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Poly(pyridinium salt)s with Stilbene or Distyrylbenzene Chromophores

IOAKIM K. SPILIOPOULOS, JOHN A. MIKROYANNIDIS

Chemical Technology Laboratory, Department of Chemistry, University of Patras, GR-26500 Patras, Greece

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ABSTRACT: A new series of poly(pyridinium salt)s that contained side stilbenyl groups or *p*-distyrylbenzene segments in the main chain were synthesized from the reactions of bis(pyrylium salts) with diamines. They were characterized by viscometry, Fourier transform infrared spectroscopy, NMR, X-ray scattering, differential scanning calorimetry, thermomechanical analysis, ultraviolet–visible analysis, and luminescence spectroscopy. The polymers were amorphous and soluble in polar aprotic solvents such as dimethylacetamide, dimethylformamide, and dimethyl sulfoxide. The glass-transition temperatures were in the range of 59–123 °C. These polymers had initial decomposition temperatures of 240–295 °C and afforded anaerobic char yields of 29–53% at 800 °C. Both the absorption and photoluminescence (PL) spectra of the polymers were studied, and the PL quantum yields in solution were determined. The polymers showed violet-blue fluorescence in solution with PL maxima at 408–416 nm and violet-green fluorescence in thin film with PL maxima at 454–523 nm. The structure of the diamine utilized for the preparation of the polymers did not influence their PL maxima. © 2001 John Wiley & Sons, Inc. *J Polym Sci Part A: Polym Chem* 39: 2454–2462, 2001

Keywords: poly(pyridinium salt)s; photoluminescence; light-emitting polymers; pyridinium; pyrylium

INTRODUCTION

Extensive research interest was focused on PPV and its derivatives since the discovery of electroluminescence in conjugated polymers.¹ PPV and its derivatives are still the most popular class of conjugated polymers used for fabrication of light-emitting diodes (LEDs). Certain new applications of conjugated polymers such as photovoltaic diodes,^{2,3} light-emitting electrochemical cells,^{4,5} and laser devices^{6–8} have initiated new research.

Completely conjugated polymers without substituents are neither soluble nor meltable. Processability of aromatic conjugated polymers can be achieved by the introduction of flexible chains

either as side groups along the polymer backbone or as moieties into the main chain.

Polymers bearing quaternary nitrogen atoms in the backbone are usually known as ionenes⁹ or poly(pyridinium salt)s. Although these polymers are unstable under certain conditions being susceptible to substitution and elimination reaction, they continue to be of interest. These materials, which belong to a class of reduction–oxidation or redox polymers,^{10,11} can be used in electron- or ion-exchange membranes,¹² as semiconducting materials and ionic conductors.¹³

A literature survey revealed that several poly(pyridinium salt)s have been synthesized, but most of them were of low molecular weight. Specifically, it has been reported that 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

Correspondence to: J. A. Mikroyannidis (E-mail: mikroyan@chemistry.upatras.gr)

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polymerization of only 3–4.¹⁴ In addition, the polymerization of bis(pyrylium salt)s with various aliphatic or aromatic diamines in CH_2Cl_2 or dimethylformamide (DMF) at room temperature under catalytic conditions (addition of Et_3N at the start of the polymerization and CH_3COOH at the middle of the polymerization period) gave polymers with inherent viscosities (n_{inh}) of 0.07–1.4 dL/g.¹⁵ However, Harris and colleagues^{16,17} had prepared rigid-rod poly(pyridinium salt)s having n_{inh} 's as high as 18.7 dL/g from the reaction of bis(pyrylium salt)s with aromatic diamines in a dimethyl sulfoxide (DMSO)/toluene mixture of 150 °C. The water generated by this transformation reaction had distilled from the mixture as a water/toluene azeotrope. The temperature of the mixture had increased to 195 °C for the last 24 h of this reaction.

The present investigation deals with the synthesis and characterization of a new class of poly(pyridinium salt)s containing side stilbenyl groups or *p*-distyrylbenzene segments in the main chain. They were prepared from the reactions of bis(pyrylium salts) with diamines via an effective and general synthetic route. Aliphatic diamines were utilized for polycondensation to enhance the solubility of polymers. In addition, it has been shown that the quaternization of the pyridine nitrogen with aliphatic amines affords pyridinium salts with a higher PL quantum yield than those obtained by quaternization with aromatic amines.¹⁸ Because PL spectra and quantum yields give relevant information for electroluminescence properties in LEDs, PL properties in solution and thin film were investigated.

This contribution is a continuation of our work on the development of new polymers that can be prepared through pyrylium salts. The present polymers were synthesized by a convenient synthetic route utilizing inexpensive and readily available starting materials. Aliphatic moieties were introduced into their backbone both to interrupt the conjugation and increase their solubility and flexibility. In certain cases, long alkoxy groups were attached as side substituents along the main chain to further increase their solubility and flexibility. These polymers are expected to combine the properties of the poly(pyridinium salt)s with those of the stilbenoid compounds. By stilbenoid compounds we mean systems that are made up of stilbene units.

