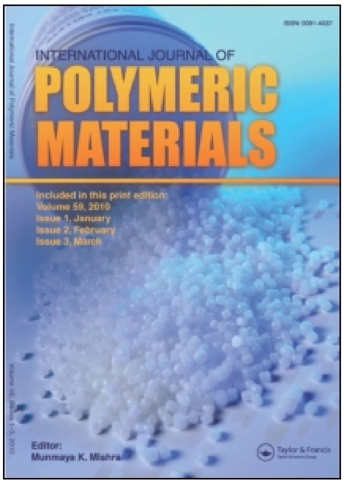

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The Temperature Dependence of the Peculiar Behaviour of Poly(N-vinyl-2-pyrrolidone) in Water. Specific Effect or Conformational Transition?

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Intrinsic viscosity [η], measurements in water at different temperatures were carried out for one fraction of poly(vinylpyrrolidone) (PVP). An anomalous behaviour of [η] at 30°C is observed. The shape of the plot of [η] vs T seems to indicate that PVP undergoes a peculiar change in water. Values of the partial specific compressibility (LC) for PVP at various temperatures are compared with the intrinsic viscosity results. This anomalous behaviour of [η], can be interpreted in terms of the different amount of hydration and the break of water structure with temperature obtained through the LC values for PVP as function of temperature.

Keywords: Poly(N-vinyl 2-pyrrolidone); conformational transition; thermal effects; solution properties; water

INTRODUCTION

A mumber of results about the conformational transitions in polymer chains in dilute solution have been described [1–15]. Reiss and Benoit reported in 1961 a conformational transition of poly(styrene) in dilute solution [1] which could be tentatively linked to the existence of a helix-like ordered conformation at low temperatures and a more random one at higher temperatures. This hypothesis was later challenged because a conformational transition was also found in the dimer [16] which is unable to form helical structures. The transition was then attributed to an increase in the rotational freedom of the phenyl groups at higher temperatures. A similar transition observed in poly (α-methylstyrene) was explained in terms of a correlation between the rotational motion of the skeletal bonds and that of the lateral phenyl groups [3].

A conformational transition was reported for the poly(*p*-tert-butylstyrene) (PtBS/toluene) system in the vicinity of 30°C. This transition was observed via both [η] and dn/dc determinations. No evidence of a conformational transition was observed by Mays *et al.* [17] in the same system. This peculiar case is one example of how conflictive is this aspect. Recently, Hadjichristidis *et al.* [18] have observed no evidence of a number of conformational transitions for flexible polymers in solutions reported in the literature. Undoubtedly, the observed phenomena show that some conformational transitions do exist for some homopolymers dissolved in a single solvent, provided the solvation power with regard to the chain is low enough. As Dondos and coworkers stated a long time ago, well solvating solvents not allow any of some helical sequences forming [4, 11].

In this communication we present a peculiar effect of temperature on the intrinsic viscosity [η] of poly(N-vinyl-2-pyrrolidone) (PVP) in water. Comparisons are made with previously published data about the partial specific compressibility of the same polymer.

EXPERIMENTAL METHODS

Viscometric measurements. The viscosities were measured with a Desreux-Bischoff dilution viscometer. The intrinsic viscosities [η] were determined according to the classical Huggins equation by plotting $\eta sp/c$ versus concentrations, *c*, and extrapolating to zero concentrations. They were obtained with an accuracy of the order of 1%. The temperature range investigated was 20°C to 45°C in water.

Poly(N-vinyl-2-pyrrolidone) was obtained by radical polymerization in bulk at 50°C using, α,α'-azobisobutyronitrile as initiator under N_2. The sample selected for this study has been the F_2 fraction with a weight-average molecular weight $\bar{M}_w = 2.6 \times 10^5$.

RESULTS AND DISCUSSION

The intrinsic viscosities [η] and their dependence on the temperature for the polymer fraction F_2 in water are shown in Figure 1. The form of this curve seems to indicate that F_2 undergoes some special change in water. An anomalous behaviour of the intrinsic viscosity [η] (coil volume) occurs about 30°C.

