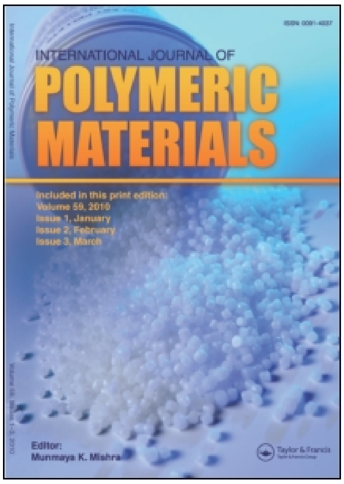

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# Viscosity Behaviour of Dilute and Moderately Concentrated Solutions. 1. Poly(vinylpyrrolidone) in 2-propanol

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# Viscosity Behaviour of Dilute and Moderately Concentrated Solutions.
# 1. Poly(vinylpyrrolidone) in 2-propanol

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The zero-shear viscosity of dilute to moderately concentrated poly(vinylpyrrolidone) solutions in 2-propanol were measured at different temperatures in the newtonian flow range. The viscosity data were analyzed in terms of Martin's and Fedor's equations. The viscosity-concentration data were generalized in terms of reduced variables. The relation between the $K_M$ parameter for the rheological interaction and some characteristics of polymer solutions such as the flexibility of the PVP chain is discussed. The temperature dependence of viscosities was expressed by the Arrhenius-Frenkel-Eyring equation and the activation energy of viscous flow of polymer solutions ($\Delta Gv$) was calculated. It was shown that $\Delta Gv$ increases with concentration and it is independent of the temperature.

KEY WORDS Zero-shear viscosity, master curve, Martin's constant, free energy activation, viscous flow

## INTRODUCTION

The zero-shear viscosity, $\eta_0$, is one of the parameters describing the rheological properties of polymer solutions or melts in the linear region of deformation and is also a complex function of many interacting variables: molecular structure ($k$), molecular weight ($M$), concentration ($C$), solvent ($S$), and temperature ($T$).[1]

Physical chemists have been interested in the dilute polymer solutions for molecular characterization, where interpolymer interaction may be considered as absent or only incipient. However in industrial applications, chemists and engineers are interested in systems of moderated to high concentrations or melts.

In dilute solutions the intrinsic viscosity $[\eta]$, depends directly on chain dimensions. At moderated concentrations the viscosity is primarily controlled by the extent of coil overlap as characterized by the product ($C[\eta]$). At high concentrations, the effect of chain entanglements, which are partly responsible of causing changes in chain dimensions, became important.[2]

A number of methods for correlating $\eta_0$ with $k$, $M$, $C$, $S$ and $T$, have been devised to describe the viscosity of dilute to moderately concentrated polymer solutions and master curves including these variables have been developed.[3]

A literature survey reveals that poly(vinylpyrrolidone) (PVP) has been studied extensively. Particularly its complexing ability towards many types of small-molecules. Its unperturbed dimensions in pure solvents (water and 2-propanol) and in binary mixtures (water/acetone, $CHCl_3$/acetone and $Na_2SO_4$/water 0.55 M) have been reported together with the rigidity factor $\sigma$ value.[4]

Poly(vinylpyrrolidone) (PVP) has been the subject of numerous reviews and general surveys.[5,6,7] From the scientific viewpoint, PVP is interesting because it presents an amphiphilic character since it contains a highly polar amide groups, and also apolar methylene and methyne groups in the backbone and the ring. PVP is also interesting from biological view point, since it has structural features similar to those of proteins.[8] Because its use in different kind of pharmaceutical formulations and in practical applications, we have considered important to know the viscometric behaviour of this polymer in different experimental conditions.

In the present work, the zero-shear viscosity of dilute to moderately concentrated solutions of poly(vinylpyrrolidone) (PVP), in 2-propanol at temperature ranging from 10° to 50°C in the newtonian flow range has been studied in order to analyze the influence of these variables.

The data obtained are treated according to Martin's and Fedor's classical equations and the temperature dependence of viscosity has been examined in the light of the Arrhenius-Frenkel-Eyring equation.[9,10]

## EXPERIMENTAL

Two commercial samples of PVP, K-30, $M_w$: 40.000 and K-90, $M_w$: 360.000 from Aldrich Chemical Co., were studied in this work.

The zero-shear viscosity of 2-propanol solutions of both fractions of PVP were determined in a Brookfield Digital Viscometer Model DV-II at concentrations from 0.25 to 18.0 g/dL and temperature ranging from 10 to 50°C.

