

Linear Viscoelasticity of Associative Polymers: Sticky Rouse Model and the Role of Bridges

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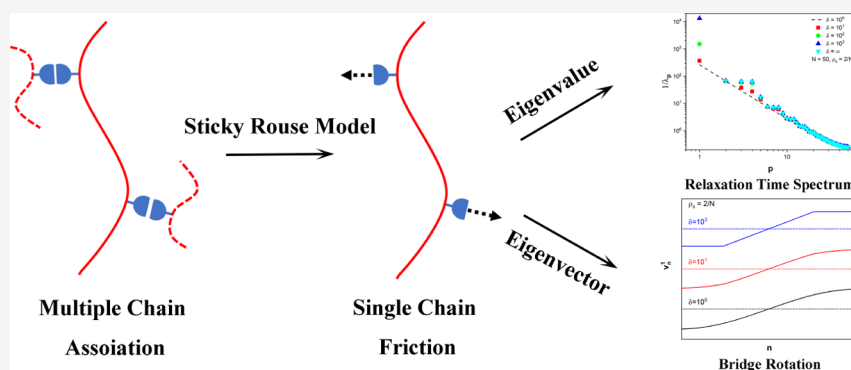
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ABSTRACT: Polymers bearing associative groups can exhibit fascinating rheological behaviors. A modified version of the Rouse model, which is originally used in block copolymers and called the sticky Rouse model here, is proposed to describe the linear viscoelasticity (LVE) of this kind of polymers without the effect of entanglement. By replacing the lifetime of a transient bond by the effective friction on stickers, the calculation of LVE functions is turned into the eigenvalue problem of the sticky Rouse–Zimm (RZ) matrix. The results show that only two parameters, sticker concentration representing the network microstructure and association interaction strength, can understand the LVE for associative polymers. In particular, the description of LVE from previous theories can be integrated in this unified theoretical framework. From the analysis of eigenvectors, it is further inferred that the rotational motion of bridge structures should be responsible for the longest relaxation times in rheology.

1. INTRODUCTION

Associative polymer (AP) is special kind of polymer whose precursor chains are hinged with associative groups, called stickers, which can form transient bonds with each other through a variety of interactions, including hydrogen bonding, π – π stacking, van der Waals interactions, or metal–ligand coordination. Compared with covalent bonds, these transient bonds can break and reconstruct under thermal fluctuations. Such a property and the complexity in association chemistry give rise to the applications of AP in a wide range of fields. Materials with special functionalities such as self-healing and shape memory are achieved by manufacturing associative interactions.^{1–3} On the other hand, solutions or melts of AP are also typical kinds of non-Newtonian fluids. The most fascinating aspect of AP is that the turning of these abundant rheological behaviors can be realized by incorporating only a small amount of stickers. Therefore, understanding the role of association in AP will greatly help us in functionality control and utilization.

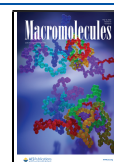
Experimentally, the viscoelastic behavior of a large variety of APs has been investigated. Here, we introduce some typical types among them. One is poly(*n*-butyl acrylate) (PnBA) functionalized with hydrogen-bonding groups like acrylic acid

and ureidopyrimidine (UPy).^{4,5} Stickers of this kind can cover a wide range of bonding energies, which results in different properties of APs. For systems with weak hydrogen bonds, they behave as their precursor systems with increased storage and loss modulus. However, for those with strong hydrogen bonds, they show the properties of an entangled network.⁴ The other widely investigated type of AP is the ionomer polymer, like the sulfonated polystyrene (SPS) neutralized with alkali metals.^{6–8} Some typical ionomer polymers like SPS-Na have higher bonding energies than the typical PnBA–UPy hydrogen-bonding system, and the association strength is influenced by the type of counterions.⁸ Thus, the nature of association chemistry in SPS is not the long-range ionic interaction but the aggregation of the sulfonic group in the low dielectric matrix.⁹

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Another type of AP we want to mention is the hydrophobically modified ethoxylated urethane (HEUR). The aqueous solution of this telechelic-style AP is a model system used in investigating the nonlinear viscoelastic (NLVE) properties of AP because of its extraordinary shear thickening behavior at a certain frequency range. Moreover, finding out the molecular origin of this thickening behavior has always been a hotspot in this area.

In spite of the effort in both theories and experiments, there are still confusions about the viscoelastic behavior of APs. The aim of the present work is an attempt to provide a unified framework to understand the LVE of unentangled APs from rigorous calculations. The article is structured as follows. In Section II.I, we first give a brief review on the present theories of AP. In Sections II.II and III, we will show, after replacing the lifetime of a transient bond by the effective friction on stickers, that the predictions about LVE made by other theories can all be integrated into a unified framework by the modified sticky Rouse model. In Section IV, the conclusions of the present work are summarized.

II. THEORETICAL MODEL

II.I. Review on Theories of AP. Since the pioneering works of Green and Tobolsky,¹⁰ Yamamoto,¹¹ and Lodge,¹² abundant theoretical efforts have been proposed to explain the viscoelastic behavior of AP. Some of them have been organized in the review articles.^{13,14} In this brief review on these theories, we focus on their connections between each other. In the next section, we will see how these theories are integrated and reproduced in the universal framework we are going to propose.

The gelation behavior of AP is well described by the mean-field theory, which is originally used in the vulcanization of a chemical gel.¹⁵ Compared to a chemical gel, a physical gel formed by AP is characterized by the finite lifetime of cross-linkers or the time scales of elasticity. In this way, some properties like gel point and plateau modulus are not influenced by the dynamics of the association reaction. The validity of the mean-field theory in AP has been confirmed by many experiments.^{14,16,17} In spite of that, it has been mentioned¹⁴ that such an extension requires a binding energy (or apparent activation energy) $E_a > 10k_B T$ (where k_B is the Boltzmann constant and T is the absolute temperature) to form an effective association, which covers most hydrogen bonding and ionic associated systems, but excludes those associated with π – π stacking or weak hydrophobic interactions.¹⁸

In the mean-field theory, the amount of stickers is always expressed as the relative extent of reaction: $\nu = (\rho_s - \rho_c)/\rho_c$, where $\rho_s (=n_s/N)$ is the concentration of stickers and $\rho_c = 1/(N - 1)$ is the gel point with the assumption that all stickers are equally likely to associate. n_s is the number of stickers per chain, and N is the polymerization degree of polymers. According to the value of this gel point, when a chain on average contains more than one sticker, the system will have the ability to form a gel. The state before the gel point, whose component chains have not formed a percolated network but isolated aggregates of chains, is called SOL. Above the gel point, the systems can be further classified into two states: the SOL + GEL state when $0 < \nu < 1$ and the GEL state when $\nu \geq 1$. In the SOL + GEL state, a giant aggregate composed of a large number of chains can be found, and at the same time, some small isolated aggregates still exist. The fraction of GEL is approximately equal to ν .¹⁷ Usually, a SOL + GEL system is a mixture of 1-sticker polymers and multiple-sticker polymers. In particular, if strictly each chain contains two stickers and the association style is binary, the

associative system should still be a SOL + GEL because of the possibility of forming an isolated loop configuration. Regarding the GEL state where more than two stickers are distributed along the chain backbone, all chains belong to a single giant percolated network. The crossover point from SOL + GEL to GEL ($\nu \geq 1$ or $\rho_s \geq 2\rho_c$) is the fully grown gel point. Exceptionally, if the functionality of the transient cross-linkers is large, or saying an aggregate of stickers can bear more stickers, the 2-sticker polymer system should be considered to be a GEL, even in the presence of loop chains. Thus, the functionality of cross-linkers is also a key factor in the ability of gelation. The above predictions about gelation are based on pure statistics. A more complicated version, which takes into account the chain configuration, phase separation, and excluded volume interaction in solutions of AP, can be found in the work of Semenov and Rubinstein.¹⁹ In addition to the other physical quantity, the plateau modulus G_N^0 , which is the measure of elasticity in a gel network, is given by the expression¹⁶

$$G_N^0 = \frac{\rho}{N} k_B T \nu \quad (1)$$

where ρ is the density of monomers. When the distribution of stickers on the chain is in a periodic or random style, this equation is equivalent to the standard one with the Flory correction term²⁰

$$G_N^0 = \frac{\rho k_B T}{\bar{N}_s} \left(1 - \frac{2N_d}{N} \right) \quad (2)$$

where \bar{N}_s is the average spacing between stickers, equal to $1/\rho_s$, and N_d is the length of the dangling end. The concept behind eq 2 is that only the bridge-forming portions contribute to the elastic behavior. They are also called the elastically effective strands. In the periodically distributed case, \bar{N}_s is equivalent to the length of a single bridge structure N_s , namely, the length of strand between neighboring stickers in the same chain. In addition, a whole elastically effective strand is composed of several bridges in the multiple-sticker chains. Comparing eqs 1 and 2, it is clear that the relative extent of reaction ν can also be regarded as the number of bridges per chain. There is no doubt that eq 2 should be more universal because it predicts that G_N^0 will be changed with different distributions of stickers. However, usually it is not so easy to precisely control the position of a sticker or characterize the exact length of the dangling ends. However, experimentally the value of ν can be evaluated via some methodologies like ¹H NMR^{4,7} if the stickers are designed to be randomly distributed.

