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LAMELLAR GELS: STRUCTURAL PECULIARITIES

The possibility of the existence of lamellar gels has been formulated using the topological approach. The structural peculiarity of the gels of this type consists in that their framework is formed by lamellae. A model of an ideal lamellar gel has been proposed, and its structural parameters have been calculated. The type of defects that can emerge in a real lamellar gel has been determined. A formula has been derived that describes water transport through the surface of lamellar hydrogels. The possibility of the existence of lamellar gels has been confirmed experimentally via light scattering in the aqueous solution of hydroxypropyl cellulose.

Keywords: lamellar gel, hydroxypropylcellulose, light scattering.

1. Introduction

As is known [1], two types of structures can exist in a polymer solution: the sol and gel ones. The difference between them consists in that the interaction between the chains is short-term in the former case. In the latter case, this interaction leads to the formation of a long-term framework in the solution, with the indicated framework consisting of polymer chains. Such a solution is called "gel". If the solvent is water, the term "hydrogel" is also used.

The challenging character of gel studies arises, first of all, from the needs of medicine [2–5]. In particular, just the possibility of implementing the obtained results in medicine has stimulated the intensive development of gel studies. Their results (see works [6–9] and references therein) allow us to assert today that there appeared a new scientific direction, gel physics.

The specific behavior of gels is mainly a result of the structural features of their framework. One of the many issues related to gel physics is the creation of theoretical models describing the gel framework, and this task is a key point of this article.

It is generally accepted [1] that the polymer framework is a network (see Fig. 1). The latter is formed by chains *1* connecting with one another at nodes *2*. A chain can pass through several nodes. A chain segment between two neighboring nodes is called the subchain. The schematic diagram of chains in Fig. 1 corresponds to the continuous (persistent) chain model [10]. According to this model, a chain is considered to be an elastic rod. By order of magnitude, the diameter of such a rod is assumed to equal the polymer link size b. Such rods are depicted in Fig. 1 by curves, and such a representation is associated with the condition

$$b \ll h, \qquad (1)$$

where h is the size of the chosen spatial scale. In other words, under condition (1), any chain is considered to be a one-dimensional object.

As was already mentioned, a network is assumed to be the only possible type of gel framework. Instead, in this paper, we will demonstrate that another type of framework, which is principally different from the network, must also exist in gels.

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2. Gel Framework from the Topological Viewpoint

In what follows, polymer links will be called polymer particles. Let b_s denote the size of the solvent particle (molecule or ion). As a rule, the sizes of the polymer and solvent particles are of the same order of magnitude, which allows us to consider that the equality

$$b \approx b_\mathrm{s} \tag{2}$$

holds. Taking into account condition (1), let us consider the polymer and solvent particles to be point-like force centers. By M, we denote a set whose elements are the polymer and solvent particles.

Following work [11], let us introduce a topology in the space occupied by the solution by partitioning the set M into subsets according to the expression

$$M = \bigcup_{j=0}^{3} M_j, \tag{3}$$

where M_0, M_1, M_2, and M_3 are subsets whose elements are zero-, one-, two-, and three-dimensional cells, respectively. By definition, a zero-dimensional cell is a point. One-, two-, and three-dimensional cells are homomorphic to an open segment, a circle, and a sphere, respectively. In other words, as a result of the partitioning, the space becomes split into three-dimensional regions. The surfaces separating these regions from one another are two-dimensional cells. The curves where the indicated surfaces intersect are one-dimensional cells. Finally, such curves intersect at points, i.e., zero-dimensional cells.

Only some part of the system is usually called the framework: it does not include regions into which the framework partitions the system. According to this statement, the set M' whose elements are the framework particles (polymer particles) should be defined by the expression

$$M' = \bigcup_{j=0}^{2} M_j. \tag{4}$$

As was already mentioned, the network consists of subchains connected by nodes. The latter act as zero-dimensional cells, whereas the subchains play the role of one-dimensional cells. Thus, in the case where the framework is a network, the framework particles are elements of the set

$$M'' = \bigcup_{j=0}^{1} M_j. \tag{5}$$

Below, the network will be called the chain framework (abbr. C-framework), and a gel with such a framework the chain gel (abbr. C-gel).

