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Unexpected discovery of the formation of high-molecular-weight aromatic polyamides from unstoichiometric diacyl chloride/diamine components

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Abstract

Two bis(ether-benzoyl chloride)s, 4,4′-(1,4-phenylenedioxy)dibenzoyl chloride (**I**) and 4,4′-(1,4-naphthalenedioxy)dibenzoyl chloride (**II**), were unexpectedly synthesized through nucleophilic substitution reaction of *p*-fluorobenzonitrile with 2-(6-oxido-6H-dibenz⟨c,e⟩⟨1,2⟩oxaphosphorin-6-yl)-1,4-benzenediol (**1**) and 2-(6-oxido-6H-dibenz⟨c,e⟩⟨1,2⟩oxaphosphorin-6-yl)-1,4-naphthalenediol (**2**), respectively, followed by hydrolysis and chlorination. A series of aromatic poly(ether-amide)s, having inherent viscosities of 0.65–0.99 dl g^{-1}, prepared by the low-temperature solution polycondensation from the diacid chloride **I** with various aromatic diamines in an initial feeding molar ratio of diamine:diacyl chloride of 1:1 and 1:1.55, respectively. All resultant poly(ether-amide)s showed high and similar inherent viscosity regardless of the great stoichiometric imbalance. The unexpected results could be attributed to the very slow dissolution rate of the diacid chloride **I** in the reaction solvents such as N-methyl-2-pyrrolidone and N,N-dimethylacetamide.

1. Introduction

It has been known for many years that phosphorus-containing polymers exhibit flame retardancy and they are gaining increasing popularity over their halogen counterparts because they generally generate less toxic combustion products. Several systems have been reported for poly(arylene ether)s, polyimides, polyamides, polyesters, and bismaleimide and epoxy networks [1–22]. Kannan *et al* [6] have developed flame-retardant phosphorus-containing polyester amides; however, their degradation temperatures (T_d), from 250 to 300 °C, are not high enough. This phenomenon could be attributed to the polyphosphate amides having a O=P–O bond in the main chain. The polymers degrade rapidly during heating due to the cleavage of O=P–O bonds in the main chain. Thus, in order

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to increase the thermal stability while maintaining flame retardancy, the O=P–O group should be covalently incorporated into polymeric systems in side chains as pendant groups [1, 2, 14–22]. To enhance solubility with the retention of high performance and flame resistance, we attempt to synthesize phosphorus-containing poly(ether-amide)s with a bulky biphenylenephosphonato [O=P–O(Ph)$_2$] group in the side chain while maintaining a high aromatic content and symmetrical 1,4-phenylene or 1,4-naphthalene structure simultaneously in the main chain. Recently, it was discovered that aromatic bis(ether-carboxylic acid)s can be readily synthesized through nucleophilic displacement reaction of *p*-fluorobenzonitrile with the bisphenoxide ion followed by hydrolysis [23, 24]. The present study follows that synthetic route to prepare ether-containing diacid monomers, starting from biphenylenephosphonato-substituted hydroquinone and 1,4-naphthalenediol, i.e. 2-(6-oxido-6H-dibenz⟨c,e⟩⟨1,2⟩oxaphosphorin-6-yl)-1,4-benzenediol (**1**) and 2-(6-oxido-6H-dibenz⟨c,e⟩⟨1,2⟩oxaphosphorin-6-yl)-1,4-naphthalenediol (**2**). However, the side chain P–Ar bonding of the phosphorus-containing aromatic diols (**1** and **2**) was cleaved by alkaline hydrolysis during the nucleophilic fluoro-displacement reaction due to the presence of basic potassium carbonate. Therefore, the approach to synthesizing the phosphorus-containing bis(ether-carboxylic acid)s by the nucleophilic substitution of biphenylenephosphonato-substituted aromatic diols (**1** and **2**) with *p*-fluorobenzonitrile followed by hydrolysis of the resulting dinitrile compounds is infeasible. Rather than biphenylenephosphonato bis(ether-acyl chloride), the non-phosphoro diacid chloride, 4,4′-(1,4-phenylenedioxy)dibenzoyl chloride (**I**), was obtained through nucleophilic substitution reaction of *p*-fluorobenzonitrile with diol **1** followed by hydrolysis and chlorination. In this article, we describe an unexpected discovery of the formation of aromatic poly(ether-amide)s with high molecular weight by low-temperature solution polycondensation from stoichiometric ratio imbalanced diacyl chloride **I** and aromatic diamines. In general, we consider two equivalent linear step-growth reactions, assuming difunctional monomers and stoichiometric equivalence, where A and B represent the complementary functional groups. The degree of polymerization (Xn) is proportional to $1/(1-P)$, where P is the fractional extent of the reaction. This rather simple conclusion was proposed by W H Carothers in the 1930s. If the restriction on stoichiometric equivalence is removed, similar reasoning leads to $Xn = (1+r)/(1+r-2rP)$, where $r = N_{B0}/N_{A0}$ is the stoichiometric ratio of functional groups present (B is taken to be limiting reactants, so r is less than one). To examine the effect of stoichiometric imbalance, consider the limiting case of complete conversion, $P = 1$, for which $(Xn)_{\max} = (1+r)/(1-r)$; reducing r by the deliberate introduction of an excess of one of the monomers provides a convenient means of molecular-weight control in a step-growth polymerization [25]. Contrary to expectation, a series of aromatic poly(ether-amide)s was synthesized by the low-temperature solution polycondensation of diacid chloride **I** and various aromatic diamines in polar aprotic solvents such as N-methyl-2-pyrriolidone (NMP) or N,N-dimethylocetamide (DMAc) at -10–$0\,^{\circ}$C. The initial feeding mole ratios of diamine/diacyl chloride **I** were 1.0/1.0 and 1.0/1.55. All the resultant polyamides showed high and very similar inherent viscosities regardless of the great stoichiometric imbalance. The unexpected results could be attributed to the slow dissolution behaviour of the diacid chloride in NMP or DMAc.

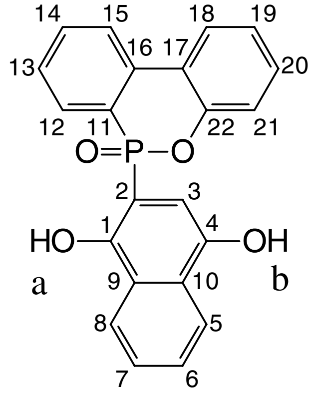
2. Experiment

2.1. Materials

9,10-Dihydro-9-oxa-10-phosphaphenanthrene 10-oxide (DOPO) (from TCI), *p*-benzoquinone (from Aldrich), 1,4-naphthaquinone (from TCI), toluene (from Acros), and *p*-fluorobenzonitrile were used without further purification. Isophthaloyl chloride (**Ia**) (from TCI) was purified by recrystallization before use. Reagent-grade aromatic diamines such as 4,4′-oxydianiline (**IIIa**, from TCI), 2,2-bis(4-aminophenyl)hexafluoropropane (**IIIb**, from Aldrich), 2,2-bis[4-(4-aminophenoxy)phenyl]propane (**IIIc**, from Aldrich), and 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (**IIId**, from Aldrich) were used as received. Commercially obtained anhydrous calcium chloride and potassium carbonate were dried under vacuum at 180 °C for 10 h. NMP, DMAc, and pyridine were purified by distillation under reduced pressure over calcium hydride. Triphenyl phosphite (TPP, from TCI) was purified by distillation under reduced pressure.

