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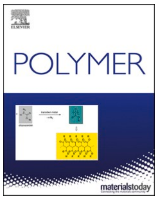

Swelling behavior of sodium lignosulfonate grafted polyacrylic acid highly absorbent hydrogels with two-phase structure

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ABSTRACT

There exist two theories on the swelling behavior of cross-linked polymer networks treated by statistical thermodynamic and scalar methods, respectively. These two theories predict inconsistent network chain length dependence of the swelling ratio. The swelling of biopolymer gels is analysed with scaling laws from polymer physics, as an alternative for the classical Flory-Rehner theory. In this paper, the swelling data of sodium lignosulfonate grafted polyacrylic acid cross-linked networks in good solvents are reanalyzed, and it is pointed out that these networks are a typical model network conforming to the two-phase structural picture. For the swelling behavior of gels in the semi-dilute regime we derive the scaling theory based swelling equations, which make them compact and universal character.

1. Introduction

Since Flory initiated the gelation theory in the 1940s to initially reveal the relationship between the swelling behavior of hydrogels and their network structure parameters, research of hydrogels has entered a rapidly developing period in the promotion of mean-field theory [1–6]. As a typical hydrophilic polymer network, super absorbent hydrogels (SAHs) is widely used in medical dressings, nursing absorption, garden water retention, and other fields, all of which are based on its unique super absorbent water retention performance [7–10]. Unfortunately, attribute to limitations on material degradability, despite their significance in numerous applications, SAHs were also considered a significant environmental pollution source due to the non-sustainable/non-renewable properties attributed to the carbon main crosslinking networks [11,12]. Though the combination of petrochemically-based monomers and natural biomass is a practical solution to create the SAH exhibiting degradable characteristics towards application, the application practice and theoretical research of semi-synthesis SAHs still faced with a rigorous challenge [13–16].

On the one hand, Flory-Huggins theory, known as the mean-field model [17–19], only depends on the primary chemical structure of the molecular chains. Due to the entropy change caused by swelling [20,21], there are still unacceptable large differences between the theory and experimental result with the different kinds of biomass raw materials [22,23]. On the other hand, mean-field for polymer solutions is intrinsically associated with ideal chains [24,25]. It is formally applicable to the concentrated region of polymer entanglement [26,27]. Considering the huge difference in branched structure between biomass macromolecules and linear polymer molecular chains and the fact that semi-synthetic hydrogel with high swelling is usually in the semi-dilute regime, we question whether our Free-Volume-Flory-Huggins (FVFH) extension of the Flory-Huggins theory can be used in the description of the water holding capacity of biopolymer gels [28,29]. It seems obvious that the lack of theory have made semisynthetic SAH one of the few subjects that theory behind the practice [28,30]. Present research methods were primarily built in the vast processing and experiment conditions, operated complicated, and lacked flexibility in performance exploration and development. The theoretical research of semisynthetic SAHs is getting more and more urgent [31–34].

Actually, some thermodynamic models have been proposed to incorporate the influence of hydrogen bonding and describe the phase behavior of these systems. Prange and collaborators [23], for instance, extended Guggenheim's quasi-chemical partition function with three categories of interaction sites: hydrogen-bond donors, hydrogen-bond

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acceptors, and dispersion force contact sites [35,36]. One of the advantages of this model is its similarity to the classical Flory–Rehner theory for hydrogels and the specific oriented interactions are bundled into a pair of interaction-dependent parameters [37]. But their molecular interaction parameters are empirically defined and their roles are difficult to be completely determined [38,39]. With the experimental data of Prange, the sponge tends to display an atypical absorbency exceeding theoretical prediction after the phase inversion desiccation technique. So, the exact dependence on molecular structure remains an open question [40,41].

It was only later when we looked to the theory of polymer physics for guidance again, that we could find that the abnormal discontinuous volume change behavior of semi-synthetic biomass gel in aqueous solutions is strongly related to "sea-island" phase separation structure which is the biggest limitation of mean-field theory in explaining water absorption mechanism [42–44]. Fortunately, there has been a lot of research on homogeneous phase separation theory [45]. As a tractable solution in renormalization theory [9,46,47], the coarse-grained molecular dynamics (CGMD) method removes the constraint on regional and global correlations, many properties of polymer solutions can be quantified using simple power-law relationships. However, researches on the "sea-island structure" of semisynthetic SAHs and some accurate signals show that in some cases, over coarse-graining may distort the theoretical analysis and lead to spurious results [43,48], which is why we have to exploit a *trans*-scale study method that combines molecule scale study and mesoscale study together [49].

