Results

The results for the system polystyrene (PS)/poly(dimethylsiloxane) (PDMS) are shown in Figure 4. The solubility of PDMS (M_w = 71 800) in PS (M_w = 500 000) is 4×10^{-6} g of PDMS/g of PS. The range of repeat runs is typically 10% of the mean. Clearly, this demonstrates the usefulness of this technique to measure the very low miscibilities typically found in polymer blends; however, with the currently used detection technique, only polymers with different refractive indices can be used.

Although a major portion of the solvent is removed from the blend near the hopper, there is a small quantity left. To minimize any solvent effect, we intend to use a two-stage screw with ring restriction in the extruder and apply vacuum at a vent to devolatilize the blend completely.

Acknowledgment. This material is based upon work supported by the National Science Foundation under Grant DMR 78-18078, Polymers Program.

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Dilute-Solution Parameters for a Fluorene-Containing "Cardo" Polyquinoline

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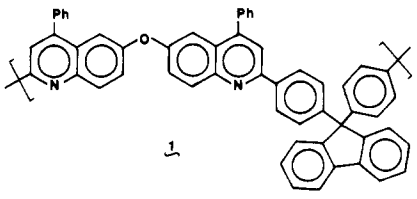
Polyquinolines with totally aromatic bulky cyclic groups serving as loops along the main chain have been prepared.[1] These "cardo" polyquinolines, which are highly amorphous, exhibit high glass transition temperatures (300–420 °C), excellent thermal stability (T_d > 500 °C in air, TGA), and good solubility. Because of this excellent solubility, "cardo" polyquinoline **1**, derived from 9,9′-bis(4-acetylphenyl)fluorene and 4,4′-diamino-3,3′-dibenzoyldiphenyl ether, was chosen to study the effect of incorporating a cardo fluorene group on the dilute-solution properties. Polyquinoline **1** is soluble in chloroform, in *sym*-tetrachloroethane (TCE), and in the polymerization medium consisting of di-*m*-cresyl phosphate and *m*-cresol.[2]



1

Experimental Section

Polymer Synthesis. Polyquinoline **1** was synthesized by the acid-catalyzed Friedlander polycondensation of 4,4′-diamino-3,3′-dibenzoyldiphenyl ether with 9,9′-bis(4-acetylphenyl)fluorene in a polymerization medium consisting of di-*m*-cresyl phosphate and *m*-cresol at 135–140 °C for a period of 48 h according to the general procedure.[1,2]

Table I
Molecular Weight and Viscosity Data for Fractionated Samples of Polymer 1

fraction no.	$[\eta]_{TCE}$, dL/g	$\bar{M}_n \times 10^{-5}$	$A_2 \times 10^3$, $(cm^3 \cdot mol)/g^2$
1	3.34	5.25	1.36
2	2.63	3.14	1.38
3	1.97	1.59	1.36
4	1.25	1.07	1.38

Intrinsic Viscosity. Solution viscosity measurements on polymer solutions were carried out in Cannon-Ubbelohde microdilution viscometers No. 50 (chloroform) and No. 75 (TCE) at 25.0 ± 0.2 °C. The intrinsic viscosity was obtained from extrapolation of the plots of η_{inh} and η_{red} vs. concentration to zero concentration.

Molecular Weight Determination. A Hewlett-Packard high-speed membrane osmometer (HP-501) equipped with a Schleicher and Schull membrane (S&S Type 08) conditioned in TCE was used to determine $\bar{M}_n$ on fractionated samples. To a stirring solution of 9.1 g of the polymer in 910 mL of chloroform at room temperature was added slowly the nonsolvent ethanol, until the appearance of a slight turbidity. This solution was allowed to stand at room temperature overnight. The clear solution was decanted from the gel phase and the process repeated several times. The gel was dried, redissolved in chloroform, and precipitated into ethanol containing a small amount of triethylamine. The fibrous polymer was suspended in a small amount of ethanol containing triethylamine and chopped in a blender. The polymer was collected by filtration, air-dried, and dried further at 110 °C (0.1 mm) for 24 h. Thus, four fractions were obtained. Intrinsic viscosity and number-average molecular weight for each of the fractions in TCE were obtained at 25.0 ± 0.2 °C and the results are shown in Table I.

