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Molecular Mobility, Structural Organization and Complexing Properties of Copolymer Macromolecules[1]

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SUMMARY: Intramolecular mobility, an intramolecular structure formation, and complexing properties of VP-VC (N-vinylpyrrolidone and N-vinylcaprolactame) copolymer macromolecules with a low content of the “hinge” VP units in aqueous solutions upon heating, phenol or SDS (sodium dodecyl sulfate) adding were studied by luminescence. The data obtained show that a slight modification of a polymer chain structure with the aid of the “hinge” units inclusion leads to a considerable change in structural and complexing properties of the copolymers.

Introduction

Molecular mobility of macromolecules in solution, nanosecond intramolecular mobility, IMM, is a fundamental polymer property. Macromolecular physics and chemistry are related to nanosecond mobility. IMM is a sensitive indicator of structural transformations in macromolecules$^{1)}$. IMM influences the course of chemical reactions in polymer chains$^{2)}$. These data were obtained for styrene-α-methylstyrene copolymers. It was found that the reagent —chloromethylanthracene – chooses the mobile parts of polymer chains. It means that the copolymer chains contain parts with different IMM. It is also known that the inclusion of the mobile “hinge” units into polymer chains is important for the formation of the intramolecular ternary structure in protein molecules. In order to investigate the role of “hinge” units in the polymer chains of synthetic copolymers the structural and functional characteristics of (co)polymer macromolecules were studied. For this investigation copolymers N-vinylpyrrolidone (VP) and N-vinylcaprolactame (VC) were chosen. In (VP-VC) copolymers with high content of VC units VP are “hinge” units. They are less loaded than VC units. This follows from data obtained by measuring IMM of homopolymers – poly-N- vinylpyrrolidone (PVP) and poly-N-vinylcaprolactame (PVC). The relaxation times characterizing the IMM of PVP and PVC in aqueous solution actually differ considerably – 16 and 40 ns re-

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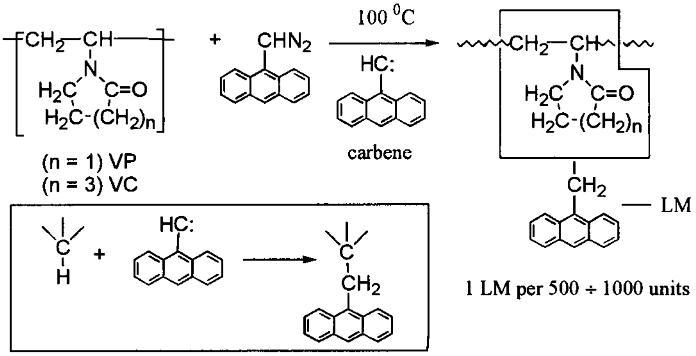
spectively. VC units are structure forming. Structure formation in aqueous PVC solutions upon heating and its influence the complexing properties of PVC were established early3, 4).

Experimental Part

VP-VC copolymers with a different composition were synthesized by method described in3). The content of VP units was varied from 5 to 85 mol.%. The effect of “hinge” units in copolymer molecules on the intramolecular structurization in aqueous solutions was studied under conditions favoring increasing hydrophobic interactions between nonpolar groups affecting a compact structure formation. The formation of an intramacromolecular structure was studied by the changes in the intramolecular mobility characterized by nanosecond relaxation times. The nanosecond relaxation times were measured using polarized luminescence at the steady state excitation and the copolymers with covalently attached luminescent markers containing anthracene groups1). Luminescently labeled (co)polymers were obtained according to scheme:



Scheme. The reaction of obtaining homo- and copolymers VP and VC with covalently attached anthracene containing luminescent groups – luminescent markers (LM).

The spectrophotometer LS-100 (PTI-Canada) was used to measure the luminescence spectra and intensity. Polarized luminescence was measured using equipment described in1). The effect of “hinge” units on functional characteristics of copolymers is represented by data characterizing the copolymer interaction with low molecular weight compounds – phenol, organic ions – Acridine Orange (AO), 8-Anilinonaphtalene –1-sulfonic acid Magnesium salt Dehydrate (ANS), Sodium dodecyl sulfate (SDS). For these compounds the molecular mechanism of their inclusion into the polymer complex was investigated in detail5, 6). For measuring the parameters of this interaction the luminescence methods were used. The part of bonded AO ions - Θ_{AO} was measured by polarized luminescence using equation (1):

