**Invited Review**

**Structure and Dynamics of Critical Polymer Clusters Formed with Tetra-Armed Star-Polymers**

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Critical polymer clusters are massive randomly branched polymers formed near the gelation threshold. Because of their universal physical properties, such as the size distribution, mass fractal dimension, and viscoelastic properties, these clusters have drawn the great attention of many physicists. This review briefly introduces a few recent remarkable experimental results, which shed light on remaining questions of the critical clusters. The static structure and dynamics of these critical clusters were investigated using small angle neutron scattering (SANS), static light scattering (SLS), and dynamic light scattering (DLS). The reviewed studies primarily focused on the data analysis for the critical clusters in the intermediate concentrations between dilute and semidilute limits. An intermediate model developed by Bastide and Candau well explained the observed static scattering profiles, indicating a coexisting state of the dilute and semidilute solutions. The dilute and semidilute features were also observed in dynamic studies as a superimposed translational motion of small dilute clusters and cooperatively diffusion of large semidilute clusters. These fundamental understanding may contribute to the applications of the critical clusters and further studies for the percolation process.

**Key Words:** Percolation / Gelation / Fractal / Slow mode / Polydispersity

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1. **INTRODUCTION**

Percolation has been an essential topic from both scientific and industrial perspectives. Despite various chemical differences between percolating systems, universal structural and physical properties were found in polymer solutions near the percolation threshold. These polymer solutions consist of highly randomly branched polymers, called critical clusters. The critical clusters are very polydisperse and have self-similar structures; the clusters range from a single monomer unit to a massive polymer cluster as large as the reaction bath. Numerous important universal scaling relations have been theoretically proposed and experimentally observed. However, most studies focused on the clusters either in the reaction bath (semidilute limit) or in highly diluted solutions (dilute limit). There is little information for the critical clusters in the intermediate concentrations, which are the concentrations range essential in the recent application of the critical clusters.

2. **PREPARATION OF CRITICAL CLUSTERS**

Recently, Sakai et al. developed a new type of critical clusters synthesized by mixing two types of mutually reactive four-armed polyethylene glycol (PEG) (Fig. 1). Because of their stable crosslinking chemistries, these critical clusters can be easily prepared with better reproducibility than conventional ones using quenching techniques. Li et al. performed a series of fundamental studies using these critical clusters. They synthesized the critical clusters at different as-prepared polymer concentrations near the corresponding gelation thresholds (Fig. 2). Then, the semidilute critical clusters were diluted to various concentrations for subsequent measurements.

3. **STATIC STRUCTURES**

The static structures of the critical clusters were typically studied at highly diluted conditions, where the interactions between the critical clusters are negligible. At this dilute limit, the scattering profiles exactly overlap after the normalization by the polymer concentration (e.g., lowest concentration in Fig. 3). The profiles show a constant value at low q-limit and gradually decays as q increasing. The weight-averaged
molecular weight and z-averaged gyration radius can be obtained from the low-\(q\) profiles\(^7\). As \(q\) increasing, the scattering profiles decay following an apparent power law relation as \(I \sim q^{-(3-f)D_s}\), where \(f\) is the Fischer exponent (relating to the size distribution) and \(D_s\) is the mass fractal dimension of dilute critical clusters. According to the tremendous studies\(^7\), \(f\) and \(D_s\) were known to be 2.25 and 2.0, yielding a scattering profile \(I \sim q^{-1.5}\). On the other hand, at the semidilute limit, the unique characteristics of the critical clusters disappear from the scattering profiles and the Ornstein-Zernike type profiles \(I \sim 1/(1 + \xi^2 q^2)\) should be observed (e.g., highest concentration in Fig. 3), where \(\xi\) is the static correlation length. However, the scattering profiles of critical clusters were typically not presented for the semidilute limit, probably because the scattering profiles do not contain the characteristics of the critical clusters.

Fig. 1 A schematic illustration of the critical polymer clusters formed by the mutual reaction four-armed PEG polymers. (a) A branch of the critical clusters. (b) As-prepared critical clusters in the reaction bath. (c) Highly diluted critical clusters. Reprinted (adapted) with permission from\(^{14}\). Copyright 2019 American Chemical Society.

Fig. 2 A schematic illustration of sol-gel phase diagram of four-armed PEG with \(M_n = 10\) k. Reprinted (adapted) with permission from\(^{15}\). Copyright 2017 American Chemical Society.

Fig. 3 Static scattering profiles of a type of critical clusters diluted at various concentrations. The critical clusters were synthesized at a polymer volume fraction \(\phi = 0.050\). The solid curves denote the scattering intensities measured with SLS and the dotted curves show the SAXS intensities. All SLS curves were vertically scaled by a factor of 0.025 to match the SAXS profiles at the low-\(q\) limit. The scattering intensities were normalized by the corresponding polymer volume fractions. Reprinted (adapted) with permission from\(^{14,15}\). Copyrights 2017 and 2019 American Chemical Society.
Figure 3 shows the static scattering profiles of critical clusters synthesized at a polymer volume fraction $\phi = 0.050$. All the concentration normalized profiles at different dilution levels overlapped at a large scattering vector $q$ region ($q > 0.1$ Å$^{-1}$, approximately 1 nm in real space), reflecting that the local polymer structures were unchanged after the dilution. This result suggests that the mass fractal dimension of the critical clusters may change as the dilution, which was widely observed in previous studies$^7$, but the structure of the basic units of the clusters remained unchanged. The basic unit suggested from the scattering profiles is a single four-armed prepolymer. During the model fit analysis, most scattering profiles could not be reproduced by the Ornstein-Zernike function$^{17, 18}$, a popular model to account for the scattering profiles of semidilute polymer solutions. The discrepancy from the OZ function suggests that these solutions were not in simple semidilute conditions. However, these solutions were also not in the simple dilute conditions because the concentration normalized scattering profiles should overlap at any concentrations in the dilution limit$^{19}$. Therefore, Li et al. tested an intermediate model for the coexisting condition of dilute and semidilute polymers, developed by Bastide and Candau$^7$. The detail of the fit equations was introduced elsewhere$^{14}$. All the scattering profiles could be perfectly reproduced by the dilute-semidilute coexisting model. The excellent agreement between the experimental results and the model fits suggests the coexisting state of the dilute and semidilute clusters in the highly polydisperse solutions; the large clusters are in the semidilute condition, but the small clusters are in the dilute conditions.

