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How Double Dynamics Affects the Large Deformation and Fracture Behaviors of Soft Materials

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Abstract

Numerous mechanically strong and tough soft materials comprising of polymer networks have been developed over the last two decades, motivated by new high-tech applications in engineering and bio-related fields. These materials are characterized by their dynamic complexities and large deformation behaviors. In this review, we focus on how chain dynamics affects the large deformation and fracture behaviors of soft materials. To favor readers without a rheology background, first we review the linear rheology behaviors of several simple networks. We show that, by playing with the physical entanglement, chemical crosslinking, and physical association of the building polymers, a very rich panel of dynamic responses can be obtained. Then we show examples of how chain dynamics affects the deformation and fracture behaviors of dually crosslinked hydrogels having chemical crosslinkers and physical bonds. We also provide examples on the unique deformation behavior of physical double-network gels made from tri-block polymers. Thereafter, examples of the influence of chain dynamics on the crack initiation and growth behaviors are presented. We show that even for chemically crosslinked double-network hydrogels that exhibit elastic behaviors in common deformation window, the chain dynamics influences the damage zone size at the crack tip. Finally, we conclude the review by proposing several directions for future research.

I. Introduction

In recent two decades, there is a spectacular development in designing network polymers with excellent mechanical properties, in particular in hydrogels.[1–24] Conventional hydrogels, typically composed of chemically crosslinked polymers, are mechanically weak and brittle owing to their structural heterogeneities and lack of energy dissipation mechanisms, which severely limit their applications.[25–29] Efforts have been made to synthesize homogeneous network structures, which improve the strength and stretchability of the materials[2,30,31]. On the other hand, more effects have been made to introduce energy dissipation mechanism in network polymers, which increases the toughness, i.e., the resistance against crack propagation.[32,33]

The first successful example to introduce energy dissipation in network materials is double-network (DN) hydrogels invented in 2003 (Fig. 1A).[1] By combining two covalently crosslinked networks, a stiff/brittle network and a soft/stretchable network, the resulting elastic gels exhibit extremely high strength, stretchability, and toughness.[17,34–41] Extensive studies have elucidated that the unprecedented toughness of DN gels results from the synergistic effect of the two networks with contrasting properties.[42–45] The covalent bonds in the brittle first network sacrificially rupture, dissipating energy, and the stretchable second network maintains the integrity of the material, redistributing stress. Chemically crosslinked hydrogels, including DN gels, usually exhibit rate-independent or elastic

deformation behavior at common experimental window, because of the low molecular friction and fast dynamics of the network strands.

DN hydrogels put forward a general sacrificial bond strategy/mechanism towards designing/understanding robust soft materials. That is, one can toughen soft materials by incorporating a brittle/weak structure. Recently, various physical associations were introduced as dynamic sacrificial bonds to dissipate energy, resulting in materials with rate-dependent and unprecedented mechanical performances (Fig. 1A). For example, a single network dually crosslinked by chemical bonds and physical associations exhibits remarkable enhancement in mechanical performance compared to its counterpart of chemical network.[46,47] A combination of a covalent network and a dynamic network brings high toughness, self-recovery, and self-healing of the materials.[32,48] A combination of two dynamic networks realizes recyclability, along with high toughness and self-healing.[49–52] Apart from the reformability that results in self-recovery and self-healing, a great advantage of dynamic sacrificial bonds is their superior versatility. The physical associations, which is also usually named as dynamic bonds in material community, or reversible stickers in rheology community, can be hydrogen bonding,[53–56] π - π stacking,[57–59] hydrophobic,[60–65] ionic interaction,[66–69] or metal-ligand interactions (Fig. 1B).[70–73] Hereafter, we follow the rheology convention and denote these physical associations as stickers. These stickers have different binding energies (Fig. 1C) and consequent associating lifetimes, endowing the materials with rich dynamic mechanical behaviors on demand.

FIG. 1. (A) Schematic diagrams of typical double dynamic networks, including double covalent networks, a covalent network with stickers, an entangled network with stickers, and a sliding network. [Adapted with permission from [15,74–76]] (B) Schematic illustrations of a covalent bond, metal-ligand coordination, ionic bonding, hydrogen bonding, hydrophobic interactions ($R = \text{alkyl}$), and π - π stacking. Inset shows the energy of a pair of stickers as a function of their distance. E_a is the activation barrier. [Adapted with permission from [16,17] with modification] (C) Binding energies of various bonds. [Adapted with permission from [77] with modification]

Despite great successes in developing various soft materials by combining different static/dynamic networks, however, the most important feature of soft materials, i.e., how the chain dynamics affects the deformation and fracture behaviors has not received much attention as it deserves. In fact, material chemists usually rely on an empirical, trial-and-error approach to develop soft materials, and material mechanists usually use a static picture to discuss the deformation and fracture behaviors of soft materials. This is at least partly owing to the poor understanding of the intrinsic relationship between chain dynamics and large deformation as well as fracture behaviors where the nonlinear rheology effect becomes important. The establishment of this intrinsic relationship is rather challenging and requires the combined efforts from rheology, material chemistry, polymer physics, and mechanics communities.

The objective of this review focuses on how the microscopic chain dynamics governs the macroscopic large deformation and fracture behaviors of network materials. The potential readers could be rheologists or mechanists who are interested in the relationship between chain dynamics and large deformation as well as fracture behaviors of soft materials or

material scientists who are interested in developing tough soft materials from the viewpoint of chain dynamics. Here, we mainly focus on network polymers with double dynamics, because tough soft materials with different crosslinking structures have at least two distinct dynamic modes of the polymer network. This review is structured as follows. First, to favor the readers unfamiliar with rheology, we introduce some textbook knowledge regarding the chain dynamics of several typical polymers and networks, including entangled polymer melts, entangled polymer melts with stickers, chemically crosslinked network, and chemically crosslinked network with stickers. Then, we present several selected examples to demonstrate the role of double dynamics on large deformation and fracture behaviors. We show the nonlinear rheology effect of dynamic network. Thereafter, we give examples to show the influence of chain dynamics on the damage zone formation in DN gels. We will also show how chain dynamics influence crack growth as well as the intrinsic coupling between chain dynamics and chain scission. Finally, we propose some future directions in this research area.

II. Dynamic mechanical spectra of polymer networks

To favor the readers from material and chemistry fields, we first briefly introduce the rheological behaviors of polymer networks. The dynamics of polymeric networks are fundamentally governed by their network structures. The polymer networks used in fabricating materials generally contain entanglements, chemical crosslinkers, or stickers, or their combinations (Fig. 2A). The interplay between the thermodynamics and kinetics of stickers, entanglements, and/or chemical crosslinkers yields a rich rheological behavior of

such type of materials. Even for polymers containing only stickers, their rheological behaviors can range from rubberlike to liquidlike, depending on the lifetime and rate of deformation. Furthermore, the density and position of stickers, as well as the structure of building polymers such as linear, ring, comb, star, and so on, influence the dynamic behaviors of these materials.[75,78–82] Here, we discuss the chain dynamics of four basic network structures: entangled polymer network, entangled network with stickers, chemical network, and chemical network with stickers. For simplicity, the discussion is limited to networks without solvent.

FIG. 2. (A) Schematic illustration to show a polymer network containing chemical crosslinkers, physical entanglements, and stickers (dynamic bonds). τ_s , τ_c , and τ_e are the lifetimes of stickers, relaxation time of chemical network strands, and relaxation time of entanglement network strands, respectively. (B) A graphical illustration of storage modulus versus frequency (logarithmic scale) of four simple networks. The molecular masses of strands between neighboring stickers, entanglement points, and chemical crosslinking points, are denoted as M_s , M_e , and M_c , respectively. Here, only the subcases with $M_s < M_e$ or $M_s < M_c$ (many stickers on each entanglement or chemical network strand) and the lifetime of the sticker is longer than the Rouse time of the associating strand are given. Here, M_c of the chemically crosslinked network is smaller than M_e of entanglement network for better demonstration. [B: Modified with permission from[75]]

It has been well-established that a highly entangled network comprising linear polymers has a dynamic storage modulus spectrum specified by three relaxation times[83]: (1) the relaxation time of the Kuhn segment, τ_0 , which is the shortest relaxation time in the Rouse

model; (2) the longest relaxation time of an entangled strand by Rouse motion, $\tau_e = \tau_0 \left(\frac{M_e}{M_0}\right)^2$, where M_e and M_0 are the molecular masses of an entangled strand and a Kuhn monomer, respectively; and (3) the reptation time required for the whole chain to escape from its tube, $\tau_{rep} = 6\tau_e \left(\frac{M}{M_e}\right)^3$, where M is the molecular mass of the whole chain. Several relaxation steps can be pointed out through time, as illustrated in Fig. 2B.

At timescales smaller than τ_0 , the Kuhn monomers cannot relax, and the material shows a glassy behavior with a storage modulus $G_0 \approx \frac{\rho RT}{M_0}$, where ρ is the polymer density, R is the gas constant, and T is the temperature. At timescales between τ_0 and τ_e , Rouse motions of subchains occur, featured by a slope of 0.5 in the plot of storage modulus versus frequency in log-log scale. At timescales between τ_e and τ_{rep} , free Rouse motion of the chain is impossible due to the topological confinement, and the material reaches the rubbery region, with a plateau modulus $G_e = \frac{\rho RT}{M_e}$. At timescale larger than τ_{rep} , the chain escapes from the entanglement constraints, and global motion of the chain occurs, which gives rise to a power-law dependence of storage modulus against frequency with a slope of 2.

