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# Conformational Changes in Poly(vinyl alcohol)-*graft*-Polyacrylamide in Aqueous Solutions vs Graft Content

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**Summary:** Conformational changes have been studied in intramolecular polymer-polymer complexes (intraPC) of graft copolymers of poly(acrylamide) and poly(vinyl alcohol) (PVA-*g*-PAA) with various numbers of grafts (4-42) per molecule as a function of temperature and copolymer concentration. It is shown that the magnitude of conformational change depends on the grafts content while the temperature range over which the conformation changes occur is essentially determined by copolymer concentration. The conformational changes are reversible on heating and cooling.

**Keywords:** conformational change; graft copolymer; hydrogen bond; polymer-polymer complex; structure

## Introduction

Graft copolymers with chemically complementary main and graft chains rank among intramolecular polymer-polymer complexes (intraPC).[1] They are among the most perspective polymer materials for stabilization of dispersed systems, such as matrices in biotechnology, drug delivery in living organisms, and the like.[2,3] A number of such intraPC based on poly(vinyl alcohol)-*graft*-poly(acrylamide) (PVA-*g*-PAA) with various numbers of grafts per molecule were investigated in the present work. The formation of these intraPC occurs through H-bonds between the main and the graft chains.[3] The way the intramolecular bonds are destroyed or established is worth investigating in order to characterize the solution properties of these systems. A rise in temperature is one of the parameters which favours the breaking of H-bonds. For instance, a sharp change of intrinsic viscosity [η] is observed for similar graft copolymers in aqueous solutions when increasing temperature.[4] The disruption of H-bonds

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together with the alteration of solvent quality trigger a conformational change of the type statistical coil→ partial collapse.[4] A similar conformational transition is expected to take place in graft copolymers PVA-*g*-PAA after destruction of the intraPC structure.

## Conformational Transition of Type: IntraPC→ Main Chain Collapse

The techniques and methods used for PVA-*g*-PAA synthesis and characterization are described elsewhere.[3] Molecular parameters of graft copolymers used in this work are shown in Table 1.

Table 1. Molecular parameters of graft copolymers.

| Sample | $M_{v\,\mathrm{PAA}}\cdot 10^{-5}$ a) | $M_{v\,\mathrm{PVA}}\cdot 10^{-4}$ b) | $M_{n\,\mathrm{PVA\text{-}g\text{-}PAA}}\cdot 10^{-6}$ | $N$ c) |
|---|---|---|---|---|
| PVA-*g*-PAA1 | 11,2 | 8 | 4,8 | 4 |
| PVA-*g*-PAA2 | 3,722 | 8 | 9,385 | 25 |
| PVA-*g*-PAA3 | 2,767 | 8 | 7,828 | 28 |
| PVA-*g*-PAA4 | 1,633 | 8 | 6,939 | 42 |

a) the molecular weight of grafts determined by viscometry method

b) the molecular weight of main chain

c) the number of grafts per polymer molecule

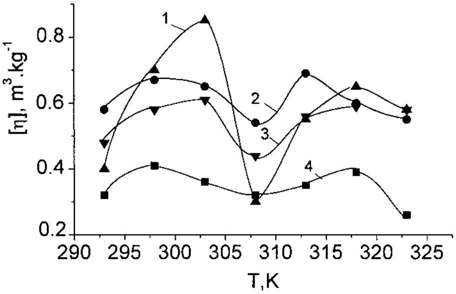

Fig. 1.Temperature dependence of intrinsic viscosity [η] for PVA-g-PAA1 (1), PVA-g-PAA2 (2), PVA-g-PAA3 (3), PVA-g-PAA4 (4).

The copolymers were characterized in dilute solution by photon correlation spectroscopy (dynamic light scattering DLS)[5] and viscometry. Viscosity of PVA-g-PAA dilute solutions was measured by means of an Ostwald type viscometer ($\tau_0$=94 s at T=298 K). The diffusion coefficient distribution was measured with Malwern 4700 automated system operating with a He-Ne laser (λ = 632 nm) at fixed angle $\theta$=90° and in the temperature range 298-313 K.

