The properties of weak solutions of N-vinylpyrrolidone and methyl methacrylate copolymers in dimethylformamide

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Summary

The rheology of solutions of N-vinylpyrrolidone and methyl methacrylate copolymers in dimethylformamide in the temperature range 20–35°C was studied. The influence of temperature and of the molecular weight and composition of the copolymers on their interaction with the solvent was shown, expressed quantitatively in terms of intrinsic viscosity, the Huggins constant, and the mean square distance between the ends of the macromolecular chains.

The creation of new functional materials based on different copolymers modified with macrocyclic compounds (MHCCs) remains an urgent and challenging problem. The immobilisation on a polymer support of compounds having a certain functional activity that is imparted to the finished material makes it possible to produce polymers with the necessary combination of properties [1]. From this viewpoint, a great deal of attention is being paid to copolymers of N-vinylpyrrolidone (VP), which are widely used in different areas of science, engineering, and medicine [2]. The reactivity and complexing capacity of N-vinylpyrrolidone make it possible to fix MHCCs on the polymer support. To develop procedures for synthesising and investigating functional materials based on tetrapyrrole MHCCs, information is required about the properties of their macromolecules: conformations, configurations, and the molecular weight and rheological characteristics.

Copolymers based on VP are contained in a large number of drugs, act as carriers of biologically active substances, and form the base material for separating membranes, sorbents, coagulants, flocculants, and so on. MHCCs, in particular porphyrins and their metal complexes, are of interest as the base for the creation of materials of this kind with catalytic, optical, sensory, and other properties [3].

Recently, researchers have paid a great deal of attention to the copolymerisation of VP, as this reaction makes it possible broadly to modify the properties of PVP. The copolymerisation of VP with a number of monomers differing in structure – with styrene, with vinyl acetate, and with diethylaminomethyl methacrylate – has now been studied [2, 4, 5]. By comparison with most vinyl monomers, VP is less active in copolymerisation reactions. The medium has a considerable influence on the activity of VP in copolymerisation reactions. The presence in the VP molecule of conjugation between the unshared electron pair of nitrogen, the double bond, and the carbonyl group makes it possible during copolymerisation to control to a significant degree the activity of the systems being copolymerised by using solvents of different nature and to produce polymers with high compositional homogeneity by copolymerisation with monomers, even monomers differing significantly in reactivity from N-vinylpyrrolidone (styrene, vinyl acetate, methacrylic acid) [5]. As all these processes proceed most effectively in organic solvents, it is expedient first of all to study the properties of copolymer solutions.

A certain amount of experience has been gained [6–11] in studying the properties of weak solutions of homopolymers of styrene, methyl acrylate, methyl methacrylate, and glycidyl methacrylate and solutions
of copolymers of styrene with different comonomers: 
acrylate, allyl alcohol, acrylic acid, and oxidized methacrylate, and also with 4-vinylpyridine, and so on. 
In a continuation of these investigations, in this work we 
studied copolymers of N-vinylpyrrolidone and methyl 
acrylate (I) obtained by suspension polymerisation 
using the standard procedure [12]:

![Chemical structure of copolymer](image)

The solvent of the polymers was dimethylformamide 
(DMF), which is most widely used as the medium for 
immobilisation of MHCCs [13]. The extremely poor 
solubility of the copolymers in solvents such as water, 
ethyl alcohol, toluene, isopropanol, chloroform, and 
tetrahydrofuran must be noted. The aim was to investigate 
the behaviour of the copolymers in a DMF solution and 
to determine the main characteristics of the polymers in 
weak solutions, namely their intrinsic viscosity, $[\eta]$, and 
Huggins constant, $K_H$, which make it possible to assess 
the hydrodynamic resistance to flow and the interaction of 
the polymer and solvent, and the mean square distance 
between the ends of the macromolecular chains, $(h^2)^{3/2}$.

The molecular weight obtained and rheological 
characteristics of N-vinylpyrrolidone and methyl 
acrylate copolymers synthesised by suspension 
copolymerisation are presented in Table 1.

With an increase in temperature, the values of $[\eta]$ 
decrease for all the copolymers (Table 1). The copolymers 
given in DMF form systems with a lower critical solution 
temperature (LCST), the macromolecular coil decreases 
with increase in temperature, and the hydrodynamic 
resistance to flow falls [14] (Figure 1).

A similar effect is observed for polystyrene and for 
styrene and vinylpyridine copolymers in DMF and toluene 
[15]. An effect of this kind naturally depends both on the 
composition of the copolymer and on the solvent. Thus, 
styrene and methyl methacrylate copolymers in DMF 
form systems with an upper critical solution temperature 
(UCST) [9].

As all the investigated copolymers possess different 
molecular weights, it is extremely difficult to compare

<table>
<thead>
<tr>
<th>Specimen number</th>
<th>Composition of initial blend (composition of copolymer)</th>
<th>Molecular weight, amu</th>
<th>Temperature, °C</th>
<th>Intrinsic viscosity $[\eta]$</th>
<th>$[\eta] = \ln \eta_{rel} / c$</th>
<th>$K_H$</th>
<th>$(h^2)^{3/2} \times 10^{-17}$, m²</th>
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values of $[\eta]$ and the composition of the solvent. Therefore, it is expedient to consider a specific index that takes into account the molecular weight of the polymer, i.e. $[\eta]/M$, where $M$ is the molecular weight of the copolymer. Accordingly, $[\eta]/M = f(\text{VP content})$ dependences were obtained in this work (see Figure 2).

As indicated by the results obtained, the introduction into the composition of a copolymer with methyl methacrylate of a fairly large amount of vinylpyrrolidone (20–70%) leads to a very small change in the $[\eta]/M$ values.

