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Improved syntheses of poly(oxy-1,3-phenylenecarbonyl-1,4-phenylene) and related poly(ether–ketones) using polyphosphoric acid/P_2O_5 as polymerization medium

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Abstract

Based on the model-compound studies, the composition of polyphosphoric acid (PPA)/P_2O_5 mixture as an effective catalytic/dehydrative medium for the preparation of poly(ether–ketones) was optimized. Thus, with the optimal weight ratio of 4:1 (PPA:P_2O_5), the electrophilic substitution polycondensation of 3-phenoxybenzoic acid and related AB monomers was substantially promoted at 130 °C to yield the subject polymer abbreviated as *m*PEK and related poly(ether–ketones) with significantly higher molecular weights. In the cases where the polymerization systems were completely homogeneous, the ensuing polycondensation was rapid and yielded high molecular weight polymers (e.g. *m*PEK $[\eta] = 2.10$ dl/g) at 130 °C within 30 min., as compared to PPMA (phosphorus pentoxide/methanesulfonic acid) method which gave only moderate molecular weight polymers, e.g. *m*PEK ($[\eta] = 0.64$ dl/g). In some cases, where the monomers and PPA/P_2O_5 were not fully compatible, polycondensation did proceed and reasonable molecular weight range ($[\eta] = 0.69–0.76$ dl/g) could be achieved. However, the complete incompatibility between the poly(ether–sulfone) and PPA/P_2O_5 medium precluded the successful polymerization of 4-phenoxybenzenesulfonic acid.
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1. Introduction

Polyetherketones (PEKs) and polyethersulfones (PESs) are important classes of engineering thermoplastics with a good balance in the material properties and processing characteristics [1]. Both aromatic electrophilic substitution (Friedel–Crafts acylation reaction) and aromatic nucleophilic substitution reactions are versatile methods to synthesize PEKs and PESs (Scheme 1). Acid-catalyzed polymer-forming reaction involves an aromatic bis(carboxylic acid) or bis(acid chloride) and an aromatic bis(sulfonic acid) or bis(sulfonyl chloride) (Scheme 1(a)) [2]. Base-promoted polymer-forming reactions involve the salt form of phenol replacing activated halogen or nitro group (Scheme 1(b)) [3,4]. Aromatic nucleophilic substitution reaction is a more preferred route because of the availability of monomers, non-corrosive reaction media, and the operational convenience in conducting the synthesis. In some cases, however, it fails to yield high-molecular weight polymers because of the substitution position on aromatic ring and the exceedingly low solubility of resulting polymer, especially in the case of semi-crystalline material [2,5].

Although the early investigations of electrophilic route were unsuccessful in producing high molecular weight polymers because of the limited solubility of growing polymer chains in chlorinated solvents such as dichloromethane [6], the utilization of superacid systems such as boron trifluoride (BF_3) in anhydrous hydrofluoric acid (HF) as polymerization medium did result in high molecular weight polymers [7,8]. An important key to achieve high molecular weight polymer through electrophilic substitution even in the case of semi-crystalline material is to use a reaction medium that can provide the enthalpy of solvation by the protonation of carbonyl [9] or sulfonyl groups [10].

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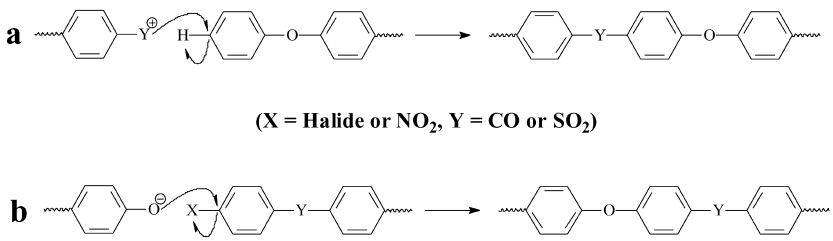


Scheme 1. Synthetic routes to PEKs and PESs: (a) aromatic electrophilic substitution; (b) aromatic nucleophilic substitution.

As a result, the solvation by strong acid make it possible to retain polymer in solution even at low temperatures, preventing premature precipitation. Similarly, in the case of nucleophilic displacement route, to achieve high molecular weight semi-crystalline PEKs, high boiling polar solvent such as diphenylsulfone (DPS, b.p. 379 °C) is commonly used and heated around polymer melting temperatures to prevent premature precipitation caused by crystallization [5].

Unfortunately, the superacid systems such as BF_3/HF [7,8], phosphorous pentoxide(P_2O_5)/methanesulfonic acid (MSA) [11], aluminum chloride ($AlCl_3$)/polyphosphoric acid (PPA) [12], trifluoromethanesulfonic acid [9], etc. are relatively expensive as well as hazardous to handle because of their volatility, corrosiveness, and toxicity. Thus, the uses of these systems are limited and only for small lab-scale preparation. Furthermore, most of these systems can only afford moderate molecular weight polymers.

We report herein an improved process utilizing a polymerization medium based on PPA that is non-toxic, relatively less corrosive, and non-volatile to prepare high molecular weight PEKs from several AB monomers. Although PPA has been used in the preparation of a wide-range of high molecular weight aromatic poly(hetero-cycles), surprisingly its utilization in the synthesis of high molecular weight poly(ether–ketones) has not been documented [13,14]. The preparation of poly(oxy-1,3-phenylenecarbonyl-1,4-phenylene), abbreviated as *m*PEK and related copolymers via aromatic fluoride-displacement route have been reported [15].

2. Experimental

2.1. Materials

All reagents and solvents were purchased from Aldrich Chemical Co. and used as received, unless otherwise specified. MSA was distilled under reduced pressure prior to use. The monomers, 3-phenoxybenzoic acid and 4-phenoxybenzoic acid, were purified by recrystallization from toluene/heptane (5/5, v/v) mixture to give shiny colorless needles (m.p. 147–148.5 and 162–164 °C, respectively). 2-Phenoxybenzoic acid was recrystallized from heptane to give colorless white flakes (m.p. 111–112 °C). The sodium salt of 4-phenoxybenzenesulfonic acid was prepared by the sulfonation of diphenylether and recrystallized from water to give white crystals (m.p. > 350 °C). The free acid was obtained from acidification of the sodium salt to give pearl flakes (m.p. > 350 °C). PPMA solution (available as Eaton's reagent, 7.7 wt% of P_2O_5 in MSA) was used as received.

2.2. Instrumentations

Proton and carbon-13 nuclear magnetic resonance (^{1}H NMR and ^{13}C NMR) spectra for the intermediates and monomer were obtained at 270 and 50 MHz on a Jeol-270 spectrometer. Infrared (FT-IR) spectra were recorded on a Bruker IFS 28 Equinox Fourier transform spectrophotometer. Elemental analysis and mass analysis were performed by System Supports Branch, Materials Directorate, Air Force Research Laboratory, Dayton, Ohio. All melting points (m.p.) were determined on a Mel-Temp melting point apparatus and the values are uncorrected. Intrinsic viscosities were determined with a Cannon-Ubbelohde No. 150 viscometer. Flow times were recorded for MSA solutions with polymer concentrations of 0.5–0.1 g/dl at 30.0 ± 0.1 °C. Differential scanning calorimetry (DSC) was performed in nitrogen with a heating rate of 10 °C/min using a Perkin–Elmer DSC-7 thermal analyzer. Thermogravimetric analysis (TGA) was conducted in helium and air atmospheres with a heating rate of 10 °C/min using a TA Hi-Res TGA 2950 thermogravimetric analyzer.

