Molecular Understanding of Viscoelasticity in Transient Polymer Networks Based on Multiple Methods

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Transient polymer networks are formed by dynamic crosslinks with a finite lifetime and therefore exhibit significant viscoelasticity, including non-Newtonian behaviors. Using the combination of multiple experimental techniques, such as viscoelastic measurements and spectroscopic analyses, these properties can be understood at the molecular level. This review classified transient polymer networks as side-chain and end-chain crosslinks, and viscoelastic studies of each type were presented. A combination of linear viscoelastic and spectroscopic methods revealed deviations between the viscoelastic properties of transient polymer networks and the molecular model. These deviations are sometimes attributed to dynamic heterogeneities potentially contained in the transient polymer network. These unexpected heterogeneous structures are challenging to control and impact viscoelasticity. Controlling and discussing these heterogeneities based on multiple experimental approaches is essential for a better molecular understanding of transient networks in the future.

Key Words: Viscoelasticity / Transient networks / Associative polymer / HEUR / Host-guest gel

1. INTRODUCTION

Transient networks are three-dimensional networks formed by dynamic crosslinks through supramolecular interactions, namely coordinate bonds, hydrogen bonds, ionic interactions, host-guest interactions, and hydrophobic interactions. The bond energies of these supramolecular interactions (several tens of kJ·mol⁻¹) are lower than those of covalent bonds (several hundred kJ·mol⁻¹ for C-C bonds). Thus, these supramolecular interactions exhibit associative and dissociative kinetics driven by thermal fluctuations and form crosslinks with a finite lifetime. As a result, transient polymer networks exhibit rich viscoelastic properties compared to entangled polymer solutions and polymer gels. They possess network structures based on the topological constraints between the polymer chains and covalently bonded crosslinks.

Recently, several studies have developed tough hydrogels and self-healing materials by utilizing dynamic crosslinks in the network structure. A mechanism to dissipate the applied energy in the hydrogels was incorporated by the inclusion of dissociative dynamic crosslinks, the reproductivity of the crosslinks prompting self-healing of the materials. Therefore, it is essential to understand the molecular mechanism of viscoelastic properties in transient networks and control their molecular dynamics when designing novel soft materials.

Viscoelasticity of transient networks is highly complex due to the interplay between the dissociation dynamics of the crosslinks and the rich dynamics of the polymer chains. However, a theoretical explanation was provided more than 50 years ago by the pioneering work of Green, Tobolsky, and Yamamoto. The authors assumed that viscoelasticity was predominantly determined by the lifetime of the bonds and that other viscoelastic modes, such as the Rouse and reptation modes, were negligible. Following their work, various models have considered the interplay between polymer- and crosslink dynamics as stickers, including the sticky Rouse mode, sticky reptation mode, and reversible gelation model. Alternatively, considerable experimental studies have been conducted to elucidate the viscoelasticity of the transient networks by using thermoresponsive ABA block copolymers, hydrophobically end-capped polymers, ionomers, “slime”, etc. In addition, some studies reported the use of wormlike (threadlike) micelles, which are also strongly relevant.

The difficulty in studying transient polymer networks originates from the fact that dynamic crosslinks, including the species, bond energy, and crosslinking site, are available in wide varieties. This review classified the transient polymer networks into two groups: side-chain crosslinked and
end-chain crosslinked, as shown in Fig. 1. For a complete understanding of the molecular mechanism of the viscoelastic properties, multiple experimental methods (not only rheology) are essential to avoid misinterpreting molecular dynamics based on limited information.

In Section 2, the viscoelastic properties of host-guest (HG) gels (side-chain crosslinked) are discussed using measurements obtained by 2D nuclear magnetic resonance (NMR) spectroscopy. In Section 3, a comprehensive evaluation of the relationship between viscoelasticity and diffusivity of transient polymer networks, using hydrophobically modified ethoxylated urethane (HEUR) (end-chain crosslinked), is provided.

