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A Molecular Theory of Polymer Gels

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ABSTRACT: A new theory for polymer gels is developed on the basis of the single-chain mean-field (SCMF) theory. This theory takes the mesh chain or the star polymer as the characteristic unit of polymer gels, and it allows the study of chain conformation properties for gels in their different states. The preparation condition effect is conveniently described by the current theory, and the gels with complex chain structures can also be studied since the SCMF theory take realistic chain conformations into consideration. In this work, the theory is compared with the widely used Flory-type gel theory and with experimental observations. It is shown that the star polymer is a more natural basic unit of the gel structure. The current theory is found to provide a better description of the gels than the Flory-type theory as well as better agreement with gel swelling experimental data for poly(ethylene oxide) gels.

I. Introduction

We define a polymer gel as a chemically cross-linked network of polymer chains and exclude networks formed through interchain physical association. The objective of this work is to construct a theory for polymer gels, based on the single-chain mean-field theory, to study these complex and important materials at the molecular level.

Chemically cross-linked polymer gels can be prepared via the following three methods:[1] (i) random cross-linking of existing polymer chains, such as chemical or irradiation vulcanization; (ii) polymerizations of multifunctional monomer systems; and (iii) end-linking reactions of well-defined precursor polymer chains. The different preparation methods result in different polymer gel structures and hence different properties. Polymerization from monomers involves complex reaction kinetics. End-linking methods can be regarded as special and simplified cases for the random cross-linking method. Therefore, we will start from polymer gels made by the end-linking process. It will be shown that even for this apparently simple system there are important unsolved questions.

As a typical example for gels made by end-cross-linking, linear α,ω-dihydroxyl-PEG chains with a narrow distribution of molecular weights are reacted with multiisocyanate in stoichiometric amounts in dioxane solutions,[2] as shown in Figure 1. The precursor chains form the gel mesh chains, and their average configuration changes with the macroscopic gel (Figure 1).

The important parameters of the system include (i) the length N_c of the precursor chains, (ii) the volume fraction of the polymer ϕ_0 just before the cross-linking, (iii) the functionality ω of the cross-links, and (iv) the interaction parameter χ_0 between the polymers and the solvent used in the preparation.

Flory provided the most widely used theory for gels,[3] which is based on a simplified picture of hydrogels. The hydrogel is treated as a special solution system where the mesh chains cannot move freely relative to each other, but the chains can become elongated in a noninteracting way in the swelling process. Correspondingly, the free energy is divided into the mixing and elastic terms.

The mixing term of the gel system is treated by Flory−Huggins polymer solution theory, and the corresponding free energy per unit volume, f_{mix}, is

$$f_{\mathrm{mix}}/kT = (1 - \phi)\ln(1 - \phi) + \chi\phi(1 - \phi) \qquad (1)$$

k is the Boltzmann constant, T is the absolute temperature, ϕ is the polymer volume fraction of the swelling gel, and $1 - \phi$ is the solvent volume fraction. The parameter χ is the Flory polymer−solvent interaction parameter. In the right side of eq 1, the first term represents the translational entropy of solvent molecules and the second term is the interaction between polymer chains and solvent molecules.

It has been known that eq 1 underestimates the monomer correlation of polymer chains and hence overestimates the intrachain monomer repulsion in good solvent.[4] The polymers are treated in Flory's theory as unconnected monomers, and the conformational entropy of polymer chains and their interactions with the environment are separated.[5,6] However, it is their ability to change conformations with the environmental conditions that give polymers fascinating properties and numerous applications. Therefore, it is very desirable to have a polymer solution theory that can correlate the chain conformations with the thermodynamic properties of the system.

In the Flory gel theory, the treatment of the elastic term was based on the rubber elasticity theory, which in turn was derived from the Gaussian chain model.[3] The expression for the elastic free energy density was obtained as

$$f_{\mathrm{el}}/kT = \frac{3}{2}\nu_{\mathrm{e}}(\alpha_{\mathrm{s}}^{2} - 1 - \ln \alpha_{\mathrm{s}}) \qquad (2)$$

