Theoretical Model of Polymer Network Chain Formation under Strain

Yong Yu,* Shunping Yan,* Ye Fang, Qinshu He, Huyi Wang, Yong Qiu, and Qiang Wan

Institute of Systems Engineering, China Academy of Engineering Physics, Mianyang, Sichuan 621999, P. R. China

ABSTRACT: In this article, the polymer network chain formation through cross-linking and scission under n strain stages is studied based on the thermal fluctuation principle. The aim is to clarify the effects of chemical reactions, especially the network chain cross-linking, dangling chain cross-linking, cross-link scission, and network chain scission, on the free energy of network chain to generalize the classical two-network model. In our model, the free energy change for a chain formation is associated with the reaction sequences, except network chain cross-linking or cross-link scission reactions under the same strain stage. A new constitutive expression for network chain formed under two strain stages is derived according to affine deformation theory in which independent network hypothesis and stress-transfer function are not required. Comparison between our model and previous experimental data about recovered stretch ratio of γ-irradiated silicone elastomer validates that our model can give more precise result than previous two-network model.

1. INTRODUCTION

In general, most elastomeric polymer products are practically used under strain. And, the occurrence of cross-linking and scission is inevitable when the polymer is used at high temperature, irradiation condition, or long time duration, resulting in permanent changes in the chain property and network topology. This is termed as “chemical relaxation” effect for changes of the mechanical behavior with time. Based on the changes in average network chain property, Tobolsky and co-workers first proposed the two-network model to describe the relaxation behavior of rubber under strain. Independent network hypothesis is applied in Tobolsky’s two-network model, where the new cross-links formed by cross-linking are treated as an additional independent network to balance the stress of the original network. As the scission reaction is ignored, Berry et al. and Scanlan and Watson discovered that the Tobolsky’s two-network model cannot describe the stress relaxation behavior of aging rubber. Therefore, Flory and Fricker introduced stress-transfer function to describe the memory or feedback effect caused by the cross-link scission. Up to date, two-network model is widely used to describe elastic behavior for polymer temperature aging, oxidative aging, radiation aging, double network, transient network, and so on. In addition, molecular dynamics simulations have confirmed the two-network model and explained the stress-transfer function.

Although the two-network model has been successfully employed in many fields, it still cannot completely characterize the chemical reactions of a network chain formation. In Figure 1, we list several important chemical reactions during chain formation. First, the reaction from state of Figure 1a to state of Figure 1b or from state of Figure 1c to state of Figure 1d is network chain scission, which will form the stress-free dangling chains. Second, the reaction from state of Figure 1a to state of Figure 1c or from state of Figure 1b to state of Figure 1d is the network chain cross-linking, which will improve the cross-link density and therefore increase the material modulus. Especially, network chains formed by cross-linking of dangling chains are in the state of ease as sketched from state of Figure 1c to state of Figure 1d. Moreover, the reaction from state of Figure 1c to state of Figure 1a or from state of Figure 1d to state of Figure 1b is the cross-link scission, which will result in the feedback or memory effect. Additionally, it should be noted that there is another special reaction of cross-link scission, which is different from the reaction as shown in state of Figure 1c to state of Figure 1a. As shown in Figure 1e, chain AB and chain CD can be reorganized into chain AC and chain

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BD by the bond-exchange reaction, which yields covalent adaptable networks.\(^{10,17}\) Unfortunately, two-network model uses only two parameters, scission ratio \(\xi_{\text{sci}}\) and cross-linking ratio \(\xi_{\text{cl}}\) to describe the scission and cross-linking reactions.\(^{6,18,19}\) Obviously, the parameter \(\xi_{\text{sci}}\) does not distinguish effects of network chain scission and cross-link scission, and the parameter \(\xi_{\text{cl}}\) does not distinguish network chain cross-linking and dangling chain cross-linking.

Chemical reactions not only affect the property of network chain, but also affect the network topology. To study the effect of chemical reactions on the formation of a network chain, a lot of theoretical analyses\(^0\)\(^{-25}\) and numerical simulations\(^{21,26\text{--}31}\) have paid the main attention to the length or molecular weight of the chains and the topology of networks. Here, we focus on the effects of chemical reactions on the property of average network chains. Although numerical simulations\(^{32,33}\) can calculate the free energy of a network chain with the given formation history, there is not a systematic theoretical model for network chain formation due to arbitrary chemical reactions under \(n\) strain stages. To the best of our knowledge, only Baxandall and Edwards\(^{25}\) have given the theoretical function for the free energy changes of the network chains after cross-linking under \(n\) strain stages.