For an entangled network with multiple interchain stickers, chain relaxation occurs via a sticky-reptation mechanism, i.e., through the repeated breakup-association process of all stickers within it.[74,75,84–86] Depending on the density and lifetimes of stickers, entanglement relaxation, and chain reptation, there are several subcases for chain relaxation mechanisms. Readers interested in this topic are strongly recommended to read the review

paper by Chen and co-workers[75] and the special issue on *Associating Polymers* in the *Journal of Rheology* in 2017.[55,87–103]

Here, we give one subcase that many stickers on each entanglement strand and the lifetime of the sticker is longer than the Rouse time of the associating strand.[75] For this case, there are two plateau modulus regimes. For timescales smaller than the sticker lifetime τ_s , the stickers do not break up and contribute to the plateau modulus. Therefore, the plateau modulus before τ_s is $G = \rho RT \left(\frac{1}{M_e} + \frac{1}{M_s} \right)$, where $M_s (< M_e)$ is the molecular mass between stickers.[84] For timescales larger than τ_s , stickers start to dissociate, and the modulus decreases. At timescales larger than the sticky Rouse time $\tau_s \left(\frac{M_e}{M_s} \right)^2$, the modulus returns to the plateau modulus due to entanglements. The reptation of the whole chain is also delayed by the stickers, which gives the sticky reptation time $\tau_{rep} = \tau_s M^3 M_e^{-1} M_s^{-2}$.

For the chemically crosslinked network, it has a similar dynamic behavior like an entanglement network, except that no chain reptation occurs due to the permanent confinement by the chemical crosslinkers. Assuming no entanglements in the chemical network for simplification, one gets a set of similar relations for the two plateau modulus regimes as those of the entanglement network by changing M_e to the molecular mass of chemical network strand M_c .

In reality, polymeric materials usually contain both chemical crosslinking and physical entanglement. Furthermore, sticker lifetimes could have a distribution. Therefore, polymeric

materials often exhibit a richer panel of dynamic behavior, which can be understood by the combinations of the simple cases described in Fig. 2B.

As shown in Fig. 2B, the mechanical behaviors of polymeric materials depend on the observation timescale or the deformation rate in relative to the characteristic relaxation times. All network materials can be glassy when the deformation rate is sufficiently high. Therefore, soft materials are defined by their responses to conventional observation timescales or experimental deformation rates, which are generally in the range of 10^{-3} to 10^1 s⁻¹. Here we limit ourselves to the viscoelastic or rubbery polymer networks (elastomers or gels) under this deformation rate range.

III. Large deformation and fracture behaviors in dually crosslinked gels

To obtain tough soft materials, the strategy of dually crosslinked network with chemical crosslinkers and stickers has been widely adopted in recent years,[46,104] as the stickers can enhance energy dissipation, while chemical crosslinking can prevent irreversible plastic flow of the material at long timescales. For swollen network polymers without stickers, the relaxation of the polymer strands is very fast and the relaxation times τ_c and τ_e are usually much shorter than 10^{-3} s.[105] Therefore, the materials exhibit elastic responses in common observation window. With the presence of stickers, the relaxation of polymer strands is slowed down. Depending on lifetimes of the stickers, the materials could show elastic or viscoelastic responses in the common observation window.

A. Weak stickers

First, we show the case of weak stickers that having short associating lifetimes τ_s and low bond density so that the imposed deformation rates are smaller than the inverse of $\tau_s \left(\frac{M_c}{M_s}\right)^2$, corresponding to the left-hand plateau modulus regime due to chemical bond in Fig. 2B. In this case, the effect of stickers is mechanically invisible in the observation window, and the materials show hyperelastic deformation behavior. However, recent experimental results show that, even in this case, the presence of stickers substantially enhances the stretchability of the material, as illustrated in Fig. 3A. This interesting phenomenon has been observed in several dually crosslinked networks that differ in their underlying chemistry.[16,106–108]

One example is the work reported by Kean et al.,[106] wherein they judiciously chose the binding strength of stickers and allowed them to be elastically ineffective under the experimental deformation rate. The polymers are poly(4-vinylpyridine), and the stickers are Van Koten-type pincer complexes (Fig. 3B). The complex can form one or two coordination bonds with the monomeric groups along the chains of the chemically crosslinked network. As shown in Fig. 3C, the dually crosslinked gels, PN2·PdEt and PN2·PdMe, are elastic in the frequency ranging from 0.01 to 4 s⁻¹, and they have the same storage modulus as the chemical gel, PN2. However, the large deformation behaviors of the dually crosslinked gel and chemical gel are significantly different. Under a deformation rate of 0.04 s⁻¹, the chemical gel (PN2) is fairly brittle. In comparison, the dually crosslinked gel, with PN2·PdEt as an example, shows the same stress response to strain as the chemical gel but has a dramatic

increase in failure strain at the same deformation rate. The behavior is more obvious at high sticker concentrations (Fig. 3E).

FIG. 3. (A) Schematic illustration to show the stress–strain curves for a chemically crosslinked network without (red curve) and with (green curve) stickers. The green and red curves collapse. However, the chemically crosslinked network with stickers failures at a much larger strain. That is, the effect of stickers is mechanically invisible at deformation, but the presence of stickers delays the fracture. (B) An example of covalent organogel (left) incorporated with pincer stickers (right) by coordination with pyridine side-groups (blue circles). (C) Storage and loss moduli of the chemical gel, PN2, dually crosslinked gels, PN2·PdMe, and PN2·PdEt at 25 °C. The sticker concentrations of PN2·PdMe and PN2·PdEt are the same of 5 mM. (D-F) Stress-strain curves and mechanically generated chemiluminescence from covalent failure under loading in a compression geometry. (D) Strategy used for the measurements. (E) Representative stress-strain and emission intensity-strain plots of gels as a function of sticker concentration, [PdEt]. (F) Strain of emission max and stress max versus [PdEt]. Loading rate: 0.04 s⁻¹. [B-E: Reprinted with permission from [106]]

In the PN2·PdEt gel, Kean et al. used a bis(adamantyl) dioxetane mechanophore crosslinker, which behaves as a chemiluminescent indicator of covalent failure and enables the direct study of the fracture behavior of the covalent network (Fig. 3D). As shown in Fig. 3F, the onset of emission due to the failure of the covalent network occurs at the stress maximum, in concert with the strain at break. Although the onset of emission shifts with sticker concentration, the integral emission intensity and duration of emission remain constant. This suggests that the stickers, even not bear stress at deformation, can delay the catastrophic crack propagation.

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In the work of Kean et al.,[106] the dually crosslinked gels have different sticker concentrations and binding strengths but were subjected to the same loading rates. In the work of Mayumi et al.,[16] a complementary perspective was taken. They used a constant sticker concentration and binding strength but changed the deformation rate. The gels were composed of polyvinyl alcohol, PVA.[16,109,110] The gels are chemically crosslinked by glutaraldehyde and transiently crosslinked by borate ions as stickers. Each borate ion can form up to four transient bonds with the polyvinyl alcohol chains. In the limit of low deformation rate, the dually crosslinked gel shows the same elasticity as the reference chemical gel. However, the failure stretch ratio of dually crosslinked gel is at least two times larger than that of the reference chemical crosslink gel under uniaxial tension.[16] A similar result was also reported by Zhao et al. in dually crosslinked gels made from a random copolymer of poly(acrylamide-co-vinylimidazole) with metal-ligand coordination as stickers.[107]

The above three studies differ in their underlying chemistry, but all show the same clear result—the presence of stickers allows the materials to be more stretchable, although these stickers do not contribute to elasticity in the observation window. One plausible explanation for this interesting phenomenon is that the stickers play a role at the crack tip during failure where complex and fast processes are involved. When the dually crosslinked gel is homogeneously deformed, the stickers do not contribute to crosslinking because the imposed strain rate is slower than the inverse of the sticky Rouse time $\tau_s^{-1}M_c^{-2}M_s^2$. Therefore, the chemical gel and dually crosslinked gel show the same stress responses. However, once the microcrack starts to propagate, the deformation rate at the crack tip is much larger than that

of the bulk. The stickers at the crack tip start to carry load and protect the sample from failure. Although the underlying mechanism remains unclear, these studies inspire the tailoring of material performance, i.e., tuning the stretchability and toughness of a material, without changing its elasticity at use.

B. Strong stickers

Next, we show the case of strong stickers having long lifetimes and high bond density such that the frequency range between $\tau_s^{-1}M_c^{-2}M_s^2$ and τ_s^{-1} in Fig.2B falls in the common observation window. In this case, the material exhibits strong viscoelasticity over a broad frequency range. With increasing loading rate, the material modulus and toughness increase. Moreover, the materials usually exhibit strain softening or yielding behavior and mechanical hysteresis, distinctly different from hyperelastic materials.

