reaction of oleum-chloroform on maleic anhydride according to the Russian procedure.[7]

(Chlorocarbonyl)-β-sulfoacrylic anhydride (3) was prepared by the reaction of fumaryl chloride with SO_3.[7] The lower boiling isomer was collected by careful fractionation through a packed column using a high reflux ratio. The fraction bp 91 °C, n^{20}_D 1.5162 contained the desired product with only a small amount of contamination by the high boiler (**2**). (See Figures 5 and 6.)

(Methoxysulfonyl)maleic anhydride (6) was prepared by the reaction of methylchloroformate on purified sulfomaleic anhydride (method A) and by addition of methyl chloroformate to a mixture of SO_3 and maleic anhydride (method B).

Method A: A combination of sulfomaleic anhydride (15 g (0.084 mol)) and methyl chloroformate (19.8 g (0.21 mol)) was heated at reflux under a nitrogen purge overnight. Evolution of CO_2 and HCl was observed. The mixture was distilled, and 12.1 g (75% yield) of **6** was obtained, bp 120-123 °C (0.6 mm).

Method B: Under a nitrogen blanket or a drybox, 98.06 g (1 mol) of maleic anhydride and 80.06 g (1.01 mol) of SO_3 were combined and heated in a ~55 °C oil bath. When the temperature rose past 60 °C, cooling was provided until the exotherm ceased. Heating was maintained for about 20 h.

The reaction mixture was cooled at ambient, and 236.3 g (2.5 mol) of methyl chloroformate was added in two portions. After the exotherm ceased the mixture was heated at ~75 °C overnight. Excess methyl chloroformate was removed on a rotary evaporator. Distillation gave 35.6 g of unreacted maleic anhydride (63.7% conversion) and 110-122 g of product, 90-101% selectivity.

Polymer Modification with Sulfomaleic Anhydride. A typical polymer modification reaction was conducted as follows. A solution of 50 g of a dry EPDM rubber such as Vistalon 2504 in 1000 mL of dry xylene was heated at 130 °C and stirred under nitrogen and 2.67 g (15 mmol) of sulfomaleic anhydride was added. The anhydride was tightly wrapped in a parafinic film to prevent moisture pickup. Heating was continued for 4 h. After cooling, excess methylamine was added (21 g) to neutralize the sulfonic acid and react with the anhydride. The polymer solution became extremely viscous and 50 mL of methanol was added to attenuate the viscosity. After standing overnight, the polymer was precipitated in a high-speed mixer with 4000 mL of isopropyl alcohol-water (70:30), collected by filtration, and washed again in the mixer with another portion of IPA-H_2O. A small quantity of Irganox 1010 (~0.1 g) antioxidant was added, and the polymer was filtered and vacuum-dried at 50 °C.

Microanalysis indicated that the polymer contained 0.46% S (14.2 mmol/100 g) and 0.265% N (19.9 mmol/100 g). Treatment of a solution of the modified polymer with excess sodium methoxide in methanol to free ionically bound methylamine and isolation of the polymer by the above procedure gave the sodium sulfonate product, whose analysis showed 0.40% S (12.5 mmol/100 g) and 0.115% N (8.2 mmol/100 g).

All polymer samples used in this study contained about 1.5-2.0 mol % unsaturated monomer. Thus the available unsaturated monomer was in excess of the sulfomaleic anhydride reagent utilized. The unsaturation in EPDM is obtained from ethylidenenorbornene while butyl rubber utilizes isoprene as the comonomer. Conjugated diene butyl is made by chlorination and dehydrohalogenation of butyl rubber.

Registry No. 6, 40336-90-1.

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Conducting Polyquinolines

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ABSTRACT: Polyquinolines containing stilbene, diphenyl sulfide, thianthrene, and biphenyl connecting groups as well as AB polyquinolines, with either phenyl or a thiophene pendent group, were prepared and doped with arsenic pentafluoride, iodine, sodium naphthalide, or sodium anthracide. The highest conductivities obtained were for the right-rod polyquinolines poly[2,6-(4-phenylquinoline)] and poly[2,2′-(*p,p*′-biphenyl)-6,6′-bis(4-phenylquinoline)], both of which gave conductivities of approximately 10 S/cm on doping with sodium anthracide. Modification of these two polyquinolines resulted in lower conductivities.

Introduction

Many polymers and metals have a number of characteristics in common such as strength, elasticity, plasticity, and toughness. However, one of the more important properties of metals, their high conductivity, is not shared with polymers except for a few isolated examples. The possibility of conducting polymers was suggested[1] over 20 years ago, although only recently have organic polymers with conductivities approaching those of metals been synthesized.

The discovery that a free-standing film of polyacetylene, prepared by a Ziegler-Natta polymerization of acetylene,[2] could be oxidized with strong oxidants to give a conducting organic polymer[3] and the discovery that poly(*p*-phenylene) could be oxidized to an organic conducting polymer[4] stimulated research on a series of conducting organic polymers. These polymers, including poly(*p*-phenylene),[4] poly(*p*-phenylene sulfide),[5] polypyrrole,[6] polythiophene,[7] and polyaniline,[8] can be doped to give conductivities of up to 10^2 S/cm (conductivity is expressed in Siemens per centimeter, S/cm). Recently, it has been shown that polyquinolines can be doped to give conductivities of approximately 10 S/cm.[9,10]

High molecular weight polyquinolines ($M_n = 5 \times 10^5$) can be prepared by an acid-catalyzed reaction of aromatic *o*-amino ketones with keto methylene compounds.[11] The polymerization reaction is versatile, and the synthetic pathways to the monomers are abundant, such that a wide variety of structural features can be incorporated into the polymer (vide infra). Rigid-rod polyquinolines such as poly[2,2′-(*p,p*′-biphenyl)-6,6′-bis(4-phenylquinoline)] are highly crystalline ($T_m \sim 500$ °C) and are soluble in the