*2.2. Synthesis of 2-(6-oxido-6H-dibenz⟨c,e⟩⟨1,2⟩oxaphosphorin-6-yl)-1,4-benzenediol (**1**) and 2-(6-oxido-6H-dibenz⟨c,e⟩⟨1,2⟩oxaphosphorin-6-yl)-1,4-naphthalenediol (**2**)*

Into a 1 l three-neck flask equipped with a nitrogen inlet, a Dean–Stark trap, and a condenser, was charged 1.00 mol of DOPO and 700 ml toluene. The solution was heated with stirring at 140 °C for 3 h under nitrogen to facilitate dehydration. After most of the water was removed, 0.9 mol of powdery 1,4-naphthaquinone was added incrementally. The reaction mixture was maintained at 120 °C for 4 h after the complete addition of 1,4-naphthaquinone. The reaction mixture was allowed to cool, and the precipitate was filtered. The crude product was recrystallized twice from DMAc and dried in a vacuum oven at 180 °C for 8 h to afford ivory coloured crystals of **2** (70% yield), m.p. 294–295 °C (by DSC). The IR spectrum (KBr) exhibited characteristic absorptions at 944, 1165 (P–O–Ph), 1199 (P=O), 1328 (C–O), 1597 (P–Ph), and 3200 cm^{-1} (O–H). Analytically calculated for $C_{22}H_{15}O_4P$ (374.33): C, 70.59; H, 4.04; found: C, 70.45; H, 4.10. ^{1}H NMR (400 MHz, DMSO-d_6): 6.57 (d, J_{HCP} 11.9 Hz, 1H, H^3), 7.36–8.34 (m, 12H, ArH), 9.78 (s, 1H, –OH$_{\mathrm{b}}$), 10.89 (s, 1H, –OH$_{\mathrm{a}}$). ^{13}C NMR (100 MHz, DMSO-d_6): 154.50 (d, J_{CCCP} 4.9 Hz, C^4), 150.05 (d, J_{COP} 7.9 Hz, C^{22}), 147.12 (d, J_{CCP} 16.8 Hz, C^1), 136.05 (d, J_{CCP} 5.9 Hz, C^{16}), 134.88 (C^{13}), 132.04 (C^{20}), 131.85 (C^{15}), 130.03 (C^5), 129.89 (C^{14}), 129.56 (C^8), 126.97 (d, J_{CP} 115 Hz, C^{11}), 126.60 (C^{18}), 125.92 (C^{19}), 125.78 (C^{10}), 124.98 (d, J_{CCP} 9.9 Hz, C^{12}), 124.46 (C^9), 123.95 (C^6), 123.34 (C^7), 121.88 (d, J_{CCOP} 11.9 Hz, C^{17}), 121.10 (d, J_{CCOP} 6.9 Hz, C^{21}), 106.64 (d, J_{CCP} 10.9 Hz, C^3), 103.50 (d, J_{CP} 145 Hz, C^2).



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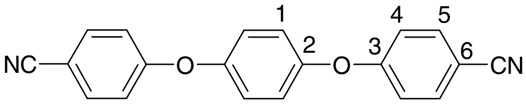
Structure 1.

2-(6-Oxido-6H-dibenz⟨c,e⟩⟨1,2⟩oxaphosphorin-6-yl)-1,4-benzenediol (**1**) was synthesized from DOPO and *p*-benzoquinone according to a similar procedure as described above. Pure **1** (75% yield) was obtained by recrystallization from DMAc twice as off-white crystals, m.p. 255–256 °C (by DSC) (literature [17] m.p. 255–256 °C). Analytically calculation for $C_{18}H_{13}O_4P$ (324.3): C, 66.67; H, 4.04; found: C, 66.56; H, 4.09. IR and NMR spectroscopic data are as reported [17].

*2.3. Nucleophilic fluoro-displacement of p-fluorobenzonitrile with phosphonato aromatic diols **1** and **2***

In a 300 ml round-bottomed flask, potassium carbonate (14.08 g; 0.1 mol) was added to a solution of the biphenylenephosphonato-hydroquinone **1** (16.21 g; 0.05 mol) in 200 ml of a 1:1 volume mixture of NMP and toluene. The suspension mixture was heated at reflux temperature using a Dean–Stark trap to remove the water by azeotropic distillation. After most of the toluene had been removed, *p*-fluorobenzonitrile (12.33 g; 0.102 mol) was added and heating was continued at 170 °C for 8 h. The reaction mixture was allowed to cool and poured into 1 l of water. The precipitate was filtered and recrystallized from acetonitrile twice and then dried *in vacuo* at 100 °C for 8 h to afford colourless needles (12.2 g), m.p. 214–215 °C (by DSC). IR (KBr): 2223 cm^{-1} (C≡N) and 1243 cm^{-1} (C–O). At first, the product was wrongly regarded as the biphenylenephosphonato containing bis(ether nitrile) PBCN as shown in scheme 2. In fact, further characterization revealed that this product is 4,4′-(1,4-phenylenedioxy)dibenzonitrile (**3a**). Analytically calculated for $C_{20}H_{12}N_2O_2$ (312.33): C, 76.91; H, 3.87; N, 8.97; found: C, 76.80; H, 3.84; N, 8.89. ^{13}C NMR (100 MHz, $CDCl_3$): 162.48 (C^3), 152.63 (C^2), 134.93 (C^5), 122.59 (C^1), 119.16 (C≡N), 118.35 (C^4), 106.35 (C^6). The m.p. of this compound is similar to that reported previously (literature [26] m.p. 212–213 °C). X-ray crystallography also confirmed the structure of **3a**.

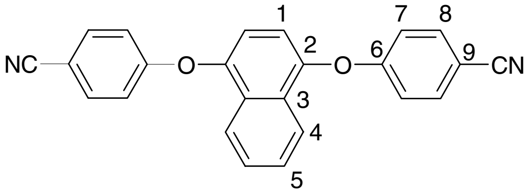


Structure 2.