In light of this, in this paper, based on the mean-field theory and renormalization theory of hydrogels, a novel thermodynamic research model of the equilibrium swelling of hydrogel was proposed in considering the crosslinking efficiency and the elastic contribution of physical crosslinking. Achieved the *trans*-scale theoretical formula of semi-synthetic SAHs by modifying diffusion coefficient between "sea-island structure", [50–52] respectively. As the semi-dilute description holds, it is considerably more convenient to deal with a scaling law that depends on a reference state that can be readily characterized in accordance with fewer experiments.

2. Theory

2.1. Equilibrium conditions for the swelling behavior of hydrogels

During the swelling behavior of most hydrogel materials there exists a pair of mutually constrained osmotic pressure swelling driving force and elastic reaction binding force [53–55]. The osmotic pressure, as a parameter describing the strength of the interaction force between the polymer hydrogel and the solvent, can be traditionally calculated using the Flory-Huggins theory, which obtains the osmotic pressure of a hydrogel from the polymer solution thermodynamics by equating the hydrogel polymer network with the corresponding polymer solution [56–59]. The difference in osmotic pressure inside and outside the polymer network is the driving force for the swelling behavior of hydrogel materials. Of course, no hydrogel can be infinitely swollen; there are cross-linked structures in the polymer network structure, and the swelling behavior will eventually be limited because the stretching of the cross-linked structures generates a counteracting elastic pressure. Eventually, under the condition that the total pressure or external pressure is zero indicates that the osmotic pressure swelling driving force exactly balances the elastic reaction binding force, and the hydrogel behaves as if it has reached the equilibrium state of swelling [60,61]. When we use Π_{ext} to denote the external pressure, Π_{mix} to denote the osmotic pressure driving force, and Π_{elas} to denote the elastic reaction force, the equilibrium conditions for hydrogel swelling can be simply described by the following equation:

$$\Pi_{ext} = \Pi_{mix} + \Pi_{elas} \tag{1}$$

Considering the Flory-Rehner hypothesis, it was pointed out that the osmotic pressure lysis driving force and the elastic reaction binding force are two thermodynamic factors that are independent of each other and have a Flory mean field theory and a scalar law theory, respectively [62–64]. After that, we will analyze the contribution of the two factors to the swelling behavior from different theoretical aspects.

2.2. Equilibrium conditions for the dissolution behavior of FVFH theory

As an extension of the classical Flory-Huggins theory [6,65], the FVFH theory describes the additional osmotic pressure contribution of water and the macromolecular polymer network due to changes in hydrogen bonding forces by means of the Flory-Huggins interaction parameters between the macromolecular polymer network and water. The osmotic pressure following the classical Flory-Huggins theory equals:

$$\frac{\Pi_{mix} v_w}{RT} = \ln\left(1-\varphi_p\right) + \left(1-\frac{v_w}{v_p}\right)\varphi_p + \chi_{p,w}\varnothing_p^2 \tag{2}$$

v_w is the molar volume of water, R is the universal gas constant, T is the temperature, φ_p is the polymer volume fractions, v_p is the molar volume of the polymer, and $\chi_{p,w}$ is the Flory-Huggins interaction parameter between polymer and solvent (water).

In the FVFH theory, $\chi_{p,w}$ is considered to be related only to the composition of the polymeric macromolecular network, and this assumption holds true for most low-swelling hydrogels based on natural polysaccharides such as starch and cellulose. However, for some protein-based highly absorbent resins the variable temperature swelling behavior deviates significantly from the theoretical value. For, protein-like natural macromolecules, the $\chi_{p,w}$ depend strongly on temperature, and temperature-induced protein denaturation tends to cause abrupt changes in the $\chi_{p,w}$ [66].

At the same time, the value of $\chi_{p,w}$ is often calculated from the isothermal adsorption curves of hydrogels, and for the case of high swelling or water activity $a_w > 0.8$, it is often difficult to obtain sufficient and accurate experimental data for the isothermal adsorption curves, which poses a considerable problem in pre-calculating the osmotic pressure of biomass highly absorbent resins and thus predicting their water absorption and retention capacity [67–69].

For elastic reaction bonding, the original Flory-Rehner theory was based on the swelling behavior of isotropic linear Gaussian chains, where the elastic contribution to the free energy is given by a strain energy function, which is expressed according to the stretching of the polymer in three main directions and is considered to be effective for highly swollen gel networks with isotropic deformation.

$$\frac{\Pi_{elas}\nu_w}{RT} = -\frac{G\nu_w}{RT}\tilde{\varnothing}^{1/3} \tag{3}$$

G is the bulk elastic modulus, and $\tilde{\varnothing} = \varphi_p / \varnothing_{ref}$ with $\varnothing_{ref}$ the volume fraction at which the chains between the crosslinks are relaxed, i.e. at zero stress. Note that $\tilde{\varnothing}^{1/3}$ is linear with the relative stretch of the polymers, which is the governing state variable in the models describing non-isotropic deformation of gels.

