Relationships between viscoelastic relaxation and network connectivity in transient networks with well-controlled network structures

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ABSTRACT

Polymers crosslinked by reversible interactions form transient networks, which show fascinating viscoelasticity due to a finite lifetime of crosslinks. However, the molecular understanding of such viscoelasticity has remained incomplete because of the difficulty of experimentally evaluating bond lifetimes and heterogeneous structures in conventional transient networks. In this study, we developed a model system of transient networks with well-controlled structures (Tetra-PEG slime) to overcome these problems. We demonstrate an experimental comparison of the bond lifetime, estimated using surface plasmon resonance (SPR) and the viscoelastic relaxation time as a function of network connectivity. With decreasing network connectivity, the viscoelastic relaxation time accelerated and became shorter than the bond dissociation time. With increasing polymer concentration, the connectivity at which the viscoelastic relaxation time matched the dissociation time shifted to the high-connectivity region. The dependence of viscoelastic relaxation on connectivity can be adequately explained within the framework of the lifetime of a "backbone." The backbone has numerous breakage points in low-connectivity region nearby the gelation point, resulting in a shorter lifetime than the dissociation time. These findings provide a crucial foundation for the molecular comprehension of transient network materials.

INTRODUCTION

Transient networks formed through reversible crosslinking show fascinating viscoelasticity due to a finite lifetime of crosslinks. Recently, there have been reports that temporary crosslinks play an essential role in polymeric materials' toughness and self-healing ability, making it important to understand the correlation between micro-kinetics and macro-viscoelasticity.[1] However, the molecular understanding of such viscoelasticity has remained incomplete because of the difficulty of evaluating bond lifetimes and heterogeneous structures in conventional experimental systems. Primarily, heterogeneities are comprised of static structures (dangling chains, heterogeneous distribution of network strand length, and branching number), and dynamics (mixture of slow dynamics from network components and fast dynamics from micellar or unimer structures in one system).[2] These heterogeneities are impossible to evaluate quantitatively and prevent molecular understanding the viscoelastic properties of transient networks. In this study, we developed a model system of transient networks consisting of mutually associative star-armed polymers to control the network structures precisely (called Tetra-PEG slime).[3] Using this system, we demonstrate an experimental comparison of the bond lifetime, estimated using surface plasmon resonance (SPR) and the terminal relaxation time for

the Tetra-PEG slime. Here, to control the network connectivity precisely, we mixed the precursors in an imbalanced ratio (Figure 1).[4]
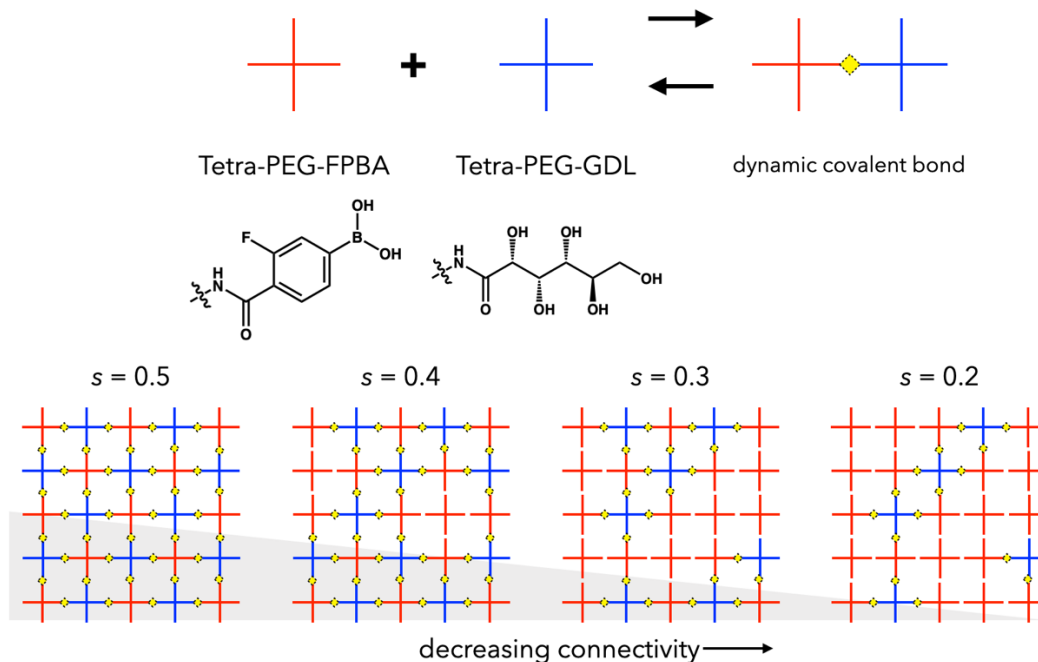