Similarly, 4,4′-(1,4-naphthalenedioxy)dibenzonitrile (**3b**), rather than PBCN (scheme 2), was obtained from the condensation of biphenylenephosphonato-1,4-naphathalenediol **2** and *p*-fluorobenzonitrile according to a similar procedure as described above. Pure **3b** (60% yield) was obtained by recrystallization from acetonitrile twice as colourless needles, m.p. 197–198 °C (by DSC) (literature [27] m.p. 197–198 °C). Analytically calculated for $C_{24}H_{14}N_2O_2$ (362.38): C, 79.54; H, 3.89; N, 7.73; found: C, 79.46; H, 3.86; N, 7.55. ^{13}C NMR (100 MHz, $CDCl_3$): 162.87 (C^6), 148.47 (C^2), 134.81 (C^8), 128.62 (C^3), 128.02 (C^4), 122.52 (C^5), 119.03 (C≡N), 117.92 (C^7), 116.43 (C^1), 106.28 (C^9). The structure of **3b** was also confirmed by x-ray crystal analysis.

*2.4. Synthesis of 4,4′-(1,4-phenylenedioxy)dibenzoic acid (**4a**) and 4,4′-(1,4-naphthalenedioxy)dibenzoic acid (**4b**)*

The bis(ether-carboxylic acid)s were prepared from alkaline hydrolysis of the corresponding bis(ether nitrile)s. A representative synthetic procedure for **4a** is described as follows. Bis(ether nitrile) **3a** (31.2 g; 0.10 mol) was added to a mixed ethanol/water solution (300 ml/300 ml)



Structure 3.

containing 80 g (1.43 mol) of potassium hydroxide dissolved in the solution. The suspension was refluxed for 3 days until the evolution of ammonia had ceased. The resulting hot clear solution was filtered to remove any insoluble impurities. The hot filtrate was allowed to cool and was acidified with concentrated HCl to pH = 2–3 to precipitate a white solid which was filtered out, thoroughly washed with water, and dried *in vacuo* to afford 31.5 g (90% yield) of **4a**; m.p. 324–326 °C (by DSC) (literature [26] m.p. 322–324 °C). 4,4′-(1,4-Naphthalenedioxy)dibenzoic acid (**4b**) was synthesized from bis(ether nitrile) **3b** with a similar procedure as described above. White powder of **4b** was obtained (94% yield); m.p. 354–355 °C (by DSC) (literature [27] m.p. 354–355 °C).

*2.5. Synthesis of 4,4′-(1,4-phenylenedioxy)dibenzoyl chloride (**I**) and 4,4′-(1,4-naphthalenedioxy)dibenzoyl chloride (**II**)*

The diacyl chloride monomers were prepared by chlorination with thionyl chloride of the corresponding bis(ether-carboxylic acid)s. A representative synthetic procedure for diacyl chloride **I** is described as follows. 4,4′-(1,4-Phenylenedioxy)dibenzoic acid (**4a**) (17.5 g; 0.05 mol) was added to 150 ml of thionyl chloride in the presence of a few drops of DMF as the catalyst [28]. The mixture was heated with stirring at 70 °C for 8 h and excess thionyl chloride was removed by distillation. The resulting crude product was purified by sublimation to afford colourless needles (15.5 g, 80% yield) of 4,4′-(1,4-phenylenedioxy)dibenzoyl chloride (**I**); m.p. 209–210 °C (by DSC) (literature [29] m.p. 207-209C). Analytically calculated for $C_{20}H_{12}O_4Cl_2$ (387.30): C, 62.02; H, 3.12; found: C, 62.27; H, 3.19. 4,4′-(1,4-Naphthalenedioxy)dibenzoyl chloride (**II**) was prepared from 4,4′-(1,4-naphthalenedioxy)dibenzoic acid (**4b**) by a similar procedure as above. Colourless needles of **II** were obtained by recrystallization from a mixture of toluene and hexane (80% yield); m.p. 166–167 °C (by DSC) (literature [30] m.p. 167–168 °C). Analytically calculated for $C_{24}H_{14}O_4Cl_2$ (437.60): C, 65.90; H, 3.20; found: C, 66.27; H, 3.31.

2.6. Polymer synthesis

2.6.1. Phosphorylation direct polycondensation method. A typical example of polycondensation is as follows. A mixture of 0.334 g (1.00 mmol) of diamine **IIIb**, 0.564 g (1.61 mmol) of **4a**, 0.2 g of calcium chloride, 0.7 ml of TPP, 0.8 ml of pyridine, and 4 ml of NMP was heated with stirring at 105 °C for 3 h. The reaction mixture was slowly poured into 300 ml of methanol. The precipitated powder was collected by filtration, washed with hot methanol, and dried at 100 °C under vacuum. The inherent viscosity of the polymer was 0.06 dl g^{-1}, measured at a concentration of 0.5 g dl^{-1} in DMAc containing 5 wt% LiCl at 30 °C.

2.6.2. Low-temperature solution polycondensation method. A typical example of polycondensation is as follows. A solution of 0.334 g (1.00 mmol) of diamine IIIb in 8 ml of DMAc was cooled to $-10\,^{\circ}$C on an ice–acetone bath. After 0.3 ml of propylene oxide was added to the solution, 0.601 g (1.55 mmol) of diacyl chloride I was added. The mixture was stirred at -10 to $0\,^{\circ}$C for 1 h and then $25\,^{\circ}$C for 15 h under nitrogen. The reaction mixture was slowly poured into 300 ml of methanol. The fibre-like precipitated polymer was collected by filtration, washed with hot methanol, and dried at $100\,^{\circ}$C under vacuum. The inherent viscosity of the polymer was 0.65 dl g^{-1}, measured at a concentration of 0.5 g dl^{-1} in DMAc containing 5 wt% LiCl at $30\,^{\circ}$C. IR (film): 3306 (N–H), 1653 (C=O), 1400–1600 (arom. C=C), 1250 cm^{-1} (C–O).

Other polymers were synthesized by similar procedures.