To describe precisely the formation history of an ideal chain over complex bond reactions, here we generalize the two-network model based on thermal fluctuation principle. In Section 2, we propose a fluctuation deformation-based method to describe the effect of cross-linking and scission on the free energy change of a network chain and build the theoretical formation model of the network chain under strain. In Section 3, based on our formation model, we discuss the relationship between the free energy change of a network chain and its formation history. In addition, we reconstruct the constitutive model for the network undergone two strain stages based on affine deformation and derive the recovered stretch ratio function. After the comparison between our theoretical model with previous experimental data about recovered stretch ratio of silicone elastomer, conclusions are given in the end.

2. THEORETICAL MODEL

2.1. Fluctuated Chain Model. Here, we adopt the assumptions as Flory’s two-network model to describe the chemical reactions of ideal chains based on affine deformation:\(^{14}\) (1) the positions of chemical bonds cross-linking and scission are independent and distributed uniformly in the network; (2) the cross-links deform as if they were embedded in a homogeneous and isotropic elastic continuum.

For ideal chains, the free energy is decided by the conformation entropy.\(^{20}\) Moreover, the Gaussian distributed conformation of ideal chains can be equivalent with an average chain composed of thermal fluctuated monomers. Hence, a fluctuated chain is introduced here as a representative chain to describe the mechanical behavior of polymer network. As shown in Figure 2a, monomers on chain AB fluctuate randomly from their thermal equilibrium positions except cross-links A and B pinned on the background. When cross-linking takes place on the monomer C, it is pinned on the elastic continuum background and its instantaneous location \(C_1\) is fixed. For example, if the instantaneous location \(C_1\) is at thermal equilibrium location \(C_0\) (free energy of this state is not changed), where the end-to-end distance ratio \(|R_{\text{AB}}|/|R_{\text{AB}}|\) equals Kuhn length ratio \(N_{\text{AC}}/N_{\text{BC}}\), the two subchains AC and BC have the same elastic property with the parent chain AB and permanent deformation is nonexistent. If cross-linking happens at \(C_1\), where the monomer C fluctuates from \(C_0\) with a fluctuation displacement \(\delta\), the elastic properties of two subchains AC and BC are different from that of parent chain AB and permanent deformation occurs. It should be noted that for an instantaneous location \(C_0\), the two subchains AC and BC are no longer Gaussian. In Section 2.2, we will introduce the statistical behavior of monomer C to keep the Gaussian property of subchains and make affine theory to be applicable. Based on affine theory, the deformation of the average chain is coincident with the macrodeformation. Therefore, the fluctuation displacement \(\delta\) can affect the macrodeformation and change the free energy. In other words, fluctuation-induced macrodeformation can be applied to describe the effect of cross-linking reaction on the free energy of a chain. Cross-link scission as the inverse reaction of cross-linking can also be handled by the fluctuation deformation. In the following, we use fluctuation deformation to describe the chemical reactions shown in Figure 1.

2.2. Cross-Linking Reaction. First, we analyze the cross-linking reaction. To simplify the model, Figure 2b shows that a one-dimensional chain AB with length \(N\) (number of Kuhn units) deforms from original end-to-end distance \(R_0\) to current end-to-end distance \(R\). The stretch ratio \(\lambda\) is defined as \(\lambda = R/R_0\). For the ideal chain in the one-dimensional space, we have \((R_{\text{AB}}^2) = Nb^2/3\), where the sign \((\cdot)^2\) expresses the mean value of a random variable and \(b\) is the Kuhn length. If cross-linking occurs at the equilibrium position \(C_0\) of monomer C, the chain AB is divided into two subchains AC and BC, whose Kuhn numbers are \(N_1\) and \(N_2\), respectively. Accordingly, the splitting ratios are defined as \(\theta_1 = N_1/N\) and \(\theta_2 = N_2/N\). So, the end-to-end distances of the two subchains AC and BC are \(R_1' = R\theta_1\) and \(R_2' = R\theta_2\), respectively. Obviously, this linear splitting does not change the total free energy.

Figure 2. (a) Illustration of the chain AB under thermal fluctuation. The red nails represent the cross-links pinned on the elastic continuum background. The blue dot line represents the conformation of the chain with monomer C at equilibrium location \(C_0\). The red line represents a random conformation of the chain after the monomer C pinned at location \(C_1\) with displacement \(\delta\) from \(C_0\). (b) Sketch of the one-dimensional model for a network chain cross-linking. (c) Schematic of the equivalent relationship between deformation free energy change \(\Delta F^b\) of cross-linking and fluctuation stretch ratio \(\lambda_{\delta}\).
Practically, the instantaneous position of monomer C deviates from the equilibrium position \( C_0 \) with the thermal fluctuation displacement \( \delta \). When cross-linking happens, monomer C is pinned on the instantaneous position \( C_1 \) in the elastic continuum background based on assumptions (2). So, we have the end-to-end distances \( R_{n} = R_{n}^{'} \pm \delta \), where the subscript \( n \) = 1 or 2 for subchains AC or BC. The additional stretch ratios imposed by fluctuation displacement \( \delta \) for AC and BC are

\[
\lambda_{\delta_{n}} = \frac{R_{n}^{'} \pm \delta}{R_{n}^{'}} = 1 \pm \frac{\delta}{R_{n}^{}}
\]

