



Interrelation of Hierarchy of Structures at Comparison of Linear and Cross-linked Polymer Compounds

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Abstract

The comparison of behavior of a linear polymer compounds and cross-linked networks are carried out. It is shown, that the correspondence between rheological behavior of a linear polymer compound and macroscopic behavior of its cross-linked analog is determined by topology of structures describing a hydrogel as qualitatively new object as well as by the type of polymer – solvent interactions. In this situation swelling degree is completely described by the Katchalsky – Lifson's theory. Moreover it is possible to predict microscopic behavior of macromolecular chains on the base of experimental studies of macroscopic specimens of the gel. Such investigations may be carried out in direct way for organogels. When the gel is charged (polyelectrolyte effect takes place) it is necessary to make some correction. The fact is due to so called effect of concentration redistribution, which occurs when surface of the gel acts as a membrane. In such situation the concentration of low-molecular salt inside gel may be quite more low then the concentration of the salt outside specimen. Thus in the solutions of ionogenic salts real behavior of the specimen is determined not average concentration of salt, but the real concentration of salt inside of the gel. Measuring this concentration experimentally it is possible to carried out investigations of charged macromolecular chains on the base of macroscopic specimens too.

Introduction

At present a number of different theories describing the swelling of polymer gel are known well. Thus, Katchalsky and Lifson's theory describes polymer gel as a collection of macromolecular chains [1]. This theory interprets the polyelectrolyte effect as a result of electrostatic repulsion of charged monomer units of the same sign. Consequently it is necessary to describe the free energy of electrostatic energy in details taking into account real configuration of macromolecular coil. Oppositely, in modern theories a gel is usually considered as some homogeneous object. This supposition may be employed in two ways: thermodynamical description [2] and diffusional theory [3]. Depending on the type of the hydrogel under consideration, its behavior may be described by one or another approach [4].

Let us suppose that different structures may be realized in the gel system. Then, Katchalsky and Lifson's theory may be considered as one limit case

[1]. The opposite limit case is the subject of diffusional theory [3] which describes strongly charged polyelectrolyte networks. Consequently the main difference between mentioned limit cases is likely to be determined by topology of gel structures. Indeed, the homogeneous hydrogel specimen has the simplest topology. The only topological sign (gel – solution boundary) determines the behavior of such system and the swelling of hydrogel may be interpreted as surface phenomenon [3-5]. Oppositely all the hydrogels, which may be successfully described by Katchalsky and Lifson's theory, have much more complicated topological structures (at least one have to take into account real spatial distribution of charged macromolecular units). One can suppose that many intermediate gel structures may exist in the nature. Of course, the concrete topology of a gel depends on chemical composition of both polymer network and solvent. The different theoretical approaches should be used in different cases. The choice ab initio may be made in evident situations only. For example, long-range Coulomb interactions give possibility to

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consider strongly charged polymer network as a sufficiently homogeneous object because the scale of such interactions is much longer than the scale of spatial variations of charge density. (Every gel really is a collection of macromolecular chains independently on theoretical description.) Such situations are very important but quite rare. There is no possibility to suppose any evident suggestion in all the mentioned above intermediate cases. Real topological structure of a gel (in general case) may be investigated only experimentally. In present paper we'll show that the comparison of gels and their linear analogs behavior may give important information about internal topological structure of the systems under consideration.

Results and Discussion

The comparison of behavior of concrete gel and its linear analog were carried out, for example, in [6] for PAAmide gel placed in $\text{H}_2\text{O} - (\text{CH}_3)_2\text{CO}$ intermixture (Fig. 1). One can see that the scale of the measuring values is the only difference between the presented curves. A similar result was given in [7]. In this paper the systems synthesized on the base of poly(N-vinyl-2-pyrrolidone) (**1** – cross-linked, **1a** – linear) and poly(acrylic) acid (**2**) were investigated. It was shown that the dependence of swelling ratio K_s of polymer gel on chemical composition of the surrounding media is similar to the dependence of reduced viscosity $[\eta]$ of linear polymer on the same parameter (Fig. 2). It is of importance, that the calculation of coefficients of the linear regression ($K_s = A + B \times [\eta]$) gives non-zero value of coefficient A. Thus, the diagram analogous to Fig. 1 can not be plotted in this case.