2.3. Model comopond I: 4,4′-dibenzoyldiphenylether (*4*)

Into a 250 ml resin flask equipped with a high-torque mechanical stirrer, a nitrogen inlet and an outlet, PPA (83% assay, 63.2 g) was placed and stirred under dried nitrogen at room temperature for 2 h. Benzoic acid (4.0 g, 0.033 mol) and diphenylether (2.65 g, 0.016 mol) were added. The resulting mixture was stirred for an hour, and P_2O_5 (15.8 g, 0.111 mol) was then added. The mixture was stirred at room temperature for 12 h and then heated in a stepwise fashion at 60 °C for 12 h, 100 °C for 12 h, and 130 °C for 12 h, when it finally became homogeneous. The color of mixture was initially white at room temperature and upon thorough mixing, it became light yellow indicating that the Friedel–Crafts reaction was taking place to some extent even at this temperature. At the end of the reaction, the mixture was

poured into cold water. The resulting white precipitates were collected by suction filtration, washed with 5% ammonium hydroxide (100 ml) and then with water (1 l), dried in air, and recrystallized from ethanol to give 5,75 g (98% yield based on diphenylether) of white flakes, m.p. 162–163 °C. Anal. Calcd. for $C_{26}H_{18}O_3$: C, 82.52%; H, 4.79%; O, 12.68%. Found: C, 82.56%; H, 5.00%; O, 12.10%. FT-IR (KBr, cm^{-1}): 1595, 1646. Mass spectrum (m/e): 378 (M^+, 100% relative abundance), 301. ^1H NMR ($CDCl_3$; δ in ppm): 7.13–7.16 (d, 4H, Ar), 7.47–7.52 (t, 4H, Ar), 7.57–7.60 (t, 2H, Ar), 7.78–7.82 (d, 4H, Ar), 7.86–7.90 (d, 4H, Ar). ^{13}C NMR ($CDCl_3$; δ in ppm): 118.59, 128.32, 128.44, 129.85, 132.52, 133.16, 137.62, 159.82, 195.36.

2.4. Model compound II: 4,4′-dibenzenesulfonyldiphenylether (7)

Into a 250 ml resin flask equipped with a high torque mechanical stirrer, a nitrogen inlet and an outlet, PPA (83% assay, 55 g) was placed and stirred under dried nitrogen purging at room temperature for 2 h. Benzenesulfonic acid (4.0 g, 0.025 mol) and diphenylether (1.79 g, 0.011 mol) were added, stirred for an hour, and P_2O_5 (13.8 g, 0.097 mol) was added. The mixture was stirred at room temperature for 12 h and then heated in a stepwise fashion at 60 °C for 12 h, 100 °C for 12 h, and 130 °C for 12 h. Contrary to the preparation of 4,4′-dibenzoyldiphenylether, the mixture remained heterogeneous throughout the course of reaction, even though its color had changed from white to light yellow at room temperature. At the end of the reaction, water was added into the flask. The resulting precipitates were collected by suction filtration, washed with 5% ammonium hydroxide (100 ml) and then with water (1 l), dried in air, and recrystallized from heptane to give 4.68 g (98.5% yield based on diphenylether) of white powder: m.p. 168–170 °C. Anal. Calcd. for $C_{24}H_{18}O_5S_2$: C, 63.98%; H, 4.03%: Found: C, 63.84%; H, 4.28%. FT-IR (KBr, cm^{-1}): 1487, 1579. Mass spectrum (m/e): 450 (M^+, 100% relative abundance), 351, 325. ^1H NMR ($CDCl_3$; δ in ppm): 7.07–7.10 (d, 4H, Ar), 7.49–7.59 (m, 6H, Ar), 7.93–7.94 (d, 4H, Ar), 7.95–7.97 (d, 4H, Ar). ^{13}C NMR ($CDCl_3$; δ in ppm): 119.51, 127.60, 129.39, 130.22, 133.30, 137.16, 141.54, 159.71.

2.5. 2-(2,6-Dimethylphenoxy)benzonitrile (10)

Into a 250 ml three-necked round bottom flask equipped with a magnetic stirrer, nitrogen inlet and outlet, and a Dean–Stark trap with a condenser, 2,6-dimethylphenol (4.91 g, 40.2 mmol), 2-fluorobenzonitrile (4.87 g, 40.2 mmol), potassium carbonate (6.67 g, 0.48.3 mol), and a mixture of NMP (80 ml) and toluene (60 ml) were placed. The reaction mixture was then heated and maintained at 140 °C for 4 h. During this time, the water formed was removed together with toluene by azeotropic distillation. After complete removal of toluene by forced nitrogen purging, the orange solution was then heated at 150 °C for 4 h. The mixture was filtered through glass filter while the mixture was still warm (80–90 °C). The filtrate was poured into distilled water containing 5% hydrochloric acid. The resulting organic phase was diluted with dichloromethane, and separated. The organic mixture was washed with 5% sodium hydroxide twice in a separatory funnel, dried over magnesium sulfate and filtered. The solvent was removed and the viscous light yellow residue was freeze-dried in liquid nitrogen under reduced pressure and recrystallized from heptane to give 8.31 g (93% yield) of milky flakes, m.p. 86–87.5 °C. Anal. Calcd. for $C_{15}H_{13}NO$: C, 80.69%; H, 5.87%; N, 6.27%; O, 7.17%. Found: C, 80.48%; H, 6.08%; N, 6.25%; O, 7.05%. FT-IR (KBr, cm^{-1}): 2230 (ν C≡N). Mass spectrum (m/e): 223 (M^+, 100% relative abundance). ^1H NMR ($CDCl_3$; δ in ppm): 2.13 (s, 6H, CH_3), 6.43–6.46 (d, 1H, Ar), 6.93–6.96 (d, 1H, Ar), 7.02–7.08 (t, 1H, Ar), 7.11 (s, 2H, Ar), 7.35–7.41 (t, 1H, Ar), 7.63–7.66 (d, 1H, Ar). ^{13}C NMR ($CDCL_3$; δ in ppm): 16.16, 113.32, 116.14, 121.67, 125.99, 128.44, 129.24, 130.94, 133.94, 150.14, 152.68, 159.48.

2.6. 4-(2,6-Dimethylphenoxy)benzonitrile (13)

Into a 250 ml three-necked round bottom flask equipped with a magnetic stirrer, nitrogen inlet and outlet, and a Dean–Stark trap with a condenser, 2,6-dimethylphenol (10.1 g, 82.68 mmol), 4-fluorobenzonitrile (10.0 g, 82.57 mmol), potassium carbonate (14.0 g, 0.101 mol), and a mixture of NMP (100 ml) and toluene (60 ml) was placed. The reaction mixture was then heated and maintained at 140 °C for 4 h. During this time, the water formed was removed together with toluene by azeotropic distillation. After complete removal of toluene by drastic nitrogen purging, the orange solution was then heated at 150 °C for 4 h. The mixture was filtered through glass filter while the mixture was still warm (80–90 °C). The filtrate was poured into distilled water containing 5% hydrochloric acid. The resulting organic phase was diluted with dichloromethane, and separated. The organic mixture was washed with 5% sodium hydroxide twice, separated again, and dried over magnesium sulfate, and filtered. The solvent was removed and the viscous light yellow residue was freeze-dried in liquid nitrogen under reduced pressure to give 17.7 g (96% yield) of light yellow oil which was analytically pure and used without further purification. Anal. Calcd. for $C_{15}H_{13}NO$: C, 80.69%; H, 5.87%; N, 6.27%; O, 7.17%. Found: C, 80.75%; H, 6.05%; N, 6.25%; O, 7.23. FT-IR (KBr, cm^{-1}): 2227 (νC≡N). Mass spectrum (m/e): 223 (100% relative abundance). ^1H NMR ($CDCl_3$; δ in ppm): 2.09 (s, 6H, CH_3), 6.80–6.85 (d, 2H, Ar), 6.95–6.98 (d, 1H, Ar), 7.10–7.12 (s, 2H, Ar), 7.53–7.58 (d, 2H, Ar). ^{13}C NMR ($CDCl_3$; δ in ppm): 15.95, 115.48, 123.17, 125.87, 129.30, 130.94, 134.28, 150.06, 152.34, 161.18.

2.7. 2-(2,6-Dimethylphenoxy)benzoic acid (**11**)

Into a 250 ml three-necked round bottom flask equipped with a magnetic stirrer, nitrogen inlet and outlet, 4-(2,6-dimethylphenoxy)benzonitrile (8.20 g, 36.73 mmol), PPA (56.0 g, 83% assay), and water (10 ml) were placed. The reaction mixture was then heated and maintained at 130 °C for 12 h. After cooled down, the homogeneous light yellow mixture was poured into distilled water. The resulting precipitate was collected by suction filtration, air dried, and recrystallized from toluene to give 4.9 g (55% yield) of white needles, m.p. 186–188 °C. Anal. Calcd. for $C_{15}H_{14}O_3$: C, 74.36%; H, 5.82%; O, 19.81%. Found: C, 74.33%; H, 5.88%; O, 19.69%. Mass spectrum (m/e): 242 (100% relative abundance). ^{1}H NMR ($CDCl_3$; δ in ppm): 2.11 (s, 6H, CH_3), 6.45–6.49 (d, 1H, Ar), 7.03–7.06 (d, 1H, Ar), 7.12–7.14 (t, 1H, Ar), 7.21 (s, 2H, Ar), 7.39–7.41 (t, 1H, Ar), 7.83–7.88 (d, 1H, Ar). ^{13}C NMR ($CDCl_3$; δ in ppm): 16.08, 111.45, 113.88, 122.44, 125.76, 127.36, 129.01, 129.11, 131.21, 150.15, 155.33, 166.41.

