Preparation and properties of new π-conjugated polyquinoxalines with aromatic fused rings in the side chain

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Summary

New π-conjugated polyquinoxalines with aromatic fused rings in their side chain have been prepared. Dehalogenative organometallic polycondensation of 5,8-dibromo[2,3-*b*]-acenaphthenequinoxaline and 5,8-dibromo[2,3-*b*]phenanthrenequinoxaline with a zerovalent nickel complex afforded poly([2,3-*b*]acenaphthenequinoxaline-5,8-diyl) (P(5,8-Qx(ace))) and poly([2,3-*b*]phenanthrenequinoxaline-5-8-diyl) (P(5,8-Qx(phen))) in high yields. P(5,8-Qx(ace)) had an [η] value of 0.23 dL g^{-1} and showed absorption and photoluminescence peaks at 445 and 565 nm, respectively. (P(5,8-Qx(phen))) gave absorption and photoluminescence peaks at 400 and 514 nm, respectively. XRD data indicated formation of ordered structures of the polymers in the solid. Preparation of related copolymer with thiophene is also reported.

Introduction

Preparation of π-conjugated polymers and revealing their chemical and physical properties are the subject of recent interest (1, 2). Poly(*p*-phenylene), PPP, is one of the basic π-conjugated polymers, and introduction of various substituents such as alkyl and alkoxy side chains to PPP has been carried out. However, introduction of a planar fused aromatic ring unit as the side chain of PPP has not been paid much attention, in spite of potential interesting properties of such PPP type polymer with the fused aromatic ring. Preparation of such polymers may not be easy. Recently, it was reported that poly(quinoxaline-5,8-diyl) (P(5,8-Qx)) and its alkyl and aryl derivatives could be prepared by dehalogenation polycondensation of the corresponding dihalo monomers (3, 4). In the case of P(5,8-Qx), introduction of the planar fused aromatic ring as the side chain in the dihalo monomer is not difficult, and preparation of the PPP type polymers with the fused aromatic ring as the side chain would be possible by using the monomer. This paper reports preparation of such new derivatives of poly(quinoxaline-5,8-diyl), P(5,8-Qx(ace)) and
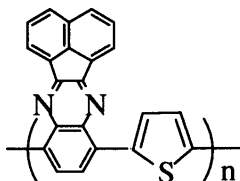
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P(5,8-Qx(phen)), with acenaphthene and phenanthrene groups as the side chain. Preparation of a copolymer with thiophene will also be reported.
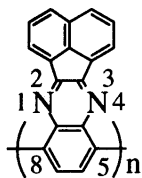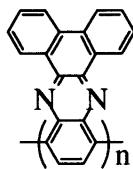
P(5,8-Qx(ace))   P(5,8-Qx(phen))


P(Th-5,8-Qx(ace))

Experimental

Materials

Bis(1,5-cyclooctadiene)nickel(0) (5), and 1,4-dibromo-2,3-diaminobenzene (6) were prepared as previously reports. Acenaphtenequinone and phenanthrenequinone were purchased from Aldrich, Inc. 2,5-Bis(trimethylstannyl)thiophene was prepared according to a method given in the literature (7).

Synthesis of monomers

5,8-Dibromo[2,3-*b*]acenaphtenequinoxaline (Monomer-1) was prepared from 1,4-di-bromo-2,3-diaminobenzene and acenaphtenequinone by modifing a reported method used for preparation of quinoxalines (8).

