeOH), ethanol (EtOH), and 2-propanol (IPA)

* Corresponding author. E-mail: itaru_natori@yahoo.co.jp.

10.1021/ma802561j CCC: $40.75
Published on Web 02/24/2009

were used without further purification. All reagents were purchased from Aldrich.

Anionic Polymerization of 1,3-CHD. A well-dried 50 mL Schlenk tube was purged with dry argon, and toluene (or cyclohexane) and *t*-BuLi were added at room temperature (*ca.* 25 °C) using syringes. 1,3-CHD was then added to the solution with a syringe, and the reaction mixture was magnetically stirred under dry argon at room temperature. After polymerization, in order to terminate the reaction, dry MeOH was added in an equimolar amount to the total 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 separated by filtration. The product was dried under reduced pressure in dry argon at room temperature for 24 h to give the polymer in the form of a white powdery substance.

Dehydrogenation of PCHD. 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. Dry DCBz (20 mL) was added with a syringe, and the mixture was stirred until the polymer was completely dissolved. TOQ (10 mmol, 400% with respect to CHD units) was added under dry argon at room temperature and the reaction mixture was magnetically stirred under dry argon at 90 °C for 96 h. After dehydrogenation, the reaction mixture was poured into a large volume of IPA to precipitate the product, which was then separated by filtration. The product was washed with excess EtOH and dried under reduced pressure in dry argon at room temperature for 24 h to give a dark red-brown powdery compound.

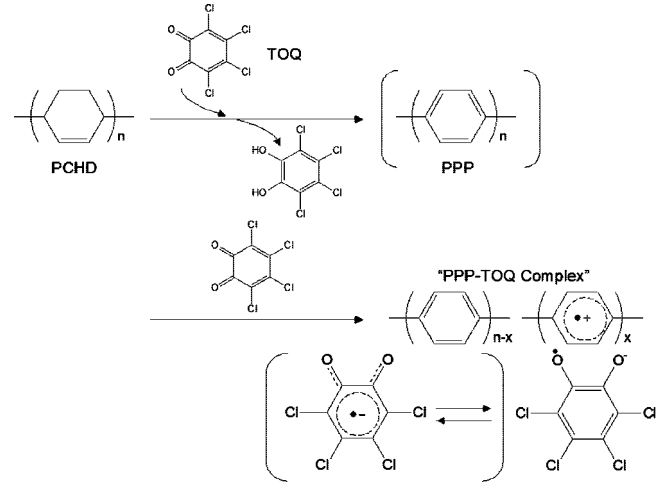
Measurements. The number average molecular weight (M_n), weight average molecular weight (M_w), and polydispersity index (PDI, M_w/M_n) were determined using gel permeation chromatography (GPC) apparatus equipped with a differential refractometer detector using a Shimadzu Shim-pack GPC-80 M column (length 300 mm, diameter 8 mm, effective molecular weight range 100−4 000 000) at 40 °C. Tetrahydrofuran (THF) was used as the eluent, and the flow rate was 1.0 mL/min. A molecular weight calibration curve was obtained using PSt standards. The apparent molecular weights obtained are quite close to absolute molecular weights determined by size exclusion chromatography coupled with a multiangle laser light scattering photometer (SEC-MALS).[15] ^{1}H NMR spectra of the polymers were measured in deuterated chloroform ($CDCl_3$) or THF (THF-d_8) at 500 MHz using a JEOL ECA500 spectrometer. UV/vis spectroscopic measurements were performed in THF using a Shimadzu UV-3101 PC with quartz cells. Photoluminescence (PL) spectra of the polymers were measured in THF using a Shimadzu RF-5300 PC with quartz cells. The infrared (IR) spectroscopic measurements were performed in KBr using a JASCO FT/IR-4100 type A spectrometer. Elemental analysis of chlorine (Cl) was performed using a combustion ion chromatography (a Shimazu HIC-10A ion chromatograph coupled with a Mitsubishi AQF-100 automation combustion system).

