Aromatic poly(pyridinium salt)s: synthesis and structure of organo-soluble, rigid-rod poly(pyridinium tetrafluoroborate)s*

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A series of phenylated, aromatic poly(pyridinium tetrafluoroborate)s has been prepared by the polymerization of 4,4′-(1,4-phenylene)bis(2,6-diphenylpyrylium tetrafluoroborate) with aromatic diamines in a dimethylsulfoxide/toluene mixture at 145–150°C. The water generated by the transformation of the pyrylium rings to pyridinium rings was distilled from the reaction mixture as a water/toluene azeotrope. All-*para*-catenated, rigid-rod polymers with inherent viscosities as high as 4.9 dl g^{-1} were obtained that were soluble in polar aprotic solvents. The polymers could be solution cast into tough, flexible films. Although the glass transition temperatures of the poly(pyridinium salt)s were difficult to detect with differential scanning calorimetry, they displayed distinctive melting endotherms with minima above 380°C. Thermogravimetric analysis showed that the polymers began to decompose near 360°C prior to melting. Wide-angle X-ray diffraction analysis revealed that the chains were packed in a structure similar to that of a smectic liquid crystalline glass.

(Keywords: poly(pyridinium salt)s; rigid-rod polymers; aromatic ionenes)

INTRODUCTION

Polymers containing quaternary nitrogen atoms in the backbone are referred to as ionenes[1]. The ionenes comprised of positively charged pyridine rings are generally referred to as aromatic ionenes, even though they usually contain aliphatic units in the polymer backbone. Such polymers can also be classified as poly(pyridinium salt)s. These materials, which belong to a class of polymers known as oxidation–reduction or redox polymers[2,3], have considerable potential for use as easily removable oxidizing or reducing agents, in electron-exchange membranes[4] and as semiconducting materials[5]. Aromatic ionenes containing 4,4′-dipyridinium cations, so-called polyviologens, are of particular interest due to their extremely low cationic redox potentials[6]. Owing to the positive charges located along their backbones, aromatic ionenes also may be utilized as ionic conductors and in ion-exchange membranes.

The major goal of this work was the synthesis of a new series of high molecular weight, phenylated, aromatic poly(pyridinium tetrafluoroborate)s. Phenylated heterocyclic polymers are known for their solubility in organic solvents and their film-forming abilities[7–9]. All-aromatic systems were sought because of their thermal and chemical stability[10]. In fact, it was postulated that owing to their phenyl substituents and the formal positive charges located along their backbones, all-*para*-catenated, rigid-rod poly(pyridinium salt)s would be soluble in common organic solvents. Although rigid-rod polyheterocyclics such as polybenzazoles[11] and polyimides[9] have been prepared previously, they have been found to be soluble only in strong acids or phenols.

The route to the desired ionene polymers involved the reaction of a bis(pyrylium tetrafluoroborate) with aromatic diamines[12]. Amines are known to react with pyrylium salts to afford pyridinium salts in high yields[13,14]. Since the pyrylium ring is converted to a pyridinium ring in these reactions[14], they are known as ring transformation reactions. However, previous attempts to utilize these reactions as modes of propagation in polymerizations have generally been unsuccessful. For example, an attempt to polymerize 2,2′,6,6′-tetraphenyl-4,4′-bis(pyrylium perchlorate) with hexamethylenediamine in refluxing methanol resulted in the formation of oligomers with an average degree of polymerization of only 3 to 4[15]. The product's low molecular weight was attributed to its premature precipitation from the reaction medium. During the course of this work, an attempt was made to polymerize bis(pyrylium tetrafluoroborate)s with aliphatic and aromatic diamines under catalytic conditions in *N*,*N*-dimethylformamide (DMF) at ambient temperature[16]. In this procedure triethylamine was added to the polymerization mixtures followed by acetic acid. These mild reaction conditions were identical to those reported to be optimum for preparing simple pyridinium salts[17]. However, the aromatic polymers obtained under these conditions had inherent viscosities of only 0.5–0.6 dl g^{-1}

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*Presented at the Americal Chemical Society, Division of Polymer Chemistry '17th Biennial Symposium on Advances in Polymerization and High Performance Polymeric Materials', 22–25 November 1992, Palm Springs, CA, USA
Paper based on the PhD dissertations of K. C. Chuang and S. A. X. Huang, The University of Akron, OH, USA, 1990 and 1993, respectively
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0032-3861/94/23/4940–09

and softening points below 100°C. This strongly suggests that the products were low molecular weight oligomers. The only polymer with an inherent viscosity greater than 1.0 dl g^{-1} was obtained from an aliphatic diamine. Thus, one of the initial objectives of this work was the determination of reaction conditions that would afford high molecular weight polymers.

EXPERIMENTAL

Instrumentation

All i.r. spectra were recorded on a Beckman FT-2100 spectrometer using film or KBr pellet samples. Proton nuclear magnetic resonance (^{1}H n.m.r.) and carbon nuclear magnetic resonance (^{13}C n.m.r.) spectra were measured at 200 MHz on a Varian Gemini-200 spectrometer using tetramethylsilane as an internal standard. All u.v. and visible spectra were recorded using a Perkin–Elmer model 559A spectrophotometer. Melting points were measured using a Meltemp capillary apparatus and are uncorrected. Inherent viscosities were determined with a Cannon-Ubbelohde no. 75 viscometer. Flow times were recorded for DMF solutions with polymer concentrations of approximately 0.5 g dl^{-1} at 30 ± 0.1°C. High pressure liquid chromatography (h.p.l.c.) was performed on a Varian 5000 Liquid Chromatograph equipped with a C_{18} reverse-phase column and a Varian UV-50 wavelength-adjustable detector; acetonitrile was used as the eluent. Differential scanning calorimetry (d.s.c.) data were recorded using a DuPont model 9900 thermal analyser equipped with a differential scanning calorimetry cell. Thermogravimetric analyses (t.g.a.) were obtained in nitrogen and in air with a DuPont model 951 at a heating rate of 10°C min^{-1}. Elemental analyses (t.g.a.) were performed by Galbraith Laboratories, Inc., Knoxville, TN, USA. Wide angle X-ray diffraction (WAXD) experiments were performed with a 40 kV Philip X-ray generator (PR 1301/03) and a Laue vacuum flat-film camera using perpendicular transmission. The wavelength of the Cu Kα X-ray incident beam was 1.54178 Å. The sample to film distance was approximately 40 mm, and the exposure time was 2–10 h.