Monomer-1
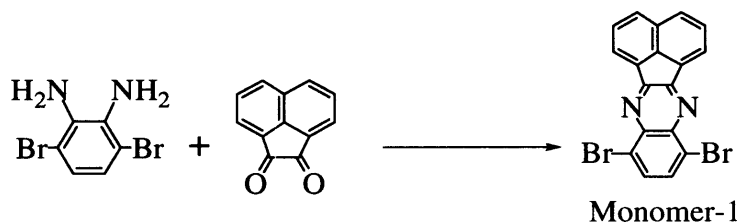
To a solution of 1,4-dibromo-2,3-diaminobenzene (0.80 g, 3.0 mmol) in 30 cm^3 of methanol at room temperature, was added acenaphtenequinone (0.55 g, 3.0 mmol) and 1 cm^3 of glacial acetic acid. After stirring for 10 h at 85 °C, the mixture was cooled. The precipitate was collected by filtration, washed with ethanol (3 times), and dried under vacuum. Yield = 0.99 g (79%). ^{1}H NMR (CF$_3$COOD): δ 8.12 (m, 2H), 8.22 (d, 2H), 8.55 (d, 2H), 8.96 (d, 2H). Anal. Calcd. for C$_{18}$H$_8$N$_2$Br$_2$: C = 52.5, H = 2.0, N = 6.8, Br = 38.8%. Found: C = 52.5, H = 2.1, N = 6.8, Br = 38.7%. 5,8-Dibromo[2, 3-*b*]phenanthrenequinoxaline (Monomer-2) was prepared analogously by using phenan-

threnequinone. Yield = 1.22 g (92%). ^{1}H NMR (CF$_3$COOD): δ 7.95 (m, 2H), 8.11 (m, 2H), 8.53 (d, 2H), 8.74 (d, 2H), 9.14 (d, 2H). Anal. Calcd. for C$_{20}$H$_{10}$N$_2$Br$_2$: C = 54.8, H = 2.3, N = 6.4, Br = 36.5%. Found: C = 55. 1, H = 2.3, N = 6.4, Br = 36.9%.

Polymerization

Polymerization of 5,8-dibromo[2,3-*b*]acenaphtenequinoxaline and 5,8-dibromo[2,3-*b*]-phenanthrenequinoxaline were carried out in a manner similar to that previously reported for the preparation of polyquinoxalines (3, 4). For example, the polymerization of 5,8-di-bromo[2,3-*b*]acenaphtenequinoxaline was carried out as follows. To a solution of Ni(cod)$_2$ (0.62 g, 2.25 mmol) in 5 cm^3 of dry *N,N*-dimethylformamide (DMF) were added 0.35 cm^3 of 1,5-cyclooctadiene and 2,2'- bipyridine (0.35 g, 2.25 mmol), and 5,8-dibromo[2, 3-*b*]acenaphtenequinoxaline (0.62 g, 1.5 mmol). After stirring at 60 °C for 48 h under N$_2$, the mixture was poured into aqueous ammonia. The precipitate was washed with warm NH$_4$OHaq (3 times), a warm aqueous solution of disodium ethylenediaminetetraacetate (3 times), warm water, methanol (3 times), and CHCl$_3$ (once) in this order. The yellow powder of P(5,8-Qx(ace)) was collected by filtration and dried under vacuum. Yield = 0.35 g (92%). Anal. Calcd. for (C$_{18}$H$_8$N$_2$· 0.7 H$_2$O)$_n$: C = 81.6, H = 3.6 , N = 10.6, O = 4.2%. Found: C = 81.4, H = 3.4, N = 10.8, O = 4.5, Br = 0.25%.

Brown powder of P(5,8-Qx(phen)) was prepared analogously by using 5,8-dibromo[2, 3-*b*]phenanthrenequinoxaline (yield 72%). Anal. Calcd for (C$_{20}$H$_{10}$N$_2$· 1.0 H$_2$O)$_{14}$Br$_2$: C = 78.1, H = 3.9, N = 9.0, O = 5.2, Br = 3.7%. Found: C = 77.9, H = 3.9, N = 8.6, O = 5.2, Br = 3.8%.