4. DYNAMIC STRUCTURES

The dynamics of the critical clusters were commonly evaluated using DLS, which is a powerful tool to study polymer dynamics. The field correlation function $g^{(1)}(r)$ typically shows a power-law type decay at a high polymer concentration, then changed to a two-relaxation-modes decay (fast and slow mode) at intermediate concentrations, and finally became a single stretched exponential decay at dilute limit$^{20, 21}$. The power law type decay was suggested because of the size-dependent dynamics of high entangled critical clusters$^{21}$. The fast and slow mode in the intermediate concentrations were not clear yet. The stretched exponential decay, whose relaxation time typically scaled with $q^3$, was attributed to an internal motion (Zimm mode) of the critical clusters$^{10}$.

The dynamics of the tetra-PEG critical clusters were evaluated using DLS at multiple scattering angles, i.e., multiple scattering vector $q$. Two relaxation modes were observed on each field correlation function $g^{(1)}(r)$ (Fig. 4). $g^{(1)}(r)$ was displayed to $r_0 q^2$ and $r_0 q^3$ to visualize the $q$-dependence of each relaxation mode. The fast modes depend on $q^2$ and are therefore diffusive. However, as diluting the polymer solutions, the relaxation time of the fast modes became slower, contrary to that of typical translational motion. The possible motion that satisfies the above experimental results is the concentration fluctuations, also known as cooperative diffusion, widely observed in semidilute polymer solutions$^{22-25}$. The dynamic correlation length ($\xi_{DLS}$) is a screening length of the hydrodynamic interaction can be estimated from the relaxation time of the cooperative diffusion. On the other hand, the static correlation length ($\xi_{SANS}$), which is a screening length of the excluded volume effect, can be estimated from the shoulder position on the static scattering profiles. However, as the intermediate concentrations were not well experimentally investigated, the scaling relationship between the correlation lengths of the critical clusters and the

![Fig. 4](image-url)
polymer concentration was not determined until recently.

The studies of Li et al revealed that both dynamic correlation lengths and the static correlation length fell on a single master line, indicating a scaling relation $\xi \sim \phi^{-1}$ (Fig. 5). This scaling relation is consistent with the theoretical prediction for the concentration fluctuations of semidilute monodisperse randomly branched polymers by Daoud and Leibler26). Although there is no theoretical prediction for the semidilute highly polydisperse critical cluster solutions, the monodisperse theory can be applied to the critical clusters because semidilute solutions do not contain the individual characteristics of the critical clusters. The agreement between the theory and the experimentally observed scaling relation strongly supports that the fast mode in DLS originates from the concentration fluctuations. As the intermediate concentrations were not systematically investigated so far, the origin of the fast mode remained unsolved for decades.

Next, we move on to the slow modes. Most of the critical cluster solutions showed $q^3$-dependent slow relaxation modes in both as-prepared and extremely diluted concentrations. Because their characteristic relaxation time always depends on $q^3$, researchers have often recognized the slow modes as the Zimm mode (an internal motion of polymers) of the large polymer clusters10, 21) because the Zimm mode scales with $q^3$. However, Li et al. denied the conventional discussion14). They suggested that the $q^3$ should be the superimposed translational motion of the highly polydisperse critical clusters because the hydrodynamic interaction, a crucial interaction for Zimm mode, should have been screened out within the dynamic correlation length. Therefore, the Zimm mode should not relax slower than the concentration fluctuation does. The theoretical explanation and an explicit calculation for the $q^3$-dependent translational motion were given by Martin a long time ago27) but were for the first time experimentally verified.

5. CONCLUSIONS

Recent studies for a series of critical clusters synthesized using four-armed star polymers as the basic units were briefly reviewed. The universal scaling relationships observed in the other chemical systems were confirmed in the star polymer system. A detailed analysis for the intermediate concentrations solved a few remaining mysteries: (1) There are wide concentration ranges where small dilute clusters and large semidilute clusters coexist, making the solutions have both dilute and semidilute features. (2) The large clusters were in the semidilute state and diffused cooperatively with no structural information (fast mode). In contrast, the dilute clusters diffused translationally and were observed as the superimposed dynamics of individual clusters (slow mode). The dilute and semidilute coexisting conditions may be found in other polymer solutions with high polydispersity and in biosystems such as cells and extrasellar matrices. The author envisions that these fundamental understandings may contribute to the applications of the critical clusters and understanding of highly polydisperse systems.

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