

Novel polyimide ionene: synthesis and characterization of polyimides containing aromatic bipyridinium salt

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A series of 4,4'-(1,4-phenylene)-bis(*N*-aminoaryl-2,6-diphenyl pyridinium perchlorate)s were synthesized by the reaction of 4,4'-(1,4-phenylene)-bis(2,6-diphenyl pyrylium) with aromatic diamines. They were used as monomers to react with various aromatic tetracarboxylic dianhydrides, to prepare polyimides via a two-stage procedure that included a ring-opening condensation in *N,N*-dimethylformamide (DMF) to give poly(amic acid)s, followed by thermal cyclodehydration to polyimides. The inherent viscosities of these poly(amic acid)s and polyimides were in a range of 1.03–0.07 dl g⁻¹ (0.5% in DMF at 25°C). All polyimides had good solubilities in several polar aprotic solvents, such as DMF, *N,N*-dimethylacetamide (DMAc), etc. Polyimides derived from 4,4'-oxydiphthalic anhydride could form transparent flexible and tough films. They had a tensile strength range of 42–80 MPa, and an elongation around 5%. The glass transition temperatures of all polyimides were between 181 and 206°C (differential scanning calorimetry). Thermogravimetric analyses indicated that they were fairly stable up to 300°C, and 5% weight loss temperatures were recorded in the range of 337–367°C in nitrogen. These polyimides were semi-conductors with conductivities around 10⁻⁸ ohm⁻¹ cm⁻¹ and their conductivities could be further increased up to 10⁻⁷ ohm⁻¹ cm⁻¹ by I₂-doping. These bipyridinium-based poly(amic acid)s and polyimides could reversibly develop colour by u.v. irradiation. © 1997 Elsevier Science Ltd.

(Keywords: bipyridinium salt; soluble polyimides; polyimide ionene)

INTRODUCTION

Polyimides are well known for their excellent mechanical properties, chemical inertness, thermal stability and electrical properties. They are primarily used as high temperature coatings, adhesives, foams and matrices for high performance composites^{1–3}. Recently, more and more studies have turned to their functional applications, such as for gas separating membranes and as photoconductive materials^{4,5}. Bipyridinium salts known as ionenes are a class of redox compounds. They can add two electrons stepwise with obvious colour change by chemical, electrochemical or photochemical methods. Thus, they are very useful electron transfer catalysts in many systems and as reversible imaging materials⁶. They have played important role in artificial conversion of solar energy to chemical and electrical energy⁷. In this paper, we will report on the synthesis and characterization of polyimides with bipyridinium salts in their main chains. This is also the first time ionic polyimide is reported. Polyimides containing a positively charged pyridine ring in their main chain can be referred to as ionenes, which have considerable potential for use as easily removable oxidizing or reducing reagents, electron-exchange membranes, ion-exchange membranes, or ionic conductor materials. The high polarity of the backbone will increase the doping possibility of polyimides and may further broaden modification of polyimides.

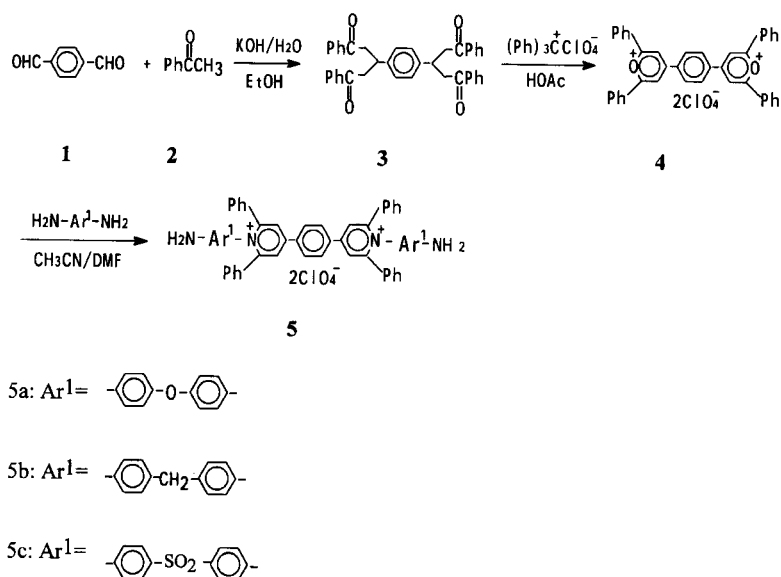
The widespread route for the preparation of linear condensation polyimide is the addition polymerization of a dianhydride with a diamine in an aprotic solvent followed by cyclodehydration. Generally, synthesis of dianhydride is somewhat more complex than that of the diamine. Our route to the desired ionic polyimides involved synthesis of bipyridinium aromatic diamines. Attempts to prepare 4,4'-bipyridinium diamine failed in our experiment, because 4,4'-bipyridiniums are a class of oxidant and can be reduced by aromatic amine. 1,1'-Diaryl-4,4'-(1,4-phenylene)bis(2,6-diphenyl pyridinium) salts were chosen, due to their relatively low cationic redox potentials. They could not be reduced by aromatic amine even in refluxing dimethylformamide (DMF). The synthetic routes of the monomer **5** and desired polyimide **8** are shown in *Scheme 1* and *Scheme 2*.