Copolymerization

Copolymerization was carried out between 5,8-dibromo[2,3-*b*]acenaphtenequinoxaline (0.41 g, 1.0 mmol) and 2,5-bis(trimethylstannyl)thiophene (0.44 g, 1.0 mmol) by using Pd(PPh$_3$)$_4$ (58 mg, 0.05 mmol) as the catalyst in 10 cm^3 of DMF at 90 °C for 48 h under N$_2$. The obtained polymer was washed with diluted hydrochloric acid (3 times), NH$_4$OH (once), warm water, MeOH (3 times), and acetone (once) in this order. The black powder of the copolymer, P(Th-5,8-Qx(ace)), was collected by filtration and dried under vacuum. Yield = 0.23 g (70%). Anal. Calcd. for Br(C$_{22}$H$_{10}$N$_2$S·0.7 H$_2$O)$_{14}$C$_{18}$H$_8$N$_2$Br: C = 74.3, H = 3.2, N =7.9, Br = 3.0, S = 8.5%. Found: C = 74.8, H = 3.1, N =7.6, Br = 3.1, S = 8.7%.
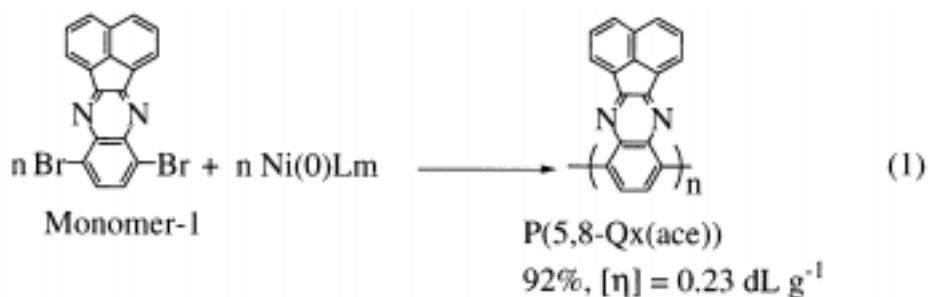
Measurements

IR, NMR, and UV-vis spectra were recorded on a JASCO IR - 810 spectrometer, a JEOL EX-400 spectrometer, and JASCO Ubest-35 or Shimadzu UV-2100 PC spectrometer, respectively. Photoluminescence spectra were obtained using a Hitachi F-4010 spectrometer. Powder X-ray diffraction (XRD) patterns were recorded on a Philips PW1000 X-ray

diffractometer. Viscosity was measured with a Ubbelohde viscometer. Gel permeation chromatography (GPC) analysis was carried out on a Toso HLC-8020 gel permeation chromatograph (polystyrene standards; eluent = DMF). MALDI-TOF MS analysis was performed using a Thermo Quest LASERMAT 2000 equipped with a 337 nm laser. Dithranol was used as the matrix.

Results and discussion

The dehalogenation polycondensation of the Monomer-1 with the zerovalent nickel complex gave the corresponding polymer in a good yield (Eq. 1).

$$n \, Br\text{-}\square\text{-}Br + n \, Ni(0)Lm \longrightarrow \left(\square \right)_n \quad (1)$$

Monomer-1

P(5,8-Qx(ace))

92%, $[\eta] = 0.23$ dL g^{-1}

P(5,8-Qx(phen)) was prepared analogously from Monomer-2, and the following copolymer, P(Th-5,8-Qx(ace)), was prepared by using Stille coupling (Eq. 2).