$$\alpha_{\mathrm{s}}^{3} = \phi_0/\phi \qquad (3)$$

Here, α_{s} is the linear deformation factor of mesh chains

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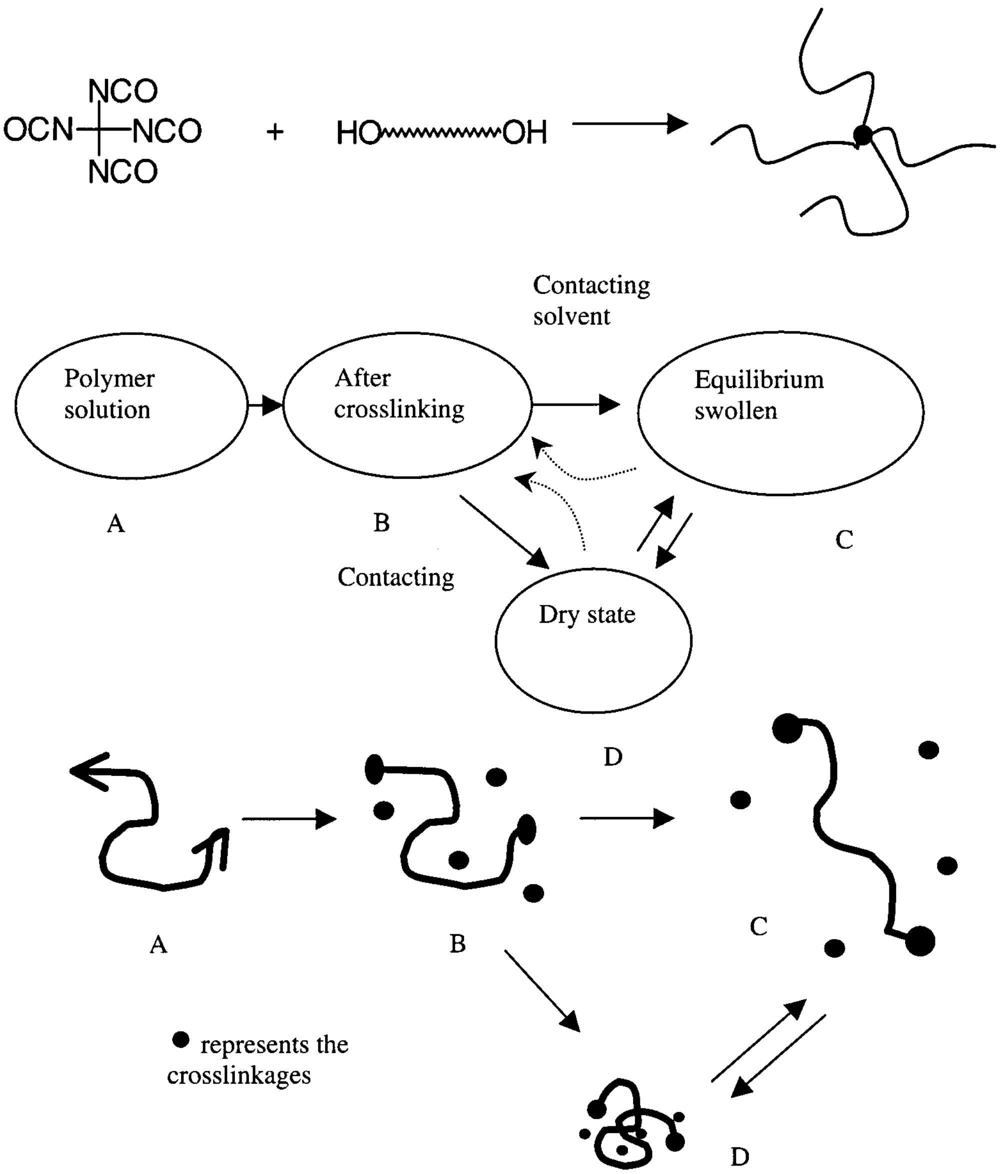

Figure 1. Schematic illustration of the different states of gels and their mesh chain conformations: A is the free mesh chain solution, B is the newly formed gel in the relaxed state, C is the equilibrium swollen state after contacting with solvent molecules, and D is the gel in the dried state. An example of the chemical reaction is shown on top of this figure for the preparation of end-linking poly(ethylene glycol) gels.

in the swelling process, and α_s^3 equals the swollen ratio of the hydrogel relative to the preparation state; ϕ_0 is the polymer volume fraction at the relaxed state (which might be taken as the same as the preparation state, see discussion below); and ν_e is the number of effective mesh chains per unit volume. For perfect networks with uniform mesh chain length but without dangling chain ends, ν_e can be expressed as follows, assuming that the molar volume of solvent molecules is the same as that of monomers of the polymer:

$$\nu_e = \phi/N_c \tag{4}$$

N_c is the number of monomers in each mesh chain.

Based on eqs 1–4, the relations among N_c, ϕ_0, the interaction parameter between polymer and the swelling agent χ, and the polymer volume fraction at the equilibrium swelling state ϕ_e have been derived. A few different forms of this relationship exist in the literature.[1,7] According to Peppas and Merrill,[8] the relation is

$$N_c = \frac{-\phi_0\left[\left(\frac{\phi_e}{\phi_0}\right)^{1/3} - \frac{1}{2}\left(\frac{\phi_e}{\phi_0}\right)\right]}{\ln(1-\phi_e) + \phi_e + \chi\phi_e^{2}} \tag{5}$$

and we cite this as the PMF (Peppas–Merrill–Flory) model in the following discussion. If the gels are made in the bulk polymer state, i.e., if $\phi_0 = 1.0$, then eq 5 reduces to the original Flory theory. Note that the only parameter characterizing the preparation condition in eq 5 is ϕ_0, the polymer volume fraction.