Regarding the time scales determined by association dynamics, the terminal relaxation time in rheology τ_{\max} , some scaling demonstrations are provided as a complement of the mean-field theory.^{16,17,21} τ_{\max} , which is attributed to the slowest relaxation mode of chain monomers, is considered to be related to the lifetime of the associative bond τ_{sti} and the bridge number ν .^{22,23}

$$\tau_{\max} \sim \nu^2 \tau_{\text{sti}} \quad (3)$$

In the solution theory proposed by Rubinstein and Semenov,²¹ a different scaling relation can be found, where τ_{\max} is a growing function of the lifetime of chain aggregates during which it breaks into two comparable parts but reversed with the single association relaxation time. According to eq 3, τ_{sti} becomes the substitution of τ_{\max} if the AP chain only contains a single bridge ($\nu = 1$), and the intrinsic Rouse relaxation time τ_R (maximum

Rouse relaxation time of the precursor polymer without stickers) is much shorter than τ_{sti} . The relaxation at different time scales is thought to be still Rouse-like, giving a relaxation time spectrum composed of two distinct groups of Rouse modes: the slow modes determined by association dynamics and the fast modes determined by the intrinsic relaxation of precursor chains, which are thought to be unaffected by association. Such a relaxation spectrum gives the expression of the linear relaxation modulus $G(t)$ ^{7,22}

$$G(t) = \frac{\rho k_B T}{N} \left\{ \sum_{p=1}^v \exp(-tp^2/\tau_{\text{max}}) + \sum_{q=v+1}^N \exp(-tq^2/\tau_R) \right\} \quad (4)$$

where the first term in the right-hand side represents the slow modes and the second term represents the fast modes. The so-called “sticky Rouse model” is used to describe the above concept.⁷ Except for the theory considered from scaling, the characteristics mentioned above can also be obtained from a model that incorporates the time-evolution function of the chain state.^{24–26} In this chain-state evolution model, monomers or chain portions in the associated or unassociated state are denoted by an order-parameter-like state number or vector. From the solution of the equation of monomer motion coupled with the distribution function of the chain state, the expression of LVE functions can be directly obtained.

In the theories above, entanglement effect is not considered. When entanglement is included in AP, it is straightforward to model chain motions as reptation,^{27–32} as the treatment in the classic tube model.³³ In fact, in the sticky reptation model first proposed by Leibler et al.,²⁷ the linear relaxation modulus is described by appending a reptational term in addition to the classic Rouse and sticky Rouse modes,³⁰ which predicts a dual network characterized by a double plateau moduli regime. The highest plateau in the intermediate-frequency regime is attributed to both chain entanglement and transient network formed by association, whose value scales with both entanglement length N_e and associative bridge length \bar{N}_s : $G_N^0 \sim \rho k_B T(1/N_e + 1/\bar{N}_s)$. At the same time, the low-frequency plateau reflects the effect of chain entanglement, where the total chain length becomes the determinant factor.

The above theories focus on the LVE of AP. Most proofs in experiments come from the melt state where the strong overlap of chains has overwhelmed the complicated distribution of configurations. For the NLVE of HEUR systems, theoretical treatment is conducted under the framework of the transient network model,^{34–43} pioneered by Tanaka and Edwards.^{34–36,44} It seems that the theories of LVE and NLVE are much different, but in fact they are connected. The NLVE behavior in solutions is always coupled with the change of configurational distribution. As has been pointed out, a wide range of configurations, including isolated loop, flower loop, isolated chain, and dangling and bridge chain, can be identified.^{45,46} However, among these, only the bridge configuration is thought to contribute to the elasticity, which is the same as the idea of the Flory correction term in eq 2. In addition, typical HEUR systems contain short-length chains, and a single-Maxwellian behavior is observed in the LVE regime.^{39,47} This behavior can be expected if the fast modes in eq 4 are neglected. So for the simplicity of theoretical treatment, a HEUR chain is always modeled as a

dumbbell with associative ends, whose intrinsic Rouse time τ_R has been overwhelmed by τ_{sti} . In addition, a single distribution function of chain end-to-end vector \mathbf{R}_{ee} will be sufficient to describe the chain configuration. The key issue that lies in NLVE is the interplay between chain motions and associative reaction dynamics. To predict the NLVE behavior, especially shear thickening, many mechanisms have been proposed, which can be classified into two factors:⁴⁸ flow-induced enhancement in the association structure or dynamics,^{39,48–50} non-Gaussian stretch of the network strand,^{37,51} or both.^{43,52,53} In spite of these efforts, further proofs for the molecular origin of shear thickening are still needed.

II.II. From Association to Friction: Sticky Rouse Model.

In this section, we would like to show that the LVE of unentangled AP, especially in a melt state, can be directly predicted from a modified version of the Rouse model, which was simultaneously proposed by Hansen and Shen,⁵⁴ Wang and DiMarzio,⁵⁵ and Stockmayer and Kennedy⁵⁶ in 1975. This model is originally used to describe the LVE of block copolymers without microphase separation such as poly(styrene-*b*- α -methylstyrene), where different constituents are considered to be experiencing different frictions during translational diffusion of the chain. Considering that an AP is actually some kind of a copolymer, it is straightforward to apply this block copolymer model to AP comprising an arbitrary type of associative interaction with different interaction degrees. The key point to conducting this extension is to relate the lifetime of a transient bond to the effective friction acting on a sticker. Based on this idea, the calculation of LVE functions will be accomplished by following a similar approach as the classic Rouse bead-spring model.⁵⁷ Therefore, it will be quite clear in the microscopic origins of viscoelasticity for the AP in which the association of stickers influences the rheological properties via changing the normalized relaxation modes of monomers, which are always the direct determinants of mechanics. In fact, the concept of relating association to friction has been used by Rubinstein and Semenov.^{21,28} Here, we still use the sticky Rouse model for the present work but proceed via a single-chain approach.

The main idea of the sticky Rouse model here is to simplify the coupled motions in an associative system through the effective friction concept, so that the LVE properties of AP can be understood from a single-chain perspective. Although the polymer chains in real AP may have different states of association, they are thought to be identical because the associative interactions from other chains are all enclosed in the effective frictions. For example, in the simplest associative system where the component chains can only experience head-to-head binary association, usually the conversions between unimers and dimers are considered.⁵⁸ However, in the present model, the unimer and dimer chains are identical, using the magnitude of the effective friction to stand for the equilibrium between the two association states. The other assumption of the sticky Rouse model is about the style of motions. In AP, the translation of polymer chains can be decomposed into two independent processes. One is the self-diffusion of aggregates or transient cross-linkers. The other is the motion where association reactions are involved, that is, the translation relative to the aggregates of stickers, for example, the hopping process between different aggregates, which has been proved to be the dominant style in many associative systems,⁵⁹ or the disengagement of an associated sticker to a free one in a dilute solution. Here, only the latter kind of motions is enclosed. These motions are considered to be the key factors in the viscoelastic behavior

of AP. That is, the association sites are regarded as the background of chain motions.

With the above assumptions, we briefly reformulate the sticky Rouse model based on the work of Hansen and Shen.⁵⁴ The equation of motion of an unentangled Gaussian bead-spring chain in the background media can be expressed in a matrix form as follows

$$\xi \Xi \frac{d\mathbf{Q}}{dt} = -k\mathbf{Z}\mathbf{Q} + \mathbf{F}\mathbf{I} \quad (5)$$

where ξ is the frictional coefficient of the background and k is the entropic spring constant. \mathbf{Q} is the column vector of the monomer position relative to the center of the related aggregates

$$\mathbf{Q} = \begin{bmatrix} \mathbf{r}_1 \\ \mathbf{r}_2 \\ \vdots \\ \mathbf{r}_N \end{bmatrix} \quad (6)$$

\mathbf{Z} is the RZ matrix, describes the connectivity of the beads

$$\mathbf{Z} = \begin{bmatrix} 1 & -1 & & \\ -1 & 2 & -1 & \\ & & \ddots & \\ & & & -1 & 1 \end{bmatrix} \quad (7)$$

Moreover, \mathbf{F} is the random force term that satisfies the fluctuation–dissipation correlation

$$\begin{aligned} \langle \mathbf{f}_n(t) \rangle &= \mathbf{0} \\ \langle f_{n\alpha}(t) f_{m\beta}(t') \rangle &= 2\xi_n k_B T \delta_{nm} \delta_{\alpha\beta} \delta(t - t') \end{aligned} \quad (8)$$

A diagonal matrix Ξ is written out, which represents the relative friction force for each segment (bead)

$$\Xi = \begin{bmatrix} \delta_1 & & & \\ & \delta_2 & & \\ & & \ddots & \\ & & & \delta_N \end{bmatrix} \quad (9)$$

where $\delta_i = \xi_i/\xi$ is the relative frictional coefficient for the i th segment. The diagonalization of eq 5 draws the normalized form of the motion equation

$$\xi \frac{d\mathbf{X}}{dt} = -k\mathbf{\Lambda}\mathbf{X} + \mathbf{T}^{-1}\Xi^{-1}\mathbf{F}\mathbf{I} \quad (10)$$

where \mathbf{X} is the vector of normal coordinates

$$\mathbf{X} = \mathbf{T}^{-1}\mathbf{Q} = \begin{bmatrix} \mathbf{X}_0 \\ \mathbf{X}_1 \\ \vdots \\ \mathbf{X}_{N-1} \end{bmatrix} \quad (11)$$

with the eigenvalue matrix $\mathbf{\Lambda}$ of $\Xi^{-1}\mathbf{Z}$

$$\mathbf{\Lambda} = \begin{bmatrix} \lambda_0 & & & \\ & \lambda_1 & & \\ & & \ddots & \\ & & & \lambda_{N-1} \end{bmatrix} \quad (12)$$

where $\lambda_0 < \lambda_1 < \dots < \lambda_{N-1}$. In addition, \mathbf{T} is the corresponding matrix of the eigenvector, which satisfies $\mathbf{T}^{-1}(\Xi^{-1}\mathbf{Z})\mathbf{T} = \mathbf{\Lambda}$ with its elements

$$\mathbf{T} = [\mathbf{v}^0 \quad \mathbf{v}^1 \quad \dots \quad \mathbf{v}^{N-1}] = \begin{bmatrix} v_1^0 & v_1^1 & \dots & v_1^{N-1} \\ v_2^0 & v_2^1 & & \\ \vdots & & \ddots & \\ v_N^0 & & & v_N^{N-1} \end{bmatrix} \quad (13)$$