$$n \, Monomer\text{-}1 + n \, Me_3Sn\text{-}\square_S\text{-}SnMe_3 \xrightarrow{Pd(PPh_3)_4} P(Th\text{-}5,8\text{-}Qx(ace)) \quad (2)$$
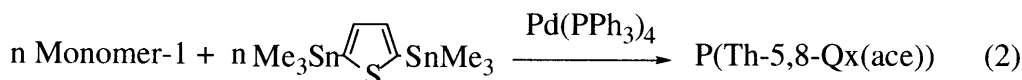
P(5,8-Qx(ace)) is soluble in CF$_3$COOH, however, it is only partly soluble in formic acid, DMF, and CHCl$_3$. The polymer gave an $[\eta]$ value of 0.23 dLg^{-1} (dL = 100 cm^3) in CF$_3$COOH. Since drying up the chloroform solution gave a sample whose IR spectrum agreed with that of original sample, a fraction with lower molecular weight was considered soluble in chloroform. The GPC analysis (eluent = DMF) indicated that the DMF soluble part (about 20 wt%) of P(5,8-Qx(ace)) had a number average molecular weight, Mn, of 3870 and weight average molecular weight, Mw, of 4100. TOF mass spectrum showed peaks in a mass range of about 1000-6000 with peak separation of 252 agreeing with the mass of the repeating unit. P(5,8-Qx(phen)) was partially soluble in CF$_3$COOH and only slightly soluble in DMF. Copolymer was also only slightly soluble in DMF.

Figure 1 exhibits IR spectra of Monomer-1, P(5,8-Qx(ace)), P(Th-5,8-(ace)), and P(5,8-Qx(phen)). As shown in Fig. 1, the IR spectrum of P(5,8-Qx(ace)) gives peaks originated from the quinoxaline unit. However, a peak of Monomer-1 at 886 cm^{-1}, which is assigned to the ν(C-Br) peak, is not obsevable in the IR spectrum of P(5,8-Qx(ace)). The polymer contained only a small amount of Br as described in the experimental part.

Figure 2 shows ^{1}H-NMR spectrum of P(5,8-Qx(ace)). Peak a is assigned to hydrogens of the *p*-phenylene unit in the main chain by comparing ^{1}H-NMR spectra of P(5,8-Qx)s with phenyl or *p*-tolyl substituents at the 2,3-positions (3, 4).

Table 1 shows UV-vis and photoluminescence data of the polymers, and Fig. 3 exhibits UV-vis and photoluminescence data of P(5,8-Qx(ace)) in DMF. P(5,8-Qx(ace)) in the DMF solution gave the lowest energy π-π^* absorption peak at 445 nm, which is shifted to a longer wavelength from those of P(5,8-Qx)s with alkyl or aryl groups (λmax = about 380 nm in non acidic solvents) (4).

P(5,8-Qx(ace))		P(5,8-Qx)s with substituents at the 2- and 3-positions (3, 4)
λmax = 445 nm	>	380 ± 7 nm
(in DMF)		(in CHCl$_3$ or NMP)

