

Dynamics of thermoresponsive conetwork gels composed of poly(ethylene glycol) and poly(ethyl glycidyl ether-co-methyl glycidyl ether)



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HIGHLIGHTS

- Fabrication and the dynamics of temperature-sensitive conetwork gels.
- Keeping transparent and isovolume state across the LCST of temperature-sensitive component.
- Ensemble averaged correction function analysis as a function of temperature.
- Good correlation in the correlation lengths obtained by DLS with those by SANS.

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ABSTRACT

The dynamics of thermoresponsive conetwork gels consisting of poly(ethylene glycol) (PEG) and poly(ethyl glycidyl ether-co-methyl glycidyl ether) (PEMGE) (PEG-PEMGE gel) was systematically investigated as a function of temperature and the mole fraction of the thermoresponsive modules (PEMGE) r using dynamic light scattering (DLS). The PEG-PEMGE gels were prepared by end-linking of four-armed hydrophilic modules (Tetra-PEG) and four-armed lower critical solution temperature (LCST)-type modules (Tetra-PEMGE) in water by the molar ratio of $(1 - r): r$, where r was varied from 0.1, to, 0.2, 0.3, and 0.4. The dynamics of the conetwork gels was discussed with the ensemble-average of the field correlation function, $g_E^{(1)}(r)$, which was classified to three temperature regions: at low temperatures below LCST of PEMGE ($\approx 23^\circ\text{C}$) (region I), the dynamics was insensitive to r . On the other hand, strong r -dependence was observed for temperatures \geq LCST (regions II and III). By approaching the LCST (region II), the slow dynamics component in $g_E^{(1)}(r)$ became more pronounced due to formation of hydrophobic domains. Additionally, the power-law exponent of the slow mode decreased in region II (near the LCST). In region III, the slow dynamics disappeared as a result of the further growth and immobilization of the hydrophobic domains.

1. Introduction

Block copolymers are a class of multi-component polymers in which different kinds of polymer chains are covalently bonded to form a single long polymer chain [1]. Because of this connectivity, block copolymers undergo microphase separation in the order of a few to a few tens nanometers. The morphology and the size of microphase separation can be tuned by the molecular lengths of the constituent block chains and the interaction parameter(s) of these components. As a result, spherical, cylindrical, lamellar, and even more complicated morphologies are observed and these structures have been intensively investigated for

more than a half century since 1970s [2].

“Conetworks” are rather a new class of multi-component polymers, which are polymer networks with two or more components [3–6]. Because of the nature of the component polymers, new functions can be bestowed to the network, such as amphiphilicity or temperature sensitivity [5]. Hence, the conetworks have unique structures and physical properties. In the literature, conetworks have been extensively investigated for more than a decade [7–11]. More recently, a “non-swelling” conetwork was developed by Kamata et al. [12] where the term “non-swelling” means that a gel does not change its volume from the preparation state even in aqueous condition. The conetwork was

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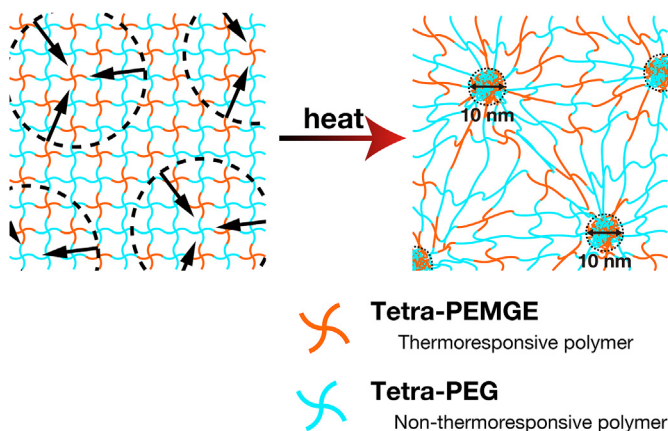


Fig. 1. Schematic illustration of PEG-PEMGE gel consisting of tetra-PEG and thermosensitive polymer (PEMGE). By heating the gel, PEMGE chains shrink to form hydrophobic domains while PEG chains remain swollen, resulting in the formation of a highly-frustrated network structure.

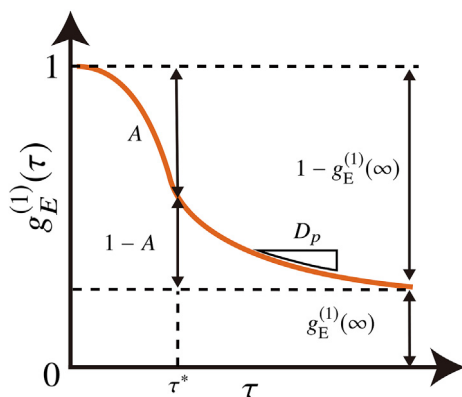


Fig. 2. Schematic illustration τ -dependence of $g_E^{(1)}(\tau)$, and a graphical separation of its dynamic and static components. The dynamic component in this study was further separated into a fast mode reproduced by a simple exponential function, and a slow mode decaying in the manner of a power-law function.