EXPERIMENTAL

Characterization Methods

Melting temperatures were determined on an electrothermal melting point apparatus IA6304 and were uncorrected. IR spectra were recorded on a PerkinElmer 16PC Fourier transform infrared (FTIR) spectrometer with KBr pellets. ^1H NMR spectra were obtained using a Bruker spectrometer (400 MHz). ^{13}C NMR (100 MHz) spectra were also obtained with a Bruker spectrometer. The NMR spectra were recorded using dimethyl sulfoxide ($\text{DMSO}-d_6$ or CDCl_3) as a solvent. Chemical shifts (δ values) are given in parts per million with tetramethylsilane as an internal standard. Ultraviolet–visible (UV–vis) spectra were recorded on a Varian Cary 1E spectrometer. The PL spectra were obtained with a PerkinElmer LS50B spectrometer. The DSC thermograms were obtained at a heating rate of 10 °C/min in N_2 atmosphere. Dynamic thermogravimetric analysis (TGA) measurements were made at a heating rate of 20 °C/min in atmospheres of N_2 or air at a flow rate of 60 cm^3/min . Thermomechanical analysis (TMA) was recorded on a DuPont 943 TMA instrument using a loaded penetration probe at a scan rate of 10 °C/min in N_2 with a flow rate of 60 cm^3/min . The TMA experiments were conducted at least in duplicate to ensure the accuracy of the results. The TMA specimens were pellets of 8 mm diameter and 2 mm thickness prepared by pressing powder of polymer for 3 min under 5–7 kpsi at ambient temperature. The inherent viscosities of the polymers were determined for solutions of 0.5 g/100 mL in dimethylacetamide (DMAc) at 30 °C using an Ubbelohde suspended level viscometer. Elemental analyses were carried out with a Hewlett–Packard model 185 analyzer. The wide-angle X-ray diffraction patterns were obtained for powder specimens on an X-ray PW-1840 Philips diffractometer.

To measure the fluorescence quantum yields, a degassed solution of the polymer in tetrahydrofuran (THF) was prepared. The concentration was adjusted so that the absorbance of the solution was lower than 0.1. The exciting wavelength was 330 nm, and a solution in 1N H_2SO_4 of quinine sulfate, which has a quantum yield of 0.546, was used as standard.

Reagents and Solvents

1,4-Benzenedicarboxaldehyde was recrystallized from distilled water. 4-Acetylstilbene was synthe-

sized according to a reported method¹⁹ from a palladium-catalyzed Heck coupling between styrene and 4'-bromoacetophenone with palladium(II) acetate and tris(2-tolyl)phosphane as the catalyst and cocatalyst, respectively, in triethylamine. It was recrystallized from ethanol 95%. Pure *p*-divinylbenzene was isolated from a commercial mixture of isomers following the literature procedure.²⁰

4-Dodecyloxyacetophenone was synthesized from the reaction of 4-hydroxyacetophenone (1 equiv) with 1-bromododecane (1.12 equiv) in the presence of K₂CO₃ (1.06 equiv) using DMF as a solvent. The mixture was refluxed for 15 h under N₂. It was subsequently concentrated under reduced pressure, and water was added to the concentrate. The solid was filtered, washed with water, and then washed with cold *n*-hexane to afford 4-dodecyloxyacetophenone in 98% (mp 50–52 °C).

Preparation of the Starting Materials and the Polymers

4,4'-(1,4-Phenylene)bis[2,6-di(*p*-styrylbenzene)-pyrylium tetrafluoroborate] (1)

A flask was charged with a mixture of 1,4-benzenedicarboxaldehyde (0.30 g, 2.24 mmol), 4'-styrylacetophenone (1.96 g, 8.96 mmol), and 1,2-dichloroethane (15 mL). Boron trifluoride etherate (1.4 mL) diluted with 1,2-dichloroethane (5 mL) was added portionwise to the stirred mixture at room temperature, and it was refluxed for 5 h under N₂. The solution was concentrated under reduced pressure, and ether was added to the concentrate. The dark red solid obtained was filtered, washed with ether, then washed with water, and finally dried to afford **1**. It was recrystallized from a mixture of 1,4-dioxane-ether (1:1 v/v) (1.82 g, 74%, mp 225–227 °C).

IR (KBr, cm⁻¹): 3024, 1620, 1598, 1484, 1452 (aromatic and pyrylium structure); 1082 (BF₄⁻); 962 (trans HC=CH). ¹H NMR (DMSO-*d*₆) δ: 9.20 (s, 4H, aromatic meta to O⁺); 8.20–7.21 (m, 40H, other aromatic); 7.15 (m, 8H, trans HC=CH).

Poly(pyridinium salt)s 2

A mixture of compound **1** (0.4000 g, 0.36 mmol), 1,12-diaminododecane (0.0714 g, 0.36 mmol), and DMAc (10 mL) was stirred and refluxed under N₂ overnight. The color of the reaction solution changed from dark red to orange during the heating period. The mixture was subsequently concen-

trated under reduced pressure, and water was added to the concentrate. The orange solid obtained was filtered, washed with water, and dried to afford **2a** (0.41 g, 89%).

n_{inh} = 0.22 dL/g in DMAc (0.5 g/dL). ELEM. ANAL. Calcd. for (C₈₄H₇₆B₂F₈N₂)_{*n*} (1287.15)_{*n*} C, 78.38; H, 5.95; N, 2.18. Found: C, 77.73; H, 6.12; N, 2.06.

