Reversible Structure Destruction of Intramolecular Polycomplexes Formed by Poly(acrylamide) and Poly(vinyl alcohol), under Hydrodynamic Shear Flow

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SUMMARY: A set of rheologic and thermodynamic researches of diluted and semi-diluted aqueous solutions of poly(acrylamide) to poly(vinyl alcohol) grafted copolymers (PVA-PAA$_N$) forming intramolecular polycomplexes (Intra PC) by the methods of static light scattering, interferometry and rheology (for gradients of shear rate $j \leq 1312$ s^{-1}) was carried out. It is established, that the thermodynamic water quality towards the copolymers improves, when the quantity N of grafts increases, but on the whole it remains close to θ-solvent. In PVA-PAA$_N$ solutions under action of a hydrodynamic shear field two level of reversible structure destruction are shown. The first level is destruction of network of pinnings and the second one is destruction of Intra PC structure together with destroying of primary associates of copolymer macromolecules. It is shown, that the character of destruction (gradual or uneven) and its depth depend on intensity of the hydrodynamic shear field action, concentration of solution and also copolymer structure. Possible reason of reversibility of PVA-PAA$_N$ structure destruction in strong hydrodynamic fields is pointed out.

Introduction

The significant number of experimental and theoretical works is devoted to problems of behavior of polymer solutions or melts in external mechanical fields. It is conditioned by study and use of such phenomena as the change of a phase condition of polymer solution or melt in a longitudinal or shear hydrodynamic field $^{1)}$, Thoms effect $^{2)}$, effect of negative thixotropy $^{3)}$ and some others. The deformation (unfolding) of macromolecules induced by hydrodynamic field is the basis of all these phenomena. That is why the establishment of character and conditions of such transition as *macromolecular coil → unfolded chain* depending on a profile and on gradient of flow rate, became important aspect of researches$^{4-5)}$. Main attention in these works is given to solutions of linear homopolymers. At the same time, the behavior in a hydrodynamic field of macromolecules of graft copolymers, especially those having chemically complementary main and grafted chains and thus forming intramolecular polycomplexes (Intra PC), represents significant interest.

It was established, that graft copolymers of poly(acrylamide) to poly(vinyl alcohol) (PVA-PAA$_N$), which form Intra PC, show in semi-diluted aqueous solutions significant effect of negative thixotropy. At small stirring the solutions thicken or completely lose fluidity (depending on copolymer structure), however their viscosity reduce up to initial value after several hours of standing. In diluted solutions PVA-PAA$_N$ show significant Thoms effect (~60% at C~0.02 kg•m^{-3} and Re~5000) $^{6)}$. Moreover, the copolymer solutions appear steady to degrading action of strong hydrodynamic flow, as against of poly(ethylene oxide) and poly (acrylamide) solutions, which show instability in hydrodynamic fields side by side with high

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hydrodynamic activity. In present work a number of rheologic and thermodynamic researches of PVA-PAA$_N$ solutions by the methods of static light scattering, interferometry and rheology was carried out to establish the processes occurring with copolymer macromolecules of various structure in hydrodynamic shear field.

PVA-PAA$_N$ macromolecules in static conditions and in a process of flow

Synthesis of PVA-PAA$_N$ and definition of molecular weight of grafts were carried out according to Ref. 7). The quantity N of grafts and molecular weight of copolymers were determined on the data of elemental analysis and of static light scattering. The copolymer samples (Tab.1) have comparable length of grafted chains (with point of view of possible change of their properties in such range of molecular weights), but essentially various N.

Table 1. Molecular characteristics for grafted copolymer samples.

Sample	$M_{VPVA} \bullet 10^{-6}$	$M_{VPAA} \bullet 10^{-6}$	$M_{PVA\text{-}PAAN} \bullet 10^{-6}$	N
PVA-PAA$_N$1	0.08	0.12	0.12	25
PVA-PAA$_N$2	0.08	0.06	0.06	31
PVA-PAA$_N$3	0.08	0.08	0.08	49

The change N is major factor determining the change of copolymers properties in a solution. Samples 2 and 3 dissolved in water at room temperature. To dissolve completely the sample1, temperature of solution was raised up to ~353 K. Taking into account a possible change of structure and thermodynamic properties of sample 1 in solution at its heating, only samples 2 and 3 were used for researches of copolymer solutions by the method of light scattering.

The intensity of surplus scattering of vertically polarized light by copolymer solutions was measured at λ=436 nm, θ=20-160°, T=293 K. The increment of refraction index ∂n/∂C in PVA-PAA$_N$ solutions was determined by interferometry method. The example of Zimm diagram calculated on the data of light scattering is submitted in Fig.1, and the copolymers characteristics obtained from diagrams, are shown in Tab.2.