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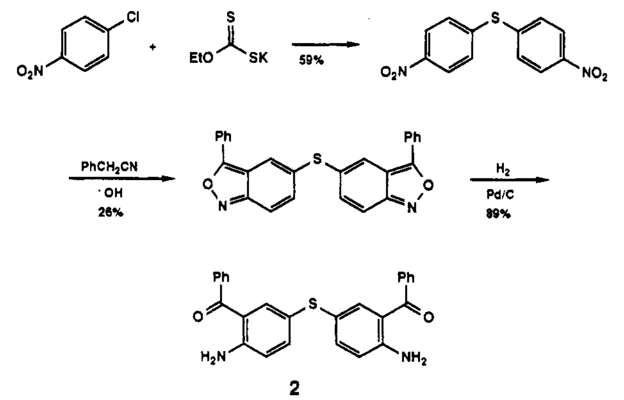
polymerization dope, *m*-cresol/di-*m*-cresyl phosphate, in which they form anisotropic solutions. Fibers of this rigid-rod polyquinoline spun from the polymerization dope containing 5–18 wt % solids have good tensile strength (>10 g/denier) and high modulus.[12]

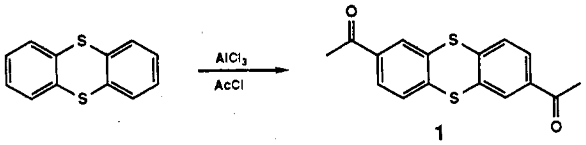
Scheme I



The crystal structure of a fiber of this polymer showed that the rodlike chains are oriented in the direction of the fiber axis and stack in parallel, nearly coplanar, sheets above one another.[13] Thus, this polyquinoline resembles, in this respect, the structure of graphite. Other rigid-rod polyquinolines prepared from A–B monomers or containing *trans*-stilbene units in the backbone form anisotropic solutions that can be spun into fibers with a high degree of crystallinity. In this paper, a series of rigid-rod and flexible polyquinolines that were prepared and doped with arsenic pentafluoride, iodine, sodium naphthalide, and/or sodium anthracide are described.

Results and Discussion

Monomers. A number of new monomers that would enable the incorporation of sulfur into the polyquinoline structure were synthesized. The acylation of thianthrene with acetyl chloride and aluminum trichloride gave diacetylthianthrene (1) (eq 1).[14] Because the isomer obtained was not obvious from the literature report[14,15] or from the spectral data, an X-ray crystal structure was carried out[16] to unambiguously assign 2,7-diacetylthianthrene (1) as the product.



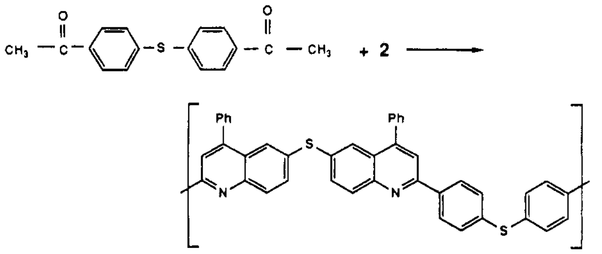
(1)

The synthesis of 4-amino-3-benzoylphenyl sulfide (2) was carried out (Scheme I) by the reaction of 4-chloronitrobenzene with potassium xanthate to give 4-nitrophenyl sulfide in 59% yield.[17] Phenylacetonitrile was condensed with 4-nitrophenyl sulfide in a basic methanol and tetrahydrofuran (THF) to give a poor yield (26%) of 5,5′-thiobis(3-phenyl-2,1-benzisoxazole). Catalytic hydrogenation gave the desired monomer (2).

The synthesis of 4-acetyl-2-(2-thienoyl)aniline (3) was carried out (Scheme II) by the condensation of 2-methyl-2-(4-nitrophenyl)-1,3-dioxolane with 2-thienylacetonitrile in basic methanol to give a low yield (15%) of the desired benzisoxazole. Although the yield was low, enough material was prepared to carry it on to monomer 3. Removal of the ketal, followed by hydrogenation of the isoxazole ring, gave 4-acetyl-2-(2-thienoyl)aniline (3).

The syntheses of 4-acetylphenyl sulfide,[18] 3,3′-dibenzoylbenzidine,[12] 4,4′-diacetylbiphenyl,[19] 4,4′-diacetylstilbene,[20] 5-acetyl-2-aminobenzophenone,[21] and 4-amino-4′-acetyl-3-benzoylbiphenyl[12] have been described elsewhere.

Synthesis and Fabrication of Polyquinolines. The polymerization[11] of 2 with 4-acetylphenyl sulfide (eq 2), 2 with 1 (eq 3), and 3,3′-dibenzoylbenzidine with 4,4′-diacetylbiphenyl (eq 4) or with 4,4′-diacetylstilbene (eq 5) in di-*m*-cresyl phosphate and *m*-cresol at 135 °C gave polyquinolines 4, 5, 6,[12,22] and 7,[23] respectively. The polymerization of the A–B monomers 5-acetyl-2-aminobenzophenone, 4-amino-4′-acetyl-3-benzoylbiphenyl, and 3 under the same conditions gave polyquinolines 8–10, respectively (eq 6–8).



(2)

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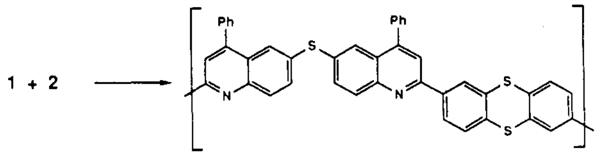

(3)

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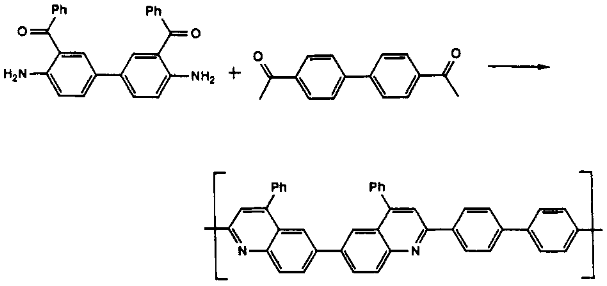

