Preparation of New Main-Chain Type Polyanthraquinones. Chemical Reactivity, Packing Structure, Piezochromism, Conductivity, and Liquid Crystalline and Photonic Properties of the Polymers

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Poly(5,8-dialkoxyanthraquinone-1,4-diyl) P(5,8-OR-1,4-AQ) (R = n-C_6H_{13} through n-$C_{16}H_{33}$), poly(5,8-dihydroxyanthraquinone-1,4-diyl) P(5,8-OH-1,4-AQ), poly(4,8-diaminoanthraquinone-1,5-diyl) P(4,8-NH_2-1,5-AQ), poly(4,8- dihydroxyanthraquinone-1,5-diyl) P(4,8-OH-1,5-AQ), and poly(4,8-dinitroanthraquinone- 1,5-diyl) P(4,8-NO_2-1,5-AQ) were prepared by dehalogenative polycondensation of the corresponding dichloro monomers with a zerovalent nickel complex or copper. They were soluble in organic solvents, and showed number average molecular weights of 3100−8600 and [η] values of 0.10−0.70 dL g^{-1}. P(5,8-OR-1,4-AQ)s and P(4,8-NO_2-1,5-AQ) afforded clear XRD peaks and their packing structures in the solid have been analyzed. P(5,8-OR-1,4-AQ) is considered to take an end-to-end packing mode and this polymer with long alkoxy side chains exhibits smectic and enanthiotropic liquid crystalline behavior and piezochromism. All the polymers were susceptible to electrochemical reduction and a linear correlation held between the reduction potentials of the polymers and electron affinity of the corresponding monomeric anthraquinones with a slope of 0.79. A photovoltaic cell using P(4,8-NO_2-1,5-AQ) and polythiophene has been constructed.

Introduction

π-Conjugated poly(arylene)s have received much attention due to their interesting electronic and optical properties and their applicability to present and future electronic and optical devices.[1,2]

Electrochemical redox reactions of π-conjugated polymers have been the subject of many recent papers. π-Conjugated polymers constituted of recurring redox active monomeric units (e.g., electrochemically active heterocyclic compounds,[1,2,3a,b] ferrocene,[3c] etc.) have received strong attention, and difference or similarity in the electrochemical behavior between the polymeric and monomeric compounds has been discussed.

Quinone belongs to one of the most attractive redox active compounds,[3d−f] and poly(arylene)s constituted of quinones are expected to show interesting electronic and optical properties. However, examples of main-chain type poly(quinone)s and studies on their electronic and optical behavior have been limited; some are shown in Chart 1).[4,5]

By the way, some π-conjugated polymers change their optical properties upon altering the solvent (solvatochromism),[6] temperature (thermochromism),[7a−c] and pressure (piezochromism).[7d−g] However, in comparison

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(1) (a) Nalwa, H. S. *Handbook of Organic Conductive Molecules and Polymers, Vol. 2*; Wiley: Chichester, 1997. (b) Skotheim, T. A.; Elsenbaumer, R. L.; Reynolds, J. R. *Handbook of Conducting Polymers*, 2nd ed.; Wiley: New York, 1997. (c) Salaneck, W. R.; Clark, D. T.; Samuelsen, E. J. *Science and Applications of Conducting Polymers*; Adam Hilger: Bristol, 1991. (d) Tolbert, L. M. *Acc. Chem. Res.* **1992**, *25*, 561.

(2) (a) Mortimer, R. *J. Chem. Soc. Rev.* **1997**, *26*, 147. (b) Scherf, U.; List, E. J. *Adev. Mater.* **2002**, *14*, 477. (c) Marsitzky, D.; Vestberg, R.; Blainey, P.; Tang, B. T.; Hawker, T. C.; Carter, K. R. *J. Am. Chem. Soc.* **2001**, *123*, 6965. (d) Monkman, A. P.; Palsson, L.-O.; Higgins, W. T.; Wang, C.; Bryce, M.; Batsanov, A. S.; Howard, J. A. *J. Am. Chem. Soc.* **2002**, *124*, 6949.

(3) (a) Schiavon, G.; Zotti, G.; Bontempelli, G. *J. Electroanal. Chem.* **1984**, *161*, 323. (b) Yamamoto, T. *J. Polym. Sci., Part A: Polym. Chem.* **1996**, *34*, 997. (c) Stanton, C. E.; Lee, T. R.; Grubbs, R. H.; Lewis, N. S.; Pudelski, J. K.; Callstrom, M. R.; Erickson, M. S.; Mclaughlin, M. L. *Macromolecules* **1995**, *28*, 8713. (d) Davidson, V. L., Ed. *Principles and Applications of Quinoproteins*; Marcel Dekker: New York, 1993. (e) O'Shea, K. E.; Fox, M. A. *J. Am. Chem. Soc.* **1991**, *113*, 611. (f) Fukuzumi, S.; Ohkubo, K.; Okamoto, T. *J. Am. Chem. Soc.* **2002**, *124*, 14147.

(4) (a) Power, G.; Hodge, P.; Clarke, I. D.; Robjohns, M. A.; Goodbody, I. *Chem. Commun.* **1998**, 873. (b) Wang, P.; Martin, B. D.; Parida, S.; Rethurisch, D. G.; Dordick, J. S. *J. Am. Chem. Soc.* **1995**, *117*, 12885. (c) Yamamoto, K.; Asada, T.; Nishide, H.; Tsuchida, E. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 1211.

(5) (a) Yamamoto, T.; Etori, H. *Macromolecules* **1995**, *28*, 3371. (b) Yamamoto, T.; Kimura, T.; Shiraishi, K. *Macromolecules* **1999**, *32*, 8886.

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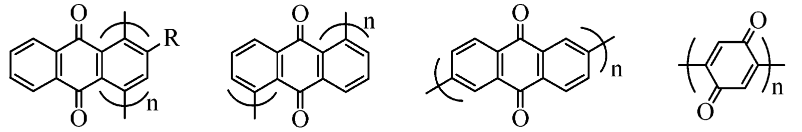
Chart 1. Examples of Reported Polyanthraquinones



R = H : P(1,4-AQ)[5a] P(1,5-AQ)[5a] P(2,6-AQ)[4a] PPBQ[5b]
(λmax = 369 nm) pale brown

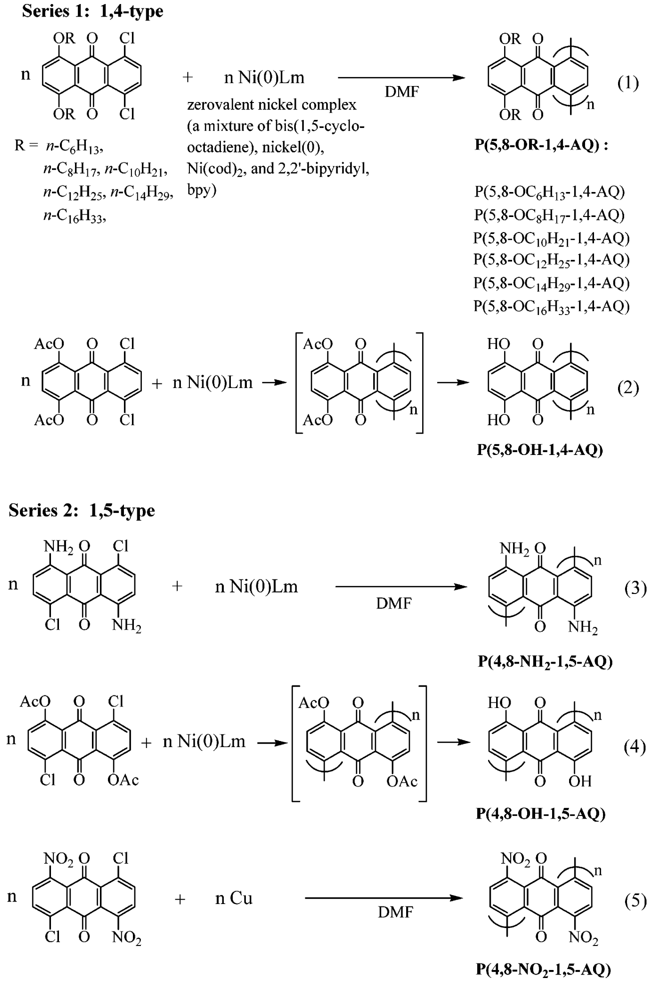
R = CH_3 : P(2-Me-1,4-AQ)[5a]
(λmax = 375 nm)

with solvatochromism and thermochromism, examples of piezochromism have been limited, despite its importance to reveal pressure dependence of molecular interaction between π-conjugated polymers. Assembly of molecules and its effect on electronic and optical properties are the subject of recent strong interest.[6c,8,9]

On these bases, we have tried preparation of new main-chain type poly(anthraquinone)s by using organometallic dehalogenative polycondensation.[5,9] Herein we report results of the preparation of the polymers, packing structure of the polymers, and basic chemical properties, (e.g., electrochemical, piezochromic, and liquid crystalline properties) of the polymer.

Results and Discussion

Preparation. Two series of new poly(anthraquinone)s, PAQs, were prepared from 1,4-dichloro- and 1,5-dichloroanthraquinones by dehalogenative polycondensation using zerovalent nickel complex, Ni(0)Lm, as shown in eqs 1 through 4.