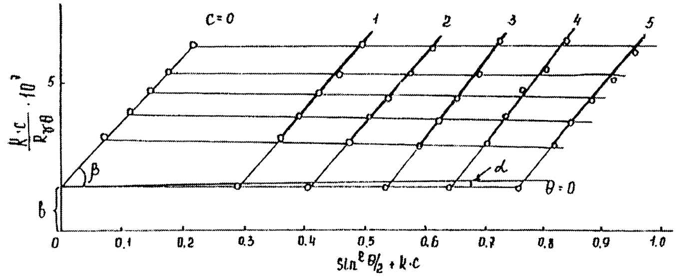


Fig. 1. Zimm diagram for PVA-PAA$_N$2, calculated for θ≤65° and C = 0,1 – 1; 0,15 – 2; 0,2 – 3; 0,25 – 4; 0,3 kg•m^{-3} – 5.

Table 2. Grafted copolymers molecular and thermodynamic characteristics, obtained by light scattering method.

Copolymer	∂n/∂C cm^3/g	M_W[a]$\bullet 10^{-6}$	$M_{PVA\text{-}PAAN} \bullet 10^{-6}$	N	Z [b]	$A_2 \bullet 10^{11}$ m^3·kmol/kg	$\langle R \rangle_z$ nm
PVA-PAA$_N$2	0,204	29,07	2,41	37	12	-2,04	362
PVA-PAA$_N$3	0,172	7,84	3,90	49	2	3,46	193

[a] Molecular weight of light scattering particles.

[b] The number of PVA-PAA$_N$ macromolecules in associate.

It is visible, that the molecular weights of scattering particles surpass essentially $M_{PVA\text{-}PAA_N}$ values found by elemental analysis (Tab.1). It means, that copolymer macromolecules even in diluted solutions are associated. Values of $M_{PVA\text{-}PAA_N}$ from Tab.1 was used to define optimum sizes N and Z (Tab.2), at which the calculated meanings of M_w particles deviated minimally from M_w particles found by light scattering method. The second virial coefficient A_2 increases with growth N, however its order testifies that the thermodynamic water quality towards to copolymers remains close to θ-solvent. This result is quite natural, as $PVA\text{-}PAA_N$ are IntraPC formed by the system of hydrogen bonds between main and grafted chains [8]) and stabilized also by H-bonds between PAA parts [8]) and hydrophobic interactions [9]). Thus, the copolymers solubility in water appreciably improves with increase N. Dissolving of the sample 1 at raised temperature and also increase A_2 and reduction Z at the transition from sample 2 to sample 3 confirm this conclusion. It is possible to believe, that such change of properties is conditioned by the reduction of quantity of H-bonds between main and grafted chains in series of copolymers, that is shown by IR spectroscopy method [10]). Really, the increase N on the main PVA chain creates the increasing spatial difficulties for it binding with PAA chains.

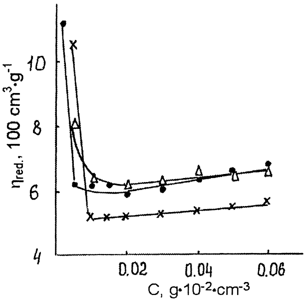


Fig. 2. The dependence of reduced viscosity from concentration for:
$PVA\text{-}PAA_N1$ – Δ,
$PVA\text{-}PAA_N2$ – • and
$PVA\text{-}PAA_N3$ – *.
T=298 K.

Concentration dependences of the reduced viscosity obtained in viscometer such as Ostwald (τ_0=94 s, T=298 K) have two characteristic sites (Fig.2). The linear sites of curves in region C>0.1 kg•m^{-3} testify to stability of molecular and supermolecular structure of copolymers in the wide area of concentrations. But values η_{sp}/C grow sharply at C<0.1 kg•m^{-3}. It can be a consequence of presence on PAA chains of small quantity of –COOH groups [8]) and also (or) Intra PC destruction under the action of gradients D of flow rate, achievable in capillary viscometer. In our case D=320 s^{-1} at C=0.1 kg•m^{-3}. $PVA\text{-}PAA_N$ hydrodynamic characteristics received by extrapolation of linear sites of curves to C=0, are shown in the left part of Tab.3. Their correlation with the data of light scattering is visible. In particular, the reduction of Huggins viscometric constant K in the series of copolymers confirms a conclusion about improvement of thermodynamic quality of water as solvent with growth N.

Table 3. Hydrodynamic parameters of grafted copolymers.