The temperature dependence of [η] for different graft copolymers is shown in Fig. 1. All the curves display a complex behavior although they all exhibit a minimum at $T$=308 K which would correspond to the conformational change arising from the breaking of H-bonds within the intraPC structure. The increase in [η] on further heating is ascribed to solvent quality.

DLS gives additional support to this assumption. We have investigated, using this technique, dilute PVA-*g*-PAA1 solutions characterized by the most important drop in [η] (Fig. 1, curve 1). Dynamic light scattering allows to measure the autocorrelation function $g(\tau)$, which is expressed through:

$$g(\tau) = \mathrm{B}\left[a\left(\int_0^\infty A(\Gamma(\exp(\Gamma\tau)\mathrm{d}\Gamma)\right)^2 + 1\right] \qquad (1)$$

The experiments were carried out at a fixed scattering angle ($\theta$= 90°) which corresponds to $q$=0.0187 nm$^{-1}$ ($q=[4\pi n\ \sin\theta/2)]/\lambda$). Equation 1 was solved by using the cumulants method, developed by Koppel.[6] Our results show the occurrence of two relaxation modes ($\Gamma_1$ slow and $\Gamma_2$ fast) (see Fig. 2).

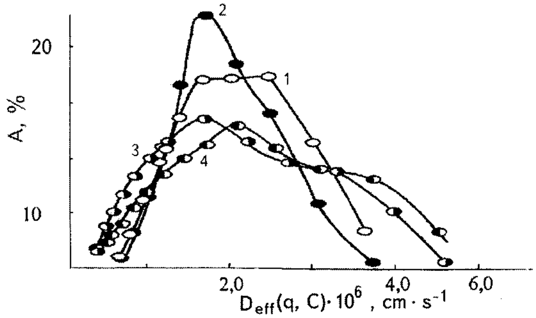

Fig. 2. Distribution of the diffusion coefficients for PVA-*g*-PAA1. $C$=0.4 kg·m$^{-3}$. $T$=298 K(1), 303 K (2), 308 K(3), 313 K (4).

As the PVA-*g*-PAA copolymers possess a narrow molecular weight distribution, high structure rigidity in water, and a sufficiently large hydrodynamic radius ($R_h$=262 nm[3]) which yields $qR_g$>1,[7] the fast and the slow decay rates can be written;[7]

$$\Gamma_1 = D_t q^2 \quad \text{and} \quad \Gamma_2 = D_t q^2 + 6D_r \qquad (2)$$

in which $D_t$ and $D_r$ are the coefficients of translational and rotational diffusion, respectively.

Slow and fast modes are well expressed and overlapped at 298 K. Increasing temperature to 303 K causes a considerable change in the distribution curve of diffusion coefficients (Fig. 2, curve 2, Table 2). It is well known that the increase in $[\eta]$ (Fig. 1, curve 1), while no aggregation occurs, is associated with enhancement of molecule asymmetry or swelling. We suspect that the increase in $[\eta]$ for PVA-*g*-PAA1 arises from swelling of the macrocoils. This is consistent with the non-variation of $D_t$ with $T$ together with a decrease in $D_r$ and of the corresponding scattering (Fig. 2, curve 2, Table 2).

The reason for such sharp swelling of polymer PVA-*g*-PAA1 in a narrow temperature range $298\ K < T < 303\ K$ is , most probably, related to the destruction of the intramolecular H-bonds between main and graft chains, while other H-bonds within the macromolecules (cis-trans-multimers of amide groups) are rather temperature-resistant.[1]

Table 2. Diffusion coefficients for PVA-*g*-PAA1.

| $T$ | $D^t_{eff}\cdot 10^{10}$ | $D^r_{eff}\cdot 10^{-3}$ |
|---|---|---|
| K | $m\cdot s^{-1}$ | $s^{-1}$ |
| 298 | 1.8 | 3.5 |
| 303 | 1.7 | 2.6 |
| 308 | 1.7 | 8.2 |
| 313 | 2.1 | 7.4 |

Increasing the temperature to 308 K produces a sharp drop in $[\eta]$ (Fig. 1, curve 1) and a major change in the distribution curve of $D$. (Fig. 2, curve 3, Table 2). The fact that $D_t$ remains practically invariable while $D_r$ increases quite dramatically suggests the formation of compact, but very asymmetric particles of graft copolymers. It is known that water is good solvent for PAA but a poor solvent for PVA. As a result, after destruction of H-bonds between the main and graft chains, which stabilized the intraPC structure, collapse of poorly soluble PVA can take place, hence the formation of very compact particles (see Fig. 3).