2.8. 4-(2,6-Dimethylphenoxy)benzoic acid (**14**)

Into a 250 ml three-necked round bottom flask equipped with a magnetic stirrer, nitrogen inlet and outlet, 4-(2,6-dimethylphenoxy)benzonitrile (17.0 g, 76.14 mmol), PPA (56.0 g, 83% assay), and water (10 ml) were placed. The reaction mixture was then heated and maintained at 130 °C for 12 h. The warm, homogeneous purple mixture was then poured into distilled water. The resulting precipitate was collected by suction filtration, air dried, and recrystallized from toluene to give 11.7 g (64% yield) of white needles: m.p. 206–208 °C. Anal. Calcd. for $C_{15}H_{14}O_3$: C, 74.36%; H, 5.82%; O, 19.81%. Found: C, 74.37%; H, 6.07%; O, 19.72. FT-IR (KBr, cm^{-1}): 1608, 1646. Mass spectrum (m/e): 242 (M^+, 100% relative abundance). ^{1}H NMR (DMSO-d_6; δ in ppm): 2.06 (s, 6H, CH_3), 6.75–6.79 (d, 2H, Ar), 7.12–7.20 (m, 3H, Ar), 7.85–7.89 (d, 2H, Ar). ^{13}C NMR (DMSO-d_6; δ in ppm): 15.75, 113.69, 125.47, 127.71, 129.13, 129.73, 130.45, 150.09, 159.42, 167.22.

2.9. Attempted formation of poly(o-phenyletherketone, o PEK)

Into a 250 ml resin flask equipped with a high torque mechanical stirrer, a nitrogen inlet and an outlet, PPA (83% assay, 80 g) was placed and stirred under dried nitrogen at 100 °C for 10 h. 2-Phenoxybenzoic acid (4.0 g) was added and the resulting mixture was then heated to 100 °C until it became homogeneous (about 1 h). The color of mixture became light yellow. P_2O_5 (20.0 g) was then added in one portion and the temperature was maintained130 °C for 6 h. At the end of the reaction, water was added into the flask. The resulting white powder was collected by suction filtration, washed with diluted ammonium hydroxide and then with large amounts of water, stirred in boiling water for 24 h, air-dried, and recrystallized from ethanol to give 2.70 g (98% yield) of colorless white needles, m.p. 174–176 °C. Anal. Calcd. for $C_{13}H_8O_2$: C, 79.58%; H, 4.11%; O, 16.31%. Found: C, 79.59%; H, 4.33%; O, 15.76%. ^{1}H NMR ($CDCl_3$; δ in ppm): 7.31–7.37 (t, 2H, Ar), 7.42–7.45 (d, 2H, Ar), 7.66–7.73 (t, 2H, Ar), 8.24–8.28 (dd, 2H, Ar). ^{13}C NMR ($CDCl_3$; δ in ppm): 117.95, 121.58. 123.86, 126.39, 134.83, 155.96, 176.87.

2.10. Poly(o-2,6-dimethylphenyletherketone, o DiMePEK)

Into a 100 ml resin flask equipped with a high-torque mechanical stirrer, a nitrogen inlet and outlet, PPA (83% assay, 20 g) was placed and stirred with dried nitrogen purging at 100 °C for 10 h. 4-(2,6-Dimethylphenoxy)benzoic acid (1.0 g, 4.13 mmol) was added and the resulting mixture heated to 100 °C until it became homogeneous. The color of the mixture became light green. P_2O_5 (5.0 g) was then added in one portion and the temperature was maintained at 130 °C for 24 h. The dark green mixture was stirred 12 h at 130 °C. At the end of the reaction, water was added into the flask. The resulting dark green precipitates were collected by suction filtration, washed with diluted ammonium hydroxide and then with large amount of water, Soxhlet extracted with water for 100 h, and finally dried in the presence of phosphorous pentoxide under reduced pressure (0.05 mm Hg) at 120 °C for 72 h to yield 0.51 g (55% yield) of dark green powder. Anal. Calcd. for $C_{13}H_8O_2$: C, 80.34%; H, 5.39%; O, 14.27%. Found: C, 56.16%; H, 4.61%; O, 19.35%.

2.11. Poly(m-phenyletherketone, m PEK) in PPA/P_2O_5 at 130 °C

Into a 250 ml resin flask equipped with a high torque mechanical stirrer, a nitrogen inlet and an outlet, PPA (83% assay, 80 g) was placed and stirred under dried nitrogen at 100 °C for 10 h. 3-Phenoxybenzoic acid (4.0 g, 18.7 mmol) was added and the resulting mixture was heated to 100 °C until it became homogeneous mixture (about 1 h). The color of the mixture became light brown. P_2O_5 (20.0 g) was then added in one portion and the temperature was maintained at 130 °C for 6 h. The mixture became very viscous after 2 h at 130 °C and started to stick to stirring rod. At the end of the reaction, water was added into the flask. The resulting purple lumps of polymeric product were taken into a Warring blender, chopped, collected by suction filtration, washed with diluted ammonium hydroxide, then with large amount of water, Soxhlet extracted with water for 100 h, and finally dried in the presence of phosphorous pentoxide under reduced pressure (1 mm Hg) at 120 °C for 72 h. The yield was essentially quantitative (>99% yield). The intrinsic viscosity of 2.10 dl/g (MSA, 30 ± 0.1 °C) was determined. Anal. Calcd. for $C_{13}H_8O_2$: C, 79.58%; H, 4.11%; O, 16.31%. Found: C, 79.57%; H, 4.33%; O, 15.40%.

2.12. Poly(m-phenyletherketone, m PEK) in PPA/P_2O_5 at 160 °C

Into a 250 ml resin flask equipped with a high torque mechanical stirrer, a nitrogen inlet and an outlet, PPA (83% assay, 80 g) was placed and stirred under dried nitrogen at 100 °C for 10 h. 3-Phenoxybenzoic acid (4.0 g, 18.7 mmol) was added and the resulting mixture was heated to 100 °C until it became homogeneous (about 1 h). The color of the mixture became light brown. P_2O_5 (20.0 g) was then added in one portion and the temperature was maintained160 °C for 3 h. The mixture became very viscous after 30 min at 160 °C and started to stick to stirring rod. At the end of the reaction, water was added into the flask. The resulting purple clusters were taken into a Warring blender and the bundles of polymeric product were chopped, collected by suction filtration, washed with diluted ammonium hydroxide, then with large amount of water, Soxhlet extracted with water for 100 h, and finally dried in the presence of phosphorous pentoxide under reduced pressure (1 mm Hg) at 120 °C for 72 h. The yield was essentially quantitative (>99% yield). The polymer was not soluble in MSA to preclude viscosity measurement. Anal. Calcd. for $C_{13}H_8O_2$: C, 79.58%; H, 4.11%; O, 16.31%. Found: C, 73.81%; H, 3.76%; O, 14.28%.

2.13. Poly(m-phenyletherketone, m PEK) in PPMA (Eaton's reagent)

Polymerization was carried out under the condition described in the literature. Into a 100 ml round-bottom flask with a magnetic stirrer, nitrogen inlet and outlet, PPMA (20 ml) and 3-phenoxybenzoic acid were placed and stirred under dried nitrogen atmosphere at 100 °C for 24 h. The color of mixture became dark brown. The mixture was poured into ice-water and the resulting purple precipitate was collected by suction filtration, washed with diluted ammonium hydroxide, then with large amounts of water, Soxhlet extracted with water for 100 h, and finally dried in the presence of phosphorous pentoxide under reduced pressure (1 mm Hg) at 120 °C for 72 h to give 1.63 g (89% yield) of purple powder. The intrinsic viscosity of 0.64 dl/g (MSA, 30 ± 0.1 °C) was determined. Anal. Calcd. for $C_{13}H_8O_2$: C, 79.58%; H, 4.11%; O, 16.31%. Found: C, 76.71%; H, 4.26%; O, 15.33%.