There are two obvious problems undermining the Gaussian chain model,[9] which is the basis of the elastic energy calculation in the Flory theory: (i) the chains in most of the cases other than under Θ-conditions do not behave in a Gaussian way, and (ii) the number of monomers between two cross-links, N_c, is often less than 100; therefore, the chains are not long enough to be taken as Gaussian. In good solvent, the Gaussian chain assumption also overestimates the elastic energy for stretched chains.[4] The separation of the mixing and elastic terms has also been criticized. These two terms both depend on the configurations of mesh chains, and therefore they are obviously connected by the nature of gel the structure.[10]

The successes of Flory's treatment depended on the cancellation of errors from the mixing and elastic terms[4] in eqs 2 and 3. Though Flory's theory has been widely used to predict the equilibrium swelling of polymer gels, it is obviously desirable to minimize the errors in this expression and develop a unified molecule theory for gels. The single-chain mean-field theory[6] seems a suitable basis for a new gel theory, which is able to describe better the mixing and the elastic term, and also correlates the chain conformations with the thermodynamics of the system.

The single-chain mean-field (SCMF) theory is based on analysis of a polymer chain in the mean field of the environment. It has the advantage of allowing both the conformational behavior of the chain molecules and the thermodynamic properties of the system to be studied within the same theoretical framework. The SCMF theory[6] has been shown to provide a better description of polymer solutions, especially in the dilute region, due to the recognition of the whole polymer chain as the basic unit in the model. The expression of the conformational entropy of mesh chains into their conformation probability distribution function (hereafter pdf) allows the removal of the Gaussian chain assumption in considering the elastic energy of the swelling gels. Moreover, as shown in the model proposed in the next section, the mixing and the elastic terms in gel systems are strongly correlated by the pdf of the mesh chain conformations. The SCMF theory also enables the study of the effect of complex geometry of mesh chains, such as branched mesh chains, which is difficult to handle in the classical theory.

In this work, we used the single-chain mean-field method to develop a new theoretical framework for polymer gels. The article is organized as follows: Section II describes the development of the theory, using linear mesh chains and star polymers as the characteristic units of polymer gels, respectively. Section III discusses the relationship among the relaxed state, the preparation condition, and the input chain conformation set, among which the last one is required to implement the theory. Following these, section IV presents several results from the theory and compares the data with PMF model as well as the experimental data. Finally, the last section includes concluding remarks.

II. Theory Development

In this section, we first develop the theory by using the mesh chain as the basic unit of polymer gels and then extend the theory by taking the star polymer as a more natural unit of the gel structure.

A. Mesh Chains as the Characteristic Gel Units. For swelling gels, the free energy of the whole system includes the following terms:

1. The translational entropy of solvent molecules expressed in eq 1.

2. The conformational entropy of the mesh chains, for which we use the form as $\nu_e \Sigma_{\{\alpha\}} P_\alpha \ln(P_\alpha)$, where ν_e is the number of effective mesh chains per unit volume, i.e., the same expression as eq 4, and P_α is the probability distribution function (pdf) of mesh chains with conformation α. This term is the Gibbs entropy for a system governed by the pdf.[11,12] This general form of the polymer conformation entropy makes it possible to remove the Gaussian chain assumption and provides the freedom to study polymers with complex structures.

3. The mixing interaction energy among polymers and solvents is expressed as $\nu_e \Sigma_{\{\alpha\}} P_\alpha n_{e\alpha} \chi(1-\phi)$, where $n_{e\alpha}$ is the total number of interactions of the mesh chain in conformation α with solvent molecules or segments belonging to other polymer chains.[6] Through this expression, the intrachain interactions are exactly accounted for, while the interchain and polymer−solvent interactions are considered in a mean-field level. This interaction expression had been shown to give better agreement with experiments than the simple mean-field theory.[6] It is through the chain property $n_{e\alpha}$ and the chain conformation pdf that the conformation of chains (entropy) and their interaction with the environment (enthalpy) become coupled.

4. Other interactions among mesh chains, which include the following two parts. The first is the interaction via the cross-links. We choose the following deformation assumption to represent it:

$$\phi^{2/3} \sum_\alpha P_\alpha R_{e,\alpha}{}^2 = \phi_0{}^{2/3} \langle R_e{}^2 \rangle_0 \qquad (6)$$

Here, parameters with subscripts 0 indicate the gel preparation condition, $R_{e\alpha}$ is the end-to-end distance of the mesh chains in conformation α, and $\langle\ \rangle$ represents the weighted average of the ensemble in the preparation state. This indicates that the end-to-end distance of mesh chains deforms to the same extent as the macroscopic sample in the swelling process. Another interchain interaction is the topological interaction by physical entanglement,[13,14] a complex term neglected for simplicity. We also neglect the so-called "entropic packing" effect[15] that describes average conformation changes due to polymer volume fraction changes.