EXPERIMENTAL

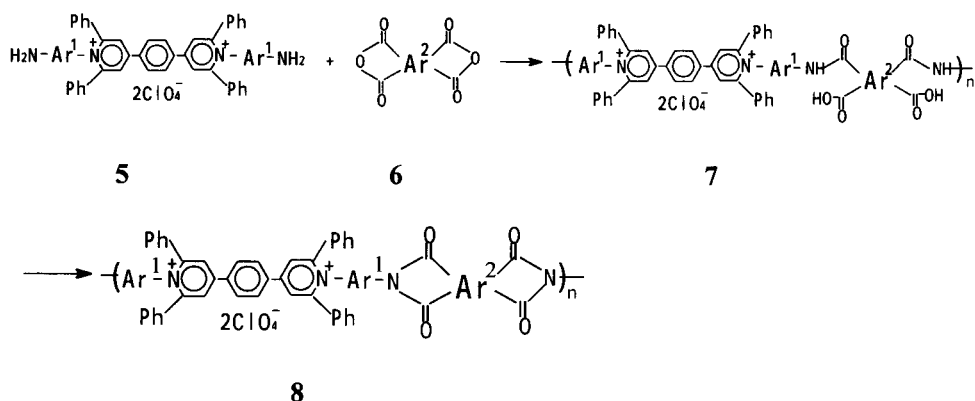
Instrumentation

All infra-red (i.r.) spectra of these samples were recorded by using a Shimadzu 340 spectrometer. All ultra-violet (u.v.) and visible spectra were recorded on a Hitachi-430 spectrophotometer. Differential scanning calorimetry (d.s.c.) data and thermogravimetric analyses (t.g.a.) were recorded using a Perkin Elmer 7 series Thermal Analysis System. Tensile strength was measured by an Instron 1122 Material Tester. Conductivity was measured by a Hioki 3520 Lcr Hi Tester. U.v.-irradiation source was a high pressure mercury lamp.

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Scheme 1



Scheme 2

Materials

All aromatic tetracarboxylic dianhydrides were recrystallized from acetic anhydride and all aromatic diamines were recrystallized from ethanol. Other reagents were used as purchased without further purification.

Monomers

3,3'-(1,4-Phenylene)bis(1,5-diphenyl-1,5-pentadione) (3). A mixture of terephthalaldehyde (10 g, 74.6 mmol) and acetophenone (54.3 g, 452 mmol) was stirred in 250 ml of 95% ethanol and heated to 65°C to dissolve the starting materials. A solution of potassium hydroxide (10.5 g, 188 mmol) in 11.3 ml water was added dropwise with vigorous stirring for 30 min. A yellow precipitate formed immediately, and the reaction mixture was heated at reflux for 5 h. Then it was filtered hot to yield 41.7 g (97%) of white powder. After the crude product was refluxed again in 250 ml ethanol and filtered hot, it was further purified by recrystallization from toluene to afford 31.0 g (74%) colourless powder: m.p. 205–207°C (lit.⁸ 205°C); i.r. (KBr) 1680 cm⁻¹ (C=O).

Triphenylmethyl perchlorate. Triphenylmethanol (26 g, 100 mmol) was added to 340 ml of acetic anhydride and the suspension was heated to 50°C until it was clear and then cooled to room temperature. Perchloric acid

(20 ml of 70%, 24 g, 240 mmol) was added dropwise to the solution. An orange precipitate formed immediately. During the exothermic process, the reaction mixture was maintained at 10–20°C with a water bath. After addition of perchloric acid, the reaction mixture was cooled to 5–10°C and maintained at this temperature for 1 h. The orange product was filtered out, washed with 50 ml of diethyl ether twice and dried in air to afford 29.8 g of orange crystals (87%).