$$\Theta_{AO} = (P - P_{free})/(P_0 - P_{free}) \quad (1)$$

in which P, P_{free}, P_0 – the polarization of luminescence for the investigated solution, and for free and bonded AO ions, respectively. The interaction ANS ions – copolymer was characterized by ANS luminescence intensity$^{5)}$. The interaction phenol-copolymer was characterized by the changes in ANS luminescence in a copolymer aqueous solution upon phenol adding. These investigations were carried out in aqueous solutions at the low (co)polymer concentration, $C_{pol.}$ = 0.2 mg/ml. The part of bonded SDS ions - Θ_{SDS} was measured using anthracene containing luminescently marked (co)polymers and luminescence quenching by Fe-ions bonded with SDS ions situated near anthracene groups in macromolecules. The luminescence quenching by Fe ions, the value of $q = I/I_0$, was measured at various concentrations of interacting (co)polymers and SDS ions. The values of [SDS]/[Pol] corresponding to the equal q values were determined at high ($C_{pol.\ high}$ = 1mg/ml) and low ($C_{pol.\ low}$ = 0.2 mg/ml) (co)polymer concentration at [Fe]/[Pol] = 0.1. The value of Θ_{SDS}:

$$\Theta_{SDS} = \{([SDS]/[Pol])_{C\ pol.\ high}\}/\{([SDS]/[Pol])_{C\ pol.\ low}\} \quad (2)$$

was used to characterize the interaction SDS ions-copolymer.

Results and Discussion

It was found that under conditions of increasing hydrophobic interactions of nonpolar groups in VP-VC copolymer macromolecules the intramolecular compact structure is formed. The values of nanosecond relaxation times increase sharply in a very narrow interval of the changes in structure forming factors – temperature, phenol or SDS content (Fig. 1A, 2A, 3A). The inclusion of "hinge" VP units into a polymer chain with a slight decrease in the content of "structurizing" VC units leads to the formation of a compact structure characterized by higher values of τ_{IMM} and higher density of nonpolar groups (Fig. 1A, 1B, 2A, 3A). The compact structure in copolymer macromolecules with "hinge" VP units, more perfect than that of homopolymer – PVC is formed upon heating (Fig. 1A), in the interaction with phenol (Fig. 2A), and in the interaction with SDS ions (Fig. 3A). An evidence of the formation of a compact, probably folded, structure is also increasing auramine luminescence intensity related to the compactness of intramolecular structure (Fig. 1C). The important result concerning