Apart from the interchain entanglement effect, at this time, our model does not consider the junction fluctuation problem, which addresses the fluctuations of junctions (tie points, cross-links) around their mean position in the gel. The discussion of this would require a detailed description of how the junction fluctuation affects the mesh chain behavior, and currently no simple formulation is given. With this discussion, the free energy per unit volume of swelling gel is expressed as

$$f/kT = (1-\phi)\ln(1-\phi) + \nu_e \sum_\alpha P_\alpha n_{e\alpha} \chi (1-\phi) + \nu_e \sum_\alpha P_\alpha \ln P_\alpha \qquad (7)$$

To obtain the pdf of chain conformations, we minimize the free energy expression subject to constraint eq 6. Introducing the Lagrange multiplier κ, we get

$$P_\alpha = q^{-1} \exp(-\chi n_{e\alpha}(1-\phi)) \exp(\kappa R_{e,\alpha}{}^2 \phi^{2/3}) \qquad (8)$$

where the normalized factor is

$$q = \sum_\alpha \exp(-\chi n_{e\alpha}(1-\phi)) \exp(\kappa R_{e,\alpha}{}^2 \phi^{2/3}) \qquad (9)$$

The entire method is described by eqs 6−9. After incorporating the pdf into eq 6, we solve the nonlinear equation by standard numerical methods to obtain the

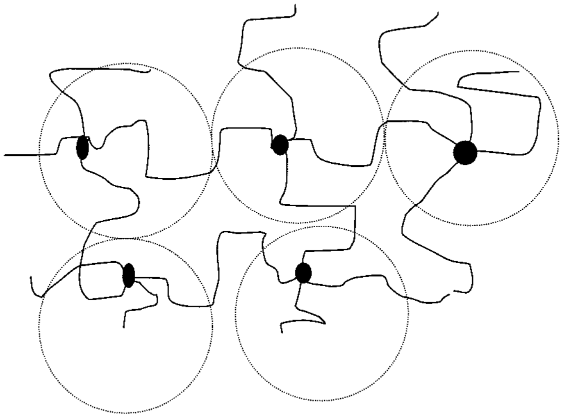

Figure 2. Star polymers consisting of cross-links and surrounding strands (each of which is a half mesh chain) are the more natural charactersitic units of a polymer gel, since they are equivalent to each other. This idea was first proposed by Silberberg.[16]

unknown parameter κ. This parameter appears in the Boltzmann factor of the pdf multiplied by the square of the end to end vector of that configuration. Thus, the physical meaning of κ is that of the elastic free energy associated with stretching the chain in conformation α away from the relaxed state (see below). The importance of this parameter is that, at difference with the classical theory of Flory, the elastic energy becomes a function of the chain model used and the relaxed state of the chain through ϕ_0 and the interactions parameter.

Once the elastic constant for the chain is known, the free energy of the system at different ϕ values can be calculated, and the minimum points are the equilibrium swelling points.[4]

B. Star Polymers as the Characteristic Gel Units. As first pointed out by Silberberg,[16] the characteristic structure units of polymer gels should not be the mesh chains, but star polymers consisting of the cross-links and the surrounding strands (each of which is a half mesh chain). As shown in Figure 2, the linear mesh chain model fails to count the special environment near the cross-links.[17,18] Therefore, both the mixing term and the elastic term and also the chain conformations could be better described by using the star polymers defined above as the characteristic units in the model.

The previously developed method can be easily modified to take star polymers as the basic unit. The swelling gel can be thought of as a special homogeneous solution of star polymers instead of mesh chains. As the gel swells, these star polymers expand. We define by r_α the effective diameter of the star polymers under conformation α, and we have

$$r_\alpha^{\ 2} = \frac{\sum_{i=1}^{\omega} r_{ie,\alpha}^{\ 2}}{\omega} \qquad (10)$$

Here, ω is the functionality of cross-links and $r_{ie,\ \alpha}$ is the end-to-center distance of the ith arm chain. Similarly, we use the simple deformation assumption to describe the interpolymer interaction caused by the cross-link topology as

$$\phi^{2/3}\sum_\alpha P_\alpha r_\alpha^{\ 2} = \phi_0^{\ 2/3}\langle r^2\rangle \qquad (11)$$

Here, the subscript 0 indicates the relaxed state.

The free energy per unit volume of the swelling gel has the same expression as in eq 7, except that the number of these star polymers per unit volume is now given by

$$\nu_{e,S} = \frac{\phi}{\omega N_c/2} \qquad (12)$$

Here, N_c is still the number of the segments each mesh chain has, and the factor $^1/_2$ indicates that only half of the segments in each mesh chain are included in the star polymer.

Following a similar derivation as above, the conformation probability distribution function of the star polymers is

$$P_\alpha = q^{-1}\exp(-\chi n_{e\alpha}(1-\phi))\exp(\kappa r_\alpha^{\ 2}\phi^{2/3}) \qquad (13)$$

κ is the unknown Lagrange multiplier as before, which again should be interpreted as the elastic constant associated with stretching the star polymer from its relaxed state. Note again that the theory incorporates the molecular structure of the polymers not only through the set of single chain configurations but also through κ, which incorporates the mean-field interactions of the swollen gel.

To implement the theory, a representative chain conformation set is required. The chain conformations can be generated by simple sampling for off-lattice chains and with the Rosenbluth and Rosenbluth (RR) algorithm for lattice chains, as previously described.[6,19,20] In the case of lattice chains we have used a simple cubic lattice, and we have generated 10^6 RR configurations. We have checked that doubling that number does not alter any of the predictions of the theory. For the off-lattice chains we used a rotational isomeric state model as described in detail in ref 20. Once the chains are generated, the probability distribution functions of the chain conformations are calculated, and all average properties such as the average chain conformation and the free energy of the system can be obtained. The details on the implementation of the theory can be found in the literature.[6,20]

III. The Preparation Condition and the Relaxed State of Gels

For gel made from solution, there are two parameters characterizing the preparation conditions: the polymer volume fraction ϕ_0 and the polymer/solvent interaction parameter χ_0. Most of the discussions in the literature focus on the effect of ϕ_0, but here we want to emphasize that the polymer/solvent interaction is also important for the relaxed state of gels made from solutions.

