STRUCTURE OF NANOCLUSTERS AND DENSITY OF SOLUTIONS OF RIGID-CHAIN POLYMERS

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INTRODUCTION

As is known, a feature of a polymer solution is the presence of nanoclusters (nano-sized aggregates consisting of a polymer chain and solvent molecules bound to it). It is also known (see, for example [1]), a polymer solution can be in two phase states, namely ,sol and gel phase. In the gel phase, the polymer chains form a network, in contrast to the sol phase, where such a network is absent. The transition between these phases is called a sol-gel transition. The gel phase of aqueous polymer solutions is called a hydrogel. The theory of first order phase transition (see, for example, [2], etc.) assumes the existence of pre-transition processes near temperature of phase transitions. The purpose of this study is to determine the mechanism of the pre-transition process that occurs near the temperature of the phase transition to the sol phase of aqueous solutions of globular polymers using the example of an aqueous solution of hydroxypropyl methylcellulose.

EXPERIMENT

The density of hydroxypropylmethylcellulose was determined in the range of 20°C÷80°C using the Density meter: Anton Paar DMA 4500 M. In Fig. 3 shown the temperature dependence of the density of hydroxypropylmethylcellulose (black circles). For comparison, in Fig.3 shown the temperature dependence of the density of bidistillate (white circles). To check changes in the structure of the boundary layer, it was proposed to introduce the characteristic θ, which was called shrinkage. This parameter was associated with the process of molecular reorientation with increasing density. The value θ should be negative and remain a constant value at the absence of changes in the structure of the boundary layer. Shrinkage θ was calculated according to the formula

$$\theta = \frac{\dfrac{M}{\rho} - \dfrac{M_M}{\rho_M} - \dfrac{M_0}{\rho_0}}{\dfrac{M_0}{\rho_0}}, \qquad (1)$$

where M and ρ are the mass and density of the solution, M_M and ρ_M are the mass and density of hydroxypropylmethylcellulose, which is in the range of $1.29 \div 1.32$ gr/cm3, M_0 and ρ_0 are the mass and density of bidistillate. The temperature dependence of θ(T) is presented in Fig. 4.
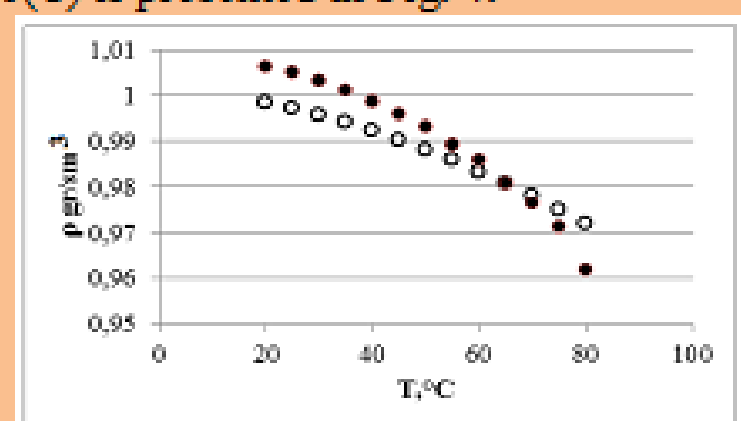

Fig.3.The temperature dependence of the density of hydroxypropylmethylcellulose (black circles) and bidistillate (white circles).
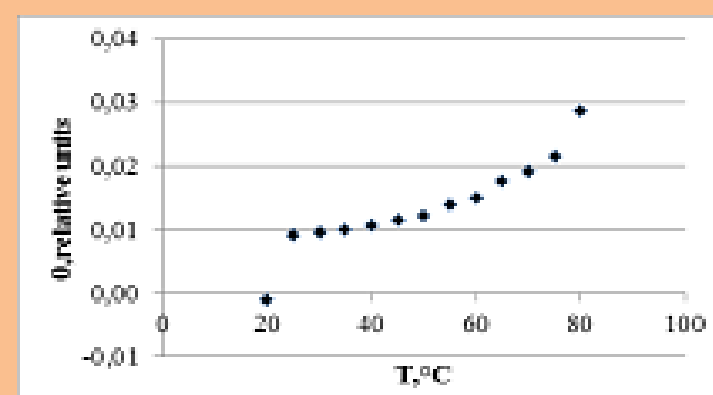
Fig.4. The temperature dependence of θ(T).