Results and Discussion

The dependence of the osmotic pressure (π) on concentration (C) was found to be linear. Therefore, the data were analyzed according to the equation[3]

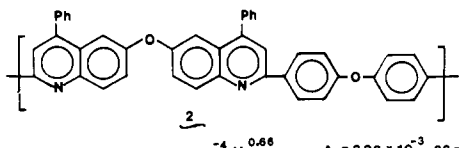
$$\pi/C = RT(1/\bar{M}_n + A_2C) \quad (1)$$

The intercept obtained by a plot of π/C vs. C was used to calculate $\bar{M}_n$ (Table I). From the number-average molecular weights and the intrinsic viscosities of the various fractions (Table I) it was possible to calculate the constants in the Mark–Houwink equation:

$$[\eta] = KM^a \quad (2)$$

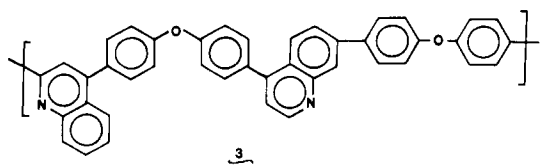
Thus, for **1** in TCE at 25 °C, $K = 1.63 \times 10^{-3}$ and $a = 0.58$. This exponent a, in conjunction with the A_2 value of 1.3×10^{-3} $(cm^3 \cdot mol)/g^2$, indicated good polymer–solvent interaction.

The Mark–Houwink parameters that have been reported[4,5] for other polyquinolines are



2

$[\eta]_{CHCl_3} = 9.0 \times 10^{-4} Mn^{0.66}$ $A_2 = 2.96 \times 10^{-3}$ cc-mol/gram²



3

$[\eta]_{CHCl_3} = 5.5 \times 10^{-3} Mn^{0.44}$ $A_2 = 1.48 \times 10^{-3}$ cc-mol/gram²

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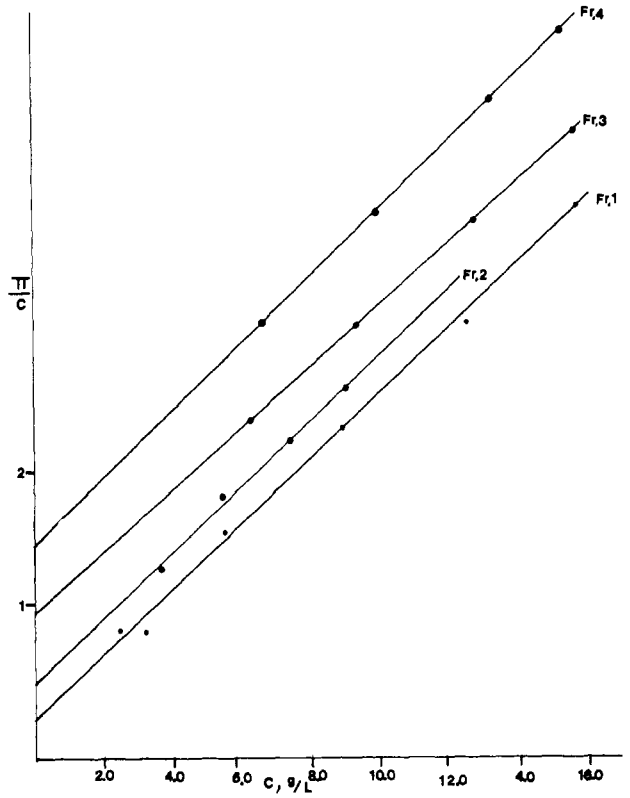

Figure 1. Plot of π/C vs. C for polymer 1.