In the case of 1,5-dichloro-4,8-dinitroantraquinone, however, its polycondensation using Ni(0)Lm did not proceed well, probably due to side reactions of the nitro group with the zerovalent nickel complex, and the resultant polymer showed broad IR absorption peaks. As shown in eq 5, polycondensation of 1,5-dichloro-4,8-dinitroanthraquinone was carried out using metallic copper (Ullmann coupling) at 100 °C in DMF to give the corresponding polymer, P(4,8-NO_2-1,5-AQ), quantitatively. It is known that Ullmann coupling proceeds especially well with haloaromatic compounds bearing NO_2 group(s).[10] Application of Ullmann coupling to the other monomers shown in eqs 1 and 3 did not give good results, and the polymers were obtained using Ni(0)-Lm. In eqs 2 and 4, PAQs bearing hydroxy groups were prepared from the corresponding acetoxyantraquinone monomers. Results of the polymerization are given in Table 1.

Previously reported nonsubstituted P(1,5-AQ) and P(1,4-AQ) exhibit only low solubility in organic solvents such as $CHCl_3$, CH_2Cl_2, and *N*-methyl-2-pyrrolidone (NMP).[5a] Introduction of substituents increases the solubility,[5] and polyanthraquinones shown in eqs 1−5 are soluble in organic solvents as exhibited in the Supporting Information.

IR spectra of polymers resembled those of the corresponding monomeric compounds, however, the ν(C−Cl)

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(6) (a) Yoshino, K.; Nakajima, S.; Gu, H. B.; Sugimoto, R. *Jpn. J. Appl. Phys.* **1987**, *26*, L2046. (b) Inganäs, O.; Salaneck, W. R.; Österholm, J.-E.; Laskso, J. *Synth. Met.* **1988**, *22*, 395. (c) Yamamoto, T.; Komarudin, D.; Maruyama, T.; Arai, M.; Lee, B.-L.; Suganuma, H.; Asakawa, K.; Inoue, Y.; Kubota, K.; Sasaki, S.; Fukuda, T.; Matsuda, H. *J. Am. Chem. Soc.* **1998**, *120*, 2047.

(7) (a) Inganäs, O.; Gustofsson, G.; Salaneck, W. R. *Synth. Met.* **1989**, *28*, C377. (b) Salaneck, W. R.; Inganäs, O.; Jhemans, B.; Nilsson, J.-O.; Sjögren, B.; Österholm, J.-E.; Bridas, J.-L.; Svensson, S. *J. Chem. Phys.* **1998**, *89*, 4613. (c) Nanos, J. I.; Kampf, J. W.; Curtis, M. D.; Gonzalez, L.; Martin, D. C. *Chem. Mater.* **1995**, *7*, 2332. (d) Yoshino, K.; Nakao, K.; Onoda, M. *Jpn. J. Appl. Phys.* **1989**, *28*, L323. (e) Hess, B. C.; Kanner, G. S.; Vardeny, Z. *Phys. Rev. B.* **1993**, *47*, 1407. (f) Iwasaki, K.-I.; Fujimoto, H.; Matsuzaki, S. *Synth. Met.* **1994**, *63*, 101. (g) Kaniowski, T.; Niziol, S.; Sanetra, J.; Trznadel, M.; Pron, A. *Synth. Met.* **1998**, *94*, 111.

(8) (a) Hu, J.; Zhang, J.; Liu, F.; Kittredge, K.; Whitesell, J. K.; Fox, M. A. *J. Am. Chem. Soc.* **2001**, *123*, 1464. (b) McCullough, R. D.; Tristam-Nagle, S.; Williams, S. P.; Lowe, R. D.; Jayaraman, M. J. *J. Am. Chem. Soc.* **1993**, *115*, 4910. (c) Noveron, J. C.; Lah, M. S.; Del Sesto, R. E.; Arif, A. M.; Miller, J. S.; Stang, P. J. *J. Am. Chem. Soc.* **2002**, *124*, 6613.

(9) (a) Yamamoto, T. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 621. (b) Yamamoto, T. *Prog. Polym. Sci.* **1992**, *17*, 1153. (c) Yamamoto, T.; Morita, A.; Miyazaki, T.; Maruyama, T.; Wakayama, H.; Zhou, Z.-H.; Nakamura, Y.; Kanbara, T.; Sasaki, S.; Kubota, K. *Macromolecules* **1992**, *25*, 1214. (d) Yamamoto, T. *Synlett* **2003**, 425.

(10) Fanta, P. E. *Chem. Rev.* **1946**, *38*, 139.

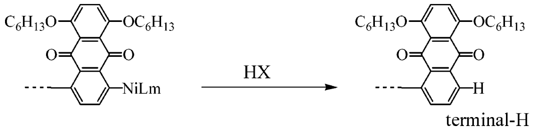
Table 1. Preparation of New Polyanthraquinones

no.	polymer	mol. wt.[a] M_n	mol. wt.[a] M_w	$[\eta]$,[b] dL g^{-1}	λ_{max}, nm solution[c,d]	λ_{max}, nm film	photoluminescence,[c] nm
1	P(5,8-OC_6H_{13}-1,4-AQ)	4.0×10^3 (V) 5.5×10^3 (NM)			402	412	
2	P(5,8-OC_8H_{17}-1,4-AQ)	3.1×10^3 (V)			415	428	510
3	P(5,8-$OC_{10}H_{21}$-1,4-AQ)	3.3×10^3 (G)	4.1×10^3 (G)		402		510
4	P(5,8-$OC_{12}H_{25}$-1,4-AQ)	5.9×10^3 (G)	6.6×10^3 (G)		410	419	509
5	P(5,8-$OC_{14}H_{29}$-1,4-AQ)	3.3×10^3 (G)	4.1×10^3 (G)		410		510
6	P(5,8-$OC_{16}H_{33}$-1,4-AQ)	7.2×10^3 (G)	1.5×10^4 (G) 6.8×10^4 (LS)	0.20	413	428	511
7	P(5,8-OH-1,4-AQ)	4.6×10^3 (G)[e]	5.2×10^3 (G)[e]	0.19	430, 530 (2600)[g]		
8	P(4,8-NH_2-1,5-AQ)[f]	3.7×10^3 (G)[e]	4.3×10^3 (G)[e]	0.10	511 (7200)[g]		
9	P(4,8-OH-1,5-AQ)	3.9×10^3 (G)[e]	4.3×10^3 (G)[e]	0.16	431		530
10	P(4,8-NO_2-1,5-AQ)	8.6×10^3 (G)	1.3×10^4 (G)	0.70	340 (3100) 480 (480)	342 505	440

[a] M_n = number average molecular weight. M_w = weight average molecular weight. (G): determined by gel permeation chromatography. (V): determined by vapor pressure osmometry. (NM): determined by ^{1}H NMR spectroscopy. (LS): determined by light scattering method. [b] $[\eta]$ = intrinsic viscosity; dL g^{-1} = 100 mL g^{-1}. [c] In chloroform unless noted. [d] Molar absorption coefficient is given in the parentheses. [e] In DMF. [f] For DMF-soluble part. [g] In NMP.

absorption peak of monomer at about 1100 cm^{-1} was not observed in the IR spectrum. The ν(C=O) peak of P(5,8-OH-1,4-AQ) (1627 cm^{-1}), P(4,8-OH-1,5-AQ) (1625 cm^{-1}), and P(4,8-NH_2-1,5-AQ) (1611 cm^{-1}) appears at somewhat lower frequency compared with that of P(5,8-OR-1,4-AQ) (about 1660 cm^{-1}), presumably due to intramolecular hydrogen bonding[11] of the OH and NH_2 group to the C=O group. ^{1}H NMR spectra of the polymers also agree with their structures (cf. the Experimental Section and Supporting Information). Because IR spectra of P(5,8-OH-1,4-AQ) and P(4,8-OH-1,5-AQ) showed no peak assigned to ν(C=O) of the OAc group at about 1750 cm^{-1} and resembled those of the corresponding dihydroxy-anthraquinones, the OAc group was considered to be transformed into the OH group according to cleavage of the acetoxyphenyl bond in the reaction with Ni(0)Lm[12a] during the polymerization and/or reactions that occurred during the workup including washing with hydrochloric acid.

P(5,8-OR-1,4-AQ)s showed only low content of Cl, and P(5,8-OC_6H_{13}-1,4-AQ) showed no Cl. The as-prepared P(5,8-OC_6H_{13}-1,4-AQ) is considered to have Ni-terminated polymer ends, which are converted into H-terminated polymer ends during workup using protic acid, similar to polyarylenes prepared analogously.[12b]



(6)

P(5,8-OR-1,4-AQ)s showed a number average molecular weight M_n of 3100−7200 as estimated by vapor pressure osmometry and gel permeation chromatography (GPC; vs polystyrene standards). The ^{1}H NMR spectrum of P(5,8-OR-1,4-AQ) exhibited a peak of terminal-H (eq 6) at δ 8.2, and M_n of P(5,8-OC_6H_{13}-1,4-AQ), which included no Cl, was evaluated as 5500 from its peak area; the M_n value roughly agreed with the M_n value estimated from GPC (M_n = 4000; no. 1 in Table 1).