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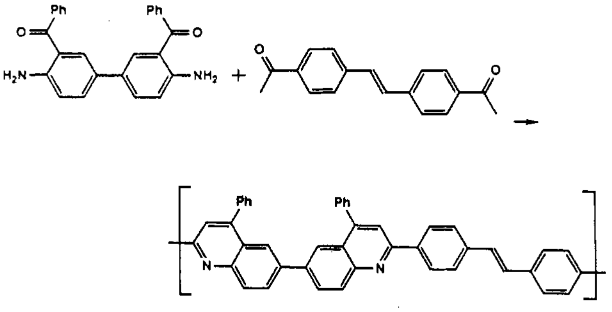

(5)

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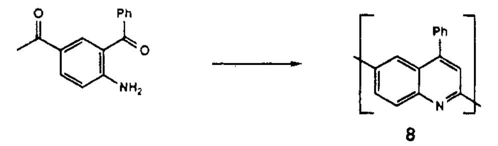
Polyquinolines 4 and 5 were soluble in chloroform, tetrachloroethane, and other organic solvents. Clear transparent films of polyquinolines 4 and 5 were cast from tetrachloroethane. Polyquinolines 6–10 are rigid-rod polyquinolines which are soluble only in strong acid (sulfuric, methanesulfonic, etc.) or the polymerization dope.[11] For the conductivity measurements, fibers and films of polyquinolines 6–10 were fabricated from the polymerization dope. Fibers of these polyquinolines were spun from 35%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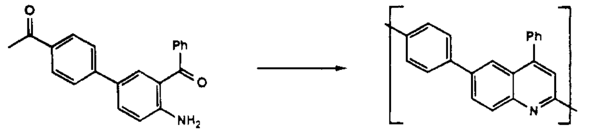
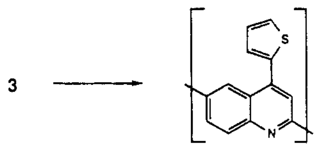

9 (7)

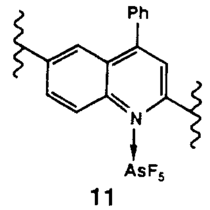

10 (8)

(w/w) di-*m*-cresyl phosphate and *m*-cresol into a triethylamine/ethanol solution. Solids contents are listed in Table I. Films of polyquinolines 6 and 7 were cast from a 0.5% (w/w) solution of polymer in a 16.6% solution of di-*m*-cresyl phosphate and *m*-cresol by pouring the solution on a glass plate. The coated plate was then heated to 50 °C to remove the *m*-cresol, and the residual film was placed into a triethylamine/ethanol solution to extract the di-*m*-cresyl phosphate.

Conductivity Measurements. Films and fibers of the polyquinolines were doped with arsenic pentafluoride, iodine, sodium naphthalide, or sodium anthracide (Table I). Exposure of polyquinolines 4–7 and 10 to arsenic pentafluoride did not result in any significant increase in conductivity. The highest conductivity (ca. 10^{-6} S/cm) was obtained from doping fibers of polyquinolines 6 and 7 for 19 days with arsenic pentafluoride.

Iodine increased the conductivity of polyquinolines 4, 6, and 10 by about 10 orders of magnitude but did not give a highly conductive material. Iodine increased the conductivity of polyquinoline 6 by 10 orders of magnitude, but after removal of the iodine by evacuation of the doping chamber, the conductivity of polyquinoline 6 returned almost to the original value. This is an example of reversible doping, which has been observed in a number of cases for iodine-doped polymers.[24] It was anticipated that the pendent thiophene in 10 would increase the electron density on the quinoline such that arsenic pentafluoride or iodine would oxidize the polymer to give a highly conducting p-type conductor. However, there was no difference in the conductivity obtained on doping 10 as compared with doping polyquinolines 4 and 6.

Lewis acids, such as arsenic pentafluoride and iodine, are poor oxidants for polyquinolines, probably as a result of Lewis salt formation with the nitrogen lone pair (11),



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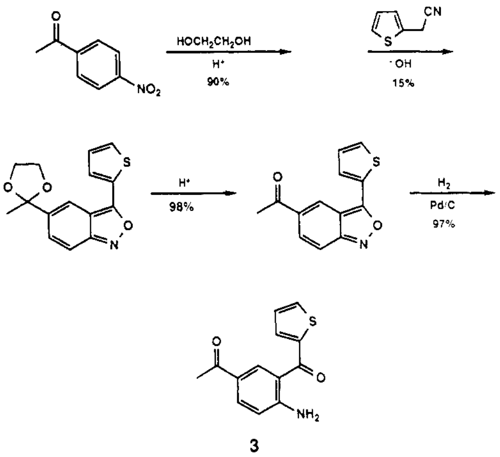
making it even more difficult to remove an electron from the quinoline ring. Comparison of the large increase in conductivity of poly(*p*-phenylene sulfide) exposed to arsenic pentafluoride to the small increase in conductivity of polyquinolines 4 and 5 illustrates the problem in oxidizing poly(arylene sulfide)s containing the quinoline ring. Although iodine is a weaker Lewis acid, it also is a weaker oxidant[25] incapable of doping polyquinolines.

Scheme II



Exposure of polyquinolines 4 and 5 to sodium naphthalide decomposed the polymer to subunits that were soluble in THF. The instability of polyquinolines 4 and 5 to sodium naphthalide in THF was not surprising in view of similar results obtained with poly(*p*-phenylene sulfide).[5,26] These results are not without precedent in small-molecule chemistry, since alkali metal cleavage of aromatic thioethers is known.[27]

Doping fibers and film samples of polyquinoline 6 with a 1 M solution of sodium naphthalide in THF gave conductivities (ca. 10^{-2} S/cm) that did not vary with sample preparation. A fiber of 6, spun from a 5% solution, was annealed to increase the amount of crystallinity and doped with the sodium naphthalide solution; only a slight decrease in conductivity was noted.

The conductivities of samples of polyquinoline 7 doped with a 1 M solution of sodium naphthalide in THF were dependent on sample preparation. Films of 7 cast from solution gave the highest conductivity (ca. 10^{-1} S/cm) when doped with sodium naphthalide. Fibers of 7, spun either from 5% or 10% solutions, gave the same conductivity (ca. 10^{-2} and 10^{-3} S/cm, respectively) with sodium naphthalide. Thus the most random sample (films cast from solution) gave the highest conductivities, while the most ordered sample (fibers from a 10% solution) gave the lowest conductivities.