However, considering that the molecular chains connected between the crosslinking points in the cross-linked network must take into account the effect of polymer concentration fluctuations and cannot be treated as Gaussian chains in the case of polymer networks that fail to swell sufficiently or have a high cross-link density, Horkay and McKenna point out that the strain energy function can only be used if 1) the elastic free energy is independent of the other terms, and 2) the molecular chains between the crosslinking points behave as Gaussian chains, neglecting volume effects, which are after these two assumptions, the elastic reactive binding forces of the isotropic model affine deformation can be discussed [70–72].

In summary, we can see that the self-consistent calculation of the

Flory mean field theory has obvious deviations in the calculation of both osmotic pressure and elastic force, and there are many prerequisites in the use of the process. However, the results of the Flory method are close to the actual values in many cases, mainly because the errors of the two important parameters in the self-consistent calculations cancel each other out in an unusual way [8,23].

(1) The repulsive energy is enonnously overestimated when correlations are omitted.
(2) The elastic energy is also largely overestimated.

Long ago, Flory devised a simple and brilliant scheme for computing the repulsive energy, which gives excellent values for all dimensionalities (Polymer, 35 (1994), 2167). We briefly describe his method and the approximations involved. The starting point is a chain, with a certain unknown radius R and an internal monomer concentration

$$C_{int} = \frac{N}{R^d} \tag{4}$$

C is the monomer concentration, N is the number of chain segments, R is the radius of rotation, and d is the number of spatial dimensions.

There is a certain repulsive energy in the chain due to monomer interactions. If C is the local concentration of monomers, the repulsive energy per cm^3 is proportional to the number of pairs present to C^2. We write it (per unit volume) as:

$$F_{rep} = \frac{1}{2} Tv(T)C^2 \tag{5}$$

where v has the dimension of a (d dimensional) volume and is positive. We call v the excluded volume parameter. [In the Flory notation v =(1-2 χ) a^d where a^d is the monomer volume and χ is an interaction parameter. For good solvents $\chi < 1/2$ and $v > 0$.]

One essential approximation is to replace the average of c (inside thecoil) by the square of the average.

$$\langle C^2 \rangle \to C_{int}^2 \tag{6}$$

This is typical of a *mean field* approach: all correlations between monomers are ignored. The overall repulsive energy after integration over a volume R^d, scales as:

$$F_{rep} = Tv(T)C_{int}^2 R_d = Tv\frac{N^2}{R^d} \tag{7}$$

This tends to favor large values of R (i.e., to swell the chain). However, if the distortion is too large, the chain entropy becomes too small, and this is unfavorable. Flory includes this through an elastic energy term derived from the ideal chain result.

If we think for example of the end-to-end elongation of the chain, since the distribution function $p_N(r)$ is a function of $(r/\ R_F)$ only, this implies that the entropy at fixed r is also a function of $r/\ R_F$ only. Finally, the elastic energy should be written Tr^2/R_F^2, rather than $Tr^2/\ R_0^2$. Again, this brings in a large reduction.

As is often the case in self-consistent field calculations (e.g., in Hartree atomic theory), the errors in (1) and (2) mostly cancel each other out, and much of Flory's subsequent work has attempted to improve either (1) or (2) without changing the other, leading to less accurate results.

2.3. Equilibrium conditions for the dissolution behavior of scaling law

The study of the osmolarity of polymer hydrogels is mainly based on the general scaling law proposed by Cloizeaux in 1975 to describe the osmolarity of polymer solutions in the semi-dilute state.

$$\frac{\Pi_{elas}\nu_w}{RT} \sim \varnothing^{\beta} \tag{8}$$

The scalar index β is obtained from another scalar index b related to another scalar law, i.e., the scalar law for the hydrodynamic radius r_H of the polymer in the dilute state.

The swelling behavior of highly swollen hydrogels acts as a typical critical behavior, where the polymer chains happen to start overlapping at the time of swelling equilibrium of the hydrogel network in the solvent, when it can be seen as a polymer solution in a semi-dilute state. In such a case for b there exists the relation $\beta = 3\nu/(3\nu - 1)$. In earlier studies on many glucose homopolymers, the value of ν was around 0.49 attachment, so we can predict that for hydrogels composed of biomass $\beta \approx 3$ [73].