The poly(pyridinium salt) **2b** was similarly prepared from the reaction of compound **1** (0.8600 g, 0.77 mmol) with 4,4'-diaminodicyclohexylmethane (0.1611 g, 0.77 mmol) in DMAc (15 mL). After heating, the reaction solution was filtered to remove a small amount of insoluble material, and water was added to the filtrate. Polymer **2b** precipitated as a yellow-brown solid in 75% yield (0.74 g).

n_{inh} = 0.31 dL/g in DMAc (0.5 g/dL). ELEM. ANAL. Calcd. for (C₈₅H₇₄B₂F₈N₂)_{*n*} (1297.15)_{*n*} C, 78.71; H, 5.75; N, 2.16. Found: C, 78.15; H, 5.96; N, 2.04.

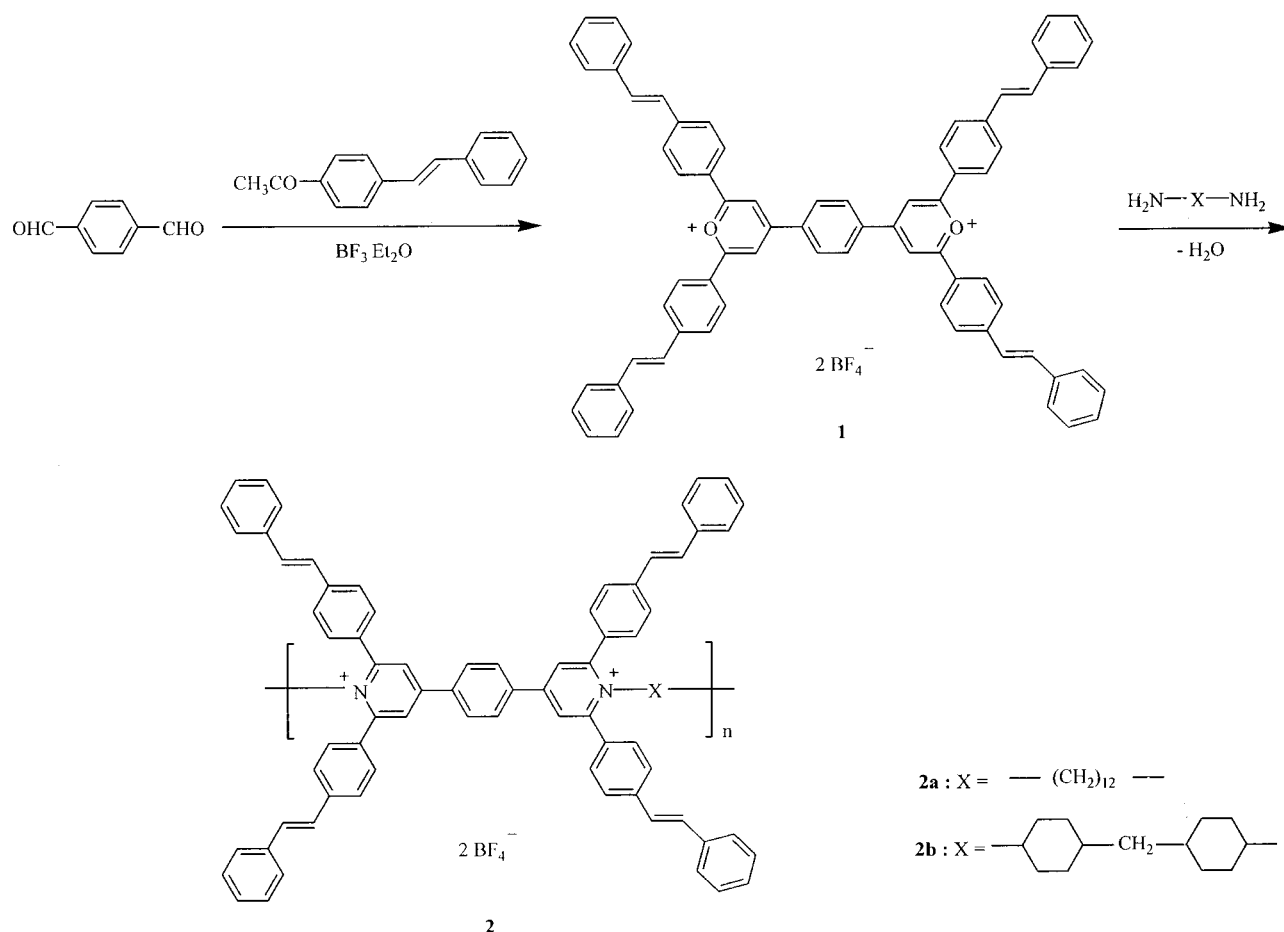
1,4-bis(*p*-Formylstyryl)benzene (3)

A flask was charged with a mixture of *p*-divinylbenzene (0.4440 g, 11.06 mmol), 4-bromobenzaldehyde (4.0931 g, 22.12 mmol), palladium(II) acetate (0.0498 g, 0.22 mmol), tri(*o*-tolyl)phosphine (0.1350 g, 0.44 mmol), and triethylamine (13 mL). The mixture was stirred and refluxed under N₂ for 24 h. Triethylamine was subsequently removed by distillation. Water containing 5% by volume hydrochloric acid was added to the residue. The solid obtained was filtered, washed thoroughly with water, and dried to afford **3**. It was recrystallized from DMF (2.10 g, 56%, mp 253–255 °C).