At this stage in our work a report appeared[9b] showing that sodium anthracide could produce polyquinolines of higher conductivities than sodium naphthalide doped polyquinolines. Doping the same series of samples of polyquinoline 6 with a 0.1 M solution of sodium anthracide in THF gave conductivities (ca. 10^{-1}–10^{-2} S/cm) that were about an order of magnitude higher than the conductivities obtained from doping with sodium naphthalide. As was the case with sodium naphthalide doping, the conductivities did not vary with sample preparation for all samples except the fiber spun from an 18% solution. This fiber gave conductivities 2 orders of magnitude higher (ca. 10 S/cm) than those of any other sample of 6. An 18% solution of 6 is anisotropic and should give fibers with a relatively higher degree of crystallinity. Annealing this fiber prior to doping produced a slight decrease in conductivity.

Samples of polyquinoline 7 doped with a 0.1 M solution of sodium anthracide in THF gave conductivities that depended on sample preparation. As was the case with sodium naphthalide doping, films of 7 cast from solution

Table I
Conductivities of Doped Polyquinolines

polymer	form	wt % solids[a]	dopant[b]	S/cm	time,[d] days	comments
4	film		AsF_5 (400)	3×10^{-7}	6	
			I_2	1×10^{-3}	5.5	
			Na naph	*i*		
5	film		AsF_5 (400)	3×10^{-7}	4	
			Na naph	*i*		
6	fiber	5	AsF_5 (390)	6×10^{-8}	19	
		10		8×10^{-6}	19	
	film		I_2	1×10^{-2}	23	*e*
			Na naph	1×10^{-2}		
	fiber	5		6×10^{-3}		
				1×10^{-3}		*f*
		10		1×10^{-2}		
	film		Na anth	3×10^{-2}		
	fiber	5		2×10^{-1}		
		10		1×10^{-1}		
		18		8		
				5		*g*
7	fiber	10	AF_5 (390)	8×10^{-6}	19	
	film		Na naph	1×10^{-1}		
	fiber	5		1×10^{-2}		
		10		1×10^{-3}		
	film		Na anth	3×10^{-1}		
	fiber	5		2×10^{-2}		
		10		4×10^{-3}		
8	fiber	5	Na anth	11		
				2×10^{-4}		*h*
		18		3		
9	fiber	5	Na anth	4×10^{-2}		
10	fiber	5	AsF_5 (480)	6×10^{-8}	7	
			I_2	3×10^{-2}	14	
			Na anth	2×10^{-2}		

[a] The number represents the percentage of solids dissolved in 35% (w/w) di-*m*-cresyl phosphate/*m*-cresol. [b] The number in parentheses gives the pressure (Torr) of the arsenic pentafluoride; Na anth means the dopant was 0.1 M sodium anthracide in THF. [c] The initial conductivity of all undoped samples was ca. 10^{-12} S/cm. [d] The doping times for Na/naph and Na/anth were chosen arbitrarily, but long doping times did not increase the conductivity. [e] On removing the iodine with dynamic vacuum, the conductivity dropped to the original value. [f] The fiber was annealed at 370 °C for 5 min under 20 g of stress prior to doping. [g] The fiber was annealed at 450 °C for 10 min under 20 g of stress prior to doping. [h] The fiber was annealed at 470 °C for 10 min under 20 g of stress prior to doping. [i] The samples decomposed; see text for discussion.

gave the higher conductivity (ca. 10^{-1} S/cm).

Fibers of polyquinolines **9** and **10** doped with sodium anthracide gave moderate conductivities (ca. 10^{-2} S/cm). Fibers of polyquinoline **8**, spun from a 5% solution and then doped, showed the highest conductivity (11 S/cm). It was expected that fibers spun from an 18% solution would have higher conductivity, as was the case with polyquinoline **6**; however, a fiber spun from an 18% solution gave a slightly lower conductivity (3 S/cm). A fiber spun from a 5% solution was annealed to increase the amount of crystallinity and was doped with sodium anthracide. The surprising result was a drop of 6 orders of magnitude in conductivity (10^{-4} S/cm).

To determine a crude value for the amount of dopant taken up by these polyquinolines, a simple weight uptake experiment was carried out. Preweighed fibers of **6** and **8** were treated for 1 h with a 0.1 M sodium anthracide solution. The fibers were washed with THF until the washings were colorless, and the fibers were then dried and weighed. The fibers were then exposed to air, extracted with technical benzene (wet) for 3 days, dried, and weighed. The weight uptake at this point was assumed to be sodium hydroxide, since the extraction with benzene should remove any anthracene or 9,10-dihydroanthracene, leaving behind sodium hydroxide. The calculations (Table II) give the ratio of sodium to recurring unit of 3.8 for **6** and 1.0 for **8**.

Table II
Weight Uptake, Sodium Anthracide

	polyquinoline	
	6	**8**
initial weight, mg	40.8	47.9
mmol of repeat unit	0.0731	0.236
weight after THF washes, mg	64.8	80.4
weight after benzene extract, mg	51.9	57.6
weight increase, mg	11.1	9.7
mmol of NaOH	0.278	0.243
ratio NaOH/repeat unit	3.8	1.0
ratio NaOH/aromatic unit	0.63	0.5

Conclusions

Lewis acids (iodine and arsenic pentafluoride) are poor oxidants for polyquinolines due to the Lewis basicity of the quinoline nitrogen. For reasons not understood, anthracene is a better electron carrier than naphthalene for reducing polyquinolines. The conductivity of polyquinolines is sensitive to sample preparation and thermal history, but each polyquinoline is unique, the best conductivities being obtained with polyquinolines **6** and **8**. Derivatives of these polyquinolines have lower conductivities.

Electrochemical reduction of polyquinoline films on a platinum electrode have been reported to give conductivities as high as 40 S/cm.[9] Changing the pendent group on the A–B polyquinoline lowers the conductivity by ca. 1 order of magnitude, regardless of the pendent group and electron donating or withdrawing.