4,4'-(1,4-Phenylene)bis(2,6-diphenyl pyridinium perchlorate) (4). Compound 3 (15.28 g, 26 mmol) and triphenylmethyl perchlorate (22.64 g, 66 mmol) were added to 305 ml of acetic acid, then the mixture was heated to reflux and maintained at this temperature for 18 h. After the reaction mixture was cooled to 80°C, the precipitate was filtered and washed with acetic acid and diethyl ether to yield crude product 18.45 g (94%). The crude product was recrystallized from formic acid to give 15.1 g of yellow crystals (77%): i.r. (KBr) 1620, 1600, 1100 (br, ClO₄⁻) cm⁻¹.

General procedure for the preparation of 4,4'-(1,4-phenylene)bis(1-aminoaryl-2,6-diphenylpyridinium perchlorate)s (5). Aromatic diamine (2.5 mmol) and 4 (0.74 g, 1 mmol) were dissolved in 25 ml of a mixture of acetonitrile and

Table 1 Elemental analysis of bis(aminoaryl pyridinium perchlorate)s **5**

Monomer	Elemental analysis (%)					
	Calculated			Found		
	C	H	N	C	H	N
5a	69.6	4.35	5.08	69.2	4.51	5.12
5b	72.1	4.73	5.10	71.5	5.12	5.10
5c	64.1	4.00	4.17	63.6	4.15	4.25

DMF, then the solution was heated with stirring under nitrogen for 7 h. The yellow precipitate formed during this course. After the reaction mixture was cooled to room temperature, 300 ml diethyl ether was poured to it and a yellow product was filtered out and dried in reduced pressure (see Table 1).

4,4'-(1,4-Phenylene)bis{1-[4-(4-aminophenyleneoxy)-phenyl]-2,6-diphenylpyridinium perchlorate} (**5a**)⁶. The reaction temperature was between 65 and 70°C. The pale yellow powder was obtained in 92% yield. The i.r. (KBr) spectrum of **5a** shows the bands at 3450, 3400, 3250, 1620 and 1100 cm⁻¹.

4,4'-(1,4-Phenylene)bis{1-[4-(4-aminophenylmethyl)-phenyl]-2,6-diphenylpyridinium perchlorate} (**5b**)⁶. The reaction temperature was between 70 and 75°C. The pale yellow powder was obtained in a 92% yield. The i.r. (KBr) spectrum of **5a** shows the bands at 3450, 3400, 3250, 2900, 1620 and 1100 cm⁻¹.

4,4'-(1,4-Phenylene)bis{1-[4-(4-aminophenylsulfonyl)-phenyl]-2,6-diphenylpyridinium perchlorate} (**5c**). The reaction temperature was between 100 and 105°C. The bright yellow powder was obtained in a 98% yield. The i.r. (KBr) spectrum of **5c** shows the bands at 3450, 3400, 3250, 1620, 1590 and 1100 cm⁻¹.

Polymerizations

General procedure for preparation of poly(amic acid)s solution (7). A solution of the 1,1'-diaminoarylidene-4,4'-(1,4-phenylene)bis(2,6-diphenyl pyridinium perchlorate) **5** (0.60 mmol) and aromatic dianhydride **6** (0.60 mmol) in 6 g DMF was stirred at ambient temperature or 70°C under nitrogen for 4 h to give a brown-red sticky prepolymer.

Preparation of polyimide films (8). The solution of polyamic acid in DMF was diluted to 10% and then cast upon a clean glass surface, heated at 60°C, 100°C and 225°C for 1 h respectively under protection of argon. The films were removed from a glass plate by soaking in water and then dried. The thickness of the films were about 25 μm.

Preparation of I₂-doped polyimide films. The polyimide films were treated with I₂ crystals in a sealed desiccator for 2 h, to saturate the films with I₂ vapour.

Measurement of the conductivity of the polyimides

The conductivity was measured in a 10 kHz alternating electric field using polyimide films.

