

THERMOSENSITIVE WATER–POLYMER SYSTEMS STUDIED BY LUMINESCENT SPECTROSCOPY Copolymers of N-vinylcaprolactam and N-vinylpyrrolidone

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Abstract

Thermosensitive aqueous solutions of N-vinylcaprolactam/N-vinylpyrrolidone (co)polymers were investigated by luminescent spectroscopy. Investigation of the luminescent intensity and the bound fraction of luminescence indicators interacting to the (co)polymers in water showed that the chemical structure of the water-soluble poly-N-vinylamides defines their functional and structural characteristics such as conformation, intramolecular mobility, compactization and complexation. It was established that the complexing ability of VCL-VP copolymers exceeds that of PVP even at a low content of VCL units. At 85 mol% of VCL the complexation and compactization of the macromolecules were found to be higher than that of pure PVCL. A hinge-like action of VP units incorporated in PVCL structure is suggested to be a reason of the extreme behavior observed for 85:15 VCL:VP composition.

Keywords: intramolecular mobility, luminescent spectroscopy, thermosensitive water–polymer systems

Introduction

Water-soluble carbon chain polymers with amide groups in side chains, mainly poly-N-vinylpyrrolidone (PVP) and VP copolymers, are widely used in industry, medicine, pharmacology, and biotechnology. Carriers of biologically active compounds, separating membranes, sorbents, coagulants and flocculants have been prepared on their basis [1].

Poly-N-vinylcaprolactam (PVCL) is a structural homologue of PVP having two extra methyl groups in the side chain. Aqueous solutions of PVCL, unlike those of PVP, display thermosensitive properties in the range of physiological temperatures exhibiting phase separation at 31–37°C. A peculiar feature of the phase transition is that the change in turbidity during the thermoprecipitation of PVCL proceeds in a very narrow temperature range ($\Delta T=1-1.5^\circ\text{C}$).

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It is well known that the change in a content of non-polar groups leads to a considerable change of properties of the water-soluble macromolecules. It has been reported in our previous publication [2] that VCL-VP copolymers exhibit their precipitation from aqueous solutions at higher temperatures than pure PVCL. The aim of the present work is to study the temperature induced changes in properties of VCL-VP copolymers of different composition using luminescent methods.

Luminescent spectroscopy has been found to be one of the most informative methods in studying the intramolecular structure of water-soluble polymers and their conformational transformations at heating. Briefly, these methods use luminescent ionic indicators, for instance 8-anilinoanthracene-1-sulfonic acid magnesium salt dihydrate (ANS) or acridine orange (OA), soluble in water. Change of their luminescent characteristics (intensity (I) and bounded fraction (θ)) in the presence of polymers indicates the complex formation ability of the dissolved macromolecules. Polarized luminescent spectroscopy studying relaxation times (τ) of anthracene-containing luminescent structures covalently attached to macromolecules gives information on intramolecular mobility of the polymer [3].

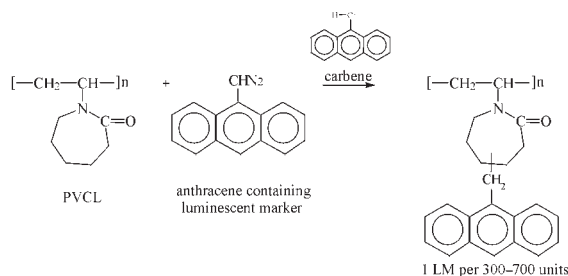
Experimental

Materials

VCL-VP copolymers containing 15, 45, 75, 80, 85, 90 and 95 mol% of VCL units and PVCL homopolymers with molecular mass of 20 000 were synthesized by free radical (co)polymerization of corresponding monomers in isopropanol at 75°C. AIBN was used as an initiator. The products were precipitated into diethyl ether and dried under vacuum at 50°C. The unreacted monomers were removed using Soxhlet extraction by diethyl ether. Copolymer composition were detected by NMR¹³C and IR spectroscopy [4].

PVP homopolymers with molecular mass of 11 000 was synthesized by free radical polymerization of VP in isopropanol at 75°C. AIBN and H₂O₂ were used as an initiator and as a molecular mass regulator, respectively.

Luminescently marked VCL-VP copolymers were obtained by chemical attachment of anthracene-containing luminescent markers (LM) to the macromolecules. For this purpose the reaction of 9-anthrylcarbene with C-H bonds of the chain or with side rings was used as it is described in [5] (Scheme 1).