Results and Discussion

Charge-Transfer Complex Formation. In a previous paper,[16] we studied the reactivity of quinones, which are strong electron acceptors, in the dehydrogenation of PCHD with a controlled polymer chain structure. It was found that the order of reactivity was TOQ > 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) > TCQ; in other words, TOQ was the strongest electron acceptor among these quinones. In addition, it has been reported that aromatic polymers (e.g., PSt, poly(*N*-vinylcarbazole), and polyaniline) and TOQ readily form charge-transfer complexes.[17−21] Therefore, it was expected that dehydrogenation of PCHD with excess TOQ would result in the formation of a PPP-TOQ charge-transfer complex (Scheme 3). In order to confirm this, the preparation and dehydrogenation of PCHD were carried out as follows.

Preparation of Prepolymer PCHD. In recent work, we modified the anionic polymerization reaction of 1,3-CHD with *t*-BuLi as an initiator.[22,23] In this polymerization system, the type of solvent used affected the microstructure of the polymer chain. When polymerization was carried out in an aromatic hydrocarbon solvent (e.g., toluene) at room temperature (ca. 25 °C), the molar ratio of 1,2-CHD to 1,4-CHD units was around 5/95.[23] PCHD containing only 1,4-CHD units was obtained using an aliphatic hydrocarbon solvent such as cyclohexane at room temperature.[22,24] On the basis of this information, two types of PCHD with different 1,2-CHD/1,4-CHD unit molar ratios were prepared by anionic polymerization of 1,3-CHD using *t*-BuLi as an initiator. The results obtained are shown in Table 1.

Scheme 3. Formation of PPP-TOQ Complex



The first type of PCHD (shown as PCHD-1 to PCHD-4 in Table 1), which was obtained by anionic polymerization in toluene, had a polymer chain consisting of 1,2-CHD and 1,4-CHD units. The M_n of these polymers was in the range 1390−14800, and the 1,2-CHD/1,4-CHD unit molar ratio was around 5/95. The second type of PCHD (PCHD-5 to PCHD-8 in Table 1) was synthesized by anionic polymerization in cyclohexane and contained only 1,4-CHD units. The M_n of these polymers was in the range 1240−13200. These two types of PCHD were thought to be appropriate prepolymers for the synthesis of soluble high molecular weight PPP in the form of a charge-transfer complex.

Dehydrogenation of PCHD with TOQ. Dehydrogenation of the two types of PCHD with different M_n values was performed using excess TOQ (CHD units/TOQ = 1/4) under dry argon at 90 °C for 96 h (a typical reaction condition to obtain the completely dehydrogenated PCHD).[12−14,16] After dehydrogenation, a dark red-brown powdery compound was obtained. In this reaction system, the yields of the products (PPP-1 to PPP-8) were greater than 100 wt % (165−292 wt %), which demonstrates the formation of the PPP-TOQ charge-transfer complex (Scheme 3). The results obtained are summarized in Table 2.

For both types of PCHD, the yields of the products (PPP-1 to −4 and PPP-5 to −8) increased as the M_n of the original PCHD increased. In addition, for PCHD with similar M_n values (e.g., PCHD-1 and PCHD-5), the yield of the product obtained from PCHD containing only 1,4-CHD units (PPP-5) appears to be somewhat higher than that of the product obtained from PCHD containing 1,2-CHD and 1,4-CHD units (PPP-1).

In order to determine the conversion from CHD units to Ph units in this dehydrogenation reaction, ^{1}H NMR measurements were carried out on PCHD and the dehydrogenation products.[12,13,16] As shown in Figure 1, the olefinic signals of PCHD (H_o at ca. 5.7 ppm) completely disappeared and the aromatic