It has been proved by Eichinger⁶⁰ that the smallest eigenvalue λ_0 is always 0. So v_i^0 is a constant, and the time evolution of the zeroth normal coordinate \mathbf{X}_0 will always stand for the diffusion of the chain center-of-mass relative to the migration of aggregates, which does not contribute to the viscoelasticity. If the normalized random force is still time-independent, eq 10 will give the relaxation mode, that is, the time correlation function of each normal coordinate \mathbf{X}_p for any $p > 0$

$$\langle X_{p\alpha}(t) X_{q\beta}(0) \rangle = \delta_{pq} \delta_{\alpha\beta} \frac{k_B T}{k \lambda_p} \exp\left(-\frac{t}{\tau_p}\right) \quad (14)$$

where

$$\tau_p = \frac{\xi}{k \lambda_p} \quad (15)$$

where τ_p is the Rouse-like relaxation time for the chain section containing N/P springs. According to the expression of stress, with the knowledge of τ_p or $\mathbf{\Lambda}$, we can draw out any properties related to the LVE. The linear relaxation modulus $G(t)$ is expressed as follows

$$G(t) = \frac{\rho k_B T}{N} \sum_{p=1}^{N-1} \exp\left(-\frac{t}{\tau_p}\right) \quad (16)$$

The dynamic modulus in the frequency space ω is given in a similar way

$$G'(\omega) = \frac{\rho k_B T}{N} \sum_{p=1}^{N-1} \frac{(\omega \tau_p)^2}{1 + (\omega \tau_p)^2} \quad (17)$$

$$G''(\omega) = \frac{\rho k_B T}{N} \sum_{p=1}^{N-1} \frac{\omega \tau_p}{1 + (\omega \tau_p)^2} \quad (18)$$

Bulk properties like the zero-shear viscosity η_0 and the steady-state recoverable compliance J_e^0 can also be calculated as

$$\eta_0 = \frac{\rho k_B T}{N} \sum_{p=1}^{N-1} \tau_p \quad (19)$$

$$J_e^0 = \sum_{p=1}^{N-1} \tau_p^2 / \left(\sum_{p=1}^{N-1} \tau_p \right)^2 \quad (20)$$

For a homopolymer chain, all segments are subjected to the same friction, that is, $\delta_i = 1$ for any $i = 1, 2, \dots, N$. Ξ becomes the unit matrix, and the eigenvalues and eigenvectors of \mathbf{Z} have explicitly analytical solutions, which return to the usual Rouse dynamics.³³ However, in the case of AP, a sticker feels the dragging force from not only the background polymers but also the associated chains. Thus, the frictional coefficient of a sticker

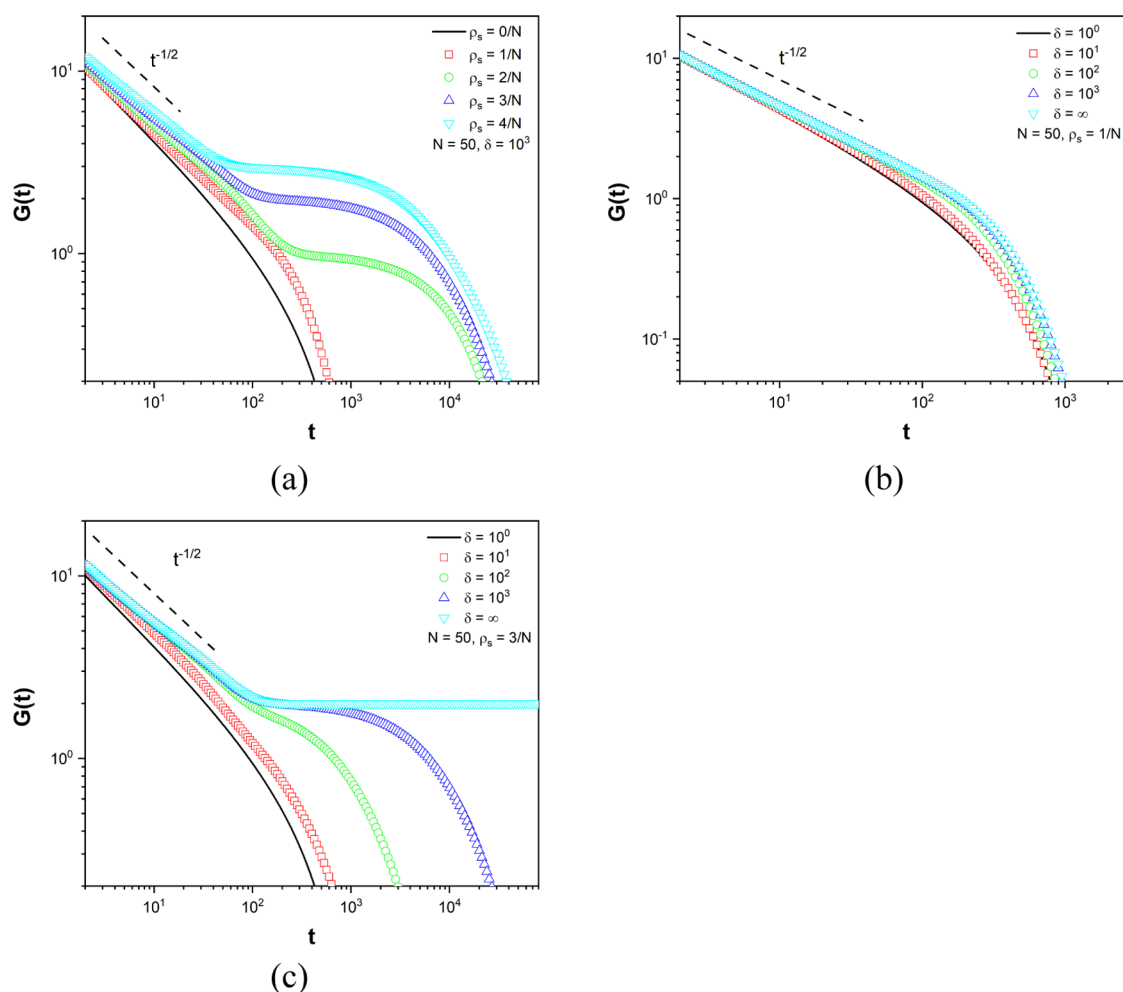


Figure 1. Linear relaxation modulus $G(t)$ of AP as a function of (a) ρ_s at $\delta = 10^3$ and δ in the (b) 1-sticker and (c) 3-sticker chain models.

is much larger than that of a precursor segment, for example, $\delta = \xi_s/\xi \gg 1$. Unlike the original idea, when this model is applied to a block copolymer, a nonunit Ξ arises from the difference in the molecular weight of each component (α -methylstyrene is heavier than styrene). In the case of AP, δ is directly related to the lifetime of the transient bond or the dynamics of association. In particular, for an AP system that mainly adopts the hopping style of motion, δ is thought to be the substitute of the frequency of hopping, whose reciprocal is the relaxation time of association and should be equivalent to the lifetime of the associative bonds.

To obtain the LVE functions of AP, the key step is to solve the eigenvalues of $\Xi^{-1}\mathbf{Z}$. We denote $\Xi^{-1}\mathbf{Z}$ as the sticky RZ matrix. Provided the positions of stickers, it seems straightforward to obtain a numerical solution. However, for some chain topologies like dendrimer, it is not so easy to find the appropriate forms of sticky RZ matrixes. An analytical method to solve the eigenvalues in any case is still necessary. Except for the rigorous analysis provided by Hall and De Wames⁶¹ and Tang,⁶² Yang⁶³ has also proposed a form of solution using the graph theory. It has been shown that a matrix that stands for a type of chain connectivity like \mathbf{Z} is equivalent to the adjacency matrix or the admittance matrix in the graph theory. So the algebraic problem of solving the eigenvalues can be simplified by some graph operations after replacing a matrix by its graph. An AP chain here is a kind of a color graph in this method. Using the graph theory, the eigenvalue problem of AP with any chain topology can all be solved, like ring, star, and dendrimer.^{63,64} In the Appendix, we

give an example of the graph theory calculation for a chain model with two periodically distributed stickers.

It has to be noted that the form of the RZ matrix in eq 7 is used to describe a configuration where all stickers are located in different aggregates to form the bridge configuration, if there are multiple stickers in a single chain and all stickers are assumed to be associated. Such a configuration contributing the maximum elasticity will be our focus in the rest of the work. The LVE of another configuration can be considered from a different chain topology. For example, a loop configuration has a ring topology, with sticky sites and some dangling ends. So configuration and chain topology are thought to be equivalent in our description for AP. Moreover, the calculated LVE functions are for a system where all of the chains adopt the same configurations. It is usually not the case in the solutions of AP but can be an approximation of the melts. In addition, the hydrodynamic interaction is also not considered. So the results directly calculated from the above approach are best suited for a condensed melt. An alternative approach to consider a solution of AP is to independently calculate the contribution to LVE from different configurations and then combine them according to their portions in the equilibrium state. The hydrodynamic interaction can be enclosed after considering the hydrodynamic screening length and referring to some approximation methods like the effective medium theory.³³ The scaling theory of Rubinstein and Semenov²¹ has successfully revealed the concentration dependence of AP, by putting all of the

configurations into the effective breakup concept. However, here the sticky Rouse model deals with a specific configuration in exchange of accurate solutions.