For the elastic reaction binding force of hydrogels, De Gennes' so-called critical crosslinking concentration hypothesis states that the size of the crosslinking lattices of polymer gels is similar to the average polymerization in semi-dilute polymer solutions in the uncrosslinked state where the molecular chains happen to be in contact with each other. Since the elastic force is formed precisely by the polymer lattice swelling behavior, the proportional relationship between polymer concentration and elastic force for the equilibrium condition of gel swelling behavior can be calculated from this. For gel equilibrium, the sum and elastic pressure of the osmotic pressure is exactly zero, which determines the proportionality

$$G \sim \frac{1}{M_c} \sim \varnothing_{p,0}^{\beta} \tag{9}$$

It can be observed that the scalar relationship between the elastic modulus and the osmotic pressure has the same exponent. Therefore the condensation and swelling behavior should have shown a linear relationship. However, for the same reason, polymer chains cannot be regarded as Gaussian chains when the length of molecular chains between the crosslinking points is too short, and there are a large number of crosslinking defects such as dangling chains in the polymer macromolecular network, which all contribute to the deviation of the index. For example, some literature states that for synthetic polymer-based gel materials, β range from about 2.3 to 2.9 [74,75].

It can be seen that the scalar theoretical approach also has some errors for describing the swelling behavior of cross-linked polymer networks. Although the prediction of the swelling behavior of cross-linked polymer networks by the Flory statistical thermodynamic approach and the scalar theoretical approach is based on the molecular weight between the crosslinking points, the dependence of the two theoretical swelling ratios on the network chain length is not consistent. Moreover, since both theories are based on homogeneous cross-linked networks with homogeneous structures, they also impose high prerequisites for the use of the theories [48,75,76].

In our previous work [77,78], a series of highly absorbent resin hydrogels with good cross-linked structures were synthesized by modified sodium lignosulfonate and bifunctional supramolecular cross-linkers, which are suitable for analyzing and verifying the applicability of the theories.

3. Materials and methods

3.1. Preparation of hydrogels

All hydrogels were prepared from aqueous stock solutions of the following chemicals.

3.2. Materials

Pentaerythritol (PER), sodium methoxide (MeONa), methanol (MeOH), dichloromethane (DCM), acetic anhydride (Ac_2O), 2.3-epoxypropyltrimethylammonium chloride (GTA), and triethylamine (TEA) were purchased from Sinopharm Chemical Reagent Co. Ltd. Allyl glycidyl ether (AGE), sodium percarbonate (SPC), sodium lignosulfonate (SL), 2,3-epoxy-1-propanol (glycidol), acrylic acid (AA), ammonium persulfate (APS), and sodium hydrate (NaOH) were purchased from Shanghai Aladdin Biochemical Technology Co. Ltd. All compounds were utilized without additional purification.

3.3. Synthesis of hyperbranched crosslinker with tunable molecular structure

Under nitrogen atmosphere, PER (0.1361 g, 1 mmol), MeONa (0.0162 g, 0.3 mmol), and MeOH (1 mL) were placed in a 50 mL reaction tube. After magnetic stirring for 30 min, MeOH was distilled off under reduced pressure. The system was heated to 95 °C and glycidyl (5.9264 g, 80 mmol) monomers were slowly added within 5 h. After dropping, the system was reacted for a further 3 h. A small amount of MeOH was used to dissolve the reaction product. Subsequently, it was neutralized using a cation exchange resin activated by hydrochloric acid. Transfer the solution to 10 vol of acetone to precipitate hyperbranched macromolecules. After vacuum drying, hyperbranched polyglycerol macromolecules are obtained. The hyperbranched polyglycidol macromolecules (containing 0.01 mol of terminal hydroxyl), AGE (1.1985 g, 0.0105 mol), and accelerator TEA (0.05 g) were added to the flask and reacted at 130 °C under a nitrogen atmosphere for 5 h. The product was dissolved in MeOH and transferred to an ether solution to induce precipitation. The hyperbranched crosslinker with the monofunctional vinyl group was obtained after the removal of ether by rotary evaporation. Finally, the number of terminal double bonds was determined using the bromination method [79].

The general procedure for the epoxidation process using sodium percarbonate is as follows. A terminal olefin (0.01 mol) and sodium percarbonate (4.0 g, containing approximately 15% active oxygen) were mixed in DCM (30.0 mL). Add Ac_2O (5.0 mL) through the constant pressure funnel, and the rate of Ac_2O addition was controlled to ensure the reaction temperature did not exceed 40 °C. After the reaction was completed, the solvent was removed by distillation and a dual functional hyperbranched crosslinker was obtained and coded as HPG. Crosslinkers with different functional group ratios of epoxy and vinyl groups could be obtained according to the abovementioned procedure by changing the amount of sodium percarbonate oxidant.