RESULTS AND DISCUSSION

The synthesis of bipyridinium-based polyimides

The terephthalaldehyde **1** was condensed with four equivalents acetophenone **2** by using a base as a catalyst to give tetraketone **3**. The tetraketone was then cyclodehydrated to bis(pyrylium perchlorate) **4** by treatment with triphenylmethyl perchlorate in boiling acetic acid. In order to get pure bis(pyridinium salt), a long time of cyclodehydration reaction, which was about 18 h, was needed, because the recrystallization could only slightly improve its purity. The monomer 4,4'-(1,4-phenylene)bis(2,6-diphenyl-*N*-aminoarylidene-) pyridinium perchlorate **5** was synthesized by reacting **4** with excess aromatic diamine⁶. Compared with the reference, the reaction temperatures of **4** with 4,4'-diaminodiphenyl ether and 4,4'-diaminodiphenyl methane were decreased to 60–80°C, to avoid oxidation of amino groups, while the temperature for 4,4'-diaminodiphenyl sulfone had to be kept above 100°C to carry out the reaction.

The bis(aminoarylidene)pyridinium **5** was reacted with various aromatic dianhydrides **6** in DMF to afford polyamic acid **7** (see Table 2). Compounds **7a–7f** could be prepared at ambient temperature, but **7g–7i** had to be prepared at a temperature above 70°C because **5c** is less active. This indicated that the amino group of monomer **5** still had enough reactivity despite the electron withdrawing effect of the pyridinium cation. The transparent polyimide films **8** (see Table 2) were obtained by casting polyamic acid solution on a glass surface and then curing under argon at 60, 100 and 230°C for 1 h each (see Table 3). The disappearance of absorption at 3450 cm⁻¹ in the

Table 2 Bipyridinium-based polyimides

Polyamic acid	Polyimide	Ar ¹	Ar ²
7a	8a		
7b	8b		
7c	8c		
7d	8d		
7e	8e		
7f	8f		
7g	8g		
7h	8h		
7i	8i		

i.r. spectra was used as a monitor to assure complete transformation of polyamic acid to polyimide. Although flexible films could be obtained from their polyamic acid solution, it is unfortunate that most of the ionic polyimides were brittle after curing. But **8a–8c** could form flexible films, which were able to be folded. This could be explained by the high density of rigid-rod structures, bipyridinium and imide groups located in the main chain of these polyimides. When polymers had more ether linkages, they had more flexibility.

Table 3 Elemental analysis for bipyridinium-based polyimides

Polyimide	Elemental analysis (%)					
	Calculated			Found		
	C	H	N	C	H	N
8a	69.1	3.58	4.36	69.1	4.46	4.07
8b	70.0	3.60	4.03	69.7	3.71	3.45
8c	69.7	3.63	4.07	69.1	4.00	3.83
8d	71.2	3.90	4.37	70.8	4.18	4.60
8e	71.9	3.90	3.90	71.4	3.94	3.95
8f	71.7	3.93	3.93	71.3	4.06	3.70
8g	64.3	3.35	4.05	63.9	3.67	3.85
8h	65.5	3.39	3.77	64.6	3.56	4.03
8i	65.2	3.42	3.80	64.7	3.55	4.05

Table 4 Solubility of bipyridinium-based polyimides **8^a**

Solvent ^b	Polyimide									
	8a	8b	8c	8d	8e	8f	8g	8h	8i	
Acetone	–	–	–	–	–	–	–	–	–	
AN	–	+/-	–	–	+/-	+/-	–	–	–	
Py	+	+	+	+/-	+	+	+/-	+/-	+	
DMF	+	+	+	+	+	+	+	+	+	
DMAc	+	+	+	+	+	+	+	+	+	
DMSO	+	+	+	+	+	+	+	+	+	
NMP	+	+	+	+	+	+	+	+	+	

^a Solubility: +, soluble at room temperature; +/-, soluble by heat; –, insoluble even by heat.

^b AN, acetonitrile; Py, pyridine; DMF, *N,N*-dimethylformamide; DMAc, *N,N*-dimethylacetamide; DMSO, dimethyl sulfoxide; NMP, *N*-methyl-pyrrolidone.