Table 1. Poly(1,3-cyclohexadiene) Prepolymers[a]

no.	$[1,3\text{-CHD}]_0/[\text{Li}]_0$	solvent	polymerization time (h)	M_n	PDI	1,2-/1,4-CHD units (mol %)[b]	yield (wt %)
PCHD-1	16	toluene	2	1390	1.21	5/95	100
PCHD-2	82	toluene	4	7120	1.32	6/94	100
PCHD-3	135	toluene	4	12300	1.67	6/94	100
PCHD-4	250	toluene	24	14800	1.72	5/95	88
PCHD-5	16	cyclohexane	2	1240	1.20	0/100	100
PCHD-6	74	cyclohexane	4	4810	1.30	0/100	89
PCHD-7	130	cyclohexane	4	9620	1.38	0/100	82
PCHD-8	200	cyclohexane	24	13200	1.57	0/100	78

[a] Anionic polymerization of 1,3-CHD with *t*-BuLi was carried out under dry argon at room temperature. [b] Estimated by ^{1}H NMR.[12,13]

Table 2. Dehydrogenation of Poly(1,3-cyclohexadiene) with Tetrachloro-1,2(*o*)-benzoquinone[a]

no.	PCHD prepolymer	yield[b] (wt %)	solubility[c]	M_n	PDI	1,2-Ph/1,4-Ph units (mol %)[d]
PPP-1	PCHD-1	165	soluble	2370	1.29	5/95
PPP-2	PCHD-2	203	soluble	6550	1.69	6/94
PPP-3	PCHD-3	243	soluble	7710	1.94	6/94
PPP-4	PCHD-4	269	soluble	8090	1.98	5/95
PPP-5	PCHD-5	196	soluble	2280	1.26	0/100
PPP-6	PCHD-6	213	soluble	4620	1.66	0/100
PPP-7	PCHD-7	262	soluble	7650	1.70	0/100
PPP-8	PCHD-8	292	soluble	8520	1.88	0/100

[a] Dehydrogenation of PCHD with TOQ was carried out under dry argon at 90 °C for 96 h. [b] Product (g)/PCHD (g)) × 100. [c] Sample/THF = 30.0 mg/5.00 mL. [d] Estimated by ^{1}H NMR of PCHD prepolymer.[12,13]

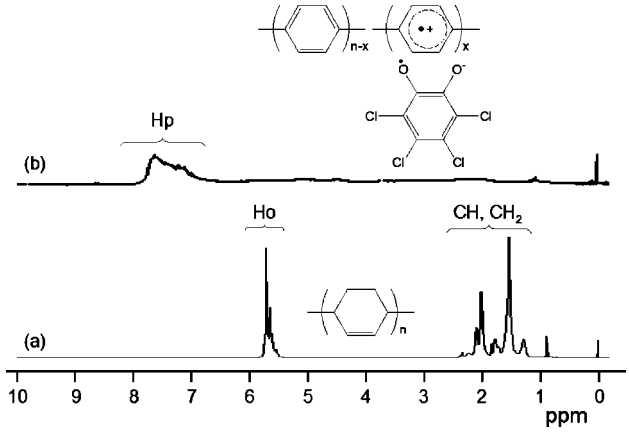


Figure 1. ^{1}H NMR spectra of PCHD and dehydrogenated polymer (PPP-TOQ complexe): (a) PCHD-8 (1,2-CHD/1,4-CHD units = 0/100) in a 3.0 wt % solution of $CDCl_3$ at 50 °C; (b) PPP-8 (1,2-Ph/1,4-Ph units = 0/100) in a 3.0 wt % solution of THF-d_8 at 50 °C.

signals of PPP (H_p at ca. 7.5 ppm) appeared definitively for each polymer. At the same time, the methylene (CH_2) and methine (CH) signals of PCHD (from 1.0 to 2.5 ppm) disappeared. Thus, it was confirmed that the conversion was 100%, and that the product obtained in the dehydrogenation reaction was the PPP-TOQ complex.

As shown in Figure 2, some obvious differences were observed in the IR spectra of the PPP-TOQ complex (PPP-6, Figure 2a) and *p*-quaterphenyl (a neutral PPP model compound, Figure 2b). New absorption peaks were observed at ~1560 and ~1050 cm^{-1}, caused by the C═O and C−C(═O)−C bonds in the quinone anion-radical.[25] Other absorption peaks in the IR spectrum of the PPP-TOQ complex were similar to those observed for PPP obtained by Kovacic's method.[26,27]

In order to obtain strong experimental evidence, ^{13}C NMR measurements and elemental analysis of the Cl content were conducted.