Hydrogels composed of polyampholytes (PA) reported by Sun et al. were chosen as an example to show the rate-dependent behavior arising from strong stickers.[111] PA gels were synthesized by the radical copolymerization of positively and negatively charged monomers at charge balanced point. Each polymer chain bears randomly dispersed cationic and anionic repeat groups that can form ionic bonds (Fig. 4A).[68,112–116] PA gels show strong viscoelasticity in an extremely wide frequency range from 10^{-6} to 10^5 s⁻¹ (Fig. 4B). The slope of storage modulus versus frequency in log-log scale is weaker than 0.5, deviating from the simple Rouse relaxation shown in Fig. 2B. This could be attributed to the distribution in strength of ionic bonds in PA gel, as seen by the 100 nm-scale phase separation

structure.[117–125] The high density of ionic bonds, which results in a large $\tau_s \left(\frac{M_c}{M_s}\right)^2$, could be another reason for the wide frequency range of viscoelasticity. Since the reptation of the whole chain is significantly delayed by the ionic bonds, PA gels do not flow under large deformation, even without chemical crosslinking. However, a distinct difference in creep behaviors under moderate stress has been observed for PA gels with and without the chemical crosslinking.[126]

As shown in Fig. 4C, the PA gel shows strong rate-dependent tensile behavior in the experimental deformation rates ranging from 0.014 to 1.25 s⁻¹. The increase in stress with the deformation rate is because more ionic bonds survive as crosslinkers at high deformation rates. This viscoelastic feature is critical to the design of materials with high shock absorption and toughness.

FIG. 4. (A) Schematic illustration of the reversible ionic bonds in polyampholyte (PA) gels. (B) Storage modulus, loss modulus, and loss factor against frequency of a chemically crosslinked PA gel at 24 °C. The gel was synthesized from random radical copolymerization of sodium p-styrenesulphonate (NaSS) and 3-(methacryloylamino)propyl-trimethylammonium chloride (MPTC). (C) Tensile stress-strain curves of the PA gel under different deformation rates from 0.014 to 1.25 s⁻¹. (D) Self-recovery of PA gel for different waiting times performed by cyclic loading test. Deformation rate: 0.14 s⁻¹. (E) Waiting time dependence of the residual strain and hysteresis ratio (area ratio of the second hysteresis loop to that of the first). (F) Pictures of the self-healing behavior of a PA gel at room temperature: Two freshly cut surfaces (red and blue) merged together within several minutes. The data of C-F are from a PA gel without chemical crosslinker. This gel shows the similar mechanical behavior as typical dually crosslinked gels, because the strong and high-density ionic bonds in this gel bring very long terminal relaxation time and the entanglements act as quasi-permanent crosslinking points in the observation time window. [C-F: Reprinted with permission from[111]]

The ionic bonds also endow the PA gels with mechanical hysteresis and self-recovery. As shown in Fig. 4D, when subjected to a loading-unloading cycle, PA gel shows a large hysteresis loop, suggesting the energy dissipation due to the breaking of the ionic bonds. The gel has a residual strain immediately after unloading. The mechanical stress and residual strain can completely recover after a certain waiting time. Fig. 4E presents the waiting time dependence of the hysteresis ratio and residual strain, which involves a fast process and a slow process. The time required for the gel to be fully recovery is much longer than the associating lifetimes of the ionic bonds, which could be explained by the re-organizing of the reformed bonds. One more function of PA gels arising from ionic bonds is self-healing after damage or cutting (Fig. 4F), which is important for prolonging the material lifetime but not being discussed in detail here, as this review focus on chain dynamics and large deformation behavior.

C. Constitutive model for stickers

The most important and challenging problem is how to quantitatively relate the rate dependent large deformation behavior to the chain dynamics resulting from the stickers. Recently, Hui et al. developed a constitutive model by combining large-strain elasticity and time-dependent bond breaking and healing kinetics of stickers.[127–129] This theory can quantitatively describe the tensile and torsion results of dually crosslinked PVA gels in which the stickers are relatively weak, and the deformation does not influence the bonding rates of the stickers. Here we do not intend to introduce the detailed mathematical expression of this

theory but aim to describe its underlying physics. The first key assumption of this theory is that the stickers can break and reform, featured by a breaking time and a healing time, which is quite different to only one association lifetime for stickers usually used in the rheology society.[75] The second key assumption is that the dynamic equilibrium of bond breaking and healing of stickers results in a constant molar fraction of connected and broken stickers, and the breaking and healing kinetics are not influenced by the loading history. The third key assumption is that, once a sticker breaks, it is in a relaxed state and carries no strain energy. Once it reforms, it starts to carry strain energy. The stress contributed by a sticker is determined by the whole deformation history experienced by this sticker. The fourth key assumption is that the strain energy of a dually crosslinked network is a sum of those of the individual networks.

In most polymeric materials, such like PA gels, the breaking kinetics depends on the stress/strain being experienced by the ionic bonds, due to their relatively long relaxation time. Recently, Hui et al. extended their model by introducing the mechanical history-dependent breaking kinetics.[130,131] The model can describe the mechanical behavior of PA gels under various deformation modes, such as uniaxial loading, loading-unloading, and stress relaxation, as shown in Fig. 5. From the model analysis, it is clarified that the strain-softening of PA gels is attributed to the force enhanced bond breaking kinetics of stickers. These results clearly demonstrate that for the case of weak stickers, linear rheology is valid even for large deformations, while non-linear rheology effect should be taken into consideration for the

materials with strong stickers. This constitutive model gives a mathematical framework and a clear physical picture to describe the large deformation behavior of self-healing materials. However, the material parameters obtained from the model fitting to the experimental results do not directly represent the rheological parameters from molecular structure. A link between the constitutive model and the rheology should be established in future.

FIG. 5. Comparison of experimental results and model predictions of PA gels. (A–C) Simple tensile stress-stretch curves with different loading rates (LR). (D–F) Loading-unloading curves with different loading and unloading rates (UR). (G, H) Tensile-relaxation curves with different nominal stretch ratios λ_0 . [Reprinted with permission from [130]]

IV. Large non-softening deformation in hydrogels comprising two physical networks

Tough materials, regardless soft or hard, usually exhibit a strain softening behavior, that is, the stress becomes prominently sublinear after a certain strain.[132–136] This is because, in general, the high toughness originates from sacrificial structures in such materials, despite that the specific molecular mechanism depends on materials. As discussed in Section III, it is possible to toughen a soft material by introducing stickers. However, due to the strain-accelerated bond breaking kinetics of stickers, strain softening usually appears at small deformation. For example, the softening strain is only approximately 0.2 for dually crosslinked PA gels having chemical crosslinkers and stickers (Fig. 5). In case of tough DN gels consisting of two covalent networks, the stress exhibits a plateau after a critical strain, which is also called yielding or yielding-like phenomenon. The yielding strain of DN gels is usually less than 1.[36] This is because the first network in DN gels is highly pre-stretched and brittle, and the covalent bond rupture occurs at small strain. Although the propagation of

such internal damages could be effectively suppressed by the double network structure, once the deformation exceeds a critical point, that is, the average limited extensibility of first network strands, the internal damage propagates to the macroscopic level.[42–45] As a result, the material exhibits softening or yielding with further deformation. Expanding the non-softening deformation of tough soft materials is important for practical application but challenging. Here we give an example to demonstrate that, it is possible to achieve a large non-softening deformation by playing with two types of stickers in a class of hydrogels from triblock copolymers (Figs. 6A and 6B).

This class of hydrogels, named glue-B gels, have a unique structure consisting of a hyperconnective physical network and linear polymers.[49,137,138] The hyperconnective network, named B gel, is made from amphiphilic triblock copolymers that form micelles by their hydrophobic end-blocks. The micelles act as hyperfunctional crosslinkers, and each micelle connects approximately 70 hydrophilic mid-block network strands (Fig. 6A). The linear polymers form hydrogen bonds with the mid-blocks of the hyperconnective network, acting as molecular glues. The hydrogen bonds have a short lifetime, and the hydrophobic association has a long lifetime, of about 10^{-2} and 10^5 s at room temperature, respectively (Figs. 6C and 6D). Consequently, the B gel exhibits weak frequency dependent modulus, while the glue-B gel shows strong frequency dependent modulus, in the frequency ranging from 10^{-6} to 10^4 s $^{-1}$. Under a strain rate of 0.14 s $^{-1}$ where the hydrophobic associations act as quasi-permanent crosslinkers and hydrogen bonds act as reversible stickers, the uniaxial tension behaviors of B gel and glue-B gel are markedly different (Fig. 6B). The B gel is weak and brittle, whereas glue-B gel is strong and stretchable. More interestingly, the glue-B gel

exhibits a quasi-linear deformation up to the failure of the sample under uniaxial loading. The quasi-linear deformation is observed in glue-B gels under a wide strain rate range ($0.001 \sim 0.14 \text{ s}^{-1}$) and with different preparation formulations.