2.14. Poly(p-phenyletherketone, p PEK) in PPA/P_2O_5 at 130 °C

Into a 250 ml resin flask equipped with a high torque mechanical stirrer, a nitrogen inlet and an outlet, PPA (83% assay, 30 g) was placed and stirred under dried nitrogen at 100 °C for 10 h. 4-Phenoxybenzoic acid (1.5 g, 7.00 mmol) was added and the resulting mixture was heated to 100 °C until it become homogeneous (about 2 h). The color of the mixture became light pink. P_2O_5 (7.5 g) was then added in one portion and the temperature was maintained at 130 °C for 12 h. The red mixture became viscous after 6 h at 130 °C and started to stick to stirring rod. At the end of the reaction, water was added into the flask. The resulting pink clusters were taken into a Warring blender and the bundles of polymeric product were chopped, collected by suction filtration, washed with diluted ammonium hydroxide, then with large amount of water, Soxhlet extracted with water for 100 h, and finally dried in the presence of phosphorous pentoxide under reduced pressure (0.05 mm Hg) at 120 °C for 72 h to yield 1.0 g (75% yield) of pink fibrous solid. The intrinsic viscosity of 0.69 dl/g (MSA, 30 ± 0.1 °C) was determined. Anal. Calcd. for $C_{13}H_8O_2$: C, 79.58%; H, 4.11%; O, 16.31%. Found: C, 78.91%; H, 4.25%; O, 15.88%.

2.15. Poly(p-phenyletherketone, p PEK) in PPA/P_2O_5 at 165 °C

Into a 250 ml resin flask equipped with a high torque mechanical stirrer, a nitrogen inlet and an outlet, PPA (83% assay, 60 g) and P_2O_5 (15 g) were placed and stirred with dried nitrogen purging at 160 °C for 2 h. 4-Phenoxybenzoic acid (3.0 g, 14.0 mmol) was added and heated to 165 °C. The color of mixture became orange. The orange mixture became viscous after 30 min at 165 °C and started to stick to stirring rod. At the end of the reaction, water was added into the flask. The resulting pink spongy clusters were taken into a Warring blender and the bundles of polymeric product were chopped, collected by suction filtration, washed with diluted ammonium hydroxide, then with large amount of water, Soxhlet extracted with water for 100 h, and finally dried in the presence of phosphorous pentoxide under reduced pressure (0.05 mm Hg) at 120 °C for 72 h to yield 1.0 g (96.4% yield) of pink solid. The intrinsic viscosity of 0.34 dl/g (MSA, 30 ± 0.1 °C) was determined. Anal. Calcd. for $C_{13}H_8O_2$: C, 79.58%; H, 4.11%; O, 16.31%. Found: C, 78.19%; H, 4.28%; O, 15.14%.

2.16. Poly(p-phenyletherketone, p PEK) in K_2CO_3/NMP at 200 °C

Into a 100 ml three-necked, round-bottomed flask equipped with a mechanical stirrer, a nitrogen inlet and an outlet, and a Dean–Stark trap with a condenser, 4-fluoro-4′-hydroxybenzophenone (3.0 g, 13.88 mmol), potassium carbonate (3.0 g, 21.7 mmol), and a mixture of NMP (30 ml) and toluene (60 ml) were placed. The reaction mixture was then heated and maintained at 140–150 °C for 4 h. During this time, the water of condensation formed was removed by azeotropic distillation with toluene. After the complete removal of toluene by drastic nitrogen purging, the orange solution was then heated at 180 °C for 1 h. The mixture was then heated to 202 °C. After 30 min, the mixture became heterogeneous. The mixture was stirred for additional 6 h., allowed to cool to room temperature, and poured into

distilled water containing 5% hydrochloric acid. The resulting white precipitate was collected by suction filtration and Soxhlet-extracted with water for 3 days, and then with methanol for another 3 days. The pale white powder was collected and dried under reduced pressure (1 mm Hg) at 150 °C over phosphorous pentoxide. The yield was essentially quantitative. $[\eta] = 0.85$ dl/g (MSA, 30.0 ± 0.1 °C). $T_m = 360.5$ °C (DSC). Anal. Calcd. for $C_{20}H_{11}FO_3$: C, 79.58%; H, 4.11%; O, 16.31%. Found: C, 77.34%; H, 4.52%; O, 15.35%.

2.17. Poly(p-2,6-dimethylphenyletherketone, p DiMePEK)

Into a 100 ml resin flask equipped with a high torque mechanical stirrer, a nitrogen inlet and an outlet, PPA (83% assay, 20 g) was placed and stirred with dried nitrogen purging at 100 °C for 10 h. 4-(2,6-Dimethylphenoxy) benzoic acid (1.0 g, 4.13 mmol) was added and heated to 100 °C until it become homogeneous mixture. The color of the mixture became light pink. P_2O_5 (25 wt% to PPA 5.0 g) was then added in one portion and the temperature was maintained at 130 °C for 24 h. The red mixture became viscous after 6 h at 130 °C. At the end of the reaction, water was added into the flask. The resulting pink clusters were taken into a Warring blender and the bundles of polymeric product were chopped, collected by suction filtration, washed with diluted ammonium hydroxide, then with large amount of water, Soxhlet extracted with water for 100 h, and finally dried in the presence of phosphorous pentoxide under reduced pressure (0.05 mm Hg) at 120 °C for 72 h to yield 0.78 g (84% yield) of pink solid. The intrinsic viscosity of 0.76 dl/g (MSA, 30 ± 0.1 °C) was determined. Anal. Calcd. for $C_{13}H_8O_2$: C, 80.34%; H, 5.39%; O, 14.27%. Found: C, 78.59%; H, 5.44%; O, 13.75%.

2.18. Poly(p-phenylethersulfone, p PES)

Into a 250 ml resin flask equipped with a high torque mechanical stirrer, a nitrogen inlet and an outlet, PPA (83% assay, 60 g) was placed and stirred under dried nitrogen purging at 100 °C for 10 h. 4-Phenoxybenzenesulfonic acid (3.0 g, 11.99 mmol) was added and heated to 100 °C for approximately, 2 h and P_2O_5 (25 wt% to PPA 15.0 g) was then added in one portion and the temperature was maintained at 130 °C for 48 h. The mixture remained heterogeneous as milky suspension from the beginning and the polymer was isolated from the mixture and stuck to the stirring rod after 6 h. At the end of the reaction, water was added into the flask. The resulting light yellow clusters were dissolved in warm water and filtered. The filtrate was poured into 10% cold hydrochloric acid. The precipitate were collected by suction filtration, Soxhlet-extracted with water for 100 h, and dried under phosphorous pentoxide under reduced pressure (0.05 mm Hg) at 120 °C for 72 h to yield 2.1 g (76% yield) of yellow clear solid. The intrinsic viscosity of 0.05 dl/g (MSA, 30 ± 0.1 °C) was determined. Anal. Calcd. for $C_{12}H_{18}O_3S$: C, 62.06%; H, 3.47%. Found: C, 58.41%; H, 3.68%.

2.19. Estimated yields with TLC and HPLC

When reaction was incomplete, the model reaction mixture had three very distinct spots on a thin-layer chromatography (TLC) plate with EtOAc/Hexane (90/10) elution solvent. The top spot ($R_f = 0.95$) was the unreacted substrate (diphenylether). The middle spot ($R_f = 0.55$), which had a trace at $R_f = 0.50$ (diacylated product), was mono-acylated product. The bottom spot corresponded to the acid endcapping agent (benzoic or benzenesulfonic acid). When an excess amount of acid was used and the reaction was driven to a quantitative conversion, there were only two spots, with one corresponding to the diacylated product ($R_f = 0.50$) and the other correspond to the excess acid ($R_f = 0.05$), were detected on TLC. The excess amount of acid was simply washed away with water and the some crude products were subject to liquid chromatography (HPLC) analysis. The relative yields were estimated based on the intensities of TLC spots cross-referenced with HPLC results.