The peak at 445 nm is not observed in the monomer, and is considered to originate from expansition of the π-conjugation system due to arylene-arylene interaction along the polymer chain. The appearance of the peak at a longer wavelength than those of other P(5,8-Qx)s indicates a more effective arylene-arylene electronic coupling in P(5,8-Qx(ace)). A dichroic experience of P(5,8-Qx(ace)) in a stretched PVA film, which was carried out similarly to cases of other P(5,8-Qx)s (10), revealed that the peak of P(5,8-Qx(ace)) at 445 nm had a transition moment along the polymer main chain.
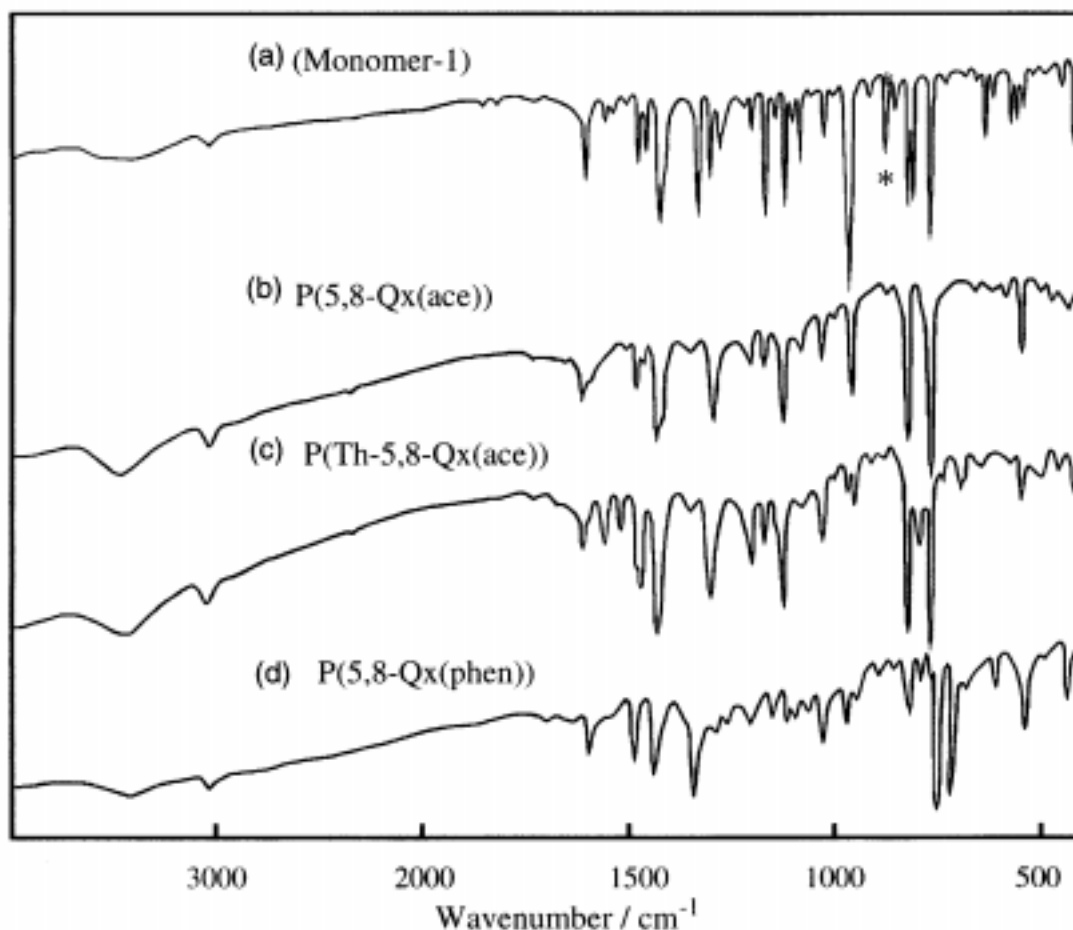

Figure 1 IR spectra of (a) 5,8-dibromo[2,3-*b*]acenaphtenequinoxaline (Monomer-1), (b) P(5,8-Qx(ace)), (c) P(Th-5,8-Qx(ace)), and (d) P(5,8-Qx(phen)). The absorption peak with * (at 886 cm^{-1}) is assigned to v(C-Br).

Table. 1 Optical properties of the polymers (in DMF)

polymer	absorption λ max/nm	photoluminescence λ max/nm	excitation spectrum λ max/nm
P(5,8-Qx(ace))	322, 445	560	327, 450
P(Th-5,8-Qx(ace))	321, 471 (498)[a]	600	323, 474
P(5,8-Qx(phen))	311, 400	514	310, 400

[a] For vacuum deposited thin film.