Copolymer	[η]	C* [a]	K	J* [b]	η_{j*}/η_0 [d]
	m³/kg	kg/m³		1/s	
$PVA\text{-}PAA_N1$	0,61	1,63	0,50 (0,32) [c]	146	84
$PVA\text{-}PAA_N2$	0,57	1,76	0,49	243	68
$PVA\text{-}PAA_N3$	0,51	1,96	0,30	146	100

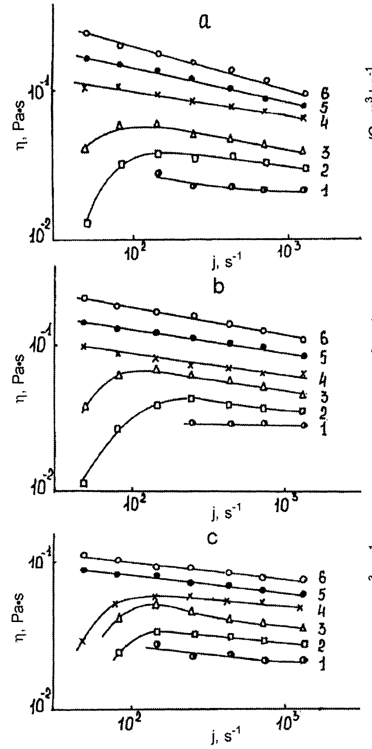
[a] The crossover concentration.

[b] The critical shear rate gradient by C=0,5 kg•m^{-3}.

[c] K values for the soluble in water part of sample 1 and for the sample 1 solution obtained at 353 K (in brackets).

[d] The value η_0 was taken from the data of viscometry.

Rheologic behavior of PVA-PAA$_N$ solutions was studied on rheoviscometer with coaxial cylinders in the field of shear rate gradients j=49-1312 s^{-1}. The ratio of cylinders diameters was equaled 1.02, T=298 K. The time of measurement of one solution made ~1 hour. As show results (Fig.3), flow curves submitted in double logarithmic coordinates, have nontraditional character.



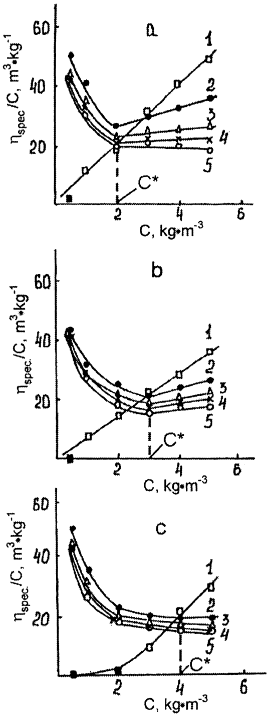


Fig. 3. The dependence of effective viscosity of PVA-PAA$_N$1 (a), PVA-PAA$_N$2 (b) and PVA-PAA$_N$3 (c) solution from the shear rate gradient by C = 0,5 – 1; 1 – 2; 2 – 3; 3 – 4; 4 – 5 and 5 kg•m^{-3} – 6.

Fig. 4. Concentration dependence of reduced viscosity of PVA-PAA$_N$1 (a), PVA-PAA$_N$2 (b) and PVA-PAA$_N$3 (c) solutions by j = 49 –1; 146 – 2; 437 – 3; 729 – 4 and 1312 s^{-1} – 5.

The typically nonneuthonian flow of solutions, but without appearance of greatest and least neuthonian viscosities, is observed in the region of relatively large concentrations (Fig.3a, b, curves 4-6, Fig.3c, curves 5-6). In the range of lower C values, which depends on a sample, the flow curves are essentially changed namely: the effective viscosity as function of j passes through a maximum, which position depends on copolymer structure (on N) and its concentration in a solution (Fig.3a, b, curves 2-3, Fig.3c, curves 2-4). At last, at C=0.5 kg•m^{-3}

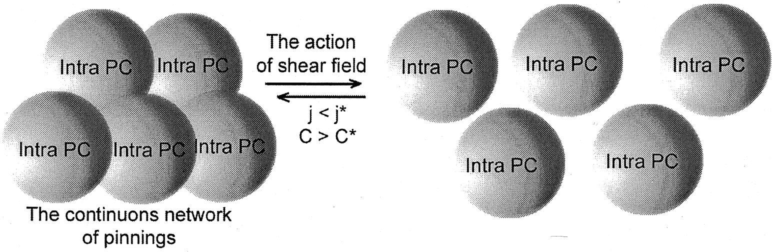
(area of diluted solutions) the value η at small j is not measured in general, as it is outside of sensitivity of rheoviscometer. However, the viscosity raises in steps in tens-hundreds times at some critical value j^* (the right part of Tab.3) and it does not vary practically at the further j increase. It is visible, that the value j^* is maximum for the sample 2. Let's note, that all flow curves were completely reversible. Besides, in the field of j values, where the viscosity gradually or in steps grew, significant fluctuations of tangential stress caused by formation of polydispersed gel particles [3)] were observed.