Figure 3 shows the typical ^{13}C NMR spectra of the PPP-TOQ complex (PPP-6; Figure 3a) and TOQ (Figure 3b).Verhoeven et al. reported a ^{13}C NMR study of the charge-transfer complexes between TOQ and some aromatic electron donors, and showed that complexation led to a general diamagnetic shift of the ^{13}C NMR signals of the TOQ.[28]

As shown in Figure 3b, the ^{13}C NMR signals of the free TOQ were observed around 169(C1), 141(C3), and 133(C2) ppm.[28] Therefore, the peaks at 133, 131, and 129 ppm in Figure 3a were assigned to the 1, 3, and 2 carbons, respectively, on the TOQ anion-radical as an electron acceptor. The peaks around 140 and 128 ppm seemed to be assigned to the 5 and 4 carbons on the 1,4-Ph unit in the main chain. The peaks around 126 and 122 ppm were likely from the 7 and 6 carbons on the 1,4-Ph radical-cation as an electron donor.

In addition, the result of elemental analysis showed that the Cl content detected in the PPP-TOQ complex (PPP-4) was 33 wt %, which was near to the value calculated from the yield of PPP-4 (Cl; 37 wt %).

The solubility of the PPP-TOQ complexes (PPP-1 to PPP-8) in THF, a typical polar organic solvent, was examined using a sample/THF ratio of 30.0 mg/5.00 mL. In contrast to previously synthesized PPP,[1,6,14] every PPP-TOQ complex obtained (PPP-1 to PPP-8) was readily soluble in THF. The solubility of the PPP-TOQ complexes seemed not to be limited by the length of the 1,4-Ph sequence.

The stability of the PCHD polymer chain during the dehydrogenation process was indicated by the fact that no peaks corresponding to low molecular weight compounds formed by decomposition of the polymer chain were observed in the GPC analysis, although the PDIs of the PPP-TOQ complexes were quite broad compared with those of the PCHD prepolymers due to the formation of the charge-transfer complex. The number of repeating units in the polymer chain appeared to be the same before and after dehydrogenation of PCHD.

In a previous paper,[15] we revealed that the M_n of PCHD estimated by GPC measurements under the analytical conditions described in this paper was close to the absolute molecular weight of PCHD. Therefore, the numbers of 1,4-CHD units in the polymer chains of PCHD-5 to PCHD-8 were determined using the following formula:

$$\text{number of 1,4-CHD units} = (M_n - 58)/80$$

where 58 is the sum of molecular weight of the *tert*-butyl end-group (57) and the other chain end (1), and 80 is the molecular weight of the 1,4-CHD unit. According to this formula, the polymer chains of PCHD-5 to PCHD-8 consisted of 15, 59, 120, and 164 1,4-CHD units, respectively, and thus PPP-5 to PPP-8 consisted of 15, 59, 120, and 164 1,4-Ph units, respectively.

