Degradation Kinetics of Poly(N-Vinyl-2-Pyrrolidone) by Persulphate Anion in Aqueous Solutions

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ABSTRACT

A kinetic study was achieved for poly(N-vinyl-2-pyrrolidone) (PVP) aqueous solutions in presence of persulphate anion by viscometry. At a low and fixed concentration of persulphate, various viscometric magnitudes were evaluated on the basis of specific viscosity, logarithmic viscosity and intrinsic viscosity. These values showed a decreasing trend with time and temperature. During the first few hours of the reaction period a levelling off was observed for the curves at 293, 298 and 303 K for various polymer concentrations. Kinetics of the reaction was followed by employing intrinsic viscosity values with respect to progressing time as an indirect measure of concentration from which degradation kinetics was found to be first order reaction yielding rate constants, k, for 3 different polymer concentrations (2.00, 2.29, 2.67 g/dL⁻¹) at varying temperatures of 293, 298 and 303 K, respectively. Finally, activation energies of degradation were determined as 21.5, 25.3, and 39.2 kJ/mol⁻¹ at increasing polymer concentrations. The results obtained from the kinetics of the reaction imply strongly, the probability of chain scission and/or degradation in the polymer chain by the persulphate anion in aqueous solutions.

Key Words: poly(N-vinyl-2-pyrrolidone), aqueous solutions, persulphate containing PVP solutions, degradation kinetics

INTRODUCTION

The dynamics and thermodynamic behaviour of poly(N-vinyl-2-pyrrolidone), PVP, in presence of inorganic salts have been studied previously [1–3] and no significant changes, capable of affecting the structure of the polymeric chain by anions in aqueous solutions, have been observed. Persulphate anion is being widely used with the purpose of initiating polymerization. However, it is known from literature that this anion exhibits a distinguished behaviour than the other ions.

Thermal decomposition of persulphate anion in aqueous solution yields two different species, one being persulphate ion radical and the latter being hydroxyl radical. It has been previously reported that
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these species abstract a hydrogen atom from the polymer molecule, consequently resulting in changes in the structure/hydrodynamic volume of the polymer chain [4]. These changes may be interpreted both by chain scission and/or intramolecular cross-linking leading to a decrease in the hydrodynamic volume of the polymer molecule [5]. Obviously, in presence of oxygen, macroradicals may decay by oxidative degradation, again resulting in chain scission.

In the related studies, it has been reported that cross-linking may occur only at high persulphate concentrations [6,7]. However, no interpretation is present for studies achieved at low persulphate concentrations involving only the first few hours of the experimentation period.

The aim of this work is to determine the behaviour of PVP aqueous solutions in presence of persulphate employed at low concentrations and to provide an interpretation to the kinetics and changes occurring in the structure of polymer chain. The facility and sensitivity of viscometric method have made it preferably available for the hydrodynamic volume measurements of the polymer in solution.

EXPERIMENTAL

Poly(N-vinyl-2-pyrrolidone) (PVP), used in this study, was purchased from BDH with nominal molecular weight of 700,000 g mol⁻¹. The weight average molecular weight, Mw, was determined from light scattering measurements in chloroform at room temperature. A Brice-Phoenix light scattering photometer, 2000 Series was used for measuring the Rayleigh ratios of the polymer solutions where a high-pressure mercury lamp (AH-3), 85 W, was employed as a light source of vertically unpolarized light at 436 nm wavelength. The evaluation of the data was achieved by the Zimm method expressed in the general form:

\[ \frac{K_{\theta}}{R_0} = \frac{1}{M_w} \left[ 1 + \left( \frac{16 \pi^2}{3 \lambda^2} \right) \langle s^2 \rangle_{z} \sin^2 \theta/2 \right] + 2 A_2 c + \ldots \]  

(1)

The refractive index increment value, dn/dc, of the polymer in chloroform was taken as 0.108 mL g⁻¹ [8]. The weight average molecular weight of the PVP sample, M_w, was calculated as 548,000 g mol⁻¹.

K₂S₂O₈ was obtained from Merck and used without further purification. Viscosity measurements were achieved by an Ubbelohde type capillary viscometer at 293, 298 and 303 K in a constant water bath of sensitivity at ±0.1 °C. The solutions were prepared at 4.00% constant persulphate concentration and varying polymer concentrations of 2.00, 2.29 and 2.67 g dL⁻¹, respectively, in double distilled deionized water.

RESULTS AND DISCUSSION

Viscometry is the simplest and most useful tool for the measurement of hydrodynamic volume of the polymers in solution which yields precise and accurate results [9-11]. It is a known fact that the role of solution concentration is very important in PVP-persulphate aqueous solutions, both for PVP and persulphate individually.

In this work, persulphate concentration was kept constant at 4.00 % since an increase in persulphate concentration resulted in the formation of insoluble polymer fragments in solution which gave rise to difficulties during viscosity measurements. It is quite obvious that a decrease in polymer concentration will cause a decrease in viscosity values due to the dilution of polymer molecules in a huge volume of solvent thus decreasing the probability of hydrogen bonding between PVP and water.

However, intrinsic viscosity values remain unchanged with dilution of the polymer solution, although in presence of persulphate a decrease is expected since the persulphate anion will tend to break the present hydrogen bonds penetrating into the polymer chain. On the other hand, it should be kept in mind that persulphate is a negative ion which has the ability to destroy the hydrogen bonds of water as well while the resulting species may very well interact with the polymer chain.