The intrinsic viscosity $[\eta]$ were determined in a flow-capillary viscometer of the Desreux-Bischoff type at concentrations from 0.25 to 1.0 $g/dL^{-1}$ at the same temperatures.

## RESULTS AND DISCUSSION

### Effect of the Concentration

The relevant data of zero-shear viscosities of PVP solutions of varying concentrations and temperature in 2-propanol are listed in Table I for the fractions studied.

It is seen from Table I that for a particular temperature, the viscosity increases with the concentration and for a particular concentration it decreases with increasing temperature as has been reported for other polymers.[11,12]

TABLE I

Zero-shear viscosity ($\eta_0$) of PVP in 2-propanol solutions in function of the concentration at different temperatures for two fractions

| | $\eta_0$ (centipoises) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C | 10° | | 20° | | 25° | | 30° | | 40° | | 50° | |
| (g dL$^{-1}$) | K-30 | K-90 | K-30 | K-90 | K-30 | K-90 | K-30 | K-90 | K-30 | K-90 | K-30 | K-90 |
| 4.00 | - | 73.3 | - | 49.8 | - | 41.1 | - | 35.2 | - | 25.8 | - | 18.9 |
| 6.00 | 13.6 | 162 | 9.61 | 109 | 7.8 | 90.6 | 6.7 | 76.8 | 5.2 | 55.1 | - | 41.4 |
| 8.00 | 19.2 | 319 | 13.2 | 209 | 11.0 | 172 | 9.31 | 144 | 6.9 | 109 | 5.1 | 82.5 |
| 10.00 | 26.1 | 558 | 17.7 | 361 | 14.8 | 299 | 12.4 | 247 | 9.3 | 174 | 7.0 | 126 |
| 12.00 | 35.4 | 929 | 23.7 | 598 | 19.7 | 484 | 16.4 | 401 | 12.3 | 284 | 9.0 | 207 |
| 14.00 | 47.1 | 1360 | 30.9 | 854 | 25.9 | 688 | 21.4 | 568 | 15.7 | 384 | 11.2 | 304 |
| 16.00 | 61.1 | 2270 | 39.1 | 1400 | 32.6 | 1120 | 27.4 | 915 | 19.4 | 621 | 14.2 | 431 |
| 18.00 | 76.8 | - | 48.3 | - | 39.4 | - | 33.6 | - | 23.7 | - | 16.9 | - |

The zero-shear viscosity-concentration data were analyzed according to the parameters of the well known Martin's equation

$$\ln(\eta_{sp}/C) = \ln[\eta] + K_M C[\eta] \tag{1}$$

where $\eta_{sp}$ is the specific viscosity, $C$ the concentration (in $g$ dL$^{-1}$), $[\eta]$ is the intrinsic viscosity (in $g$ dL$^{-1}$) and $K_M$ is the Martin's constant, a typical parameter of the polymer-solvent pair which has been considered as an adjustable one or in the same way as the Huggins's constant. This relation was found to be linear, as is shown in Figure 1 over the whole concentration range studied for the two PVP fractions. These data were also analyzed according to Fedor's equation, which is given by Equation (2):

$$\frac{1}{2}(\eta r^{1/2} - 1) = \frac{1}{[\eta]C} - \frac{1}{[\eta]C_m} \tag{2}$$

where $\eta_r$ is the relative viscosity and $C_m$, Fedor's constant.

The values of $[\eta]$ obtained from Martin's and Fedor's equations are in very good agreement and they decrease with increasing in temperature as it is normally observed.

## Reduced Variables

The usual method of generalization of experimental results for different polymer systems consists in using reduced variables. In the case of the viscosity-concentration data this parameter is the product $(C[\eta])$,[13] the product of the volume concentration $C$ (in $g$ dL$^{-1}$) multiplied by the intrinsic viscosity $[\eta]$ (in dL $g^{-1}$) as a reduced variable where the reduced viscosity function can be defined by Equation 3.

$$\tilde{\eta} = \eta_{sp}/(C[\eta]) = (\eta_0 - \eta_0^s)/\eta_0^s C[\eta] \tag{3}$$