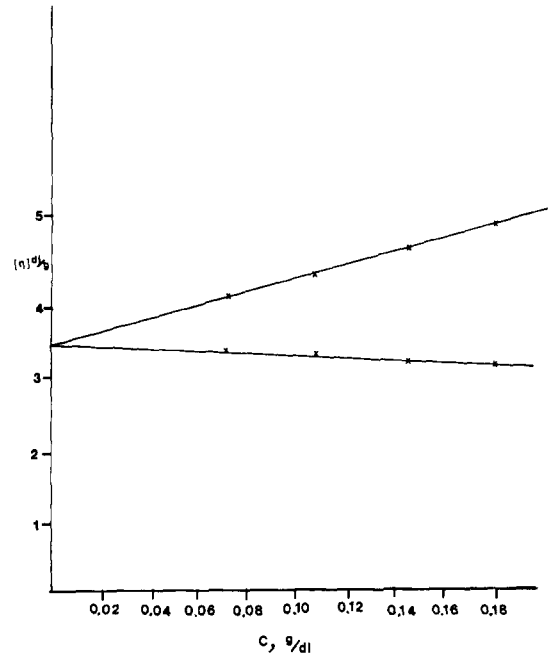

Figure 2. Plot of η_{sp}/C and ln η_r/C vs. C for polymer 1, fraction 1.

The nature of the polymer–solvent interaction for the cardo and noncardo polyquinolines, even though in different solvents, seems to be similar, as shown by their A_2 values. This enables a comparison of the exponent a values, which are very nearly the same for both the cardo and noncardo polyquinolines, implying similar flexibility.

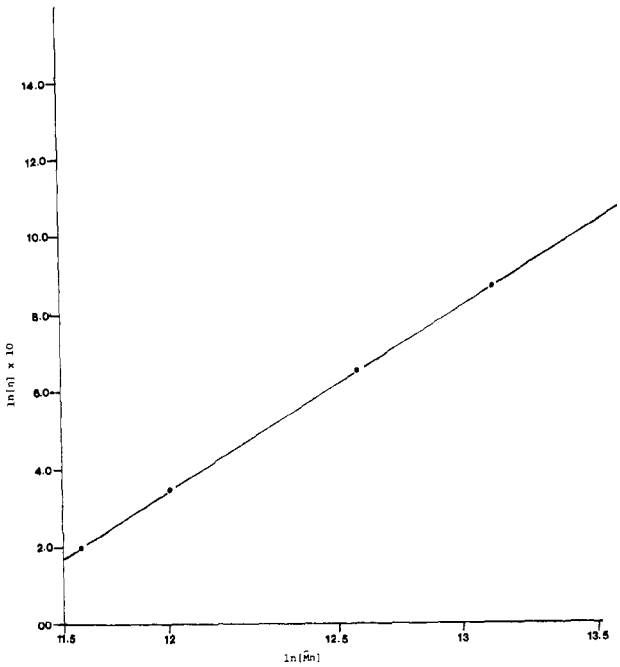

Figure 3. Plot of ln $[\eta]$ vs. ln $\bar{M}_n$ for polymer 1.

Dilution of polymer solutions would be expected to break up aggregation, if present, and deviation from linearity would result for any solution property, such as specific viscosity (η_{sp}) or osmotic pressure (π) as a function of concentration. The linearity of the plots of π/C vs. C and η_{sp}/C vs. C for polymer 1 suggests no aggregation (Figures 1 and 2).

The intrinsic viscosity as expressed by the Huggins equation

$$[\eta] = [\eta_0](1 + [\eta]C + K'[\eta]^2C^2 + \ldots) \qquad (3)$$

gives a value of the Huggins constant K' that is usually in the range $0.3 < K' < 0.7$. Generally, K' is found to increase with decreasing solvent power; for a Θ solvent, experimentally determined values range from 0.5 to 0.7. The value of $K' = 0.43$ obtained by a plot of η_{sp}/C vs. C (Figure 2) for 1 in TCE complements the data from osmometry in establishing the good polymer–solvent interaction.

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