3. Results and discussion

3.1. Model reactions

In order to establish the optimal conditions for synthesis of either PEKs or PESs via Friedel–Crafts polymerization of the respective AB monomers, two model reactions were conducted (Scheme 1). Three important parameters were investigated: (i) the P_2O_5 content as modulated by the weight ratio of PPA:P_2O_5, (ii) reaction temperature, and (iii) reaction time at a constant temperature. The total solid content of the reaction medium (83% PPA or mixtures of PPA (83%)/P_2O_5) and the reactants was arbitrarily fixed at 10 wt%. The progress of each reaction was monitored with TLC and the products were analyzed with liquid chromatography. The results are summarized in Table 1.

When the reaction was conducted in ‘as received PPA(83%)’ at room temperature, only starting materials were detected. However, as the reaction temperature was elevated to 100 °C, the mono-acylated product (**3**) started to appear (approximately less than 5%). Upon heating at a higher temperature (160 °C), no substantial increase in the yield of **3** was observed (approximately less than 10%). Since the resultant carbonyl formation reduced the susceptibility toward the electrophilic substitution on the other phenyl ring, it is apparent that these conditions were not strong enough to promote second Friedel–Crafts reaction (Scheme 2).

It is clear from the results depicted in Table 1, the increase in the P_2O_5 content of PPA has a great influence on

Table 1
Reaction conditions and yields of **4** based on liquid chromatograph

PPA/P_2O_5 (wt/wt)	Temperature (°C)	Time (h)	**4** Yield (%)
100/0	100	6	0
		12	0
	130	6	Trace
		12	Trace
	160	6	Trace
		12	Trace
100/5	100	6	15
		12	20
	130	6	40
		12	80
	160	6	50
		12	90
100/10	100	6	80
		12	97
	130	6	85
		12	97
	160	6	90 (+by-products)
		12	97 (+by-products)
100/15	100	6	97
		12	98
	130	6	99
		12	99
	160	6	90 (+by-products)
		12	97 (+by-products)
100/20	100	6	98
		12	98
	130	6	99
		12	>99
	160	6	98 (+by-products)
		12	99 (+by-products)
100/25	100	6	98
		12	99
	130	6	>99
		12	>99
	160	6	98 (+by-products)
		12	99 (+by-products)
100/30	100	6	99
		12	99
	130	6	>99
		12	>99
	160	6	98 (+by-products)
		12	99 (+by-products)

the course and the kinetics of Friedel–Crafts reaction. As the weight ratio of PPA/P_2O_5 was varied from 100/5 to 100/30, the yield of the bis-acylated product, 4,4′-dibenzoyldiphenylether (**4**) improved dramatically. **4** was characterized with ^1H and ^{13}C NMR (see Fig. 1), FT-IR and mass spectroscopy as well as elemental analysis (see experimental Section 2.3). It is particularly noteworthy that when the PPA/P_2O_5 ratio was 100/30 and the mixture was still heterogeneous but pink in color (indicating the presence of acylium cation), the reaction was proceeding even at room temperature. For the cases where the weight ratios of PPA/P_2O_5 were greater than 100/15, the reaction time became the driving factor toward the quantitative yields of **4**. In the cases where the weight ratio of PPA/P_2O_5 exceeded 100/25, the high bulk viscosity and the heterogeneity of the mixture rendered the stirring and mixing ineffective. In the 'PPA/P_2O_5 = 100/25' case, the system became homogeneous at the temperature 130 °C, and the reaction was essentially completed in about 8 h with quantitative yield of the bis-acylated product **4**. When the reaction temperature was kept constant at 160 °C, all the cases where the PPA/P_2O_5 weight ratios were greater than 100/5 showed the generation of 1–5% of unidentified side-products, depending on the duration of heating. It appears that the gelation would be most likely if the PPA/P_2O_5 weight ratio $\geq$100/10 and the polymerization temperature is set $\geq$160 °C. Therefore, it is recommended that the optimal conditions for polymerization be: (i) PPA/P_2O_5 weight ratio ~100/25; (ii) reaction temperature at 130 °C. Under these conditions, the heating time can be prolonged beyond 6–12 h without the concern for any side reactions.

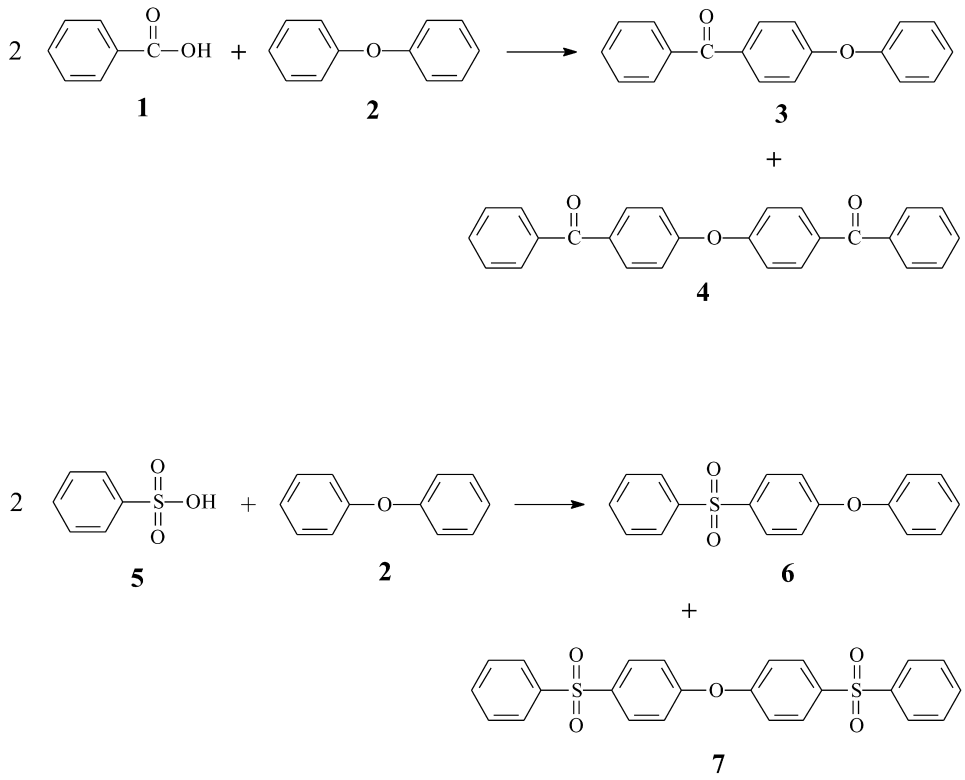
For the Friedel–Crafts reaction between benzenesulfonic acid (**5**, generated in situ from the corresponding sodium salt) and diphenylether (**2**), the PPA/P_2O_5 weight ratio of 100/25 was selected since it was optimal for the acylation reaction [16]. However, at this PPA/P_2O_5 weight ratio, the reaction mixture remained heterogeneous at temperatures $\leq$130 °C throughout the course of the reaction. In spite of heterogeneity, the reaction did indeed go to completion after 8 h to give 4,4′-dibenzenesulfonyldiphenylether (**7**) in quantitative yield (Scheme 2 and Fig. 2). Similarly, when the reaction temperature was 160 °C, some unidentified side-products were also observed (see Table 2).

3.2. AB monomers

It is known that the *meta*-AB monomer, namely, 3-phenoxybenzoic acid (**18**) can be polymerized in a mixture of MSA and 10 wt% P_2O_5 (PPMA; also known as Eaton's reagent) to form *m*PEK with relatively high molecular weight (η_{inh} = 1.0 dl/g, in H_2SO_4, at 0.5 dl/g, 30 °C) [11]. However, similar polymerization of the *para*-AB monomer, 4-phenoxybenzoic acid (**20**) by two separate research groups only yielded low molecular weight *p*PEK [11,17]. Since the *ortho*-AB monomer (**15**) is known to form the corresponding xanthone (**16**) in 83%PPA via intramolecular Freidel–Crafts reaction [18], the 2,6-positions of the phenoxy moiety were blocked with the methyl groups. The AB monomers (**11** and **14**) were synthesized as showed in Scheme 3. Thus, the reaction of 2,6-dimethylphenol with

Table 2
Reaction conditions and yields of **7** based on liquid chromatograph

PPA/P_2O_5 (wt/wt)	Temperature (°C)	Time (h)	**7** Yield (%)
100/25	100	6	92
		12	95
	130	6	97
		12	>99
	160	6	98 (+by-products)
		12	99 (+by-products)



Scheme 2. Syntheses of model compounds.