The relaxed state of gels is defined as the state where the mesh chains do not exert elastic forces on the cross-links,[21] and it is generally accepted that the nascent gel beyond the gelation point is in the relaxed state.[21−24] Gels made under different conditions have their unique relaxed states and hence have different molecular structures. For example, as shown in Figure 3, even with the same solvent volume fraction, the different polymer/solvent interactions result in different average chain conformations in the relaxed states and therefore different $\langle R_e^2\rangle_0$ that will influence the final (swollen) chains through the elastic term, κ, by means of eq 6.

The thermodynamic expression for the relaxed state is that the conformational entropy of polymer chains is

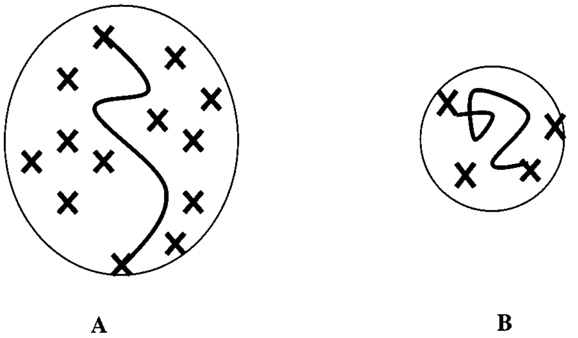

Figure 3. Representation of chain conformations in various relaxed states. The lines represent the mesh chains, while the crosses are the cross-links within the chain volume. The polymer volume fractiones of the gel in the relaxed state may be the same, but the polymer/solvent interactions are different in the two cases. The average chain conformation in the relaxed state is more expanded in the good solvent (case A) than in the bad solvent (case B).

at the maximum. We designate the conformation pdf of polymer chains in the relaxed state as $P_{\alpha 0}$. The change of the environment condition will cause the gel to deviate from its relaxed state and make the polymer chains exert forces on the cross-links. Thermodynamically, it changes the polymer chain conformation pdf from $P_{\alpha 0}$, which results in an increase of the elastic free energy.

The pdf of the polymer chains of the nascent gel is generally unknown. For gels made through the end-linking method, we further assume that it is equal to the pdf of polymer chain conformations just before the gelation. The chain conformations of free chains in the preparation solution can be written as[6]

$$P_{\alpha 0} \propto \exp(-\chi_0 n_{\mathrm{ea}}(1-\phi_0)) \qquad (14)$$

Here, the subscript 0 represents the parameters in the relaxed state. This assumption neglects the change of pdf needed for polymer chains to get cross-linked but is indirectly justified by the fact that the end-to-end distance of mesh chains does not change much across the gelation.[21-24]

The representative chain conformation set, which is used in the calculation, should represent exactly the mesh chain conformations in the relaxed state. The implicit assumption behind the conformation generation process is that all the conformations have the same probability in the set without further constraints. This corresponds to the entropy maximum of the unconstrained chains. For example, if the gel is prepared in a good solvent with $\chi_0 = 0$, we use a simple self-avoiding chain conformation set to represent the chains in the relaxed state. For other cases, we may still use the self-avoiding chain conformations, but with $P_{\alpha 0}$ to the conformation probability that will now minimize the free energy of the chain in the relaxed chain due to the presence of an interaction term.

IV. Results and Discussion

Representative chain conformation sets have been generated by simple sampling mostly on a cubic lattice model.[25] Comparisons are made among the predictions from PMF model, current theory with mesh chains (hereafter the mesh chain model), and star polymers (hereafter the star polymer model) as characteristic units. A more realistic chain conformation set based on off-lattice flexible star polymers[20] is also used for the comparison between theoretical predictions and experimental data.

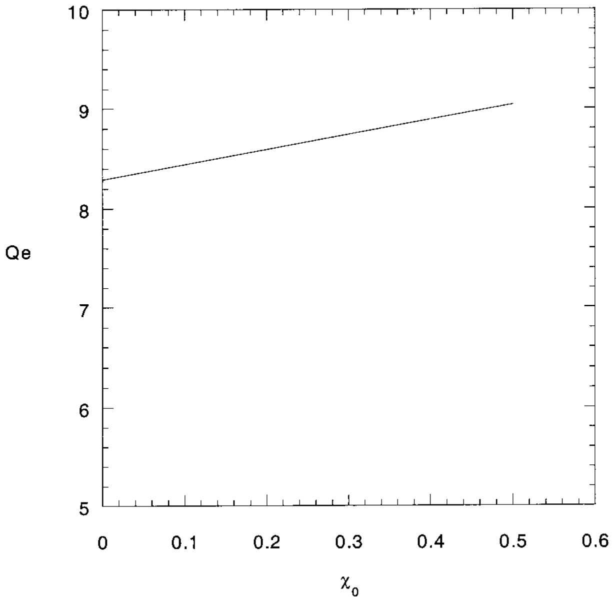

Figure 4. Equilibrium swelling ratio Q_e as a function of polymer/solvent interaction parameter χ_0 in the relaxed state. The solid line represents the prediction from the current model using linear mesh chains as basic units and assuming the gels are made from solution with $\phi_0 = 0.4$ and $\chi = 0.0$. The mesh chains have 40 segments.