2.7. Measurements

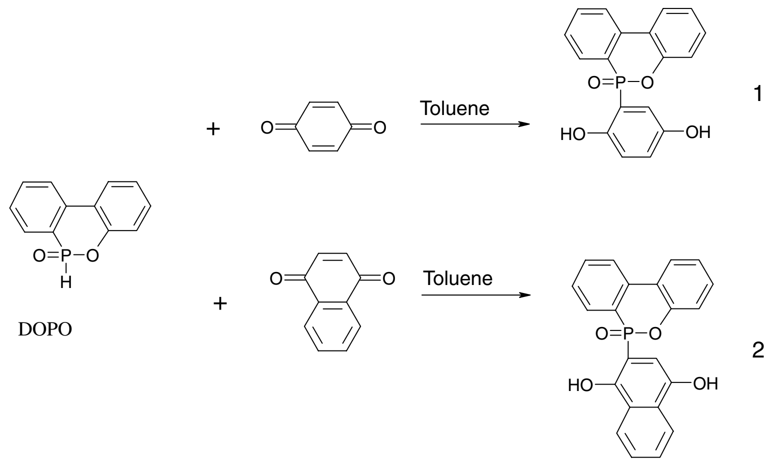
Infrared spectra were recorded on a Horiba FT-720 Fourier transform infrared spectrometer. Elemental analyses were run ion a Perkin–Elmer model 2400 CHN analyser. ^{1}H and ^{13}C NMR spectra were measured on a Jeol EX-400 Fourier transform nuclear magnetic resonance spectrometer with $CDCl_3$ or DMSO-d_6 as the solvent and external reference, working at 400 and 100 MHz, respectively. The x-ray crystallographic data were collected on a CAD-4 diffractometer. The inherent viscosities were determined at 0.5 g dl^{-1} concentration using a Cannon–Fenske viscometer. DSC analyses were performed on a Perkin–Elmer DSC 7 differential scanning calorimeter in flowing nitrogen (30 cm^3 min^{-1}) at a heating rate of $20\,^{\circ}$C min^{-1}.

3. Results and discussion

3.1. Monomer synthesis

The biphenylenephosphonato aromatic diols **1** and **2** were successfully synthesized from the addition reaction of DOPO with *p*-benoquinone and 1,4-naphthaquinone, respectively, (scheme 1), according to a modification of the method reported by Endo *et al* [31] and Wang *et al* [14–22]. After the reaction, the distinctive absorption at 2384 cm^{-1} for P–H stretching in DOPO disappeared while a broad absorption around 3200 cm^{-1} for phenolic OH appeared in **2**. Consequently, this addition reaction could be monitored by means of these absorptions. The yields were satisfactory and the structures of **1** and **2** were confirmed by elemental, IR, and NMR analysis. The IR and NMR spectra of diol **2** are illustrated in figures 1 and 2, respectively.

The fluoro-displacement reactions of *p*-fluorobenzonitrile with diols **1** and **2** were carried out in order to obtain the originally desired biphenylenephosphonato-bis(ether nitrile)s PBCN and PNCN (scheme 2), which may be further converted into biphenylenephosphonato bis(ether-carboxylic acid)s PBCA and PNCA and bis(ether-acid chloride)s PBCl and PNCl (scheme 3). Because the synthesis was straightforward and all the expected key functional absorptions appeared in the IR spectra of the intermediates and the final products (figure 3), for a time we considered that the syntheses of these phosphorus-containing monomers have been well done. However, further characterizations revealed that the results are not as expected. At first, the ^{13}C NMR spectra (figure 4) of the products of the fluoro-displacement reactions exhibited only seven and ten peaks, respectively. The relatively more simple spectra compared to that of diol **1** or **2** imply that the compounds have a highly symmetric structure. Moreover, the results of elemental analysis and x-ray diffraction analysis (figures 5 and 6) confirm the stuctures of



Scheme 1.

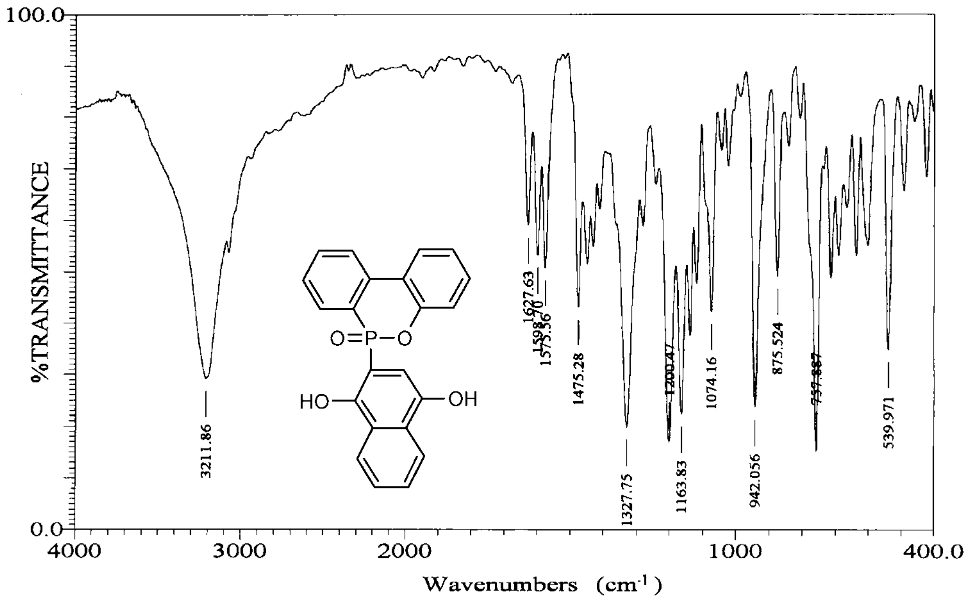


Figure 1. The IR spectrum of 2-(6-oxido-6H-dibenz⟨c,e⟩⟨1,2⟩oxaphosphorin-6-yl)-1,4-naphthalenediol (**2**).

the compounds as **3a** and **3b**, but not the originally designed PBCN and PNCN. Obviously, the side chain P–Ar bonding of biphenylenephosphonato-containing aromatic diols **1** and **2** was cleaved by alkaline hydrolysis during the nucleophilic fluoro-displacement reaction due to the presence of basic potassium carbonate. Thus, the approach to synthesize the phosphorus-containing bis(ether-carboxylic acid)s PBCA and PNCA by a nucleophilic substitution of the phosphorus-containing diol **1** or **2** with *p*-fluorobenzonitrile, followed by hydrolysis of the resulting dinitrile compounds (PBCN and PNCN) seems to be infeasible.

Bis(ether-carboxylic acid)s **4a** and **4b** were readily prepared by the alkaline hydrolysis of the bis(ether nitrile)s **3a** and **3b**. These bis(ether-carboxylic acid)s were converted to