Monomers

3,3′-(1,4-Phenylene)bis(1-phenyl-2-propen-1-one)(p-bischalcone) (2). A mixture of terephthalaldehyde (6.7 g, 0.05 mol) and acetophenone (12.0 g, 0.1 mol) was dissolved in 200 ml of 95% ethanol at 60–70°C. Sodium hydroxide (3.0 g, 0.075 mol) in 32 ml of water and 19 ml of 95% ethanol was added dropwise to the solution. The *p*-bischalcone product precipitated in 5–10 min. After the heterogeneous solution was heated at 60–70°C for an additional 20 min, it was cooled to room temperature. The product was collected by filtration, washed with 95% ethanol and a mixture of toluene and hexane. The crude product was recrystallized from toluene to afford 15.6 g (95%) of yellow needles: m.p. 194–195°C (lit.[18] m.p. 201°C); i.r. (KBr) 1660 cm^{-1} (C=O).

3,3′-(1,4-Phenylene)bis(1,5-diphenyl-1,5-pentadione) (*3*). A mixture of terephthalaldehyde (40.0 g, 0.3 mol) and acetophenone (217.0 g, 1.8 mol) was stirred in 1 l of 95% ethanol and heated to 65°C. After the starting materials dissolved, a solution of potassium hydroxide (42.0 g, 0.75 mol) in 45 ml of water was added dropwise over 30 min with vigorous stirring. A yellow precipitate formed immediately. The heterogeneous reaction mixture was then heated at reflux until it turned pink, which took 4–5 h. During this time, the *p*-bischalcone redissolved and reacted with two additional equivalents of acetophenone to form the tetraketone, which precipitated. The reaction mixture was filtered hot, and the pink solid was collected by filtration to afford 164.0 g (96%) of crude product. (The crude product was sometimes obtained as a yellow-brown solid.) The crude product was recrystallized from toluene to afford 159.0 g (92%) of colourless crystals: m.p. 205–206°C (lit.[19] m.p. 205°C); i.r. (KBr) 1683 cm^{-1} (C=O).

4,4′-(1,4-Phenylene)bis(2,6-diphenylpyrylium tetrafluoroborate) (**4**). (a) *Triphenylmethyl tetrafluoroborate method*[16,19]. A suspension of triphenylmethanol (62.4 g, 0.24 mol) in 700 ml of acetic anhydride was placed in a three-necked round-bottom flask equipped with a mechanical stirrer. The mixture was warmed to 65°C until it became clear and then cooled to room temperature. To the cloudy mixture was added carefully 44 ml of 48 wt% fluoroboric acid (55 g, 0.3 mol) dropwise. The reaction mixture, which became homogeneous, was also maintained at 20–25°C with a water bath during the exothermic process. After the addition of fluoroboric acid, solid 3,3-(1,4-phenylene)bis(1,5-diphenyl-1,5-pentadione) (57.8 g, 0.1 mol) was added portionwise. After the solid dissolved, the yellow product precipitated in 5–10 min. The heterogeneous reaction mixture was stirred at ambient temperature overnight to ensure a complete reaction. The yellow precipitate was collected by filtration, washed extensively with acetic anhydride, and dried at 110°C under reduced pressure to afford 70.8 g (99%) of a yellow powder. A small sample was recrystallized from acetic acid to afford light yellow needles: m.p. > 350°C (decomposition), (lit.[16] m.p. > 350°C); i.r. (KBr) 1620, 1600, 1500, 1465, 1400, 1090 and 1060 cm^{-1} (broad, BF_4^-); ^{1}H n.m.r. (deuterated dimethylsulfoxide (DMSO-d_6)): δ 7.5–9.0 (m, 24H, aromatic) and 9.35 ppm (s, 4H, 3,5 aromatic). Analysis calculated for $C_{40}H_{28}B_2F_8O_2$: C 67.26; H 3.93; found: C 66.96; H 4.20.

(b) *Boron trifluoride etherate method.* To a suspension of the *p*-bischalcone **2** (3.38 g, 0.01 mol) and acetophenone (2.4 g, 0.02 mol) in 100 ml of toluene, boron trifluoride etherate (100 ml, 0.082 mol) was added carefully at ambient temperature. Although the suspended solids dissolved immediately, a yellow precipitate formed in 10–15 min. The heterogeneous reaction mixture was heated at reflux for 2–3 h. The water that formed in the reaction was removed as a toluene/water azeotope with a Dean-Stark trap. During this time, the yellow suspension first changed to orange and then become a clear orange solution, which darkened to brown-orange at the end of the reflux period. Fumes also evolved from the condenser. The reaction mixture was evaporated to dryness on a rotary evaporator. The dark-brown residue was triturated with 95% ethanol, and the resulting solids were collected by filtration to yield 4.5 g (63%) of a yellow-orange product.

1,4-Bis(4-nitrophenyl)benzene. To a suspension of *p*-terphenyl (20.0 g, 0.087 mol) in 80 ml of nitrobenzene at ambient temperature was added 24 ml of fuming nitric acid portionwise over 2–3 min. Initially the *p*-terephenyl dissolved to form a cloudy solution, from which a yellow solid gradually precipitated. The heat generated by the exothermic reaction raised the temperature to 90°C. The reaction mixture was then stirred without external heating for 1 h. Brown fumes evolved from the condenser throughout the reaction. After the heterogeneous mixture was cooled in an ice-bath, the precipitate was collected by filtration. The crude product was recrystallized from 120 ml of nitrobenzene and dried at 100°C under reduced pressure to afford 7.3 g (35%) of yellow needles: m.p. 276–278°C (lit.[20] m.p. 270–271°C); i.r. (KBr) 1340, 1520 cm^{-1} (NO_2).

