NOTE

Polyelectrolyte Behavior of a Polybenzimidazole in Formic Acid

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Instead of the expected linear relationship between reduced viscosity and concentration, such as has been observed for dilute solutions of poly[2,2'-(4,4'-oxydiphenylene)-5,5'-bibenzimidazole] (PBI) in aprotic polar solvents,[1] the reduced viscosity of PBI in formic acid (FA) is characterized by anomalous upswings as the concentration decreases (see Figure 1). This behavior can be repressed by the addition of inorganic salts such as lithium bromide (LiBr) and is similar to the polyelectrolyte behavior of polyamides[2-4] in FA
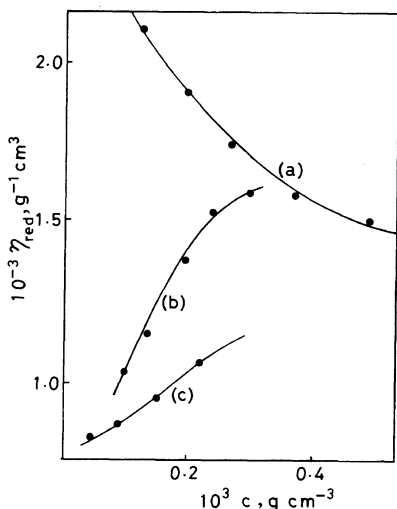

Figure 1. Viscosity curves of PBI ($M_w = 15.0 \times 10^4$) in FA: (a), without LiBr; (b), with 0.13 g/g PBI of LiBr; (c), with 1.3 g/g PBI of LiBr.

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solution; it can thus be understood as arising from the imidazole rings of the polymer in FA solution. A considerable number of these rings reacts with solvent molecules to produce a polyelectrolyte in
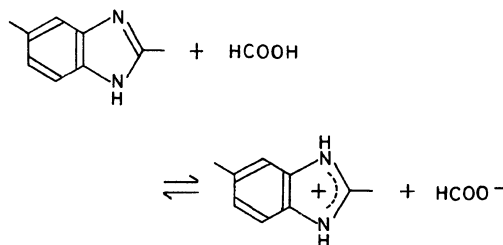
solution.

In order to find the intrinsic viscosity of the polyion by the extrapolation of the data for reduced viscosity to zero concentration, the equation of Fuoss and Strauss,[5,6]

$$\eta_{sp}/c = A/(1 + Bc^{1/2})$$

has been generally used.[2-7] For strong polyelectrolytes, the plot of the reciprocal of the reduced viscosity (η_{sp}/c) *vs.* the square root of the concentration gives a straight line. The value of A, when extrapolated to zero concentration, gives a limiting value corresponding to the intrinsic viscosity.

Fuoss constants for PBI of various molecular weights in FA solutions are listed in Table I, which also shows the data[2,7] for other typical polyelectrolytes. The values of B, assumed to be a measure of the electrostatic forces between the polyion and its counter ions, are close to those for typical polyelectrolytes, though these values tend to

Table I. Fuoss constants for various polyelectrolytes

| Polymer | Molecular weight | Solvent | A | B | Ref |
			cm³ g⁻¹	cm³ᐟ² g⁻¹ᐟ²	
Poly(ε-caproamide)	2.6×10^4	FA	2.84×10^2	19.6	2
Linear Poly[3,3′-(4,4′-diamino-diphenylene)pyromellit-amide]	—	DMAc[a] (0.5 MEt₃N)	3.45×10^2	17.3	7
PBI	4.5×10^4	FA	0.36×10^3	10.2	Present work
	9.7×10^4	FA	1.21×10^3	11.8	
	15.0×10^4	FA	2.44×10^3	13.3	
	23.3×10^4	FA	4.87×10^3	14.2	

[a] DMAc, *N,N*-dimethylacetamide.

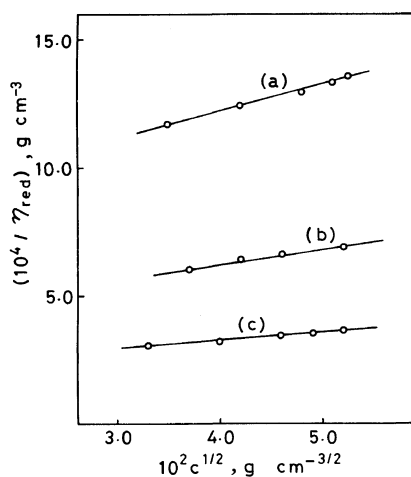**Figure 2.** Plots of reciprocal of reduced viscosity *vs.* the square root of concentration for PBI with various molecular weights: (a), 9.7×10^4; (b), 15.0×10^4; (c), 23.3×10^4.

become larger with molecular weight.

The approximate intrinsic viscosity $[\eta]$ of PBI in FA is plotted as a function of weight-average molecular weight in Figure 3. The slope of the line gives the value of a in the equation:

$$[\eta] = k(M_w)^a$$

The value obtained for $a(a = 1.58)$ is larger than the value 1.41 obtained for polyamides in formic acid,[3] and indicates a considerable uncoiling of the polymer chain due to the presence of charges along them. That is, polyion chains of PBI in FA solution behave more as rod-like chains at lower con-
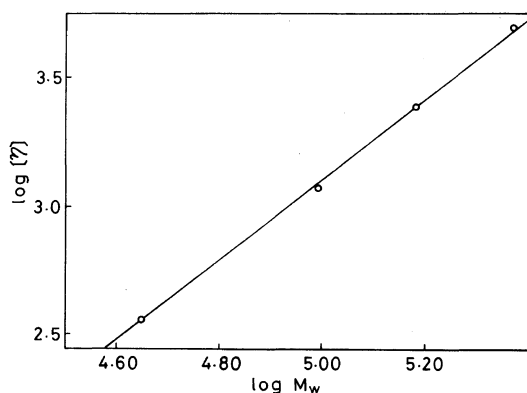

Figure 3. Intrinsic viscosity of polyions as a function of weight-average molecular weight.

centrations. The relatively larger value of a for PBI in FA, compared with other polyelectrolytes, is interpreted in terms of the long stiff repeating units within the main chain of PBI.

EXPERIMENTAL

PBI was prepared by the polycondensation of 3,3′-diaminobenzidine tetrahydrochloride and dimethyl 4,4′-oxybibenzoate in poly(phosphoric acid). This polymer, dissolved in *N,N*-dimethylacet-amide, was purified and dried by the method of Helminiak *et al.*[8] Its molecular weight was controlled by varing the reaction time or the proportion of reactants in the feed, and was determined by light scattering. The details of the experimental procedure are described in a previous paper.[1]

The four samples with different molecular weights ($10^{-4} M_w = 4.5, 9.7, 15.0,$ and 23.3), for which a plot of log $[\eta]$ vs. log M_w was found to be independent of the draining effect in the previous work,[1] were used in this work.

Viscosities were measured with an Ubbelohde viscometer at 303 K. In measurements on solutions containing added LiBr, dilutions were made with pure solvent, in order to keep the mole ratio of LiBr to PBI constant. Analytical grade 99.8% formic acid (Wako Pure Chemicals, Ltd.) from the same source was used through out the viscometry.

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