IR (KBr, cm⁻¹): 1688 (CHO); 3022, 598, 1566 (aromatic); 968 (trans HC=CH); 832 (C—H deformation vibration of the 1,4-disubstituted benzene ring). ¹H NMR (DMSO-*d*₆) δ: 9.98 (s, 2H, CHO); 7.89 (s, 4H, aromatic ortho to CHO); 7.81 (s, 4H, aromatic meta to CHO); 7.68 (s, 4H, aromatic of the central phenyl ring); 7.44 (d, 4H, trans HC=CH).

4,4'-[1,4-(Bistyryl)benzene]bis[2,6-di(4-dodecyloxyphenyl)pyrylium tetrafluoroborate] (4)

A mixture of **3** (0.20 g, 0.59 mmol), 4-dodecyloxyacetophenone (0.72 g, 2.36 mmol), 1,1,2,2-tetrachloroethane (15 mL), and boron trifluoride etherate (0.37 mL, 2.95 mmol) was stirred and refluxed in a stream of N₂ for 5 h. It was subsequently concentrated under reduced pressure, and meth-



Scheme 1

anol was added to the concentrate. The dark red-brown solid obtained was filtered, washed with water, then with cold ether, and dried to afford **4** (0.58 g, 59%, mp 118–120 °C).

IR (KBr, cm⁻¹): 2922, 2852 (C—H stretching of aliphatic segments); 1622, 1600, 1510, 1456 (aromatic and pyrylium structure); 1252, 1176 (ether bond); 1089 (BF₄⁻); 964 (trans HC=CH). ¹H NMR (DMSO-*d*₆) δ: 9.18 (s, 4H, aromatic meta to O⁺); 8.19–7.20 (m, 20H, other aromatic except those ortho to O); 6.90 (m, 8H, aromatic ortho to O); 7.12 (m, 4H, trans HC=CH); 4.01 (m, 8H, OCH₂); 1.10–1.97 [m, 80H, OCH₂(CH₂)₁₀]; 0.90 [m, 12H, OCH₂(CH₂)₁₀CH₃].

Poly(pyridinium salt)s 5

A mixture of compound **4** (0.4000 g, 0.24 mmol), 1,12-diaminododecane (0.0484 g, 0.24 mmol), and DMAc (10 mL) was stirred and refluxed under N₂ overnight. The mixture was subsequently poured into water, and polymer **5a** precipitated as a yel-

low-brown solid. It was filtered, washed with water, and dried (0.31 g, 71%).

*n*_{inh} = 0.28 dL/g in DMAc (0.5 g/dL). ELEM. ANAL. Calcd. for (C₁₁₆H₁₆₀B₂F₈N₂O₄)_{*n*} (1820.17)_{*n*} C, 76.55; H, 8.86; N, 1.54. Found: C, 75.93; H, 9.12; N, 1.68.