(1)

Define \( \lambda_{\delta_{n}} \) as the “fluctuation stretch ratio”. The end-to-end distances for AC and BC can be rewritten as

\[
R_{n} = R_{n}^{'} \theta_{n} \lambda_{\delta_{n}}
\]

(2)

For an ideal chain, the free energy can be expressed as

\[
F(N, R) = \frac{3k_{B}T}{2N} R^{2}_{a} + F(N, 0)
\]

(3)

in which \( k_{B} \) is the Boltzmann constant and \( T \) is the absolute temperature.\(^{10}\) The first term on the right of eq. 3 is \( R \)-dependent free energy and can be expressed as a function of \( \lambda \) with the form \( F^{R}(\lambda) = k_{B}T\lambda^{2}/2 \). Here, we named \( F^{R} \) as the deformation free energy. The second term \( F(N, 0) \) is the \( R \)-independent free energy for zero end-to-end distance chain and depends only on the Kuhn units number \( N \).\(^{35}\) Because the total number of Kuhn units is not changed by the chemical reactions, the equation \( F(N, 0) = F(N_{0}, 0) + F(N_{0}, 0) \) for the subchains AC and BC must be held. Therefore, the free energy change caused by chemical reactions depends only on the deformation free energy change, which means \( \Delta F = F(N, R) - F(N_{0}, R_{1}) - F(N_{0}, R_{2}) = \Delta F^{R} \). For a subchain in one-dimensional condition, free energy change caused by the fluctuation stretch ratio is \( \Delta F(\lambda_{\delta_{n}}) = k_{B}T\lambda_{\delta_{n}}^{2}(\lambda_{\delta_{n}}^{2} - 1)/2 \). It is noted that the stretch ratio of each subchain \( \lambda_{n} = \lambda\sqrt{\theta_{n}} \) because original end-to-end distance of the subchain is \( R_{n}^{0} = R_{n}\sqrt{\theta_{n}} \). Therefore, free energy changes of the two subchains are

\[
\Delta F_{n}(\lambda_{\delta_{n}}) = \frac{3k_{B}T}{2N\theta_{n}} \left( \frac{\delta^{2}}{\theta_{n}} \pm 2\delta R \right)
\]

(4)

Hence, all the free energy change caused by the fluctuation displacement \( \delta \) reads

\[
\Delta F(\delta) = \Delta F(\lambda_{\delta_{n}}) + \Delta F(\lambda_{\delta_{n}})
\]

\[
= \frac{3k_{B}T\delta^{2}}{2N\theta_{n}} \left( \frac{1}{\theta_{n}} \right)
\]

(5)

Based on the theory of thermodiffusion, \( \Delta F(\delta) \) must conform to Boltzmann distribution. So, the probability of \( \delta \) is \( P(\delta) = A \exp(-\Delta F(\delta)/k_{B}T) \), where \( A \) is the normalized constant. The mean values of \( \delta \) and \( \delta^{2} \) can be derived as \( \langle \delta \rangle = 0 \) and

\[
\langle \delta^{2} \rangle = \frac{N\theta_{n}^{2}}{3\theta_{n}}
\]

(6)

Taking the value of \( \langle \delta^{2} \rangle \) into eq 5, we have \( \langle \Delta F(\delta) \rangle = k_{B}T/2 \), which is independent of the deformation state. In the remaining of this paper, we directly use the free energy change \( \Delta F \) to express the mean value of free energy change. Equivalently, we can obtain the value of \( \Delta F \) by the theorem of energy equipartition theory. When the number of chains increases by one, the free energy of system increases by \( k_{B}T/2 \) per space dimension. Thus, the effects of the reactions, including cross-linking or scission, on the free energy change of the system can be linked to the fluctuation stretch ratio through eqs 4–6. Taking the value of \( \langle \delta^{2} \rangle \) into eq 2 and choosing \( \lambda = 1 \), the mean square values of end-to-end distances for AC and BC are \( \langle R_{1}^{2} \rangle = N\theta_{0}\lambda^{2}/3 \) and \( \langle R_{2}^{2} \rangle = N\theta_{0}\lambda^{2}/3 \), respectively, which satisfy the characteristic of Gaussian chains. With the help of the statistical behavior about monomer C, subchains hold the Gaussian property and affine theory is applicable.