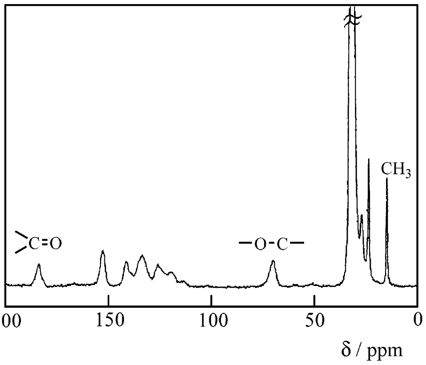


Figure 1. CP/MAS solid ^{13}C NMR spectrum of P(5,8-$OC_{16}H_{33}$-1,4-AQ).

^{1}H NMR spectra of polymers often give complicated absorption patterns for various reasons (e.g., due to difference in conformation of the polymer and regio- and stereo- regularity).[12c,d,13] P(5,8-OR-1,4-AQ) also exhibits a complex ^{1}H NMR pattern which, for example, gives two $-OCH_2-$ peaks at δ 4.05 and 3.72 for P(5,8-$OC_{16}H_{33}$-1,4-AQ) (cf. the Supporting Information). For this polymer, for example, the presence of −O−R cis and trans conformations with regard to the relation to the quinone carbonyl group is conceivable. The presence of rotamers around the main chain is also conceivable. In addition, the terminal and penultimate units may give peaks at different positions.

P(5,8-OR-1,4-AQ) is considered to form an ordered structure in the solid as discussed below. Therefore, the conformation of the OR chain and the main chain, which may not be fixed in the solution as discussed above, is considered to be fixed in the solid state, and a solid state ^{13}C NMR spectrum is expected to give a simpler pattern. The CP/MAS solid ^{13}C NMR spectrum of P(5,8-$OC_{16}H_{33}$-1,4-AQ) shown in Figure 1 exhibits only one peak for the carbonyl (δ 183.95), $-OCH_2-$ (δ 70.02), and terminal $-CH_3$ (δ 14.77) groups, respectively. These data support the structure of P(5,8-OR-1,4-AQ).

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(11) (a) Brown, C. J.; Mitchel, G. R. *Acta Crystallogr. Sect. B* **1982**, *38*, 3149. (b) Baitey, M.; Brown, C. J. *Acta Crystallogr.* **1967**, *22*, 488. (c) Yoshida, Z.; Takabayashi, F. *Tetrahedron* **1968**, *24*, 933. (d) English, D. S.; Zhang, W.; Krauss, G. A.; Petrich, J. W. *J. Am. Chem. Soc.* **1997**, *119*, 2980. (e) Yasukouchi, K.; Ono, Y. *Nippon Kagaku Kaishi* **1967**, *88*, 538.

(12) (a) Yamamoto, T.; Ishizu, J.; Komiya, S.; Yamamoto, A. *J. Am. Chem. Soc.* **1980**, *102*, 3758. (b) Yamamoto, T.; Maruyama, T.; Zhou, Z.-H.; Ito, T.; Fukuda, T.; Yoneda, Y.; Begum, F.; Ikeda, T.; Sasaki, S.; Takezoe, H.; Fukuda, A.; Kubota, K. *J. Am. Chem. Soc.* **1994**, *116*, 4832. (c) Bovey, F. A. *Polymer Conformation and Configuration*; Academic Press: New York, 1969. (d) Slonim, I. Y.; Lyubimov, *The NMR of Polymers*; Plenum: New York, 1970.

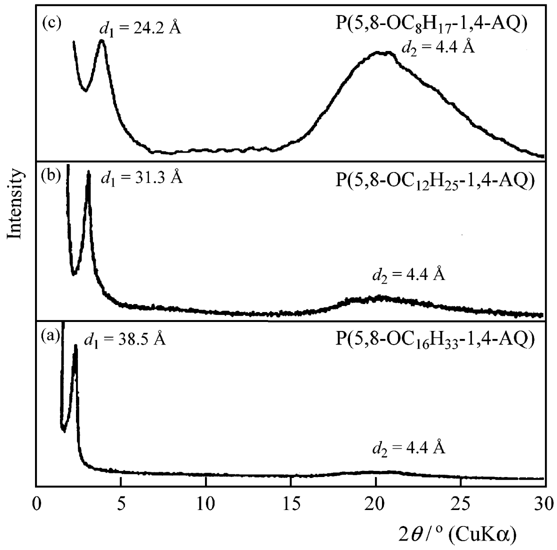


Figure 2. Powder X-ray diffraction patterns of (a) P(5,8-OC$_{16}$H$_{33}$-1,4-AQ), (b) P(5,8-OC$_{12}$H$_{25}$-1,4-AQ), and (c) P(5,8-OC$_8$H$_{17}$-1,4-AQ).

Light scattering analysis of a chloroform solution of P(5,8-OC$_{16}$H$_{33}$-1,4-AQ) gave a larger molecular weight (weight average molecular weight $M_w = 6.8 \times 10^4$) than that obtained by GPC ($M_w = 1.5 \times 10^4$) (no. 6 in Table 1), suggesting occurrence of partial aggregation in a static solution, similar to cases of regioregular π-conjugated poly(alkylthiophene)s.[6c,13−15]

P(5,8-OH-1,4-AQ), P(4,8-NH$_2$-1,5-AQ), and P(4,8-OH-1,5-AQ) gave M_n of 4600, 3700, and 3900, respectively, as shown in Table 1. PAQs shown in nos. 6−9 in Table 1 exhibited intrinsic viscosity [η] of 0.10−0.20 dL g^{-1} (dL = 100 mL) in chloroform. Considering [η] of 0.20 dLg^{-1} corresponds to M_w of 5.3×10^4 for polystyrene,[16a] the polyanthroquinones seem to assume a somewhat stiffer structure than polystyrene in the solution. P(4,8-NO$_2$-1,5-AQ) showed a larger [η] value of 0.70 dL g^{-1} in *N*-methyl-2-pyrrolidone (NMP) at 30 °C and gave higher M_n and M_w of 8600 and 13 000, respectively, than the polymers listed in nos. 7−9 in Table 1. All of the polymers afforded films with good quality when cast from solutions on Pt and ITO glass plates, and the cast films were suited for optical and electrochemical analysis.

XRD Data, Packing Structure, and Liquid Crystalline Behavior. Figure 2 shows powder X-ray diffraction (XRD) patterns of P(5,8-OR-1,4-AQ). All the polymers exhibit a clear d_1 diffraction peak in a low-angle region below $2\theta = 7°$. Recently it was reported that various π-conjugated poly(arylene)s with long side chains gave a similar XRD peak in the low angle region,[6c,8b,13−15] and the appearance of this peak suggests that P(5,8-OR-1,4-AQ) takes an ordered structure assisted by side chain crystallinity[13−15,16b−d] (or cohesive force between the long alkyl groups), similar to that of previously reported poly(arylene)s with long side chains.[6c,8b,9,13−15]

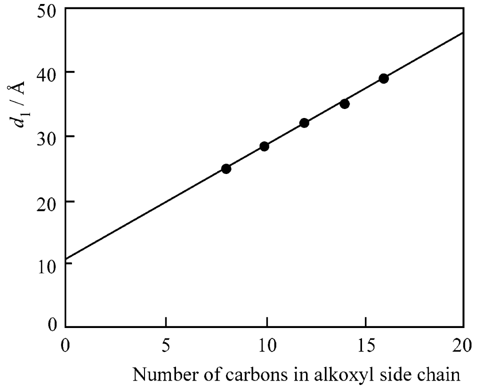
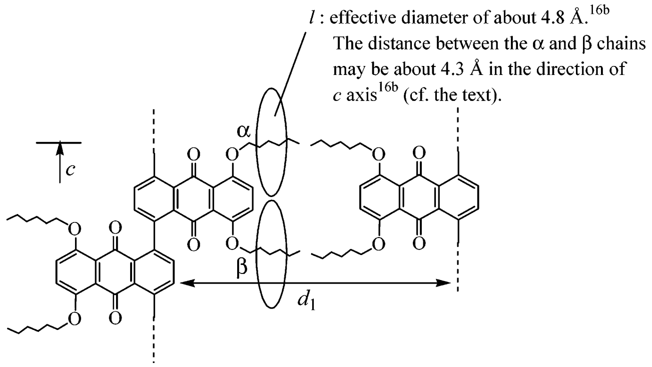


Figure 3. Plots of d_1 space of P(5,8-OR-1,4-AQ)s vs the number of carbons in the alkoxyl side chain in the polymer.

Plots of the d_1 value obtained from the XRD pattern vs the number of carbons in the OR side chain give a straight line as shown in Figure 3. The linear increase of the d_1 value with the length of the OR group strongly suggests that the d_1 value corresponds to a distance between the π-conjugated main chain separated by the OR group as shown in Chart 2.[15d]

Chart 2. Packing Model of P(5,8-OR-1,4-AQ) with Long OR Groups. Only one layer is shown



The intercept of the linear line in Figure 3 (ca. 10 Å) is considered to correspond to the thickness of the core main chain. The slope of the linear line, 1.8 Å/carbon, roughly agrees with those (1.8−2.0 Å/carbon) observed with regioregular poly(3-alkylthiophene-2,5- diyl)[6c,13,14] and poly(4-alkylthiazole-2,5-diyl)[6c] which are considered to take an end-to-end packing mode[16b,c] (not an interdigitation packing mode).