2- and 4-fluorobenzonitriles (**9** and **12**) in NMP at elevated temperatures in the presence of potassium carbonate afforded 2- and 4-(2,6-dimethylphenoxy)benzonitriles (**10** and **13**). The benzonitrile intermediates were subsequently converted to the respective carboxylic acid monomers (**11** and **14**) with the aid of 100% phosphoric acid.

3.3. Polymerizations

On the basis of the foregoing model-compound studies, all self-condensations of the phenoxybenzoic acid monomers and 4-phenoxybenzenesulfonic acid were conducted at 130 °C with the additional 25 wt% of P_2O_5 and in 5 wt% monomer concentration (see Scheme 4); both percentages are relative to the amount of PPA used.

The reaction mixture of monomer **18** was purple-colored. When the reaction temperature approached 130 °C, it became a very viscous and homogeneous mixture that stuck onto the stirring rod after 30 min. The polymer (*m*PEK, **19a**) was obtained in quantitative yield with intrinsic viscosity up to 2.10 dl/g. The adverse effect of higher reaction temperature can be illustrated by the following observation: when the reaction temperature approached 160 °C, the system was too dry and non-fluid to allow stirring effectively, and a small portion of the mixture was gel-like. For comparison purposes, the polymerization of monomer **18** was also conducted in PPMA (Scheme 5) following the procedure reported in literature [11]. The polymerization mixture was dark purple and the resulting polymer **19b** (*m*PEK) was also dark purple with a substantially lower intrinsic viscosity ($[\eta] = 0.64$ dl/g). It is noteworthy that while **19b** is very soluble in methylene chloride, **19a** is not soluble at all in haloalkanes and polar amide solvents tested, suggesting the effect of higher molecular weights. The reaction mixture of monomer **20** was red and heterogeneous throughout the entire polymerization process. Stirring 24 h at 130 °C resulted in some moderate build-up of the bulk viscosity and the polymerization dope eventually clung around stirring rod. However, the polymer **21a** (*p*PEK) was obtained in 75% yield (based on the initial amount of AB monomer) with an intrinsic viscosity of 0.69 dl/g that is significantly higher than the values previously reported for *p*PEK obtained using PMMA polymerization medium ($\eta_{inh} = 0.15–0.32$ dl/g [11]; $[\eta] = 0.18$ dl/g [17]).

A similar phase separation was also observed during the polymerization of the dimethyl-blocked monomer **14**. This system was slightly pink-colored and heterogeneous. The yield of polymer **22** (DiMe-*p*PEK) after work up was 84% with an intrinsic viscosity of 0.76 dl/g. Thus, relatively high molecular weight was achieved even at heterogeneous phase, reminiscent of the polymerization process of rigid-rod benzobisazole polymers in PPA [14]. Apparently, the lower than quantitative yield was due to incomplete consumption of the monomer. Furthermore, the result indicated that the methyl groups were not effective in promoting solubilization of the polymer chains in PPA.

For comparison, the synthesis of *p*PEK (**21b**) via an

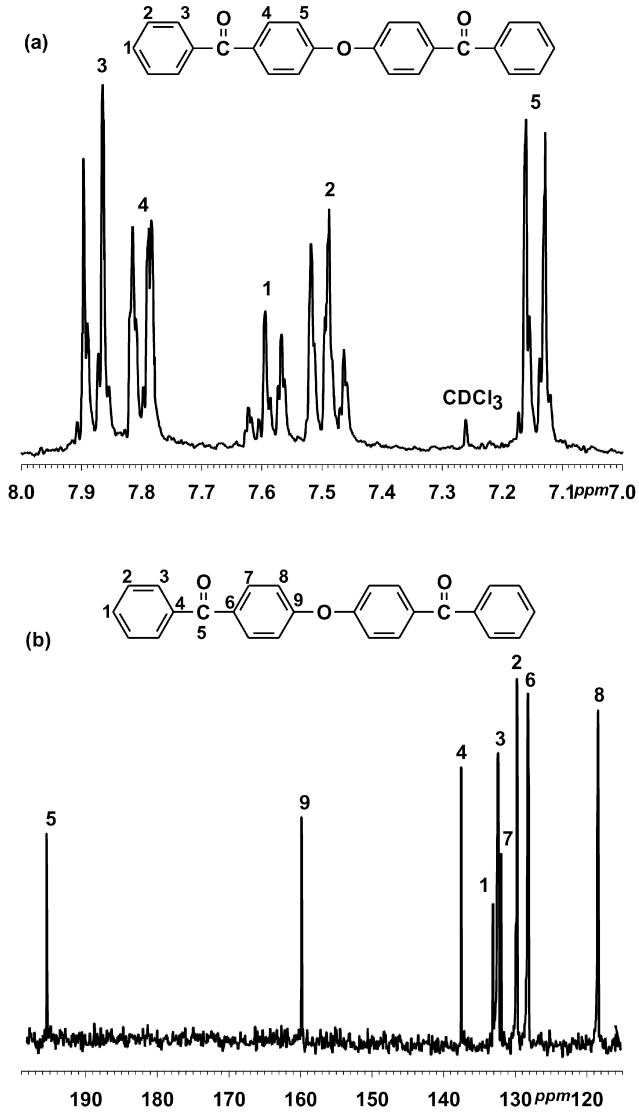


Fig. 1. ^{1}H and ^{13}C NMR spectra of 4,4′-dibenzoyldiphenylether (**4**): (a) proton; (b) carbon.

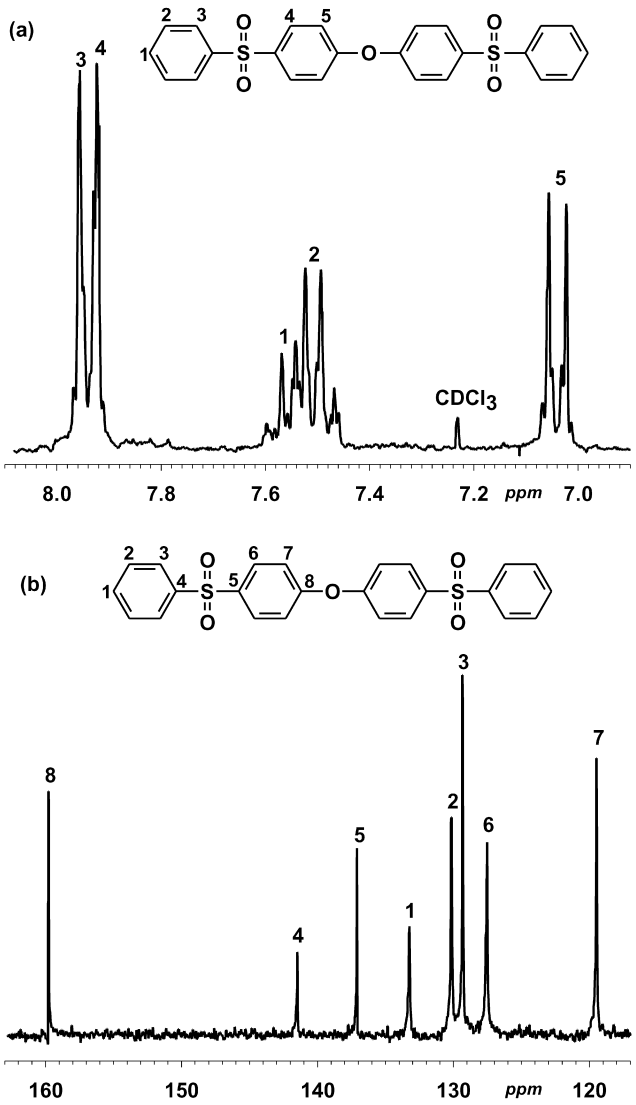


Fig. 2. ^{1}H and ^{13}C NMR spectra of 4,4′-dibenzenesulfonyldiphenylether (**7**): (a) proton; (b) carbon.

