Note

A HYBRID POLYMER GEL AND ITS STATIC NONERGODICITY[*]

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Abstract We used a thermally reversible hybrid gel made of billions of physically jam-packed swollen thermally sensitive poly(N-isopropyl-acrylamide) chemical microgels. Laser light scattering study on a series of such hybrid gels formed at different gelling rates and temperatures revealed that the position-dependence of the scattering speckle pattern (static nonergodicity) came from large voids formed during the sol-gel transition. With a proper preparation, such a nonergodicity could be completely removed, indicating that the static nonergodicity generally observed in a gel is not intrinsic, but comes from the clustering "island" structure formed during the gelation process.

Keywords Polymer gel, Nonergodicity, Dynamic light scattering

INTRODUCTION

A gel is generally considered to be a three-dimensional polymer network swollen by a large amount of solvent. Polymer chains in chemical gels are crosslinked by covalent bonds. A chemical gel is normally formed by a copolymerization of monomers with a crosslinking agent[1–4]. In contrast, the formation of a physical gel usually starts with a polymer solution. In physical gels, polymer chains are interconnected via physical interactions (*e.g.*, hydrogen bonding, electrostatic interaction, and coordination) and the gelation is often induced by an alternation of physical conditions, such as temperature and ionic strength[5]. It has been well known that in the formation of chemical gels, short linear chains are first formed, then large branched clusters, and finally a network in which the interconnected clusters look like "islands" in a three-dimensional solvent "sea"[6–10]. Such an inhomogeneous clustering structure should be absent when long polymer chains uniformly distributed in a solution are randomly associated to form a physical gel.

Recently, it has been shown that there also exists a scattering speckle pattern when an aqueous mixture of poly(vinyl alcohol) and Congo red is gelled at 43 °C or below[5]. The question is whether this static nonergodicity is intrinsic for all thermally reversible physical gels or only for this particular one. In order to have a better understanding of the gelation of physical gels, we have developed a novel hydrogel made of billions of jam-packed thermally sensitive poly(N-isopropylacrylamide) (PNIPAM) microgels when they swell at ~25 °C or lower temperatures. Inside each microgel, the polymer chains were chemically crosslinked, but the interaction between the microgels was purely physical. This is why it is named "hybrid". It resembles a glass in which spherical swollen soft microgels replaces small atoms or molecules. It is actually formed via a volume concentration-induced gelation.

There are several advantages of using this hybrid gel as a model system to study the sol-gel transition and

structures of physical gels, such as the structural inhomogeneity from the chemical crosslinking. It is limited within a volume of dimensions much smaller than the wavelength of our laser light, so that individual swollen microgels are transparent; the microgels as building blocks are narrowly distributed and well characterized; and the gelation is completely thermally reversible without any hysteresis. Using a combination of static and dynamic laser light scattering, we studied a series of such hybrid gels formed at different gelling rates and temperatures. It has been found that the observed scattering speckle pattern in thermally reversible physical gels was not intrinsic, but strongly depends on whether large voids were formed during the gelation. The details are reported in this communication as follows.

EXPERIMENTAL

Narrowly distributed spherical poly(N-isopropylacrylamide) (PNIPAM) microgels were prepared by emulsion polymerization of N-isopropylacrylamide in the presence of N,N'-methylenebis-(acrylamide) as crosslinker and anionic surfactant (sodium dodecyl sulfate, SDS) as dispersant. The unreacted monomers and SDS were removed by three successive centrifugation-decantation-redispersion cycles in deionized water. The zeta potential of the resultant dispersion was close to zero. The synthesis has been detailed before[11, 12]. A commercial LLS spectrometer (ALV/SP-125) equipped with an ALV-5000 multi-τ digital time correlator and a solid laser (DPSS, output power $\cong$ 400 mW at λ = 532 nm) was used in this study. The details of LLS instrumentation and theory can be found elsewhere[13–15].