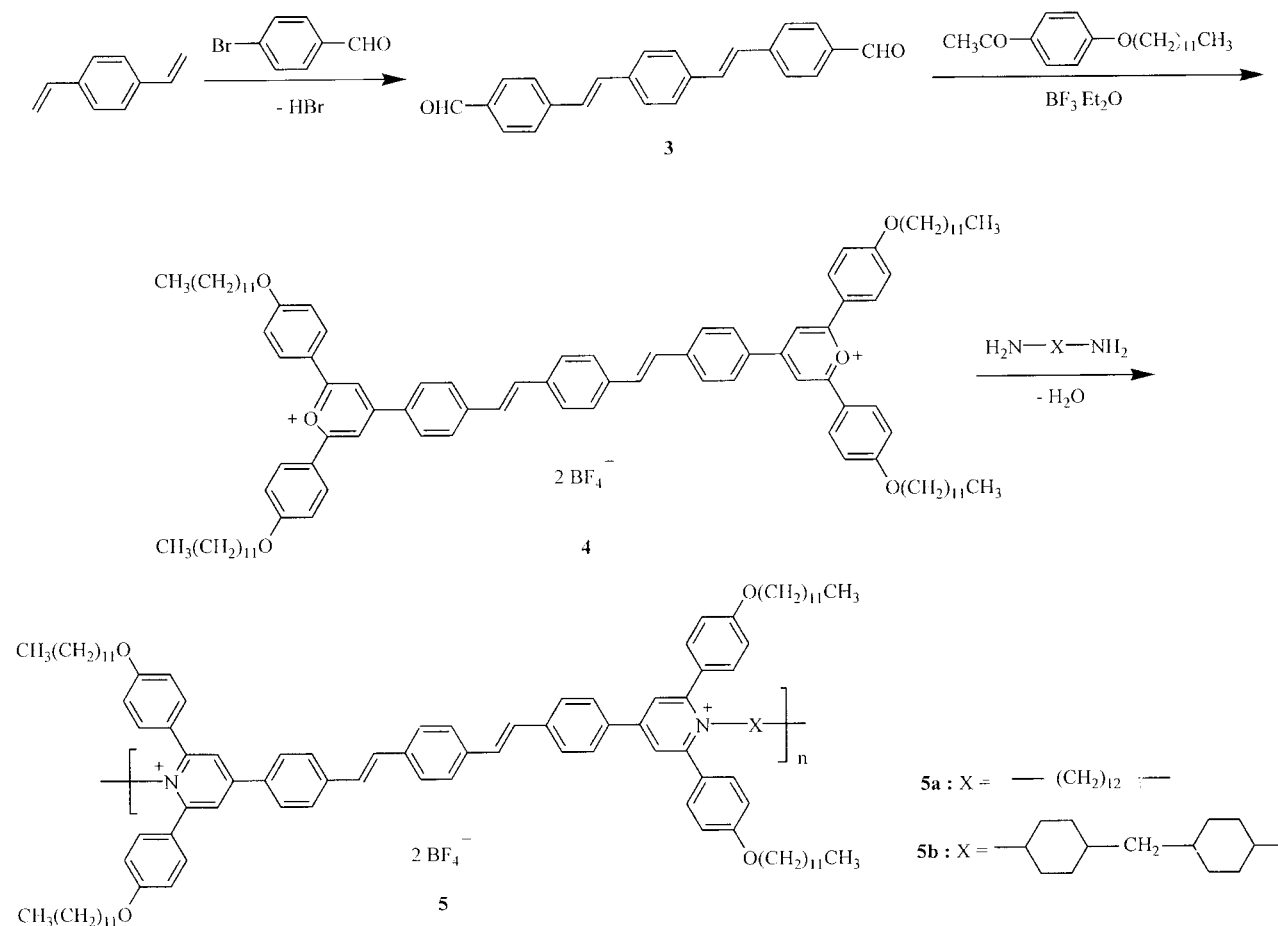
The poly(pyridinium salt) **5b** was similarly prepared from the reaction of compound **4** (0.3849 g, 0.23 mmol) with 4,4'-diaminodicyclohexylmethane (0.0489 g, 0.23 mmol) in DMAc (10 mL). Polymer **5b** was obtained as a brown solid in 78% yield (0.33 g).

*n*_{inh} = 0.32 dL/g in DMAc (0.5 g/dL). ELEM. ANAL. Calcd. for (C₁₁₇H₁₅₈B₂F₈N₂O₄)_{*n*} (1830.16)_{*n*} C, 76.79; H, 8.70; N, 1.53. Found: C, 76.10; H, 9.08; N, 1.60.

RESULTS AND DISCUSSION

Synthesis of Polymers

Scheme 1 outlines the reaction sequence applied for the synthesis of the poly(pyridinium salt)s **2**.



Scheme 2

Specifically, 1,4-benzenedicarboxaldehyde was reacted with four equivalents of 4-acetylstilbene in the presence of boron trifluoride etherate to afford the bis(pyrylium salt)s **1**. Numerous pyrylium salts have been prepared by reacting an aromatic aldehyde with acetophenone in the presence of $\text{BF}_3 \cdot \text{Et}_2\text{O}$.²¹ The polycondensation of **1** with an equimolar amount of a diamine such as 1,12-diaminododecane or 4,4'-diaminodicyclohexylmethane gave the poly(pyridinium tetrafluoroborate)s **2**. The polymerization reaction was carried out in DMAc and heated at approximately 150 °C. A transformation of the pyrylium ring to that of pyridinium occurred during this reaction, and therefore the removal of the evolved water could be useful. As previously mentioned, Harris and colleagues^{16,17} showed that the removal of the evolved water as an azeotrope from the reaction mixture increased the degree of polymerization of the obtained poly(pyridinium salt)s. Because the reaction conditions have been investigated in detail by Harris and colleagues,^{16,17} no optimization of the reaction was undertaken. The polyconden-

sation took place in a homogenous reaction mixture, and the polymer was isolated by pouring the mixture into a nonsolvent.

Scheme 2 shows the synthetic route utilized for the preparation of the poly(pyridinium salt)s **5**. Particularly, a Heck reaction between *p*-divinylbenzene and 4-bromobenzaldehyde afforded dialdehyde **3**. The reaction was carried out in triethylamine, and dialdehyde **3** precipitated during the heating period. The latter was reacted subsequently with 4-dodecyloxyacetophenone in the presence of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ to yield the bis(pyrylium salt)s **4**. Finally, they were polycondensed with diamines by the method previously described to afford the poly(pyridinium tetrafluoroborate)s **5**.