Finally, the difference between the gels and their linear analogs is most pronounceable for polyelectrolyte systems. Indeed, the dependence $K_s(C)$, where C is the low-molecular salt concentration (or ionic strengths) has a plateau at the low concentrations of the salt [5]. Oppositely, the viscosity of any polyelectrolytes falls down sharply with the increasing of salt concentration at the very beginning of the curve [8].

One can suppose that in the case described in [6] Katchalsky and Lifson's theory is applicable. Oppositely, in the last cases [5,7] some effects connected with the electrostatic interactions take place. In order to investigate this problem let us consider the next systems: poly(ethylenglicol) in $\text{CH}_3\text{OH} - \text{CCl}_4$ intermixture and poly(acrylic) acid in NaCl (0.1N) –

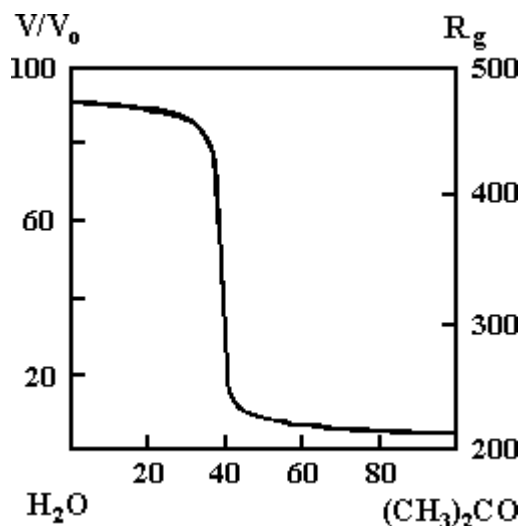


Fig. 1. Dependence of swelling ratio K_s of the PAAmide gel and hydrodynamic radius R_g (Å) of its linear analog in water – acetone intermixture. In chosen scale the curves duplicate each other.

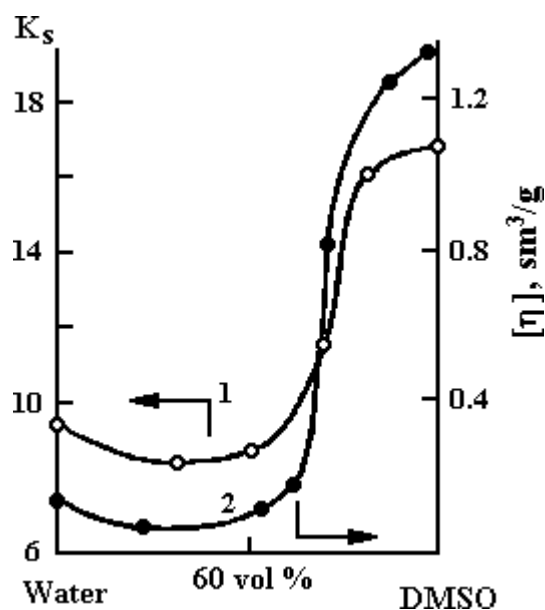


Fig. 2. Dependence of K_s of the 1a-2 complex (**1**) and $[\eta]$ of the 1-2 complex (**2**) on water/dimethyl sulfoxide mixtures.

$\text{C}_4\text{H}_8\text{O}_2$ intermixture. The curves that demonstrate the behavior of these systems in cross-linked and linear modifications are presented in Fig.3 and Fig.4 respectively. One can see that the behavior of the gels and their linear analogs visually is much like. The difference becomes observable when the linear regressions are used. First of all, we have to note that linear regressions (with acceptable errors) might be obtained only when different segments of the curves are considered independently. The results of calcula-

tions are plotted in Fig.5 and Fig.6 respectively. One can see that the linear approximations of different segments of the curves have the different slope. Segments correspond to experimental points before and after maximums of the curve were considered independently.