RESULTS AND DISCUSION

Figure 1 shows that, in the gel state, the time average scattered intensity $<I>_T$ randomly varies with the sample position. In contrast, the scattering speckle pattern disappears at 30°C because the bulk hybrid gel melts into a microgel dispersion (*i.e.*, the sol state) due to the shrinking of individual microgels. It is worth noting that in the temperature range 15–33°C, the microgels in a dilute dispersion can reversibly swell and shrink with a size change between ~45 nm and ~106 nm, corresponding to a 13-time variation in volume. This is why the swelling could induce the sol-gel transition. Note that $<I>_E$ increases with the temperature, very different from previous observations in which $<I>_E$ decreased when a physical gel melted into individual less scattered polymer chains[5],
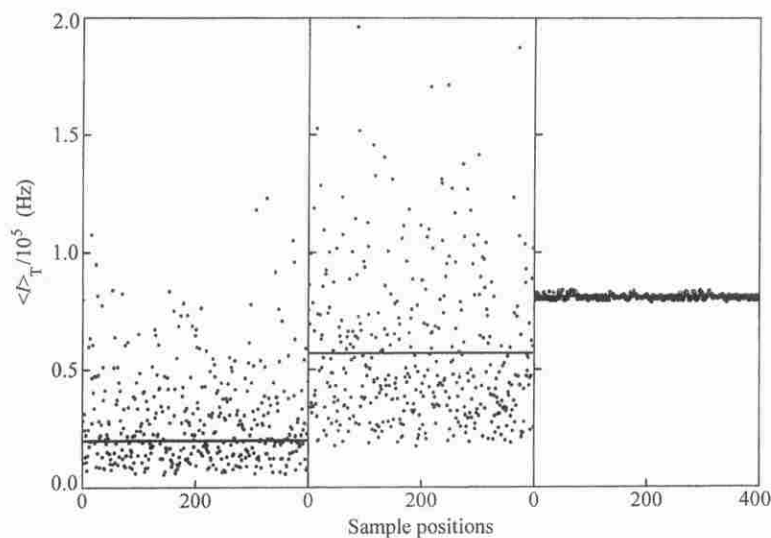
Fig. 1 Sample position dependence of time-average scattered intensity $<I>_T$ of hybrid PNIPAM gel after the microgel dispersion was quickly cooled down from 40°C to different setting temperatures, where each solid line represents an ensemble-average intensity $<I>_E$ defined as $(\Sigma_i <I>_{T, i})/N$ with N being the total number of the sample positions measured.

but similar to a concentration induced sol-gel transition. This difference can be attributed to the fact that in this study, individual collapsed microgels are stronger scattering objects than the swollen gel network, especially when the temperature approaches its LCST. Besides $<I>_T$, for each chosen sample position, we also measure a normalized intensity-intensity time correlation function $S(q, \tau)$ defined as[16, 17]:

$$S(q,\tau) = \frac{<I(q,0)I(q,\tau)>}{<I(q,0)>^2} - 1 \tag{1}$$

where q is the scattering vector and τ is the delay time. We found that in the gel state, the plot of "$\lg[S(q, \tau)]$ versus $\lg(\tau)$" had a typical power-law behavior with a critical exponent close to ~0.8, higher than ~0.4 reported in [5], indicating that the hybrid gel is a better resemblance of glasses[18]. As shown in [16, 17, 19, 20] for a nonergodic gel, $<I>_T$ is a summation of the static component $<I_s>_T$ and the dynamic component $<I_d>_T$, so that

$$S(q,\tau) = \left(\frac{<I_d>_T}{<I>_T}\right)^2 \exp(-2Dq^2\tau) + 2\left(\frac{<I_d>_T}{<I>_T}\right)\left[1 - \left(\frac{<I_d>_T}{<I>_T}\right)\right]\exp(-Dq^2\tau) \tag{2}$$