It should be noted that the fluctuation stretch ratio \( \lambda_{\delta} \) does not affect the mean value of end-to-end distance because of \( \langle \lambda_{\delta_{n}} \rangle = 1 \) based on eq 1. But \( \lambda_{\delta} \) plays an important role in relating the cross-linking with deformation of the chain and makes the subchains following the Gaussian distribution. Figure 2c illustrated the relationship between the deformation free energy change and fluctuation stretch ratio. For a network chain in the state of \( S_{1} \) with stretch ratio \( \lambda_{1} \), the relationship between deformation free energy and stretch ratio can be described by the function \( F_{1}(\lambda_{1}) \). After cross-linking, the network chain changes from state \( S_{1} \) to \( S_{2} \) with deformation free energy increment \( k_{B}T/2 \). The relationship of deformation free energy and stretch ratio for \( S_{2} \) can be described by another function \( F_{2}(\lambda_{2}) \). For equivalence, the deformation free energy of state \( S_{2} \) equals that of state \( S_{1} \) according to the relationship \( F_{1}(\lambda_{1}) = F_{2}(\lambda_{2}) \). The deformation in state \( S_{3} \) has an increment \( \lambda_{\delta} \) compared with state \( S_{1} \), where \( \lambda_{\delta} \) represents the fluctuation stretch ratio due to cross-linking. So, the description of cross-linking reaction can be unified in the deformation-dependent free energy function of \( F(\lambda_{\delta}) \).

We generalize the cross-linking model of one deformation stage to \( n \) discrete deformation stages, where one cross-linking reaction happens at each deformation stage. This problem has been discussed by Baxandall and Edwards with the replica theory.\(^{34}\) Assume that the end-to-end distance of an original network chain \( R_{0} \) after \( i \)-th cross-linking is \( R_{i} \) and the splitting ratio of \( R_{i} \) relative to \( R_{i-1} \) is \( \theta_{i} \) where \( i = 1, 2, ..., n \). The fluctuation stretch ratio caused by the cross-linking in \( i \)-th deformation stage is \( \lambda_{\delta_{i}} \) and we have \( \lambda_{\delta_{i}} = 1 + \delta/(R_{i}/\theta_{i}) \) based on eq 1. Generalizing eq 2 to the \( n \)th stage, we have

\[
R_{n} = R_{0}\prod_{i=1}^{n}(\lambda_{i}\theta_{i}/\lambda_{\delta_{i}})
\]

(7)

where \( \lambda_{i} \) is the stretch ratio of the \( i \)-th stage related to \( (i-1) \)-th stage. Introducing variables

\[
\Lambda_{\delta_{i}} = \prod_{i=1}^{n}(\lambda_{\delta_{i}}^{2})
\]

\[
\Lambda_{\lambda} = \prod_{i=1}^{n}\lambda_{i}
\]

\[
\Theta_{\lambda} = \prod_{i=1}^{n}\theta_{i}
\]

(8)

which represent the accumulated values of the mean-square fluctuation stretch ratio, stretch ratio, and splitting ratio after
original network chain cross-linking $n$ times, respectively, the mean-square end-to-end distance $R_n$ of eq 7 yields

$$\langle R_n^2 \rangle = \langle R_0^2 \rangle \Lambda_n^2 \delta \Lambda_n^2$$

(9)

Using the recursive method, we obtain the mean-square fluctuation stretch ratio as (see Appendix for detail)

$$\Lambda_{\delta_i}^2 = 1 + \sum_{i=1}^{n} \left( \frac{B_i}{\Lambda_i^2} \right)$$

(10)

where $B_i = 1/\Theta_i - 1/\Theta_{n-i}$ is named as the multiplication factor for the $i$th stage, representing the incremental number of network chains from $(i - 1)$th stage to the $i$th stage. Obviously, the deformation free energy of a single network chain is

$$F^R = \frac{3k_B T}{2} \langle R_n^2 \rangle / 3 = \frac{k_B T}{2} \Theta_n \Lambda_n^2 \Lambda_{\delta_i}^2$$

(11)

Explicitly, the value of $1/\Theta_n$ denotes the total number of subchains formed after the $n$th stage. If the subchains experience additional deformation $\lambda$ after $n$ deformation stages, the final deformation state is $\Lambda = \Lambda_\lambda \Lambda_n$. Therefore, the free energy change of a network after $n$ deformation stages is the difference between the total free energy of the current state $P^n/\Theta_n$ and the state without chemical reactions $k_B T \Lambda^2/2$, which yields

$$\Delta F = \frac{k_B T}{2} \sum_{i=1}^{n} B_i \left( \Lambda_i^2 \Lambda_{\delta_i}^2 \right)$$

(12)

The result of eq 12 coincided with the Baxandall and Edwards’ model, but the derivation here does not use the replica theory. Especially for one time cross-linking condition of $n = 1$, we have $\Delta F = (k_B T/2)(\Lambda^2/\Lambda_n^2)$.