III. RESULTS AND DISCUSSION

III.I. Gelation. We first show the overall performance of the sticky Rouse model from the modulus, and we will see the gelation behavior of AP predicted by previous theories is also captured in this single-chain model, after we have only considered the motions caused by association reactions. We choose the linear relaxation modulus as a representative of the rheological functions. The regulations found in $G(t)$ should also exist in other functions. In the following, the reduced temperature $k_B T$, chain density ρ/N , and characteristic time ξ/k are all set to unity. So eq 16 is expressed in the simplest form: $G(t) = \sum_{p=1}^{N-1} \exp(-t/\tau_p) = \sum_{p=1}^{N-1} \exp(-\lambda_p t)$. We discuss chain models with 1–4 stickers, periodically distributed along the backbone: for the 1-sticker chain, we have one sticker in the middle; for the 2-sticker chain, we have stickers in positions $N/4$ and $3N/4$; for the 3-sticker chain, stickers are set in $N/6$, $N/2$, and $5N/6$; for the 4-sticker chain, the four stickers are in $N/8$, $3N/8$, $5N/8$, and $7N/8$. These chain models with strict positions of stickers are thought to be the substitutes of completely random cases, which are usually designed in experiments. Based on this sticky Rouse model, only with parameters δ and ρ_s can we determine the LVE properties of the AP.

The modulus profiles for different association parameters with a fixed chain length are plotted in Figure 1a–c. It is clear that the result is in mutual agreement with what has been predicted by previous theories. A Rouse-like regime for AP can always be observed at short time scales, but its scaling dependence is slightly shifted from the usual $t^{-1/2}$ form. This is also observed in the model of Indei et al.²⁶ For the 1-sticker chain ($\rho_s = 1/N$), which is thought to be a SOL, the $G(t)$ does not show much difference from homopolymer chains (black solid line), except for a hump in the terminal regime. In addition, this hump converges when $\delta \rightarrow \infty$, as shown in Figure 1b. While for $\rho_s \geq 2/N$, as shown in Figure 1a, a distinctive plateau regime appears, showing the characteristics of a network, as long as the value of δ is above a certain threshold. The associative system with $\rho_s = 2/N$, which may be possibly a SOL + GEL according to the mean-field theory, completely behaves as a GEL. So the SOL behavior in the SOL + GEL mixture state is not contributed by such a bridge configuration. The range of the plateau regime is determined by δ when the content of stickers is fixed, as can be seen in Figure 1c. When $\delta \rightarrow \infty$, the behavior of a covalently cross-linking system occurs, characterized by a constant plateau in the modulus. Indeed, the parameter δ reflects the association time, which influences the system dynamics. There is an interesting phenomenon in GELS: although the outermost terminal is relatively larger in a chain model with more numbers of stickers, the position where the plateau starts to decline is shifted to a smaller time scale. Or we can say that the entire terminal regime is more expanded. The reason for this expansion is that the longest relaxation times become degenerated with the increase of ρ_s , which will be discussed in detail in the following. The dependence of $G(t)$ on δ is very similar to the demonstration of previous theories about how τ_{\max} is influenced by τ_{sti} in eq 3. In addition, the plateau values of the modulus G_N^0 in Figure 1a for $\rho_s = 2/N$, $3/N$, and $4/N$ are 1.0, 2.0, and 3.0, respectively, which is exactly the number of bridges and the same as the results calculated from eqs 1 and 2. All of these results in $G(t)$ show that the LVE behaviors of an unentangled AP

predicted by previous theories are well included in this sticky Rouse model, where only one parameter, namely, the frictional coefficient δ , is preassumed and no further parameters are involved except for the basic concepts of the classic Rouse model.

III.II. Diffusion. Although the zeroth eigenmode is not included in the theoretical expression of viscoelasticity, the center-of-mass diffusion is still an important aspect in dynamics and also observable in experiments. The sticky Rouse model in the present form partially reveals the style of diffusion in AP. Moreover, the predicted form of diffusion is also found to rely on the gelation behavior. Although v_i^0 is always a constant at any topology and association strength, the zeroth normal coordinate X_0 changes its form at a large value of δ , which becomes

$$\mathbf{X}_0 \approx \frac{1}{n_s} \sum_{i=1}^{n_s} \mathbf{r}_{is} \quad (21)$$

where \mathbf{r}_{is} means the position of the i th sticker. So the diffusion of center-of-mass of an associative chain relies mostly on the motion of stickers. This is very similar to the model proposed by Baxandall,²² who described an AP chain as multiple stickers connected by massless arcs and so the stickers form an effective center. Therefore, the calculation for diffusion turns back to the single equation of motion for stickers. According to the fluctuation–dissipation relationship of eq 8, the random force acting on a sticker should also grow with effective friction. So the motion of a sticker will be governed by the random force if δ is large, which is

$$\delta \xi \frac{d\mathbf{r}_{is}}{dt} = -k(2\mathbf{r}_{is} - \mathbf{r}_{is-1} - \mathbf{r}_{is+1}) + \mathbf{f}_{is} \approx \mathbf{f}_{is} \quad (22)$$

Replacing the real positions of stickers by the normal coordinate, we have the mean-square displacement of \mathbf{X}_0

$$\langle (\mathbf{X}_0(t) - \mathbf{X}_0(0))^2 \rangle = \frac{6k_B T}{n_s \delta \xi} t \quad (23)$$

Because the migration of aggregates is independent of the motions caused by association reactions, the overall diffusion constant of the center-of-mass should be expressed as

$$D = \frac{k_B T}{n_s \delta \xi} + \frac{D_A}{n_s} \quad (24)$$

where D_A is the diffusion constant of a single aggregate, whose value depends on the viscoelasticity of the system. So evidently gelation becomes a critical factor in the expression of a diffusion constant. For a SOL system where $n_s = 1$, the viscosity will not grow much according to the form of $G(t)$ in Figure 1b, so the self-diffusion of aggregates will always be significant. However, in a strongly associated state, the diffusion caused by association reactions becomes trivial, making the first term on the right side of eq 24 negligible, that is, $D \approx D_A$. As a result, experimentally, we should observe a retarded diffusion of AP chains, determined by the aggregation number of the association site. However, for a GEL system, the aggregates are fixed because of the formation of the network. So eq 24 should be approximated as $D \approx k_B T/n_s \delta \xi$, that is D is inversely proportional to both the sticker number and the amplitude of friction in a fully gelled associative network.

It seems that the expression of the diffusion constant for the GEL does not match with experiments. According to the work of Colby et al.,²³ the scaling dependence between D and n_s in the SPS ionomers is $D \sim n_s^{-2}$, which is stronger than that predicted