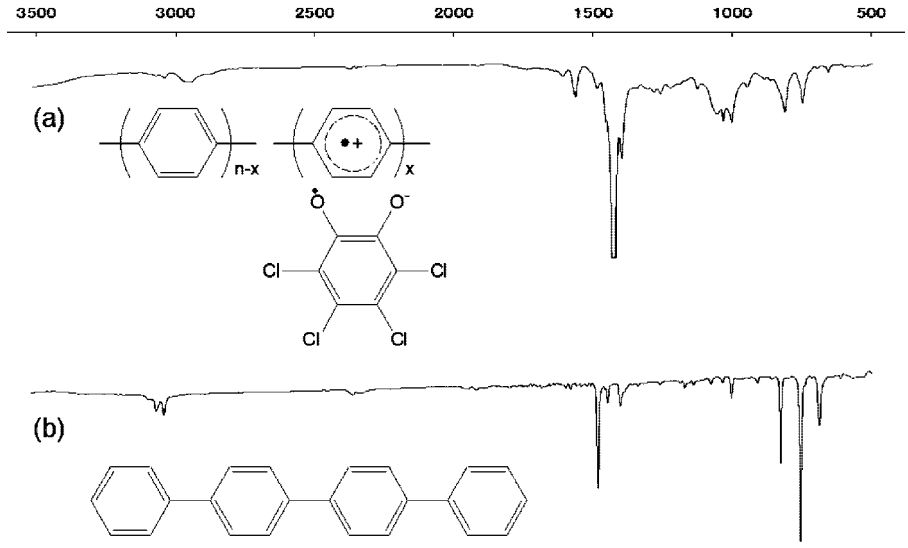


Figure 2. IR spectra of PPP-TOQ complex and *p*-quaterphenyl: (a) PPP-6; (b) *p*-quaterphenyl.

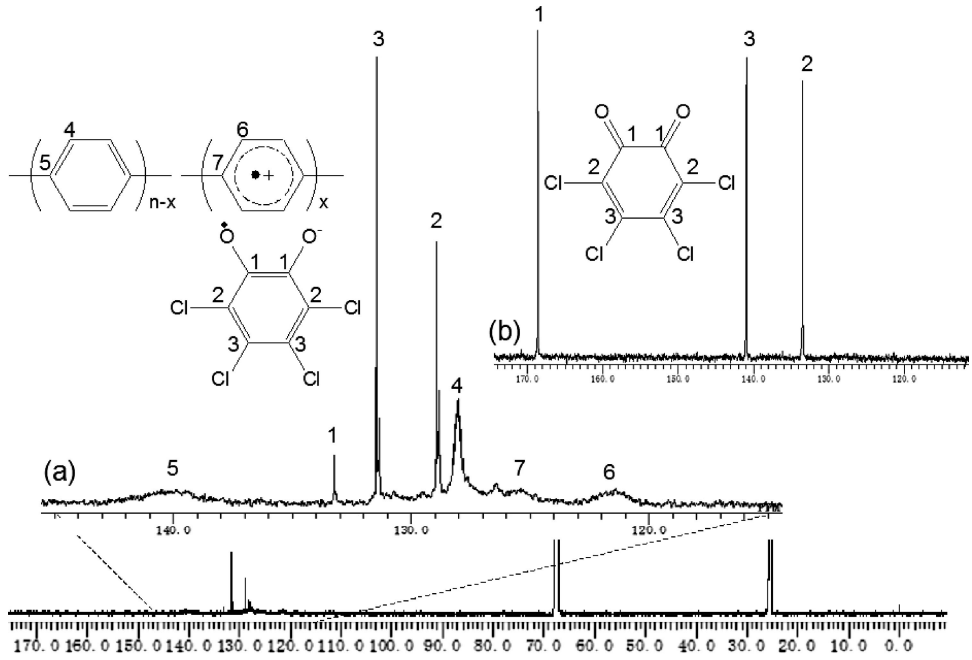


Figure 3. ^{13}C NMR spectra of PPP-TOQ complex and TOQ: (a) PPP-6 in a 7.0 wt % solution of THF-d_8 at 50 °C, (b) TOQ in a 7.0 wt % solution of THF-d_8 at 50 °C.

Although the samples of PPP-6 to PPP-8 had long 1,4-Ph sequences (i.e., higher M_n) and contained only 1,4-Ph units, these PPP-TOQ complexes showed good solubility. The formation of the PPP-TOQ complex is thought to effectively suppress the crystallization of PPP. To our knowledge, the highest molecular weight soluble PPP homopolymer obtained previously consisted of 16 1,4-Ph units.[14] Therefore, PPP-6 to PPP-8 are regarded as the first successful examples of soluble high molecular weight PPP.