2.3. Cross-Link Scission Reaction. Now, we consider the cross-link scission reaction. As sketched in Figure 3a, the uncross-linking state $S_1$ has one network chain with free energy $F_1$, and the cross-linking state $S_2$ has two network chains with free energy $F_2$. The progress of cross-linking reaction is from state $S_1$ to $S_2$, and the inverse progress is the cross-link scission reaction. According to the view of the chemical reaction kinetics, these two reactions have different energy barriers to overcome. However, according to the view of the chemical reaction thermodynamics, the energy difference between $S_1$ and $S_2$ is fixed as $k_B T/2$, which is independent of reaction paths and deformation state. If we set a cross-link break in deformation state of $\Lambda_\delta$, the total free energy change of chains is $-(k_B T/2)(\Lambda^2/\Lambda_{\delta_i}^2)$ when the network deforms to stretch ratio $\Lambda$, which is the reverse value of cross-linking for $n = 1$.

Figure 3b shows an ordinary network chain $AB$ formed from cross-link scission of $AC$ and $BC$. Network chain $AC$ is formed from chain $L_1$ by $n_1$ stages cross-linking and $BC$ is formed from chain $L_2$ by $n_2$ stages cross-linking. Assume that the system is undergone $n$ strain stages before cross-link scission, we have $n \geq n_1$ and $n \geq n_2$. Introduce null stage (no chemical reaction) with the $B_{n_1}^{AC} = 0$ or $B_{n_2}^{BC} = 0$ into $L_1$ or $L_2$ to make sure $n_1 = n_2 = n$. Cross-linking history of $AC$ and $BC$ are defined as $\Theta_n^{AC}$, $\Lambda_n^{AC}$, $\Theta_n^{BC}$, and $\Lambda_n^{BC}$, respectively. $\Lambda_n^{AC}$ and $\Lambda_n^{BC}$ can be obtained from eq 10, and the free energy for $AC$ and $BC$ can be derived from eq 11. When the cross-link scission happens at $(n + 1)$ step with strain state $\Lambda_{n+1}$, the free energy change by cross-link scission is $-(k_B T/2)(\Lambda^2/\Lambda_{n+1}^2)$, and the total free energy of chain $AB$ is

$$F_{AB}^R = F_{AC}^R + F_{BC}^R = \frac{k_B T}{2} \frac{\Lambda^2}{\Lambda_{n+1}^2}$$

with

$$\Theta_{n+1}^{AB} = \Theta_n^{AC} + \Theta_n^{BC}$$

$$B_{n+1}^{AB} = \left( \frac{\Theta_n^{AC} B_{n+1}^{AC} + \Theta_n^{BC} B_{n+1}^{BC}}{\Theta_{n+1}^{AB}} \right)$$

with $i \leq n$

$$B_{n+1}^{AB} = -\frac{1}{\Theta_{n+1}^{AB}}$$

(13)

(14)

in which $B_{n+1}^{AB}$ $(i = 1, 2, \ldots, n + 1)$ are the equivalent multiplication factors, and $\Lambda_{n+1}^{AB}$ is the mean-square fluctuation stretch ratio of chain $AB$. Here, $(\Lambda_{n+1}^{AB})^2$ has the same functional form as the $(\Lambda_{n+1}^{AC})^2$ in eq 10, which indicates that the cross-link scission can also be described by the fluctuation stretch ratio. Therefore, if we choose chain $AB$ experiencing $n$ times cross-linking and one time cross-link scission as the average chain, the free energy change of network has the same form as eq 12, which is

$$\Delta F = \frac{k_B T}{2} \sum_{i=1}^{n+1} B_{n+1}^{AB} \left( \frac{\Lambda^2}{\Lambda_i^2} \right)$$

(15)

Explicitly, we have $B_{n+1}^{AB} < 0$ in eq 15, which represents the total decrement of cross-links due to the cross-link scission reaction, and we no longer need the stress-transfer function to describe the cross-link scission reaction. Although Baxandall and Edwards have obtained eq 12, they have not extended the equation to describe the cross-link scission reaction. Additionally, for any cross-linking and cross-link scission sequence, we
can obtain multiplication factors from eq 14 and the total free energy change from eq 15.