where D is the collective diffusion coefficient. Therefore, for a nonergodic system at a given q, one has four different scattered intensities, $<I>_T$, $<I_s>_T$, $<I_d>_T$ and $<I>_E$, but the former three are not independent. $<I>_T$ and $<I_s>_T$ vary with the sample position, but not $<I>_E$ and $<I_d>_T$ by their definitions. Only in an ergodic system, $<I_s>_T$ = 0, so that we have $<I>_T = <I_d>_T = <I>_E$. Experimentally, the initial slope of "$\ln S(q, \tau)$ versus τ" leads to an apparent diffusion coefficient D_A in the range of $D/2 < D_A < D$. It has been shown that D and $<I_d>_T$ are related to D_A and $<I>_T$ as[2, 7]

$$\frac{<I>_T}{D_A} = \frac{2<I>_T}{D} - \frac{<I_d>_T}{D} \tag{3}$$

For each chosen sample position at a given q, we can measure one $<I>_T$ from static LLS and calculate one D_A from $S(q, \tau)$ measured in dynamic LLS. Figure 2 shows that D_A decreases as $<I>_T$ increases and approaches a constant when $<I>_T$ is sufficiently high. The inset is a corresponding plot on the basis of Eq. (3). A least-squares fitting of the data leads to D and $<I_d>_T$, respectively, from its slope and intercept.
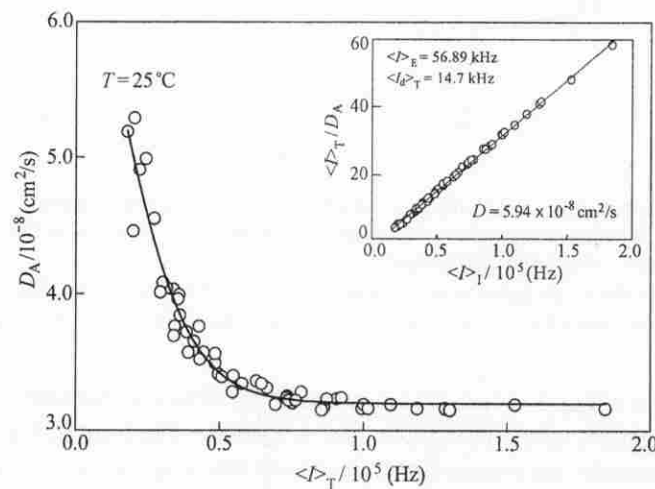
Fig. 2 Time-average scattered intensity $<I>_T$ dependence of apparent diffusion coefficient D_A of hybrid PNIPAM gel at 25 °C, where D_A was obtained from the initial slope of the intensity-intensity time correlation function
The inset shows a decomposition plot on the basis of Eq. (3).

Figure 3 shows that when $T < 25\,°C$, $<I>_E$ increases with the setting temperature, but $<I_d>_T$ does not; while in the higher temperature range, $<I_d>_T$ increases sharply and catches $<I>_E$ at ~30 °C, indicating a progressive melting of the hybrid gel into individual collapsed microgels, *i.e.*, from a nonergodic bulk gel to a completely ergodic microgel dispersion. The extrapolations of $<I_d>_T$ in the two temperature regions lead to a temperature close to the gelation temperature (T_{gel}) observed in a flow test. Note that a high value of $<I>_E$ was often used in the past as an indication of the inhomogeneity. However, our result tells a different story because we know that the microgel dispersion at ~30 °C is homogeneous and ergodic even $<I>_E$ is higher.
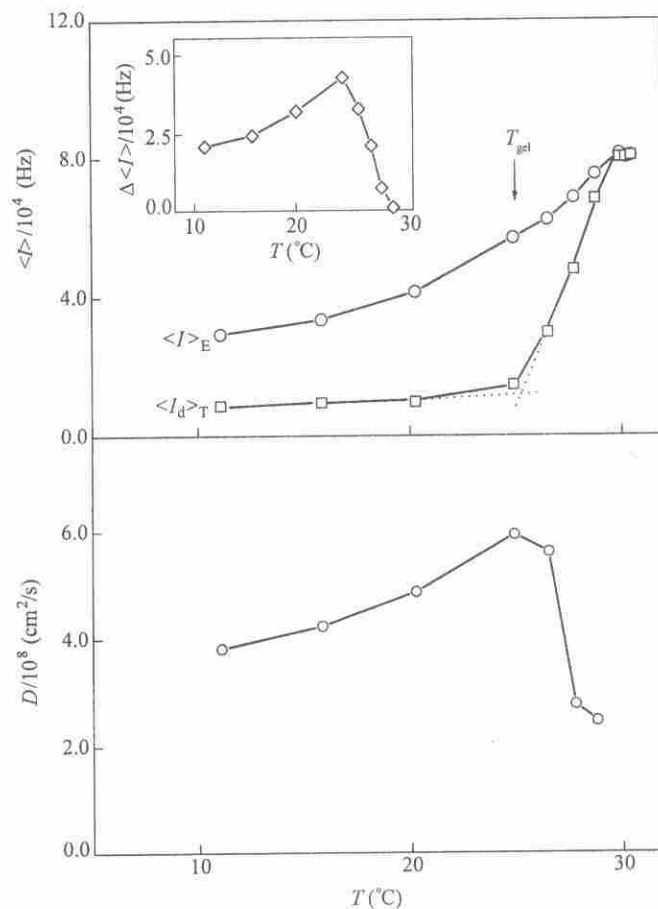

