PROPERTIES OF DILUTE POLYPYRROLIDONE SOLUTIONS

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Molecular weights of unfractionated samples and fractions of polypyrrolidone ($M_w = 10^4 - 3 \cdot 10^5$) were determined by the light scattering method in a mixed solvent, 2,2,3,3-tetra-fluoropropanol/50 vol. % water. Their intrinsic viscosities in m-cresol and in the mixture 2,2,3,3--tetrafluoropropanol/10 vol. % water were also measured. The constants of the Mark-Houwink equation and the constants K_0 were compared with those of polycaprolactam. The selective sorption coefficients were measured in mixtures of 2,2,3,3-tetrafluoropropanol with water and lithium chloride and compared with analogous values obtained for polycaprolactam.

The polymerization of pyrrolidone has been studied more attentively only in recent years. Little attention has so far been devoted to the properties of polypyrrolidone in solutions (particularly diluted ones). The reason should probably be sought in that owing to great similarity between the chemical structure of polypyrrolidone and that of thoroughly investigated polycaprolactam, the solution behaviour of both polyamides may be expected to be quite similar.

Sekiguchi[1] has reported that polypyrrolidone can be dissolved in common solvents of polyamides, such as phenol, cresol, halogenated phenols, strong acids, saturated salt solutions in methanol, etc. The same author has measured the number average molecular weight (by chemical determination of the end groups) and intrinsic viscosity in cresol for several unfractionated samples, and calculated the constants of the Mark-Houwink equation.

It has been the objective of this work to find appropriate conditions for measuring the basic molecular parameters of polypyrrolidone by the light scattering method, to determine the relationship between the weight average molecular weight and the intrinsic viscosity of fractions over the widest possible range of molecular weights, to determine the selective sorption coefficients in some binary solvents, to estimate the rigidity of polypyrrolidone and polycaprolactam.

EXPERIMENTAL

The polypyrrolidone samples were obtained by the heterogeneous bulk anionic polymerization of polypyrrolidone catalyzed with its potassium salt (0·4 mol %) and activated with N-benzoyl-pyrrolidone (0·4 mol %) in sealed ampoules at 40°C according to a procedure described in ref.[2]. The products of polymerization completed to various conversion (28—56%) were dissolved in cresol, reprecipitated into diethyl ether and dried in vacuo. The molecular weights of unfractionated

samples were determined as follows:

Sample:	A	B	C	D	E	F
$M_{\overline{W}} \cdot 10^{-3}$:	33·5	43·5	45	48·5	64·5	68

Fractions of the samples A, C and E (5—8 fractions of each) were obtained by the equilibrium precipitation fractionation with petroleum ether from 1% solutions in cresol.

2,2,3,3-Tetrafluoropropanol (Schuchardt, Munich) was rectified and its purity was checked chromatographically. Technical m-cresol contained 60% m-cresol. Lithium chloride and petroleum ether (Lachema, Czechoslovakia) were analytical purity grade.

The light scattering was measured with a French Sofica apparatus within the usual angular range. The data thus obtained were represented as the ratio Kc/R_0, K being the optical constant including the refractive index increment dn/dc (v), c the polymer concentration in g/ml, and R_0 the reduced intensity extrapolated to zero angle of observation. Determination of refractive index increments of the polymer in mixed solvents at a constant concentration of the solvent components and at a constant chemical potential of the solvent component in solution and in solvent by means of differential refractometry (Brice-Phoenix, a BP-2000 V model) and dialysis has been described earlier[3]. All measurements were carried out at 25°C; green light $\lambda = 546$ nm was used for optical measurements.

The intrinsic viscosity was measured (25°C) with Ubbelohde viscometers by employing the standard procedure.

RESULTS AND DISCUSSION

Choice of a Suitable Solvent

Pure or technical m-cresol is the solvent mostly employed for viscosity measurements of practically all polyamides. However, this solvent is not suitable for light scattering measurements owing to its high refractive index ($n_D = 1\cdot54$) which is close to that of polypyrrolidone ($n_D = 1\cdot564$, measured by the Becke line method). Our previous experience[4] has led us to use 2,2,3,3-tetrafluoropropanol (TFP), the low refractive index of which ($n_D = 1\cdot3217$) ensures good accuracy even with relatively low molecular weight polycaprolactam samples.