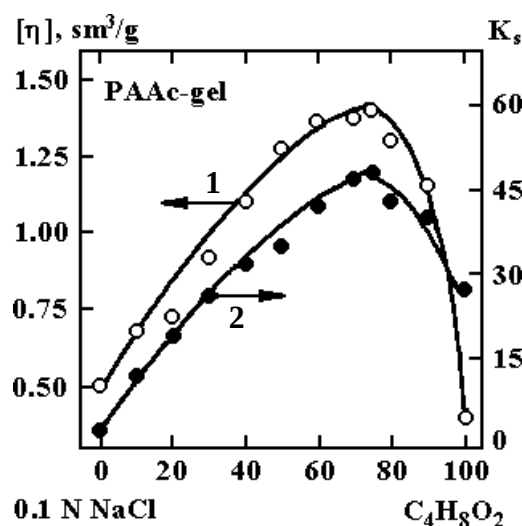


Fig. 3. Dependence of $[\eta]$ of linear PAA and K_s of the PAA gel in shown system.

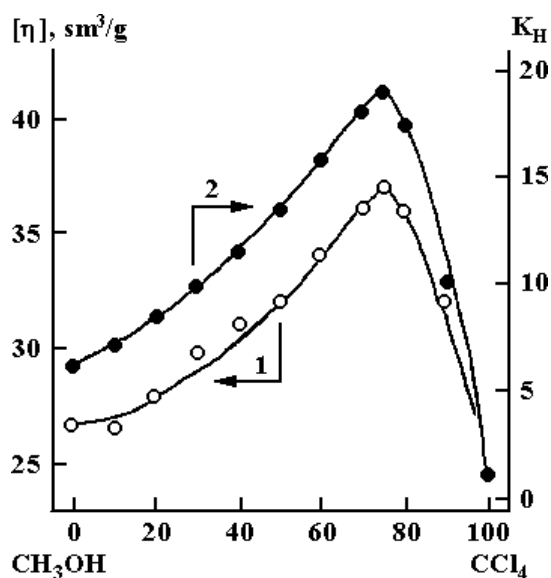


Fig. 4. Dependences of $[\eta]$ of linear PEG and K_s of the PEG gel in shown system.

Nevertheless all used linear regressions may be presented in the form:

$$\alpha = Q [\eta] + [\eta]_0 \quad (1)$$

Let us consider one of the limit cases (Katchalsky's and Lifson's theory). Here we'll suppose that the hydrogel swelling is determined by swelling of the

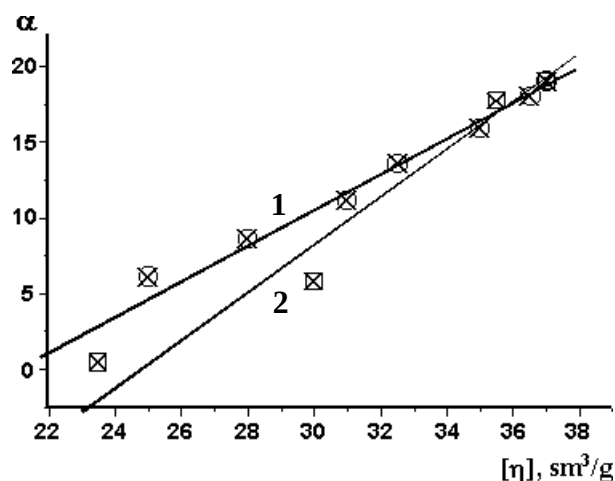


Fig. 5. Linear regressions for Fig. 3.

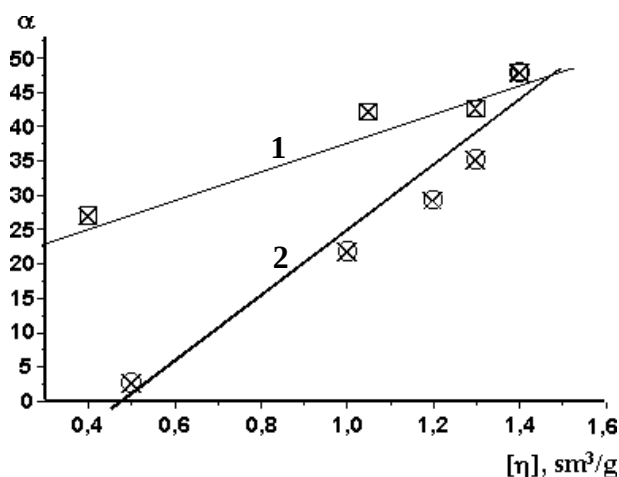


Fig. 6 Linear regressions for Fig. 4.

single macromolecular coil.