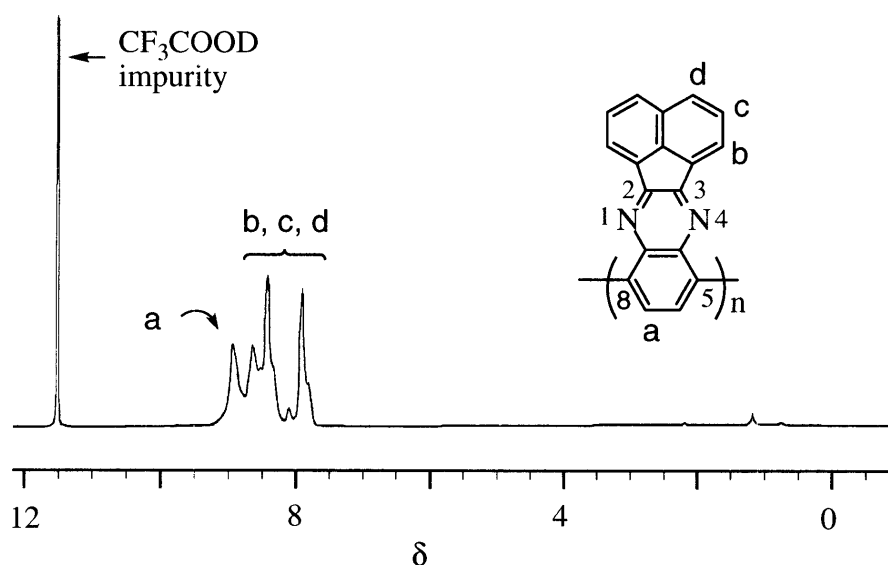**Figure 2** ^{1}H-NMR spectrum of P(5,8-Qx(ace)) in CF_3COOD.

P(5,8-Qx(ace)) gives a photoluminescence peak at 565 nm (Fig. 3), which locates near the onset position of the absorption band at 445 nm, similar to cases of usual aromatic compounds and polymers. The excitation spectrum monitored at 565 nm shows two peaks at 327 and 450 nm in accord with the absorption spectrum. P(5,8-Qx(ace)) also shows photoluminescence in a PVA film and gives a quantum yield of about 10%.

The copolymer, P(Th-5,8-Qx(ace)), shows the lowest energy absorption peak at a longer wavelength than the homopolymer, presumably due to an intramolecular charge-transferred structure of the copolymer (Table 1). The quinoxaline unit is a π-accepting unit whereas the thiophene unit serves as a π-donor. Similar shifts to a longer wavelength has been reported for other quinoxaline copolymers with thiophene (11) and has been explained by the intramolecular charge transferred structure. A vacuum deposited thin film of P(Th-5,8-Qx(ace)) gives a peak at a longer wavelength (498 nm ; Table 1) than that of P(Th-5,8-Qx(ace)) in the solution, suggesting the presence of intermolecular interaction in

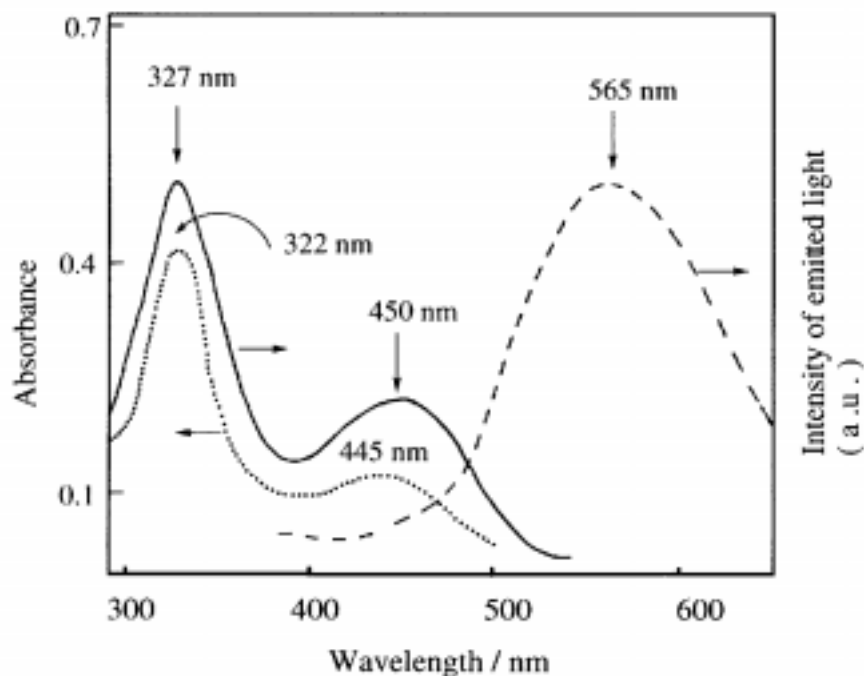the solid state through the aromatic fused ring side chain.