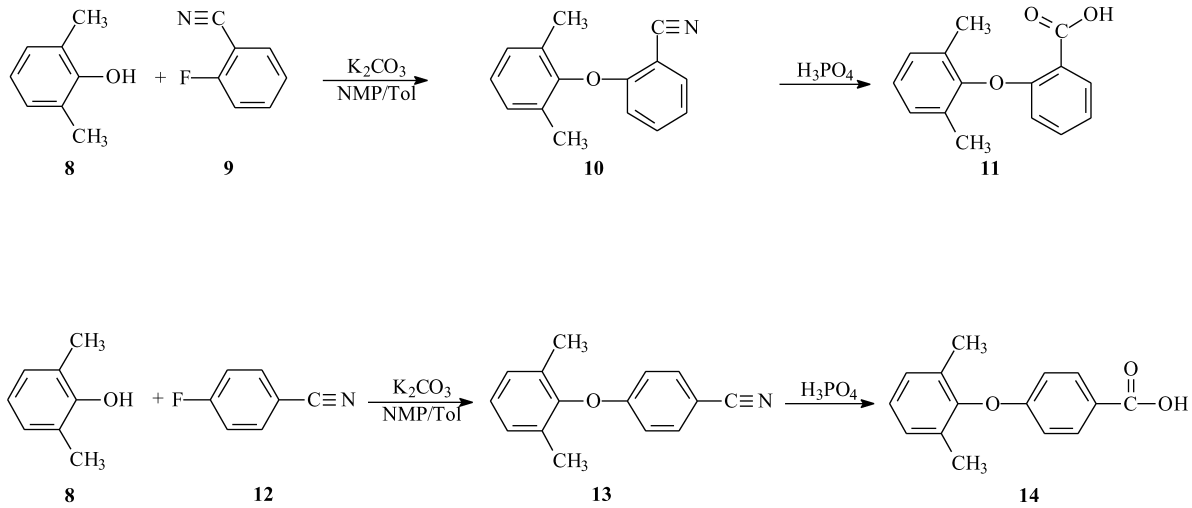
aromatic nucleophilic substitution reaction from the monomer, 4-fluoro-4′-hydroxybenzophenone (**12**) was also conducted under similar conditions reported (Scheme 6) [5]. The resulting *p*PEK had intrinsic viscosity value as high as 0.85 dl/g.

Despite the presence of the blocking groups at 2,6 positions to preclude intramolecular cyclization process, the polymerization of monomer **11** only led to the isolation of a low molecular weight material as green powder, which was not characterized.

The polymerization mixture containing either sodium 4-phenoxybenzenesulfonate **23** or 4-phenoxybenzenesulfonic acid was also heterogeneous. As the polymerization proceeded, the polymer was observed to phase-separate from the bulk and eventually formed an isolated lump that stuck to the stirring rod. The phase separation and ineffective mixing during the early stage of polymerization may account for the result in a very low-molecular weight product **24** ($[\eta] = 0.05$ dl/g). However, much higher molecular weight PES **24** had been prepared in PPMA ($\eta_{inh} = 0.85$ dl/g, N,N′-dimethylacetamide) [10].

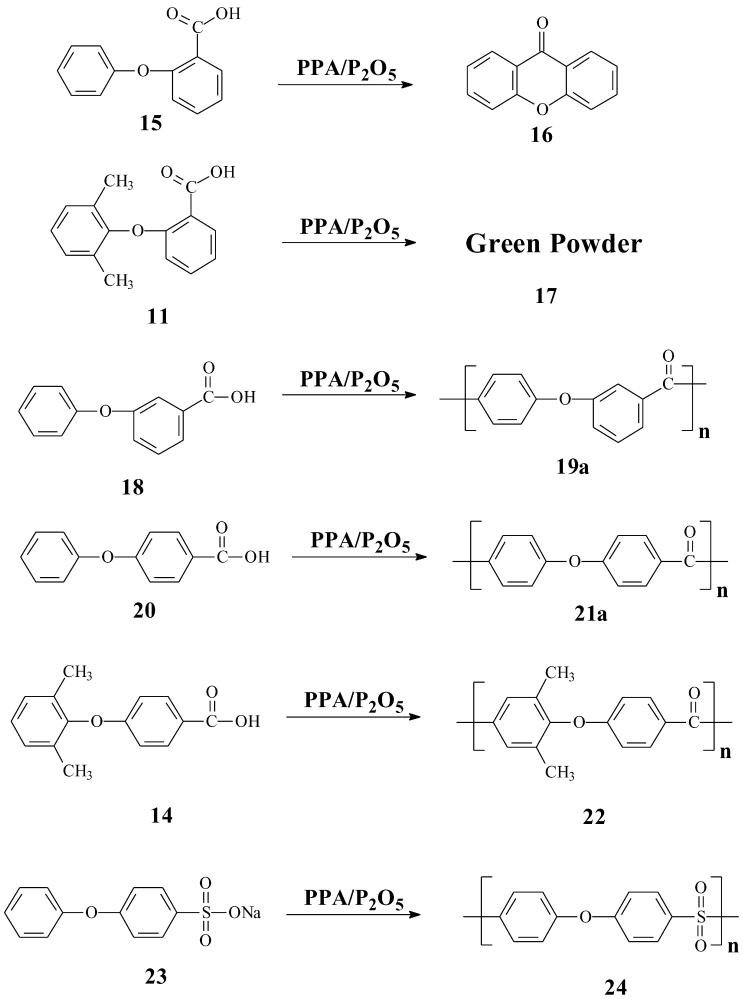
3.4. Thermal properties

The glass-transition temperatures (T_gs) of the polymers were obtained from DSC. The DSC samples (powder form) were subjected to two cycles of heating from room temperature to 340–400 °C and then cooling to 20 °C, with heating and cooling rate of 10 °C/min. The T_g value was taken as the mid-point of the maximum baseline shift from the second run. The results are summarized in Fig. 3 and Table 3, the *m*PEK samples **19a** ($[\eta] = 2.10$ dl/g) and **19b** ($[\eta] = 0.64$ dl/g), which were prepared from different acidic media, exhibited T_gs at 137 °C and 129 °C. Similar *m*PEK ($\eta_{inh} = 2.40$ dl/g, at 0.5 g/dl in MSA, 30 °C) prepared via aromatic nucleophilic displacement method

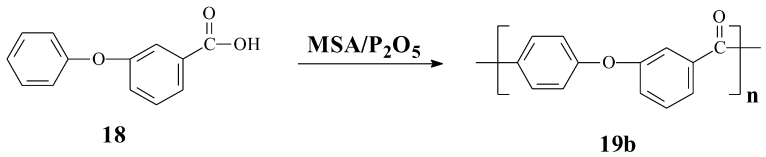


Scheme 3. Syntheses of dimethyl-blocked AB monomers.

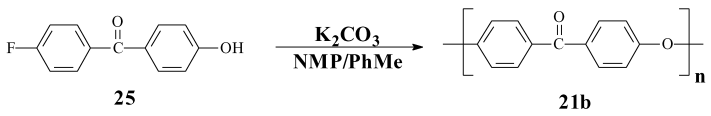
was reported to have a T_g value of 132 °C [15]. **19a** also displayed a broad exotherm whose peak value was at 250 °C during the first run, but shifted to 305 °C during second run. The semi-crystalline *p*PEK **21a**, which was prepared from PPA/P_2O_5 route, displayed a broad melting endotherm centered at 344 °C during the first heating scan. The all *para*-substituted polymer **21b**, prepared from aromatic nucleophilic substitution reaction [5], had a relatively



Scheme 4. Polymerization in PPA/P_2O_5 medium.



Scheme 5. Polymerization in MSA/P_2O_5 (PPMA) medium.



Scheme 6. Polymerization in NMP/Toluene mixture in the presence of potassium carbonate.

sharp melting endotherm at 360 °C during the first heating run. Surprisingly, **21a** showed a T_g at 159 °C and two exothermic peaks at 192 and 275 °C, attributable to the thermally-induced crystallization process. This also implicated that the **21a** had retained its amorphousness during the polymerization and work-up. On the first cooling scan, **21a** displayed a broad exotherm (crystallization) with peak value at 221 °C and a T_g at 159 °C, and **21b** showed a sharp crystallization exotherm centered at 272 °C and T_g at 175 °C. On the second heating run, **21a** and **21b** showed T_g at 165 and 169 °C as well as the melting endotherms with peak values at 326 and 344 °C, respectively. However, only **21a** had a crystallization exotherm centered at 227°. Overall, **21a** has broader and lower melting temperature, lower and broader recrystallization temperature, slower crystallization rate, and lower T_g than **21b**. This is very likely because of isomeric defect in **21a** originated from a small portion of *ortho*-substituted structures via Friedel–Crafts reaction. The polymer **22**, which is the 2,6-dimethylsubstituted version of **21**, was amorphous, displaying a T_g at 200 °C.