As one can see from expressions (4) and (5), in addition to the chain framework, a framework of another type, which includes surfaces, can exist in the polymer gel. In reality, every such surface is a wide thin plate. Following the accepted terminology [12], we will call such a plate the lamella in order to describe the exterior view of the crystals. The corresponding framework will be called the lamellar framework (abbr. L-framework). A gel with such a framework will be called the lamellar gel (abbr. L-gel).

3. Ideal Gels: Chain and Lamellar

As is known [1], the gel structure is characterized by a substantial disorder. It is clear that this term remains undefined until the term “order” is defined. In other words, when talking about the disorder in the gel, we thereby assume the existence of some ideal, i.e., completely ordered, structure. Let us call it the ideal gel and consider a possible variant of such a structure.

When solving this task, we should keep in mind that, by their properties, gels occupy an intermediate position between the liquid and the solid, with certain peculiarities inherent to solids being also observed in gels [1]. This fact gives us an idea to determine the structure of ideal gel by analogy with how the issue of ideal structure is resolved in solid-state physics. In solid-state physics, the role of such

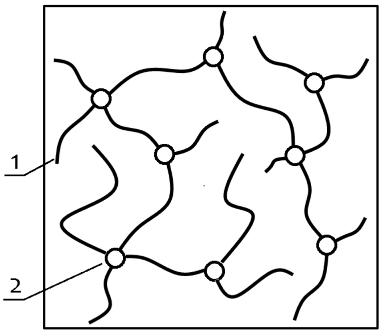

Fig. 1. Gel network as a model of polymer framework: chain (*1*), node (*2*)

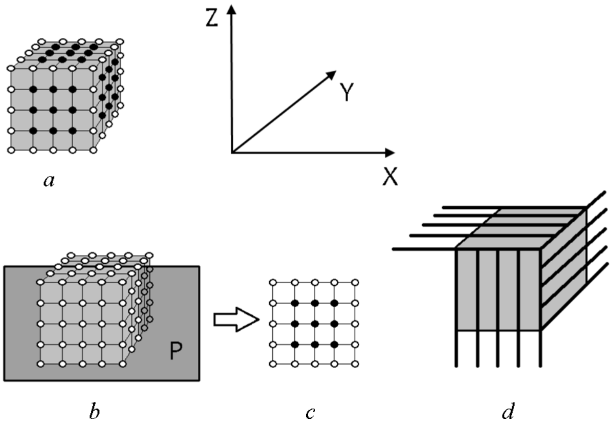

Fig. 2. Ideal gel types: chain (a) and lamellar (b, c, d)

a structure is played by the lattice of an ideal crystal [12, 13], which is characterized by the long-range order by definition. So, following the path of analogies with solids, we have to reasonably assume that there exists a lattice in an ideal gel. However, only the framework can form such a lattice.

As was shown above, there are two types of frameworks; therefore, they must form two lattices. One of them will be called the ideal C-framework, and the other the ideal L-framework. The gels with these frameworks will be called the ideal C-gel and the ideal L-gel, respectively. The unit cells of the both gels are exhibited in Fig. 2 (panels a and b). Fig. 2, c illustrates a cross-section of the unit cell shown in Fig. 2, b in the plane P. The polymer particles are shown as hollow circles, and the solvent particles as solid ones.

One can see from Fig. 2, a that the chains have a completely straightened configuration in the ideal C-gel: they are directed along the crystallographic axes X, Y, and Z. According to Figs. 2, b and c, in the ideal L-gel, the polymer particles fill the unit cell faces. The chains consisting of those particles are directed along the axes X, Y, and Z (Fig. 2, d). As one can see from Figs. 2, b and c, the solvent particles are locked within the unit cell of the L-framework; they cannot move over their volume occupied by the ideal L-gel.