FIG. 6. (A) Schematic illustration to show the molecular structure of B gel and glue-B gel. [Reprinted with permission from [138]] (B) Stress-stretch curves for the B gel and glue-B gel in uniaxial tension. Initial strain rate: 0.14 s^{-1} . The inset in B shows the enlarged view of the small stretch ratio. (C, D) Frequency dependent storage modulus, loss modulus, and loss factor of B gel (C) and glue-B gel (D) at $24 \text{ }^\circ\text{C}$. [B-D: Adapted with permission from [49]]. (E, F) Schematics to show the deformation and fracture of B gel and glue-B gel. (E) For the B gel, once a strand is pulled out from micelle, the neighboring strands should be overloaded. As a result, local stress concentration and local strain amplification occur, inducing the catastrophic sample failure. (F) For the glue-B gel, when a network strand is pulled out, the load is transferred to the glue polymers, which effectively suppress local stress concentration. Consequently, further rupture does not occur at the neighboring strands but occurs randomly in the network with increasing deformation. [E-F: Reprinted with permission from [138]]

Based on the toughening mechanism of DN gels, the large non-softening deformation of glue-B gels consisting of two physical networks can be explained as a synergistic effect of the low pre-stretch of the first network and the suppression of stress concentration by the double dynamic structure, as revealed by Ye et al. with time-resolved small-angle X-ray scattering.[138] Ye et al. found that, under uniaxial stretching, the nanoscale micellar network deformation of the B gel is smaller than the bulk deformation, suggesting local strain amplification during deformation. However, in the glue-B gel, the nanoscale network deformation is exactly the same to the bulk deformation over the entire deformation range. The affine deformation indicates no strain amplification at the network scale until sample failure. The ability to suppress local strain amplification of glue-B gels is related to the

interplay between the hydrogen bonding, hydrophobic interaction, and network hyperconnectivity. At the beginning of deformation, the fast breaking and reforming of hydrogen bonds dissipate energy. With increasing deformation, the endblock chain with the shortest midblock is pulled out from the micelles through the breakage of hydrophobic association. In the case of B gel (Fig. 6C), the stress redistributes to neighboring strands, resulting in local stress concentration and local strain amplification. In the case of the glue-B gel (Fig. 6D), the long chain glue polymers form hydrogen bonds with multiple midblock chains of the hyperconnective network. When the endblock chain is pulled out, stress is redistributed far more diffusively over many strands and over much longer length through the physically bonded glue linear chains. Consequently, no local stress concentration and strain amplification occur. Instead, further chain pullout occurs randomly in the skeleton network. In addition, the hyperconnectivity of micelle gives its loading carry ability even many of its strands are pulled out. Furthermore, the midblock chains in hyperconnective network are not highly pre-stretched, which allows a large deformation before reaching its pull-out limit. Accordingly, the glue-B gels show an extremely large non-softening deformation.

V. Dynamic effects on damage zone and crack propagation

Understanding the fracture mechanism of soft material is critical for their applications. Generally, fracture in soft materials involves multiple time and length scales, including molecular-scale covalent bond scission, nanoscale polymer strand dynamics, mesoscale energy dissipation, and macroscale crack blunting.[139–141] Owing to experimental difficulties, understanding of the network scale chain dynamics on fracture of soft materials

is very limited. The tensile behaviors of all examples in Section III indicate that stickers play a role in fracture. Recent results also suggest that chain dynamics on the network scale affects the fracture behavior of soft materials even without stickers.[142–145] In this section, we focus on the onset of crack propagation and the size of the damage zone. In the next section, we will discuss the crack growth behavior.

A. Effect of chain dynamics on damage zone size in DN hydrogels

DN gels, with a structure as schematically shown in Fig. 7A, are known for their extremely high toughness and rate-independent behavior at conventional strain rates.[36] The high toughness of DN gels originates from the sacrificial rupture of the first brittle network over a wide zone (damage zone) ahead of the crack tip, while the second stretchable network maintains the structural integrity of the material. Such a DN architecture suppresses local stress concentration and dissipates a significant amount of mechanical energy at the crack tip. Typical DN gels, consisting of two chemically crosslinked networks, are strain rate independent in storage moduli, as shown in Fig. 7B as a typical example. The rate-independence behavior originates from the fast dynamics of the polymer network strands that cannot be observed at the conventional strain rates. Recent work by Zheng et al. suggests that the dynamics of the polymer network strands in DN gels influences the load transfer and the damage zone formation, thereby influences the onset of crack propagation and toughness.[142]

Fig. 7. (A) Schematic illustration to show the structure of a DN gel comprising a stiff/brittle first network and a soft/stretchable second network. (B) Frequency dependence of storage modulus, loss modulus, and loss factor of a DN hydrogel at 24 °C. [Reprinted with permission from [42]] (C) Uniaxial tensile stress-strain curves of DN gels swelled in EG/water mixture with volume fraction of EG (ϕ_{EG}) varied from 0 (pure water) to 1.0 (pure EG). Strain rate: 0.14 s^{-1} . (D) Young's modulus calculated from the stress-strain curves in (C). (E) Schematic illustration to show the necking zone and its network structure ahead of the crack tip at crack initiation with stretch ratio λ_c . The necking zone size, h_c , is calculated from the necking zone area S_c in the deformed state with the relation $h_c = S_c^{0.5}/\lambda_n$, where λ_n is the deformation ratio where necking finishes in uniaxial tension. (F) Change of necking zone size h_c versus solvent viscosity η_s . [C-F: Adapted with permission from [142]]

Zheng et al. studied the role of chain dynamics in DN gels comprising chemical networks, poly(2-acrylamido-2-methylpropane sulfonic acid sodium salt) (PNaAMPS) as the first network and polyacrylamide (PAAm) as the second network.[142] To slow down the chain dynamics, the solvent in the DN gel was changed from water to ethylene glycol (EG)/water mixtures or glycerol/water mixtures. The EG and glycerol have a comparable solvent quality with water, whereas the viscosity of the mixed solvents is 10^0 – 10^3 times higher than that of water. Because the chain dynamics of the network strands is governed by the friction between the monomer units and solvent, the dynamics of the polymer chains can be tuned over 3 orders of magnitude. At a strain rate of 0.14 s^{-1} that the gels stay in the rubbery plateau region, uniaxial tensile results show that DN gels do not change in stress-deformation response with the solvent viscosity (Figs. 7C and 7D). However, the onset of crack propagation, the size of the damage (necking) zone, and consequently the toughness of DN gels, distinctly decreases with increasing solvent viscosity at the same strain rate (Fig. 7E and 7F). Specifically, the fracture energy Γ decreases from 3000 to 700 J m^{-2} for changing EG volume fraction from 0 to 1.0 of EG/water mixtures.

These results suggest that despite DN gels are made up of chemical networks and show rate-independent tensile deformation, the dynamics of the network strands strongly influences on the fracture behavior. In the tensile test, the global stretch rate is much smaller than the longest relaxation dynamics of the network strands (the Rouse mode of polymer strands), thereby changing chain dynamics has negligible influence on the tensile behavior. However, in the fracture experiments, the local strain rate at the crack tip is considered much faster than the global stretch rate, and the chain dynamics of the network strands play a role. Once the first brittle network ruptures around the crack tip, the stress is transferred to the second network strands. When the chain dynamics of the second network strands is fast, the load is quickly picked up by the second network and then transferred to surrounding networks to cause further internal damage of the first network, which effectively prevents local stress concentration at the crack tip. Consequently, the gel has a large damage zone and high toughness. However, when the chain dynamics is slowed down by the more viscous solvent, it requires longer time for the second network to pick up the load, and stress concentration activates the scission of the second network at the crack tip. As a result, the crack starts to propagate at a smaller damage zone, and the fracture energy decreases.

B. Coupling of chain dynamics and chain scission in single network polymers

Even in a simple network, chain dynamics is also critical to fracture behavior. For a simple chemically crosslinked network staying in the rubbery plateau region (for frequency smaller than τ_c^{-1} in Fig. 2B), the fracture energy is rate independent. This intrinsic fracture energy, Γ_0 , is well explained by the Lake-Thomas model.[146] According to Lake-Thomas

theory, Γ_0 is the energy required to break one layer of the network strands crossing the fracture plane, which is related to the strand length and number density of network strands. For the network stays in the viscoelastic region (for frequency between τ_c^{-1} and τ_0^{-1} in Fig. 2B), the fracture energy is rate dependent, and it is usually described as $\Gamma = \Gamma_0 + \Gamma_{diss}$, where Γ_{diss} is from viscoelastic dissipation of network strands, and it is rate dependent.[147] It has been considered that the chain scission of network strands was not influenced by viscoelasticity.

Recently, Sloodman et al. incorporated a new mechanophore as a chain scission-reporting crosslinker into a series of acrylate elastomers comprising of ethyl acrylate (EA) or methyl acrylate (MA) monomers (Fig. 8A).[143] This new mechanophore has high fluorescence and stability, allowing them to quantitatively detect chain scission even in a simple network, with high spatial resolution and sensitivity (Fig. 8A). They changed the viscoelasticity and thus the chain dynamics of the elastomer by changing the experimental temperature and deformation rate, where the fracture energy could be changed from about 100 to 10000 J m⁻². Their results showed that, the chain scission is far beyond a single layer of network strands. The chain scission region can delocalize up to hundreds of micrometers, 100 folds of the size of single layer of network strands. Figs. 8B and 8C give an example at low viscoelasticity and high viscoelasticity of the network, by stretching the sample at the same speed but setting the experimental temperature at 80 and 25 °C, respectively. When the viscoelastic dissipation is low, chain scission occurs in a region a few micrometers wide at the crack surface. When viscoelastic dissipation is high, chain scission occurs over a hundred micrometers. These

results suggest that the chain dynamics and chain scission are intrinsically coupled during the fracture process (Fig. 8D).