Because of a fairly strong steric hindrance between the phenylene rings, it seems difficult for P(5,8-OR-1,4-AQ) to take a coplanar main chain which is advantageous to form a π-stacked structure. However, these polymers are still considered to be loosely stacked in the end-to-end packing mode assisted by side chain crystallization. In addition to this, it was reported that a torsion angle of biphenyl could become 0° when it had appropriate substituents.[16d]

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(13) (a) McCullough, R. D.; Lowe, R. D.; Jayaraman, M.; Anderson, D. L. *J. Org. Chem.* **1993**, *58*, 904. (b) Chen, T.-A.; Wu, X.; Rieke, R. D. *J. Am. Chem. Soc.* **1995**, *117*, 233.

(14) Ezqurra, T. A.; Sánchez-Cuesta, M.; Ungar, G.; Feijoo, J. L.; López-Cabaros, E. *J. Polym. Sci, Part B: Polym. Phys.* **1998**, *36*, 49.

(15) (a) Morikita, T.; Yamaguchi, I.; Yamamoto, T. *Adv. Mater.* **2001**, *13*, 1862. (b) Yamamoto, T.; Kokubo, H.; Morikita, T. *J. Polym. Sci., Part B: Polym. Phys.* **2001**, *39*, 1713. (c) Yamamoto, T.; Shiraishi, K. *Chem. Lett.* **1998**, 895. (d) Yamamoto, T.; Saitoh, Y.; Anzai, K.; Fukumoto, H.; Yasuda, T.; Fujiwara, Y.; Choi, B.-K.; Kubota, K.; Miyamae, T. *Macromolecules* **2003**, in press. (e) Yamamoto, T.; Arai, M.; Kokubo, H.; Sasaki, S. *Macromolecules* **2003**, *36*, 7986−7993.

(16) (a) Oth, J.; Desreux, V. *Bull. Soc. Chim. Belg.* **1954**, *63*, 285. (b) Hsieh, H. W.; Post, B.; Morawetz, H. *J. Polym. Sci. Polym. Phys. Ed.* **1976**, *14*, 1241. (c) Jordan, E. F., Jr.; Feleisen, D. W.; Wrigley, A. N. *J. Polym. Sci., Part A-1* **1971**, *9*, 1835. (d) Tashiro, K.; Hou, J.-A.; Kobayashi, M.; Inoue, T. *J. Am. Chem. Soc.* **1990**, *112*, 8273.

The R group in OR has an effective diameter (*l* in Chart 2) of about 4.8 Å when its cross section is regarded as a circle.[16b] However, if the OR groups are densely packed by taking a herringbone-type arrangement as in a crystal of linear polyethylene and paraffins,[16b,c] the distance between the neighboring OR groups (e.g., α and β chains in Chart 2) may become about 4.3 Å in the direction of the polymer chain (or *c* axis) This distance agrees with repeating height of the *p*-phenylene unit (about 4.2 Å)[9c,17a] Another broadened diffraction peak centered at about $d_2 = 4.4$ Å in Figure 1 is considered to originate from the side chain packing,[16b,c] although it may include contribution from face-to-face packing of the π-conjugated polymer chains which is considered to give a diffraction peak at $d = 3.6-3.9$ Å.

Differential scanning calorimatery revealed that P(5,8-OC_6H_{13}-1,4-AQ) had a relatively low glass transition temperature (T_g) which rose with increase in the length of the OR group; P(5,8-OC_6H_{13}-1,4-AQ): $T_g = -71.8$ °C; T_i (transition temperature to/from isotropic phase) = 243.1 °C (heating), 224.2 °C (cooling). P(5,8-OC_8H_{17}-1,4-AQ): $T_g = -64.0$ °C; $T_i = 170.2$ °C (heating), 156.2 °C (cooling). P(5,8-$OC_{12}H_{25}$-1,4-AQ): $T_g = -37.5$ °C; $T_i = 158.7$ °C (heating), 153.5 °C (cooling). P(5,8-$OC_{16}H_{33}$-1,4-AQ): $T_g = -7.0$ °C; $T_i = 174.2$ °C (heating), 160.6 °C (cooling). Polarized optical microscopy indicated formation of smectic liquid crystalline texture between T_g and T_i, and the liquid crystalline behavior was enantiotropic. Rigid rodlike polymers, especially π-conjugated polymers, with flexible side chains and liquid crystalline properties are the subject of recent interest,[2c,17a−f] and smectic phase was reported for π-conjugated poly(1,6-heptadiyne)s and polyacetylenes.[17c,d]

It has recently been reported that liquid crystalline π-conjugated polymers such as poly(dialkylfluorene) can be aligned on a rubbed polyimide film when treated above T_i and such alignment is important for construction of superior polymer electronic devices.[18] Figure 4 exhibits dichroism caused by P(5,8-$OC_{12}H_{25}$-1,4-AQ) molecules laid on a rubbed polyimide film. The as-cast film of P(5.8-$OC_{12}H_{25}$-1,4-AQ) on the rubbed polyimide film did not show dichroism; however, after once heated beyond T_i the polymer showed the dichroism for its UV−vis absorption band as depicted in Figure 4, which was measured after cooling to room temperature. At the temperature higher than T_i, the P(5,8-$OC_{12}H_{25}$-1,4-AQ) molecules seem to be rearranged. However, the observed dichroism was a reverse type, compared with that reported for liquid crystalline poly(9,9-bis(2-ethylhexyl)-fluorene-2,7-diyl)[2b,18] (cf. the data shown in the inset in Figure 4). P(5,8-$OC_{12}H_{25}$-1,4-AQ) is considered to be aligned rather in a perpendicular mode (the (α) mode in Figure 4) than in a parallel mode (the (β) mode). Delicate sterical requirement of the long side chains in P(5,8-$OC_{12}H_{25}$-1,4-AQ) and poly(9,9-bis(2-ethylhexyl)-fluorene-2,7-diyl) seems to control the direction of alignment. Electronic effect of P(5,8-$OC_{12}H_{25}$-1,4-AQ) may also affect the direction of alignment. Alignment of π-conjugated polymers on substrates has been the subject of recent interest.[8b,9,12b,18,19]

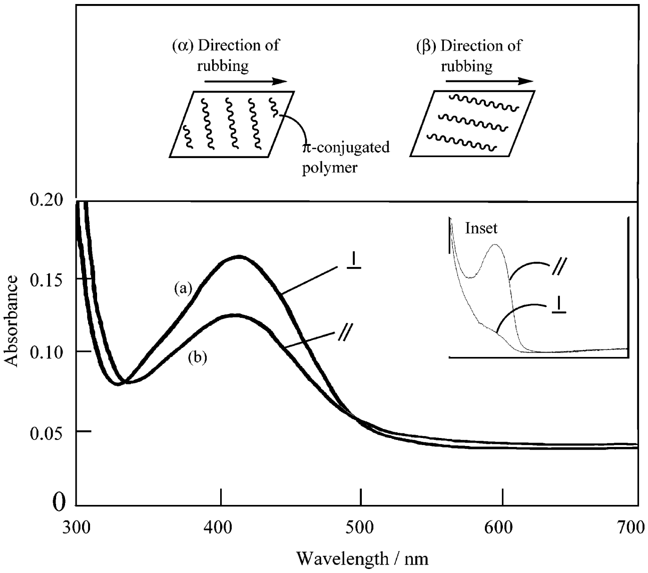

Figure 4. Dichroism caused by P(5,8-$OC_{12}H_{25}$-1,4-AQ) molecules laid on a rubbed polyimide film; after annealing at 170 °C for 1 h. These UV−vis dichroic data suggest alignment of P(5,8-$OC_{12}H_{25}$-1,4-AQ) in the (α) mode shown in the top part of the figure. Inset: Analogous data for poly(9,9-bis(2-ethylhexyl) fluorine-2,7-diyl) laid on the same rubbed polyimide film. These data in the inset agree with reported results,[18] and suggest alignment in the (β) mode. || and ⊥ indicate the UV−vis spectra taken by irradiation with parallelly and perpendicularly polarized light (toward the direction of rubbing), respectively.

P(4,8-NO_2-1,5-AQ) showed XRD peaks at $d = 7.2$ Å and 4.2 Å, whereas P(4,8-OH-1,5-AQ) gave XRD peaks at $d = 4.9$ Å and 3.9 Å. The XRD pattern of P(4,8-NO_2-1,5-AQ) has been analyzed by the linked-atom Rietveld whole-fitting method,[20] which indicates that P(4,8-NO_2-1,5-AQ) assumes the packing structure shown in Figure 5.