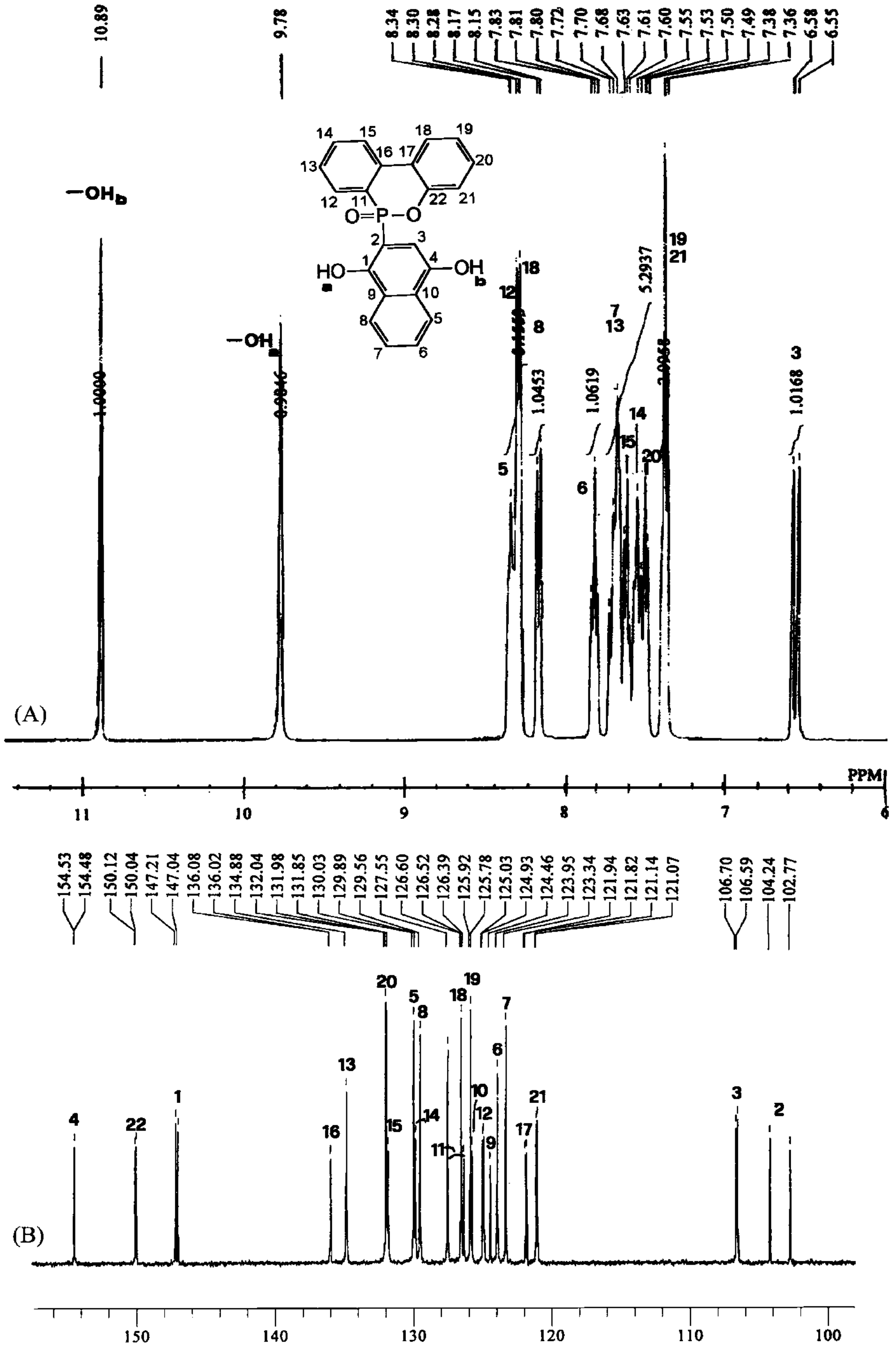
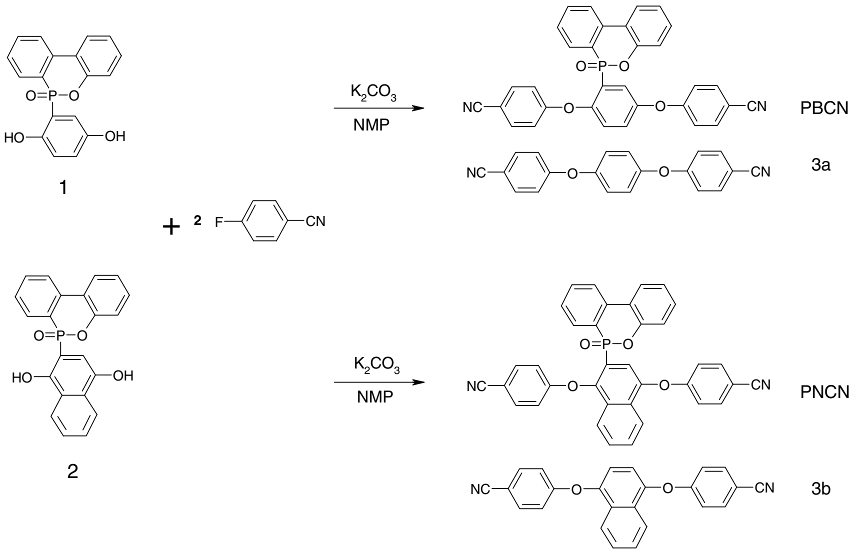
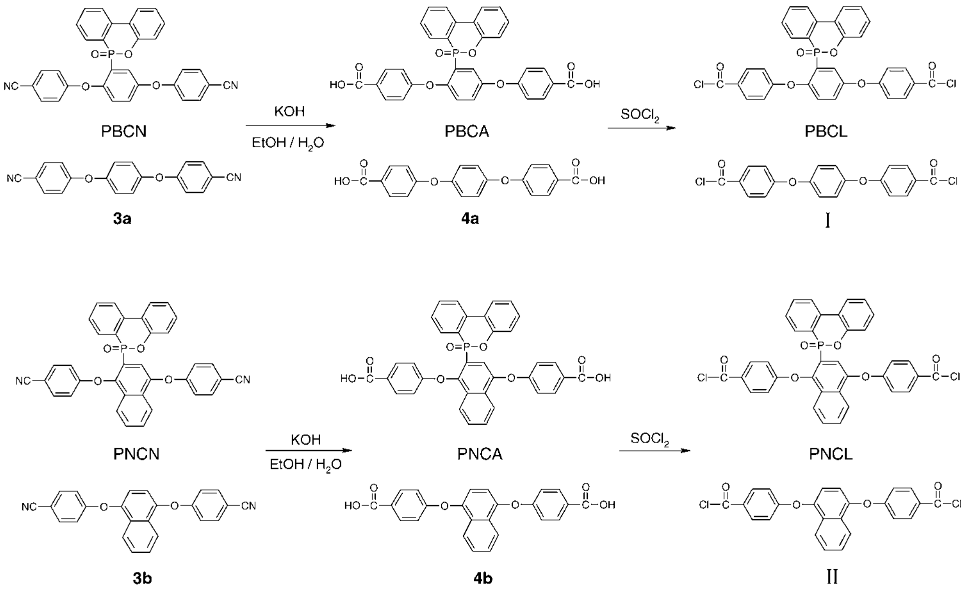


Figure 2. (A) ^{1}H NMR (DMSO-d_6) spectrum of **2**. (B) ^{13}C NMR (DMSO-d_6) spectrum of **2**.

the corresponding bis(ether-acyl chloride)s **I** and **II** by treatment with thionyl chloride in the presence of a few drops of DMF. The synthetic route is outlined in scheme 3. The characterization data of these diacids and diacid chlorides are similar to those reported previously [26, 27, 29, 30].