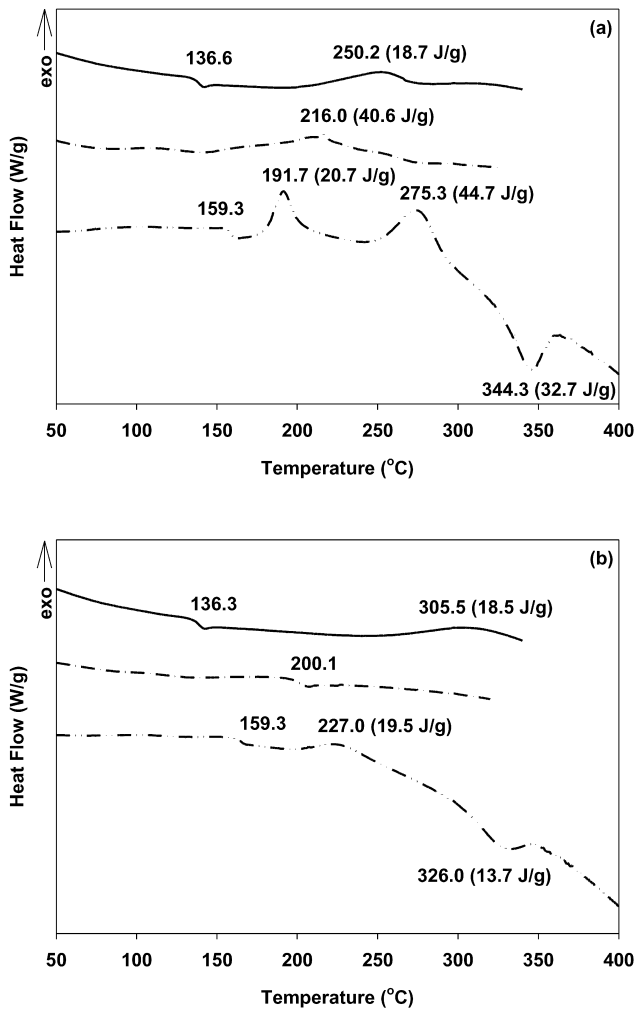


Fig. 3. DSC thermograms for the poly(ether–ketones) with heating rate of 10 °C/min: (a) first heating scan; (b) second heating scan: **19a** (solid line), **21a** (dash–dot), and **22** (dash–dot–dot).

The polymers were subjected to determine their thermo-oxidative stability and thermal stability by TGA on the powder samples in air and helium, respectively. The results are depicted in Fig. 4. In general, polymers are thermally stable as indicated by the fact that the temperatures at which a 5% weight loss occurred are in the range of 414–503 °C in air and 365–516 °C in helium (see Table 3).

4. Conclusion

In summary, we have developed an improved polymerization medium by optimizing the P_2O_5 content of PPA for the electrophilic synthesis of *m*PEK and related polymers. Although we have demonstrated the effectiveness of such polymerization medium for generating high molecular weight PEKs from AB-type monomers, it is applicable to AA + BB polymerization as well. For example, poly(ether–ketones) prepared from either 1,4-diphenoxybenzene or diphenylether and terephthalic acid have intrinsic viscosity values of 0.66–0.73 dl/g (MSA). Our focus on AB polymerization primarily because of a parallel effort in the synthesis and characterization of novel ABA triblock (coil–rod–coil) copolymers where A blocks are linear or hyperbranched poly(ether–ketones) and B block is rigid-rod poly(p-phenylenebenzobisthiazole) [19]. Although the model compound study indicated the suitability of PPA/P_2O_5 for effecting aromatic sulfonylation, the

Table 3
Intrinsic viscosity data and thermal properties of PEKs and PES

Entry	$[\eta]$[a] (dl/g)	T_{gh}[b] (°C)	T_{gc}[c] (°C)	T_m[b] (°C)	ΔH_f (J/g)	T_c[c] (°C)	ΔH_c (J/g)	TGA[d] Air $T_{d5\%}$ (°C)	Char at 900 °C	Helium $T_{d5\%}$ (°C)	Char at 900 °C
19a	2.10	136.6	135.2	ND	ND	ND	ND	414	0.8	365	41.2
19b	0.64	129.2	127.0	ND	ND	ND	ND	–	–	–	–
21a	0.69	159.3	165.0	344.0(326.0)	32.7(13.7)	221.3	13.1	503	0.3	516	44.0
21b	0.85	174.6	169.3	360.5(344.8)	36.9(17.0)	272.0	34.6	461	0.1	463	37.6
22	0.76	200.1	198.4	ND	ND	ND	ND	435	0.3	418	49.1
24	0.05	–	–	ND	ND	ND	ND	–	–	–	–

[a] Intrinsic viscosity measured in MSA at 30 ± 0.1 °C.
[b] Glass transition temperature (T_g) and melting temperature (T_m) determined by DSC with heating rate of 10 °C/min. ND = Not detected. T_m values in parentheses are from second heating scan.
[c] Glass transition temperature (T_g) and crystallization temperature (T_c) determined by DSC with cooling rate of 10 °C/min.
[d] 5% weight temperature ($T_{d5\%}$) determined by TGA with heating rate of 10 °C/min.

analogous polymerization was not successful, presumably because of the incompatibility/immiscibility [20] of the poly(ether–sulfone) chains with the medium at the early stage of polymerization. Finally, we have also noted that there are distinct differences in the thermal and morphological behaviors of both the *m* PEK and *p* PEK depending on the polymerization conditions (electrophilic versus nucleophilic, and viscousness of the reaction media). The results for the comparison studies will be described in a forthcoming paper.

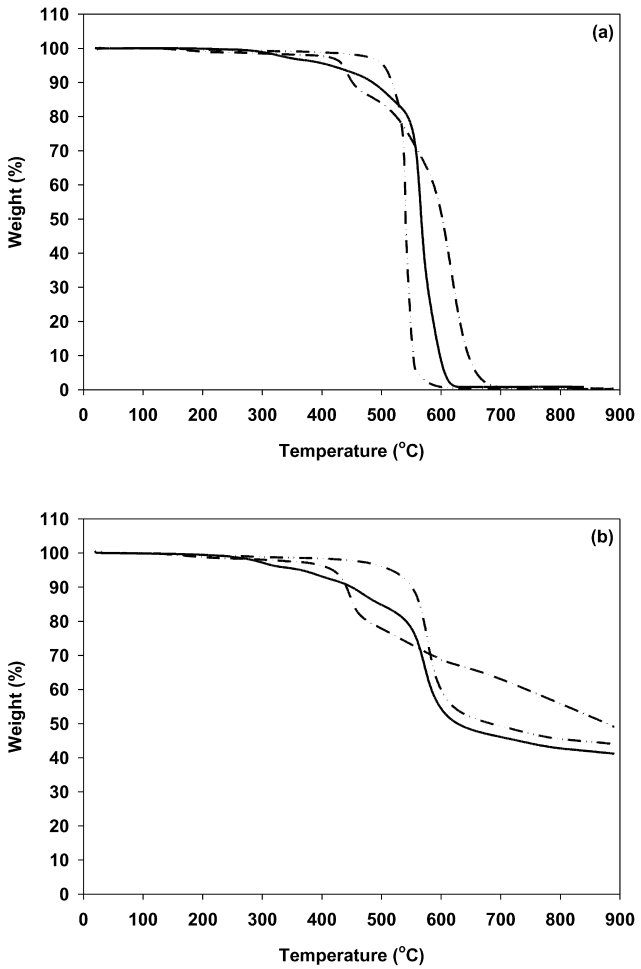


Fig. 4. TGA thermograms for the poly(ether–ketones) with heating rate of 10 °C/min under (a) air and (b) helium atmospheres: **19a** (solid line), **21a** (dash–dot), and **22** (dash–dot–dot).

Acknowledgements

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[20] The insufficient protonation as the enthalpic driving force may be accounted for the incompatibility of PESs and polyphosphoric acid. Consider the following order of acidity: carbonic acid, HO(C=O)OH < phosphoric acid, $HO(P{=}O)(OH)_2$ < sulfuric acid, HO(O=S=O)OH, then the order of basicity (oxygen lone-pair electrons) should be reversed: carbonyl > phosphoryl > sulfonyl. Thus, it would not be a surprise that poly(phosphoric acid) cannot protonate the sulfonyl group to the same extent as it does the carbonyl group.