Use of crystallographic parameters of $a = 8.7$ Å, $b = 10.1$ Å, $c = 12.7$ Å, $\alpha = 142°$, $\beta = 123°$, and $\gamma = 71°$ in a triclinic packing gives a similated XRD pattern which essentially agrees with the observed XRD pattern. The crystallographic parameters afford a calculated density of 1.68 g cm^{-3}, and the observed density of 1.58 g cm^{-3} is reasonable considering a polymer sample usually exhibits an observed density somewhat lower than a

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(17) (a) Watanabe, J.; Ono, H.; Uematsu, I.; Abe, A. *Macromolecules* **1985**, *18*, 2141. (b) Ballauff, M. *Makromol. Chem. Rapid Commun.* **1986**, *7*, 407. (c) Jin, S.-H.; Kim, S.-H.; Cho, H. N.; Choi, S. K. *Macromolecules* **1991**, *24*, 6050. (d) Oh, S.-Y.; Akagi, K.; Shirakawa, H. *Macromolecules* **1993**, *26*, 6203. (e) Koide, N.; Hirai, Y. *Mol. Cryst. Liq. Cryst.* **1999**, *332*, 2873. (f) Katsis, D.; Geng, Y. H.; Ou, J. J.; Culligan, S. W.; Trajikovska, A.; Chen, S. H.; Rothberg, L. J. *Chem. Mater.* **2002**, *14*, 1332.

(18) (a) Bauer, C.; Urbasch, G.; Giessen, H.; Meisel, A.; Nothofer, H.-G.; Neher, D.; Scherf, U.; Mahrt, R. *ChemPhysChem* **2000**, 142. (b) Grell, M.; Knoll, W.; Lupo, D.; Meisel, A.; Miteva, T.; Neher, D.; Nothofer, H.-G.; Scherf, U.; Yasuda, A. *Adv. Mater.* **1999**, *11*, 671.

(19) (a) Fukuda, T.; Yamamoto, T.; Kurihara, T.; Ooba, N. *Synth. Met.* **1993**, *60*, 259. (b) Sirrnghaus, H.; Brown, P. J.; Friend, R. H.; Nielsen, M. M.; Bechgaard, K.; Langeveld-Voss, B. M. W.; Splerlag, A. J. H.; Janssen, R. A.; Meijer, E. W.; Horwings, P.; deLeauw, D. M. *Nature* **1999**, *401*, 685. (c) Cai, C.; Bösch, M. M.; Tao, Y.; Müller, B.; Gan, Z.; Kündig, A.; Basshard, C.; Liakatas, I.; Jäger, M.; Günter, P. *J. Am. Chem. Soc.* **1998**, *120*, 8563. (d) Yamamoto, T.; Kokubo, H.; Morikita, T. *J. Polym. Sci., Part B: Polym. Phys.* **2001**, *39*, 1713. (e) Yamamoto, T.; Kanbara, T.; Mori, C. *Synth. Met.* **1990**, *38*, 399. (f) Yamamoto, T.; Wakayama, H.; Fukuda, T.; Kanbara, T. *J. Phys. Chem.* **1992**, *96*, 8677. (g) Yamamoto, T.; Fang, Q.; Morikita, T. *Macromolecules* **2003**, *36*, 4262.

(20) (a) Rietveld, H. M. *J. Appl. Crystallogr.* **1969**, *2*, 65. (b) Sasaki, S.; Yamamoto, T.; Kanbara, T.; Morita, T.; Yamamoto, T. *J. Polym. Sci.* **1992**, *30*, 293. (c) Brückner, S.; Prozio, W. *Makromol. Chem.* **1988**, *189*, 961.

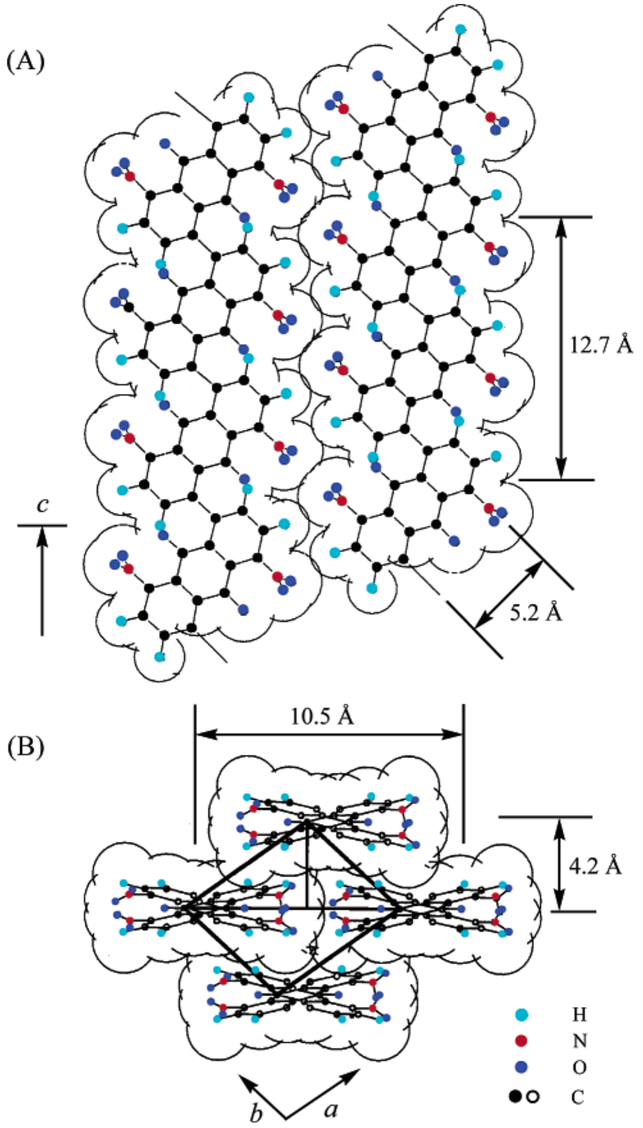

Figure 5. Packing model of P(4,8-NO_2-1,5-AQ). Top: A sheet of the polymer plane is depicted. Bottom: Side view seen from the direction of the polymer maincahin (*c* axis).

calculated density due to the presence of amorphous parts. Because P(4,8-NO_2-1,5-AQ) molecules do not have a significant $\pi-\pi$ interaction in the solid as depicted in Figure 5B, the polymer affords the UV−vis peak essentially at the same position in $CHCl_3$ and in film.

UV−Vis and Photoluminescence Data. Basic optical data of polyanthraquinones are included in Table 1. P(4,8-NO_2-1,5-AQ) was soluble in various organic solvents, and its least-transition-energy absorption peak at about 500 nm moved depending on the kind of the solvent. Plots of the transition energy of the absorption peak vs donor number[21] of the solvent afford a linear line as depicted in Figure 6. The highly electron-accepting dinitroanthraquinone monomeric unit seems to have a donor−acceptor interaction with the solvents and this is considered to be the origin of the solvatochromism. Higher solubility of P(4,8-NO_2-1,5-AQ) in the solvent with a larger donor number supports this view. Other polyanthraquinones did not exhibit such an obvious solvatochromism.

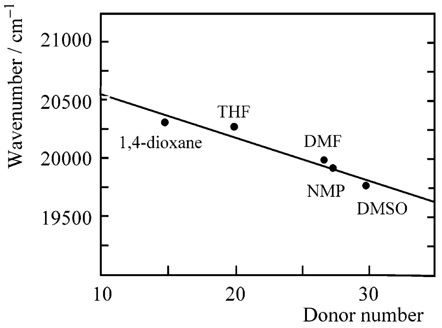

Figure 6. Solvatochromism of P(4,8-NO_2-1,5-AQ): dependence of ν_{max} on donor number of the solvent.

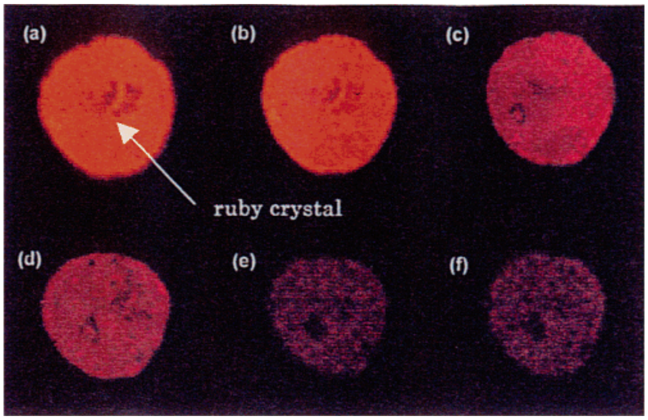

Figure 7. Images of P(5,8-$OC_{16}H_{33}$-1,4-AQ) at (a) 0.55 GPa, (b) 1.1 GPa, (c) 3.3 GPa, (d) 6.1 GPa, (e) 6.9 GPa, and (f) 11.0 GPa. Shadows in the images are due to nonuniformity of the film due to the presence of ruby for monitoring pressure.

As shown in Table 1, λ_{max} position of cast film of P(5,8-OR-1,4-AQ) is shifted by about 10−15 nm to a longer wavelength compared with that of the polymer in solutions, presumably due to an increase of the coplanarity and the expansion of the π-conjugation system in the film. All PAQs exhibited a photoluminescence peak at the onset position of the absorption peak as usually observed with π-conjugated molecules and polymers. P(4,8-OH-1,5-AQ) and P(4,8-NH_2-1,5-AQ) gave relatively high quantum yields of 6−10% for the photoluminescence.