FIG. 8. (A) Schematic illustration of acrylate elastomers with mechanophore as a crosslinker. When the mechanophore is under tension, no fluorescent forms. When the scission of mechanophore occurs, it releases a fluorescent anthracene moiety, reporting for strand breakage. (B) Frequency dependence of storage and loss moduli of an elastomer at 25°C and 80°C. Dashed vertical line corresponds to the strain rate in fracture experiment. (C) Confocal images of fluorescence activation in an elastomer at temperatures of 80 and 25 °C. The samples were fractured at a rate of $3 \times 10^{-3} \text{ s}^{-1}$. The scale bar is 100 μm . The direction of crack propagation is along the x direction. (D) Schematic illustration to show the coupling between viscoelasticity and chain scission at the crack tip. [Adapted with permission from [143]]

C. Crack propagation in sliding-ring gels

Here, we give one example of sliding-ring (SR) gels to demonstrate the importance of chain dynamics on crack growth behavior. SR gels were fabricated by crosslinking two cyclic molecules on different necklace-like supramolecular structures, named as polyrotaxanes.[148,149] The cyclic crosslinkers are threaded onto an axis polymer chain and can move freely in the polymer network until they hit an end-cap. Upon deformation, the cyclic crosslinkers can slide on the axial polymer to equalize the tension of polymer chains like pulleys. In typical SR gels, the timescale of cyclic crosslinker sliding is much longer than of the Brownian motion of network strands.[150,151] The dynamics of an SR gel, has a state named as “sliding state” at higher temperature or lower frequency than the rubbery state (Fig. 9A).[77,152] In this state, the Brownian motion of the sliding ring contributes to elasticity (sliding elasticity).

Liu et al. compared the crack propagation behaviors between pre-cut SR gels and fixed crosslink (FC) gels at the same modulus.[144] Uniaxial stretching was performed at a constant speed of 0.1 mm/s, where both of two gels stay in rubbery region. Both the SR and FC gels first show slow and then fast crack propagations. The crack velocities between these slow and fast stages are almost 20-fold different. This velocity jump from slow to fast is usually explained by the non-linear effect such as local glass transition or viscoelastic dissipation.[153,154] However, when plotting the crack velocity against the initial modulus in these two stages (Figs. 9B and 9C), a difference between SR and FC gels can be observed. In the slow mode fracture (Fig. 9B), SR gels show weak or almost no modulus dependence of crack velocity, while FC gels show strong modulus dependence of crack velocity. In the fast mode fracture (Fig. 9C), both SR and FC gels show similar strong modulus dependence of crack velocity. This result suggests that the crack propagation behavior of SR gels is controlled by the competition between the crack tip opening and sliding movement of cyclic crosslinkers (Fig. 9D). In the slow mode fracture, the cyclic crosslinkers have time to slide before encountering the crack tip. In this case, crack velocity is related to the slidable range of crosslinker on axial polymer, which is modulus independent. In the fast mode fracture, the crack tip motion has faster dynamics than the sliding motion, and the cyclic crosslinkers can be considered as fixed ones. As a result, SR gels and FC gels fracture in the same way. Determination of the timescale of chain relaxation and cyclic molecule sliding motion could confirm this explanation.

FIG. 9. (A) Schematic illustration of dynamic modulus of sliding-ring materials. Different from typical crosslinked amorphous polymers, the sliding-ring materials have a sliding transition and a sliding elasticity, where the cyclic molecules and axis polymer chains are sliding actively. This sliding state appears at higher temperature or a lower frequency than the rubber state for typical sliding-ring materials due to the slow sliding motion of cyclic molecules. [Reprinted with permission from [77]] (B, C) The change of crack velocity against initial modulus of SR and FC gels in (B) slow mode and (C) fast mode fracture stages. (D) Schematic illustration to show the chain deformation and sliding motion of SR gels during slow mode and fast mode fractures. [Reprinted with permission from [144]]

VI. Concluding remarks

In recent decades, soft materials made from polymeric networks have achieved spectacular developments in terms of new materials with high mechanical performance, which allows them promising applications in diverse fields. In this review, we focused on one specific aspect: how chain dynamics affects the large deformation and fracture behaviors. Despite many examples have shown the critical role of chain dynamics on deformation and fracture behavior of soft materials, however, the underlying mechanisms are still poorly understood. More efforts should be made towards to resolve this fundamental and challenging problem.

Molecular theory describing the viscoelasticity of a simple entangled polymer network has been well established. However, for materials containing stickers (dynamic bonds), the chain dynamic behavior is still far from being fully understood, especially for the materials comprising of two or multiple networks. One important challenge is due to the lack of the molecular details of the polymer network. Another important challenge is due to the complex morphology or microstructure of these materials. Associative groups have been reported to

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have nano or microphase separation. [81] Model system with well-defined network structure and the precise placement of stickers will be the first step to resolve this problem. [155] In addition to the linear chain dynamics, the nonlinear effect is more closely relevant to the large deformation and fracture behaviors of soft materials. Understanding on nonlinear rheology of polymer network, especially for complex networks, will benefit the understanding of this question.

From the material viewpoint, one promising future opportunity is to harness control over the chain dynamics within polymer network(s) through rational molecular design, leading to unprecedented, tunable mechanical performance of bulk materials. For example, many engineering materials require high toughness to resist fracture but low mechanical hysteresis to save energy. However, these two requirements usually conflict, as high toughness requires high energy dissipation while low mechanical hysteresis requires low energy dissipation. As demonstrated in Section III, by judiciously choosing the binding strength of dynamic crosslinker, it is possible for the dually crosslinked gels to have the same elasticity at use as the chemically crosslinked gels but with higher stretchability. This means, this type of dually crosslinked materials could have little energy dissipation or low hysteresis in the normal operation of cyclic loads, but dissipate energy at the crack tip once the crack starts to propagate.

Future efforts should also towards to the accurate description of chain dynamics and the large deformation behavior of complex networks. The challenge is that complex networks usually combine flow properties, exhibited by viscous fluids, with large strain elasticity that

characterized by solids. From a modeling viewpoint, they, therefore, fall at the boundary of solid and fluid mechanics, as pointed out by Hui et al.[156] The situation is even more challenging with increasing the complexity of the network. Another fundamental challenge is modeling the fracture of soft materials. Classical fracture theory assumes small deformation and linear viscoelasticity, which is not the case for polymer networks with large deformation. In addition, classical fracture theory assumes that the local fracture process is rate independent. This may not be true even in chemically crosslinked network, as demonstrated in Fig. 7, let alone in complex networks with chemical and dynamic bonds.

There are also opportunities for studying the fracture behavior of polymer networks with two or multiple dynamics. So far, there have been extremely few reports on the fracture behavior of this type of materials. Intuitively, one would expect that the fracture behavior of DN gels is less influenced by the chain dynamics, as they are chemically crosslinked and elastic at usual experimental observation window. However, as shown in Section V, the chain dynamics in the second network determines the stress transfer between the two networks and thus influence the crack initiation. It would be very interesting to study the fracture behavior of dually crosslinked gels with chemical crosslinking and physical bonds. The interplay between time-independent chemical network and time-dependent dynamic network ahead of crack tip is expected to give unique fracture behaviors of this type of materials. Furthermore, the dually crosslinked materials show a rich panel of dynamic responses. As shown in Fig. 2B, not only the lifetime but also the density of stickers influences the chain dynamics and should be paid attention in molecular design.

We expect the current review will inspire material design through tuning chain dynamics of polymeric networks to achieve the desired mechanical performance. Furthermore, we hope this review will provoke interdisciplinary discussions on a fundamental question: how chain dynamics affect the large deformation and fracture behaviors of soft materials. We think the integration of various efforts from rheology, chemistry, polymer physics, and continuum mechanics communities is required to reveal the picture behind this fundamental question. We believe such a picture will provide a solid foundation for the rational design of next-generation polymeric soft materials, including elastomers, hydrogels, and organogels.