1,4-Bis(4-aminophenyl)benzene (***9e***). To a yellow suspension of 1,4-bis(4-nitrophenyl)benzene (12.2 g, 0.038 mol) in 300 ml of 2-methoxyethanol (methyl cellosolve) at 110°C, a hot solution of stannous chloride dihydrate (87.0 g, 0.385 mol) in 140 ml of concentrated hydrochloric acid (preheated to 60–70°C) was added. The reaction mixture was heated at reflux for 3 h during which time the yellow needles of 1,4-bis(4-nitrophenyl)benzene were gradually replaced by white platelets. The reaction mixture remained heterogeneous during the entire process. The white solids were collected by filtration and then treated with 20% aqueous sodium hydroxide to neutralize the diamine dihydrochloride salt. The pink product was extracted with xylene in a Soxhlet apparatus for 2 days. After the xylene extract was cooled to room temperature, orange needles crystallized. The crystals were collected by filtration and dried at 100°C under reduced pressure overnight to afford 9.5 g (96%) of 4,4″-diamino-*p*-terphenyl: m.p. 240–241°C (lit.[20] m.p. 241–242°C): i.r. (KBr) 3270, 3205 cm^{-1}.

2,2′-Bis(trifluoromethyl)-4,4′-diamino-1,1′-biphenyl (***9f***). This monomer was prepared in 75% yield from 2,2′-bis(trifluoromethyl)-4,4′-dinitro-1,1′-biphenyl by the described procedure[21]: m.p. 180–182°C (lit.[21] m.p. 181–182°C).

*General procedure for the preparation of diamines **13a,b***[22]. A mixture of 1-fluoro-4-nitrobenzene (0.54 mol), the appropriate glycol (diethylene glycol or triethylene glycol; 0.18 mol) and potassium carbonate (0.18 mol) was heated at reflux for 24 h under nitrogen. The mixture was cooled and then poured into water. The precipitate that formed was collected by filtration and washed with ether to remove excess 1-fluoro-4-nitrobenzene. The crude dinitro compound was recrystallized from ethanol. The dinitro compound was hydrogenated using a 5% Pd/C catalyst in 95% ethanol at 50 psi in a Parr hydrogenation apparatus.

Bis[2-(4-aminophenoxy)ethyl] ether (***13a***). The white solid was obtained in 83% yield: m.p. 59–60°C (lit.[22] m.p. 60°C); i.r. (KBr) 3450 and 3350 (NH_2); ^1H n.m.r. (acetone-d_6); δ 3.8 (m, 12H, $-OCH_2CH_2-/NH_2$) and 6.6 ppm (m, 8H, aromatic).

1,2-Bis[2-(4-aminophenoxy)ethoxy]ethane (***13b***). The white crystalline solid was obtained in 77% yield: m.p. 94–95°C (lit.[22] m.p. 93–95°C); i.r. (KBr) 3340 and 3250 cm^{-1} (NH_2); ^1H n.m.r. (acetone-d_6): δ 3.8 (m, 16H, $-OCH_2CH_2-/NH_2$) and 6.6 ppm (m, 8H, aromatic).

Model reaction studies

*Model compound **6b***. A solution of the 4,4′-(1,4-phenylene)bis(2,6-diphenylpyrylium tetrafluoroborate) (**4**) (1.428 g, 2.000 mmol) and *p*-anisidine (0.429 g, 4.000 mmol) in 6 ml of DMF was heated at reflux for 2 h. The solution was evaporated to dryness on a rotary evaporator to afford a yellow crude product in quantitative yield. A small sample was recrystallized from glacial acetic acid to afford yellow needles: m.p. 386–388°C; i.r. (KBr) 1620, 1600, 1578, 1512, 900 and 850 cm^{-1} (BF_4^-); ^1H n.m.r. (DMSO-d_6): δ 3.60 (s, 6H, $-OCH_3$), 6.72 (d, $J=1.5$ Hz, 4H, aromatic), 7.36 (d, $J=1.5$ Hz, 4H, aromatic), 7.4 (m, 20H, aromatic), 8.62 (s, 4H, 2′,6′-aromatic) and 8.82 ppm (s, 4H, 3,5-aromatic). Analysis calculated for $C_{54}H_{42}N_2B_2F_8O_2$: C, 70.15; H 4.58; N 3.03; found: C 69.87; H 4.45; N 2.73.

*Model compound **8***. A solution of 2,4,6-triphenylpyrylium tetrafluoroborate (**7**) (3.170 g, 8.000 mmol) and 4,4′-diaminobiphenyl (0.7396 g, 4.000 mmol) in 12 ml of DMSO was heated at reflux (200°C bath temperature) for 2 h. After the resulting yellow clear solution was stirred at room temperature overnight, it was slowly poured into a large excess of rapidly stirred diethyl ether. The product that precipitated was collected by filtration, washed with ether, and dried under reduced pressure at 110°C overnight to afford 3.743 g (99.5%) of a yellow powder: m.p. > 400°C (decomposition); ^1H n.m.r. (DMSO-d_6) δ 8.7 (s, 4H, 3,5-aromatic), 8.35 (s, 4H, 2′,6′-aromatic) and 7.3–7.8 ppm (m, 34H, aromatic).

Polymerizations

General procedure for the polymerization of the bis(pyrylium tetrafluoroborate) ***4*** *with aromatic diamines. Procedure 1*. A solution of the 4,4′-(1,4-phenylene)bis(2,6-diphenylpyrylium tetrafluoroborate) (**4**) (40.00 mmol) and the aromatic diamine (40.00 mmol) in 240 ml of DMSO or DMF was vigorously stirred and heated at 110°C under nitrogen for 2 h. Toluene (100 ml) was then added so that the water generated by the transformation of the pyrylium ring to the pyridinium ring could be removed as a toluene/water azeotrope. The bath temperature was increased to 150°C and the azeotrope and the excess toluene were gradually distilled from the reaction mixture using a Dean-Stark trap over 4–5 h. The bath temperature was then increased to 195°C and maintained at that temperature for 24 h. The resulting viscous solution was diluted with DMSO (200 ml) and slowly poured into a large excess (25 times in volume) of rapidly stirred diethyl ether. The fibrous yellow poly(pyridinium salt) that precipitated was collected by filtration and reprecipitated from 200 ml of hot DMF with diethyl ether. The poly(pyridinium salt), which was obtained in a quantitative yield, was washed with ether and dried at 120°C under reduced pressure overnight.