Piezochromism. As shown in Figure 7, P(5,8-$OC_{16}H_{33}$-1,4-AQ) exhibits piezochromism at high pressures in the solid state. Similar piezochromism has been reported for poly(3-alkylthiophene-2,5-diyl) P3RTh;[7d−g] P(5,8-$OC_{16}H_{33}$-1,4-AQ) presents another example of piezochromism of π-conjugated polymer. As shown in Figure 7, by applying a high pressure, the color of the pressed film of the polymer changes from orange-yellow at 1 atm to dark red at 11 GPa, and this piezochromism is reversible.

For solid-state structure of poly(3-octylthiophene), it was reported that both distance between polythiophene main chain separated by the alkyl side chains and the face-to-face distance between polythiophene planes were shortened at high pressure, e.g., about 8% shortening of the face-to-face distance at 8 GPa.[22] If such shortening of the face-to-face distance between the π-conjugated polymer planes takes place for P(5,8-$OC_{16}H_{33}$-1,4-AQ),

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(21) Gutman, V.; Wychera, E. *Inorg. Nucl. Chem. Lett.* **1966**, *2*, 257.

(22) Samuelsen, E. J.; Märdelen, J.; Konestabo, O. R.; Hanfland, M.; Lorenzen, M. *Synth. Met.* **1999**, *101*, 98.

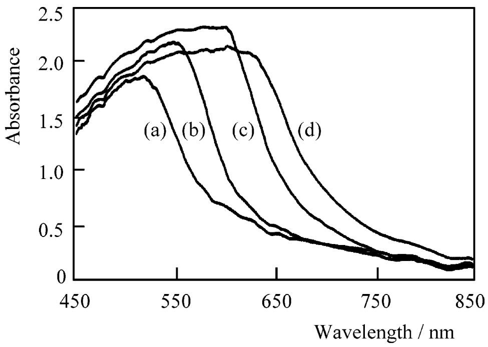
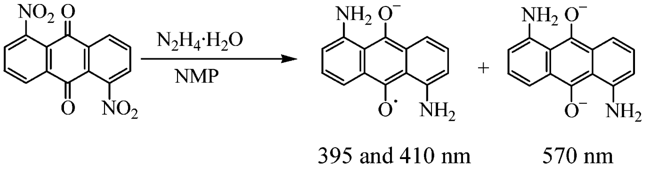


Figure 8. UV-vis spectra of P(5,8-$OC_{16}H_{33}$-1,4-AQ) at (a) 0.55 GPa, (b) 3.3 GPa, (c) 6.9 GPa, and (d) 11.0 GPa. Cf. S-10 in the Supporting Information.

it will increase interlayer $\pi-\pi$ interaction between P(5,8-$OC_{16}H_{33}$-1,4-AQ) molecules to cause the piezochromism.

Under high pressures, the absorption peak shifts to a longer wavelength (λ_{max} = 428 nm at 1 atm (Table 1) to 640 nm at 11 GPa via 520 nm at 0.55 GPa), as depicted in Figure 8. The band gap of P(5,8-$OC_{16}H_{33}$-1,4-AQ) evaluated from the onset position also decreases from 2.42 eV at 1 atm to about 1.5 eV at 11 GPa (or 0.08 eV GPa^{-1}). It has been reported that the application of high pressure to solids of planar metal complexes also leads to a red shift in their absorption bands (e.g, from about 550 nm at 0.2 GPa to 700 nm at 4.1 GPa for bis(dimethylglyoximato)nickel(II)) through the increase of the intermolecular interaction at a high pressure.[23a,24] Other P(5,8-OR-1,4-AQ)s with shorter OR group did not show such obvious piezochromism.

Chemical Reduction. P(4,8-NO_2-1,5-AQ) receives chemical reduction. Figure 9 compares UV–vis changes observed during the reduction of (a) P(4,8-NO_2-1,5-AQ) and (b) 1,5-dinitroanthraquinone (1,5-NO_2-AQ) with hydrazine hydrate in *N*-methyl-2-pyrrolidone (NMP). Reduction of 1,5-NO_2-AQ (Figure 9b) gives new absorption peaks at about 400 and 570 nm. The NO_2 group is considered to be reduced to a NH_2 group, and the new peaks are assigned to anion radical and dianion of 1,5-diaminoanthraquinone (1,5-NH_2-AQ), repectively, because they appear near those of dianion (AQ^{2-}) and anion radical ($AQ^{-\bullet}$) of anthraquinone.[25] Exposure of the solution to air gave a UV–vis spectrum shown by a broken line in Figure 9b, and this spectrum agreed with that of 1,5-NH_2-AQ (λ_{max} = 510 nm).



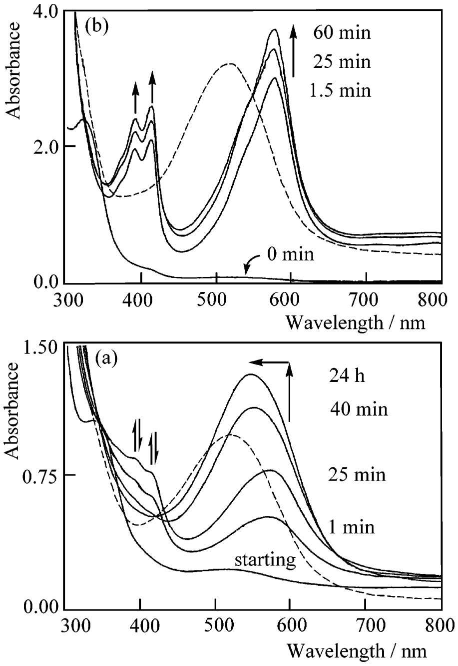


Figure 9. Changes of UV–vis spectrum during the reduction of (a) P(4,8-NO_2-1,5-AQ) and (b) 1,5-dinitroanthraquinone with excess amount of $N_2H_4 \cdot H_2O$ in NMP at room temperature under N_2. When the chemically reduced sample was exposed to air, the UV–vis spectrum finally changed to that expressed by the broken line.

Reduction with *N*,*N*-diethylhydroxylamine gave similar UV–vis spectroscopic changes. Chemical reduction of nitroanthraquinones including 1,5-NO_2-AQ to aminoanthraquinones has been reported.[26]

Reduction of P(4,8-NO_2-1,5-AQ) with $N_2H_4 \cdot H_2O$ in NMP brings about similar changes in the UV–vis spectrum, as shown in Figure 9a. Upon reducing the polymer, new peaks at 575 nm and about 400 nm assigned to the dianion and anion radical species, respectively, appear and become stronger. Further reduction leads to a shift of the dianion peak at 575 nm toward a shorter wavelength of 540 nm, and absorption peaks at about 400 nm assigned to the anion radical disappear as the chemical reduction proceeds. This behavior suggests formation of a unique new electronic state along the polymer chain. When the chemically reduced solution was exposed to air, the solution gave a UV–vis spectrum shown by a broken line in Figure 9a, which agrees with UV–vis spectrum of P(4,8-NH_2-1,5-AQ).

Electrochemical Properties. Electrochemical response of the polymers was measured with films cast on the Pt plate, and cyclic voltammetric (CV) data are summarized in Table 2.

The polymers were inert in an oxidation region. However, they showed two redox cycles characteristic of two-step reduction (the first step to form anion radical $AQ^{-\bullet}$ and the second step to form dianion AQ^{2-}) of quinones[27] in reduction region, and an average of peak reduction (or *n*-doping) potential and reoxidation (or

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(23) (a) Shirotani, I.; Kawamura, A.; Suzuki, K.; Utsumi, W.; Yagi, T. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 1607. (b) Barnett, J. D.; Block, S.; Piermarini, G. J. *Rev. Sci. Instrum.* **1973**, *44*, 1.

(24) Shirotani, I.; Suzuki, K.; Suzuki, T.; Yagi, T.; Tanaka, M. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1078.

(25) (a) Hamanoue, K.; Yokoyama, K.; Kajiwara, Y.; Kimoto, M.; Nakayama, T.; Teranishi, H. *Chem. Phys. Lett.* **1985**, *113*, 207. (b) Hamanoue, K.; Nakayama, T.; Sugiura, K.; Teranishi, H.; Washino, M.; Tagawa, S.; Tabata, Y. *Chem. Phys. Lett.* **1985**, *113*, 207.

(26) (a) Morley, J. O. *Synthesis* **1976**, 528. (b) Buecheler, P. German Pat. 2425314, 1975 (*Chem. Abstr.* **1975**, *82*, 126611). (c) Hutcheson, R.; Morley, J. O. *J. Chem. Res. Synop.* **1979**, 286; German Pat. 137782, 1990.

(27) (a) Hoang, P. M.; Holdcroft, S.; Funt, B. L. *J. Electrochem. Soc.* **1985**, *132*, 2129. (b) Degrand, C.; Miller, L. L. *J. Electroanal. Chem.* **1981**, *117*, 267.

