THE FRACTAL APPROACH TO THE STUDY OF CHITOSAN FILMS SWELLING

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The structure of crab's chitosan films depending on a degree of swelling in heavy water vapor has been studied by SANS. The films of chitosan (M_w=1,08·10^5, M_n=7.0·10^4, M_w/M_n=1.54) were poured from formic acid solution. It has been shown that their supermolecular structure greatly changes depending on a degree of swelling [1].

Dry films of chitosan containing nevertheless about 10% of water strongly bounded with the chains of chitosan have a fractal structure in the range 10^1-10^{4}Å. In this case $d_s = d = 3$, where d_s and d are surface and mass fractal dimension. The latter seems to be typical for a porous solid where there is a lot of internal surface but the pore volume is almost to disappear [1].

For the films containing 30% of heavy water we have observed the scattering where Porod's law holds $I(q) \sim q^{-4}$ what is typical for the scattering from inhomogeneities having a smooth boundary. This fact attest that water forms clusters. Their dimensions according to the formula of Debye-Bueche are about 300 nm. Still at more high water content the cluster surfaces get more developed ($d_s \to 3$). At water content of 120% the clusters disappeared and it is the chains of chitosan now that give the main contribution to the scattering. By that we obtained $d = 3$ that is typical for the scattering from a mass fractal. At last, for the films containing 170% of heavy water $d = 2.4$. It has been concluded that at this water content the chains of chitosan started to stretch (beginning of dissolving).

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SMALL-ANGLE NEUTRON SCATTERING STUDY OF THE POLYELECTROLYTE HYDROGELS STRUCTURE

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The first synthesis and small-angle neutron scattering investigations of the supermolecular structure of the superswelling polyelectrolyte hydrogels, based on sodium polyacrylate cross-linked by high molecular weight compounds (allyldextran with molecular weight M=15000 and 500000 and different concentration of cross-linker as well as allylhydroxyethylcellulose with M=135000) in aqueous solutions of heavy water over a wide range of hydrogel swelling degrees have been carried out [1–4].

The method of the structural analysis of such systems as applied to the small-angle neutron scattering has been devised, that allowed a series of important results have been obtained. The comparison of the neutron scattering patterns for polyelectrolyte hydrogels

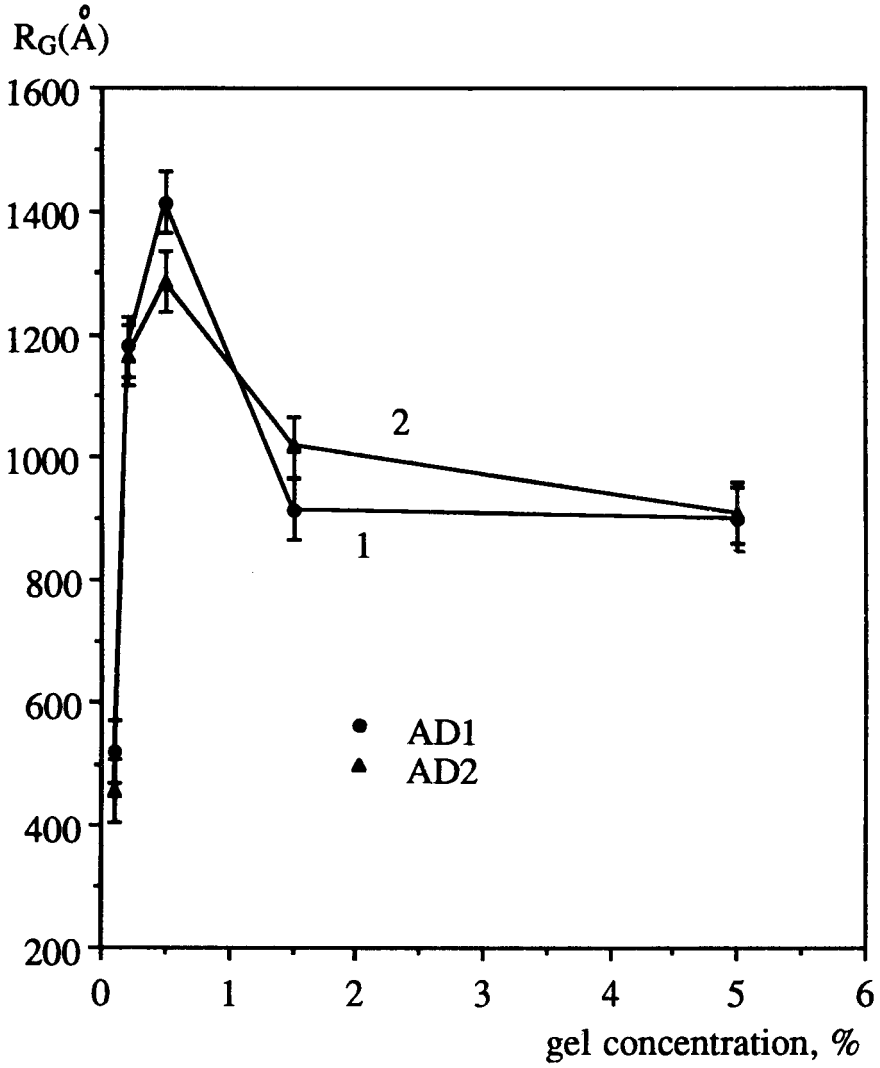

Fig. Concentration dependence of radius of gyration for the hydrogels cross-linked by low (*1*) and high (*2*) molecular weight allyldextran

cross-linked by different compounds show that there is a small difference in the size of heterogeneities in the vicinity of the junctions for used high molecular weight polyfunctional cross-linking agents (no dependence on their chemical nature and molecular weight).

It showed a anomalous dependence of of the average radius of gyration of the heterogeneities in the gels on the degree of gel swelling and a presence of the maximum on the curve of this dependence (Fig.). The total behaviour is similar to the one for linear polyelectrolytes in aqueous solution. These data allow us to propose the hypothesis of the availability of very strong fractal transition on simple gel swelling. Though one must be extremely careful with generalization of such a sort, this result still may turn a starting point for reconsideration of interrelations between properly (or usually) said phase transitions, fractal transitions and

other transitions including relaxational ones, or even deformation and fracture at stress. Being very tempting this hypothesis needs, certainly, more theoretical considerations and precise experimental studies.

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THE STRUCTURE OF POLYACRYLATE--SURFACTANT COMPLEXES

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The structure of complexes between a cross-linked polyacrylic acid (cl-PANa) and a cationic surfactant such as cetyltrimethyl-ammonium bromide (CTAB) has been studied by SANS and SAXS. The neutron scattering curves for the samples were fitted using Ornstein-Zernike correlation function $I(Q) \sim 1/(1 + Q^2\xi^2)$ (where $I(Q)$ is the intensity of scattering and ξ is the correlation length. It was found that ξ=500 Å for the sample of cl-PANa in D_2O and ξ=560 Å for cl-PANa-CTAB in 2.5% D_2O (2.5% D_2O is the matching point for CTAB). We conclude that the dimension of large-scale density fluctuations of a pure gel is approximately that of a polycomplex.

X-ray studies of the polycomplexes suggest the existence of a certain periodicity. The X-ray scattering curves of dry and swollen samples have two well-pronounced diffraction maxima associated with interplanar spacings d_1 and d_2 ($d = 2\pi/Q$, where Q is scattering vector for a maximum). The ratio of d_1/d_2 is equal to two. This suggests a lamellar structure with a period of 33 Å and 42 Å for dry and swollen samples, respectively.