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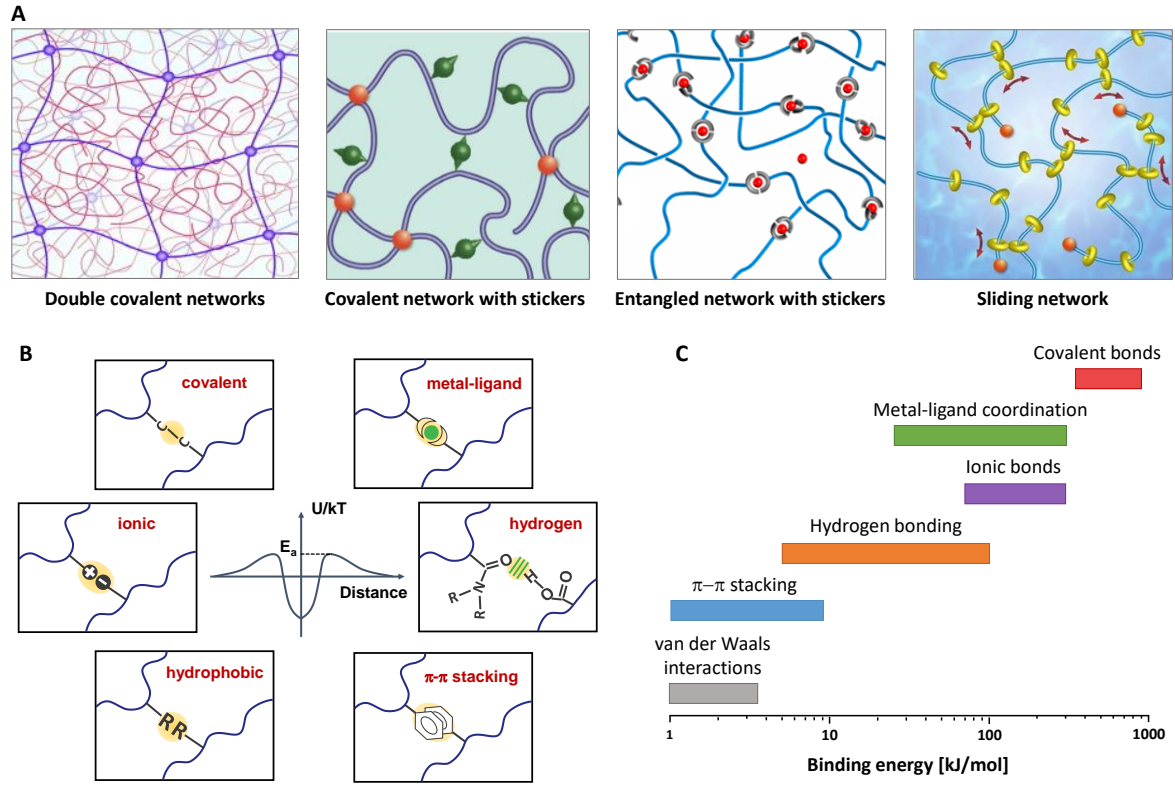
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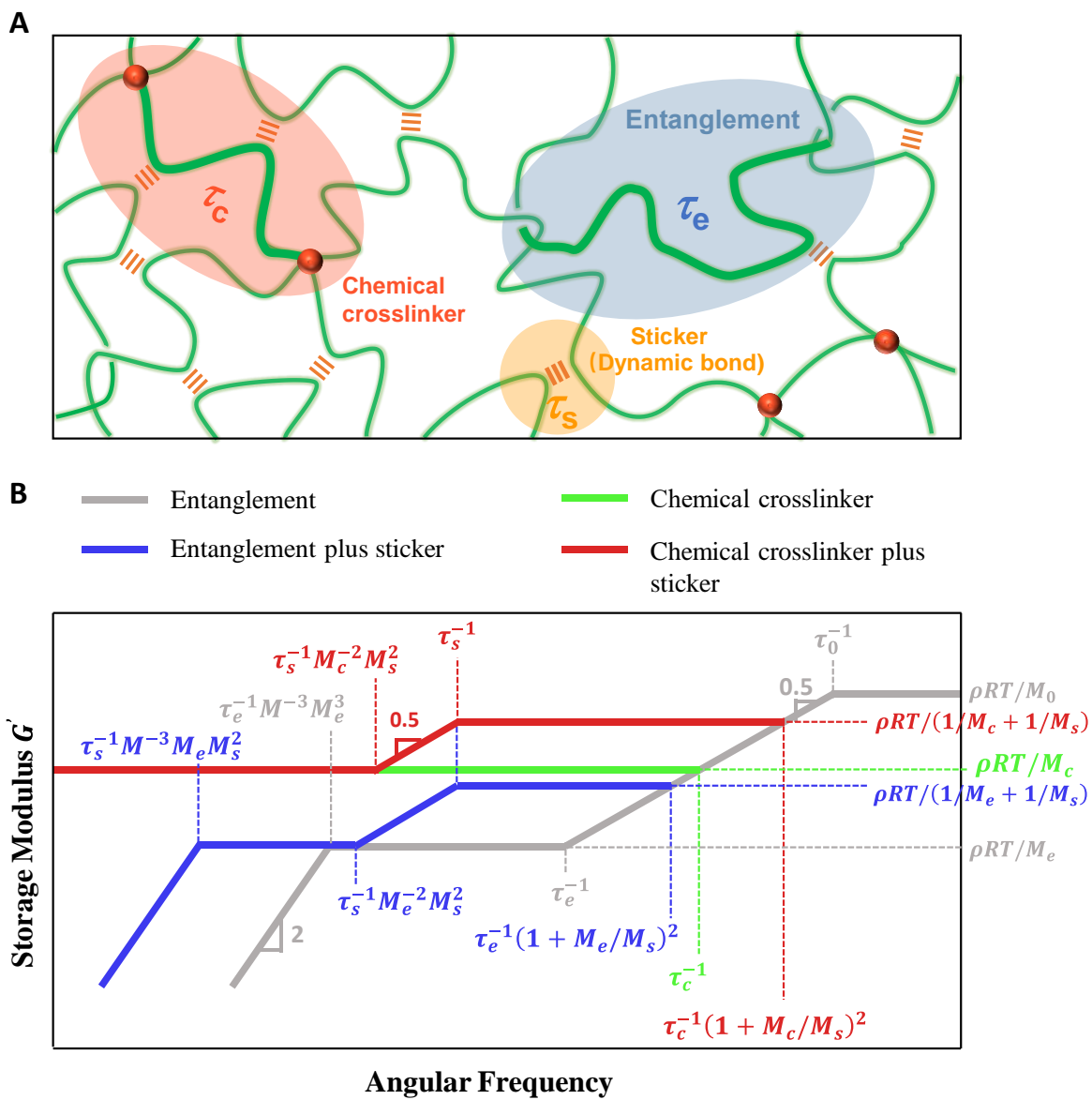
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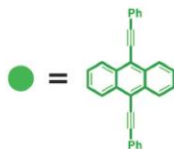
