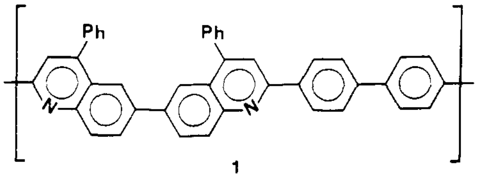
Conducting Polyquinolines

An organic polymer that combines the properties of high electrical conductivity, attractive processing characteristics, and good mechanical strength as yet has not been realized. Although poly(*p*-phenylene), for example, can be doped with either electron acceptors or donors to yield conducting polymers, it is an intractable, insoluble powder.[1-7] Although films have been formed by simultaneous polymerization and doping of oligomer films, free-standing films of structural integrity have not been produced. Poly(*p*-phenylene sulfide), which is readily processed (solution and melt), shows moderately good conductivity on doping with p-type dopants.[8-14]

High molecular weight ($\bar{M}_n = 5 \times 10^5$) polyquinolines can be prepared by an acid-catalyzed reaction of aromatic *o*-amino ketones with ketomethylene compounds.[15] 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 chain. Rigid-rod polyquinolines such as **1** are highly crystalline ($T_m \sim 500$ °C) and are soluble in the polymerization dope [*m*-cresol/di(*m*-cresyl) phosphate], in which they form anisotropic solutions. Fibers of **1** spun from the polymerization dope containing 5–18 wt. % solids have good tensile strength (~10 g/denier) and high modulus.[16]

The X-ray structure of a crystalline fiber of poly[2,2′-(*p*,*p*′-biphenylene)-6,6′-bis(4-phenylquinoline)] (**1**) showed that the rodlike chains are oriented in the direction of the fiber axis and stack in parallel, nearly coplanar sheets above one another.[17] Thus, this polyquinoline resembles, in this respect the structure of graphite. The head-to-tail, AB polyquinoline[16] as well as the polyquinoline-containing connecting stilbene units also forms anisotropic solutions and can be spun into fibers with a high degree of crystallinity.



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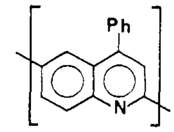

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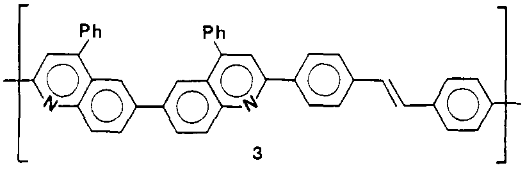

3

Thus, fibers of **1**–**3** were spun from 35% (w/w) di(*m*-cresyl) phosphate in *m*-cresol into an ethanol/triethylamine solution. Films were cast from a 0.5% (w/w) solution of polymer in either a 3.2 or 16.8% solution of the di(*m*-cresyl) phosphate/*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 solution to extract the di(*m*-cresyl) phosphate.

Fiber and film of polyquinolines **1**–**3** were doped with sodium naphthalide (1.0 M in THF) and sodium anthracide (0.1 M in THF), Table I.

The conductivity measurements were made by using a Kiethley Model 616 electrometer for large resistances and the standard dc four-probe method for low resistances. The polymers were attached to the platinum electrodes with Electrodag 502. 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 rapidly decreased in conductivity. The doping times were chosen arbitrarily but long doping times did not improve the conductivity. A sample of **2** had the same conductivity after 1 h as when it was treated for 6 h.

Several features of these studies are evident. First, sodium anthracide produced polyquinolines with higher conductivities than did sodium naphthalide. Second, the

Table I
Polyquinoline Conductivities

polymer	[η],[a] dL/g	form	soln concn wt % solids[b]	dopant (time, h)		conductivity, Ω^{-1} cm^{-1}		Na/quinoline
						initial	final[c]	
1	25	film	3.2	Na/napth		4×10^{-12}	1×10^{-2}	
			16.8		(5)	2×10^{-12}	1×10^{-2}	
			3.2	Na/anth	(26)	1×10^{-11}	3×10^{-2}	
		fiber	5	Na/napth	(17)	4×10^{-11}	6×10^{-3}	
			10			3×10^{-12}	1×10^{-2}	
			5	Na/anth	(6.5)	9×10^{-12}	2×10^{-1}	
			10		(5.5)	5×10^{-12}	1×10^{-1}	
			18[d]		(4)	6×10^{-11}	8	1.9[e]
2	4.4	fiber	5	Na/anth	(1)	6×10^{-12}	2	
					(11)	5×10^{-11}	11[f]	1.0[e]
					(11)	2×10^{-11}	1×10^{-2}[f,g]	
3	19.5	film	3.2	Na/napth		7×10^{-12}	1×10^{-3}	
			16.8		(15)	6×10^{-12}	1×10^{-1}	
			3.2	Na/anth	(9)	5×10^{-12}	6×10^{-1}	
		fiber	5		(3)	3×10^{-11}	2×10^{-2}[f]	
			10		(21)	2×10^{-11}	6×10^{-2}[f]	

[a] Intrinsic viscosities obtained in H_2SO_4 for **2** and in *m*-cresol/di(*m*-cresyl) phosphate for **1** and **3**. [b] All films cast from 0.5% (w/w); and the number represents the percent of di(*m*-cresyl) phosphate in solvent. [c] The conductivity after sample was washed of excess doping solution and dried under vacuum. [d] On extracting the fiber for 2 days with triethylamine/ethanol prior to doping, the conductivity dropped to 2 Ω^{-1} cm^{-1}. [e] The samples were weighed, doped 1 h with Na/anth, washed with THF, pumped for 1.5 days, weighed, exposed to air, extracted with technical benzene for 3 days, and weighed again. The weight uptake, at this point, is assumed to be NaOH. [f] The fiber was extracted for 2 days with triethylamine/ethanol. [g] The fiber was annealed at 380 °C for 10 min under 20 g of stress, during which time it underwent a 10% elongation.

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incorporation of a vinyl group into the backbone lowers the conductivity. Third, the conductivity was very sensitive to the preparation of the fiber or film and to its thermal history. Better conductivity was obtained when fibers were spun from solutions containing higher solids content. Under spinning conditions of high solids content, highly anisotropic solutions are observed, which lead to highly oriented fiber and apparently a higher degree of crystallinity. Annealing the fibers, however, produced a decrease in conductivity, an unexpected result, since annealing generally produces material of higher crystallinity.

The weight gain on doping was unusually high. When the doped fibers were exposed to air and then continuously extracted with benzene to leave behind sodium hydroxide in the fiber, the weight difference corresponded to 1.9 to 1.0 sodium ions per quinoline unit in **1** and **2**, respectively.

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Registry No. **1**, 75460-97-8; **2**, 59827-46-2; **3**, 86527-06-2; sodium naphthalide, 3481-12-7; sodium anthracide, 12261-48-2.

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