As can be seen from Figure 4, at a temperature T < 23°C the parameter θ takes negative values

CONCLUSIONS

A nanocluster in aqueous solutions of hydroxypropyl methylcellulose is a polymer globule surrounded by a boundary layer in which water molecules are oriented.

Their areas are perpendicular to the globule surface. Under action of thermal fluctuations, water molecules cause bending deformations of the boundary layer. The boundary layer is connected to a rigid globule, therefore, bending deformations lead to the appearance of tensile stresses under the influence of which voids appear in the boundary layer.

The volume occupied by voids increases with increasing temperature, forming an ordered water structure around the globule, which is necessary for the disintegration of the globule and subsequent formation of a polymer network.

CONTINUUM MODEL

Immersion of the polymer chain in the solvent changes its structure in the immediate surroundings of the chain. We will call the region that includes a chain and a solvent with a changed structure a nanocluster. Accordingly, we will consider the polymer solution as a system consisting of nanoclusters that are immersed in the matrix-part of the solvent. In this system the original structure of the latter has been preserved. In [3], on the basis of viscometric data interpreted with the help of hydrodynamic theory [4,5] the following is established. In an aqueous solution of a cellulose derivative - hydroxypropyl cellulose - the chains at T=20°C have the shape of a cylindrical globule. At formation globule the chain is folds as shown in Fig. 1a. The cross-section of the globule is shown in Fig. 1b.
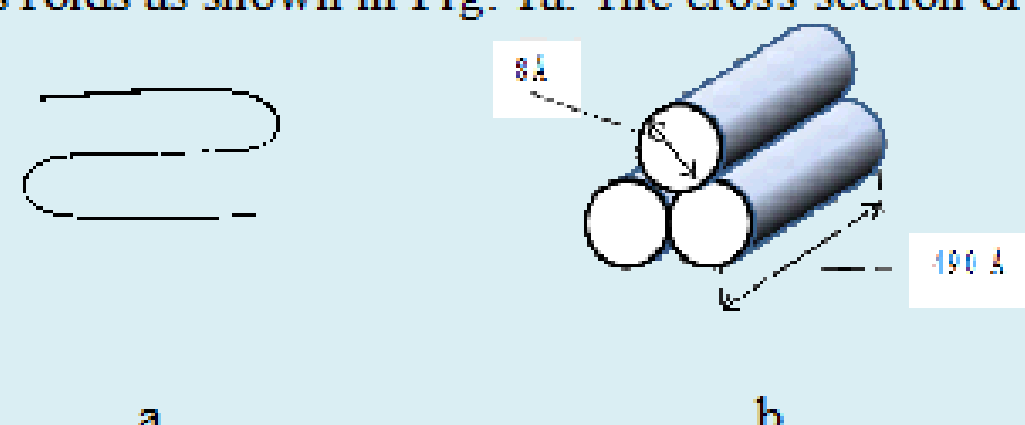

Fig. 1. Schematic (a) and dimensional (b) image of the location of the chain in the globule of hydroxypropyl cellulose
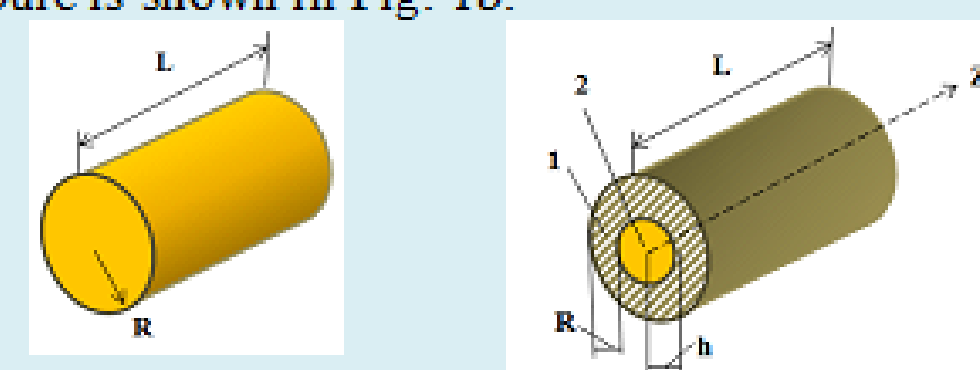
Fig. 2. Continuous models of globule (a) and nanocluster (b), where 1- boundary layer (solvent with a broken structure); 2- globule; L is the length of the globule (L= 420Å); h is the thickness of the boundary layer.