Figure 3 Absorption (. . . .), excitation (——) (monitored at 565 nm) and photoluminescence (----) spectra of P(5,8-Qx(ace)) in DMF.
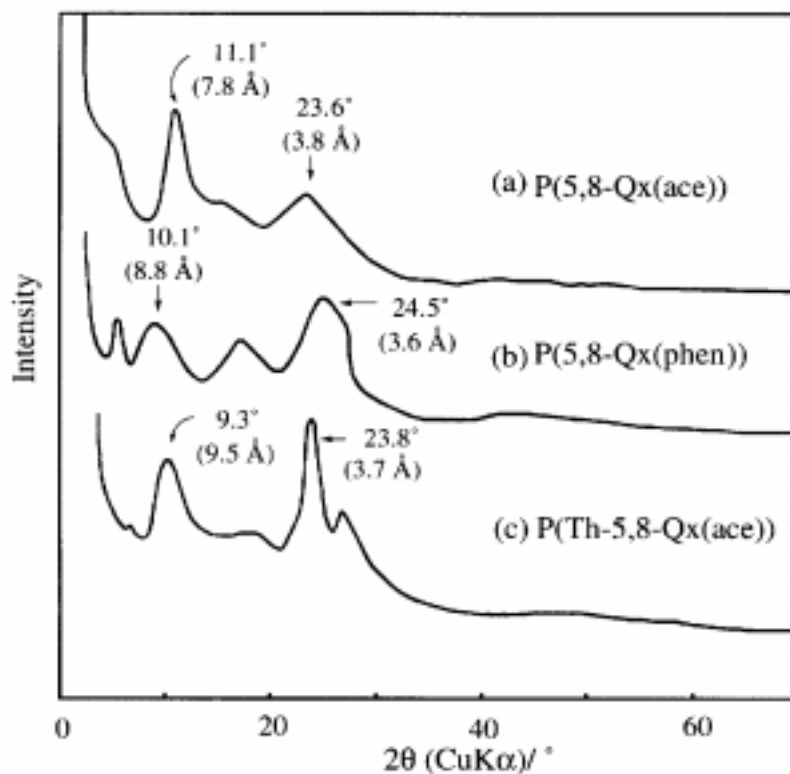

Figure 4 Powder XRD petterns of (a) P(5,8-Qx(ace)), (b) P(5,8-Qx(phen)), and (c) P(Th-5,8-Qx(ace)).

Fig. 4 shows powder X-ray diffraction (XRD) patterns of the polymers. The XRD patterns reveal that they take ordered structures in the solid. Although detailed analysis is

required for their pocking structures, the peak at about d = 3.7 Å may correspond to a face -to-face packing distance between coplanar π-conjugated polymers. It is reported that some π-conjugated polymers such as head-to-tail type poly(3-alkylthiphene), HT-P3RTh, give such a face-to-face distance in their XRD patterns (12). The appearance of the peaks at about d = 3.7 Å for the present polymers suggests the presence of similar π-π stacking force between the polymer molecules possibly assisted by the fused aromatic side chains. On the other hand, the π-stacking of HT-P3RTh in the solid is considered to be assisted by the long 3-alkyl chains. Although preparation of various polyquinoxalines has been reported (3, 4, 13-15), formation of an ordered structure in the solid has not been paid much attention. As described above, a new type of π-conjugated polymers with aromatic fused side chain can be obtained by using the quinoxaline monomers.

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