Figure 1: Schematic illustration of tuning the network connectivity, where two precursors are mixed at either a stoichiometric ratio ($s = 0.5$) or an imbalanced ratio ($s \neq 0.5$).

RESULTS AND DISCUSSION

The temperature dependence of the terminal relaxation time (τ) followed the Arrhenius-type equation over a wide range, independent of the detailed network structures. On the other hand, the dissociation time of the end groups estimated from SPR measurements also showed a similar temperature dependence, strongly suggesting that the elementary reaction of the viscoelastic relaxation is the dissociation process.

Figure 2 shows the relationship between τ and p. The termination relaxation time was delayed with increasing p. Furthermore, the degree of delay was more pronounced at lower polymer concentrations. The relaxation time was also delayed by increasing the molecular weight of the precursor. The solid line in the figure indicates the dissociation time obtained from SPR. Interestingly, τ was larger than the dissociation time in the high-p region. On the other hand, as p decreased, τ decreased and became smaller than the dissociation time.

This is well explained by the durability of the "backbone," which essentially supports the stress in the networks. At high connectivity, one dissociation cannot kill the backbone since the other strands support the stress. Meanwhile, at low connectivity near the gelation point, the backbone resembles a linear chain with some breakable points and has a shorter lifetime than the dissociation time. Conventional theoretical models[5] do not predict the concentration dependence, indicating that network formation in the semi-dilute region is far from a random branching process. The reported direct comparison of bond lifetime-viscoelasticity-relaxation times provides essential information for the molecular design of transient network materials.
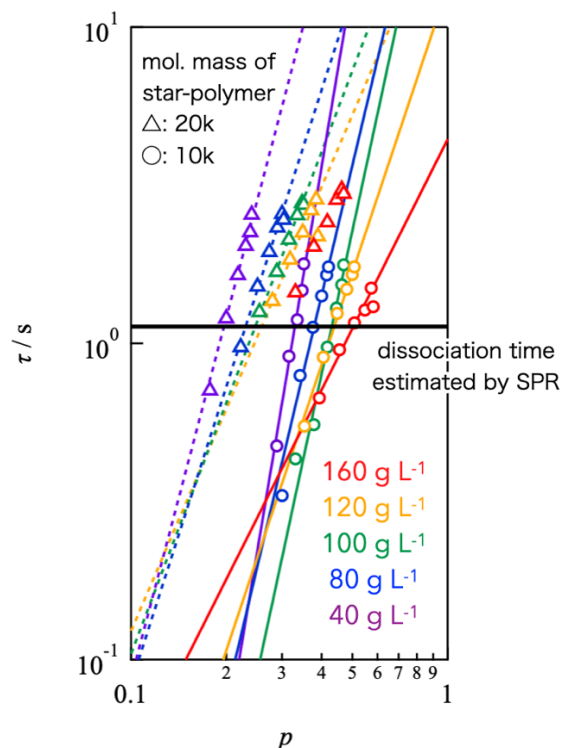
Figure 2: Double logarithmic plot of viscoelastic relaxation time against network connectivity (p). Circles and triangles represent the data of different molar masses of precursors of 10,000 and 20,000 g mol^{-1}, respectively. The solid line represents the bond lifetime estimated by SPR.

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