Scheme 2.



Scheme 3.

3.2. Polymer synthesis

A series of high molecular weight poly(ether-amide)s **IVa–d** were synthesized from diamines **IIIa–d** with aromatic diacyl chloride **I** by the low-temperature solution polycondensation in DMAc in the presence of propylene oxide as an acid acceptor (scheme 4). The initial feeding molar ratios of diamine/diacyl chloride **I** were 1.0/1.0 and 1.0/1.55, and the results are summarized in table 1. Four kinds of poly(ether-amide)s (**IVa–d**) were successfully obtained with similar inherent viscosities, regardless of the great stoichiometric imbalance.

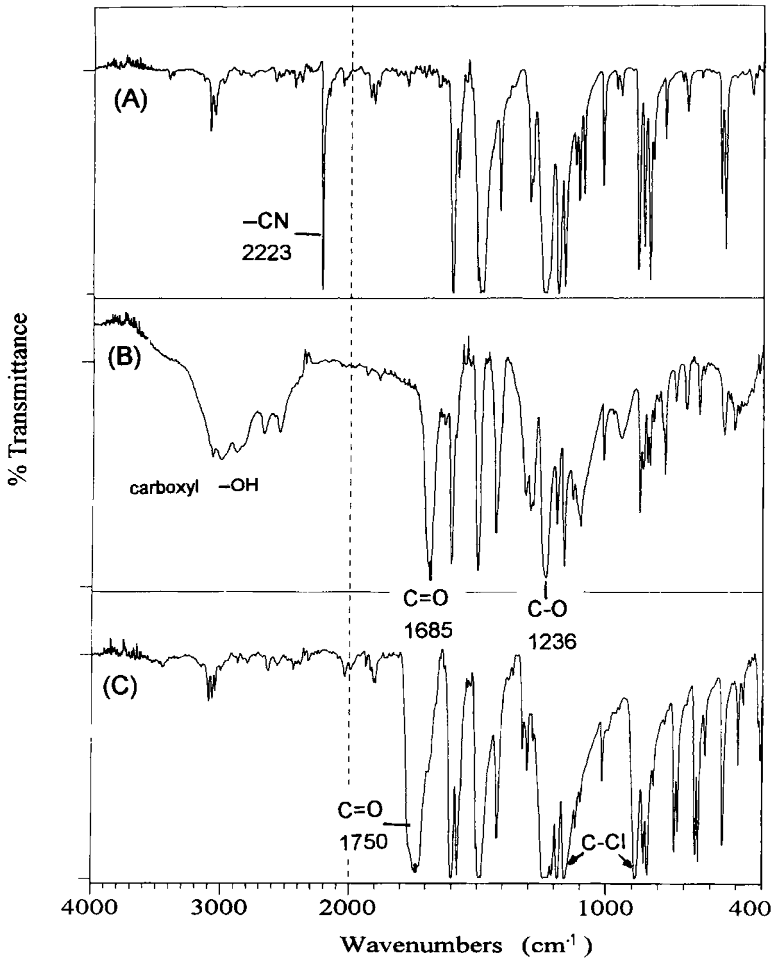


Figure 3. IR spectra of (A) bis(ether nitrile) **3a**, (B) bis(ether-carboxylic acid) **4a**, and (C) bis(ether-acyl chloride) **I**.

The molecular weights of all polymers are sufficiently high to permit the casting of tough and flexible films. The formation of poly(ether-amide)s was confirmed by means of IR spectroscopy, and FTIR spectra of these poly(ether-amide)s showed characteristic amide absorption bands at 3300–3340 and 1680 cm^{-1}. As shown in table 1, the polymer preparation was first conducted by the direct polymerization method in the molar ratio of 1.0:1.61 of diamine **IIIb**:diacid **4a**. The diacid **4a**, derived from the phosphorus-containing aromatic diol **1** with *p*-fluorobenzonitrile followed by the hydrolysis of the intermediate product (**3a**, in fact), was mistaken as the phosphorus-containing diacid PBCA in the beginning. Therefore, the molar ratio of diamine **IIIb** to the mistaken diacid PBCA was thought to be 1:1 owing to PBCA having a much higher molecular weight than diacid **4a**. It was found that the inherent viscosity of the resulting poly(ether-amide) **IVb** was very low, and that the unfavourable result was probably caused by the phosphorus-containing group of diacid (PBCA) which took part in the direct polymerization (Yamazaki–Higashi phosphorylation polycondensation) at around 100 °C. The inherent viscosities of the poly(ether-amide)s (**IVb**) synthesized from diamine **IIIb**/diacyl chloride **I** by low-temperature solution polycondensation significantly differed

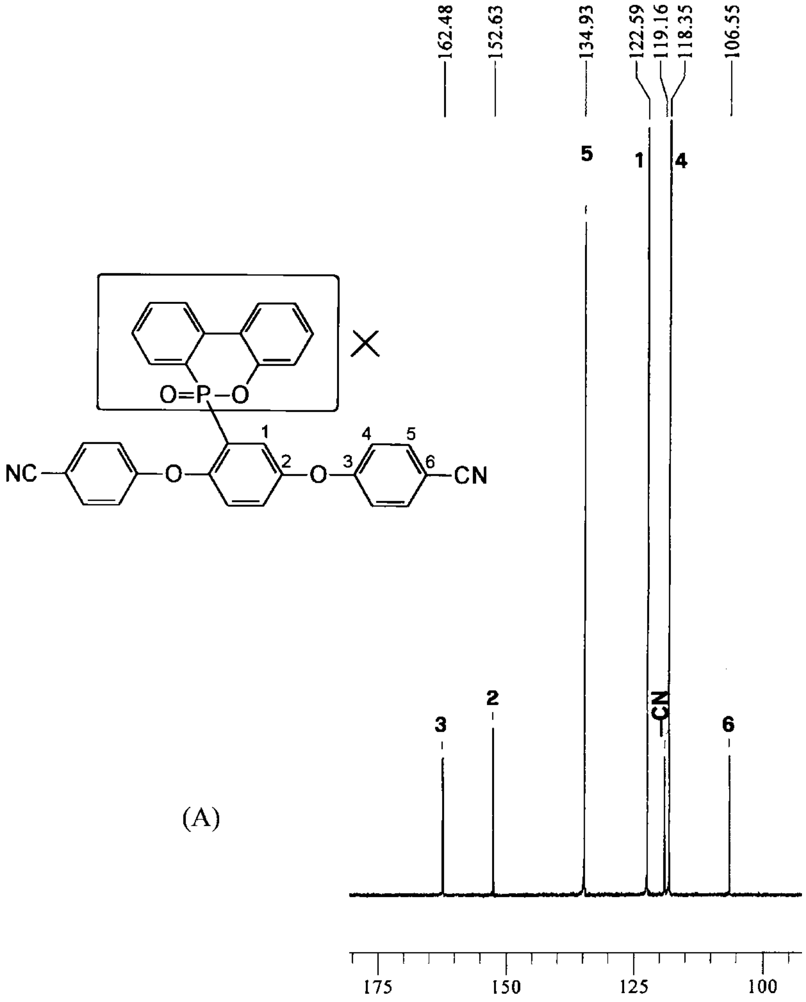


Figure 4. (A) ^{13}C NMR (CDCl$_3$) spectrum of the product of the nucleophilic substitution reaction between *p*-fluorobenzonitrile and **1**. (B) ^{13}C NMR (CDCl$_3$) spectrum of the product of the nucleophilic substitution reaction between *p*-fluorobenzonitrile and **2**.