Characteristics of the PPP-TOQ Complex. The products obtained in the dehydrogenation reaction of PCHD with excess TOQ are thought to consist of PPP and TOQ arranged as shown in Scheme 3. Therefore, the PPP and TOQ contents (g) in the reaction products can be estimated using the following formulas:

$$\text{PPP (g)} = \text{PCHD (g)} \times 76/80; \quad \text{TOQ (g)} = \text{reaction product (g)} - \text{PPP (g)}$$

$$\text{Ph units (mol)} = \text{PPP (g)}/76; \quad \text{TOQ (mol)} = \text{TOQ (g)}/246$$

where 76 is the molecular weight of the Ph unit, 80 is the molecular weight of the CHD unit, and 246 is the molecular weight of TOQ. Using these formulas, the TOQ/Ph molar ratios (mol/mol) of PPP-1 to PPP-8 were calculated as 0.23, 0.35, 0.48, 0.57, 0.33, 0.39, 0.54, and 0.64, respectively.

Figure 4 shows the relationship between the M_n of the PCHD prepolymers and the TOQ/Ph molar ratios (mol/mol) of the PPP-TOQ complexes. The TOQ/Ph molar ratio increased linearly with the M_n of the PCHD, representing an increase in TOQ content. In addition, for PCHD with similar M_n values, the TOQ/Ph molar ratio of the PPP-TOQ complex obtained from PCHD containing only 1,4-CHD units was greater than that of the complex obtained from PCHD consisting of 1,2-CHD and 1,4-CHD units. Therefore, the addition of TOQ to the PPP polymer chain seems to occur mainly at the 1,4-Ph units. From the viewpoint of the polymer chain structure, it is thought that the degree of electron mobility in the PPP polymer chain increases as the length of the 1,4-Ph sequences increases. As a result, charge (i.e., electron) transfer from PPP to TOQ increases with the length of the 1,4-Ph sequences. Accordingly, PPP with a

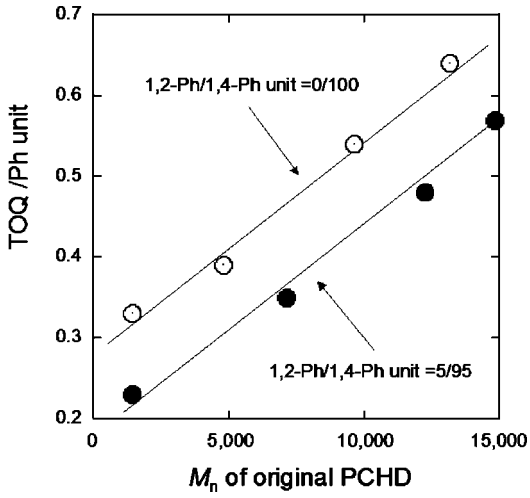


Figure 4. Relationship between the M_n of the PCHD prepolymers and the TOQ/Ph molar ratios (mol/mol) of the PPP-TOQ complexes.

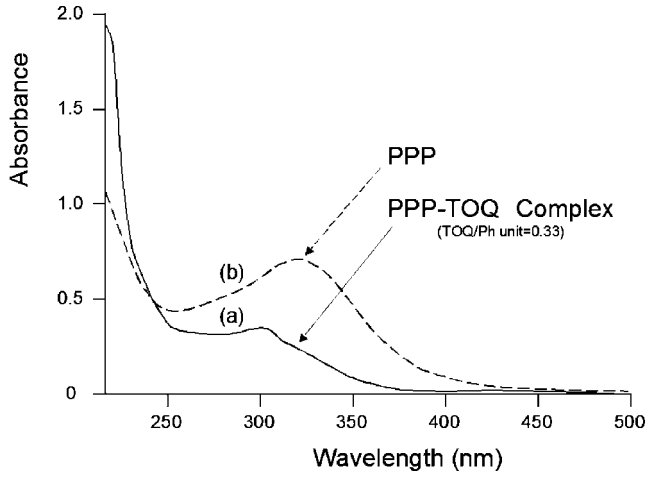


Figure 5. UV/vis spectra of PPP-TOQ complex and PPP: (a) PPP-5; (b) PPP (M_n 1610, PDI 1.26)[29] in THF. Sample/THF = 0.10 mg/10.0 mL.

higher M_n and 1,4-Ph molar ratio is expected to have a higher TOQ/Ph molar ratio.