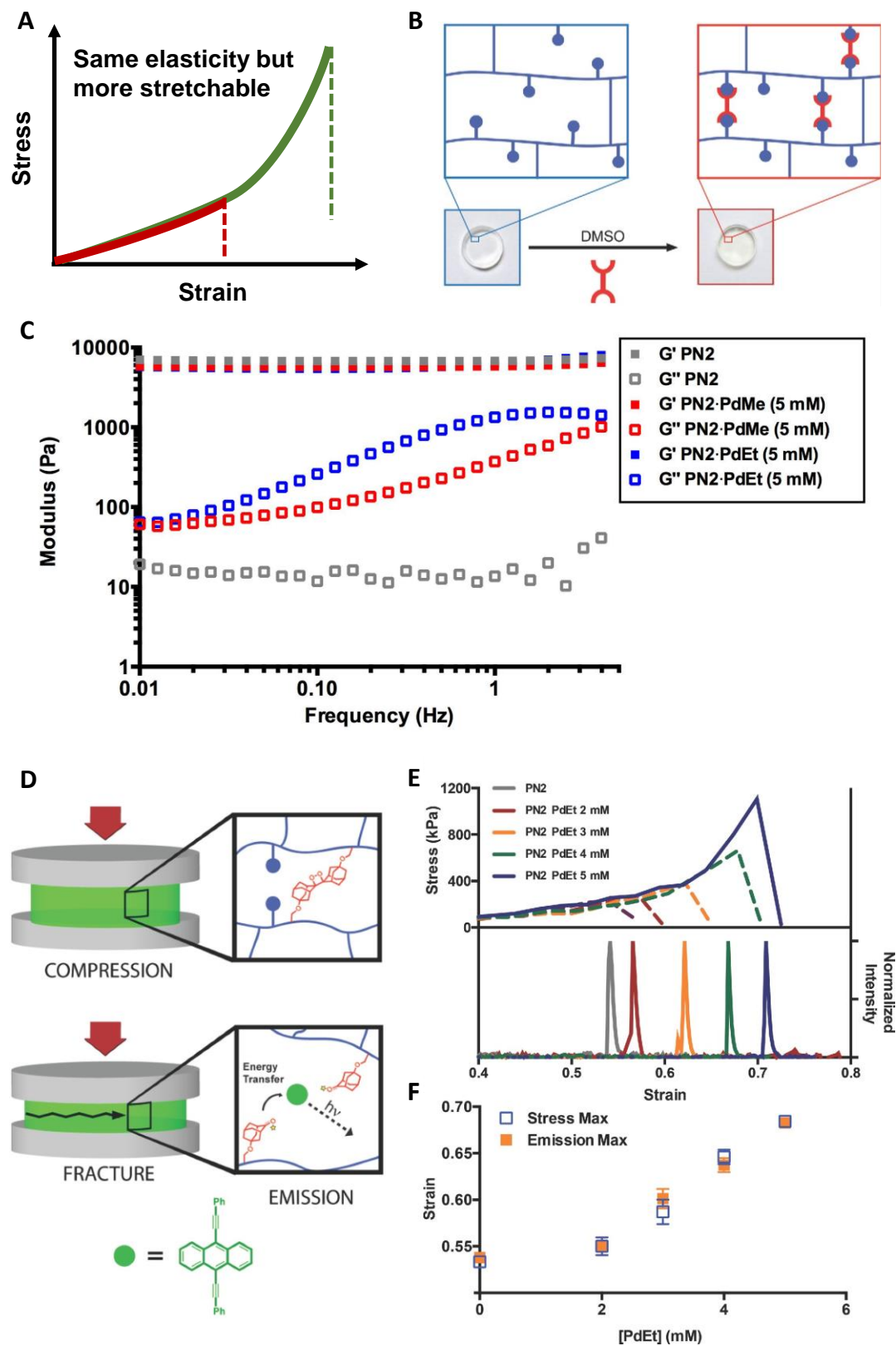
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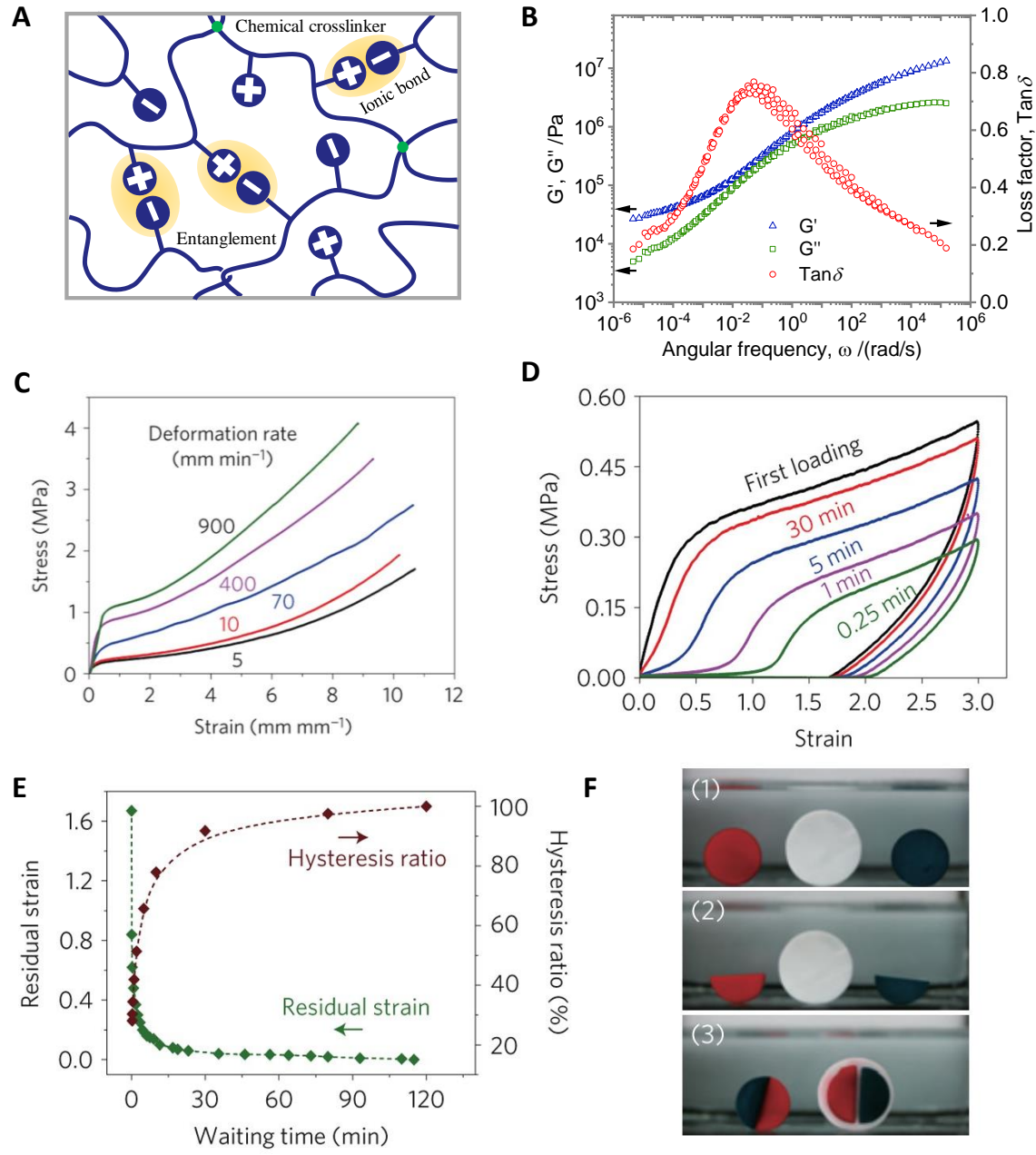
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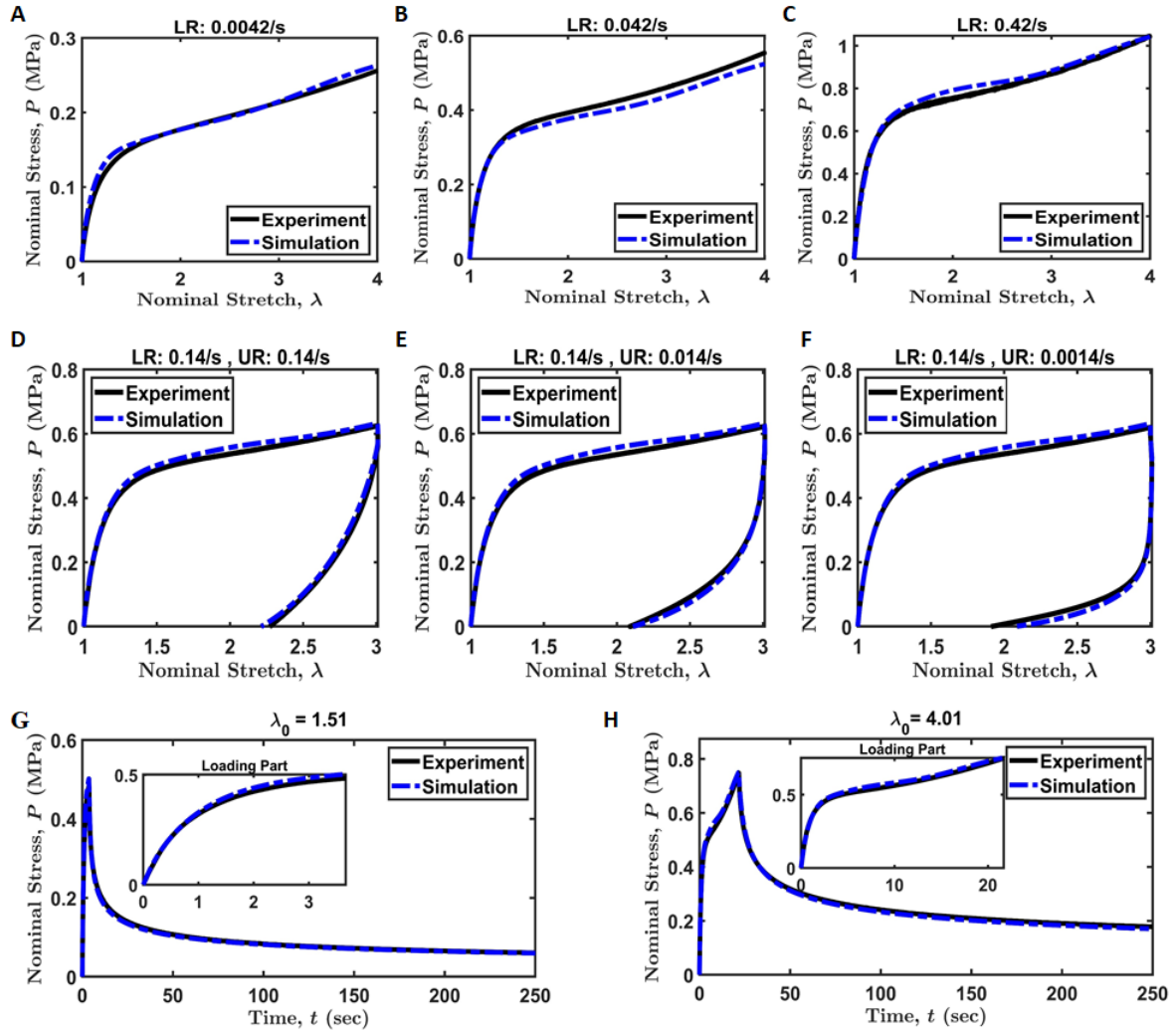
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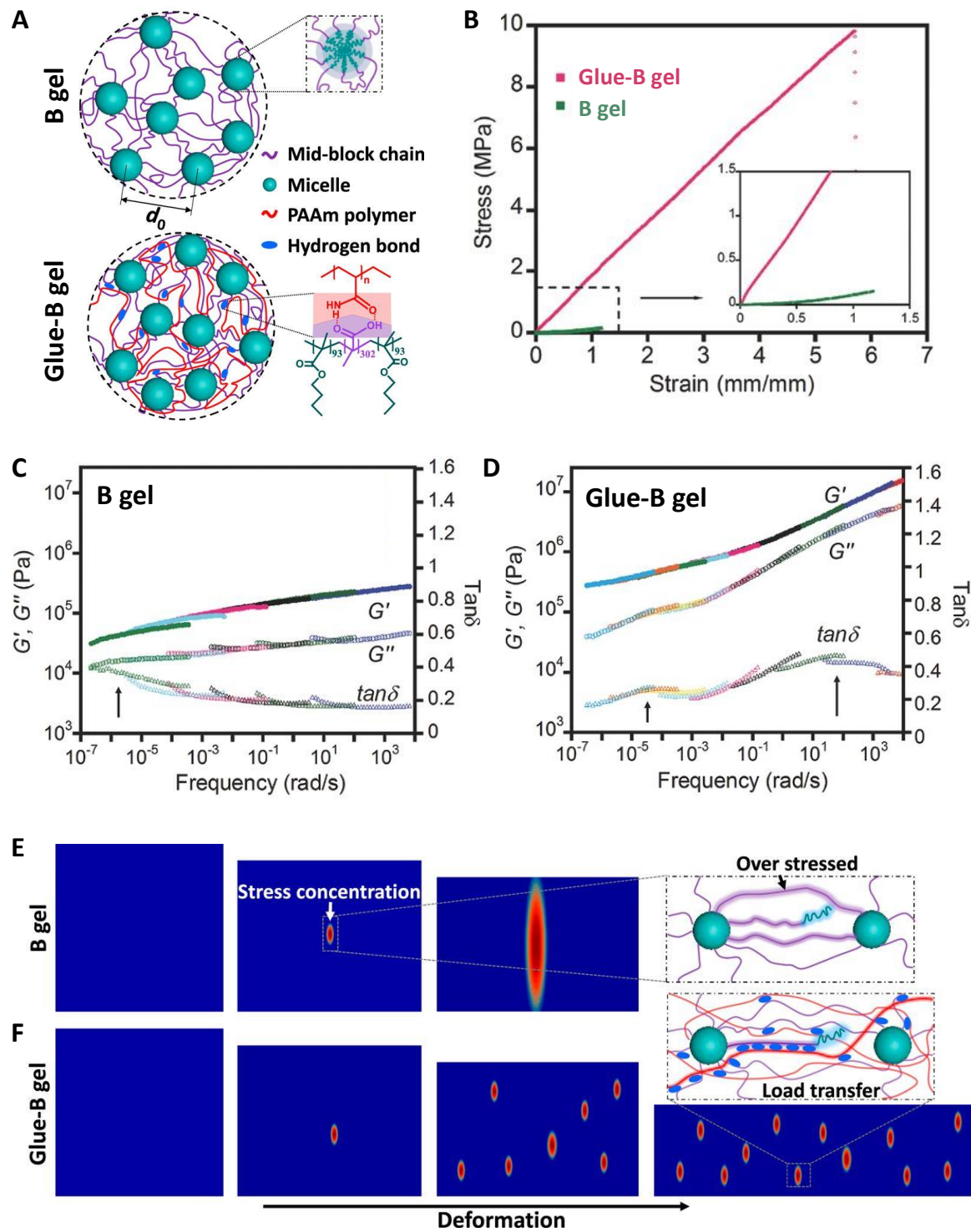