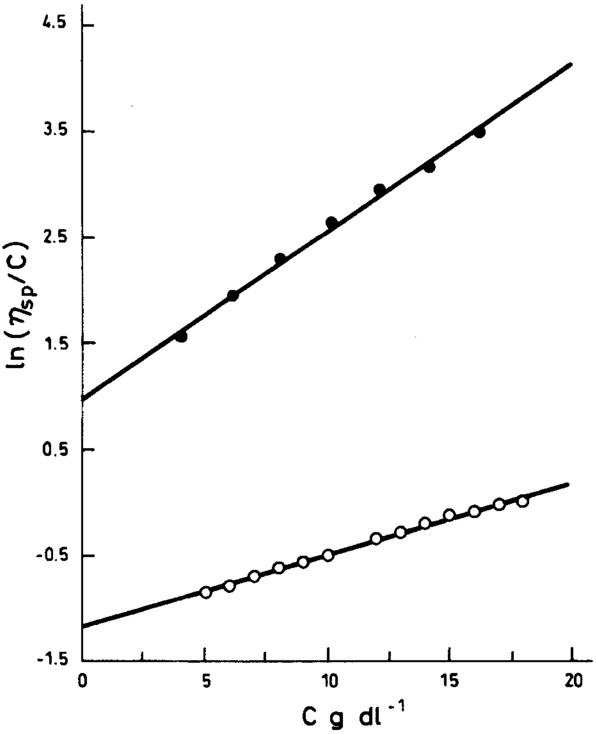

FIGURE 1 Plots $\ln(\eta_{sp}/C)$ vs. $C$ for PVP K-90 (●) and PVP K-30 (○) in 2-propanol at concentrations from 5.0 to 18.0 g dL$^{-1}$ at 298 K.

where $\eta_0^s$ is the solvent viscosity, $\eta_0$ is the zero-shear viscosity of the polymer solution. According to Drewal *et al.*,[3] the value of $\tilde{\eta}$ tends to unity as $C \rightarrow 0$, and thus it gives a common starting point for all systems.

Plots based on the viscosity-concentration data of 2-propanol PVP solutions over the entire set of experimental conditions are shown in Figure 2. Examination of these plots reveals that the points corresponding to each set of experimental conditions fall in separated lines. The differences in the shape of the dependence of $\tilde{\eta}$ on $C[\eta]$ is connected to a great extent with the effect of the temperature on the nature of the intermolecular interactions. Then, from the rheological point of view, the coefficient characterizing the concentration dependence of the viscosity can serve as a quantitative measure of these interactions.[3] The other problem is to know in what extent the interaction in dilute solutions determines the behaviour of concentrated solutions. We must consider to measure of this interaction. As it is evident from Figure 2, the experimental relations of $\tilde{\eta}$ and $(C[\eta])$ are satisfactorily described by the Martin equation over a rather wide range of the parameter.

The analysis of these values shows that $K_M$ is a function of the polymer molecular weight, concentration and temperature, therefore, it may be considered as an adjustable parameter. When it is used to normalize the dimensionless concentration $(C[\eta])$, it allows to obtain a master curve which represents the viscometric behaviour of the polymer solution in the whole range of concentration studied and, this curve is independent of the polymer molecular weight and temperature.

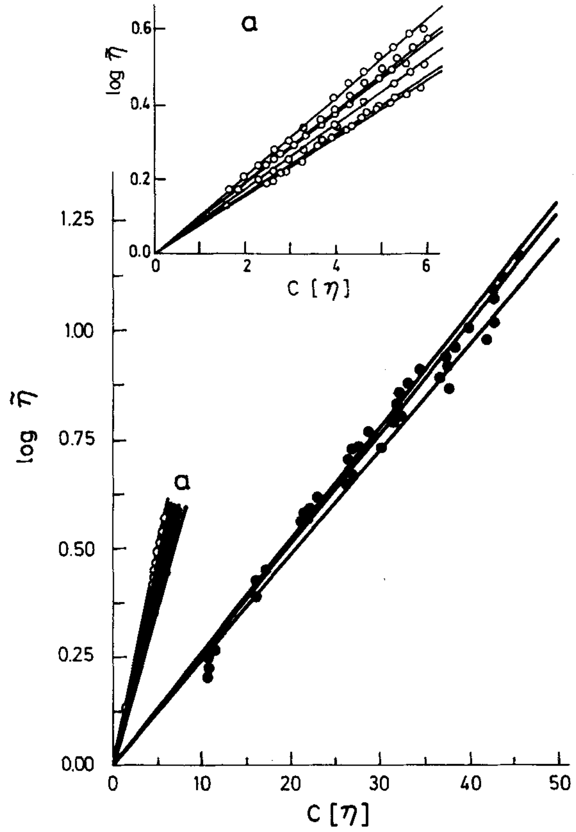

FIGURE 2 Plots log $\tilde{\eta}$ vs. $C[\eta]$ for PVK K-90 (●) and PVP K-30 (○) at concentrations from 4.0 to 16.0 g $dL^{-1}$ in 2-propanol at temperatures ranging from 10 to 50°C. (a) Plot log $\tilde{\eta}$ vs. $C[\eta]$ for PVP K-30 concentrations from 5.0 to 18.0 g $dL^{-1}$ in 2-propanol at temperatures ranging from 10 to 50°C.