Scheme 1

LM content in (co)polymers obtained by this method was 0.15–0.35 mol% (one marker per 280–700 units of the main structure). The absorption spectrum of solutions of the (co)polymers in the wavelength range of 350–4000 nm corresponds to that of compounds with 9-alkylanthracene structure.

Luminescence indicators: 8-anilinonaphtalene-1-sulfonic acid magnesium salt dihydrate and acridine orange (Fluka) were used as received.

Methods and measurements

The measurements were carried out in dilute aqueous solutions at (co)polymer concentration $2 \cdot 10^{-3}$ mol l⁻¹. Complexing ability of VCL-VP, (co)polymers was characterized by a change in luminescence intensity of ANS anions, I_{ANS} , for the complexes of the polymers with the ANS anions or by a change in the fraction of bound luminescent cations of acridine orange (AO), θ_{AO} . Investigations of the complexing ability of VCL-VP (co)polymers were carried out at ANS or AO concentrations in aqueous solutions of $2 \cdot 10^{-5}$ or $2 \cdot 10^{-6}$, respectively.

Luminescence spectra of aqueous solutions of VCL-VP copolymers with luminescent markers were measured on a LS-100 luminescent spectrophotometer (PTI company, Canada) at the excitation of luminescence with $\lambda_{\text{exc}}=365$ nm. The ANS luminescence intensity of aqueous solutions was determined at 500 nm.

The fraction of AO ions bound by the VCL-VP copolymer in an aqueous solution was determined by polarized luminescence [6] for wavelength $\lambda_{\text{lum}}=546$ nm excited by light $\lambda_{\text{lum}}=436$ nm with the aid of the Eq. (1)

$$\theta_{\text{AO}} = (P_{\text{obs}} - P_{\text{free}}) / (P_{\text{o}} - P_{\text{free}}),$$

in which P_{o} , P_{free} and P_{obs} are the values of luminescence polarization of solutions AO ions immobile (completely frozen in a viscous medium) and mobile water (in the absence of the polymer) and those of mixture of mobile and immobile ions in this polymer solution, respectively.

Relaxation times τ_{IMM} characterizing the intramolecular mobility of macromolecules in solutions were determined using the polarized luminescence at stationary light excitation [6]. (Co)polymers with covalently attached luminescent markers with the anthracene structure were used; one marker per 300–700 units of the main structure, $\lambda_{\text{exc}}=365$, $\lambda_{\text{lum}}=436$ nm.

Results and discussions

Effect of temperature on structural characteristics of VCL-VP copolymers in water

It is known that the intermolecular mobility (IMM) of the polymer chain as well as relaxation time (τ_{IMM}), being its direct characteristic, are important properties reflecting structural changes in the macromolecules [5, 6]. The increase of τ_{IMM} indicates an increase of intramolecular hindrance, which takes place with strengthening of intramolecular contacts or with an increase of their number. The increase of intramole-

cular hindrance, the τ_{IMM} value, for an individual molecule reflects its compactisation accompanied by a decrease in intramolecular mobility of the dissolved polymer.

In Fig. 1 the data on relaxation time vs. temperature for the copolymers of different compositions containing luminescent anthracene labels are present. It follows from the graph that the ' $\tau - t$ ' functions for all the copolymers and for pure PVCL has a jump indicating that their intramolecular mobility decreases significantly at heating within a narrow temperature interval. Temperature and the height of the jumps depend on the copolymer composition. Pure PVP (curve 1) demonstrates a *smooth* line where one can see that its intramolecular mobility *smoothly increases* with heating. Introduction of 15% of VCL (curve 2) first changes the slop (the mobility *decreases* with heating) and second leads to a short jump which appears at 80°C. The effect corresponds to the thermoprecipitation of the copolymer including 15 mol% of VCL links. Further increase of VCL content is followed by a decrease of the phase separation temperature and an increase of the height of the effect. At 85 mol% (curve 4) of VCL the maximum value of the ' $\tau - t$ ' function jump is observed whereas its temperature coincides exactly to that of pure PVCL (curve 3). The finding characterizes the copolymers containing 85 mol% of VCL as a system where the maximum decrease of macromolecules mobility after thermoprecipitation takes place. The decrease of the mobility is even higher than in pure PVCL.