Experimental Section

The ^{1}H NMR spectra were obtained on an IBM WP-200 spectrometer (200 MHz) or an IBM WP-270 spectrometer (270 MHz), with tetramethylsilane (0.00 ppm), dimethyl sulfoxide

(Me_2SO, 2.49 ppm), benzene (7.15 ppm), or chloroform (7.24 ppm) as the internal standard. The ^{13}C NMR spectra were obtained on an IBM WP-200 spectrometer (50.3 MHz) or an IBM WP-270 spectrometer (67.9 MHz), with tetramethylsilane (0.00 ppm), Me_2SO (39.50 ppm), chloroform (77.00 ppm), or benzene (128.00 ppm) as the internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, b = broad), coupling constant in hertz, and integration. Unless otherwise stated, the spectra where obtained in deuteriochloroform.

Starting materials were obtained from commercial suppliers or prepared according to standard procedures. Tetrahydrofuran (THF), diethyl ether (ether), and benzene were freshly distilled under nitrogen from sodium/benzophenone prior to use. All reactions were carried out under an inert atmosphere (nitrogen or argon) and in flame-dried glassware unless otherwise stated.

All melting and boiling points are uncorrected. A Du Pont 910 differential scanning calorimeter (DSC) cell base was used to perform thermal analyses on pressed polymer samples. The reported intrinsic viscosity values, $[\eta]$, were determined by dilute viscosity measurements of polymer solutions obtained with Cannon-Ubbelohde microdilution viscometers size 50 (chloroform), size 75 (tetrachloroethane), and size 200 (sulfuric acid). The reduced and inherent viscosities were calculated and graphed vs. concentration by using a least-squares approximation. The co-*y*-intercept of the two lines was the value taken for the intrinsic viscosity, $[\eta]$. Medium-pressure liquid chromatography (MPLC) was performed with an ISCO Model UA-5 absorbance/fluorescence monitor equipped with a Type 6 optical unit and a Model 1133 multiplexer–expander using Woelm silica gel, 240–400 mesh. Elemental analyses were performed by Micro-Tech Laboratories of Skokie, IL; Atlantic Microlab, Inc., of Atlanta, GA; or Galbraith Laboratories, Inc., of Knoxville, TN.

Di-*m*-cresyl phosphate,[28] 4-nitrophenyl sulfide,[17] 4-acetylphenyl sulfide,[18] 2,7-diacetylthianthrene (**1**),[14] 3,3′-dibenzoylbenzidine,[12] 4,4′-diacetylbiphenyl,[19] 4,4′-diacetylstilbene,[20] poly[2,2′-(4,4′-biphenyl)-6,6′-bis(4-phenylquinoline)] (**6**),[12,22] poly[2,2′-(4,4′-stilbene)-6,6′-bis(4-phenylquinoline)] (**7**),[23] 5-acetyl-2-aminobenzophenone,[21] 4-amino-4′-acetyl-3-benzoylbiphenyl,[12] poly[2,6-(4-phenylquinoline)] (**8**),[29] and poly[2,6-(4-phenylene)-4-phenylquinoline] (**9**)[12] were prepared according to literature methods.

5,5′-Thiobis(3-phenyl-2,1-benzisoxazole). To a solution of 112 g (2.00 mol) of potassium hydroxide in 900 mL of methanol was added 450 mL of THF, followed by 48.0 g (400 mmol) of phenylacetonitrile. To this solution was added 50.0 g (200 mmol) of 4-nitrophenyl sulfide. The dark purple reaction mixture was heated at reflux for 16 h. The mixture was cooled and poured into 1500 mL of water, and the crude product was isolated by suction filtration. The product was washed with water until the washings were colorless. The product was slurried in 1500 mL of water, filtered, slurried in 1000 mL of methanol, and filtered. The product was dried under reduced pressure to give 24.6 g (29%) of yellow solid. The product was recrystallized from toluene (30 mL/g) to give 22.4 g (27%) of yellow solid: mp 213–214 °C (lit.[30] mp 208–211 °C); ^1H NMR (270 MHz) δ 7.99–7.94 (m, 6 H), 7.61–7.47 (m, 8 H), 7.25 (dd, J = 1.6, 9.2 Hz, 2 H); ^{13}C NMR (67.9 MHz) δ 156.94, 133.55, 131.18, 130.56, 129.37, 128.10, 126.62, 122.57, 116.83, 114.80.

4-Amino-3-benzoylphenyl Sulfide (2). Into a Parr shaking hydrogenator was placed 14.0 g (33.3 mmol) of 5,5′-thiobis(3-phenyl-2,1-benzisoxazole), 1.8 g (0.83 mmol, 2.5 mol%) of 5% palladium on charcoal, 100 mL of THF, and 6 mL of triethylamine. The bottle was pressurized to 50 psig with hydrogen and shaken for 22 h. The pressure was released and the slurry was filtered through a celite pad. The solvent was removed under reduced pressure to yield a yellow syrup. The syrup was chromatographed (MPLC, silica gel, 80% chloroform/20% ethyl acetate) to give a yellow solid. The solid was recrystallized from ethanol (25 mL/g) to give 12.6 g (89%) of yellow needles: mp 136–136.5 °C (lit.[30] mp 134.5–135.5 °C); ^1H NMR (270 MHz) δ 7.52–7.34 (m, 12 H), 7.25 (dd, J = 2.2, 8.5 Hz, 2 H), 6.66 (d, J = 8.5 Hz, 2 H), 6.17 (bs, 4 H); ^{13}C NMR (67.9 MHz) δ 198.17, 150.13, 139.49, 137.84, 137.61, 131.23, 129.03, 128.10, 121.90, 118.65, 118.02.

2-Methyl-2-(4-nitrophenyl)-1,3-dioxolane. A mixture of 16.5 g (0.100 mol) of 4-nitroacetophenone, 12.4 g (0.200 mol) of ethylene glycol, and 0.2 g (0.001 mol) of *p*-toluenesulfonic acid in 150 mL of benzene was heated at reflux and the water was removed azeotropically. The benzene was removed under reduced pressure. The resulting solid was washed with 95% ethanol and dried to give 18.9 g (90%) of off-white crystalline solid: mp 75–76 °C (lit.[31] 73–75 °C); ^1H NMR (270 MHz) δ 8.20 (d, J = 8.8 Hz, 2 H), 7.68 (d, J = 8.8 Hz, 2 H), 4.16–4.01 (m, 2 H), 3.85–3.73 (m, 2 H), 1.66 (s, 3 H); ^{13}C NMR (67.9 MHz) δ 150.55, 147.52, 126.24, 123.30, 107.94, 64.56, 27.17.