The polymers were prepared in high yields (71–89%), and their inherent viscosities ranged from 0.22 to 0.32 dL/g. This strongly suggests that the polymers were of low molecular weights, identically to what has been observed in other polymerizations of this type.^{14,15} The synthetic route utilized by Harris and colleagues,^{16,17} that gave rigid-rod poly(pyridinium salt)s with high n_{inh}

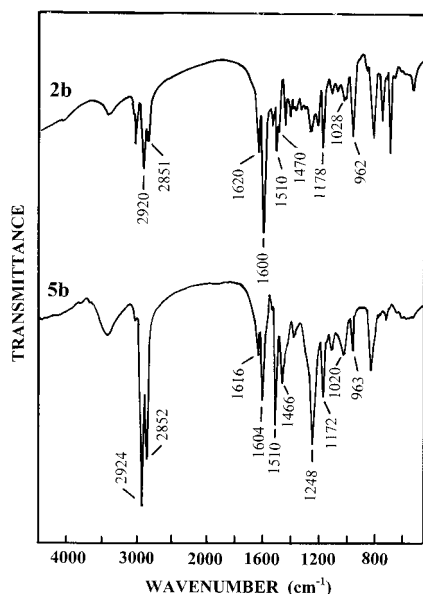


Figure 1. FTIR spectra of polymers **2b** (top) and **5b** (bottom).

values could not be applied in the present case because a crosslinking through the stilbene or the *p*-distyrylbenzene olefinic bonds will certainly take place during heating at 195 °C for 24 h. Because only traces of the resulting polymers dissolved in THF, their molecular weights were not determined by gel permeation chromatography.

Structural Characterization of Polymers

Structural characterization of the polymers was accomplished by IR and NMR spectroscopies. The FTIR spectra of the typical polymers **2b** and **5b** (Fig. 1) showed characteristic absorptions around 2920, 2850 (C—H stretching of aliphatic); 1620, 1600, 1510, 1170 (aromatic and pyridinium structure); 1020 (BF_4^-); and 962 cm^{-1} (HC=CH trans). Because polymer **5b** contained aliphatic parts both in backbone and side groups, its absorptions at 2924 and 2852 cm^{-1} exhibited higher intensity than the corresponding absorptions of **2b**, which carried aliphatic parts only in the backbone. Both polymers showed a C—N stretching band near 1470 cm^{-1} . The absorption band at 1248 cm^{-1} of **5b** was assigned to the ether bonds.

Figure 2 presents the ^1H NMR spectrum of the representative polymer **2a** in $\text{DMSO-}d_6$ solution. It displayed peaks at 8.14 (s, 4H, aromatic meta to N^+); 7.80–7.20 (m, 40H, other aromatic and 8H, trans HC=CH); 3.40 (m, 4H, N^+CH_2); 1.10 [m, 20H, $\text{N}^+\text{CH}_2(\text{CH}_2)_{10}$].

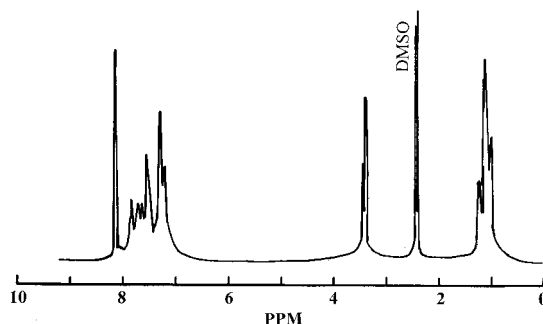


Figure 2. ^1H NMR spectrum of polymer **2a** in $\text{DMSO-}d_6$ solution.

The ^{13}C NMR spectrum of **2a** in $\text{DMSO-}d_6$ solution and the assignments of peaks are shown in Figure 3. It seems that the carbons of the aromatic and stilbenyl moieties resonated between 160 and 120 ppm, whereas those of the aliphatic segments resonated around 30 ppm.

Crystallinity and Solubility of Polymers

All polymers were generally amorphous as was evidenced by their wide-angle X-ray scattering curves of powder specimens obtained at room temperature. The polymers carried rigid blocks in their backbone as well as bulky side groups that caused loose chain packing. The aliphatic fragments, which also existed in the backbone of the polymers, reduced their stiffness but did not introduce a detectable degree of crystallinity. The amorphous character of the polymers was confirmed by the lack of melting, as was shown by DSC.

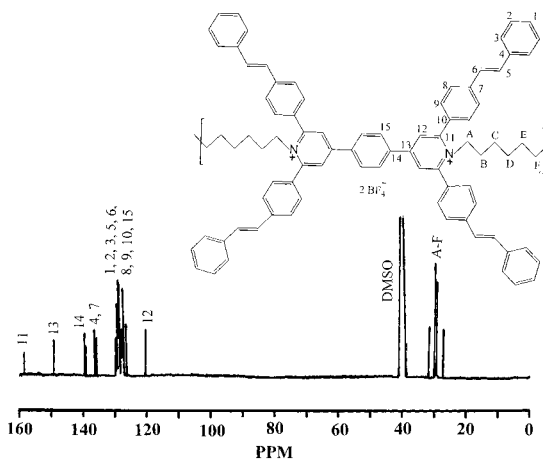


Figure 3. ^{13}C NMR spectrum of polymer **2a** in $\text{DMSO-}d_6$ solution.