The normalization of the dimensionless concentration ($C[\eta]$) with the Martin's constant, $K_M$, reduces all the experimental results obtained for PVP in 2-propanol to a master curve, as shown in Figure 3. Similar master curves for various polymers in different solvents have been reported.[3,11,12]

From Figure 3 it is seen that the value of Martin's constant, $K_M$, characterizes the influence of the solvent and temperature on the viscosity not only in dilute solutions but over the whole range of concentration. Thus, the parameter $K_M C[\eta]$, derived from Martin equation, determines the viscometric behaviour of PVP solutions in the whole range of concentrations studied.

We have tried to correlate $K_M$ with thermodynamic and conformational characteristics of the poly(vinylpyrrolidone). Dreval *et al.*[3] have established a correlation between $K_M$ and the expansion factor for a polymer coil in a dilute solution $\alpha_\eta^3$, defined by $\alpha_\eta^3 = [\eta]/[\eta]_\theta$, where $[\eta]_\theta$ is the intrinsic viscosity in a theta-solvent. Figure 4 shows this correlation taken from literature,[3] in which we have inserted our $K_M - \alpha_\eta^3$ value for PVP in 2-propanol.

For PVP K-90 in 2-propanol, we have found $K_M$ value equal 0.10. If we take a

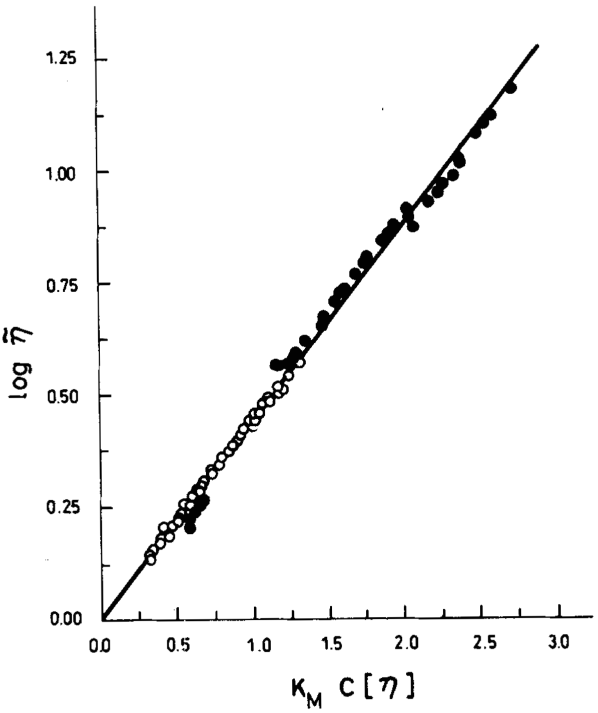

FIGURE 3 Plots log $\tilde{\eta}$ vs. $K_MC[\eta]$ for PVP K-30 (○) and PVP K-90 (●) at concentrations from 4.0 to 18.0 g $dL^{-1}$ in 2-propanol at temperatures from 10 to 50°C.

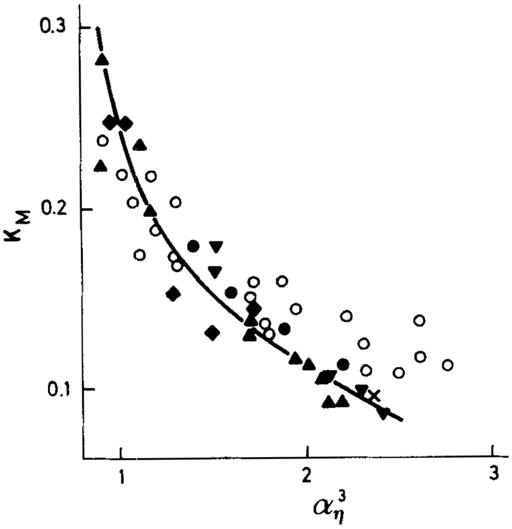

FIGURE 4 Plot of $K_M$ vs. $\alpha_\eta^3$ for: (●) polydimethyl siloxane, (▲) polyisobutene, (■) polystyrene, (▼) poly(vinylacetate); (○) data of Bohdanecký[14] for polyisobutylene and polystyrene, and (×) poly(vinylpyrrolidone) (this work).