It is likely that vinylpyrrolidone has a very weak effect on loosening (compression) of a nominal segment of a macromolecule of the copolymers. However, note that some comonomers of styrene, for example methyl acrylate [9], behave in the opposite manner.

According to data given by Usacheva et al. [15], systems with an LCST separate out into layers when they are heated. One of the reasons for the appearance of an LCST may be the rupture, during heating, of the hydrogen or donor–acceptor bonds promoting the original formation of the solution. The rupture of these bonds has an adverse effect on the compatibility of the components. A second reason for the appearance of an LCST is the difference in the coefficients of volume expansion of the polymer and solvent. During heating, the solvent expands more strongly, compressing the macromolecules and promoting the formation of associates with their subsequent precipitation into a new phase. In this case, the LCST normally lies above the boiling point of the solvent but below its critical temperature [15].

As the determination of the intrinsic viscosity, $[\eta]$, of a polymer solution by the dilution method is a fairly laborious and drawn-out process, a number of researchers have proposed different mathematical expressions making it possible to calculate $[\eta]$ from the value of the relative viscosity, $\eta_{rel}$, determined for a solution of the same concentration [16]. It is considered that the most accurate value of $[\eta]$ can be obtained by means of the formula:

$$[\eta] = \frac{\ln \eta_{rel}}{c}$$

In this work, $[\eta]$ values calculated by means of this formula are given (Table 1). Calculations show that, for all copolymers, the formula derived gives considerably higher $[\eta]$ values, with an error of the order of 30%. Thus, the use of the proposed formula for determining the value of $[\eta]$ for the same concentration of the given copolymers is unacceptable.

It is well known that $[\eta]$ and $K_H$ are connected by an inversely proportional relationship. As expected, in the present cases, with reduction in $[\eta]$ the values of $K_H$ increase with increase in temperature (Table 1). That is, owing to compression of the macromolecular coil, the interaction of its segments with each other increases, and in our view it is this factor, the Huggins constant, $K_H$, that is responsible for this parameter.

An informative quantitative index of the properties of weak solutions of copolymers is the size of the macromolecular coil, which is assessed from the mean square distance between the ends of the chain, $\langle h^2 \rangle^{3/2}$.

The parameter given depends on the temperature, the composition of the copolymer, and the molecular weight. The temperature dependence of $\langle h^2 \rangle^{3/2}$ correlates entirely with the change in $[\eta]$ and is consistent with the ideas set out above. In order to identify which factor – the composition of the copolymer or its molecular weight – makes the greater contribution to the parameter $\langle h^2 \rangle^{3/2}$, it is expedient to present a specific index that takes into account the molecular weight of the polymer, i.e. $\langle h^2 \rangle^{3/2}$, where $M$ is the molecular weight of the polymer, as a function of the composition of the copolymer (Figure 3).
It should be noted that the composition of the copolymer makes a considerable contribution to the magnitude of the mean square distance between the ends of the macromolecular chains.

On the basis of the data obtained, it can be stated that the parameter \( \langle h^2 \rangle^{3/2} \) is similar to data obtained for copolymers of styrene and methyl methacrylate and styrene and 2- and 4-vinylpyridines [9, 15].

Thus, the conducted investigations of N-vinylpyrrolidone and methyl methacrylate copolymers, namely of the behaviour of their macromolecular coils, showed the quantitative dependence of the rheological characteristics (\([\eta]\), \(K_H\), \(\langle h^2 \rangle^{3/2}\)) on the composition of the copolymer, its molecular weight, and temperature.

**EXPERIMENTAL**

N-Vinylpyrrolidone and methyl methacrylate copolymers were obtained in the presence of initiator azobisisobutyric acid by the method of suspension copolymerisation [12]. The copolymers were reprecipitated twice from DMF into water to remove residual monomer and low-molecular-weight fractions and then dried in a vacuum oven at 55°C to constant weight.

The nitrogen content was determined by elemental analysis on a FlashEA 1112 Series CHNS-0 Analyser. The composition of the copolymer was calculated from nitrogen content data and from data of titration of the ester groups [12]. The molecular weights were determined by gel permeation chromatography and from intrinsic viscosity values.

To determine the intrinsic viscosity, \([\eta]\), of the polymer solutions, the traditional procedure [17] of diluting the solution in an Ubbelohde viscometer was employed. A weighed sample of the copolymer (0.1 ± 0.0002 g) was placed in a calibrated (10 mL) pycnometer and dissolved in DMF at room temperature. The solution obtained was poured into an Ubbelohde viscometer placed in a thermostat and held for 15 min at a certain temperature (20, 25, 30, and 35°C). After each dilution, the time of discharge of the polymer solution, \(\tau_d\), was determined. On the basis of the data obtained, the following were determined:

- the relative viscosity:
  \[ \eta_0 = \frac{\tau_d}{\tau_0} \]
  where \(\tau_d\) is the discharge time of the solution at the corresponding dilution and \(\tau_0\) is the discharge time of the pure solvent.
- the specific viscosity
  \[ \eta_\text{sp} = \eta_0 - 1 \]

On the basis of the data obtained, the ratio \(\eta_\text{sp}/c\) was calculated, with concentration expressed as g/100 mL solvent. From the dependence \(\eta_\text{sp}/c = f(c)\), processed by the least-squares method, the values of the intrinsic viscosity, \([\eta]\), and the Huggins constant, \(K_H\), were obtained:

\[ K_H = \frac{tg\alpha}{[\eta]^2} \]

where \(tg\alpha\) is the slope tangent of the \(\eta_\text{sp}/c = f(c)\).

The values presented of \([\eta]\) and \(K_H\) are the averages of at least three parallel determinations. The error of determination did not exceed 3%.

**ACKNOWLEDGEMENTS**

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**REFERENCES**