2.4. Other Reactions. Network chain scission is another scission reaction, illustrated as the reaction from state of Figure 1a to state of Figure 1b. Because the dangling chains formed by network chain scission cannot bear loads, the deformation free energy must be zero, which means $F^D = 0$. Network chain scission loses all formation history of the original chain. So, we have $\Lambda_{6}^D = 0$ from eq 11. After network chain scission, the dangling chains can cross-link to form new stress-free network chains under strain $\Lambda_f$ which is the reaction illustrated in the reaction from state of Figure 1b to state of Figure 1d. In this case, the deformation free energy of the new network chain is

$$\Lambda_{6}^D = \frac{1}{\Lambda_f^2}$$

(16)

which is completely different from eq 10 for the loss of formation history. In addition, the dangling chain can form dangling cyclic chain through cross-linking by itself. The dangling cyclic chain also cannot bear loads, so we have $F^D = 0$ and $\Lambda_{6}^D = 0$ based on eq 11. For the bond-exchange reaction as shown in Figure 1e, it only changes the network topology and does not change the number of chains. So, the free energy of network chain does not change. Many researches have been done to study the changes in network topology on the network elasticity,

$$\delta = 0$$

but here we just focus on the free energy changes of average chain under isotropic condition.

From the above discussion, our model can be used to describe different chemical reactions and their effects on the free energy of network chain. The formation history of a network chain is recorded by accumulated values of fluctuation stretch ratio. We can find that the chain scission has an important effect on the formation of network chain because it makes the network chain lose the formation history until reforming the new network chain.

3. RESULTS AND DISCUSSION

3.1. Formation History of a Network Chain. In general, the formation history of a network chain is the sequence of chemical reactions under different deformation states. We first discuss the relationship between the free energy change of a network chain and chemical reaction sequence. Based on eqs 12 and 15, the total free energy changes of the system due to cross-linking and scission directly relate with $B_i$ and $\Lambda_i$ ($i = 1, 2, ..., n$). Obviously, if $B_i$ changes with $\Lambda_n$, the formation history of the chain is correlated with the cross-linking and scission sequence. If $\Lambda_i$ is fixed, the sequence of $B_i$ can be changed. This sequence-independent property has been used in the classical two-network model. It not only simplifies the theoretical analysis of cross-linking and cross-link scission
ddoes but also reduces the calculation complexity of numerical simulation greatly.

$$\delta = 0$$

When network chain scission happens, the dangling chains are formed and the strain state is released. As the lost deformation history is dependent on the sequence number of network chain scission reactions, the chain formation sequences have great effect on the free energy change. In conclusion, the free energy change for a chain formation is associated with the reaction sequences, except network chain cross-linking or cross-link scission reactions under the same strain stage.

3.2. Constitutive Model. Using our network chain formation model, we reconstruct the constitutive equation for the polymer undergone chemical reactions at deformation state $\Lambda_f$. Based on the formation history, the network chains are categorized into dangling-dependent chains whose formation history contains network chain scission and dangling-independent chains whose formation history does not include the network chain scission. Assume that the fraction of the original chains undergone chain scission reaction is $\xi_{sci}$. So, the network chains can be categorized into dangling-dependent chains with proportion $\xi_{sci}$ and dangling-independent chains with proportion $(1 - \xi_{sci})$. Set the average multiplication factor of each chain as $B$, so the increment number of chains or cross-links is $\xi_{sci} = B$. For dangling-independent chains, the mean-square fluctuation stretch ratio can be deduced from eq 10 as $\Lambda_{6}^{sci} = 1 + \xi_{sci}/\lambda_i^2$. For the dangling-dependent chains, the reaction sequence can affect the mean-square fluctuation stretch ratio but not the constitutive model. For simplification, we assume the chain breaks first and then cross-links with another chain to form a new network chain; hence, $\Lambda_{6}^{sci} = \xi_{sci}/\lambda_i^2$. After the chemical reactions, the state of each chain can be described as $\Lambda_{6}^{sci}$. Here, we use the same symbols $\xi_{sci}$ and $\xi_{sci}$ with different physical meaning to compare with classical two-network model. Because these two types of chains are independent, the stress $\sigma_{total}$ of the system can be derived by superposing their stresses as

$$\sigma_{total} = \sigma((1 - \xi_{sci}), \lambda \Lambda_{6}^{sci}) + \sigma(\xi_{sci}, \lambda \Lambda_{6}^{sci})$$

(17)

where $\sigma(\bullet)$ expresses the constitutive equation. Because the free energy changes are taken into account naturally in our formation model, the independent network hypothesis and the stress-transfer function are not needed, which coincide with the result of Weisgraber’s molecular dynamics simulation.