Table I. Glass-Transition Temperatures, Optical Energy Gaps, PL Wavelength Maxima in Solution and Thin Film, and PL Quantum Yields in Solution of the Polymers

Polymer	T_g from DSC (°C)	E_g (eV)	$\lambda_{f,max}$ in Solution (nm)	$E_{f,max}$ in Solution (eV)	$\lambda_{f,max}$ in Thin Film (nm)	$E_{f,max}$ in Thin Film (eV)	Φ_f in Solution
2a	102	3.17	408	3.04	516	2.41	0.10
2b	123	3.14	408	3.04	523	2.37	0.18
5a	65	3.21	409	3.04	471	2.64	0.19
5b	59	3.24	416	2.98	454	2.73	0.27

E_g represents the optical energy gaps calculated from the UV-vis spectra of the polymers in THF solution. $\lambda_{f,max}$ represents the PL maxima, $E_{f,max}$ the corresponding energies, and Φ_f the PL quantum yields.

The polymers displayed a limited solubility being soluble in polar aprotic solvents like DMAc, DMF, and DMSO. They were partially soluble in other less efficient solvents such as *p*-dioxane, acetonitrile, acetone, and THF. The ionic nature of the polymers affected their solubility behavior and favored their dissolution in polar aprotic solvents. The polymers with *p*-distyrylbenzene units in their backbone are especially insoluble in organic solvents. Therefore, the attachment of the side dodecyloxy groups in polymers **5a** and **5b** was necessary to make them soluble in polar aprotic solvents. When shorter alkoxy groups were introduced to these polymers, they did not dissolve even in hot DMAc.

Thermal and Thermomechanical Properties of Polymers

DSC and TMA were used to determine the transition temperatures of the polymers. No distinct endotherms associated with melting were observed in the DSC thermograms. Polymers **5a** and **5b** showed weak endotherms around 42 °C that could be attributed to the side chains melting.²² Despite repeated runs, no clear glass-transition

temperatures (T_g 's) could be detected with DSC below 300 °C. However, transitions below this temperature cannot be ruled out because aromatic polyheterocyclis often undergo very small changes in heat capacity at the T_g .¹⁷

The T_g values of the polymers were determined from the TMA method using a loaded penetration probe and are listed in Table I. The T_g is assigned by the first inflection point in the TMA curve, and it was obtained from the onset temperature of this transition. The T_g 's of the polymers ranged from 59 to 123 °C. Polymers **5a** and **5b** showed significantly lower T_g 's (59–65 °C) than **2a** and **2b** (102–123 °C) obviously owing to the existence of the four side dodecyloxy groups in each repeat unit. In any case, the present polymers displayed remarkably lower T_g 's than those prepared from the polycondensation of 4,4'-(1,4-phenylene)bis(2,6-diphenylpyrylium tetrafluoroborate) with aromatic diamines (196–220 °C).¹⁶ This behavior was attributed to the lack of aliphatic segments in the latter.

The thermal stability of the polymers was evaluated by means of TGA. The temperatures (DT) at which weight losses of 1, 5, and 50% were obtained in both N₂ and air as well as the anaerobic char yield (Y_c) at 800 °C for all polymers are summarized

Table II. Thermal Stabilities of the Polymers

Polymer	In N ₂				In Air		
	DT ₁ ^a (°C)	DT ₅ ^a (°C)	DT ₅₀ ^a (°C)	Y_c ^b (%)	DT ₁ ^a (°C)	DT ₅ ^a (°C)	DT ₅₀ ^a (°C)
2a	248	325	713	41	244	310	519
2b	260	377	— ^c	53	248	313	530
5a	246	332	563	29	240	303	478
5b	295	381	701	46	286	335	501

^a DT₁, DT₅, DT₅₀: temperatures at which weight losses of 1, 5, and 50%, respectively, were obtained.

^b Char yield at 800 °C.

^c A weight loss of 50% was not obtained up to 800 °C.

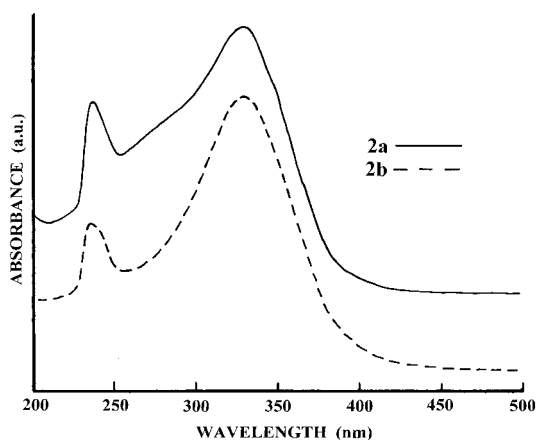


Figure 4. UV-vis spectra of polymers **2a** and **2b** in THF solution.

in Table II. They were stable up to 240–295 °C and afforded anaerobic Y_c 's of 29–53% at 800 °C. Polymers **2b** and **5b** had higher thermal characteristics than the corresponding ones of **2a** and **5a**, which indicates that they were more thermally stable.