First, it should be noticed that there is a minimum volume fraction in the preparation state to form a continuous end-linking gel.[26,27] In our calculation, we use the following equation to estimate this minimum ϕ_m:

$$\frac{4\pi}{3}\langle R_e{}^3\rangle_0 \phi_m \cong N_c a^3 \qquad (15)$$

where a is the lattice size. For example, $\phi_m \approx 0.01$ for $N_c = 40$ and $\chi_0 = 0.0$, which is very close to the value calculated based on Dusek's analysis.[26,27]

The effect of the solvent used in the preparation state is studied by the mesh chain model. Figure 4 shows the equilibrium swelling ratio as a function of χ_0, the polymer/solvent interaction parameter in the preparation state. The gel swells to a larger extent if it was prepared in a worse solvent, but the dependence is very weak. It is physically reasonable since gels made from bad solvent have a relaxed state where chains are in the less-expanded state, and therefore when the gel swells to the same extent, they have less elastic energy penalty than those made from good solvent. There is experimental evidence in the literature showing that the end-linking gels behave differently if prepared in different solvent,[28] but a more systematic experimental study is required to have a meaningful theory/experiment comparison on this preparation state effect.

Compared with the sparse experiments on the effect of solvent used in the preparation state, there are well-documented data on the effect of the polymer volume fraction ϕ_0 of the preparation solutions. Figure 5 shows the equilibrium swelling ratio as a function of ϕ_0 of the precursor polymers. The open circles in the figure are from the experimental studies of end-linking poly(ethylene glycol) (PEG) gels by Gnanou and co-workers.[2] In their system, the PEG chains had molecular weight

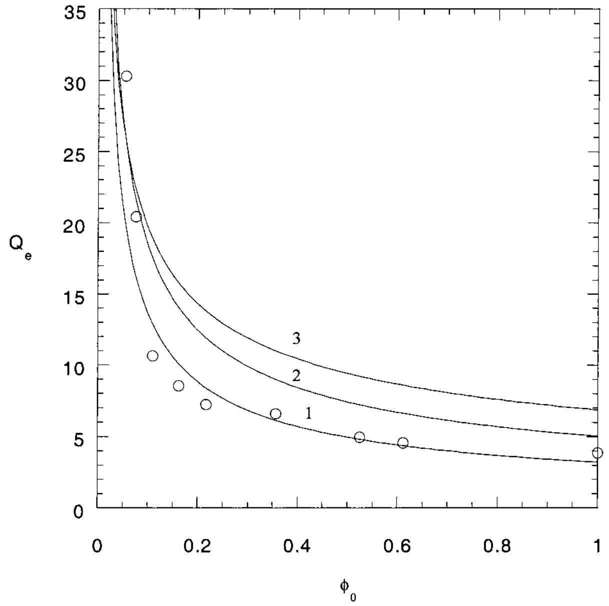

Figure 5. Equilibrium swelling ratio Q_e as a function of the polymer volume fraction of the gels in the preparation state. Curve 1 represents the prediction from the current model using lattice star polymers with $\omega = 4$ as the basic unit and assuming the gels are made from solution with $\chi_0 = \chi = 0.0$. The mesh chains have 40 segments. Curve 2 is the prediction of the linear mesh chain model, while curve 3 is that of the PMF model for the same system. The open circles are the experiemntal data from Gnanou et al.[2]

of 1800, i.e., 40 repeating units. The gels were made from dioxane solution with ϕ_0 ranging from 0.055 to 1.0, and the swelling studies were done in water. Curves 1, 2, and 3 in Figure 5 show the predictions from our star polymer model with $\omega = 4$, our linear mesh chain model, and the PMF model, respectively. In these theoretical calculations, we take the segment number in each mesh chain as $N_c = 40$ and assume the solvent molecules and the chain segments have the same volume. The polymer/solvent interaction parameters are taken as $\chi_0 = \chi = 0.0$, which is a good assumption for PEG/water interaction but may not be for PEG/dioxane interactions. However, we justify this assumption by the fact that the parameter χ_0 only has a weak effect on the results as shown in Figure 4.

All models predict very well the trend of increasing swelling ratio as increasing solvent fraction in the preparation state. It is shown that the PMF model predicts higher equilibrium swelling ratio than our models do. Padmavathi and Chatterji[29] studied the swelling of poly(ethylene glycol) diacrylate (PEGDA) gels with known mesh chain length and compared the results with the prediction from Flory-type equation. The comparison showed that the Flory theory indeed predicted higher swelling ratio, and the discrepancy with the experimental data became more significant for longer PEGDA chains, which is also compatible with our theoretical predictions (data not shown).