Fig. 3 Temperature dependence of ensemble-average scattered intensity $<I>_E$, time average dynamic component of scattered intensity $<I_d>_T$ and collective diffusion coefficient D of hybrid PNIPAM gel
The arrow shows the gelation temperature T_{gel} observed by a flow test. The inset is the temperature dependence of the intensity difference (ΔI) between $<I>_E$ and $<I_d>_T$.

A careful examination of Fig. 3 reveals that it should be the difference between $<I>_E$ and $<I_d>_T$ that reflects the extent of the inhomogeneity of a given system, not $<I>_E$ alone. The inset in Fig. 3 shows that even before reaching the gelation threshold, the system already becomes inhomogeneous, *i.e.*, $\Delta I > 0$. As the temperature decreases, the intensity difference ΔI reaches a maximum at T_{gel} and then decreases in the lower temperature range. This is because large voids are formed at the gelation threshold and further swelling of individual microgels squeezes the voids between the jam-packed microgels, leading to a more uniform hybrid gel. The temperature dependence of D shows a similar tendency. The jump-wise decrease of D near T_{gel} was also observed for other physical gels[5], but not for chemical gels[2], probably because the formation of a chemical gel is

irreversible and the size of the clusters always increases during the gelation. In the present case, as the temperature increases, individual microgels shrink so that non-jammed microgels diffuse fast. After the melting temperature, the gel network breaks into slowly diffused large clusters so that D decreases. It is worth noting that the value of D is close to that of individual microgels in a dilute dispersion. Since individual swollen microgels are transparent to the light used, the inhomogeneities observed in Fig. 1 must come from an imperfect packing of the microgels when they were suddenly jammed together. Therefore, if we slow down the cooling process, the swollen microgels would have time to arrange themselves into a more uniform structure. Ideally, if individual collapsed microgels could be closely stacked together at a high temperature before cooling them down, we might be able to obtain a uniform hybrid gel. Figure 4 shows a schematic of how the gel structure could be influenced by the gelation condition. The different inhomogeneities shown in Fig. 4 have been confirmed in terms of the scattering speckle pattern and the difference between $<I>_E$ and $<I_d>_T$, as shown in Fig. 5. It should be stated that the hybrid gel prepared under centrifugation showed a color if it was illuminated with white light even though it could not completely disperse the white light as a prism or a crystal. This imperfect dispersion might be attributed to the polydispersity in the microgel size and a small refractive index difference between water