Table 2. Electrochemical Data[a] and Electrical Conductivities (σ) of PAQs

		redox potential,[c] V vs Ag$^+$/Ag				
no.	polymer	$E_1°$ (x)	$E_2°$ (y)	ΔE	IP, eV	σ,[e] S cm^{-1} (nondoped state)
1	P(1,4-AQ)[b] yellow	−1.30 (0.64) red	−1.62 (0.51) deep red	0.32		1.8×10^{-8}
2	P(2-Me-1,4-AQ)[b] yellow	−1.38 (0.62) red	−1.69 (0.48) deep red	0.31		8.0×10^{-8}
3	P(5,8-OH-1,4-AQ) black	−1.16[d] black	−1.55[d] black	0.39		2.0×10^{-6}
4	P(1,5-AQ) yellow	−1.30 (0.82) red	−1.58 (0.76) reddish red	0.28	5.8	$< 10^{-8}$
5	P(4,8-OH-1,5-AQ) brown yellow	−1.08[d] brown	−1.39[d] dark brown	0.31		2.4×10^{-6}
6	P(4,8-NH_2-1,5−AQ) dark purple	−1.50 (0.93) purple	−1.88 (0.45) reddish purple	0.38	5.2	7.0×10^{-7}
7	P(4,8-NO_2-1,5−AQ) reddish brown	−0.74 (0.31) purple	−1.03 (0.22) dark purple	0.29	6.4	1.4×10^{-6}

[a] Measured in an CH_3CN solution of $[N(C_2H_5)_4]BF_4$, unless otherwise noted. Color of the polymer film is shown at neutral state, after the E_1 process, and after the E_2 process. [b] Measured in an CH_3CN solution of $[N(C_2H_5)_4]ClO_4$. Data from refs. 5a and 5b. [c] $E° =$ the average of n-doping and n-undoping potentials. x and $y =$ the number of negative charges stored per repeating unit or doping level. ΔE = the difference between $E_1°$ and $E_2°$. [d] Two redox peaks could not be separated well after second cycle. [e] Measured with a pressured powder at nondoped state.

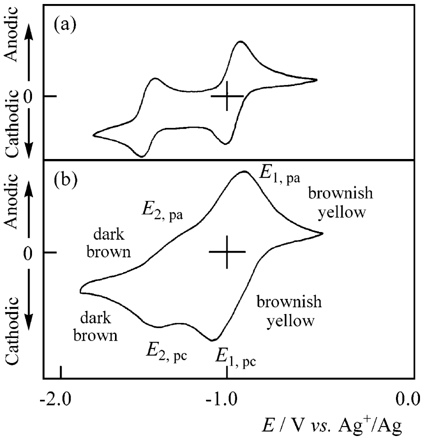
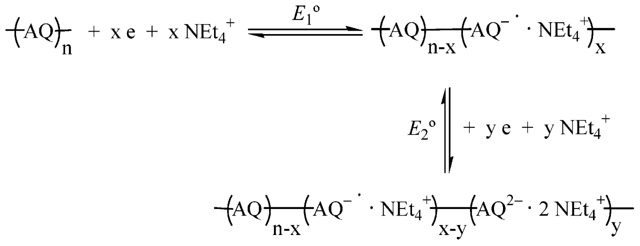


Figure 10. Cyclic voltammograms of (a) 1,5-dihydroxyanthraquinone (3.0×10^{-6} M) in a DMF solution containing $[N(C_2H_5)_4]BF_4$ (0.10 M) and (b) a film of P(4,8-OH-1,5-AQ) on a Pt plate in an CH_3CN solution of $[N(C_2H_5)_4]BF_4$ (0.10 M), Sweep rate is 100 mV s^{-1} at room temperature.

n-dedoping) potentials was calculated for $E_1°$ and $E_2°$. The CV curve was reproducible in repeated scanning.



$$-\!(AQ)_n\!- + x\,e + x\,NEt_4^+ \underset{}{\overset{E_1°}{\rightleftharpoons}} -\!(AQ)_{n-x}\!-\!(AQ^{-\cdot}\cdot NEt_4^+)_x\!- \overset{E_2°}{\underset{+\,y\,e\,+\,y\,NEt_4^+}{\rightleftharpoons}} -\!(AQ)_{n-x}\!-\!(AQ^{-\cdot}\cdot NEt_4^+)_{x-y}\!-\!(AQ^{2-}\cdot 2\,NEt_4^+)_y\!-$$

Figure 10 exhibits examples of the CV charts of the polymer and its corresponding monomeric compound. The CV data reveal the following features of the electrochemical reduction of π-conjugated PAQs.

(i) The two CV peaks are broadened and the potential difference between the two peaks, $\Delta E = E_1° - E_2°$, becomes smaller than that obtained from the monomeric compound. For example, the ΔE value of P(4,8-OH-1,5-AQ) (0.31 V) is smaller than that (0.49 V) of 4,8-dihydroxyanthraquinone. Similar results were reported for P(2-Me-1,4-AQ)[5a] and these results seem to reflect the unique electronic state of reduced PAQs. The reduced PAQs contain the AQ, $AQ^{-\bullet}$, and/or AQ^{2-} units which are mutually exchanging electron through the π-conjugated main chain and direct interaction in the solid state. When the electron exchange is ultimately rapid, the two peaks are expected to coalesce to give a single broad peak, and at a moderate exchanging velocity, the two CV peaks will become broad with a smaller ΔE value than that for monomeric quinone.

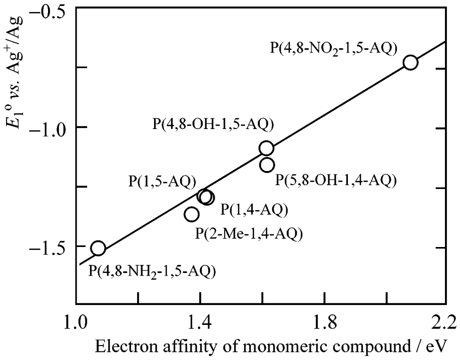
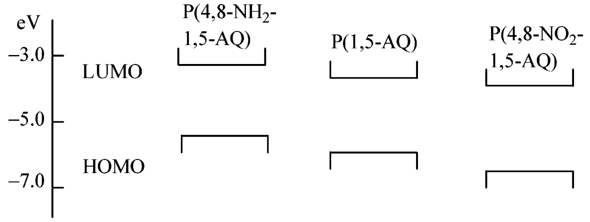


Figure 11. Plots of $E_1°$ of PAQs vs calculated electron affinity of monomeric compound.

(ii) In cases of monomeric anthraquinones, the E_1 and E_2 processes give the same peak area. On the other hand, PAQs generally give a considerably smaller peak area for the E_2 process as seen in Figure 10 and CV chart previously reported for P(2-Me-1,4-AQ).[5a] The doping level for the E_2 process (y in Table 2) is smaller than that for the E_1 process (x in Table 2), revealing that the presence of $AQ^{-\bullet}$ species in the π-conjugated polymer system makes the second step reduction difficult, presumably due to electronic repulsion.

(iii) The $E_1°$ and $E_2°$ values appear to reflect the electron accepting ability of the recurring monomer unit. Thus, P(4,8-NO_2-1,5-AQ) with the electron-withdrawing NO_2 groups gives higher $E_1°$ and $E_2°$ values than those of P(1,5-AQ), whereas P(4,8-NH_2-1,5-AQ) gives lower $E_1°$ and $E_2°$. Figure 11 exhibits plots of $E_1°$ vs electron affinity of the corresponding monomeric compound estimated by MOPAC calculation with Cache system using AM1. Similar correlation has been reported between the reduction potential of poly(arylene)s and corresponding monomeric aromatic compounds,[3b,5b] and

Chart 3. HOMO and LUMO Energies of 1,5-PAQs



the slope (0.79) of the line in Figure 11 is comparable to that (0.85 ± 0.02) observed with various poly(arylene)s. For P(4,8-NH_2-1,5-AQ), P(1,5-AQ), and P(4,8-NO_2-1,5-AQ), their ionization potentials (IP) were evaluated from ultraviolet photoelectron spectroscopy (UPS)[28a] and data are given in Table 2. Plots of the IP values of the polymer vs IP values of the corresponding monomeric compounds estimated by the MOPAC calculation also gives a linear correlation (Supporting Information). Chart 3 depicts HOMO and LUMO energies of PAQs evalulated from UPS, UV−vis, and photoluminescence data. The electronic state of 1,5-PAQs apparently reflects the inductive effect of the substituent.

(iv) Films of PAQs show electrochromism as shown in Table 2, although the electrochromism is not clear for black P(5,8-OH-1,4-AQ) whose UV−vis spectrum shows a broad absorption band covering most part of the visible region.

P(5,8-OR-1,4-AQ)s are also electrochemically active. For example, a P(5,8-$OC_{16}H_{33}$-1,4-AQ) film on a Pt plate shows E_{pc}s (or *n*-doping peaks) at −0.95 and −1.64 V vs Ag^+/Ag.

Conducting Properties. Table 2 includes data of electrical conductivities of nondoped PAQs. As shown in Table 2, PAQs show some dc conductivity even at a nondoped state. Recently it has been reported that several π-conjugated polymeric compounds (e.g., poly(2,2-bipyridine)-transition metal complexes[12b] and poly(arylene)-*N*-oxides[28b]) show similar intrinsic dc conductivity at the nondoped state, and their electrical conducting property has been attributed to the formation of carrier in the π-conjugated main chain by MLCT or by taking some resonance forms in the *N*-oxides. Evolution of carriers in the π-conjugation system of the anthraquinone unit bearing the OR, OH, NH_2, or NO_2 group by taking analogous resonance structures is also conceivable. Electrical conductivity decreased by lowering temperature. Measurement of magnetic susceptibility at low temperature showed a unique diamagnetic contribution below 70 K as described in the Supporting Information, however, measurement of electrical conductivity below 70 K was not possible because of the very low conductivity.