Let a_{C} and a_{L} denote the translational periods of the ideal C- and L-gel lattices, respectively; let n be the number of polymer particles; and let N be the total number of particles in the gel. The fraction ϕ of polymer in the gel is determined by the formula

$$\phi = n/N. \tag{6}$$

According to equalities (6) and (2), the quantity ϕ represents the relative volume occupied by the polymer in the gel. We will assume that the following condition holds:

$$\phi \ll 1. \tag{7}$$

The obvious consequences of this condition are the inequalities

$$a_{\mathrm{C}} \gg b, \quad a_{\mathrm{L}} \gg b. \tag{8}$$

In the models shown in Fig. 2, a subchain and a lamella have the dimensions $a_{\mathrm{C}} \times b \times b$ and $a_{\mathrm{L}} \times a_{\mathrm{L}} \times b$, respectively. After elementary geometric calculations, we obtain the following equalities for the relative volumes θ_{C} and θ_{L} occupied by the polymer in the ideal C- and L-gels, respectively:

$$\theta_{\mathrm{C}} = 3b^2/a_{\mathrm{C}}^2, \tag{9}$$

$$\theta_{\mathrm{L}} = 3b/a_{\mathrm{L}}. \tag{10}$$

Whence we obtain

$$a_{\mathrm{C}} = b(3/\phi)^{1/2}, \tag{11}$$

$$a_{\mathrm{L}} = 3b/\phi. \tag{12}$$

Accordingly, for the numbers of subchains n_{C} and n_{L}, we have the formulas

$$n_{\mathrm{C}} = 3N(\phi/3)^{3/2}, \tag{13}$$

$$n_{\mathrm{L}} = 3N(\phi/3)^3. \tag{14}$$

Formulas (10)–(14) describe the characteristic feature of the lattices in an ideal gel: the parameters of those lattices depend on the polymer concentration in the gel.

4. Real Lamellar Gel

As is known, in solid-state physics, along with the model of an ideal crystal, various models of real crystals are used to describe the behavior of solids. The formation of a real crystal is considered to be a consequence of defect accumulation in the lattice [12]. These are defects of different dimensions: zero-dimensional, one-dimensional, and so forth. The zero-dimensional type of defects includes the defects that are called substitutional. These are impurity particles and vacancies.

Continuing to follow the approach adopted in solid-state physics, let us apply the concept of structural defects to gel physics, keeping in mind the L-framework and using the terms "real L-framework" and "real L-gel".

By convention, the links of a polymer chain are distinguished into internal and terminal ones. The latter differ from the former by their chemical composition and the character of their interaction with neighboring particles. The terminal links violate the spatial periodicity of the gel framework lattice. Accordingly, these links play the role of impurity particles (according to the terminology adopted in solid-state physics [13]).

Figure 3, *a* illustrates one of the possible variants for the arrangement of terminal links in a lamella. In this variant, the exhibited links are the nearest neighbors, and, in principle, they can be considered as a single zero-dimensional defect, a pair of impurity particles. The terminal links can be arranged along the chain direction at a certain distance from one another. If this distance equals b, then the formed void (see Fig. 3, *b*) is a vacancy (according to the terminology adopted in solid-state physics); if the distance equals $2b$, then we deal with a bivacancy (Fig. 3, *c*); and so forth. At distances that substantially exceed b, the matter concerns the emergence of a one-dimensional defect, a complex of vacancies (a gap) (see Fig. 3, *d*). A gap can also arise as a result of the chain bending (see Fig. 3, *e*). The presence of voids in the lamellae of a real L-gel (Fig. 3), allows solvent particles to move from one cell to another, thus traveling throughout the entire volume occupied by the gel.

Let us assume that vacancies and vacancy complexes are formed via a non-fluctuation mechanism [14], so, the number of voids in the lamellae is kept at a required level that is necessary for the motion of particles over the gel volume. An answer to the question of whether a lamellar gel actually exists, as is predicted by topology, can be given by measuring the turbidity of the polymer solution during the sol-gel transition. Indeed, polymer chains act as light scatterers in the sol-structure. If a C-gel is formed, this role is transferred to subchains. Therefore, in dilute solutions, where the number of chains is insignificant, the light scattering induced by the C-gel formation cannot lead to a noticeable light reflection.