from those obtained by direct polycondensation. In spite of the great stoichiometric imbalance between diamine **IIIb** and diacyl chloride **I**, in the case of using a molar ratio of 1.00:1.55 the resultant poly(ether-amide) **IVb** also exhibited a high inherent viscosity which was similar to that obtained using an equimolar ratio.

Concerning the unexpected results, diacyl chloride **I** was also initially mistaken as the phosphorus-containing diacyl chloride PBCL, thus the initial feeding ratio of diamine/diacyl chloride was regarded to be equimolar. The polymerization reaction was carried out at −10–0 °C in the initial 1 h and then at room temperature for 15 h, but the dissolution rate of diacyl chloride **I** was found to be very slow in DMAc at the reaction temperatures. Therefore, the slow dissolution character of the diacyl chloride provides a controlled introduction of the reactant into an excess of diamine in the DMAc solution. Because amidation takes place in the liquid phase as rapidly as diacyl chloride is dissolved, the dissolution of diacyl chloride **I** is the rate-controlling step at all concentrations. Furthermore, due to the very slow dissolving

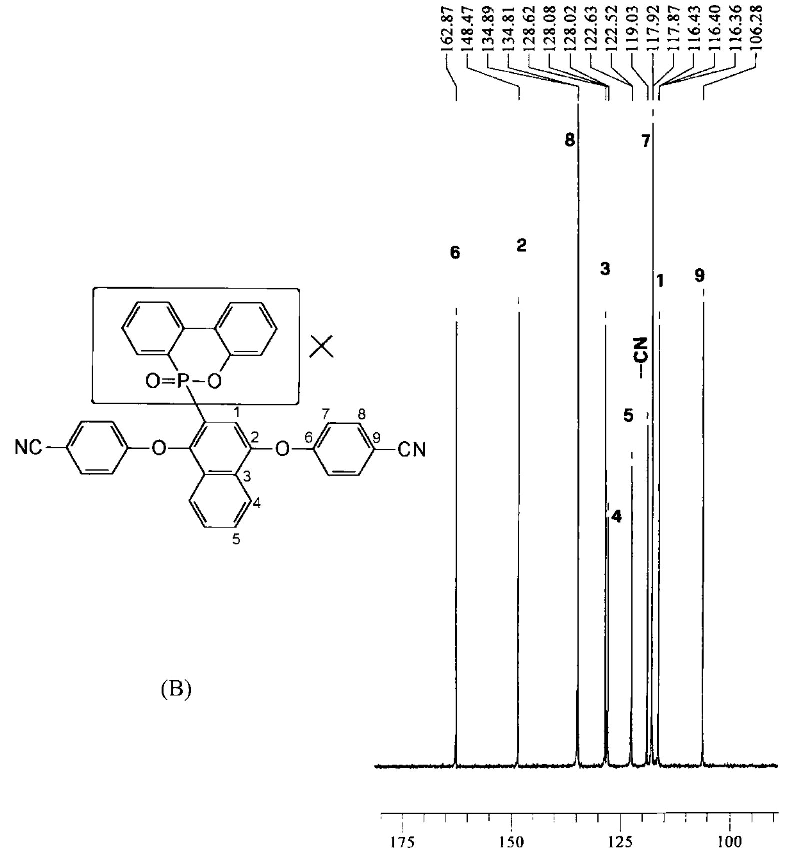


Figure 4. (Continued)

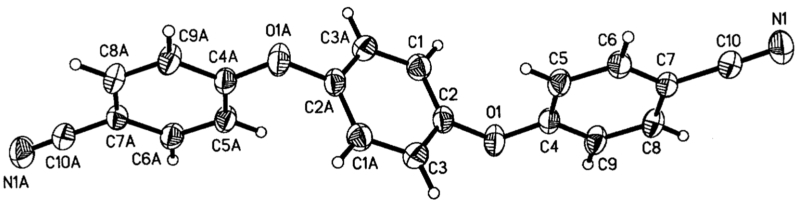


Figure 5. X-ray crystal structure of bis(ether nitrile) **3a**.

rate of this diacyl chloride, it appears that there is no need to worry about the problem of stoichiometric imbalance of the monomers. The polycondensation reaction is well self-controlled and proceeds smoothly. The reaction solution becomes gradually viscous as the limiting reactant, diamine, is used up completely. It was found that the solution became highly viscous after 15 h at room temperature but quite a lot of undissolved diacyl chloride (**I**) solids still remained in the viscous solution. Conventionally, the satisfactory synthesis of high molecular weight polymers is also strong evidence that pure diacyl chloride has been prepared if all diacyl chloride dissolved immediately after added to the diamine solution. Thus, this peculiar phenomenon of undissolved diacyl chloride solid in the viscous solution is against the Carothers' equation and inspired us to investigate the structures of the synthesized

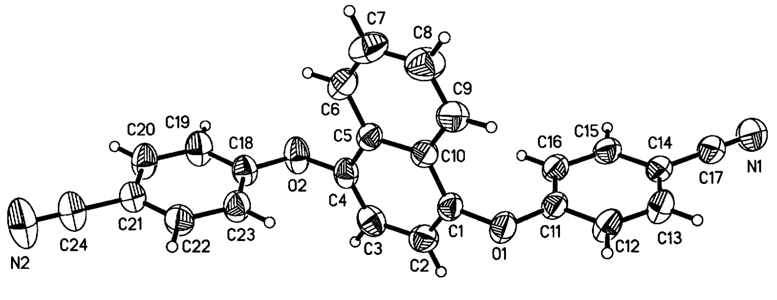
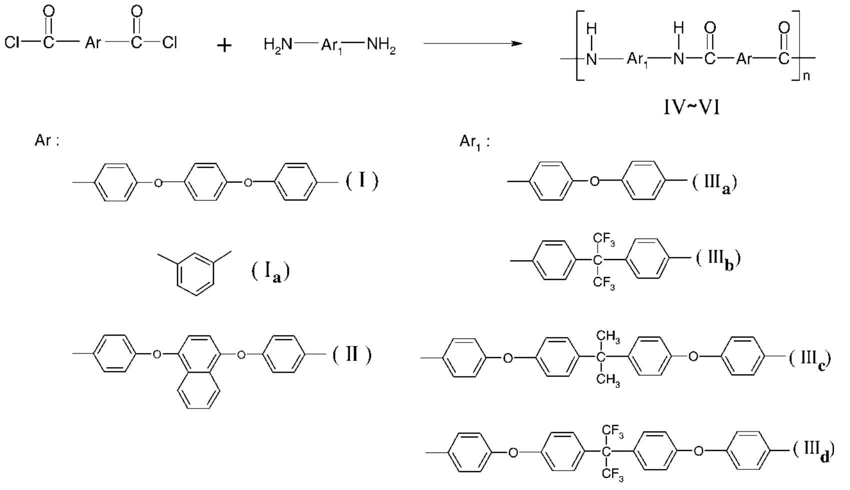