Photovoltaic Cell. Application of π-conjugated polymers to photovoltaic cell is the subject of recent interest.[29−32] By using a vacuum deposition method, an indium−tin-oxide (ITO)/vd-PTh (50 nm)/LiF (2 nm)/vd-P(4,8-NO_2-1,5-AQ) (50 nm)/LiF (2 nm)/Al photovoltaic cell was constructed (vd-PTh = vacuum deposited poly(thiophene-2,5-diyl)[33] and vd-P(4,8-NO_2-1,5-AQ) = vacuum deposited P(4,8-NO_2-1,5-AQ)). It has been reported that low molecular weight fractions (up to molecular weight of about 2000) of π-conjugated poly(arylene)s are sublimable when heated under vacuum to give vacuum-deposited thin film with good quality.[33] In this photovoltaic cell, PTh is a typical hole-carrying material, and P(4,8-NO_2-1,5-AQ) is regarded as an electron-carrying material in view of its electron accepting properties. Holes and electrons generated by irradiation of light are considered to move through the PTh layer and P(4,8-NO_2-1,5-AQ) layer to reach the ITO and Al electrodes, respectively. It is known that insertion of a LiF layer improves characteristics of various organic electric devices such as photovoltaic cells;[31] thickness of the LiF layers has been optimized in the cell shown above.

The cell or the electric device gives a rectification curve in the dark. Under illumination, a curve characteristic of a photovoltaic cell[29−32] was obtained with open circuit voltage (V_{oc}) of about 2.0 V (cf. Supporting Information). This V_{oc} value is somewhat smaller than the band gap of P(4,8-NO_2-1,5-AQ) (cf. Chart 3) and largest among reported organic photovoltaic cells, to our knowledge. The determining factors for the V_{oc} of organic photovoltaic cells is still controversial. Fill factors of the cell were 0.26 and 0.25 under illumination of 50 mW cm^{-2} and 70 mW cm^{-2} to give energy conversion efficiency of 0.20 and 0.27%, respectively.

Conclusion

Various new main-chain type polyanthraquinones have been prepared by dehalogenative polycondensation. According to the polymerization process, they have well-defined bonding between the monomeric units, and XRD analyses reveal their packing structures. P(5,8-OR-1,4-AQ) with long alkoxy side chains assumes an end-to-end stacking structure in the solid and exhibited piezochromism and liquid crystalline behavior. Cyclic voltammograms, IP data, and data obtained in chemical reduction indicate that the polymers have an electron-accepting nature based on the anthraquinone unit and the ease of reduction reflects electronic effect of the substituent. A photovoltaic cell using P(4,8-NO_2-1,5-AQ) gives an open circuit voltage of about 2 V. The polymers are soluble in organic solvents and films are easily obtained by casting from the solution. They reveal fundamental electronic and optical properties of polymers constituted of typical electron-accepting quinone units and are expected to serve as materials to support future organic devices.

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(28) (a) Miyamae, T.; Aoki, M.; Etori, H.; Muramatsu, Y.; Saito, Y.; Yamamoto, T.; Sakurai, Y.; Seki, K.; Ueno, N. *J. Electron Spectrosc. Relat. Phenom.* **1998**, *88−91*, 905. (b) Yamamoto, T.; Lee, B.-L.; Hayashi, H.; Saito, N.; Maruyama, T. *Polymer* **1997**, *38*, 4233.

(29) Yu, G.; Hummelen, J. C.; Wudl, F.; Heeger, A. J. *Science* **1995**, *270*, 1789.

(30) Graström, M.; Petritsch, K.; Arias, A. C.; Lux, A.; Andersson, M. R.; Friend, R. H. *Nature (London)* **1998**, *395*, 257.

(31) (a) Brabec, C. B.; Cravino, A.; Meissner, D.; Sariciftci, N. S.; Fromherz, T.; Rispens, M. T.; Sanchez, L.; Hummelen, J. C. *Adv. Funct. Mater.* **2001**, *11*, 374. (b) Shaheen, S. E.; Brabec, C. J.; Sariciftci, N. S. *Appl. Phys. Lett.* **2001**, *78*, 841.

(32) (a) Arias, A. C.; Granström, M.; Petritsch, K.; Friend, R. H. *Synth. Met.* **1999**, *102*, 953. (b) Tada, K.; Onoda, M. *Jpn. J. Appl. Phys.* **2000**, *39*, 3623.

(33) (a) Yamamoto, T.; Kanbara, T.; Mori, C.; Wakayama, H.; Fukuda, T.; Inoue, T.; Sasaki, S. *J. Phys. Chem.* **1996**, *100*, 12631. (b) Yamamoto, T.; Wakayama, H.; Fukuda, T.; Kanbara, T. *J. Phys. Chem.* **1992**, *96*, 8677. (c) Yamamoto, T.; Kanbara, T.; Mori, C. *Synth. Met.* **1990**, *38*, 399.

Experimental Section

Materials and Measurements. Dichloroanthraquinones were prepared by modifying the literature methods.[26,34] Bis(1,5-cyclooctadiene)nickel, Ni(cod)$_2$, was prepared according to the literature.[35] Solvents were distilled and stored under N_2. Activated copper was purchased from Aldrich or prepared according to the literature.[36] Poly(9,9-bis(2-ethylhexyl)fuluorene-2,7-diyl) was prepared according to the literature method using Ni(cod)$_2$.[18] Rubbed polyimide film on a quartz glass plate was prepared by Nissan Chemical Industries, Ltd.

NMR and IR spectra were recorded on a JEOL EX-400 or JEOL GX-270 spectrometer and a JASCO IR-800 spectrometer, respectively. UV−vis and photoluminescence spectra were recorded on a Shimadzu UV-3100 and a Hitachi F-4010 spectrometer, respectively. Cyclic voltammetry was performed with a Hokuto Denko HA-501 galvanostat/potentiostat and a Hokuto Denko KB-104 function generator. Polymer powder for piezochromism was placed in a diamond-anvil pressure cell and pressed, and the applied pressure was determined on the basis of the pressure shift in the sharp R-line photoluminescence (PL) of ruby added to the polymer sample.[23,24] *I*-voltage characteristics of the photovoltaic cell were obtained with a Hewlett-Packard 4155B semiconductor parameter analyzer.

Synthesis of Polymers. *P(5,8-OC$_6$H$_{13}$-1,4-AQ).* To a DMF solution (30 mL) containing Ni(cod)$_2$ (0.29 g, 1.1 mmol), cod (0.13 mL), and bpy (0.17 g, 1.1 mmol) in a Schlenk tube was added 1,4-dichloro-5,8-dimethoxyanthraquinone (0.43 g, 0.9 mmol) with stirring under N_2. The reaction mixture was stirred at 60 °C for 48 h to afford a yellow precipitate. The precipitate was collected by filtration, washed with diluted HCl$_{aq}$/MeOH (twice), NH$_4$OH$_{aq}$/MeOH (3 times), MeOH, warm ethylenediaminetetraacetic acid (EDTA)$_{aq}$/MeOH (twice), H_2O, and MeOH in this order. Reprecipitation of the chloroform solution of the polymer into MeOH and drying under vacuum afforded an orange powder of the polymer in 42% yield. The polymer was free from Cl. Anal. Calcd for $(C_{26}H_{30}O_4)_n$: C, 76.8; H, 7.4. Found: C, 76.9; H, 7.3; Cl, 0.0. IR (KBr, cm^{-1}): 2954, 2928, 1672, 1459, 1264, 1209. ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ 8.23 (d, terminal-H), 7.8−7.4 (Ar−2,3-H, 2H), 7.2−6.9 (Ar−6,7-H, 2H), 4.2−3.5 (Ar−OCH$_2$−, 4H), 2.1−1.0 (−(CH$_2$)$_4$−, 16H), 1.0−0.5 (−CH$_3$, 6H). $M_n = 4000$ (determined by vapor pressure osmometry in CHCl$_3$), 5500 (determined by ^{1}H NMR spectroscopy).

Other P(5,8-OR-1,4-AQ)s and dihydroxy- and diaminoanthraquinone polymers were prepared analogously, and their analytical, IR, and ^{1}H NMR data are given in the Supporting Information, which also includes the synthetic data of P(4,8-NO$_2$-1,4-AQ).

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Supporting Information Available: Table of solubility, IR and NMR spectroscopic and analytical data, XRD data, ionization potential, magnetic susceptibility, data of the photovoltaic cell, and UV−vis data of P(5,8-OC$_{16}$H$_{33}$-1,4-AQ) (pdf; 11 pages). This material is available free of charge via the Internet at http://pubs.acs.org/.

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(34) (a) Allen, C. F. H.; Frame, G. F.; Wilson, C. V. *J. Org. Chem.* **1941**, *6*, 732. (b) Thomas Winter, R.; Ssercel, A. D.; Hollis Showalter, H. D. *Synthesis* **1988**, 712.

(35) Bogdanovic, B.; Kröner, M.; Wilke, G. *Justus Liebigs Ann. Chem.* **1966**, *699*, 1.

(36) Core, P. H.; Hughes, G. K. *J. Chem. Soc.* **1959**, 1615.