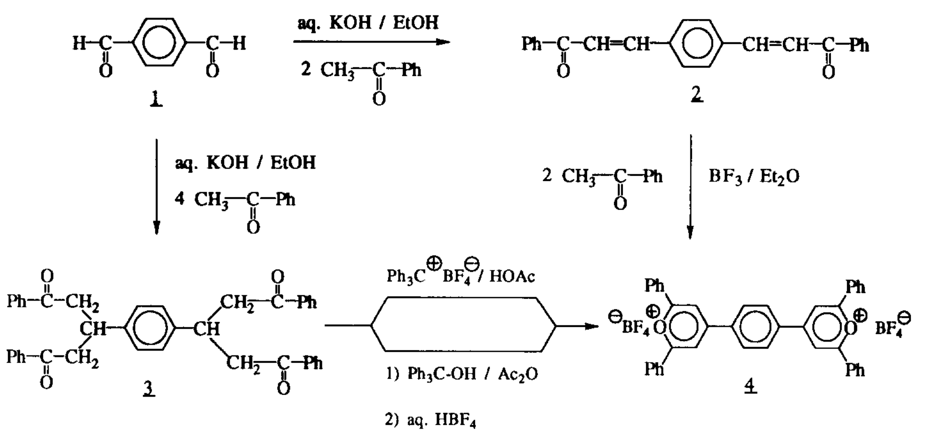
Procedure 2. The second procedure was identical to the first except that the bath temperature was maintained at 150°C after the azeotrope and excess toluene had been removed by distillation.

RESULTS AND DISCUSSION

Monomer synthesis

The monomer 4,4′-(1,4-phenylene)bis(2,6-diphenylpyrylium tetrafluoroborate) (**4**) was synthesized by the two routes shown in *Scheme 1*.

The first route involved the base-catalysed reaction



Scheme 1

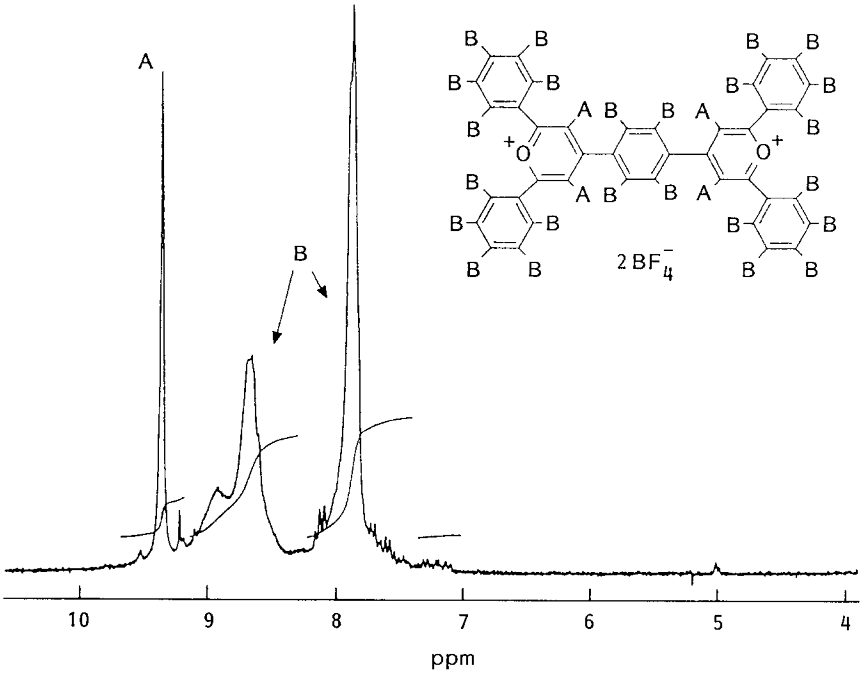


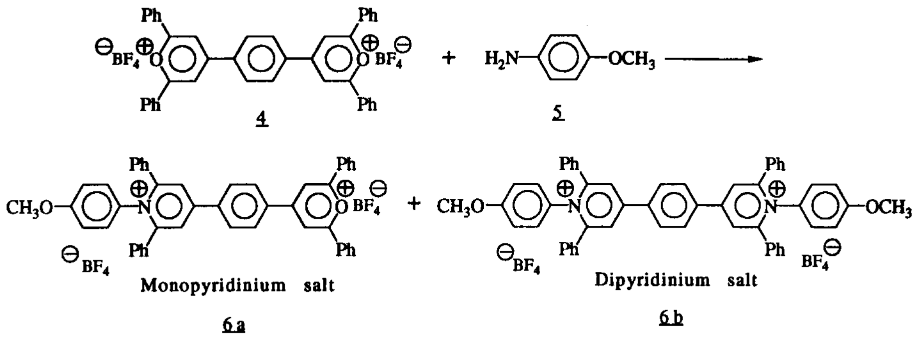
Figure 1 ^{1}H n.m.r. spectrum (DMSO-d_6) of 4,4′-(1,4-phenylene)bis(2,6-diphenylpyrylium tetrafluorborate)

of terephthalaldehyde (**1**) with two equivalents of acetophenone to form the bischalcone **2**, which was further condensed with two additional equivalents of acetophenone in the presence of boron trifluoride etherate to give a 60% yield of **4**[23]. In this route, the intermediate chalcone **2** also functions as a hydride acceptor to facilitate pyrylium ring formation. In the process, 1,3-diphenyl-1-propanone is generated as a side product, which is detrimental to both the yield and purity of the product[23].

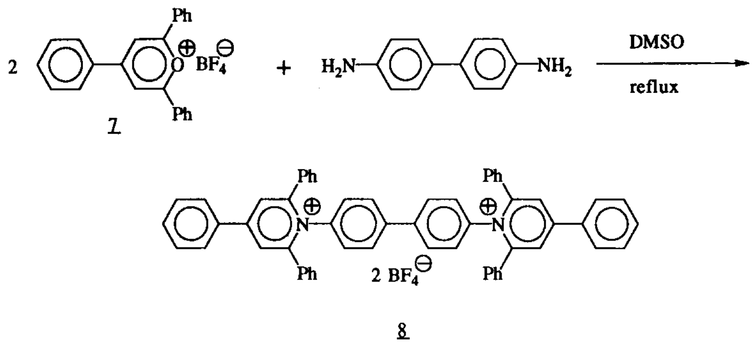
The second route involved a modification of the reported procedure[19,24] by which the corresponding bis(pyrylium perchlorate) had been prepared. Thus, terephthalaldehyde was condensed with four equivalents of acetophenone under basic conditions to afford a 95% yield of the tetraketone **3**, which was then quantitatively cyclodehydrated to **4** by treatment with triphenylmethyl tetrafluoroborate. To lower the cost of monomer synthesis, the hydride acceptor, i.e. triphenylmethyl tetrafluoroborate, was generated *in situ* from triphenylmethanol and 48% fluoroboric acid in acetic anhydride[16,25]. This route was far superior to the first.