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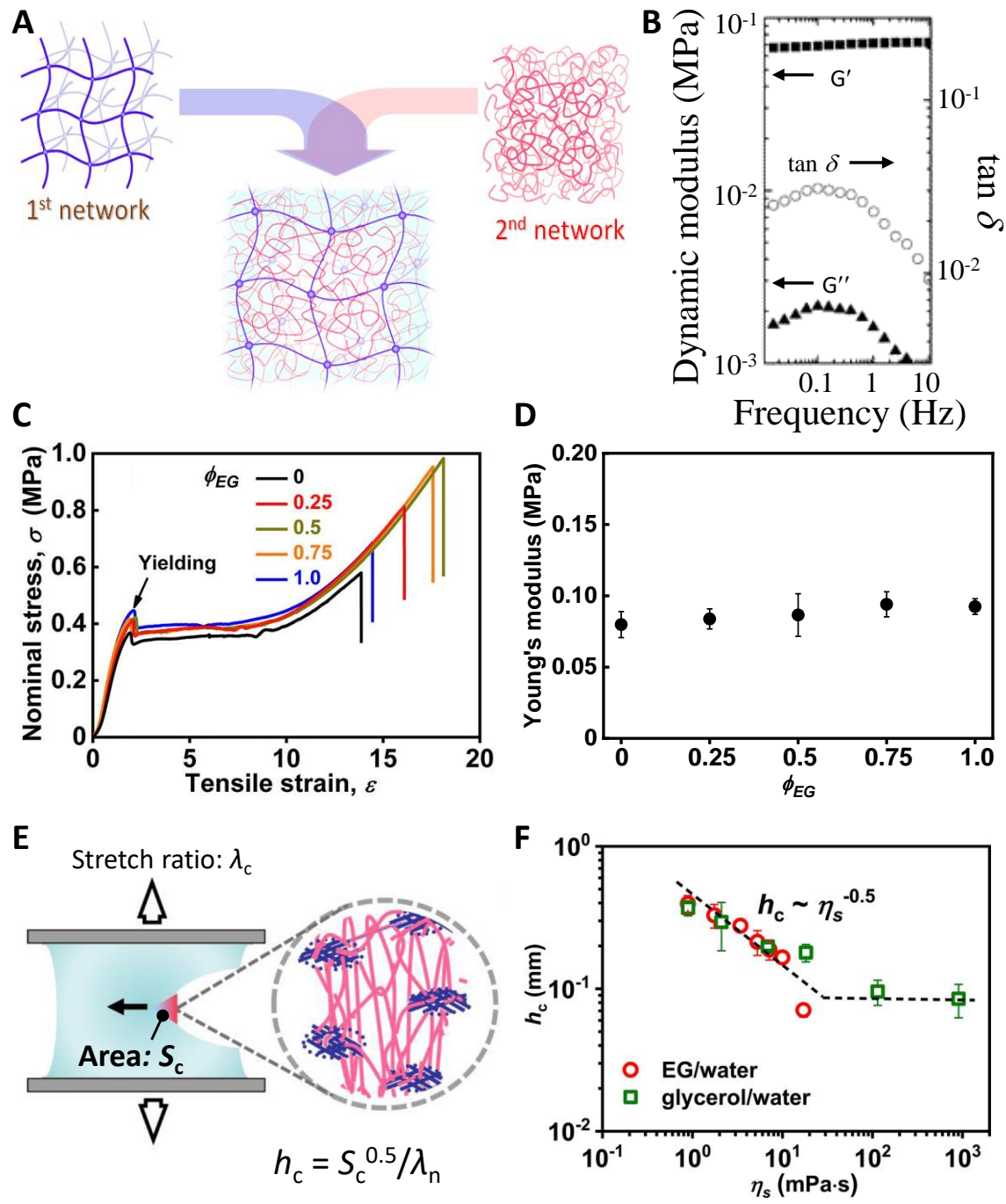
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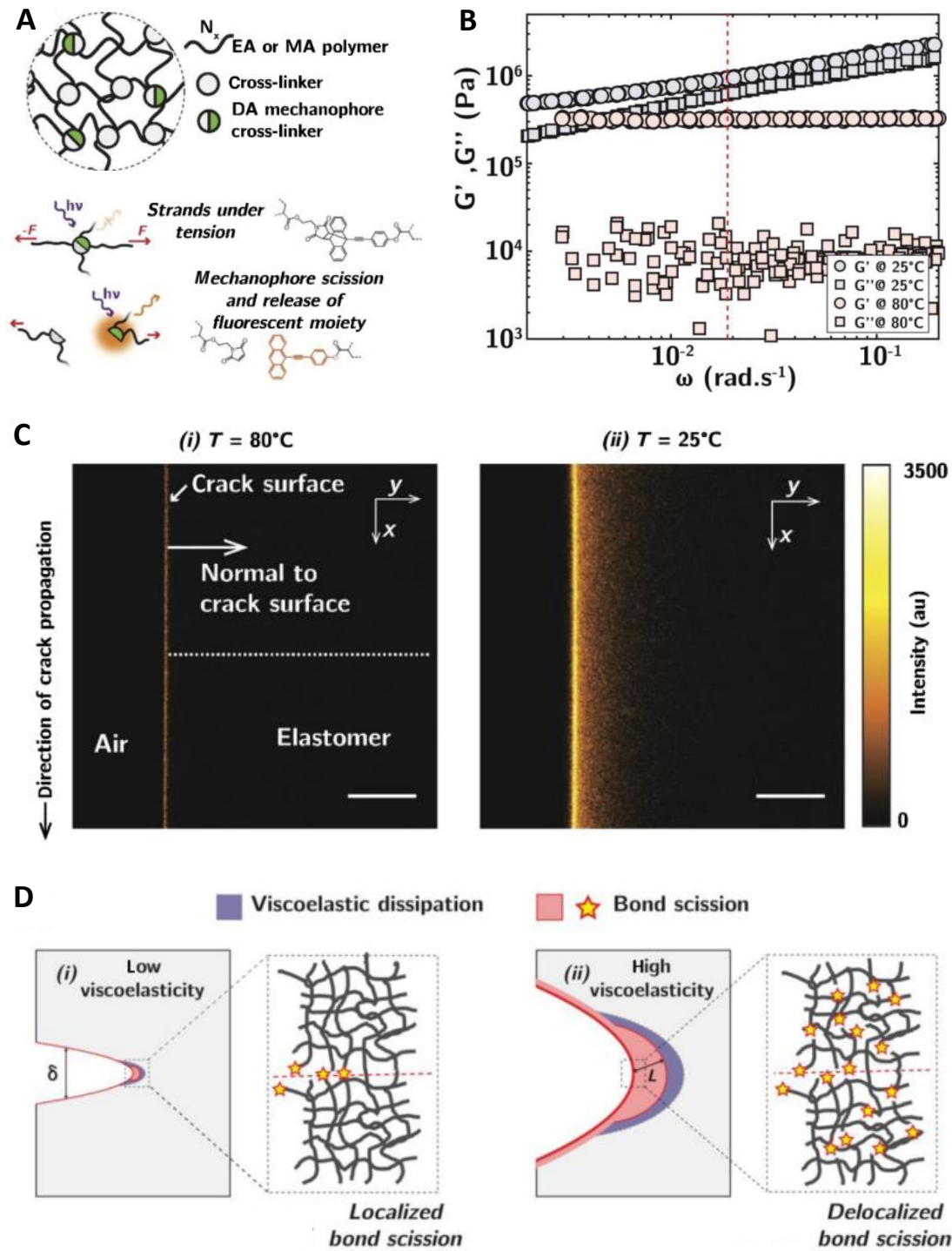
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