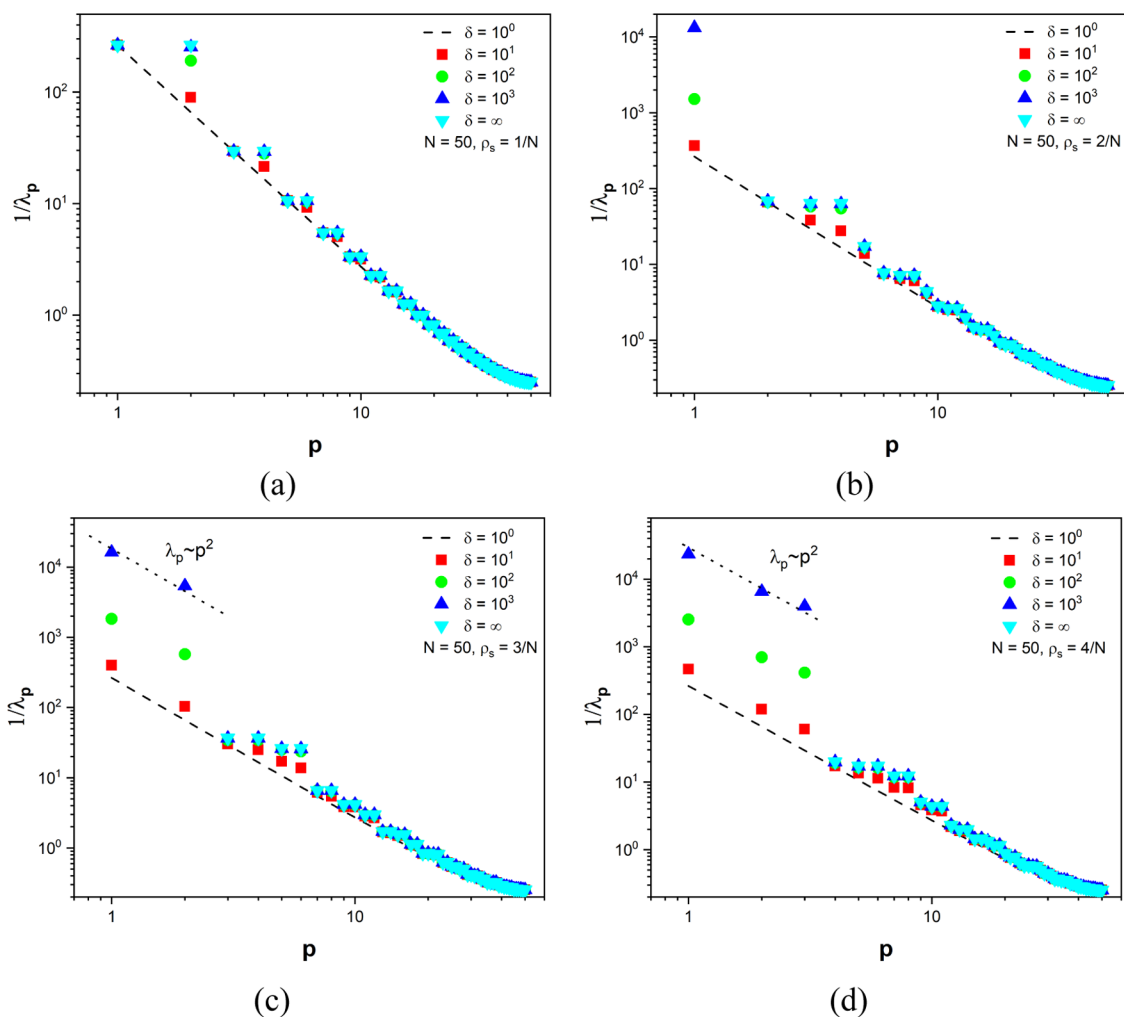


Figure 2. Relaxation time spectra $\tau_p (=1/\lambda_p)$ in unit of ξ/k calculated by our sticky Rouse model for AP with 1–4 stickers. The dashed line denotes that for the classic Rouse model with $\lambda_p = 4\sin^2(p\pi/2N)$.

by the sticky Rouse model. The explanation for such a discrepancy is that we have not considered the relationship between δ and n_s . It should be expected that changing the concentration or number of stickers will also result in the change in association dynamics. If eq 24 is the rightful expression for the mentioned experimental system, then $\delta \sim n_s^1$, that is the association relaxation time grows linearly with the content of stickers, which can be a possible case. According to the multiplet-cluster model for SPS proposed by Eisenberg and Moore,⁶⁵ the cluster zone with restricted mobility is expanded at a higher ion content. So the apparent association dynamics can be retarded in spite of the increased concentration of reactants.

III.III. Eigenvalues and Eigenvectors. Now we have seen that the overall LVE property of AP is captured in the sticky Rouse model, and the diffusion behavior of AP is also explainable according to the basic equations. In this section, we will turn to the details at the fundamental level, that is, the eigenvalues and eigenvectors of the sticky RZ matrix. The former represents the entire relaxation time spectrum, and the latter will show the molecular motion corresponding to a specific relaxation mode. These results have been rarely captured by previous theories, and we can see the advantage of the present model.

The relaxation time spectra for 1–4-sticker polymers are plotted in Figure 2a–d, respectively. In addition, the

corresponding leading terms (relatively long relaxation times) are plotted in Figure 3. The analytical expressions of $\text{Tr}(\mathbf{Z}^{-1}\Xi)$ ($=\sum_{p=1}^{N-1} 1/\lambda_p$) calculated from the graph theory, which is equal to $-\alpha_{N-2}/\alpha_{N-1}$ as shown in eq A.8 of Appendix, are also presented as dashed lines. It is found that all of these expressions (with $N = 50$) are in the following form

$$\text{Tr}(\mathbf{Z}^{-1}\Xi)(\delta) = a\delta + b + \frac{c}{d + \delta} \quad (25)$$

where the coefficients for different chain models are listed in Table 1. These coefficients also depend on topology and chain length, but here we focus on association. From the form of eq 25, it can be inferred that if δ is large, the last term is negligible and $\text{Tr}(\mathbf{Z}^{-1}\Xi)$ strictly becomes a linear function of δ . So the slope a is the key coefficient in its response to δ or association dynamics.

A general feature is found that these eigenvalues, especially for the fast modes ($p \gg 1$), become degenerated with the increase of δ . That should explain why the Rouse regime ($t^{-1/2}$ scaling regime) in the $G(t)$ of AP deviates from the precursor polymer. So the relaxation modes at small time and length scales are in fact not unaffected by association. For the SOL-state polymer with 1 sticker ($\rho_s = 1/N$) in Figure 2a, all relaxation times become twofold degenerate, namely, only $N/2$ internal relaxation times. In addition, only the even-numbered modes show a response to the value of δ . $\tau_{\max} (=1/\lambda_1)$ in unit of ξ/k is not influenced by δ ,

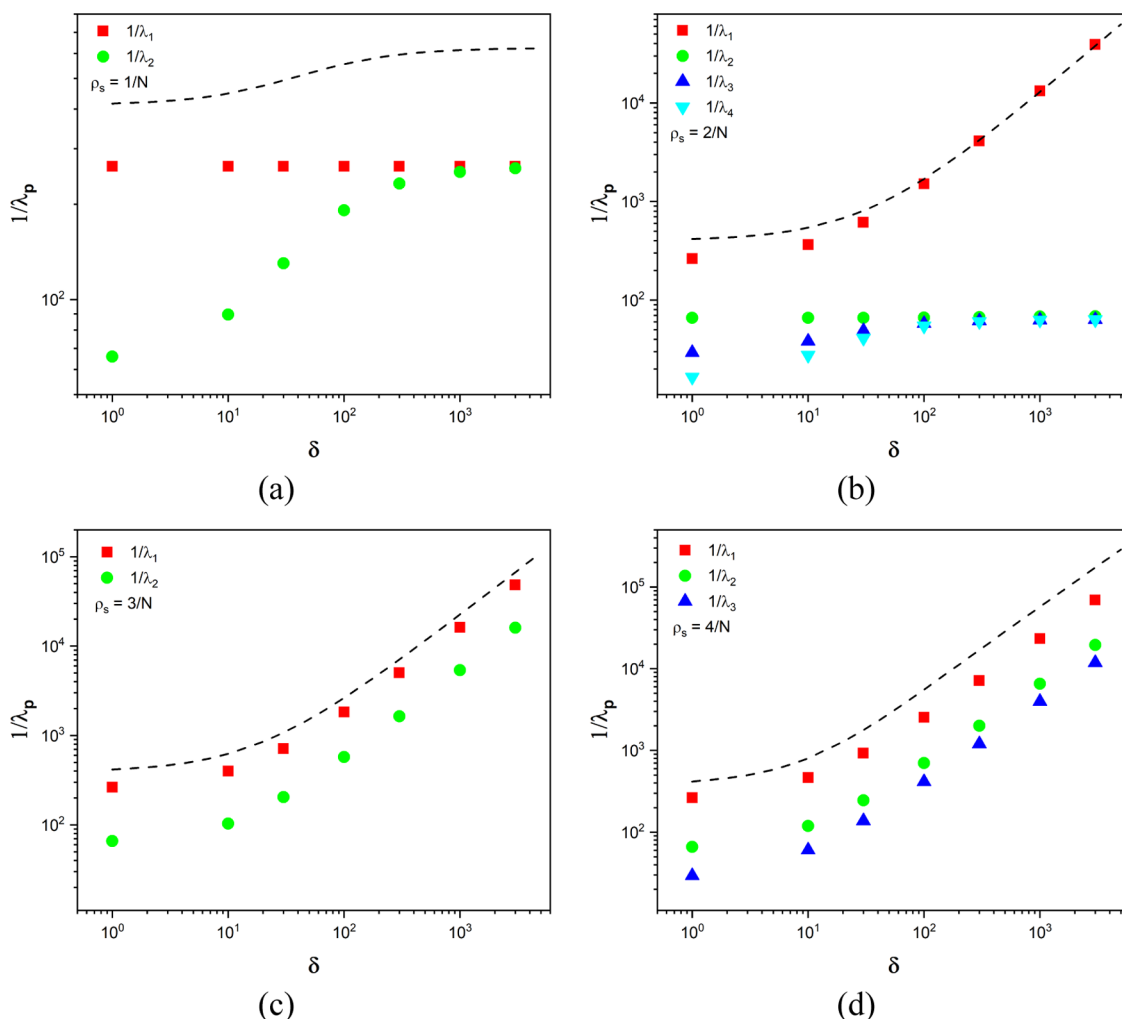


Figure 3. Relatively long relaxation times corresponding to Figure 2 as a function of δ . Dashed lines are the analytical expressions of $\text{Tr}(\mathbf{Z}^{-1}\Xi)$ from the graph theory calculation.

Table 1. Coefficients in the Analytical Expressions of $\text{Tr}(\mathbf{Z}^{-1}\Xi)$

ρ_s	a	b	c	d
1/N	0	625	−10 413	49
2/N	12.50	456	−1300	24
3/N	22.22	417	−384	15.67
4/N	57.75	−506	43 219	49

so we can always find a finite terminal in $G(t)$ even in the chemically bonded case, as shown in Figure 1b. From Figure 3a, we can see how the second longest relaxation time $1/\lambda_2$ gradually converges to $1/\lambda_1$ because of the degeneracy, which is the origin of the hump in Figure 1b. It can also be expected that two types of molecular motions, corresponding to λ_1 and λ_2 , respectively, share the same relaxation time. So the terminal relaxation in rheology is attributed to dual relaxation modes, rather than a single mode. Moreover, the value of $\text{Tr}(\mathbf{Z}^{-1}\Xi)$, which is the measure of the zero-shear viscosity η_0 , is also a converging function of δ with $a = 0$. So the bulk viscosity of a SOL polymer will never be tremendous whatever the strength of association.