2. SIDE-CHAIN CROSSLINKED TRANSIENT POLYMER NETWORKS

The rheological properties of side-chain crosslinked transient polymer networks have been studied using various model systems. For example, Chen et al. developed a model system of transient crosslinking of entangled or non-entangled partially sulfonated polystyrene and investigated the ion interactions on viscoelasticity in detail\textsuperscript{25, 39, 40}. The transient crosslinking results in the onset of elasticity depending on the degree of crosslinking and the associated large-scale delay in dynamics. The linear viscoelasticity is explained by some theoretical models, such as the sticky Rouse model\textsuperscript{20, 21, 38} and the sticky reptation model\textsuperscript{23}, depending on the molecular structures. Since such transient crosslinks result in energy dissipation in response to external deformation, many functional materials have been developed. However, it is not always the case that the transient structure is “ideally” formed. A multidisciplinary approach plays a vital role in elucidating the mechanism of such materials. Here, the viscoelasticity of host-guest gel is introduced as an example.

Host-guest gels are a type of side-chain crosslinked transient polymer network formed by the formation of host-guest specific complexes, demonstrating high flexibility and excellent toughness\textsuperscript{6, 11}. The host-guest gel is obtained by the addition of β-cyclodextrin and adamantane-modified acrylamide (βCD, Ad-AAm) during radical polymerization of the vinyl monomer. In water, hydrophobic interactions between βCD and Ad result in a stable inclusion complex, thus acting as a dynamic crosslink. Despite being a transient polymer network, the host-guest gel does not dissolve in water but remains in a swollen state, exhibiting gel-like properties\textsuperscript{49}. Therefore, viscoelasticity and NMR measurements reveal the molecular origin of the host-guest gel properties\textsuperscript{50}.

Figure 2(a) shows the dynamic viscoelasticity results when host molecules, absent in the main chain, were introduced into the host-guest gel at various concentrations. For the standard host-guest gel ($C_{\text{host}} = 0$), $G'$ and $G''$ decreased slowly with a decrease in $\omega$, while no plateau value of $G'$ was detected. The frequency dependence was weakened with the introduction of host molecules, although there was minimal change in the value at the low-frequency limit. The weakening frequency dependence indicates that inserting the host molecule inhibits the formation of the inclusion complex and reduces the transient crosslink point density. Conversely, the flat modulus at the low-frequency limit was equal to the rubbery flat modulus of the polyacrylamide solution without a crosslinking structure, suggesting that the elasticity observed in this range is not due to the crosslinking structure but instead the entanglement of the main chains. From the creep test results and other experiments conducted by the authors, a flat modulus was observed, sometimes for periods above $10^5$ s, mimicking the behavior of a trapped entanglement. Therefore, the dynamic viscoelasticity of polyacrylamide with only βCD incorporated into the main chain was herein investigated, as shown in Fig. 2(b). Increasing the concentration of βCD delayed the terminal relaxation time, the plateau modulus at the high frequency remained unchanged. This was often observed in a branched and entangled polymer\textsuperscript{51}. This similarity suggests that the βCD molecules form branching points in the polyacrylamide chain, despite the absence of Ad molecules.

Subsequently, 2D nuclear Overhauser-enhanced (NOE) NMR of the polyacrylamide solution containing only βCD was performed (Fig. 3(a)). Cross-correlation was observed between the protons inside the βCD molecules and those in the polyacrylamide main chains (red squares in Fig. 3(a)). The NOE NMR measurements showed cross-correlation between protons in proximity, which suggests that the main chain penetrates the βCD to form a rotaxane structure. These results indicate two types of crosslinks in the host-guest gel:
dynamic crosslinks, due to the host-guest complex, and static crosslinks, due to the rotaxane structure. The two types of crosslinks have different dynamics and can dissipate the deformation energy, which is thought to be the reason for the above-mentioned toughness.

3. END-CHAIN CROSSLINKED TRANSIENT NETWORKS

The rheological study of end-chain crosslinked transient networks has been developed differently from the side-chain type. Hydrophobic ethoxylated modified urethanes (HEURs) are one of the most famous end-crosslinked transient networks as a model system. HEURs consist of hydrophilic poly(ethylene glycol) chains and hydrophobic alkyl end groups. The end groups aggregate in water to form a network that consists of dynamic crosslinks. The hydrophobic interactions repeatedly form and disintegrate with thermal fluctuations and exhibit a single viscoelastic relaxation behavior (Fig. 4)\textsuperscript{51, 52}. The single viscoelastic relaxation was explained by pioneering transient network models\textsuperscript{15, 16}. However, experimental studies found several deviations from this theory, including the concentration and molecular weight dependence of the viscoelastic relaxation time\textsuperscript{53}.