$\alpha_\eta^3$ value for K-90 in 2-propanol 2.19 from reference (4), it is observed that our experimental data correlates nicely with the data for other polymers shown in Figure 4.

There is also a correlation between $K_M$ and the parameter $\sigma$ characterizing the polymer chain flexibility defined by:

$$\sigma = \frac{\langle r^2 \rangle_0^{1/2}}{\langle r^2 \rangle_{0f}^{1/2}} \tag{4}$$

and the energy of intermolecular interactions.

Figure 5 shows the correlation found between the $\sigma$ values and the contribution of the entropy to the rheological constant $K_M$ when energy interactions are excluded ($K_{M,0}$) for four polymers, taken from Reference 3.

The $\sigma$ value of PVP was taken from a previous work about the unperturbed dimensions of PVP in 2-propanol.[4] We can see that a decrease in chain flexibility of the polymer is accompanied by an increase in $K_{M,0}$.

From this $\sigma$ value, we found 11.5 as the $K_{M,0}^{-1}$ value for PVP ($K_{M,0} = 0.087$) obtained from Figure 5. If we compare the $K_M$ and $K_{M,0}$ values (0.10 and 0.087, respectively) we can conclude that an increase in the energy of intermolecular interactions gives rise to a higher $K_M$ value.

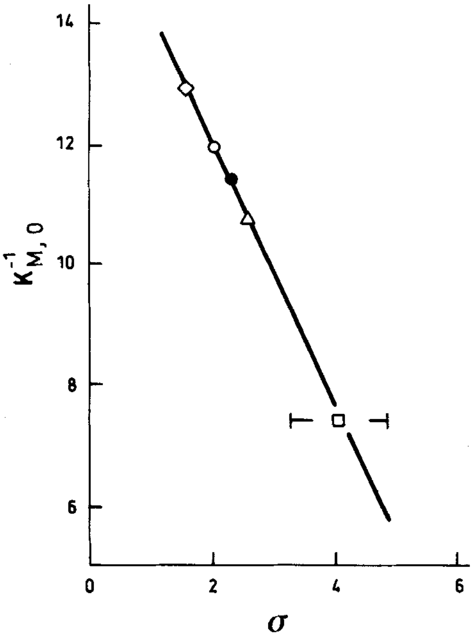

FIGURE 5 Plot of $K_{M,0}^{-1}$ (at $\chi_1 = 0$) vs. $\sigma$ for: (◇) polydimethylsiloxane, (○) polyisobutylene, (△) polystyrene, (□) cellulose acetate and (●) poly(vinylpyrrolidone) (this work). This figure was also taken from 3.

## Effect of Temperature

The temperature dependence of viscosity can be expressed by the Arrhenius-Frenkel-Eyring equation

$$\eta_0 = Ae^{\Delta Gv/RT} \tag{5}$$

where $\Delta Gv$ is the free energy activation for viscous flow and $A$ is the preexponential factor.[9,10]

The plots of ln $\eta_0$ vs. $(1/T)$ are found to be linear for PVP solutions of different concentrations as shown Figure 6 for PVP K-90, the slope and intercept yielding

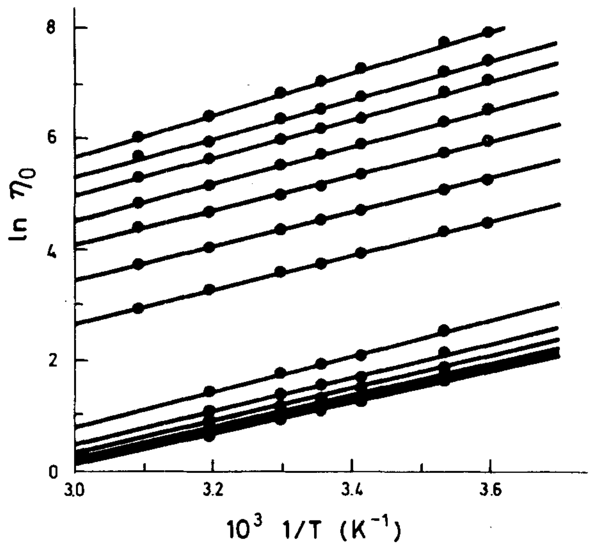

FIGURE 6 Plots ln $\eta_0$ vs. 1/T of PVP K-90 at concentrations from 0.25 to 16.0 g $dL^{-1}$ in 2-propanol.