To analyze the nature of the phenomena one should take in account the temperature behavior of PVCL and PVP homopolymers hydrated in aqueous solutions. The hydrate shells of water-soluble polymers stabilize their favorable conformations in water [7]. At heating the shells change their state. In case of PVP it leads to an increase of macromolecule flexibility and, consequently, to an increase of their intramobility (Fig. 1, curve 1). As for PVCL, it is found to form 100% syndiotactic configuration providing its favorable conformation stabilized in water by a hydrate shell consisting of two water molecules per an elementary unit [8]. Changing the hydrate shell of PVCL at heating causes the destabilizing of the favorable conformational state of the macromolecules and as a result dispersion interactions as well as di-

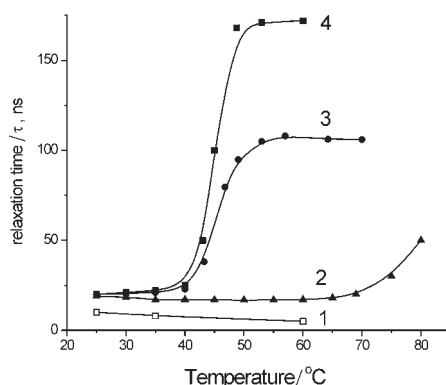


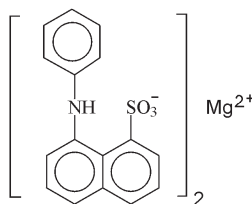
Fig. 1 τ_{IMM} vs. temperature for VCL-VP (co)polymers containing 100 (1), 85 (2), 15 (3) and 0 (4) wt% of VP links

pole-dipole ones between the caprolactam rings increase. Macromolecules form new conformations characterized by more compact structure and less number of water molecules around the polymer chain. We observe an effect of thermoprecipitation. At these conditions the intramolecular mobility decreases significantly within a narrow temperature interval inducing the jump-like increase of the relaxation time which one can see on the curves of Fig. 1.

Now let us look what happens if one incorporate 15 mol% of VP and 85 mol% of VCL into the copolymer (the maximum jump of ' $\tau - t$ ' function, curve 4). In this case 100% syndiotactic structure of PVCL is partly destroyed. From one hand it leads to deformation of the hydrate shell of PVCL and from the other hand VP units act as *hinges* which relieve the rotation mobility of the VCL consequences. At this conditions formation of more compact globules than for pure PVCL is expected. This may be the reason of the lowest intramolecular mobility of the 85:15 VCL-VP copolymer observed after the thermoprecipitation. As to the temperature of the phase separation ($T_{ph.s.}$) it does not change for the mentioned composition indicating that the stability of the hydrate shell which is responsible to the $T_{ph.s.}$ value [9] is not influenced very much. The more or less marked increase of the $T_{ph.s.}$ is observed at higher VP content (starting from 15 mol%). This effect and the decrease of the height of the jump (Fig. 1, curve 2) show that the change of the chemical structure in the copolymers results in transformations of the hydrate shell followed by higher thermostability and higher intramolecular mobility of the dissolved macromolecules.

Effect of intramolecular mobility of the VCL-VP copolymers on their interaction to ion luminescent indicator ANS

The ions of ANS (Scheme 2) exist in aqueous solutions as low luminescent hypomolecular associates. In case interaction of macromolecules to ANS ions in solution prevails the tendency to form non-luminescent associates, the macromolecular complexes with ANS ions exhibiting luminescence of high intensity are observed. Association or complexing of the ANS molecules with polymer chains reduces the moving activity of the indicator thus providing tenfold or even hundredfold increase of I_{ANS} [6]. Thus increase of I_{ANS} at polymer presence characterizes the complexing ability of the macromolecules.



Scheme 2

The change of I_{ANS} vs. composition of VCL-VP copolymers at 25°C is shown in Fig. 2. It is seen that I_{ANS} , characterizing complexing ability of the dissolved copoly-

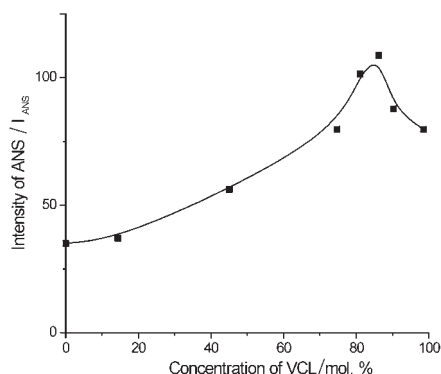


Fig. 2 Intensity of ANS vs. concentration of VCL in composition of VCL-VP copolymers

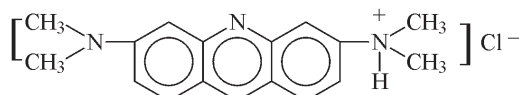
mer, increases with VCL content passing through a maximum at VCL:VP composition of 85:15. The data is in agreement with the findings on τ_{IMM} showing that the less intramolecular mobility the higher complex forming ability of the dissolved macromolecules. In other words there is a direct connection between chemical structure, conformation, intramolecular mobility and complexation of the water-soluble polymers.