5-(2-Methyl-1,3-dioxolan-2-yl)-3-thienyl-2,1-benzisoxazole. To a stirred solution of 20 g (0.50 mol) of sodium hydroxide in 25 mL of methanol was added a slurry of 5.2 g (0.025 mol) of 2-methyl-2-(4-nitrophenyl)-1,3-dioxolane and 3.1 g (0.025 mol) of 2-thienylacetonitrile in 25 mL of methanol. The dark purple reaction mixture was stirred for 51.5 h at room temperature. The product was precipitated by pouring the reaction mixture into 200 mL of water, and the black precipitate was isolated by suction filtration. The black precipitate was dissolved in 200 mL of chloroform and dried over magnesium sulfate, and the chloroform was removed under reduced pressure to give 4.3 g of black solid. The black solid was chromatographed (silica gel, 1% ethyl acetate/methylene chloride) to give 1.2 g of yellow-brown solid (second band). This yellow-brown solid was sublimed at 0.1 mmHg, 100 °C, to give 1.1 g (15%) of yellow product: mp 141.5–142.5 °C; ^1H NMR (270 MHz) δ 7.88 (dd, J = 1.0, 1.4 Hz, 1 H), 7.80 (dd, J = 1.1, 3.8 Hz, 1 H), 7.58 (dd, J = 1.1, 5.0 Hz, 1 H), 7.57 (dd, J = 1.0, 9.4 Hz, 1 H), 7.43 (dd, J = 1.4, 9.4 Hz, 1 H), 7.24 (dd, J = 3.8, 5.0, 1 H), 4.12–3.82 (m, 4 H), 1.70 (s, 3 H); ^{13}C NMR (67.9 MHz) δ 160.31, 157.45, 139.76, 129.82, 129.59, 128.59, 128.22, 127.17, 115.80, 115.49, 113.41, 108.44, 64.63, 26.85. Anal. Calcd for $C_{15}H_{13}NO_3S$: C, 62.70; H, 4.56; N, 4.87; S, 11.16. Found: C, 62.73; H, 4.61; N, 4.82; S, 11.20.

5-Acetyl-3-thienyl-2,1-benzisoxazole. A mixture of 1.15 g (4.00 mmol) of 5-(2-methyl-1,3-dioxolan-2-yl)-3-thienyl-2,1-benzisoxazole (**10**), 50 mL of THF, 10 mL of water, and 1 mL of concentrated hydrochloric acid was heated at reflux for 3 h. To the cooled solution was added 100 mL of methylene chloride, and the solution was extracted twice with water, saturated sodium bicarbonate, water, and saturated sodium chloride and was then dried over magnesium sulfate. The solvents were removed under reduced pressure to give 0.95 g (98%) of dark yellow solid, which was sublimed at 0.1 mmHg, 130 °C, to give a yellow solid: mp 140–141 °C; ^1H NMR (270 MHz) δ 8.40 (dd, J = 1.0, 1.5 Hz, 1 H), 7.88 (dd, J = 1.5, 9.5 Hz, 1 H), 7.84 (dd, J = 1.1, 3.7 Hz, 1 H), 7.66 (dd, J = 1.1, 5.0 Hz, 1 H), 7.55 (dd, J = 1.0, 9.5 Hz, 1 H), 7.27 (dd, J = 3.7, 5.0 Hz, 1 H), 2.66 (s, 3 H); ^{13}C NMR (67.9 MHz) δ 195.83, 163.08, 157.58, 133.59, 130.03, 129.16, 128.62, 128.56, 128.48, 124.20, 115.30, 113.24, 26.11. Anal. Calcd for $C_{13}H_9NO_2S$: C, 64.18; H, 3.73; N, 5.76; S, 13.18. Found: C, 64.26; H, 3.78; N, 5.69; S, 13.11.

4-Acetyl-2-(2-thienoyl)aniline (3). Into a Fischer-Porter bottle were placed 3.65 g (15.0 mmol) of 5-acetyl-3-thienyl-2,1-benzisoxazole, 0.4 g of 10% Pd/C (0.4 mmol, 2.5 mol % palladium), 70 mL of THF, and 4.8 mL of triethylamine. The bottle was pressurized to 50 psig with hydrogen and stirred for 3 h. The mixture was filtered through a celite pad, and the celite pad was rinsed with methylene chloride until the washings were colorless. The solvents were removed under reduced pressure to give 3.8 g of brown solid, which was sublimed at 0.1 mmHg, 200 °C, to give 3.7 g of brown solid. The brown solid was chromatographed (MPLC, silica gel, chloroform) to give 3.6 g (98%) of yellow solid, which was recrystallized from ethanol (with a small amount of sodium hydrosulfite) to give small yellow needles: mp 177.5–178.5 °C; ^1H NMR (270 MHz) δ 8.49 (d, J = 2.1 Hz, 1 H), 7.93 (dd, J = 2.1, 8.7 Hz, 1 H), 7.72 (dd, J = 0.8, 4.8 Hz, 1 H), 7.61 (dd, J = 0.8, 4.8 Hz, 1 H), 7.18 (dd, J = 3.9, 4.8 Hz, 1 H), 6.75 (d, J = 8.7 Hz, 1 H), 6.32 (bs, 2 H), 2.52 (s, 3 H); ^{13}C NMR (67.9 MHz, Me_2SO-d_6) δ 194.67, 187.76, 154.04, 143.61, 134.07, 133.88, 133.82, 133.20, 128.22, 123.89, 116.16, 116.11, 25.68. Anal. Calcd for $C_{13}H_{11}NO_2S$: C, 63.65; H, 4.52; N, 5.71; S, 13.07. Found: C, 63.58; H, 4.57; N, 5.67; S, 13.10.