A qualitative, preliminary evaluation of the purity of monomer **4** was carried out with ^{1}H n.m.r. As shown in *Figure 1*, the chemical shifts of the aromatic protons in the monomer are in the range of 7.0–9.5 ppm. The four protons labelled as A (3,5-aromatic), which are located closest to the positively charged oxygen, have the largest chemical shift at 9.35 ppm. All the other 24 aromatic protons labelled as B have chemical shifts of 7.0–9.0 ppm. The ratio of the integrated area under the peak at 9.35 ppm to the area under the peaks between 7.0 and 9.0 ppm should be 4:24, i.e. A:B = 1:6. By checking this ratio, the purity of the bispyrylium monomer could be estimated. For example, since the ratio of these integrated areas in the ^{1}H n.m.r. spectrum of the monomer as obtained was 1:8, an effort was made to improve its purity.

A study of recrystallization conditions determined that acetic acid and a 70/30 (v/v) mixture of DMSO/toluene were the best recrystallization solvents. Although pure light-yellow needles could be obtained from acetic acid, only a very small portion of the monomer crystallized from the saturated solution. The recovery of the monomer



Scheme 2



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Scheme 3

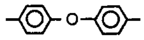
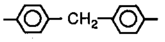
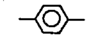
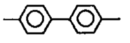
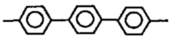
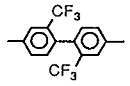
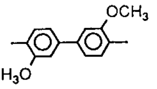
from the solvent mixture was over 80%, but the ratio of the integrated areas under the A protons and the B protons in the ^{1}H n.m.r. spectrum of the light-yellow powder was 1:7.7, which indicated that the monomer was still impure. H.p.l.c. was then employed to analyse the samples further. There were two small extraneous peaks in the h.p.l.c. chromatogram of the monomer both before and after recrystallization. In fact, it appeared that there were slightly more impurities in the recrystallized sample. Thus, the attempt to purify the monomer through recrystallization was abandoned.

In another attempt to purify the monomer, the precipitate obtained from the reaction mixture was carefully washed with acetic anhydride and then dried at 110°C under reduced pressure. As shown in *Figure 1*, integration of the areas under the A protons and the B protons in the ^{1}H n.m.r. spectrum of this sample gave the theoretical value of 1:6. The h.p.l.c. chromatogram of the sample also contained only one peak.

Model reaction studies

To determine the optimal conditions for the polymerization of the bis(pyrylium salt) with aromatic diamines, an investigation of the model reaction of **4** with two equivalents of *p*-anisidine (**5**) was carried out (*Scheme 2*). The reaction was initially carried out in refluxing ethanol and in refluxing acetonitrile. In both cases a mixture of monopyridinium and dipyridinium salts (**6a,b**) was obtained. The premature precipitation of the monopyridinium salt prevented the reaction from going to completion. Quantitative yields of model compound **6b**, which remained in solution, were obtained in both refluxing DMF and in refluxing DMSO.

Table 1 Properties of aromatic poly(pyridinium tetrafluoroborate)s

Polymer	-Ar-	η_{inh}[a] (dl g^{-1})	T_g[b] (°C)	T_m[c] (°C)	T_{dec}[d] (°C)
10a		1.8[e]			
		2.9[f]	217	400	350
		3.8[g]	220	387	350
10b		1.7[f]	196	426	362
10c		0.3[e]			
		0.8[f]	ND[h]	382, 390, 432	365
10d		2.9[f]	ND	412	366
		4.9[g]	ND	ND	
10e		2.7[f]	ND	390	368
10f		1.8[f]	ND	dec[i]	364
10g		1.9[f]	ND	dec[i]	358

[a] Inherent viscosity determined in DMF at 30±0.1°C with a concentration of 0.5 g dl^{-1}

[b] Glass transition temperature (mid-point of change in slope on d.s.c. thermogram obtained with a heating rate of 10°C min^{-1})

[c] Melting point (minimum of melting endotherm on d.s.c. thermogram)

[d] Temperature at which a 5% weight loss occurred in air when subjected to t.g.a. with a heating rate of 10°C min^{-1}

[e] Polymerization carried out in DMF/toluene according to Procedure 1

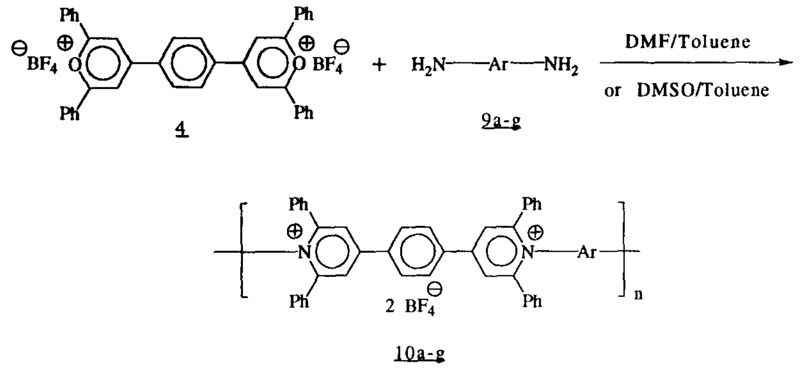
[f] Polymerization carried out in DMSO/toluene according to Procedure 1

[g] Polymerization carried out in DMSO/toluene according to Procedure 2

[h] ND, could not be detected with d.s.c.

[i] Decomposed before melting

Although the reaction of **4** with *p*-anisidine is representative of the reaction of bis(pyrylium salt)s with many aromatic diamines, it is not a good model for their reaction with 1,4-diaminobenzene or with 4,4′-diaminobiphenyl. In this case the reactivity of the first amino group that reacts in the diamine may be different from that of the second owing to the electron withdrawing effect of the generated pyridinium ring. Thus, a second



Scheme 4

study was carried out in which two moles of 2,4,6-triphenylpyrylium tetrafluoroborate (**7**) were treated with one mole of 4,4′-diaminobiphenyl in DMSO heated at reflux (*Scheme 3*). The model compound **8** was isolated from the reaction solution in quantitative yield. The compound's structure was ascertained by ^{1}H n.m.r.