Regarding the GEL-state polymer, it is evident that the relaxation modes are classified into a slow group and a fast group. The fast modes are degenerated and convergent, like those in the

SOL polymer. However, the relaxation times in the slow group are increasing functions of δ . In particular, the number of slow modes is equal to the bridge number. For $\rho_s > 2/N$, they are even satisfying a Rouse-like relationship: $\lambda_p \sim p^2$, as shown in Figure 2c,d. The classification of the fast and slow modes is close to eq 4 of the previously proposed sticky Rouse model.²² However, in the present model, fewer parameters are involved, and the fast modes are more precisely presented. From Figure 3b–d, we can find that, unlike a SOL polymer, the bulk viscosity of a GEL polymer, mainly dominated by the slowly decaying modes or the longest relaxation times, can keep growing with the binding strength or friction of stickers. In other words, $\text{Tr}(\mathbf{Z}^{-1}\Xi)$ is mainly contributed by the leading terms. In the 2-sticker polymer, it is exactly the value of τ_{\max} with an analytical expression of eq A.12. In eq 25, we have seen that $\text{Tr}(\mathbf{Z}^{-1}\Xi)$ is approximately a linear function of δ . In addition, the ratios of the relaxation times in the slow group are found to be constants (Rouse-like). So rigorously τ_{\max} is also a linear function of δ in a strongly associated case, and τ_{\max} grows faster at a higher content of stickers ($a_2 < a_3/(1 + 2^{-2}) < a_4/(1 + 2^{-2} + 3^{-2})$, where a_i is the slope for the i -sticker chain). Such a relationship is analogous to the dependence of τ_{\max} on ν and τ_{sti} in eq 3, indicating that the basic assumption of the sticky Rouse model should be reasonable. Similarly, since more than one eigenvalue can be the representation of the slowest mode in rheology, it is

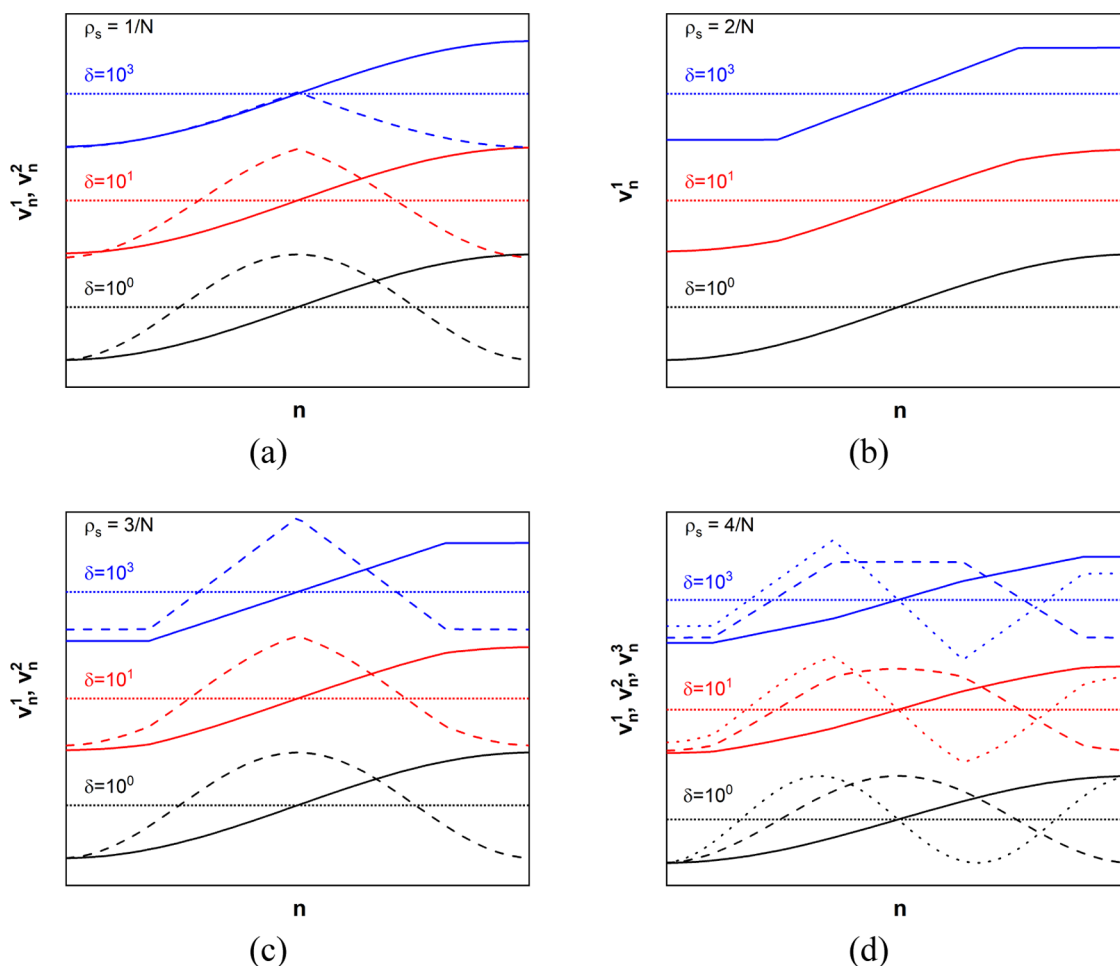


Figure 4. Profiles of eigenvectors for AP with 1–4 sticker. The horizontal lines are the positions of zero. Solid lines mean v_n^1 , dashed lines mean v_n^2 , and dotted lines mean v_n^3 .

important to identify the corresponding motions at the molecular level. This has however been neglected by previous theories.

To do so, we can use the inverse of normal coordinates of eq 11

$$\mathbf{r}_n = \sum_p v_n^p \mathbf{x}_p \quad (26)$$

A relaxation mode is always related to the rotation motion of a chain vector connecting two certain beads, $\mathbf{R}_{mn} = \mathbf{r}_m - \mathbf{r}_n$, and its time correlation function is as follows

$$\begin{aligned} \langle \mathbf{R}_{mn}(t) \cdot \mathbf{R}_{mn}(0) \rangle &= \sum_p \sum_q (v_m^p - v_n^p)(v_m^q - v_n^q) \langle \mathbf{x}_p(t) \cdot \mathbf{x}_q(0) \rangle \end{aligned} \quad (27)$$

According to eq 14, the right side of eq 27 is dominated by the slow group of relaxation modes with relatively small values of λ_p . In addition, the most appropriate choice of m and n for a certain relaxation mode is where $|(v_m^p - v_n^p)(v_m^q - v_n^q)|$ reaches the maximum. The profiles of eigenvectors corresponding to the identified slow modes are plotted in Figure 4. For AP with $\rho_s = 1/N$, the first two terms in eq 27 need to be considered. According to Figure 4a, the eigenvector v^1 is not affected by δ , consistent with the constant value of λ_1 . In spite of the value of $v_{N/2}^2$ gradually approaching 0, v^2 is always symmetric. When $m =$

1 and $n = N$, in this case, \mathbf{R}_{mn} is the end-to-end vector \mathbf{R}_{ee} , $|v_m^1 - v_n^1|$ reaches the maximum but $|v_m^2 - v_n^2|$ vanishes. So we have

$$\langle \mathbf{R}_{1,N}(t) \cdot \mathbf{R}_{1,N}(0) \rangle \sim \langle \mathbf{X}_1(t) \cdot \mathbf{X}_1(0) \rangle \quad (28)$$

where the prefactor is left out and the formula can be regarded as the normalized form. Hence, similar to what has been proposed by the classic Rouse model for homopolymers, τ_{\max} is always the rotational relaxation time of the entire chain. For the second longest time, since it stands for the symmetric situation, we find the following form

$$\begin{aligned} \langle \{\mathbf{R}_{1,N/2}(t) + \mathbf{R}_{N,N/2}(t)\} \cdot \{\mathbf{R}_{1,N/2}(0) + \mathbf{R}_{N,N/2}(0)\} \rangle \\ \sim \langle \mathbf{X}_2(t) \cdot \mathbf{X}_2(0) \rangle \end{aligned} \quad (29)$$

where $\mathbf{R}_{1,N/2}$ or $\mathbf{R}_{N,N/2}$ is the middle-to-end vector, or called the dangling vector. Here, λ_2 stands for the rotation of the cooperative vector $\mathbf{R}_{1,N/2} + \mathbf{R}_{N,N/2}$. Further considering that $\mathbf{R}_{1,N/2}$ and $\mathbf{R}_{N,N/2}$ are symmetric, we can say that it is the rotation of the dangling portion that contributes to the second longest relaxation time. In addition, this type of relaxation becomes comparable to that of \mathbf{R}_{ee} when the polymer is covalently associated with the stickers in the chain center.

For AP with $\rho_s = 2/N$, we only need to concentrate on v^1 . As can be seen in Figure 4b, although not so significant, a change in the overall profile of v^1 does exist. The values of v_n^1 for $1 \leq n \leq N/4$ and $3N/4 \leq n \leq N$ gradually become constant with the

increase of δ . According to the demonstration in the last paragraph, although it is still valid when we say τ_{\max} corresponds to the rotation of \mathbf{R}_{ee} , it is also valid to match it with the bridge vector $\mathbf{R}_{N/4,3N/4}$ that is

$$\langle \mathbf{R}_{N/4,3N/4}(t) \cdot \mathbf{R}_{N/4,3N/4}(0) \rangle \sim \langle \mathbf{X}_1(t) \cdot \mathbf{X}_1(0) \rangle \quad (30)$$

The physical picture here is obviously clear. Because the motion of stickers is greatly hindered by the association effect, the bonded dangling monomers are also subjected to suppressed movements. So apparently \mathbf{R}_{ee} or any vectors whose two ends are both located in the dangling parts will follow the rotation of the bridge vector $\mathbf{R}_{N/4,3N/4}$. This can be regarded as the molecular origin of the Flory correction term in eq 2, that is, only the bridge portions are elastically effective. From here, we start to find clues for the role of bridge whose relaxation should be responsible for the rheological terminal.