Considering these deviations, the molecular understanding of viscoelastic properties in transient networks of telechelic type polymers remains incomplete. To understand the molecular mechanism, direct evaluation of the molecular dynamics provides helpful information. In this section, the research focusing on diffusion will be introduced. There are several methods to evaluate the diffusion of molecules such as nuclear magnetic resonance and dynamic light scattering. Fluorescence recovery after photobleaching (FRAP) is helpful for evaluating slow dynamics. FRAP measurement was performed whereby a molecule with a fluorescent probe in a limited region was photobleached with intense light. The
self-diffusion of the molecule recovered the intensity in that region, and the diffusion coefficient was estimated based on this recovery process.

Figure 5(a) shows the ratio of the diffusion coefficient of HEUR polymer modified with fluorescein ($D$) to that of unconnected HUER polymer ($D_0$) as a function of the polymer concentration of HEUR ($c_{HEUR}$). $D/D_0$ was lower than unity and decreased with an increase in $c_{HEUR}$, suggesting that the stickers surrounding the polymer end restricted the movement of the HEUR chains. To interpret the viscoelasticity based on the molecular diffusion, the distance ($L$) over which the polymer chain diffuse in the viscoelastic relaxation time ($\tau_{visco}$) was evaluated. The random diffusion process provides $L$ as:

$$ L = (D\tau_{visco})^{1/2} \quad (1) $$

Figure 5(b) shows the estimated $L$ for $c_{HEUR}$. $L$ showed a constant value of 1 μm in the examined concentration regime. Figure 5(b) also showed the gyration radius of one polymer chain presented as a dashed line, less than 1/100 times smaller than $L$. This implies that the HEUR polymer moves about 100 times the polymer size within $\tau_{visco}$. $L$ is larger than the length of the elastically effective chains, which is expressed as $\xi = (k_BT/G_0)^{1/3}$.

The viscoelasticity of a flexible polymer system is mainly due to the orientation anisotropy caused by deformation. The Brownian motion of the polymer eliminates the orientation anisotropy while it diffuses about the size of the polymer. The discrepancy between diffusion and viscoelasticity in HEUR may be due to the dynamic heterogeneous structure of the transient network, such as superbridge structures, dangling chains, unconnected micelle, and unimer (Fig. 6). Highly diffusive micelle structures are also formed in transient networks, such as HEUR. In general, slow network components dominate the macroscopic viscoelasticity, although fast dynamics are dominantly detected by FRAP measurements, resulting in an inconsistency between $L$ and $\xi$. The present results suggest that some chains dissociate from the network structure and diffuse rapidly by recombination, indicating that the viscoelasticity of HEUR cannot be explained by simply considering the collapse of crosslinking points and polymer diffusion.
4. CONCLUSIONS AND PERSPECTIVES

This review presents a study on the viscoelasticity of transient polymer networks using several experimental techniques. Linear viscoelastic studies of transient networks, using NMR and FRAP, showed that dynamic heterogeneity, such as rotaxane crosslinking and micellar structures, significantly affects viscoelasticity.

In particular, controlling the viscoelastic relaxation time of transient networks has been reported to significantly affect large deformation behavior, such as rupture and ductile/brittle fracture\(^{55-57}\). In addition, natural silk materials, including cocoon silk and spider silk\(^{58-60}\) also utilize dynamic cross-links between proteins to form high-order structures and their novel physical characteristics such as toughness and heat-resistance. Therefore, understanding the dynamics of transient networks is expected to play an essential role in polymer physics and materials.

However, studies on transient networks are often complex due to heterogeneities in the network structures and limited experimental characterization. Conventional systems have a high degree of freedom in the possible structures, and unexpected structures can be created in terms of mesh size, the number of branches, loops, and micelle formation. These uncontrollable heterogeneous structures prevent a definitive discussion of molecular dynamics. Recently, a novel method to link branched polymers at the ends was developed to design an ideal network structure\(^{61}\), and was applied to fabricate transient networks\(^{62}\). These attempts to study the physical properties of ideal networks with well-defined structures will form one stream in the future. Another important aspect is the accurate and independent approach to various dynamics. Considering that transient networks have complex dynamics, such as dissociation of crosslinks, fluctuation of polymer chains, and segmental motion, interpretations based on limited experimental results can result in a flawed understanding. Multiple experimental evaluations, such as spectroscopic and viscoelastic techniques, are needed to facilitate the molecular level understanding and give critical insight into the future development of emerging transient polymer networks.

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