Poly[2,2′-(diphenyl sulfide)-6,6′-bis(4-phenylquinoline) Sulfide] (4). Into a resin kettle were placed 1.1566 g (2.7240 mmol) of 4-amino-3-benzoylphenyl sulfide (**2**), 0.7360 g (2.724 mmol) of 4-acetylphenyl sulfide, 20.0 g (71.9 mmol) of di-*m*-cresyl phosphate, and 7.1 g (66 mmol) of *m*-cresol. The resin kettle was purged with nitrogen for 15 min. The mixture was then mechanically stirred for 48 h at 135–140 °C under a static nitrogen atmosphere. The polymerization dope was then poured into 300 mL of 10% triethylamine/ethanol and chopped in a Waring blender for 2 min. The polymer was isolated by suction filtration and was then extracted in a Soxhlet with 10% triethylamine/ethanol for 25.5 h. The polymer was dried at 0.1 mmHg, 105 °C, for 24 h to give 1.6 g (95%) of polymer, [η] $CHCl_3$ = 0.82 dL/g, T_g = 238 °C. Anal. Calcd for $(C_{42}H_{26}N_2S_2)_x$: C, 81.00; H, 4.21; N, 4.50; S, 10.30. Found: C, 80.55; H, 4.32; N, 4.40; S, 10.26; residue 0.26.

Poly[2,2′-(3,8-thianthrenediyl)-6,6′-bis(4-phenylquinoline) Sulfide] (5). Into a resin kettle were placed 1.0613 g (2.5000 mmol) of 4-amino-3-benzoylphenyl sulfide (2), 0.7511 g (2.500 mmol) of 2,7-diacetylthianthrene (1), 18.9 g (67.5 mmol) of di-*m*-cresyl phosphate, and 7.3 g (68 mmol) of *m*-cresol. The resin kettle were purged with nitrogen for 15 min. The mixture was then mechanically stirred for 49.5 h at 135–140 °C under a static nitrogen atmosphere. The polymerization dope was then poured into 300 mL of 10% triethylamine/ethanol and chopped in a Waring blender for 2 min. The polymer was isolated by suction filtration and was then extracted in a Soxhlet with 5% triethylamine/ethanol for 37 h. The polymer was dried at 0.1 mmHg, 105 °C, for 24 h to give 1.58 g (97%) of polymer, [η] $Cl_2CHCHCl_2$ = 0.58 dL/g, T_g = 228 °C. Anal. Calcd for $(C_{42}H_{24}N_2S_4)_x$: C, 77.27; H, 3.71; N, 4.29; S, 14.73. Found: C, 75.21; H, 3.82; N, 4.14; S, 14.36.

Poly[2,6-(4-(2-thienyl)quinoline)] (10). Into a resin kettle were placed 1.2265 g (5.0000 mmol) of 4-acetyl-2-(2-thienoyl)aniline (3), 16.7 g (60.0 mmol) of di-*m*-cresyl phosphate, and 5.9 g (55 mmol) of *m*-cresol. The resin kettle was purged with nitrogen for 15 min. The mixture was then mechanically stirred for 50 h at 135–140 °C under a static nitrogen atmosphere. The polymerization dope was then poured into 200 mL of 10% triethylamine/ethanol and chopped in a Waring blender for 2 min. The polymer was isolated by suction filtration and was then extracted in a Soxhlet with 10% triethylamine/ethanol for 24 h. The polymer was dried at 0.1 mmHg, 105 °C, for 36 h to give 1.0 g (96%) of polymer, [η] H_2SO_4 = 2.76 dL/g, T_g = 358 °C. Anal. Calcd for $(C_{13}H_7NS)_x$: C, 74.61; H, 3.37; N, 6.69; S, 15.32. Found: C, 71.46; H, 3.77; N, 6.52; S, 14.50.

Preparation of Fibers and Films. Fibers of poly[2,2′-(4,4′-biphenyl)-6,6′-bis(4-phenylquinoline)] (6), poly[2,2′-(4,4′-stilbene)-6-6′-bis(4-phenylquinoline)] (7), poly[2,6-(4-phenylquinoline)] (8), poly[2,6-(4-phenylene)-4-phenylquinoline] (9), and poly[2,6-(4-(2-thienyl)quinoline)] (10) were spun either directly from the polymerization dope or from 35% w/w di-*m*-cresyl phosphate in *m*-cresol (solids content shown in Table I) into a triethylamine/ethanol solution.[12] Films of poly[2,2′-(4,4′-biphenyl)-6-6′-bis(4-phenylquinoline)] (6) and poly[2,2′-(4,4′-stilbene)-6-6′-bis(4-phenylquinoline)] (7) were cast from a 0.5% w/w solution of polymer in a 16.8% solution of di-*m*-cresyl phosphate in *m*-cresol solvent by pouring the solution onto a glass plate. The coated plate was then heated to 50 °C to remove the *m*-cresol, and the residual film was placed in a triethylamine/ethanol bath to extract the di-*m*-cresyl phosphate. Films of poly[2,2′-(4,4′-diphenyl sulfide)-6,6′-bis(4-phenylquinoline) sulfide] (4) and poly[2,2′-(3,8-thianthrenediyl)-6,6′-bis(4-phenylquinoline) sulfide] (5) were cast from a 10% w/v solution of polymer in tetrachloroethane.

Conductivity Measurements. The conductivity measurements were performed as described.[32] The fibers and/or films of the polyquinolines were doped with iodine, arsenic pentafluoride, sodium naphthalide,[33] and/or sodium anthracide[33] as shown in Table I. The conductivity measurements were made by using a Kiethley Model 616 electrometer for large resistances and the standard dc four-probe method[32] for low resistances. The polymers were attached to the platinum electrodes with Electrodag 502 (Acheson Colloids Co.). The doping chamber was evacuated and filled with argon at least three times prior to doping. All polyquinoline samples turned black upon doping and, upon exposure to air, showed a rapid decrease in conductivity. The doping time with sodium naphthalide or sodium anthracide was chosen arbitrarily, but long doping times did not improve the conductivity. A sample of poly[2,6-(4-phenylquinoline)] (8) had the same conductivity after it was doped with sodium anthracide for 1 or 6 h.