3.4. Synthesis of superabsorbent hydrogels

Sodium lignosulfonate grafted polyacrylic acid hydrogels (PSH) were synthesized by free radical graft copolymerization in an aqueous solution. AA, NaOH (molar ratio 4:3), SL, and HPG were dissolved in deionized water at 10 °C with stirring and nitrogen was bubbled to remove dissolved oxygen. After heating the system to 65 °C, an initiator (APS) was added and the system was reacted for 2 h to complete the polymerization reaction. A polyacrylic acid homopolymer was extracted with ethanol at the end of the reaction. For grafting efficiency calculations, the unreacted SL was separated using dimethyl sulfoxide. The hydrogel was dried at 80 °C and mechanically crushed to obtain powdered PSH xerogel, which was sieved with a steel mesh (80–100 mesh).

3.5. Characterization

The water absorption and retention properties of the gels were tested using the equilibrium swelling method. The swelling degree of the dry gel in deionized water and normal saline was calculated by using Eq (10).

$$Q_{eq} = \frac{m_2 - m_1}{m_1} \tag{10}$$

where m_1 and m_2 represent the weight of the dry and swollen samples, respectively. The swelling degree of the dry gel in deionized water and normal saline were marked as Q_{eq} and $Q_{eq}^{'}$, respectively.

The dynamic mechanical properties of the gel after swelling were tested using an extended rheometer (MCR302, Anton Paar). The hydrogels were subjected to a constant strain of 0.1% by varying the frequency from 1.0 to 1000 Hz at 25 °C. The gap width used was 0.1 mm.

4. Results

4.1. Dependence of hydrogel swelling on molecular weight between cross-linking sites

According to the Flory polymer swelling theory, the statistical thermodynamic theory of swelling behavior at equilibrium can be expressed as

$$M_c = -F_{(f)}\rho_g V_1 V_{2c}^{\frac{2}{3}} V_2^{\frac{1}{3}}\left[\ln(1 - V_2) + V_2 + \chi V_2^2\right] \tag{11}$$

where V_2 is the volume fraction of the polymer at swelling equilibrium, V_{2c} is the volume fraction of the polymer in solution when the cross-linking reaction occurs, χ is the interaction parameter, V_1 is the molar volume of the solvent, ρ_g is the dry gel density and $F_{(f)}$ is a factor related to the structural parameters of the network and the degree of restricted motion of the cross-linking point. The cross-linked network can exhibit a large swelling in a good solvent, when $V_2 \ll 1$. The following equation can be obtained after expanding the logarithmic term in Eq. (11) and keeping only the starting two terms.

$$Q = \left[\frac{\frac{1}{2} - \chi}{F_{(f)}\rho_g V_1}\right]^{\frac{3}{5}} V_{2c}^{-\frac{2}{5}} M_c^{3/5} \tag{12}$$

Obviously, the degree of swelling Q is proportional to $M_c^{3/5}$.

From the scalar theory, the equilibrium of the swelling behavior of polymer networks is based on the law of proportionality in the contact concentration C^* of polymer solutions.

The cross-linked network reaches swelling equilibrium in a good solvent when the chain ends of the macromolecular network just touch each other to form physical entanglement points. The equilibrium concentration at this point can be expressed as:

$$C_\theta = k_{(f)} C^* \tag{13}$$

$k_{(f)}$ is a constant related to the crosslinking point functionalities and the concentration of the polymer at the crosslinking reaction.

We have modified related description and made it more accurate. It can be seen from Eqs. (8) and (10) that there is a significant difference between statistical thermodynamics and scalar theory in predicting the swelling of polymer cross-linked networks. As De Gennes points out in his book Scaling concepts in polymer physics, let us start with a solution of chains (polymerization index N) in a good solvent (excluded volume parameter $v = a^3(1 - 2\chi) > 0$). The chains repel each other, and this is reflected in the existence of a positive osmotic pressure Π. When attach the chains together, for example by reaction of the chain ends with certain z-functional molecules (z being equal to 3, 4. etc.), and we let them choose their density. They would like to separatefrom each other as much as possible. However, each coil must remain incontact with its neighbors because of the crosslinks. What we have is a set of closely packed coils sealed together by the crosslinks. The situation is reminiscent of the overlap threshold in semi-dilute solutions. Thus, the gel automatically maintains a concentration c proportional to c^*. At this point, the following equation can be derived. $C = k(z)C^* = k(z)N^{-4/5}v^{-3/5}a^{-6/5}$.Since M_c is proportional to N, it can be concluded that $C^* \propto M^{-4/5}$, the exponential rule for the equilibrium swelling of the cross-linked network in a good solvent can be obtained.

$$Q \propto M_c^{4/5} \tag{14}$$

It can be seen from Eqs. (12) and (14) that there is a significant difference between statistical thermodynamics and scalar theory in predicting the swelling of polymer cross-linked networks.