It is well known that the reduced polymer solution viscosity and square-average radius of the single macromolecular coil is connected to each other through the Flory's constant. The latter value is equal to $(3.62 \pm 2.19) \times 10^{23}$ in accordance with the data obtained by different authors [8].

$$[\eta] \text{ (dm}^3/\text{g)} = \Phi_0 (h^2_0)^{1.5} / M \quad (2)$$

where M is the molecular mass of polymer chain. Formula (2) correlates with Einstein's expression obtained for the dispersion of spherical particles.

$$[\eta] \text{ (dm}^3/\text{g)} = 2.5\pi d^3 N_A / 6M \quad (3)$$

where d is the diameter of the particle. Let us suppose h^2_0 is corresponding to effective size of free part of macromolecular chain included in the network. Then, one can determine a new constant $\beta_0 = 6\Phi_0 / \pi N_A$, which allows to obtain connection between reduced viscosity and volume V_M occupied by one

mole of macromolecules.

$$[\eta] = \beta_0 V_M / M \quad (4)$$

Simple calculation gives: $\beta_0 = 0.8\text{--}1.2$ (dimensionless value). On the last step we have to connect the effective volume V_M with the swelling ratio $K_s = (m - m_0)/m_0$, where m_0 is the mass of dry gel. If swelling ratio K_s is high ($m \gg m_0$), the density of the solvent inside and outside the gel is practically the same. Then,

$$K_s = V_M \rho / M \quad (5)$$

Gathering (4) and (5) one can see that the changes of swelling ratio due to changes of composition of the solvent (in the case of non-electrostatic interactions) may be described as:

$$\Delta K_s \sim Q \Delta[\eta] \quad (6)$$

It is of importance that the part of monomer units does not interact with solvent due to polymer-polymer interactions. (This part practically does not influence on the swelling ratio). Consequently, we use relative differences of considering parameters but not their absolute values. We may write approximately $Q \approx \rho/\beta_0$. While the density of used solvents is close to 1 g/sm^3 we have $Q \approx 0.8\text{--}1.2$. This value is in a good agreement with experimental data for the system $\text{CH}_3\text{OH} - \text{CCl}_4$ in the region $[\text{CH}_3\text{OH}] > [\text{CCl}_4]$. In opposite case $[\text{CH}_3\text{OH}] < [\text{CCl}_4]$ constant Q has quite different value.

Obtained result shows that the one of the mentioned limit cases (Katchalsky and Lifson's theory) may be observed when in the system takes place non-electrostatic interactions only. However this condition is not enough. Besides, the condition of similar chemical nature of interactions between separate sections of macromolecular chains and polymer - solvent interactions is necessary. If this condition is in fault, some complicated supramolecular structures may appear and the swelling ratio may be changed. The well-known example of such structures is due to the combination of hydrophobic and hydrophilic interaction [9]. Predictions based on formula (6) are not valid at all when the membrane effects became important. Such effects take place when the interactions in the system are of electrostatic nature (polyelectrolyte gel - electrolyte solution system). In such system the effect of concentration redistribution takes place and the difference between salt concentrations inside and outside the gel is pronounceable. Due to this fact the real concentration of salt inside the gel may be quite

far from the initial (average) value and the direct comparison of behavior of cross-linked and linear polymers become senseless.

Conclusion

The direct proportionality between rheological and swelling parameters of polymer system takes place when the polymer - polymer and polymer - solvent interactions are of identical chemical nature. In this case structure of a new type does not appear. Swelling ratio of gel is determined only by size of an individual macromolecular coil. When mentioned interactions have a various nature (but are not long-range) the constant of proportionality is determined by supermolecular structures of a new type. The direct proportionality cannot be found when electrostatic interactions take place in the system. In this case the main topological indication of the system is hydrogel - solution boundary possessing membrane properties.

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Received 14 June 2001.