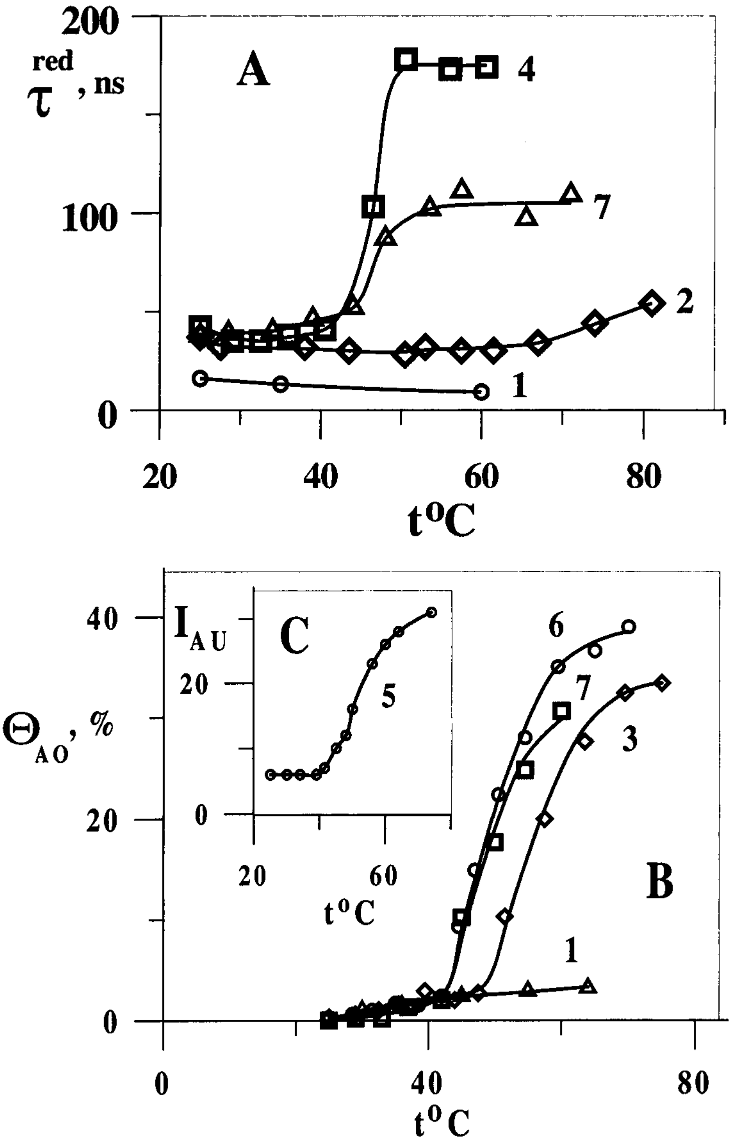


Fig. 1: τ^{red} (A), Θ_{AO} (B) and I_{AU} (C) – auramine luminescence intensity vs. temperature for VP-VC copolymers with various content of VP units (mol. %): 1 - 100; 2 - 55; 3 - 25; 4 - 15; 5 - 10; 6 - 5; 7 - 0. $\tau^{red} = \tau \cdot \eta_{red} / \eta$ (η - viscosity of the solvent). η_{red} = 0.89 cP.; C_{pol}= 0.2 mg/ml, C_{AO}= $2 \cdot 10^{-6}$ mol/l, C_{AU}= $2.5 \cdot 10^{-5}$ mol/l.

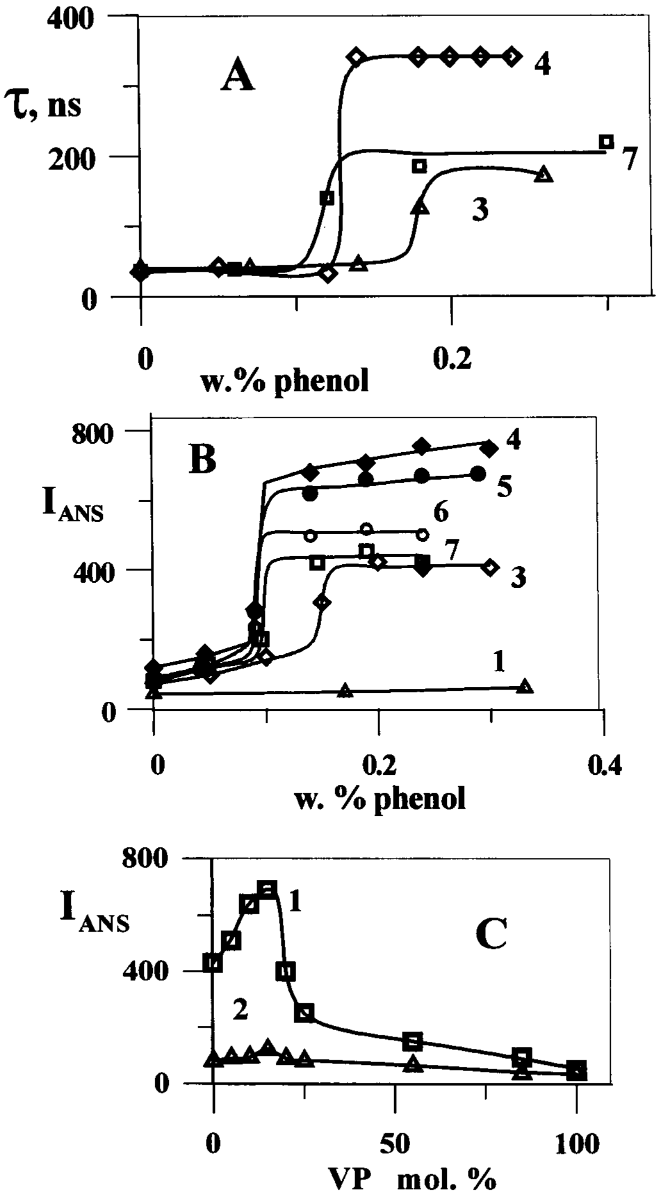


Fig. 2: τ (A) and ANS luminescence intensity – I_{ANS} (B) vs. phenol content in the aqueous solutions of VP-VC copolymers with various content of VP units (mol. %): 1 - 100; 3 - 20; 4 - 15; 5 - 10; 6 - 5; 7 - 0. C - I_{ANS} (C) vs. VP units content in VP-VC copolymers: 1 - in water-phenol (0.16 w. %); 2 – in aqueous solution. ANS concentration equal $2\cdot10^{-5}$ m/l.