4.2. Swelling behavior of polymer hydrogels in two-phase systems

The existing statistical thermodynamics and scalar swelling theories assume that polymer networks have only a homogeneous cross-linked structure, but in practice most cross-linked networks have a non-homogeneous cross-linked structure. There are often physical cross-linkages, ionic cross-linkages, covalent cross-linkages, hydrogen cross-linkages and crystalline cross-linkages in polymer networks, and the relationship between different types of cross-linkages and the degree of swelling is also different. Therefore, experimental data about hydrogels at high swelling degrees are often very scattered and difficult to correspond with the relevant theories.

If we consider the cross-linked network as a mixture of multiple homogeneous networks with equal chain lengths interconnected, where the total volume of the swollen macromolecular network is equal to the sum of the volume $V_{p,i}$ of each homogeneous component plus the volume $V_{t,i}$ of the absorbed solvent, then the actual swelling ratio q of the non-homogeneous network can be expressed as:

$$Q^{*}=\frac{\sum_{i}\left(V_{p,i}+V_{t,i}\right)}{\sum_{i}\left(V_{p,i}\right)}=\frac{V_{p,i}}{\sum_{i}\left(V_{p,i}\right)}\left(\frac{V_{p,i}+V_{t,i}}{V_{p,i}}\right)=\sum_{i}\forall_{i}Q_{i} \tag{15}$$

where $\forall_i$ and Q_i denote the volume fraction of the ith homogeneous network in the cross-linked network and its corresponding swelling degree, respectively.

Solubility ratio Assume that a cross-linked network has a two-phase structure, i.e., it is composed of a homogeneous network 1 with low cross-linkage and a homogeneous network 2 with high cross-linkage. If we express the volume fraction V occupied by the low cross-linked region by the parameter Z, then Eq. (15) can be expressed as:

$$Q^{*}=ZQ_{1}+(1-Z)Q_{2} \tag{16}$$

When the crosslinking degree in the high crosslinking zone is very high and Q_2 is approximately 1, the swelling effect is only generated in the low crosslinking zone, and the lower corner of the identification of the homogeneous network in the low crosslinking zone can be omitted at this time, then Eq. (16) can be expressed as follows.

$$Q^{*}=ZQ+(1-Z) \tag{17}$$

The above analysis shows that Eq. (17) is a special case of Eq. (15).

In the sodium lignosulfonate grafted polyacrylic acid crosslinking network system prepared in this paper, thanks to the good reactivity of sodium lignosulfonate and the nature of polyelectrolyte, it exists in aqueous solution as a cluster of polygroups, and after the polyacrylic acid molecules are grafted on the surface of sodium lignosulfonate, the sodium lignosulfonate macromolecules can be regarded as the crosslinking points of multiple polyacrylic acid molecules. Unlike the ideal crosslinking network which requires carbon-carbon bonds as crosslinking points, the sodium lignosulfonate grafted polyacrylic acid crosslinking network system can be considered as a typical inhomogeneous crosslinking system with a two-phase structure.

In this two-phase model network, the sodium lignosulfonate clusters can be considered as highly cross-linked spheres with an approximate solubility ratio of 1. In a polyacrylic acid bridged macromolecular network, since each polyacrylic acid macromolecule has two reactive end groups, if the molecular weight of the polyacrylic acid macromolecules do not differ significantly, the molar ratio of sodium lignosulfonate to the number of reactive chain ends of polyacrylic acid in the starting state of polymerization, $y=[SL]/[PAA]$, the mass fraction of sodium lignosulfonate can be expressed as can be expressed as:

$$W_{SL}=1\Big/\left[1+\frac{1}{2y}\cdot\frac{M_{c}}{M_{SL}}\right] \tag{18}$$

where M_c and M_{SL} are the molecular weights of polyacrylic acid and sodium lignosulfonate, respectively.