Under uniaxial load in the $x$-direction, we use the Neo–Hookean constitutive model to obtain the constitutive equation as

$$\sigma_{total} = G_0 (1 - \xi_{sci}) \left( \lambda^2 \Lambda_{6}^{sci} - \Lambda_{6}^{sci} \right) + G_0 \xi_{sci} \left( \frac{\lambda^2 \Lambda_{6}^{sci}}{\lambda} - \Lambda_{6}^{sci} \right)$$

(18)

where $G_0$ is the shear modulus of the pristine material. The first item on the right side of eq 18 is the stress coming from dangling-independent chains whose mean-square fluctuation stretch ratio is $\Lambda_{6}^{sci} = 1 + \xi_{sci}/\lambda_i^2$. For the uniaxial loading condition, if the stretch ratio in the $x$ direction is $\lambda_x$ and the stretch ratios in the $y$ and $z$ axes are the same as $1/\sqrt{\lambda_z}$, then the mean-square fluctuation stretch ratio in the $y$- and $z$-directions are $\Lambda_{6}^{sci} = 1 + \xi_{sci}/\lambda_i^2$. The second item on the right side of eq 18 is the stress coming from the dangling-dependent chains whose mean-square fluctuation stretch ratio is $\Lambda_{6}^{sci} = \xi_{sci} \lambda_i$. Then, eq 18 can be simplified as the following form

$$\sigma_{total} = G_0 \left( 1 - \xi_{sci} \right) \left( \frac{\lambda^2}{\lambda} - \frac{1}{\lambda} \right) + \xi_{sci} \left( \frac{\lambda^2}{\lambda} - \frac{\lambda}{\lambda} \right)$$

(19)
Obviously, eq 19 has the same form as the constitutive equation based on the two-network model. Solving eq 19 for \( \sigma = 0 \), we obtain the recovered stretch ratio as

\[
\lambda_s = \left( \frac{1 + f_{\text{eff}} \lambda_1}{1 + f_{\text{eff}} / \lambda_1^2} \right)^{1/3}
\]

(20)

where \( f_{\text{eff}} = \xi_{\text{sci}}/(1 - \xi_{\text{sci}}) \). For the constitutive equation base on two-network model, we also get the same expression of recovered stretch ratio as eq 20, but \( f_{\text{eff}} = f_{\text{sci}}/f_{\text{sci}} \). Specially, for Tobolsky’s two-network model, we have \( f_{\text{eff}} = \xi_{\text{sci}} \) and \( f_{\text{sci}} = 1 \) for just the cross-linking reaction. For Fricker’s two-network model, the additional stress-transfer function \( \Phi = \xi_{\text{sci}}/(1 + \xi_{\text{sci}}) \) is needed to describe the memory or feedback effect of cross-link scission, and we have \( f_{\text{sci}} = (1 - \xi_{\text{sci}} + \Phi \xi_{\text{sci}}) \) and \( f_{\text{eff}} = (1 - \Phi) \xi_{\text{sci}} \).

To validate our model, we compare the results of our model with the experiment and the previous two-network model. Here, we adopt the experimental data about the recovered stretch ratio of the stretched silicone elastomer after \( \gamma \)-radiation obtained by Chinn et al.\(^3\). With the assumption of the linear dependence of chain scission, cross-linking, and cross-link scission proportions on radiation dosage \( D \), we have \( \xi_{\text{sci}} = k_{\text{sci}}D, \xi_{\text{sci}} = k_{\text{sci}}D \), where \( k_{\text{sci}} \) and \( k_{\text{sci}} \) are constants. In the experiment of Chinn et al.,\(^3\) the values of stretch state for \( \gamma \)-radiation are \( \lambda_1 = 1.2, 1.4, 1.6 \), and 1.9. Using eq 20 to fit the experimental data, we have \( k_{\text{sci}} = 0.002203 \) (kGray\(^{-1}\)) and \( k_{\text{sci}} = 0.007273 \) (kGray\(^{-1}\)), which are different from the values of Maiti et al. obtained from the two-network model with \( k_{\text{sci}} = 0.002 \) (kGray\(^{-1}\)) and \( k_{\text{sci}} = 0.010 \) (kGray\(^{-1}\)). Figure 4a\(^{37}\) gives the comparison of the results of our model, the experimental data, and results from Fricker’s two-network model. Both our model and Fricker’s two-network model can give good prediction for conditions of \( \lambda_1 = 1.2, 1.4, \) and 1.6. But for \( \lambda_1 = 1.9 \), Fricker’s two-network model has a great derivation from the experimental data and our model can also give a good prediction. The reason is that our model can properly distinguish the different reactions and their effects on the free energy of network chain. Moreover, net cross-link density ratio can be calculated as \( \sigma_1/\sigma_0 = (1 - \epsilon_{\text{sci}} + \xi_{\text{sci}}) \), where \( \epsilon_{\text{sci}} \) and \( \epsilon_{\text{sci}} \) are the cross-link density of the current state and the initial state. Figure 4b\(^{37}\) gives the comparison of the experimental data measured by NMR and solvent swelling methods,\(^3\) results from Tobolsky’s two-network model,\(^6\) Fricker’s two-network model,\(^3\) and our model. It is apparent that our model is more precise than the previous models and give a better prediction of the net cross-link density ratio for all dose ranges. Here, we use the average chain to represent the property of the isotropic affine network. However, the real network is generally complex and many factors can affect the property of the system, including the pending chains, cyclic defects, entanglements, and so on. The deviations between the theoretical model and reality are included in the fit parameters, such as \( k_{\text{sci}} \) and \( k_{\text{sci}} \) used here.