Table 5 The inherent viscosities of bipyridinium-based poly(amic acid)s **7** and polyimides **8**

Polyamic acid	η_{inh}^a (dl g ⁻¹)	Polyimide	η_{inh}^a (dl g ⁻¹)
7a	0.90	8a	0.25
7b	1.02	8b	0.49
7c	1.03	8c	0.46
7d	0.51	8d	0.10
7e	0.69	8e	0.26
7f	0.77	8f	0.35
7g	0.10	8g	0.07
7h	0.26	8h	0.13
7i	0.12	8i	0.07

^a Measured in DMF at a concentration of 0.5 g dl⁻¹ at 25°C

Table 6 Thermal properties of bipyridinium-based polyimides **8**

	Polyimide									
	8a	8b	8c	8d	8e	8f	8g	8h	8i	
T_g (°C)	203	192	213	181	206	197	ND ^b	ND	ND	
T_{dec}^c (°C)	350	337	344	340	367	341	356	334	342	

^a T_g measured on d.s.c. at a heating rate of 20°C min⁻¹.

^b Cannot be detected before decomposition.

^c Temperature at which a 5% weight loss was recorded on t.g.a. at a heating rate of 20°C min⁻¹ under nitrogen.

The properties of bipyridinium-based polyimides

All of these ionic polyimides could be well dissolved in polar aprotic solvents such as DMF and *N*-methyl pyrrolidinone (NMP) (see *Table 4*). This is obviously caused by the introduction of a bulky substitute phenyl group and a pyridinium ion pair along the polymer backbone. The inherent viscosities of these polyamic acids **7** are shown in *Table 5*. The polyamic acids **7** containing flexible ether linkage had relatively higher viscosities. The inherent viscosities of the polyimides were lower than those of polyamic acids. That is because the carboxyl groups disappeared after imidization and there is no hydrogen bond between chains of polyimide.

The glass transition temperature (T_g) and thermal stability of these polyimides in nitrogen were determined by d.s.c. and t.g.a. Data are listed in *Table 6*. The glass transition was not obvious for all samples. Some of them appeared at just the same temperature as the homopolymers of these bipyridiniums⁹, the others could not be detected before decomposition. As shown in *Figure 1*, the thermal stabilities of these bipyridinium-based polyimides were quite high, but not as high as polyimide without pyridinium. They underwent a 5% weight loss between 337 and 367°C. The second step weight loss, which was of about 15%, occurred at a temperature of around 400°C. This may suggest the decomposition of counter ion ClO₄⁻ (which takes 15% in weight of these polyimides) at the beginning of decomposition¹⁰. Ion pairs located along the backbone did impair the thermal stability of the polyimide.

Good mechanical performance is an important character of polyimides, but the tensile strengths of these bipyridinium-based polyimides are lower than those of common polyimides (*Table 7*). Their elongations at break around 5% indicate that they lack good ductility and toughness. This may be the result of the introduction of the bulky rigid-rod structure of the bipyridinium group into the backbone of polyimide.

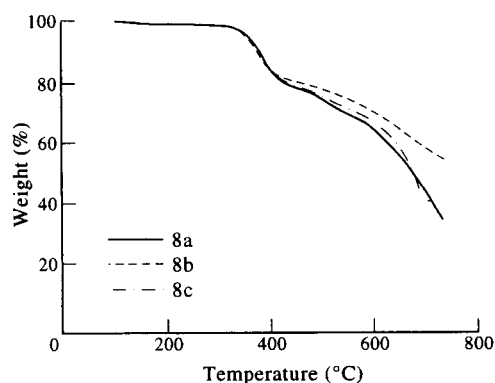
**Figure 1** T.g.a. thermograms of polyimides **8a**, **8b**, and **8c**, at a heating rate of 20°C min⁻¹ in nitrogen

Table 7 Mechanical properties of bipyridinium-based polyimides **8a–8c**

Polyimides	Tensile strength (MPa)	Elongation at break (%)
8a	41.9	4.0
8b	69.8	5.6
8c	52.0	6.7

Table 8 Conductivities of ionic polyimides **8a–8c**

Polymer	Bulk conductivity ^a (ohm ⁻¹ cm ⁻¹)	Bulk conductivity ^b (ohm ⁻¹ cm ⁻¹)
8a	2.6×10^{-8}	3.2×10^{-7}
8b	ND ^c	7.6×10^{-7}
8c	2.2×10^{-8}	5.7×10^{-7}

^a Pure polymer measured in a 10 kHz alternating electric field.

^b I₂-doped polymer measured under the same conditions.