Considering the small difference in density between the components, the mass fraction of sodium lignosulfonate can actually be regarded as the volume fraction occupied by the highly cross-linked region in the two-phase cross-linked network, which is the $(1-Z)$ part, then Eq. (18) can be expressed as：

$$Z=1\Big/\left[1+2y\cdot\frac{M_{SL}}{M_{c}}\right] \tag{19}$$

By substituting Eq. (19) into Eq. (17), the relationship between the real swelling degree and the actual swelling degree of the homogeneous network formed by the macromolecular chain with chain length M_c as：

$$Q=\frac{Q^{*}-1}{Z}+1=\frac{Q^{*}-W_{SL}}{1-W_{SL}} \tag{20}$$

To verify the swelling theory from the experimental swelling data Q^*, the swelling degree Q must first be calculated for the corresponding homogeneous network to satisfy the theoretical premise, W_{SL} represents the mass fraction of sodium lignosulfonate.

Each unit volume of the dry gel cross-linked network contains μ sodium lignosulfonate spheres as crosslinking points and ν homogeneous polyacrylic acid network chains of equal length. If each sphere is connected with f network chains, the total number of contacts between the network chains and the spheres should be μf or 2ν if the cross-linked network structure is whole and there are no suspended chains [80,81]. If the number of sodium lignosulfonate macromolecular units in each sphere is n, the starting ratio y for graft copolymerization can be expressed as

$$y=n\mu/2\nu \tag{21}$$

After combining Eq. (18), Eq. (19) and Eq. (21):

$$y=\frac{n}{f}=\frac{1}{2}\left[\frac{1-Z}{Z}\right]\frac{M_{c}}{M_{SL}} \tag{22}$$

According to the elasticity theory of cross-linked networks, the elastic deformation energy of Gaussian chain phantom networks strictly follows the following equation:

$$\Delta Gel=\frac{\xi}{2}kT\left(\sum_{i=1,2,3}\lambda_{i}^{2}-3\right) \tag{23}$$

where $\lambda_{i,i=1,2,3}$ is the deformation stretch ratio in the direction of the three tensile principal axes, and ξ is the number of independent circuits in the cross-linked network structure, and he has a simple relationship of $\xi=\nu-\mu$ between the number of network molecular chains ν and the number of crosslinking points μ. Since there is a relationship of $\nu=\rho_g/M_c$ between the number of network molecular chains ν and the molecular weight M_c between crosslinking points, where ρ_g is the dry gel density. The following equation can be obtained through Eq. (21) and Eq. (22).

$$\xi=\left(\frac{f-2}{n}\right)y\cdot\nu=\left(\frac{f-2}{n}\right)\rho_{g}\frac{y}{M_{c}} \tag{24}$$

Eq. (24) shows that ξ is not only related to the number of network chains ν, but also depends on the polymerization ratio y and the structural parameters n and f of the highly cross-linked pellets.

Although the parameters n and f are unknown, it can be assumed that under aqueous polymerization conditions, the number of sodium lignosulfonate macromolecular units per pellet of the polyelectrolyte is proportional to the solution concentration, i.e., the starting ratio y for graft copolymerization, while the number of grafted macromolecular chains on the surface of each pellet is proportional to the collision probability of acrylic acid monomers and is therefore also affected by the graft copolymerization monomer ratio y.Therefore, there will be no significant change in the ratio of $(f-2)/n$ during the polymerization process. Thus, it is reasonable to assume that when comparing the experimental data with each other and verifying the swelling theory, the proportional relationship between the swelling degree Q and the molecular weight M_c between the crosslinking points can be obtained by different graft copolymerization ratios y.

The network property parameters based on the elastic modulus provide more accurate and valid evidence for our assessment of the swelling theory. PAA is often used as a model system for super absorbent hydrogels and that their interaction with water indeed resembles that of other semi synthetic SAHs. We have collected data on equilibrium swelling degree of petroleum based and semi synthetic SAHs, which concern polyacrylic acid (PAA) and lignosulfonate-*graft*-copolymer. We have designed lignosulfonate-graft-copolymer systems to investigate the applicability of the models for the elastic pressure of biopolymer gels. We have collected network parameter data on the change of the semi synthetic SAHs subject to externally applied pressure, via either osmosis or rheometer method. The choice for SL-g-PAA hydrogels is advantageous because the crosslinking of these systems is well controlled, rendering uniform cross-linked network in the gels.