These effects may be understood conceptually as follows. The Flory theory overestimates both the intrachain repulsion in the mixing term and the elastic term with Gaussian chain assumption.[4] The overestimation in the mixing term would result in the prediction of higher equilibrium swelling ratio, which would be corrected to some extent by the overestimation of the elastic term in the free energy. However, as the mesh chains become longer, the Gaussian chain assumption becomes a better one to calculate the elastic energy. The overall effect on the prediction is a higher swelling ratio caused by the unbalanced overestimation of the intrachain repulsion in the mixing term.

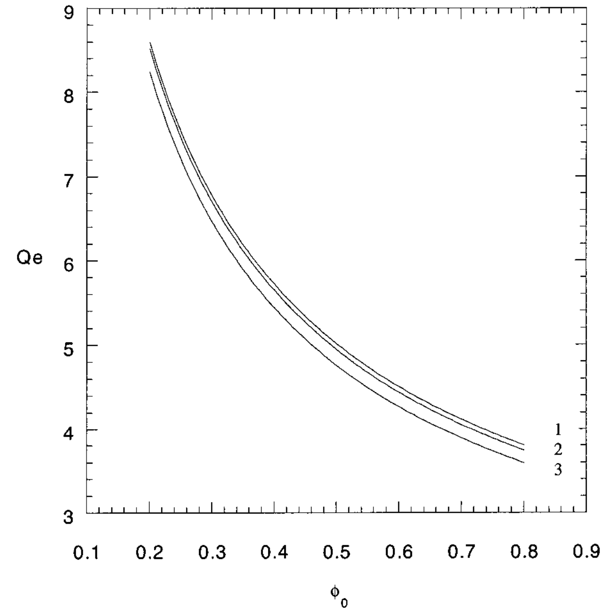

Figure 6. Equilibrium swelling ratio Q_e as a function of the polymer volume fraction of the gels in the preparation state. The lines are from the prediction of the current model using lattice star polymers with functionality $\omega = 3$ (curve 1), 4 (curve 2), and 5 (curve 3). The gels are made from solution with $\phi_0 = 0.4$ and $\chi_0 = \chi = 0.0$. The mesh chains have 40 segments.

The use of star polymers as the characteristic units of polymer gels should provide a more accurate description of gel properties. The analogy of a swollen gel and a solution of star polymers with the same geometry and concentration was mentioned in the literature.[4] However, to the best of our knowledge, this is the first time we study this idea in detail. As shown in Figure 5, the star polymer model predicts the lowest equilibrium swelling ratio. This is physically reasonable since, in their relaxed state, the chains in the star polymer conformation are more stretched than linear chains[17] and, therefore, higher elastic energy penalty when further elongated in the swelling process.

Figure 6 shows the swelling ratio as a function of ϕ_0 of the precursor polymers for three cases of different cross-link functionality. Curves 1, 2, and 3 are the prediction from the lattice star polymer model with $\omega = 3$, 4, and 5, respectively. The equilibrium swelling ratio decreases with the increase of the cross-link functionality, as previously predicted.[30] However, the effect predicted is rather small. In the relaxed state, chains of gels with higher cross-link functionality are more stretched, and they tend to elongated to a less extent when the gels contact with solvent molecules.

We have also used more realistic star polymer conformations for calculations in order to compare the predict ability of the current model. The experimental data are from the PEG gel works by Gnanou and coworkers[2] as previously described. The star polymer conformation set used in the calculations is generated by using an off-lattice model.[20] With this chain model, the SCMF theory has been shown to quantitatively predict the properties of PEG polymers such as their surface pressure isotherms at the air/water interface.[31–33]

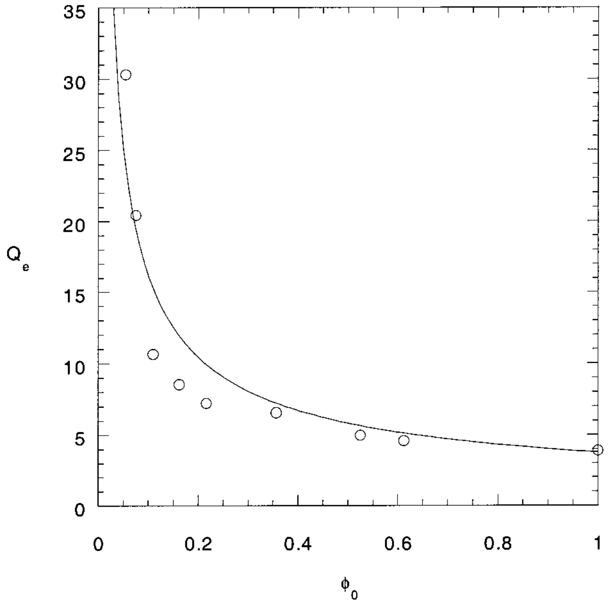

Figure 7. Equilibrium swelling ratio Q_e as a function of the polymer volume fraction of the gels in the preparation state. The curve represents the prediction from the current model using off-lattice star polymers with $\omega = 6$ as the basic unit and assuming the gels are made from solution with $\chi_0 = \chi = 0.0$. The mesh chains have 40 segments. The open circles are the experiemntal data from Gnanou et al.[2] The weight-average functionality of the cross-linkages in the experimental system is 6.4.