Figure 5 shows the UV/vis spectra of the PPP-TOQ complex PPP-5 (Figure 5a) and PPP (Figure 5b).[29] The UV/vis absorption intensity of the PPP-TOQ complex was weaker than that of PPP. Furthermore, the maximum absorption for the PPP-TOQ complex was at a shorter wavelength than that of PPP. As we revealed in a previous paper,[12] UV/vis absorption in the region from 310 to 380 nm is caused by the 1,4-Ph unit in the polymer chain, and the intensity of this absorption depends on the amount and length of the 1,4-Ph sequences; in other words, the decrease in the UV/vis absorption in the region from 310 to 380 nm (Figure 5a) is thought to be due to a decrease in the original 1,4-Ph units (i.e., an increase in 1,4-Ph cation-radicals) in the polymer chain associated with the formation of the PPP-TOQ complex (Scheme 3).

The PL spectra of the PPP-TOQ complex PPP-5 and PPP[29] are shown in Figure 6. Although the intensity of the PL emission depends on the amount and length of the 1,4-Ph sequences,[12] in contrast to the UV/vis spectra (Figure 5), the PL emission of the PPP-TOQ complex (Figure 6a) was considerably enhanced compared with that of PPP (Figure 6b). It is thought that the formation of the PPP-TOQ complex effectively suppresses the $\pi-\pi$ intermolecular interactions of the PPP molecules. Under these conditions, PL quenching, caused by the formation of an intermolecular excimer of PPP in THF solution, is not observed.

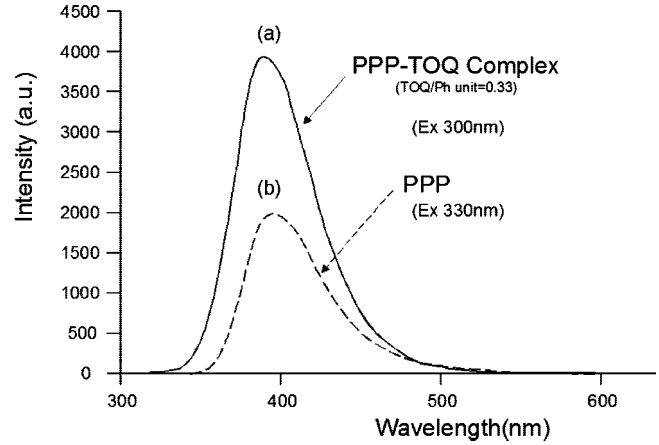


Figure 6. PL spectra of PPP-TOQ complex and PPP: (a) PPP-5; (b) PPP (M_n 1610, PDI 1.26).[29] Sample/THF = 0.10 mg/10.0 mL.

This is thought to be the reason for the strong PL emission of the PPP-TOQ complex.

The results shown in Figures 4−6 suggest that the formation of the PPP-TOQ complex has a considerable effect on π-orbital conjugation in PPP. Thus, as well as solubility, the optical and electrical properties due to π-orbital conjugation are thought to be strongly affected by the formation of the PPP-TOQ complex.

Conclusion

Soluble high molecular weight PPP, in the form of a charge-transfer complex consisting of PPP (an electron donor) and TOQ (an electron acceptor), was synthesized by complete dehydrogenation of PCHD with excess TOQ. The yield of the PPP-TOQ complex increased with the M_n of the PCHD prepolymer. The addition of TOQ to the PPP polymer chain occurred mainly at the 1,4-Ph units in the polymer chain. The PPP-TOQ complex showed good solubility in THF, which was not limited by the length of the 1,4-Ph sequence. The formation of the PPP-TOQ complex effectively suppressed crystallization of PPP due to a decrease in π-π intermolecular interactions in the PPP molecules. The UV/vis absorption of the PPP-TOQ complex was weaker than that of PPP due to the formation of the charge-transfer complex. In contrast, the PL emission of the PPP-TOQ complex was considerably enhanced compared with that of PPP. The formation of the PPP-TOQ complex also has a considerable effect on π-orbital conjugation in PPP. These results concerning soluble high molecular weight PPP should accelerate the development of new high performance materials containing 1,4-Ph units as a key molecular structure.