The dissolution data of SL-g-PAA hydrogel model network in saline were plotted against the molecular weight M_c between the crosslinking points as a double logarithmic coordinate plot as shown in Fig. 1. Although the data showed a trend of certain proportional relationship, the distribution of data points was scattered and the linear regression rate was not high. Similarly, for the SL-g-PAA hydrogel model network with a two-phase structure, the ideal network swelling degree Q can be calculated by substituting Q^* and W_{SL} into Eq. (24). However, a double logarithmic coordinate plot of Q against the molecular weight M M_c between the crosslinking points shows that the data distribution is still scattered. As mentioned earlier, the dispersion of the data points was improved to a large extent by plotting Q against M_c/y as suggested by Eq. (24). As shown in Fig. 2, with this plotting method, the experimental data distribution can be fitted to both sides of a straight line with a slope of 0.13. According to this treatment, it is equivalent to rewriting Eq. (24) as the following equation:

$$Q=\left[\frac{\frac{1}{2}-\chi}{\frac{\rho_g V_1 F_{(t)}}{y}}\right]^{\frac{3}{5}} V_{2c}^{-\frac{2}{5}}\left[\frac{M_c}{y}\right]^{0.13} \tag{25}$$

5. Conclusion

In this paper we have analysed the deswelling of biopolymer gels with both the Flory-Rehner theory and scaling laws from polymer physics for the semi-dilute regime. Our work shows that semi-dilute polymer theory can be applied to develop a simple power-law relationship between swelling and crosslinking point functionality. The simplicity of our resulting equations provides substantial utility for gel synthesis design.

CRediT authorship contribution statement

Junhao Fei: Writing – original draft, Data curation. **Tao Tang:** Writing – original draft, Investigation. **Likang Zhou:** Visualization, Investigation. **Huiwen He:** Supervision, Project administration, Investigation. **Meng Ma:** Supervision. **Yanqin Shi:** Supervision. **Si Chen:** Writing – review & editing, Supervision. **Xu Wang:** Supervision.

Declaration of competing interest

Si Chen reports financial support was provided by National Natural Science Foundation of China. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

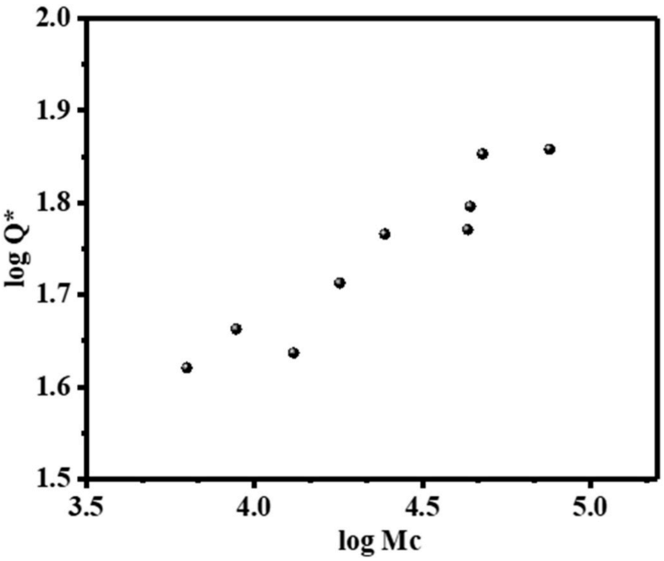

Fig. 1. Experimental swelling ratio Q^* and the correaponding molecular weight of precursor chains M_c for SL-g-PAA hydrogel model networks in normal saline at room temperature.

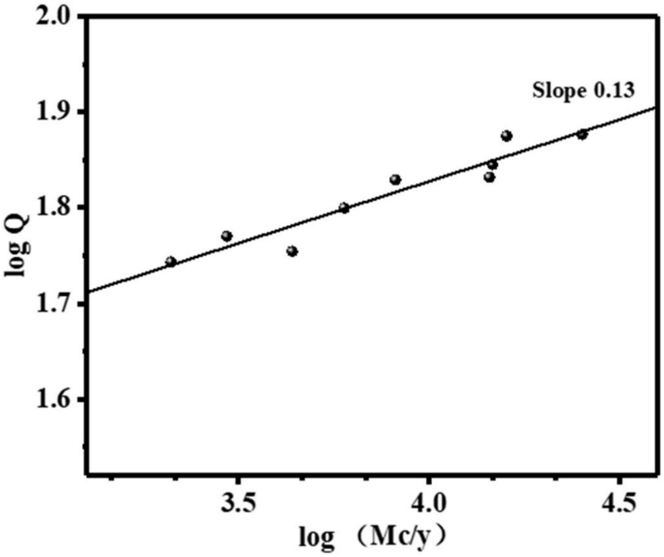

Fig. 2. Dependence of the swelling ratio Q of the homogenous areas in SL-g-PAA hydrogel model networks on the parameter (M_c/y).

Data availability

The authors do not have permission to share data.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.polymer.2024.126828.

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