Weight Uptake Experiment. A weighed amount of either poly[2,2′-(4,4′-biphenyl)-6-6′-bis(4-phenylquinoline)] (6) or poly[2,6-(4-phenylquinoline)] (8) fiber was placed into a doping chamber. The chamber was filled with a 0.1 M solution of sodium anthracide for 1 h; the doping solution was removed, and the fiber was washed with THF until the washings were colorless. The fiber was dried under reduced pressure overnight. The fiber was weighed and then extracted with technical benzene in a Soxhlet extractor open to the air for 3 days. The fiber was dried under reduced pressure and weighed. The weight uptake at this point was assumed to be sodium hydroxide.

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264 *Macromolecules* **1987**, *20*, 264-267

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Effects of Side-Chain Structure on Polymer Conformation: Synthesis and Dilute Solution Properties

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ABSTRACT: Two imidazole-containing polymers, poly(*N*-vinylimidazole) (PVI) and poly[*N*-(1,1-dimethyl-3-imidazolylpropyl)acrylamide] (PDIA), were used to study the effects of side-chain length and flexibility on backbone-chain conformation. Both polymers were synthesized by free-radical polymerization in organic media and characterized by light scattering and intrinsic viscosity in methanol and in aqueous salt solutions. For neutral PVI and PDIA, the characteristic ratios are identical, indicating that backbone-chain flexibilities of these vinyl polymers are not affected by the length and flexibility of the side chain that joins the imidazole ring to the backbone. For protonated PVI, the characteristic ratio is similar to that for uncharged PVI when the counterion of the protonated imidazolium ring is chloride but increases when the counterion is changed to acetate or propionate. This effect is diminished, however, for protonated PDIA, where the imidazole group is far removed from the backbone by a long and flexible amide linkage.

Introduction

The functions of imidazole or imidazolium groups in polymers, such as metal–ion complexation, counterion binding, and dye binding, are dictated by their distribution along or distance from the backbone chain. In an earlier paper[1] we described conformations of poly(*N*-vinylimidazole) (PVI) polymers in terms of the nature of solvent, quaternizing group, ionic strength, and counterion type. The solution behavior of these polymers was correlated with their binding characteristics to an azo dye, methyl orange.[2]

In the present study, we investigated chain dimensions of a similar polymer, poly[*N*-(1,1-dimethyl-3-imidazolylpropyl)acrylamide] (PDIA), where the imidazole moiety is linked to the vinyl backbone by a long and flexible amide side chain. The unperturbed dimensions were determined by light scattering and intrinsic viscosity for several fractionated samples. These results were compared with those for PVI to examine the effects of side-chain structure on overall chain conformation. Further correlation between conformation, counterion binding, and dye binding of these two polymers will be reported in a separate paper.[3]

Experimental Section

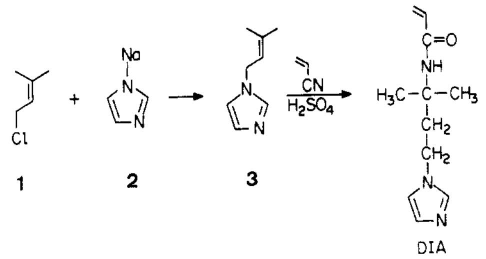
Materials. *N*-(1,1-Dimethyl-3-imidazolylpropyl)acrylamide (DIA). The vinyl monomer was synthesized by the two methods shown in Schemes I and II.

Scheme I. To sodium imidazole (300 g, 3.3 mol) in DMF (1.5 L) at 0–5 °C was added 1-chloro-3-methyl-2-butene (**1**) (346.5 g, 3.3 mol; Kodak Laboratory Chemicals). The mixture was kept overnight and then heated to 80 °C for 2 h and filtered, and the solvent was removed. The residue was distilled to give 2-methyl-4-imidazolyl-2-butene (**3**): bp 75–78 °C (0.1 mmHg); yield 75%. Anal. Calcd for $C_8H_{12}N_2$: C, 70.6; H, 8.9; N, 20.6. Found: C, 66.3; H, 8.3; N, 19.8.

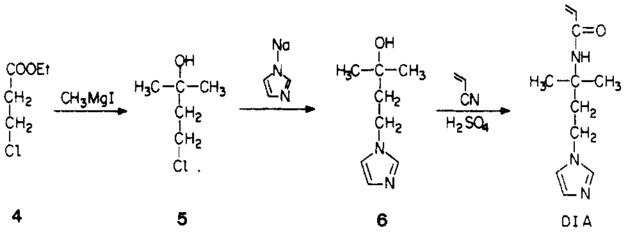
The structure of compound **3** was verified by mass and NMR spectra.

A mixture of acrylonitrile (201 g, 3.8 mol; Kodak Laboratory Chemicals), water (27.5 mL), 2,6-di-*tert*-butyl-*p*-cresol (4.5 g), and compound **3** (250 g, 1.8 mol) was cooled to 0 °C, and concentrated H_2SO_4 (468 g, 4.5 mol) was added slowly while the temperature was kept at 0–5 °C. The mixture was allowed to reach ambient temperature overnight and then heated to 80 °C for 2 h. The mixture was cooled to 0 °C and diluted with methanol (3 L). The excess acid was neutralized with anhydrous ammonia while the temperature was kept below 20 °C. The salts were filtered, and the solvent was removed. The residue was dissolved in ethyl acetate, dried over anhydrous magnesium sulfate, and filtered. On cooling to −16 °C, the product crystallized from ethyl acetate to give the vinyl monomer (DIA): mp 104–107 °C; yield 70%. Anal. Calcd for $C_{11}H_{17}N_3O$: C, 63.7; H, 8.3; N, 20.3. Found: 63.5; H, 8.3; N, 20.2.

Scheme I



Scheme II



The structure of DIA was confirmed by mass and NMR spectra.

Scheme II. 2-Methyl-4-chloro-2-butanol (**5**) (174 g, 1.4 mol), prepared[4] from **4**, was added dropwise at room temperature with constant stirring to a sodium imidazole (117 g, 1.3 mol) suspension prepared from 50% sodium hydride (75.0 g, 1.56 mol) and imidazole (88.0 g, 1.33 mol) in DMF (1.0 L). The mixture was stirred continuously at room temperature overnight and heated to 80 °C the next day for 2 h. Methanol (60 mL) was added to react with

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