References and Notes

(1) Kovacic, P.; Jones, M. B. *Chem. Rev.* **1987**, *87*, 357–359.
(2) Ivory, D. M.; Miller, G. G.; Sowa, J. M.; Shacklette, L. W.; Chance, R. R.; Baughman, R. H. *J. Chem. Phys.* **1979**, *71*, 1506–1507.
(3) Grem, G.; Leditzky, G.; Ullrich, B.; Leising, G. *Adv. Mater.* **1992**, *4*, 36–37.
(4) Grem, G.; Leditzky, G.; Ullrich, B.; Leising, G. *Synth. Met.* **1992**, *51*, 383–389.
(5) Grem, G.; Leising, G. *Synth. Met.* **1993**, *57*, 4105–4110.
(6) Ried, W.; Freitag, D. *Angew. Chem., Int. Ed.* **1968**, *7*, 835–902.
(7) Zhong, X. F.; François, B. *Makromol. Chem. Rapid Commun.* **1988**, *9*, 411–416.
(8) Zhong, X. F.; François, B. *Synth. Met.* **1989**, *29*, 35–40.
(9) Zhong, X. F.; François, B *Synth. Met.* **1991**, *41−43*, 955–958.
(10) Zhong, X. F.; François, B. W. *Makromol. Chem.* **1991**, *192*, 2277–2291.
(11) Mignard, E.; Tachon, C.; François, B. *Synth. Met.* **1999**, *102*, 1246–1247.
(12) Natori, I.; Natori, S.; Sato, H. *Macromolecules* **2006**, *39*, 3168–3174.
(13) Natori, I.; Natori, S.; Sato, H. *Polymer* **2006**, *47*, 7123–7130.

(14) Natori, I.; Natori, S.; Sekikawa, H.; Sato, H. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 5223–5231.
(15) Natori, I.; Sato, H. *J. Polym. Sci., Part B: Polym. Phys.* **2006**, *44*, 1442–1452.
(16) Natori, I.; Sato, H. *Polym. Int.* **2007**, *56*, 810–815.
(17) Pillai, P. K. C.; Rashimi, *Polymer* **1979**, *20*, 1245–1249.
(18) Kulshreshtha, Y. K.; Srivastava, A. P. *Polym. J.* **1980**, *12*, 771–775.
(19) Pillai, P. K. C.; Rashimi, *Eur. Polym. J.* **1981**, *17*, 611–614.
(20) Loh, F. C.; Tan, K. L.; Kang, E. T. *Eur. Polym. J.* **1991**, *27*, 1055–1063.
(21) Ponniah, D.; Xavier, F. *Phys. B: Condens. Matter.* **2007**, *392*, 20–28.
(22) Natori, I.; Natori, S. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 3282–3293.
(23) Natori, I.; Natori, S. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 6604–6611.
(24) Quirk, R. P.; You, F.; Zhu, L.; Cheng, S. Z. D. *Macromol. Chem. Phys.* **2003**, *204*, 755–761.
(25) Iida, Y. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 345–349.
(26) Kobryanskii, V. M.; Kotova, S. L. *Synth. Met.* **1997**, *84*, 667–668.
(27) Kobryanskii, V. M.; Kotova, S. L. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 1043–1052.
(28) Prins, I.; Verhoeven, J. W.; De Boer, T. H. J. *Org. Magn. Reson.* **1977**, *9*, 543–545.
(29) PPP was obtained by the complete dehydrogenation of PCHD with DDQ in a previous study (M_n 1610, PDI 1.26).[14]

MA802561J