Viscometric investigations were carried out for other PVA-*g*-PAA samples for studying the influence of temperature on the graft copolymer structure (Fig. 1). The conformational changes occur practically in the same temperature range irrespective of chemical structure of the copolymers, yet the chemical structure has an influence on the magnitude of molecular changes.

The smallest molecular changes are observed for the sample containing the highest number of grafts (Fig. 1, curve 4).

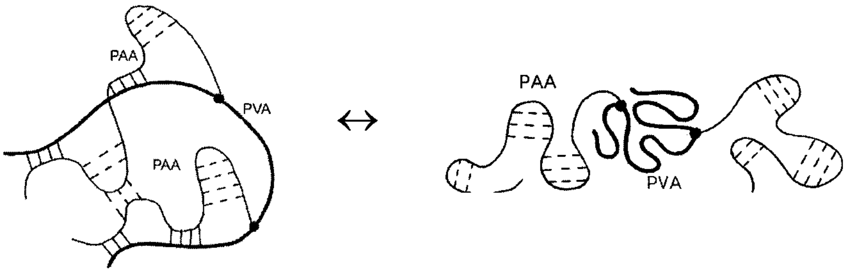

Fig. 3. Sketch of the conformation changes in PVA-*g*-PAA on heating. Note that hydrogen bonds can occur between PAA chains and PVA chains (solid line) and between different PAA chains and/or within PAA chains (broken line).

The temperature dependence of the viscometric Huggins constant and of the intrinsic viscosity are opposite (Fig. 4). The minimal value of $K$ is observed in the temperature range where swelling of graft copolymers occurs (from 293 K to 298 K), which suggests improvement of thermodynamic quality of water. The conformational changes start at $T \geq 298$ K, then the Huggins constant increases and reaches a maximum while $[\eta]$ drops to its lowest value.

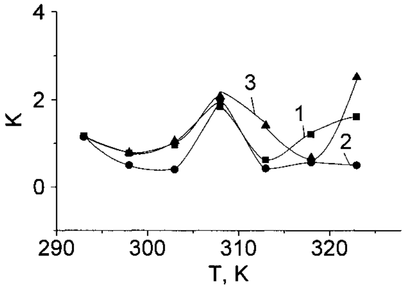

Fig. 4. Temperature dependence of viscometric Huggins constant for PVA-*g*-PAA2 (1), PVA-*g*-PAA3 (2) and PVA-*g*-PAA4 (3).

The region of conformation transition does not depend on the number of grafts but rather on the copolymer concentration. The temperature dependence of $\eta_{red}$ for PVA-*g*-PAA2 is presented in Fig. 5 as a typical example. The onset of conformation changes for all PVA-PAA samples increases with concentration increasing. Thus macromolecular contacts have certain contribution to stabilization of macrocoils structure. It should be noted that the conformational changes are perfectly reversible as ascertained from the absence of any hysteresis on the $\eta_{red}$ value in heating and cooling cycles. The process of heating and cooling was performed with the same rate.

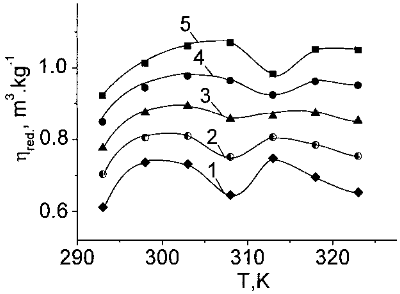

Fig. 5. Temperature dependence $\eta_{red}$ for PVA-*g*-PAA2; *C*=0.2 (1), 0.4 (2), 0.6 (3), 0.8 (4) and 1.0 kg·m$^{-3}$(5).

## Concluding Remarks

The existence of a reversible conformational transition of the type: intraPC → main chain collapse has been evidenced for graft copolymers PVA-g-PAA in a narrow temperature region. The magnitude of conformational changes depends on the chemical structure of the graft copolymers while its location depends upon concentration.

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