Polymerizations

The bis(pyrylium salt) **4** was initially polymerized with 4,4′-diaminodiphenyl ether (**9a**) and 1,4-diaminobenzene (**9c**) in DMF/toluene and DMSO/toluene mixtures (*Scheme 4*). Although toluene had not been used in the model reaction studies, it was postulated that it would be useful in removing the water generated by the transformation of the pyrylium rings to the pyridinium rings from the viscous reaction mixtures. Thus, after the 'ring transformation polymerizations' had been allowed to proceed at 110°C for 2 h in DMF or DMSO, toluene was added, and the stirred mixtures were heated to near 150°C. After the toluene/water azeotrope and excess toluene were removed by distillation, the reaction mixtures were heated at reflux for 24 h. The poly(pyridinium tetrafluoroborate)s **10a** and **10c** were isolated in quantitative yields by precipitation in diethyl ether. The polymers were purified by reprecipitation from DMF with diethyl ether and dried under reduced pressure at 120°C overnight.

The inherent viscosities of **10a** and **10c** were substantially lower when the polymerizations were carried out overnight in refluxing DMF rather than in refluxing DMSO (*Table 1*). It was postulated that during the long heating period a small portion of the DMF decomposed to form dimethylamine[26], which then reacted with the bis(pyrylium salt). Such a reaction involving a monofunctional amine would effectively interrupt chain propagation. Therefore, the polymerizations of **4** with the 1,1-bis(4-aminophenyl)methane (**9b**), 4,4′-diamino-1,1′-biphenyl (**9d**), 1,4-bis(4-aminophenyl)-benzene (**9e**), 2,2′-bis(trifluoromethyl)-4,4′-diamino-1,1′-biphenyl (**9f**) and 3,3′-dimethoxy-4,4′-diamino-1,1′-biphenyl (**9g**) were carried out in DMSO. In fact, the polymers with the highest viscosities were obtained when the DMSO polymerization mixtures were heated to only 150°C (*Table 1*). This would suggest that the bis(pyrylium salt) also underwent some decomposition in refluxing DMSO. Depending on the conditions used in their isolation, the polymers had fibrous, wood-like or sheet-like textures (*Figures 2* and *3*).

The inherent viscosities of the polymers ranged from 0.3 to 4.9 dl g^{-1} (*Table 1*). The polymer prepared from

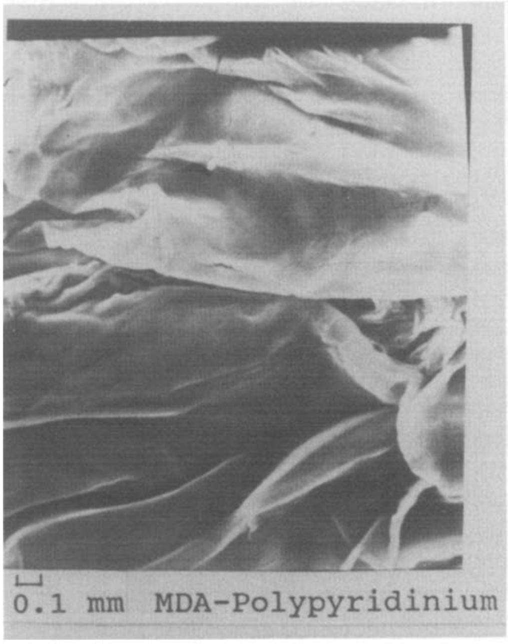
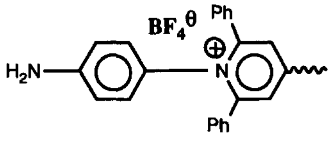


Figure 2 Photograph of poly(pyridinium tetrafluoroborate) **10b** obtained by direct addition of the polymerization mixture to diethyl ether

Figure 3 Photograph of poly(pyridinium tetrafluoroborate) **10a** obtained by addition of the diluted (DMSO) polymerization mixture to diethyl ether

1,4-diaminobenzene displayed the lowest inherent viscosity. This can be explained by considering the structure of the intermediate (**11**) generated by the reaction of the first amino group in the diamine.



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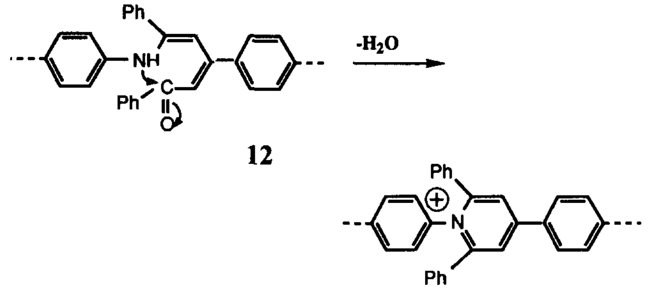
The positively charged pyridinium ring undoubtedly functioned as a strong electron-withdrawing substituent, which decreased the reactivity of the second amino group. Computer modelling results showed that the second amino group is also sterically hindered[27]. The two phenyl groups on the incoming pyrylium ring are forced to interact closely with the two phenyl groups on the initial pyridinium salt. The other diamines used in this study had at least one additional aromatic ring separating their two amino groups. Thus, the pyridinium salt that formed during their polymerizations was less effective in deactivating the remaining amino group. The rigid-rod polymer prepared from 4,4′-diamino-1,1′-biphenyl displayed the highest inherent viscosity.

The polymers' inherent and reduced viscosities increased when the concentration of their solutions was reduced below 0.1 g dl^{-1}. The magnitude of the increase was much more dramatic for the rigid-rod systems. The polyelectrolyte effect will be described in detail in a future publication.

In addition to their solubility in DMSO, the polymers were soluble in other polar aprotic solvents such as DMF and dimethylacetamide. This is particularly significant in the case of the rigid-rod polymers **10c–g**. Thin, flexible films could be cast from DMSO or DMF solutions that were 'fingernail creasible', indicating considerable toughness.