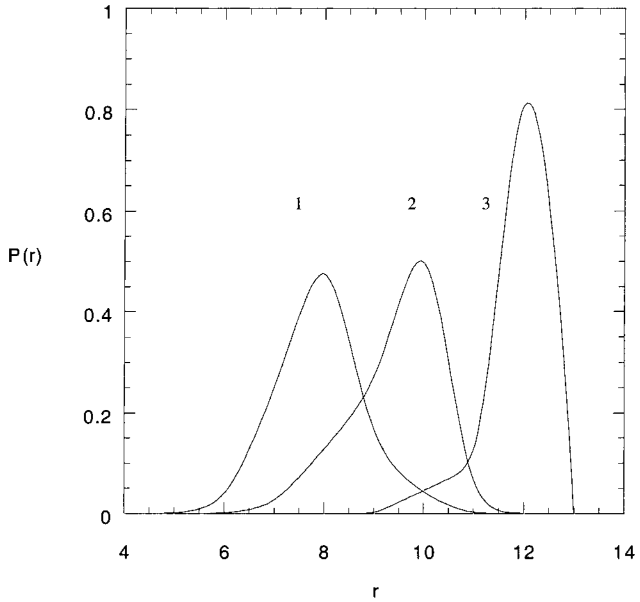

Figure 8. Probability distribution of the radius of the star polymers. The radius is in units of the monomer bond length. The curves represent the calculations of the off-lattice star polymer model: the relaxed state (curve 1); the equilibrium swelling state for gels made from solution with $\phi_0 = 0.2$ (curve 2) and 0.6 (curve 3). The gels have mesh chains of 40 segments and cross-link functionality $\omega = 6$ as the basic unit and assuming the gels are made from solution with $\chi_0 = \chi = 0.0$.

The functionality of the star polymers is chosen to be 6, which is close to the experimental data, where the weight-average functionality is 6.4 and the number-average functionality should be lower than this.

Figure 7 shows the comparison between the theoretical calculation based on the current model (curve) and the experiment (open circles) for the swelling ratio as a function of ϕ_0. The predicted swelling ratio from the current model using off-lattice star polymer units is lower than that from PMF model and very close to the experimental data. The agreement is even slightly better than the lattice model predictions over the whole range shown.

The theory also enables the study of the conformational changes of the gel chains for different thermodynamic states. As an example, Figure 8 shows the probability distribution of the star polymer radius $P(r)$ for a gel in three different states. Curve 1 represents the distribution in the relaxed state, and the distribution is independent of the solvent fraction under our assumption with $\chi = 0$. In the swelling process, the distribution should shift to larger r as shown. Curves 2 and 3 represent the distributions in the equilibrium swollen states for gels made from solutions with $\phi_0 = 0.2$ and 0.6, respectively. The distributions differ in not only their peak locations but also the shapes. Especially in the case where $\phi_0 = 0.6$, the distribution of the star polymer diameter is much narrower; i.e., they tend to have the same size in the equilibrium state.

V. Concluding Remarks

A new theoretical description of polymer gels was developed on the basis of the single-chain mean-field (SCMF) theory. Compared to the classical Flory gel theory, the new theory has the following advantages: (i) both of the mixing term and the elastic term in the free energy expression are better described; (ii) the current model can describe the chain conformation changes at the molecular level by calculating the probability distribution function of realistic chain models; (iii) the relationship between the preparation condition and the gel properties can be conveniently discussed; and (iv) within the power of SCMF theory, this model can describe gels with complex mesh chain structures or even heteropolymer chains.

In this work, we have shown that the star polymer is a more natural structure unit of polymer gels than the mesh chain, since the star polymer model takes into consideration the special environment near the cross-links. This idea, first proposed by Silberberg,[16] was here tested for the first time with a molecular level calculation. The agreement between the theoretical prediction based on the star polymer model and the experiment observation is very good.

The current model predicts a lower equilibrium swelling ratio than the Flory-type theory does for the same gel system. Experimental data suggests that the Flory theory indeed overestimates the equilibrium swelling ratio.

The effect of the solvent used in the preparation condition has been studied. The better the solvent, the average chain conformations in the relaxed state are more expanded, and hence the prepared gel swells to a less extent. For the system studied here, the dependence of the swelling ratio on the solvent used in the preparation is very weak. However, with the use of heteropolymer gels and solvent molecules with stronger polymer/solvent interactions, we may expect a stronger dependence. With the ability to describe the preparation condition effect and the chain conformation change, the current model should be able to help in the molecular design of new functional gels such as molecular imprinted gels,[34,35] where understanding the preparation condition effect and the chain conformation changes is essential.

Polymer gels are very complex materials, and the current theory is still too simple for a complete understanding of their structure–property relations. For example, a better gel theory should be able to describe the interchain entanglement effect. Nevertheless, the current model should serves as a new starting point for more studies in this field, just as the current understanding of polymer gels would not be possible without the vigorous debates of 50 years ago.[39,40]

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