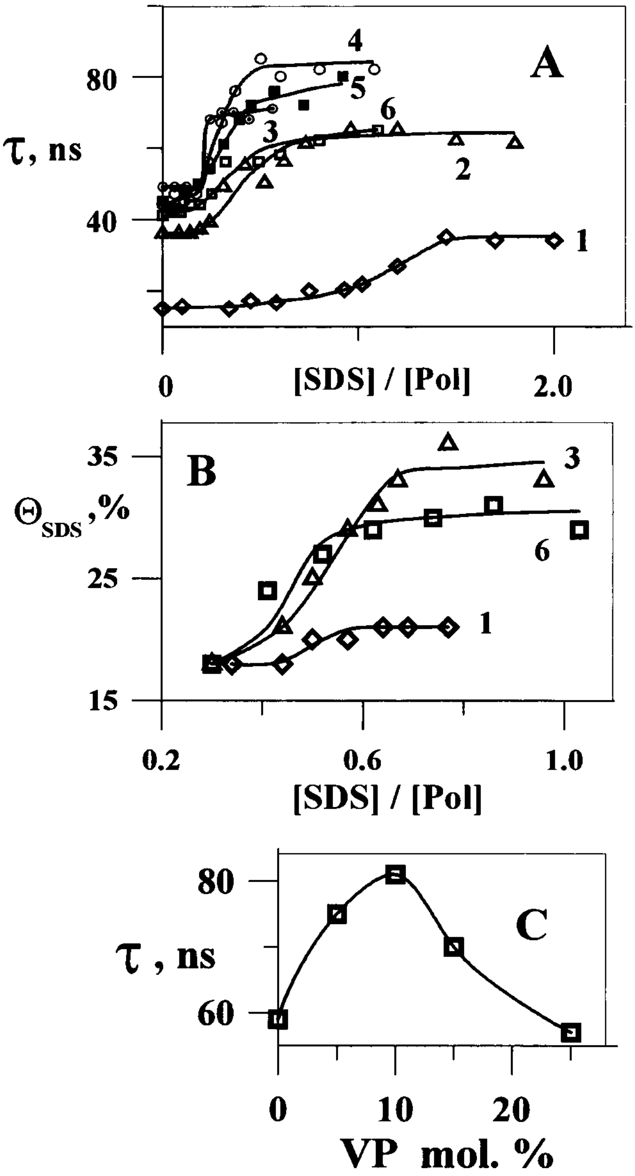


Fig. 3: τ (A) and Θ_{SDS} (B) vs. SDS concentration in aqueous solution of VP-VC copolymers with various content of VP units (mol. %): 1 – 100; 2 – 25; 3 –15; 4 – 10; 5 – 5; 6 – 0. [SDS] / [Pol] – concentrations of SDS and copolymers in moles and moles of monomers units, respectively. C - τ vs. the content of VP units in VP-VC copolymers in water-SDS solution. C_{SDS} = 265 mg/L; C_{pol} = 0.2 mg/ml.

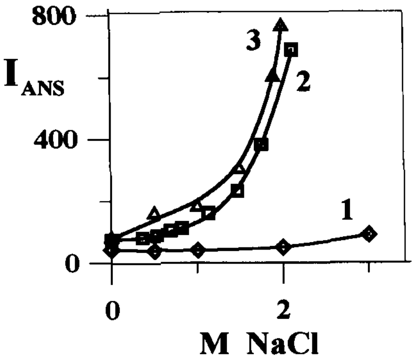


Fig. 4: I_{ANS} vs. NaCl content in aqueous solutions of 1 - PVP, 2 - PVC, 3 - (VP-VC, 5%—95%).

the (co)polymer complexing ability was also obtained. The complexing ability of the copolymers VP-VC with "hinge" VP units is greater than that of the homopolymer PVC. These data were obtained for various copolymer complexes – with AO ions, phenol and ANS ions (Fig. 2B, 2C), with SDS ions (Fig. 3B) and with ANS ions in water-salt solution (Fig. 4).

Conclusion

The above examples show that a slight modification of a polymer chain structure with the aid of a “hinge” units inclusion leads to a considerable change in structural and complexing properties of the copolymer.

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