Optical Properties of Polymers

Because the polymers contained chromophores either in the side substituents or in the main chain, their optical properties were investigated both in solution and in the solid state. Figure 4 presents typical UV-vis spectra of polymers **2a** and **2b** in dilute THF solution. They displayed absorption maxima at 235 and 330 nm associated with the aromatic structure and the π - π^* transition of the stilbenyl units. The optical energy gaps E_g of the polymers were calculated from the onset wavelength of their UV-vis spectra in THF solution and are listed in Table I. The E_g values ranged from 3.14 to 3.24 eV, comparable to those of other related polymers.¹⁸ It appears that the UV-vis spectra of **2a** and **2b** were essentially independent of the structure of the nonconjugated chain, namely, the fragment derived from diamine.

Figures 5 and 6 depict the PL spectra in THF and thin film that were obtained by excitation at 330 nm, which is the maximum of the absorption band. The films were prepared by spin coating on quartz plates from a solution of polymers. The wavelengths at peak maxima and the corresponding energies are summarized in Table I. The PL maxima were independent of the excitation wavelength.

The polymers exhibited in THF solution violet-blue PL with PL maxima at 408–416 nm. Specifically, polymers **2a** and **2b** bearing side stilbenyl groups had identical PL curves with a maximum

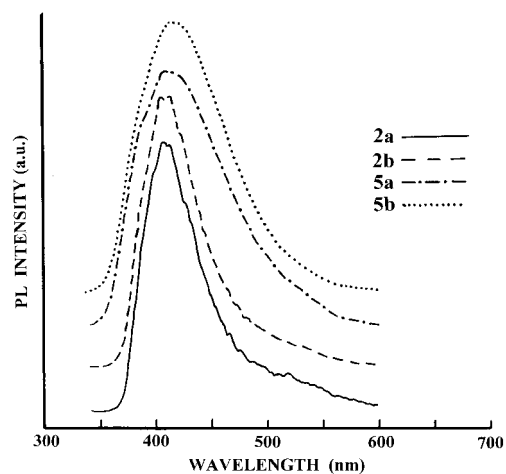


Figure 5. PL spectra for all polymers in THF solution (excitation at 330 nm).

at 408 nm. This clearly suggests that the diamine structure did not influence the emission spectra. Polymers **5a** and **5b** showed broader PL curves with maxima at 409 and 416 nm. Thus, the introduction of the *p*-distyrylbenzene segment in the polymer backbone did not influence considerably the PL maximum but broadened the PL curve to lower and mainly higher wavelengths.

The polymers showed in thin film violet-green PL with PL maxima at 454–523 nm. Upon going from solution to the thin film, the PL maxima of **2a** and **2b** were remarkably redshifted by 108 and 115 nm. This feature strongly indicates that in solid state there were significant chain interactions between the pendant stilbenyl groups. An analogous behavior has been observed with other polymers containing side stilbenyl groups.^{18,23,24} The present polymers have flexible spacers, long enough to stack in

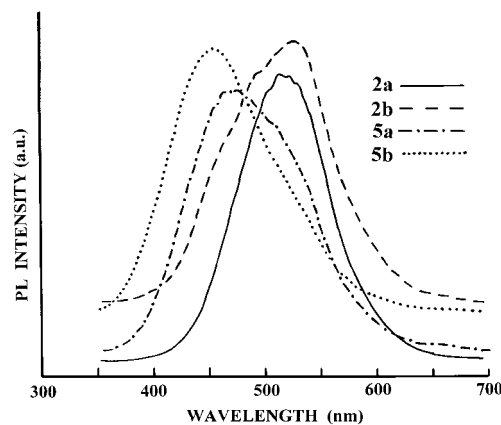


Figure 6. PL spectra for all polymers in thin film (excitation at 330 nm).

an intramolecular as well as intermolecular fashion. The large bathochromic shifts of the PL maxima in films owe to the highly ordered structure in the solid-state films. This ordered structure in the solid state arises from both intra- or intermolecular π - π interactions of chromophores.²⁵

The PL curves of **5a** and **5b** in thin film compared with those in solution displayed smaller redshifts by 62 and 38 nm. Such a behavior is reasonable because these polymers lacked side stilbenyl groups. However, stacking interactions subsisted and aggregates were formed even in this case.^{26,27}

The quantum yields (Φ) of the polymers in THF solution were determined²⁸ using quinene sulfate as a standard ($\Phi = 0.546$), listed in Table I. The Φ values ranged from 0.10 to 0.27. Polymers **2b** and **5b** obtained from 4,4'-diaminodicyclohexylmethane had higher Φ than the corresponding **2a** and **5a** derived from 1,12-diaminododecane. The present polymers compared with our previously synthesized poly(*m*-phenylene)s bearing pendant stilbene-based chromophores¹⁸ displayed lower Φ values.

CONCLUSIONS

bis(Pyrylium salts) were reacted with diamines to afford a new series of poly(pyridinium salt)s that carried side stilbenyl groups or *p*-distyrylbenzene segments in the main chain. The polymers were amorphous and soluble in polar aprotic solvents. Their T_g values were 59–123 °C. No weight loss was observed up to 240–295 °C by TGA, and their anaerobic char yields at 800 °C were 29–53%. The solutions of the polymers in THF were violet-blue fluorescent with PL maxima at 408–416 nm and quantum yields of 0.10–0.27. Thin films of the polymers showed violet-green fluorescence with PL maxima at 454–523 nm.

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