Specific viscosity, η_sp, and logarithmic viscosity, \( \ln \eta_s \), are two basic parameters which yield polymer
hydrodynamic volume specifically, being a function of temperature, pH and solution composition (polymer, and the amount of additive).

Intrinsic viscosity value is normally independent of time and no variation should be observed by progressing time for a polymer solution. However, in our case, one should be aware of the fact that the considered polymer solution contains the persulfate anion where a probable chain scission and/or degradation of the polymer chain is occurring, thus, it is quite expected that intrinsic viscosities will change with time due to the reaction taking place between the PVP chain and persulfate anion.

Figures 1 and 2 demonstrate the specific viscosity and logarithmic relative viscosity values versus time plots at constant persulfate concentration for varying polymer concentrations. As can be clearly noticed, viscosity values tend to decrease with time. Similarly, a levelling off for the curves can be observed with increasing temperature. Although a large number of studies exists in literature involving the determination of dynamic, thermodynamic properties and conformational changes of various other systems in solution by viscometry, no previous work has been reported on the nature and kinetics of the reaction involving PVP aqueous solutions in presence of persulfate anion until now. This fact has been investigated by our group for the reaction occurring in the first few hours of the reaction period and on the basis of intrinsic viscosity data (which is an indirect measure of concentration) with progressing time.

Variation of specific viscosity and relative viscosity with temperature and solution concentration has already been observed, however, these two parameters do not adequately explain the change in hydrodynamic volume of the polymer chain in solution. Thus, another important parameter, intrinsic viscosity, the intrinsic viscosity, is required to interpret the chain scission/degradation in the polymer chain kinetically.

Several equations exist in literature for evaluating the intrinsic viscosity, [η], values. Among them, Solomon-Ciuta Equation is being widely used which depends on one point measurement.

\[
[\eta] = 2(\eta_sp - \ln \eta_r)^{1/2}/C
\]  

(2)

Intrinsic viscosity values have been subsequently calculated by substituting the \( \eta_sp \) and \( \ln \eta_r \) values determined from viscometric measurements into the eqn (2) at various concentrations and temperatures.

Figure 3 displays the variation of intrinsic

![Graph](image-url)

Figure 1. Variation of specific viscosity with time, at different temperatures and polymer concentrations.
viscosity plotted as ln [η] versus time yielding straight lines with high correlation coefficients. Degradation kinetics has been found to follow first order reaction kinetics with regard to these curves.

Rate constants have been calculated from the slope of the straight lines in ln[η] versus time plots and consequently ln k versus 1/T graphs (Figure 4) have been employed to determine the activation energies of degradation at various solution concentrations of 2.00, 2.29, and 2.67 gdl⁻¹ found as 21.5, 25.3, and 39.2 kJmol⁻¹, respectively. The reason for ending up with three different activation energies may be interpreted by the change in hydrodynamic volume of the polymer chain with increasing polymer concentration and taking into account the reaction going on between the persulphate anion and PVP chain.

At low polymer concentrations, the polymer coil

![Figure 2. Variation of ln [relative viscosity] with time, at different temperatures and polymer concentrations.](image)

![Figure 3. Variation of ln [intrinsic viscosity] with time, at different concentrations and temperatures.](image)
is extended thus, the persulphate anion finds way easily to penetrate into the polymer chain to achieve degradation and/or chain scission. As a result, the obtained activation energy is lower. At higher polymer concentration the coil tends to contract due to the increased amount of hydrogen bonds formed between the polymer segments and solvent molecules, not allowing the penetration of the persulphate anion into the polymer chain for degradation. Since the task of entering into the PVP chain becomes much more difficult for the persulphate anion, the activation energy required for the degradation increases accordingly.

At higher concentrations and temperatures, no significant decrease was obtained for intrinsic viscosity values and even a slight increase was observed since chain segments approached nearer to each other, indicating the initiation of cross-linking or gelation in the polymer chain.

In this work, all experiments were carried out in presence of oxygen leading to a decrease in intrinsic viscosity values implying that chain scission is occurring both by the persulphate anion and oxygen present in the reaction medium. However, latter studies have shown that experiments achieved under vacuum result in no significant decrease in intrinsic viscosity values but vice versa in a slight increase indicating a tendency for cross-linking started due to the absence of oxygen radicals.

CONCLUSION

In this study, degradation kinetics of PVP by the persulphate anion was investigated at a fixed persulphate concentration and various polymer concentrations and temperatures employing the first few hours of the reaction period. It has been reported in literature that degradation of PVP by persulphate may either result in chain scission or oxidative degradation leading to cross-linking but no work has been reported involving the effects of increased solution composition, temperature and the presence of oxygen in the reaction medium. These three important facts were investigated in detail by our group and it was concluded that in presence of oxygen, at increasing solution concentrations and temperatures, intrinsic viscosity values showed a decreasing tendency implying that persulphate anion achieved degradation most probably by chain scission in the polymeric chain. However, after a certain threshold value of polymer composition and temperature, this trend was almost reversed to an increasing tendency of the intrinsic viscosities due to the decay of oxygen radicals consumed in the medium, leading to the cross-linking or gelation of PVP which is under current investigation of our research group as a future prospect.
REFERENCES