Let us keep attention at the fact that the homopolymer of PVCL, being a very close homologue of PVP, nevertheless exhibits twice higher complexing ability in comparison to PVP ($I_{\text{ANS}}=78$ and 38, respectively, Fig. 2). It is clear that the two extra methylene groups in the caprolactam ring result in the unique properties of PVCL. The seven-membered caprolactam ring, unlike the five-membered pyrrolidone one, has been reported to have 'chair' as the most favorable conformation [10, 11], which induces formation of very compact globules or coils by packing syndiotactically placed 'chairs' to each other in a way of 'seat-onto-back' [1]. This feature, according to the conclusions of data in Fig. 1, enables the higher complexing ability of PVCL and VCL copolymers, in comparison to PVP (Fig. 2).

The strongest interaction of the VCL-VP macromolecules to the luminescent indicator at 25°C is observed for the composition of 85:15 (maximum in Fig. 2). It proves that the small amount of VP links acting as rotating hinges partly disturbing 100% syndiotactic conformation of VCL consequences provides the formation of more compact, in comparison to PVCL homopolymer, globules not only at $T_{\text{ph.s.}}$, but also at lower temperatures.

Temperature effect on complex forming ability of VCL-VP copolymers

The influence of temperature on the complex forming ability of VCL-VP copolymers is present in Fig. 3. AO is taken as a luminescent agent dissolved in water. Unlike ANS, dynamic properties of AO ions (Scheme 3) only manifest themselves at their rotating diffusion as a whole. As a result of the rotation diffusion characterized by nanosecond time range, which is comparable to the AO life time in the activated state,



Scheme 3

the decrease of polarization of their luminescence take place. In case AO takes part into macromolecular complex its rotating diffusion is depressed dramatically leading to an increase of the luminescent polarization. So the rise of the luminescent polarization is an indicator of binding the luminescent agent by polymer chains. The parameter can be used for the quantitative estimation of a ratio of AO (Θ_{AO}) ions included into the macromolecular complexes [6].

Figure 3 shows that at room temperature the Θ_{AO} is negligible for all the compositions. It indicates that AO forms complex neither with the homopolymers nor with the copolymers. At heating the copolymers as well as pure PVCL demonstrate increasing complexing ability with a jump at temperature of the thermoprecipitation.

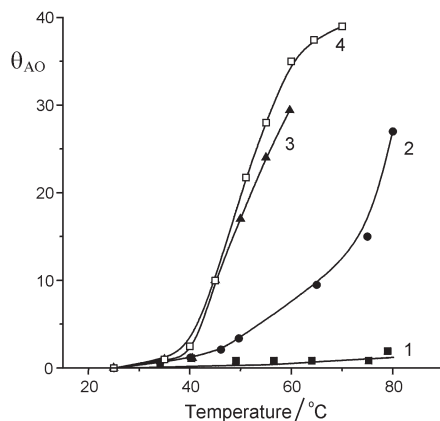


Fig. 3 Ratio of AO (Θ_{AO}) ions included into the macromolecular complexes vs. temperature for VCL-VP (co)polymers containing 100 (1), 85 (2), 15 (3) and 0 (4) wt% of VP links

It is important to note that the increase of complexation with rising temperature is not a trivial phenomenon. Just opposite, most of the water-soluble polymers, including PVP, exhibit lowering complexation at heating [12, 13]. From the data of the work it is clear that the unique behavior is induced by the progressive compactization of macromolecular structure taking place for PVCL and for its copolymers. The maximum jump of Θ_{AO} is observed for copolymers of 85:15 VCL:VP composition. It again proves our assumption about hinge-like behavior of small amount of VP links in the structure of the copolymers.

Conclusions

The analysis of the temperature induced changes in properties of PVCL, PVP and VCL-VP copolymers by luminescent spectroscopy leads to the conclusion that the chemical structure of the water-soluble poly-N-vinylamides directly defines their functional and structural characteristics such as conformation, intramolecular mobility, compactization and complexation in aqueous solutions.

Investigations of polarized luminescence allows to identify the thermoprecipitation phenomena of the VCL-VP-copolymers as a process of compactisation in macromolecule globules.

The copolymer composition (85:15 of VCL:VP), exhibiting the highest complexing ability in comparison to pure PVCL is found.

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