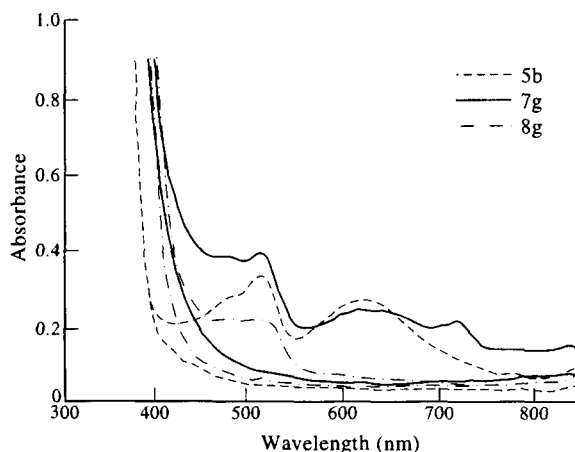
^c Cannot be determined.

It is well known that common polyimides are good insulators, but these polyimides are semi-conductors whose bulk conductivities can reach 10^{-8} ohm⁻¹ cm⁻¹ (Table 8). This behaviour can be attributed to an ionic conducting mechanism¹¹. Iodine has long been recognized as a good dopant to promote the conductivity of conjugated polymer¹². The conductivities of the I₂-doped ionic polyimides were about 10^{-7} ohm⁻¹ cm⁻¹, which was about ten times higher than that of the undoped one. The conductivities of these polymers did not change any more after exposed in air for 1 week.

The sandwiches of bipyridinium-based polyamic acids and polyimides in NMP could develop a red colour under u.v. light in air with a long inductive phase. The maximum absorption of polyimides in u.v.-vis spectra was located at 520 nm, which was different to monomer **5** and polyamic acids which had two absorption bands at 620 nm and 512 nm respectively under the same conditions (Figure 2). The colour of the sandwiches could slowly fade in the dark, but immediately disappeared after the sandwiches were opened to air. When the sandwiches were irradiated for the second time after they faded in the dark, their colour development was much faster than the first time. Further details will be published in our future work.

CONCLUSIONS

A series of ionic polyimides with bipyridinium in their backbone have been successfully prepared by the synthesis of aromatic diamines containing bipyridinium and reacting them with various aromatic dianhydrides. These bipyridinium-based polyimides can be dissolved well in aprotic polar solvents. The introduction of bipyridinium does cause a loss of thermal stability and

**Figure 2** Visible absorption spectra for monomer **5b**, poly(amic acid) **7g**, and polyimide **8g** in NMP solution before and upon u.v. irradiation

mechanical toughness of the polyimide. The T_g s of these polymers are similar to homopolymer of bipyridinium. These bipyridinium-based polyimides are semiconductors, and their conductivities can be improved by ten times by doping with iodine vapour. The solutions of these polyamic acids and polyimides in NMP or in PVP film can change their colour under u.v. irradiation.

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REFERENCES

1. St. Clair, T. L. and Maudgal, S., US Patent No. 4624888 (NASA), 1986.
2. Alvino, W. M. and Edelman, L. E., *J. Appl. Polym. Sci.*, 1975, **19**, 2961.
3. Reinhardt, B. A. and Arnara, F. E., *J. Appl. Polym. Sci.*, 1981, **26**, 2679.
4. Kim, T. H., Koros, W. J., Husk, G. R. and Brien, K. C. O., *J. Appl. Polym. Sci.*, 1987, **34**, 1767.
5. Numata, S., Oohara, S., Fujisaki, K., Imaizumi, J. and Kinjo, N., *J. Appl. Polym. Sci.*, 1986, **31**, 101.
6. Yang, Y., *Polym. Commun.*, 1985, **3**, 185.
7. Byrd, H., Suponeva, E. P., Bocarsly, A. B. and Thompson, M. E., *Nature*, 1996, **380**, 610.
8. Krivun, S. V. and Dorofeenko, G. N., *Khim. Geterotsykl. Soedi.*, 1966, **2**(5), 656; *Chem. Abstr.*, 1967, **67**, 64170w.
9. Harris, F. W., Chuang, K. C., Huang, S. A. X., Janimak, J. J. and Cheng, S. Z. D., *Polymer*, 1994, **35**(23), 4940.
10. Huang, S. A. X. and Harris, F. W., *Polym. Prepr.*, 1994, **36**(1), 519.
11. Yu, W., Shaw, M. T., Huang, X. and Harris, F. W., *J. Polym. Sci., Polym. Phys. Edn.*, 1994, **32**, 481.
12. Kanatzdis, M. G., *C&E News*, 1990, **68**(49), 36.