On the other hand, as was already mentioned, if a lamellar gel is formed, the polymer chains form surfaces composed of lamellae. A set of such surfaces is impermeable to light waves; i.e., light reflection should be observed during the lamellar gel formation.

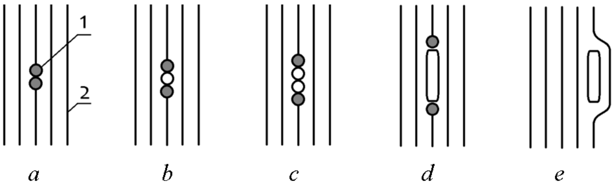

Fig. 3. Types of defects in the lamellar framework: a pair of impurity particles (*a*), a vacancy (*b*), a bivacancy (*c*), vacancy complexes (gaps) (*d, e*). Notation: chain (*1*),) terminal link (*2*)

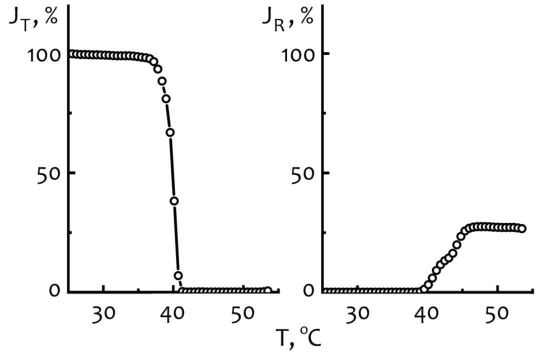

Fig. 4. Temperature dependences of the intensities of transmitted (J_T) and reflected (J_R) light beams for the 2% wt aqueous solution of hydroxypropylcellulose. The heating rate is 1.1 ° C/min

Using the technique described in work [15], we studied light scattering in a 2% wt aqueous solution of hydroxypropyl cellulose. The experimental results are presented in Fig. 4. An analysis of this figure demonstrates that the intensity of light passing through the polymer solution practically vanishes at a temperature higher than 41 °C. This fact testifies that a lamellar hydrogel is formed in the examined solutions.

According to the literature data [16], the size of a polymer unit of hydroxypropyl cellulose equals $b \simeq \simeq 0.8$ nm. Then the size of lamellae in the hydrogel studied in this experiment and calculated using formula (12) is approximately equal to 150 nm.

5. Water Transport through the Hydrogel Surface

As is known [2–5], hydrogels are widely used in medicine as a component of wound dressings. A factor that accelerates the wound healing process is the maintenance of wound moisture, so the hydrogel plays the role of a “moisture donor”. A hydrogel intended for this role must meet at least two requirements:

- it must retain water at a permanent level throughout the therapeutic action of the dressing;
- it must make it possible to regulate the amount of water entering the wound.

The lamellar hydrogel meets these requirements to a greater extent than the chain hydrogel. Indeed, the first requirement is ensured by the fact that water is present in cells with polymer walls. The second requirement can be met by changing the number of voids in the lamellae. Such changes can be achieved by introducing ions into the gel [17, 18].

In work [19], it was shown that the size of the physical infinitesimal volume (the region, where the local equilibrium is established) in liquids, is of an order of 100 nm. This means that a cell of lamellar hydrogel with the size $a_\mathrm{L} \simeq 150$ nm is a physical infinitesimal volume from the thermodynamical viewpoint. This circumstance makes it possible to consider the lamellar hydrogel as a certain continuum on which the scalar field of the concentration of water molecules $C(\mathbf{r})$, where $\mathbf{r}$ is the radius vector of the continuum points (in physical terms, this is the radius vector of the center of inertia of the cell), is defined. The behavior of such a field is described by the diffusion equation

$$\frac{\partial C}{\partial t} = D_\mathrm{e}\Delta C, \tag{15}$$

where D_e is the effective diffusion coefficient.