Spectroscopic analysis

^{1}H n.m.r., ^{13}C n.m.r. and Fourier transform i.r. spectroscopies were employed to characterize the structures of the polymers. The ^{1}H n.m.r. spectra of the polymers in DMSO-d$_6$ contained aromatic absorptions between 7.0 and 8.0 ppm and pyridinium ring absorptions between 8.0 and 9.0 ppm, and were in agreement with the proposed structures. The largest chemical shifts were assigned to the protons located closest to the positively charged nitrogens. According to the proposed mechanism for the conversion of a pyrylium salt to a pyridinium salt[16,28], the last ring-closure step involves a nucleophilic attack of a vinylogous amino group (**12**) on a carbonyl group, followed by the loss of a water molecule. The polymers' i.r. spectra did not contain any absorptions that could be attributed to olefinic protons. The spectra, which were almost identical to those of the model compounds, contained a strong aromatic stretch band at 1620 cm^{-1}, a C–N stretch at 1490 cm^{-1}, and a broad BF_4^- peak at 1100–1180 cm^{-1}. Their ^{13}C n.m.r. spectra in DMSO-d$_6$ also contained only aromatic carbon absorptions between 120 and 160 ppm. The carbonyl absorption at 186 ppm, previously attributed to a vinylogous amine structure[29], could not be detected. This suggests that the ring closure proceeded to completion. A typical ^{1}H n.m.r. spectrum of polymer **10d** is shown in *Figure 4*.



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Thermal analysis

D.s.c. and t.g.a. were used to determine the transition temperatures and the thermal stabilities of the polymers (*Table 1*). The d.s.c. thermograms of most of the samples contained distinctive melting endotherms. However, no glass transition temperatures (T_gs) could be detected during the first heating cycles on the d.s.c. When samples of **10a** and **10b** were preheated to 380°C, quenched to room temperature with ice, and then rerun, their d.s.c. thermograms contained weak baseline shifts that could be attributed to T_gs. This procedure was not successful in detecting the T_gs of the rigid-rod polymers. No evidence was found for the low softening points previously attributed[16] to aromatic poly(pyridinium tetrafluoroborate)s.

The thermal and thermo-oxidative stabilities of the poly(pyridinium tetrafluoroborate)s were very similar. Their t.g.a. thermograms showed 5% weight losses between 350 and 360°C in both air and nitrogen atmospheres (*Table 1*). Thus, the polymers began to decompose prior to melting.

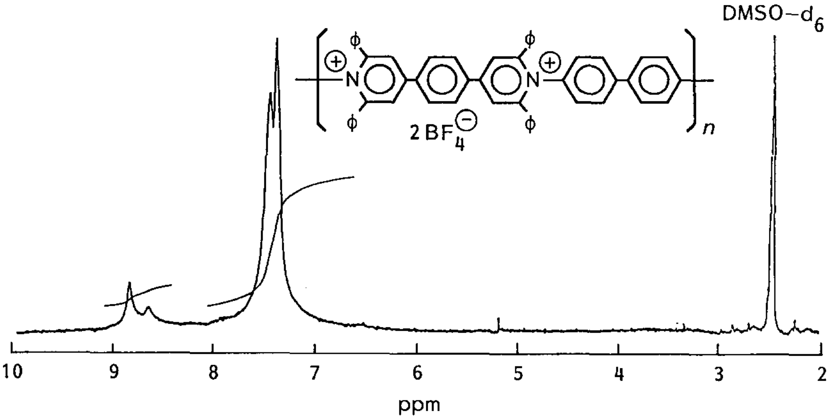


Figure 4 ^{1}H n.m.r. spectrum (DMSO-d$_6$) of poly(pyridinium tetrafluoroborate) **10d**

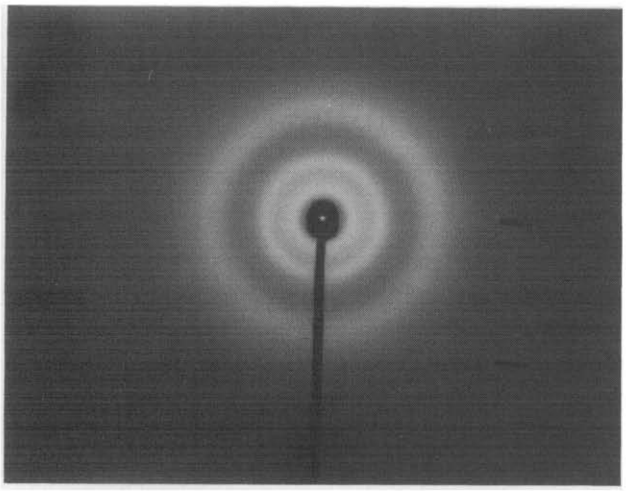


Figure 5 WAXD pattern (powder) of poly(pyridinium tetrafluoroborate) **10d**

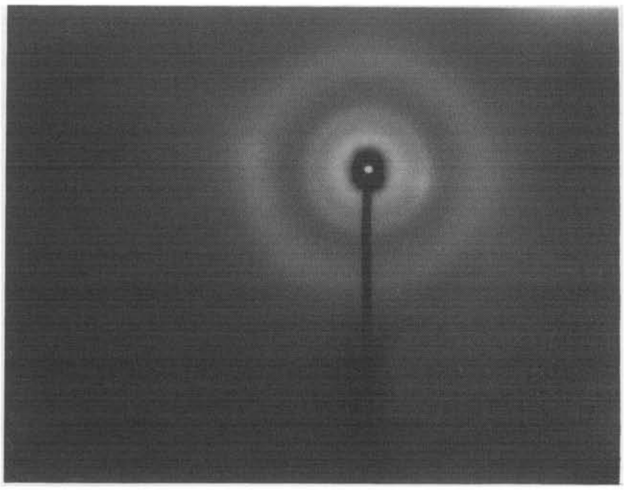
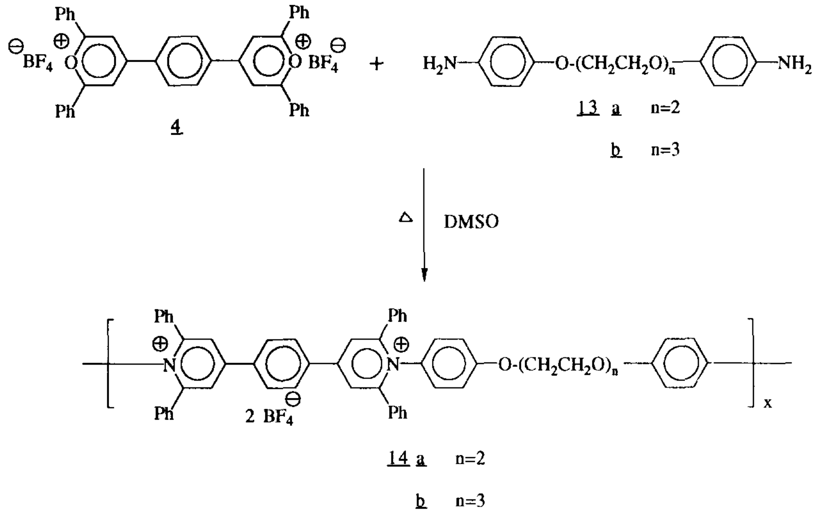