4. CONCLUSIONS

According to the principle of the thermal fluctuation, we propose the fluctuation deformation to describe the effect of the chemical reactions on the free energy change of polymer network chain under strain, including the reactions of cross-linking, cross-link scission, and chain scission. The formation history of an ideal network chain formed through chemical reactions on \( n \) strain stages is modeled as the function of the mean-square fluctuation stretch ratio. In our model, the free energy change for a chain formation is associated with the reaction sequences, except network chain cross-linking, or cross-link scission reactions under the same deformation state. Classifying network chains as dangling-dependent chain and dangling-independent chain, the constitutive equation for network chains formed under two strain stages is derived in the affine theory framework. Compared to classical two-network model, the independent network hypothesis and stress-transfer function are not needed in our model, and the recovered stretch ratio derived from our new two-network model is better able to predict the experimental results. In conclusion, the connection between the fluctuation stretch ratio and the chemical reactions in our model can give insight into the nature of the formation of network chains under strain, and can be applied to describe the mechanical behavior of polymer undergone chemical reactions in various applications.

APPENDIX: MEAN-SQUARE FLUCTUATION STRETCH RATIO AFTER \( N \) TIMES CROSS-LINKING

In Section 2.2, we consider a chain formed by \( n \) times cross-linking happening on \( n \) discrete deformation stages, where one
cross-linking occurs at each deformation stage. The end-to-end distance is expressed as eq 7. Based on the definition of splitting ratio, the Kuhn number of a network chain undergone $(n-1)$ cross-linking reactions is

$$N_{n-1} = N_0 \theta_1 \theta_2 \cdots \theta_{n-1} = N_0 \prod_{i=1}^{n-1} \theta_i$$  \hspace{1cm} (A.1)

According to eq 1 for one time cross-linking happening on one deformation stage, the $n^{	ext{th}}$ fluctuation stretch ratio is

$$\lambda_{n} = 1 + \frac{\delta_{n}}{R_0 \prod_{i=1}^{n} (\lambda_i \theta_i) \prod_{i=1}^{n-1} \lambda_i}$$  \hspace{1cm} (A.2)

When the $n^{	ext{th}}$ cross-linking reaction takes place with the splitting ratio $\theta_n$ based on eq 6 and eq A.1, the mean-square fluctuation deformation is

$$\langle \delta_{n}^2 \rangle = \frac{1}{3} N_n b^2 \theta_n (1 - \theta_n)$$

$$= \frac{1}{3} N_n b^2 (1 - \theta_n) \prod_{i=1}^{n} \theta_i$$  \hspace{1cm} (A.3)

Owing to $\langle \delta_{0} \rangle = 0$, we have $\langle \lambda_{0} \rangle = 1$ and the mean-square the $n^{	ext{th}}$ fluctuation stretch ratio is

$$\langle \lambda_{n}^2 \rangle = 1 + \frac{\delta_{n}^2}{R_0 \prod_{i=1}^{n} (\lambda_i \theta_i) \prod_{i=1}^{n-1} \lambda_i \theta_i} \quad (A.4)$$

Substituting eq A.3 and $(R_0^2) = N_n b^2/3$ into eq A.4, we have

$$\langle \lambda_{n}^2 \rangle = 1 + \frac{1 - \theta_n}{\prod_{i=1}^{n} (\lambda_i \theta_i) \prod_{i=1}^{n-1} \lambda_i}$$  \hspace{1cm} (A.5)

The above equation is multiplied by $\prod_{i=1}^{n-1} \langle \lambda_i^2 \rangle$, and it is transformed to

$$\prod_{i=1}^{n} \langle \lambda_i^2 \rangle - \prod_{i=1}^{n-1} \langle \lambda_i^2 \rangle = \frac{1 - \theta_n}{\prod_{i=1}^{n} (\lambda_i \theta_i)}$$

$$= \frac{1}{\prod_{i=1}^{n} (\theta_i)} \left( \prod_{i=1}^{n-1} (\theta_i) - \prod_{i=1}^{n-1} (\theta_i) \right)$$  \hspace{1cm} (A.6)

Introducing the variables shown in eq 8, we can obtain the following recursion equation

$$\Lambda_{n}^2 - \Lambda_{n-1}^2 = \frac{1}{\Lambda_n^2} \left( \frac{1}{\Phi_n} - \frac{1}{\Phi_{n-1}} \right)$$  \hspace{1cm} (A.7)

Using the recursive method, we can obtain the mean-square fluctuation stretch ratio as shown in eq 10.

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