Let us denote the size of a hole, a formed vacancy complex, by $f \times g \times b$ (the faces of a unit cell) and determine the dependence of D_e on the parameters f, g, and a_L of the lamellar crystal structure. Following [20], let us write down the formula for the average velocity v of the translational diffusion motion of particles in the liquid,

$$v = \frac{D}{bg}, \tag{16}$$

where D is the self-diffusion coefficient of particles. In the framework of microscopic model, for the number Q of particles (water molecules) that pass, on average, through the hole per unit time, we have the expression

$$Q = vCfg. \tag{17}$$

Accordingly, in the continuum model, the particle flux is given by the formula

$$J = \frac{Q}{a_\mathrm{L}^2} = \frac{vCfg}{a_\mathrm{L}^2}, \tag{18}$$

and the flux through the cell face by the formula

$$J = -D\frac{\partial C}{\partial x}. \tag{19}$$

Approximating the derivative in formula (19) in the form

$$\frac{\partial C}{\partial x} \approx \frac{C}{a_\mathrm{L}} \tag{20}$$

and comparing expressions (18) and (19), we obtain

$$D_\mathrm{e} = D\frac{fg}{b_\mathrm{s}a_\mathrm{L}}. \tag{21}$$

This formula together with formula (15) determines the character of water transport through the hydrogel surface.

6. Conclusions

Today, it is generally accepted in the physics of gels that the gel framework is a network formed by polymer chains that are connected to one another at nodes. In this paper, it is shown that not only a network can serve as a framework model. There are gels, where the framework is formed by lamellae consisting of closely adjacent polymer chains. Such gels can be reasonably called lamellar.

The framework of an ideal lamellar gel is a lattice. In this lattice, the walls of a unit cell are lamellae with a size of about 100 nm. The framework of a real lamellar gel is also a lattice, but its lamellae contain defects such as vacancy complexes. The latter are holes in the lamellae. Due to these holes, solvent particles can pass from one cell to another and move throughout the entire volume occupied by the gel.

As is known [2–5], hydrogels are widely used in tissue engineering. Today, there is a problem in this field concerning the creation of artificial materials that could replace rigid biotissues, such as muscles, blood vessels, and so forth. Lamellar hydrogels with their rigid framework can help one in solving this problem. For example, it was shown in works [21, 22] how lamellar polymer matrices with specified physical and mechanical properties are built on the basis of water-soluble cellulose derivatives under certain temperature conditions and the presence of polymerization binding agents.

Another issue important for applications is the creation of microgels on the basis of diluted polymer solutions with ionic impurities [18]. Such microgels consist of polymer aggregates (clusters), which also have a lamellar structure. By introducing ions into such solutions, it is possible to change the size of lamellae and the corresponding porosity of the clusters, which makes it possible to use microgels as carriers of active substances in modern technologies for the manufacture of nanocomposite films, catalysts, bactericidal polymer films, and drug delivery systems [23–26].

As follows from formula (21) obtained in this paper, the transport of the solvent through the hydrogel surface is governed by the geometric parameters of unit cell. Therefore, the drug release rate is determined by the hydrogel porosity, and the latter can be created by performing the directed polymerization in order to obtain a lamellar framework with a required structure [27].

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ЛАМЕЛЯРНІ ГЕЛІ: ОСОБЛИВОСТІ СТРУКТУРИ

На основі топологічного підходу доведено можливість існування ламелярних гелів. Особливість структури цього типу гелів полягає в тому, що їхній каркас утворено з ламел. Запропоновано модель ідеального ламелярного гелю та розраховано параметри його структури. Визначено вид дефектів, які можуть виникати в реальному ламелярному гелі. Виведено формулу, що описує транспорт води крізь поверхню ламелярних гідрогелів. Можливість існування ламелярних гелів підтверджена експериментально за допомогою розсіяння світла водним розчином гідроксопропілцелюлози.

Ключові слова: ламелярний гель, гідроксипропілцелюлоза, розсіяння світла.