The effect of reversible increase of PVA-PAA$_N$ solutions viscosity with increase j testifies to display by copolymer macromolecules of viscoelastic properties as result of destruction of the intramolecular bonds system, i.e. Intra PC structure, under action of hydrodynamic field [1,3)]. According to Fig.3 and also Fig.4 constructed on the data of Fig.3, this effect is observed not only at $j>j^*$, but also at the solution concentration, smaller some critical value $C<C^*$. Thus, the character and degree of Intra PC destruction in a shear field depend on C. So, the sharp Intra PC destruction is observed at C=0.5 kg•m-3 and $j=j^*$. It is accompanied by uneven, maximal on relative size increase of solution viscosity (Tab.2, Fig.4) and reminds phase transition of the first sort [4-5)]. The Intra PC structure destruction with growth j goes gradually in the field of $0.5<C<C^*$, and the size of destruction, which can be compared to size η_{max}/η_0 (Fig.3), becomes more and more insignificant with increase C. Finally, at $C>C^*$ the shear field destroys only separate pinnings between macrocoils, but initial Intra PC structure is kept. Such behaviour of system is possible to explain by known kinetic effects at macromolecular unfolding [11)] caused by limited time of the hydrodynamic field action, high molecular weight of polymer chains and dependence of the time of large-scale relaxation of macromolecules τ_0 on C. It is impossible to consider this question more deeply, because of absence of the theory of such transition as *macromolecular coil → unfolded chains* for branched homopolymers and considered copolymers forming Intra PC. However, proceeding from the general conceptions about increase τ_0 with growth C at the expense of increase of solution viscosity and display of the pinnings effect [11)], it is possible to believe, that existence C^* in PVA-PAA$_N$ solutions is caused by sharp enough transition of copolymer macromolecules from the condition of isolated associates to the condition of continuous network of pinnings. As it is visible from Fig.4, value C^* grows with increase N. This result correlate with the change in copolymers series of the crossover concentration (Tab.3) defined as $1/[\eta]$, according the theory for linear homopolymers [4)].

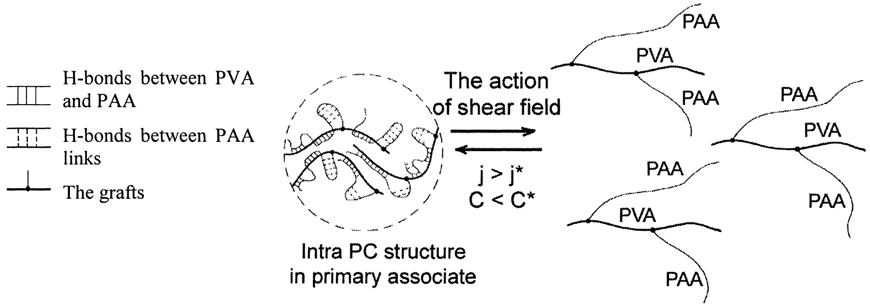
Conclusion

Thus, in PVA-PAA$_N$ solutions under action of a hydrodynamic shear field two levels of reversible structure destruction (schemes 1, 2) are shown.

Scheme 1. The destruction of continuous network of pinning.



Scheme 2. Destruction of Intra PC together with primary PVA-PAA$_N$ associate.



The character and depth of destruction depend on intensity and duration of a field action, concentration of solution and also copolymer structure. The greatest stability to influence of a hydrodynamic field is shown by macromolecules of the sample 2, in which the greatest total quantity of H-bonds between main and grafted chains and also PAA chains $^{10)}$ is revealed. Destruction of Intra PC structure proceeding together with destroying of primary associates of copolymer macromolecules, is began at low enough gradients of shear rate. It is accompanied by substantial growth of a solution viscosity, that can be used in the petroleum production technologies for the rise of oil extraction from oil containing layers. Reversibility of the PVA-PAA$_N$ structure destruction in a solution, which distinguishes such copolymers from PEO and PAA, is caused by presence of the special force returning of copolymer macromolecules in the initial condition (the condition Intra PC) after stopping of the hydrodynamic field action. Thermodynamic affinity between PVA and PAA is evidently by such "returning force".

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