TABLE II

Activation free energy values of viscosity flow ($\Delta Gv$) for PVP K-90 in 2-propanol at different temperatures and concentrations

| T/K | $\Delta G_v$ [kcal $mol^{-1}$] | | | | | | |
|---|---|---|---|---|---|---|---|
| | 4.00 g $dL^{-1}$ | 6.00 g $dL^{-1}$ | 8.00 g $dL^{-1}$ | 10.00 g $dL^{-1}$ | 12.00 g $dL^{-1}$ | 14.00 g $dL^{-1}$ | 16.00 g $dL^{-1}$ |
| 278 | 2.55 | 2.59 | 2.60 | 2.80 | 2.86 | 2.91 | 3.12 |
| 283 | 2.55 | 2.59 | 2.59 | 2.80 | 2.86 | 2.91 | 3.12 |
| 293 | 2.54 | 2.58 | 2.58 | 2.80 | 2.85 | 2.90 | 3.11 |
| 298 | 2.54 | 2.58 | 2.58 | 2.80 | 2.85 | 2.90 | 3.11 |
| 303 | 2.55 | 2.58 | 2.58 | 2.80 | 2.85 | 2.90 | 3.12 |
| 313 | 2.55 | 2.58 | 2.59 | 2.80 | 2.85 | 2.90 | 3.12 |
| 323 | 2.55 | 2.59 | 2.60 | 2.80 | 2.86 | 2.89 | 3.12 |

$\Delta Gv$ and $A$, respectively. These parameters are functions of the solvent, concentration and molecular weight of the polymer.

The Arrhenius-Frenkel-Eyring equation can be rearranged as Equation (6),

$$\Delta Gv = 2.303\mathrm{RT}(\log \eta_0 - \log A) \tag{6}$$

Thus, it can be used to calculate the values of $\Delta Gv$ if the zero-shear viscosities are known. The activation free energy of viscous flow, $\Delta Gv$, for the PVP-2PrOH systems were calculated and the results are listed in Table II. Similar results have been reported for other polymers.[2,11,12]

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## References

1. K. S. Gandhi and M. C. Williams, *J. Polym. Sci. Part C*, **35**, 211–234 (1971).
2. V. K. Sinha, K. H. Patel and H. C. Trivedi, *Angew. Makromol. Chem.*, **157**, 31–41 (1988).
3. V. E. Drewal, A. Y. Malkin and G. O. Botvinnik, *J. Polym. Sci., Polym. Phys. Ed.*, **11**, 1055–1076 (1988).
4. R. Meza and L. Gargallo, *Eur. Polym. J.*, **13**, 235 (1977).
5. D. A. Tomalia, *N-Vinylpyrrolidone, in Functional Monomers: Their Preparation, Polymerization, and Application*, Yocum, R. H. and Myquist, E. B., Eds., Marcel Dekker, New York, Vol. 2, 1974, p. 132.
6. I. Greenfield, *Ind. Chem.*, **32**, 11 (1956).
7. P. Molyneux, *Water-Soluble Synthetic Polymers: Properties and Behavior*, CRC Press, Inc., Vol. 1, 1987, p. 146.
8. B. Jorgensons, *J. Polym. Sci.*, **8**, 519 (1952).
9. J. Nizette, N. Hadjichristidis and V. Desreux, *Eur. Polym. J.*, **13**, 41–45 (1977).
10. M. Liouni, C. Touloupis and N. Hadjichristidis, *Eur. Polym. J.*, **26**, 479–483 (1990).
11. B. K. Patel, V. K. Sinha, K. K. Makhija, A. Ray and H. C. Trivedi, *J. Macromol. Sci., Phys.*, **B29(4)**, 397–409 (1990).
12. P. P. Shah and P. H. Parsania, *J. Macromol. Sci. Phys.*, **B23(4–6)**, 363–372 (1984–85).
13. P. Debye, *J. Chem. Phys.*, **14**, 636–639 (1946).
14. M. Bodhanecký, *Coll. Czech. Chem. Commun.*, **35**, 1972 (1970).