The chain of hydroxypropylmethylcellulose compared to hydroxypropylcellulose contains a small amount of side methyl groups. The chain of hydroxy propyl methyl cellulose has the form shown in Fig.2.

MECHANISM OF ARRANGEMENT OF THE INTERFACE LAYER OF NANOCLUSTER

As the conducted experiment shows, the arrangement of the boundary layer is a consequence of the temperature increase or the reason of the arrangement is the thermal movement of water molecules in the boundary layer. According to [6], water molecules in the boundary layer are oriented and deformations can occur in this layer. The rheological equation is used for the material of the layer as a moment-elastic medium

$$\sigma_{ik} = c_{iklm}\varepsilon_{lm} + g_{iklm}\omega_{lm}, \qquad (2)$$

where - σ_{ik} tensor of stresses, ε_{lm} - tensor of deformation, ω_{lm} - tensor of rotation angles, c_{iklm} - tensor of elastic moduls, g_{iklm} - tensor of torsional-bending oscillations.

The characteristics of local oscillations are determined by the solution of the equation of motion

$$\frac{\partial u_i}{\partial t} = \frac{\partial \sigma_{ik}}{\partial x_k} + f_i, \qquad (3)$$

where $\vec{u}$ is the vector of displacements, t is time, f_i is the density of volumetric forces causing oscillations

Let us denote by A the set of points located on the inner and outer surfaces with radius R, by B – the points located on other parts of the surface of the layer.

Let us have the decision of equation (3) in the case when the surface of the layer is free from external loads, that is, when the boundary conditions are fulfilled

$$\sigma_{ik} n_k = 0 \quad (\vec{r} \in A, \vec{r} \in B), \qquad (4)$$

where $\vec{n}$ is the normal to the surface, $\vec{r} = \{x, y, z\}$ is the radius vector of a point in the space occupied by the layer.

A characteristic feature of the mentioned decision is that due to the appearance of bending deformations, the layer in the direction of the Z axis undergoes contraction.

In the accepted model, the globule is considered as a absolutely rigid body. Therefore, in reality, the solution of equation (3) should be performed under boundary conditions

$$\vec{u} = 0, (\vec{r} \in A), \qquad (5) \qquad\qquad \sigma_{ik} n_k = 0, (\vec{r} \in B). \qquad (6)$$

Due to condition (5), the boundary layer cannot freely deform in the direction of the Z axis, and to fulfill this condition, tensile stresses P must occur in the area of the layer adjacent to the surface (Fig. 5)

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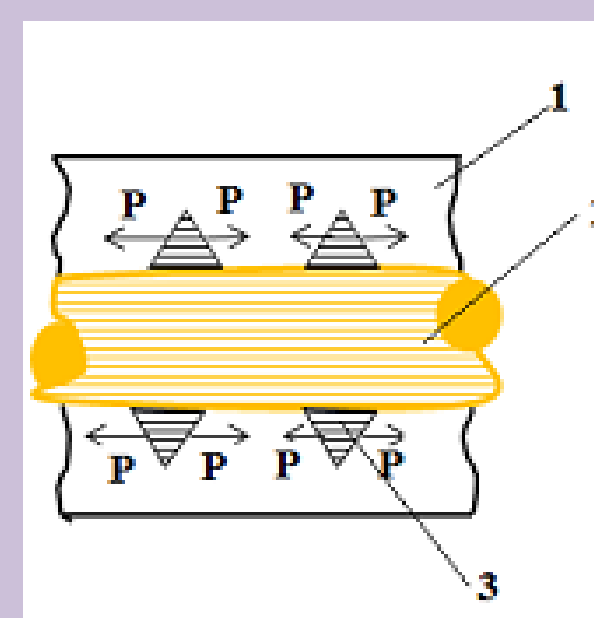

Fig. 5. Formation of cracks in the boundary layer (1 - boundary layer, 2 - globule, 3 - crack)

Under the action of these stresses, cracks appear in this area (Fig. 5) and disorder its structure. The formation of these cracks in the boundary layer is the reason for the increase in shrinkage θ with increasing temperature (Fig. 4)

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