To further clarify the role of bridge in the rheological aspect, we need to analyze the 3-sticker and 4-sticker chains. These two systems contain a superbridge (the longest bridge that starts from the first sticker to the last sticker and is composed of several single bridges) and have different symmetries. For AP with $\rho_s = 3/N$, the profile of \mathbf{v}^1 is similar to that in the 2-sticker polymer, while \mathbf{v}^2 is similar to that in the 1-sticker polymer, except that $|\mathbf{v}_{N/2}^2|$ is not vanishing, as shown in Figure 4c. According to the results in the last two paragraphs, λ_1 should be corresponding to the rotation of the superbridge vector $\mathbf{R}_{N/6,5N/6}$ which is as follows

$$\langle \mathbf{R}_{N/6,5N/6}(t) \cdot \mathbf{R}_{N/6,5N/6}(0) \rangle \sim \langle \mathbf{X}_1(t) \cdot \mathbf{X}_1(0) \rangle \quad (31)$$

However, λ_2 represents the relaxation of the cooperative vector formed by the two bridge vectors $\mathbf{R}_{N/6,N/2}$ and $\mathbf{R}_{5N/6,N/2}$

$$\begin{aligned} & \langle \{ \mathbf{R}_{N/6,N/2}(t) + \mathbf{R}_{5N/6,N/2}(t) \} \cdot \{ \mathbf{R}_{N/6,N/2}(0) \\ & + \mathbf{R}_{5N/6,N/2}(0) \} \rangle \sim \langle \mathbf{X}_2(t) \cdot \mathbf{X}_2(0) \rangle \end{aligned} \quad (32)$$

It suggests that the rheological terminal is contributed by the relaxation of both the single bridge and superbridge. Although λ_1 is several times smaller than λ_2 , they are both a decaying function of δ . So the rotations of the bridge and superbridge can both be regarded as the slowest motions in AP chains.

When $\rho_s = 4/N$, the situation becomes more complicated. Two types of bridges exist: the outer bridge $\mathbf{R}_{N/8,3N/8}$ (or $\mathbf{R}_{7N/8,5N/8}$) and the internal bridge $\mathbf{R}_{3N/8,5N/8}$. In addition, two sub-superbridges comprising two neighboring bridges $\mathbf{R}_{N/8,5N/8}$ and $\mathbf{R}_{7N/8,3N/8}$ can also be identified. To clarify their relationship with the three eigenvectors \mathbf{v}^1 , \mathbf{v}^2 , and \mathbf{v}^3 , some approximations need to be involved. For the two antisymmetric eigenvectors \mathbf{v}^1 and \mathbf{v}^3 , the relaxations of the two related vectors $\mathbf{R}_{N/8,7N/8}$ and $\mathbf{R}_{3N/8,5N/8}$ are coupled

$$\begin{aligned} & \langle \mathbf{R}_{N/8,7N/8}(t) \cdot \mathbf{R}_{N/8,7N/8}(0) \rangle \\ & \approx |\mathbf{v}_{N/8}^1 - \mathbf{v}_{7N/8}^1|^2 \langle \mathbf{X}_1(t) \cdot \mathbf{X}_1(0) \rangle \\ & + |\mathbf{v}_{N/8}^3 - \mathbf{v}_{7N/8}^3|^2 \langle \mathbf{X}_3(t) \cdot \mathbf{X}_3(0) \rangle \end{aligned} \quad (33)$$

and

$$\begin{aligned} & \langle \mathbf{R}_{3N/8,5N/8}(t) \cdot \mathbf{R}_{3N/8,5N/8}(0) \rangle \\ & \approx |\mathbf{v}_{3N/8}^1 - \mathbf{v}_{5N/8}^1|^2 \langle \mathbf{X}_1(t) \cdot \mathbf{X}_1(0) \rangle \\ & + |\mathbf{v}_{3N/8}^3 - \mathbf{v}_{5N/8}^3|^2 \langle \mathbf{X}_3(t) \cdot \mathbf{X}_3(0) \rangle \end{aligned} \quad (34)$$

Using the relations $\lambda_1 < \lambda_3$ and $|\mathbf{v}_{N/8}^1 - \mathbf{v}_{7N/8}^1| > |\mathbf{v}_{N/8}^3 - \mathbf{v}_{7N/8}^3|$, eq 33 can be written in an approximated form

$$\langle \mathbf{R}_{N/8,7N/8}(t) \cdot \mathbf{R}_{N/8,7N/8}(0) \rangle \sim \langle \mathbf{X}_1(t) \cdot \mathbf{X}_1(0) \rangle \quad (35)$$

Obviously, the longest relaxation time is still connected with the superbridge. For eq 34, we have to leave it in this coupled form. In other words, the relaxation of the internal bridge is always coupled with that of the superbridge. Regarding the second longest time, we have found two candidates

$$\begin{aligned} & \langle \{ \mathbf{R}_{N/8,3N/8}(t) + \mathbf{R}_{7N/8,5N/8}(t) \} \cdot \\ & \{ \mathbf{R}_{N/8,3N/8}(0) + \mathbf{R}_{7N/8,5N/8}(0) \} \rangle \\ & = \langle \{ \mathbf{R}_{N/8,5N/8}(t) + \mathbf{R}_{7N/8,3N/8}(t) \} \cdot \\ & \{ \mathbf{R}_{N/8,5N/8}(0) + \mathbf{R}_{7N/8,3N/8}(0) \} \rangle \sim \langle \mathbf{X}_2(t) \cdot \mathbf{X}_2(0) \rangle \end{aligned} \quad (36)$$

where $\mathbf{R}_{N/8,3N/8} + \mathbf{R}_{7N/8,5N/8}$ is the cooperative vector of the two outer bridges and $\mathbf{R}_{N/8,5N/8} + \mathbf{R}_{7N/8,3N/8}$ is the cooperative vector of the two sub-superbridges. Because the internal bridge is shared by $\mathbf{R}_{N/8,5N/8}$ and $\mathbf{R}_{7N/8,3N/8}$, the motions of the two sub-superbridges are strongly coupled with each other. So the more appropriate explanation of eq 36 is that the second longest relaxation time refers to the outer bridges. In spite of the increased complexity in the 4-sticker chain model, we are still able to identify the role of bridges whose relaxation should always be the slowest motions.

We stop our discussions in the 4-sticker chain model. The analysis of the eigenvector in AP with more stickers is more complicated, but it can be straightforwardly proceeded via a similar procedure. From the forms of these relaxation modes, it is also suggested that if we are concerned only about the slow relaxation modes, an associative chain can be modeled as a simpler molecule with only the sticky beads and the effective bonds formed by the bridge structures, which returns to the picture proposed by Baxandall.²² Moreover, the identification of these slowest motions provides clues on how to prove this model from an experimental aspect. The classic Rouse model has shown the role of \mathbf{R}_{ee} and its relaxation characterized by dynamic light scattering or neutron spin echo experiments^{66,67} has always been a strong piece of evidence of this model. Similarly, the sticky Rouse model here has shown the role of bridge, and an experiment that can directly capture bridge relaxation will also be a compelling verification of this model.

From the results and discussions in this section, we can see that the most significant aspects in the LVE of AP, including the gelation behavior, the measure of elasticity, the relaxation time spectrum, and the corresponding molecular motions, can all be related to bridges. Besides, the property dependence on the chain length, which is one of the key predictions of the classic Rouse model, is also incorporated in the discussion of bridges in the case of AP. If ρ_s is fixed, the increase of N will intersperse more stickers in each chain, which means more bridges. On the other hand, if the number of stickers is fixed, the situations for different chain length systems are very similar, except for the difference in the value of ρ_s . All of these results show that the bridge should be the most critical structure in AP.

IV. CONCLUSIONS

In summary, a modified version of the Rouse model, the sticky Rouse model, was successfully applied to describe the dynamics of polymers with associative groups. The predicted phenomena

were in mutual agreement with previous theories. Both the LVE and diffusion behavior were explained after the effect of association in AP was replaced by an effective frictional force acting on stickers. Following a similar way as the classic Rouse model, the viscoelasticity of AP was deciphered by solving the eigenvalues of the sticky RZ matrix $\Xi^{-1}\mathbf{Z}$. Analytical expressions were also given by the graph theory. Based on this concept, the following properties about the LVE of AP were predicted. (1) A network characterized by a plateau modulus can be formed when a bridge structure exists. The range of the plateau regime is determined by the magnitude of the sticker's friction, and the plateau value is proportional to the bridge number. (2) The relaxation modes are classified into a slow group and a fast group: the former is still Rouse-like, while the latter is degenerated and shifted from the intrinsic relaxation behavior of the precursor polymer. (3) The slow modes are related to the rotational relaxation of the bridge portions. These predictions have shown the role of the bridge structure in determining the LVE of AP and also provided clues on how to prove this model from measurable quantities.

In spite of these predictions, it has to be noted that some significant aspects of real AP are not included in the present work. One is the dependence of association dynamics, for example, the relationship between the effective friction δ and the sticker concentration ρ_s , which has been mentioned in Section III.II. Such a relationship relies on the specific style of association reactions. In particular, more attention needs to be paid to the aggregation of stickers, which should be a significant factor in the association dynamics and is also noted by the perspective paper of Zhang et al.¹⁴ The other is the insufficiency to describe a network from a single-chain model. A modification in the expression of stress should be considered. In our forthcoming work, we will conduct molecular dynamic (MD) simulations on AP, where direct evidence for this model will be provided, and these missing points will be addressed.