Figure 6 WAXD pattern (powder) of poly(pyridinium tetrafluoroborate) **10a**



Scheme 5

WAXD analysis

The WAXD patterns of powder samples of the poly(pyridinium salt)s contained an outer amorphous ring and two inner rings in the relatively small-angle region. The WAXD pattern of polymer **10d**, which is typical of those of the rigid-rod polymers, indicates that the chains were packed in a structure similar to that of a smectic liquid crystalline glass (*Figure 5*)[30,31]. The presence of ring patterns in the relatively small-angle region is indicative of long-range order. The amounts of long-range order was considerably higher in the rigid-rod polymers (**10c–g**) than in the polymers containing flexible ether and methylene linkages (**10a,b**) based on the intensity of X-ray diffractions generated over the 10 h exposure time (*Figure 6*). The average distance between adjacent chains in the amorphous regions and the d-spacings obtained from the WAXD patterns are listed in *Table 2*. The d_1- and d_2-spacings can be attributed to the distance between two sets of different adjacent crystalline planes. It is likely that these d-spacings are associated with the repeat unit length along the polymers' backbones. Further small-angle X-ray work on oriented samples is needed before conclusions can be reached on the crystalline morphology.

Table 2 d-Spacings of the aromatic poly(pyridinium tetrafluoroborate)s

Polymer	Average distance[a] between chains in amorphous region (Å)	d_1-Spacing (Å)	d_2-Spacing (Å)
10a	5.3	8.9	19.0
10b[b]	–	–	–
10d	5.2	9.2	19.6
10e	5.0	9.1	17.9
10f	5.3	10.4	19.0
10g	4.9	9.7	21.4

[a] Calculated from the diameter of the amorphous ring on WAXD pattern using Bragg's equation: $2d \sin \theta = n\lambda$, where $n = 1$

[b] The long-range order in this polymer was negligible. No d-spacing could be calculated from the WAXD pattern

Poly(pyridinium tetrafluoroborate)s containing flexible linkages

The results of the WAXD studies showed that the amount of long-range order in the rigid-rod polymers was considerably higher than in the polymers containing flexible ether or methylene linkages. In order to study further the effects of chain flexibility on morphology, two poly(pyridinium salt)s containing flexible oxyethylene linkages (**14a,b**) were prepared. Thus, the bis(pyrylium

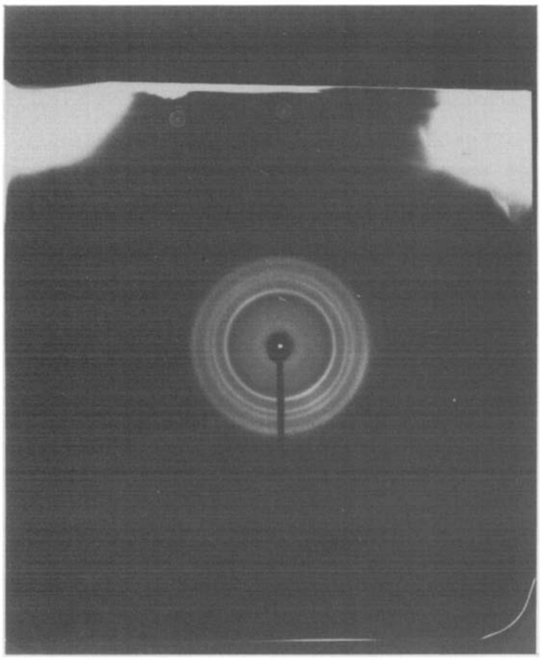


Figure 7 WAXD pattern (powder) of poly(pyridinium tetrafluoroborate) **14a**

salt) **4** was polymerized with bis[2-(4-aminophenoxy)ethyl] ether (**13a**) and 1,2-bis[2-(4-aminophenoxy)ethoxy]ethane (**13b**) in DMSO (*Scheme 5*). Polymers **14a** and **14b** had inherent viscosities of 1.70 and 1.78 dl g^{-1}, respectively.

D.s.c. analysis of **14a** and **14b** showed that they decomposed gradually above 250°C. Thus, their T_gs and melting temperatures could not be determined. However, dynamical mechanical thermal analysis on a film of **13a** clearly showed a transition near 262°C. The transition was accompanied by decomposition as the tan δ value went off the scale. The sample softened into a black tar and emitted smoke at about 260°C. The WAXD patterns of powder samples of **14a** and **14b** nevertheless, showed that these two polypyridiniums were highly crystalline (*Figure 7*). In fact, the many distinct rings indicate that the polymers were packed in highly ordered lattices. It is postulated that the flexible linkages allowed the rigid segments in the polymer chains to pack into crystalline lattices.

CONCLUSIONS

Reaction conditions have been determined for the polymerization of 4,4′-(1,4-phenylene)bis(2,6-diphenylpyrylium tetrafluoroborate) with aromatic diamines that afford film-forming polymers with inherent viscosities as high as 4.9 dl g^{-1}. These ‘ring transformation polymerizations’ have been used to prepare a series of phenylated, rigid-rod poly(pyridinium tetrafluoroborate)s that are soluble in polar aprotic solvents. To the best of our knowledge, the polymers are the first examples of organo-soluble, high molecular weight, all-aromatic, linear ionenes.

The poly(pyridinium tetrafluoroborate)s are semicrystalline with a morphology similar to that of smectic liquid-crystalline glasses. The crystalline order can be improved substantially through the incorporation of flexible oxyethylene linkages in the polymer backbone. The polymers' high melting points (over 380°C) are above their initial decomposition temperatures. The polymers' solution, redox, electrical and mechanical properties will be the subjects of future publications.

ACKNOWLEDGEMENTS

The authors thank Dr Steve O. Norris, who independently proposed this research during his graduate school career many years ago, for supplying very helpful references, and Professor A. Q. Zhang for his help with the WAXD measurements. The financial support of this work by Ballard Advanced Materials, North Vancouver, Canada, is gratefully acknowledged.

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