Figure 6. X-ray crystal structure of bis(ether nitrile) **3b**.



Scheme 4.

compounds in detail. According to the results of elemental analysis, NMR, and single-crystal x-ray diffraction analysis, the cleavage in side chain P–Ar bonding of phosphorus-containing aromatic diols **1** and **2** was confirmed during the nucleophilic fluoro-displacement reaction due to the presence of basic potassium carbonate. Therefore, we mistook diacyl chloride **I** for PBCL, and the actual initial feeding molar ratio 1.0:1.55 of diamine:diacyl chloride was incorrectly regarded as 1.0:1.0. Thus, high molecular weight aromatic poly(ether-amide)s from stoichiometric imbalanced diamine and diacyl chloride **I** were attained accidentally.

In order to get more insight into the effect of the initial feeding molar ratio of diamine/diacyl chloride on the molecular weight of aromatic polyamides, two diacyl chlorides, isophthaloyl chloride (**Ia**) and 4,4′-(1,4-naphthalenedioxy)dibenzoyl chloride (**II**) were also used to prepare polyamides for a comparative study of the stoichiometric imbalance effect with the corresponding polyamides derived from diacyl chloride **I**. By comparing the inherent viscosity results shown in table 2, except for poly(ether-amide)s which were derived from diacyl chloride **I**, all the other corresponding polyamides (**V** and **VI**) prepared from diacyl chlorides **II** and **Ia**, respectively, showed quite different results from polymer **IV**. It was found that the diacyl chloride (**II** or **Ia**) showed high solubility in DMAc or NMP solvents and dissolved completely within 10 min after addition to the diamine solution. The inherent viscosities of polyamides **Va** and **VIa** were 0.08–0.89 and 0.08–0.84 dl g^{-1}, respectively, and increased with decreasing mole ratio of diamine/diacyl chloride components. The relation

Table 1. Synthesis of poly(ether-amide)s.

Monomer code	Molar ratio	Polymer code	Method of preparation[a]	η_{inh}[b] (dl g^{-1})	T_g[c] (°C)	Remark[d]
IIIb/4a	1.0/1.61	**IVb**	A	0.06	–	Powder
IIIb/4a	1.0/1.0	**IVb**	A	0.64	–	Film
IIIb/I	1.0/1.55	**IVb**	B	0.69	229	Film
IIIb/I	1.0/1.0	**IVb**	B	0.66	229	Film
IIIa/I	1.0/1.55	**IVa**	B	0.90	–	Opaque film
IIIa/I	1.0/1.0	**IVa**	B	0.82	–	Opaque film
IIIc/I	1.0/1.55	**IVc**	B	0.77	190 (193)[e]	Film
IIIc/I	1.0/1.0	**IVc**	B	0.74	190	Film
IIId/I	1.0/1.55	**IVd**	B	0.99	214 (211)[e]	Film
IIId/I	1.0/1.0	**IVd**	B	0.87	214	Film

[a] A: polymerization was carried out by direct polymerization method. B: polymerization was carried out by low-temperature solution method.
[b] Measured at a concentration of 0.5 g dL^{-1} in DMAc containing 5 wt% LiCl at 30 °C.
[c] From the second heating, traces of DSC measurements conducted at a heating rate of 20 °C min^{-1} in N_2.
[d] Powder: the precipitated powders were obtained when the reaction solution was slowly poured into methanol; film: the flexible films could be cast from the resultant polymer solutions in DMAc.
[e] Values in parentheses are T_g data reported in the literature [26].

Table 2. Inherent viscosities of polyamides[a].

Monomer code	Mole ratio	Polymer code	η_{inh}[b] (dl g^{-1})	Remark[c]
IIIa/II	1.0/1.0	**Va**	0.89	Film
IIIa/II	1.0/1.2	**Va**	0.28	Powder
IIIa/II	1.0/1.49	**Va**	0.08	Powder
IIIa/Ia	1.0/1.0	**VIa**	0.84	Film
IIIa/Ia	1.0/1.2	**VIa**	0.22	Powder
IIIa/Ia	1.0/1.5	**VIa**	0.08	Powder

[a] Polymerization was carried out by low-temperature solution method.
[b] Measured at a concentration of 0.5 g dl^{-1} in DMAc containing 5 wt% LiCl at 30 °C.
[c] Appearance of the resultant polymers after casting from slow evaporation of the polymer solutions in DMAc.

between decreasing tendency of inherent viscosity and stoichiometric imbalance apparently follows the conclusion of Carothers' equation.

The thermal behaviour of the poly(ether-amide)s **IVa–d** was evaluated by means of DSC, and the thermal behaviour data of the polymers are given in table 1. The influence of residual water or solvent and history of thermal annealing are sometimes observed in the first heating scanning of DSC. The poly(ether-amide)s were rapidly quenched from elevated temperatures at approximately 400 °C to room temperature to form predominantly amorphous samples, so that the glass transition temperatures (T_g) of polymers could be easily measured in the DSC charts of the second heating trace. The T_g values of the poly(ether-amide)s (**IVa–d**) ranged from 190 to 229 °C, consistent with the results reported previously [26].

4. Conclusion

Aromatic poly(ether-amide)s having high molecular weights were successfully synthesized from stoichiometric imbalanced aromatic diamines with 4,4′-(1,4-phenylenedioxy)dibenzoyl chloride (**I**) by low-temperature solution polycondensation. The initial feeding mole ratios of diamine:diacyl chloride (**I**) ranged from 1:1 to 1:1.55, and all resultant poly(ether-amide)s showed high and similar viscosities regardless of the great stoichiometric imbalance. The unexpected results could be attributed to the slow dissolution rate of the diacyl chloride **I** in DMAc or NMP solvents compared with conventional aromatic diacyl chlorides.

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