In contrast with polycaprolactam, polypyrrolidone does not exhibit a polyelectrolyte effect in pure TFP; however, pure TFP as a solvent for light scattering measurements is unsuitable for two reasons: 1) Thermodynamically, it is such a good solvent of polypyrrolidone that with respect to the extremely high value of the second virial coefficient the extrapolation of measured values to zero concentration of the polymer may be rather inaccurate; 2) it is strongly hygroscopic, so that the solutions may absorb an undefined quantity of moisture during operations before measurements. These disadvantages may be avoided by adding water (as the precipitating agent) to the solvent. With increasing water content the mixture becomes a poorer solvent, which is reflected in a pronounced decrease in both the intrinsic viscosity and the second virial coefficient (Fig. 1). In the region between 50—55 vol. % of water,

when polypyrrolidone is on the threshold of precipitation, the decrease is already so steep that measurements may be subjected to a considerable error as a consequence of very small changes in the solvent composition. Therefore, a mixture TFP/50 vol. % water was chosen for the molecular weight determinations by the light scattering method. As it was confirmed by measurements of the scattered light intensity and of the viscosity of unfractionated samples, solutions in the TFP/10−53 vol. % water are aggregate-free and stable even at elevated temperatures (they were heated to 90°C up to three hours).

Selective Sorption in Mixed Solvents

In the investigations of polycaprolactam solutions by light scattering in the TFP/water mixtures with conventionally determined refractive index increments, apparent values of molecular weight are obtained owing to the selective sorption of the TFP molecules onto the polymer[4]. The real molecular weights of polypyrrolidone were determined using exclusively refractive index increments measured in the state of the dialysis equilibrium between the solution and the mixed solvent[3]. In analogy with polycaprolactam[4] no dependence of selective sorption on molecular weight was expected; therefore all dialysis and refractive measurements were performed with two samples only, E and F.

The refractive index increments of polypyrrolidone in the mixture TFP/water before (v_c) and after (v_μ) dialysis indicate the selective sorption of TFP (*i.e.* that of the better solvent with a lower refractive index) on polypyrrolidone:
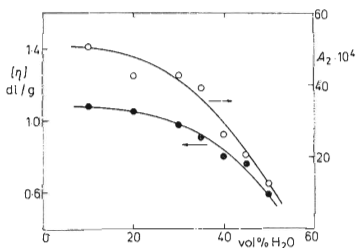

FIG. 1

Dependence of Intrinsic Viscosity $[\eta]$ (●) and of Second Virial Coefficient A_2 (○) of Sample D on the TFP/Water Composition
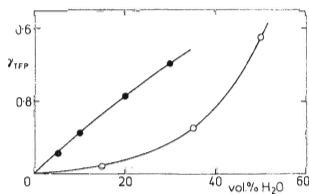

FIG. 2

Selective Sorption Coefficient of TFP (γ_{TFP}) on Polypyrrolidone (○) and Polycaprolactam[4] (●) from the TFP/Water Mixtures

Water, vol. %:   0   15   35   50

v_c: 0·202   0·193   0·191   0·187

v_μ: 0·202   0·192   0·181   0·155

Quantitatively, this sorption can be expressed as the so-called selective sorption coefficient $\gamma = (v_\mu - v_c)/v_\phi$ where v_ϕ is the refractive index increment of the better solvent in the absence of the polymer ($v_\phi = -0.021$). Compared to polycaprolactam[4], polypyrrolidone binds considerably less TFP in mixtures with less than 40 vol. % water (Fig. 2). This means that water is by far a weaker precipitant for polypyrrolidone than for polycaprolactam, which is in agreement with the data on the pronounced sorption of moisture on polypyrrolidone in the solid state[5]. The increased sorption of moisture on polypyrrolidone is assigned to a higher frequency of the —CO—NH—