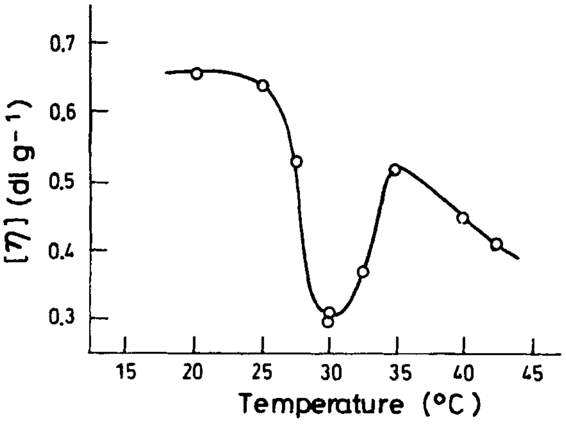

FIGURE 1 Variation of the intrinsic viscosity [η] with temperature for fraction F_2 of PVP in water.

Some years ago, it has been shown that, in the study on the solution properties of high polymers, the compressibility of the solution can be used as a valuable parameter. The data of the compressibility of a dilute solution were extrapolated to an infinite dilution to give a quantity which limits the partial specific compressibility (LC). So far the "LC" values of some polymers as poly(vinyl acetate), [19, 20] poly(styrene) [21] and dextran [22] have been determined under various conditions. The LC of dextran in aqueous solution was negative as a result of the hydration and the amount of hydration water was estimated from the LC value.

The LC of poly(N-vinyl-2-pyrrolidone) (PVP) was determined at various temperatures by ultrasonic velocity measurements. The details of the experimental procedure have been reported [19, 21]. The PVP used for LC determinations was a commercial product, PVP K-30, the molecular weight was 0.4×10^5. The experimental results taken from Reference 23 are summarized in Table I, where k_1 is the compressibility of the solvent, $\bar{v}_{20}$, the partial specific volume of the solute at infinite dilution; $\bar{k}_{20}$, the LC, defined by:

$$\bar{k}_{20} = \left(\frac{1}{\bar{v}_{20}}\right)\left(\frac{\partial v_2}{\partial p}\right)_0 \qquad (1)$$

ω, is the amount of hydration, and [η], the intrinsic viscosity.

In the Table I, it should be noted that the LC increases from a negative value to a positive with the rise in temperature. The negative value of LC can be ascribed to the hydration [22]. The amount of hydration decreases

TABLE 1 Compressibility of the solvent, k_1, partial specific volume of the polymer at infinite dilution, $\bar{v}_{20}$, the LC, $\bar{k}_{20}$, the amount of hydration, ω and the intrinsic viscosity $[\eta]$ for PVP fraction at different temperatures

T°C	$k_1 \times 10^{12}$ *cm²/dyne*	$\bar{v}_{20}$ *cm³/g*	$\bar{k}_{20} \times 10^{12}$ *cm²/dyne*	ω *cm³/g*	$[\eta]$ *cm³/g*
5	49.14	0.783	− 18.2	0.458	24.5
15	46.53	0.793	− 8.2	0.230	24.5
25	44.84	0.794	− 1.1	0.033	24.5
35	43.57	0.806	8.1		21.8
45	42.81	0.808	20.7		23.5
55	42.40	0.821	24.0		25.5

with the increases in temperature, as in the case of sucrose [24] and dextran [22], as a result of the exothermic nature of the hydration process.

It is interesting to observe that the LC value becomes positive above 30°C and also $[\eta]$ decreases, although it is not a remarkable variation because the PVP fraction has a molecular weight smaller (0.4×10^5) than the PVP fraction F_2 shown in Figure 1 (2.6×10^5).

The increasing in temperature breaks the structure of water to some extent, and at the same time it reduces the amount of hydration. According to the explanation from Nomura *et al.* [23] the behaviour of dehydrated bare molecules of PVP becomes similar to that of a synthetic chain polymer, such as polystyrene in an organic solvent, and the LC value becomes positive.

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