fabricated by end-coupling of tetra-arm poly(ethylene glycol) (Tetra-PEG) and tetra-arm poly(ethyl glycidyl ether-co-methyl glycidyl ether) (Tetra-PEMGE) (hereafter we call PEG-PEMGE gel). PEMGE in water shows a lower critical solution temperature (LCST) at $\sim 23^\circ\text{C}$. The swelling/shrinking behavior of PEG-PEMGE gels was studied by Kamata et al. [12] Below the LCST, PEG-PEMGE gels swell in water like normal PEG hydrogels, but upon raising the temperature above the LCST, PEMGE units shrink and the volume of the gel decreases. With a moderate PEMGE molar ratio (r , $r = 0.4$) to the total amount of polymers, the swollen PEG-PEMGE gel returns back to the volume at the preparation state when the temperature is above the LCST of PEMGE. Nakagawa et al. investigated the microscopic structures of PEG-PEMGE gel in isochore condition by small-angle neutron scattering (SANS) [13,14]. Above the LCST, hydrophilic domains which consist of both PEG and PEMGE units were formed (Fig. 1). These domains are

expected to have unordinary dynamics around the LCST resulting from the shrunken domains and the stretched polymer chains surrounding the domains. In this paper, we carried out a systematic study for the polymer chain dynamics of the PEG-PEMGE gels with different r at different temperatures by using dynamic light scattering (DLS).

2. Theoretical

The field correlation function of the scattering light, $g_T^{(1)}(\tau)$, is defined by

$$g_T^{(1)}(\tau) \equiv \frac{\langle E(t)E^*(t+\tau) \rangle_T}{\langle |E(t)|^2 \rangle_T} \quad (1)$$

Here, $\langle \dots \rangle_T$ denotes time average, $E(t)$ is the scattering electric field, and τ is the lag time [15]. For Brownian particles in a solution, $g_T^{(1)}(\tau)$ is correlated with the diffusion coefficient, D as

$$g_T^{(1)}(\tau) = \exp(-Dq^2\tau) \quad (2)$$

Here, q is the magnitude of the scattering vector. In most DLS measurements, the intensity correlation function of the scattering light, $g_T^{(2)}(\tau)$, is obtained instead of $g_T^{(1)}(\tau)$.

$$g_T^{(2)}(\tau) \equiv \frac{\langle I(t)I(t+\tau) \rangle_T}{\langle I(t) \rangle_T^2} \quad (3)$$

Here, $I(t)$ is the scattering intensity. The dynamics of polymer gels was first discussed as the cooperative diffusion of polymer networks by Tanaka et al. [16] Then, it was recognized that the dynamics of polymer gels is sample position-dependent due to the nonergodic nature of gels [17–22].

Hence, eq (3) cannot be directly applied for gels. For such nonergodic materials, like polymer gels, the ensemble-averaged correlation function should be used to capture the dynamics. The ensemble-average of the field correlation function, $g_E^{(1)}(\tau)$, is defined by

$$g_E^{(1)}(\tau) \equiv \frac{\langle E(t)E^*(t+\tau) \rangle_E}{\langle |E(t)|^2 \rangle_E} = \frac{\langle \langle E(t)E^*(t+\tau) \rangle_T \rangle_E}{\langle \langle |E(t)|^2 \rangle_T \rangle_E} \quad (4)$$

Here, $\langle \dots \rangle_E$ is the ensemble-average. $g_E^{(1)}(\tau)$ can be estimated by taking the ensemble average of the correlation functions of different samples, or at many different sample positions of the same sample by using the following relation between $g_E^{(1)}(\tau)$ and $g_T^{(2)}(\tau)$ [23,24].

$$g_E^{(1)}(\tau) = \frac{\langle I_T \sqrt{g_T^{(2)}(\tau) - \{g_T^{(2)}(0) - 1\}} \rangle_E}{\langle I \rangle_E} \quad (5)$$

We can obtain the fraction of the static and dynamic components of $g_E^{(1)}(\tau)$ from $g_E^{(1)}(0)$ and $g_E^{(1)}(\infty)$ as follows (also see Fig. 2) [17],

$$g_E^{(1)}(\infty) = \frac{\langle I_C \rangle_E}{\langle I \rangle_E} \quad (\text{Static component}) \quad (6a)$$

$$1 - g_E^{(1)}(\infty) = \frac{\langle I_F \rangle_E}{\langle I \rangle_E} \quad (\text{Dynamic component}) \quad (6b)$$

To analyze dynamic component of the correlation function, we used the following equations [25].

$$g_E^{(1)}(\tau) = [1 - g_E^{(1)}(\infty)]g_{E,F}^{(1)}(\tau) + g_E^{(1)}(\infty) \quad (7a)$$

$$g_{E,F}^{(1)}(\tau) = A \exp(-Dq^2\tau) + \frac{1 - A}{(1 + \tau/\tau^*)^{D_p}} \quad (7b)$$

Here, A is the fraction of the exponential term (the fast mode) that represents the cooperative diffusion of the semidilute polymer chains, τ^* is the lag time at which a power-law type relaxation starts, and D_p is the fractal dimension of scattered light [25]. The correlation length, i.e.

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