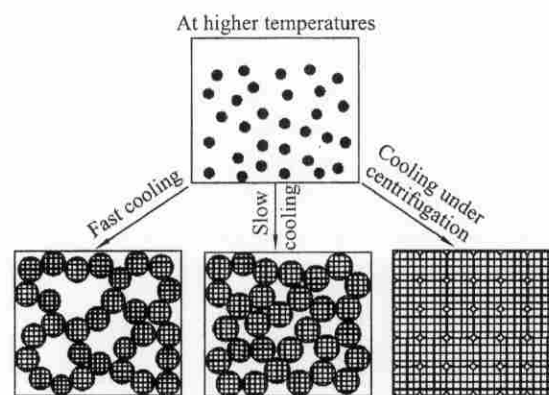
Fig. 4 Schematic of the gelation condition dependence of the structure of the hybrid gel made of spherical thermally sensitive swollen PNIPAM microgels
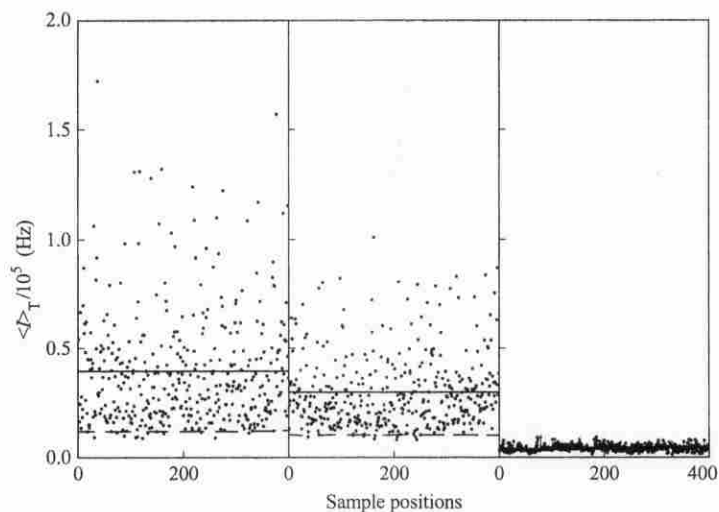
Fig. 5 Sample position dependence of time-average scattered intensity $<I>_T$ of hybrid PNIPAM gel after the microgel dispersion was cooled down from 40 ℃ to 15 ℃ under different conditions, where the solid and dashed lines represent $<I>_E$ and $<I_d>_T$, respectively.

and smollen microgel networks, but it clearly indicated a certain degree of ordering of the microgels inside the hybrid bulk gel.

Note that Figs. 1(c) and 5(c) are similar. Both of them display an ergodic behavior, *i.e.*, $<I>_E = <I_d>_T$. However, it is worth noting that they were obtained from two completely different states; namely, Figure 1c shows a measurement of a uniform and ergodic microgel dispersion in which individual collapsed microgels are under random Brownian motions in water, while Fig. 5(c) is from a uniform hybrid gel. To our knowledge, this is the first observation of such a uniform and ergodic hybrid gel.

Figure 5 clearly demonstrates that the static inhomogeneity of thermally reversible physical gels is not intrinsic, but very strongly dependent on the gelation process. It is also interesting to note that D is nearly a constant, which indicates that the voids inside the gel network are much larger than the microgels and the gel network does not affect the relaxation of individual non-jammed microgels. As expected, for a given temperature, individual non-jammed microgels with the same size relax at the same rate. How the gel network is formed can only affect the static part, *i.e.*, $<I_S>_T$, but not D. This point has been overlooked in the past.

CONCLUSION

It is not difficult to imagine that before the gelation threshold, swollen clusters look like "islands" floating in a solvent "sea", but after the gelation, the interconnected clusters become a "continent" (background) and the "sea" changes into many "lakes" (voids)[8, 9, 21, 22]. It is these large and non-uniform voids that lead to the scattering speckle pattern, static nonergodicity. Our results suggest that this kind of static nonergodicity in both physical and chemical gels might have a similar origin. The only difference is that in chemical gels, the clusters are known to be branched polymer chains and microgels, but in physical gels, they could be formed via a non-uniform interchain association of polymer chains prior to the gelation threshold.

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