■ APPENDIX: SOLVING EIGENVALUES FROM THE GRAPH THEORY

We follow the procedure proposed by Yang⁶³ to give the analytical expression of the eigenvalues of the sticky RZ matrix $\Xi^{-1}\mathbf{Z}$ from the graph theory. In a published paper,⁶⁸ the eigenvalue problem of the chain model with a sticker in the middle has been discussed. Here, we will demonstrate the graph calculation of the chain model with two periodically distributed stickers. Chain models with more stickers or other topologies can be proceeded in a similar way.

The graph theory calculation for polymers always involves two elementary graphs, which is shown in Figure 5. In addition, the eigenpolynomials for Figure 5a,b are $g_n(x)$ and $\dot{g}_n(x)$, respectively, with the form

$$\begin{aligned} g_n(x) &= g_n(2\cos\theta) = \frac{\sin[(n+1)\theta]}{\sin\theta} \\ \dot{g}_n(x) &= \dot{g}_n(2\cos\theta) = \frac{\cos[(n+1/2)\theta]}{\cos(\theta/2)} \end{aligned} \quad (\text{A.1})$$

where $x = 2 - \lambda$. The 2-sticker polymer is an $\dot{A}_m B_1 A_{2m} B_1 \dot{A}_m$ -style copolymer with $N = 4m + 2$. The graph representation G of the corresponding $\Xi^{-1}\mathbf{Z}$ is shown in Figure 6a. Following Theorem I in ref 63, we cut off the middle bond and obtained G' and the subgraphs G_i . Subsequently, the eigenpolynomial of the original graph $P_G(x)$ can be written as

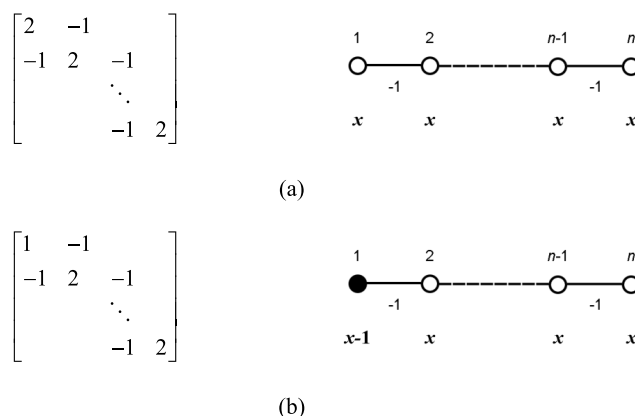


Figure 5. Two elementary matrixes and the corresponding graph representations in the graph theory calculation for polymers.

$$P_G(x) = P_{G'}(x)^2 - P_{G_i}(x)^2 \quad (\text{A.2})$$

To this means, the eigenvalue problem is simplified into the graph calculation of the $\dot{A}_k B_1 A_l$ -style chain segment. By repeating this procedure, we get its eigenpolynomial

$$\begin{aligned} P_{G_{kl}}(x) &= [(2 - 2\delta + x\delta)\dot{g}_k(x) - \dot{g}_{k-1}(x)]g_l(x) \\ &\quad - \dot{g}_k(x)g_{l-1}(x) \end{aligned} \quad (\text{A.3})$$

The final expression of $P_G(x)$ is

$$\begin{aligned} P_G(x) &= \{[(2 - 2\delta + x\delta)\dot{g}_m(x) - \dot{g}_{m-1}(x)]g_m(x) - \dot{g}_m(x)g_{m-1}(x)\}^2 \\ &\quad - \{[(2 - 2\delta + x\delta)\dot{g}_m(x) - \dot{g}_{m-1}(x)]g_{m-1}(x) - \dot{g}_m(x)g_{m-2}(x)\}^2 \end{aligned} \quad (\text{A.4})$$

If the λ expansion of P_G is

$$P_G(\lambda) = \sum_{p=0}^N \alpha_p \lambda^{N-p} \quad (\text{A.5})$$

the coefficients can be calculated via

$$\begin{aligned} \alpha_{N-k} &= \frac{1}{(k-1)!} \lim_{\lambda \rightarrow 0} \frac{d^k P_G(\lambda)}{d\lambda^k} \\ &= \frac{1}{(k-1)!} \lim_{x \rightarrow 2} \frac{d^k P_G(x)}{d(2-x)^k} \\ &= \frac{1}{(k-1)!} \lim_{\theta \rightarrow 0} \frac{d^k P_G(2\cos\theta)}{d(2-2\cos\theta)^k} \end{aligned} \quad (\text{A.6})$$

Here, using the Taylor expansion, we have these coefficients for the 2-sticker chain model

$$\begin{aligned} \alpha_N &= 0 \\ \alpha_{N-1} &= 2 - N - 2\delta \\ \alpha_{N-2} &= \frac{1}{2} - \frac{\delta}{2} - \frac{N}{24} [8 + 4N^2 + \delta(12\delta - 24) \\ &\quad + N(15\delta - 15)] \\ &\dots \dots \end{aligned} \quad (\text{A.7})$$

The following relationships will further enable us to calculate the values of λ_p

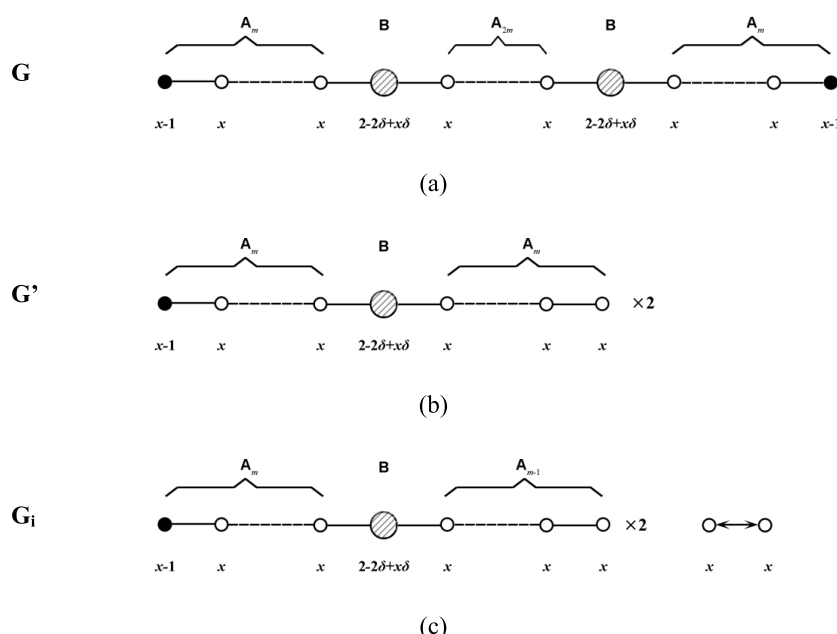


Figure 6. (a) Graph representation of the sticky RZ matrix of a 2-sticker chain. (b) Graph G' by cutting the middle bond. (c) Subgraphs G_i by removing the closed path passing through the middle bond.

$$\begin{aligned}\frac{\alpha_{N-2}}{\alpha_{N-1}} &= -\text{Tr}(\mathbf{Z}^{-1}\Xi) \\ \frac{\alpha_{N-3}}{\alpha_{N-1}} &= \frac{1}{2}\{\text{Tr}^2(\mathbf{Z}^{-1}\Xi) - \text{Tr}(\mathbf{Z}^{-1}\Xi)^2\} \\ \frac{\alpha_{N-4}}{\alpha_{N-1}} &= \frac{1}{2}\text{Tr}(\mathbf{Z}^{-1}\Xi)\text{Tr}(\mathbf{Z}^{-1}\Xi)^2 - \frac{1}{3}\text{Tr}(\mathbf{Z}^{-1}\Xi)^3 \\ &\quad - \frac{1}{6}\text{Tr}^3(\mathbf{Z}^{-1}\Xi) \\ &\dots \dots\end{aligned}\quad (\text{A.8})$$

where

$$\text{Tr}(\mathbf{Z}^{-1}\Xi)^k = \sum_{p=1}^{N-1} \frac{1}{\lambda_p^k} \quad (\text{A.9})$$

The bulk properties, including the zero-shear viscosity η_0 and the steady-state recoverable compliance J_e^0 , are directly related to $\text{Tr}(\mathbf{Z}^{-1}\Xi)^k$. They can also be expressed by these coefficients as

$$\eta_0 = -\frac{\rho \xi k_B T}{kN} \frac{\alpha_{N-2}}{\alpha_{N-1}} \quad (\text{A.10})$$

$$J_e^0 = \frac{N^2}{\rho k_B T} \left[1 - 2 \frac{\alpha_{N-3} \alpha_{N-1}}{\alpha_{N-2}^2} \right] \quad (\text{A.11})$$

If $\text{Tr}(\mathbf{Z}^{-1}\Xi)$ is dominated by several small eigenvalues, the longest relaxation times can be easily evaluated. In the present case, we have the estimation

$$\begin{aligned}\frac{1}{\lambda_1} &\approx \text{Tr}(\mathbf{Z}^{-1}\Xi) \\ &= \frac{1}{-48 + 24N + 48\delta} \{12 - 12\delta \\ &\quad + N[8 + 4N^2 + \delta(12\delta - 24) + N(15\delta - 15)]\} \\ &\quad (\text{A.12})\end{aligned}$$

which is also the expression of η_0 after being multiplied with the prefactor.

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Notes

The authors declare no competing financial interest.

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