Fig. 3

Selective Sorption Coefficient of Lithium. Chloride (γ_{LiCL}) on Polypyrrolidone (○) and Polycaprolactam[4] (●) from the Mixtures TFP/LiCl Depending on the Molarity M of Lithium Chloride
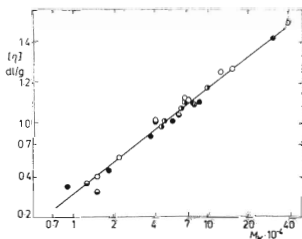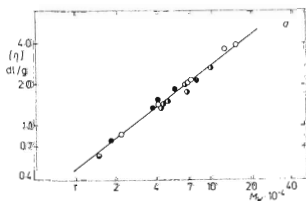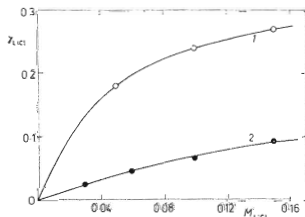

Fig. 4

Dependence of Intrinsic Viscosity of Polypyrrolidone on Molecular Weight *a*) in *m*-Cresol, *b*) in the Mixture TFP/10 vol. % Water

Unfractionated samples (◑), fractions of samples A (◐), C (●), E (○).

groups in the polyamide chain. Assuming a relatively strong complex bond between some salts and the above groups[4,6], one may expect that these salts will be more strongly sorbed on polypyrrolidone than on polycaprolactam. The markedly different selective sorption coefficients of lithium chloride from the mixtures with TFP (again obtained from the dialysis and differential refractometry data) for both polymers fully corroborate this statement (Fig. 3).

Relationship between Intrinsic Viscosity and Molecular Weight

To determine the constants of the Mark-Houwink equation $[\eta] = KM^a$ we measured the molecular weights of a number of unfractionated samples and their fractions by the light scattering method in the mixed solvent TFP/50 vol. % water, and also determined their intrinsic viscosities in *m*-cresol and in the mixed solvent TFP/10 vol % water. The plots log $[\eta]$ *vs* log M_w for both solvents (Figs 4*a, b*) are linear. The
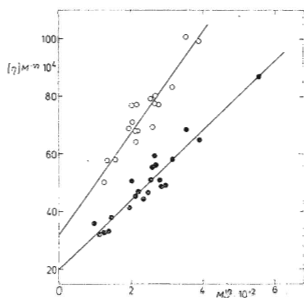
Fig. 5

Determination of the Constant K_0 of Poly-pyrrolidone in *m*-Cresol (●) and in the Mixture TFP/10 vol. % Water (○)

TABLE I

Comparison of Molecular Characteristics of Polypyrrolidone and Polycaprolactam
K, a constants of the Mark-Houwink equation, K_0 calculated from Berry's relationship[7].

Polymer	*m*-Cresol			TEP/10 vol. % Water		
	a	$K \cdot 10^4$	$K_0 \cdot 10^4$	a	$K \cdot 10^4$	$K_0 \cdot 10^4$
Polypyrrolidone	0·77	3·98	22·8	0·78	1·80	14·3
Polycaprolactam[a]	0·74	5·26	26	0·76	3·42	20

[a] *Cf.* ref.[8].

fact that the experimental points for unfractionated samples and fractions fit the same lines is apparently due to the very good thermodynamic quality of both solvents and consequently, to a small difference between the weight and viscometric average molecular weights.

From the molecular weight and intrinsic viscosity in both solvents we calculated the constants K_0 by using Berry's relationship[7] (Fig. 5)

$$[\eta]/M^{1/2} = 1 \cdot 4 \, K_0 + C M^{1/2}$$

and compared them, together with the constants of the Mark-Houwink equation, with analogous data for polycaprolactam[4,8] (Table I). The values obtained in the mixed solvents TFP/water and TFP/water/lithium chloride may be compared, because the presence of lithium chloride leaves unaffected the intrinsic viscosity of both polypyrrolidone and polycaprolactam.

Table I allows the following conclusions to be drawn: _1)_ both solvents are thermo-dynamically better for polypyrrolidone than for polycaprolactam (higher values of the exponent _a_); _2)_ the unperturbed dimensions (K_0 being their measure) of poly-pyrrolidone are smaller in the given solvent than those of polycaprolactam; _3)_ the K_0 values for both polymers are higher in _m_-cresol than in the mixture TFP/10 vol. % water (or with 0·1M lithium chloride), which is in accord with the assumed dependence of unperturbed dimensions on the dielectric constant of the solvent[8].

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