Phase Separation and Shrinking Patterns of Polymer Gels

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We have investigated the shrinking phase transition of the slightly ionized cylindrical poly(N-isopropylacrylamide) gels. The macroscopic conformation change and the phase transition velocity were obtained on the continuous heating processes with constant temperature drift rates. The phase transition can be characterized by the phase coexistence in the smaller temperature drift rates, while the phase transition starts with grain patterns, which becomes bubble patterns with time in the larger temperature drift rates. The bubbles gradually shrink to become smooth surface. Shrinking pattern has a strong correlation with the phase transition velocity.

Key words: poly(N-isopropylacrylamide) gel, phase separation, shrinking pattern, nucleation, spinodal decomposition

1. INTRODUCTION

Polymer gels can take two distinct phases in liquid, swollen and collapsed, which is characterized by the network density.[1] A lot of studies on slightly cross-linked polymer gels have shown a very sharp volume change when an environment condition is varied, and it has been considered as a first-order phase transition.[2,3] If the environment condition is properly selected, a phase coexistence of an ionized gel could be expected.[4] Although the static swelling behavior of ionized polymer gels have been extensively studied, the phase transition velocity and its fundamentals have not been fully understood yet. This paper deals with the macroscopic conformation change of slightly ionized poly(N-isopropylacrylamide) (NIPA) gels during the shrinking phase transition; the temperature was continuously increased with a temperature drift rate, v_T. We present the kinetic properties of the gels prepared in a cylindrical shape with submillimeter diameter on the continuous heating process.[5,6] The origin of the characteristic conformation, which depends on v_T, is qualitatively discussed in terms of the traditional phase-separation model.

2. EXPERIMENTAL PROCEDURE

The slighty ionized NIPA gels were prepared by the same method as described in Ref. 6. The main constituent consists of NIPA monomer (670 mM) and acrylic acid (ionizable monomer, 20 mM). The gel is chemically cross-linked by a small amount of N,N'-methylenebis(acrylamide) (8.6 mM). The gelation was carried out at the ice temperature more than 12 hours. After the gelation, cylindrical gels were removed from microcapillaries and subsequently washed in the distilled and de-ionized pure water to remove residual chemicals and unreacted monomers from the polymer networks. In order to destroy the structure formed at gelation through the hydrogen bonding by the carboxyl groups, the gels were dipped into the aqueous sodium hydroxide (pH = 14), and were successively washed in a large amount of pure water. The experimental setup was similar to that used in Ref. 5. The temperature was continuously increased with a constant heating rate, v_T using a computer controlled water-bath with an accuracy of ±0.01°C. The gel was imaged by an optical microscope apparatus with a calibrated CCD camera and a video processor.

(a) *from an edge*

Collapsed State

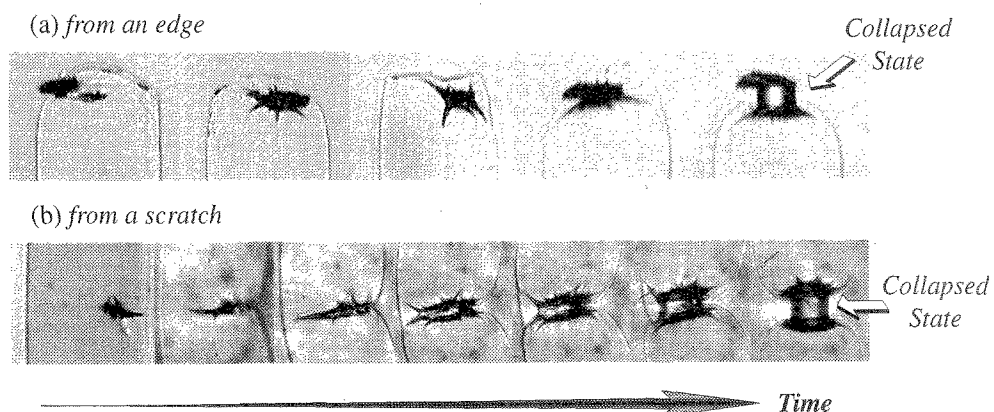(b) *from a scratch*

Collapsed State

Time

Fig. 1 Characteristic pictures on the gradual heating, where the shrinking phase transition starts from the corner of an edge (a) or from the position of a scratch (b).
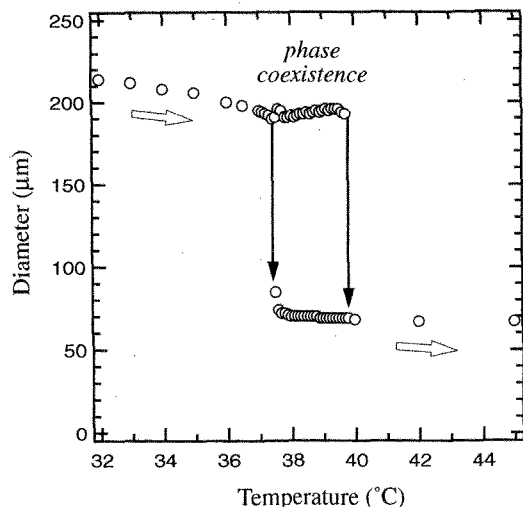
Fig. 2 Diameter change of the slightly ionized NIPA gel as a function of temperature on a quasi-static heating process. Between 37.5 and 39.7°C, the gel can take two-phase state, which is not equilibrium.

3. RESULTS AND DISCUSSION

3.1 Starting Portion of the Shrinking Phase Transition

It has been experimentally pointed out that the phase transition of polymer gels begins at the surfaces.[7,8] In the case of the present cylindrical gels, the phase transition begins at the corners of the edges (as is shown in Fig. 1(a)), since the free energy gain by the transition is largest at the corners. Note that the transition can start at the different positions from the edges, including the positions of a large scratch on the surface (Fig. 1(b)) and the cave inside the gel.

3.2 Swelling Curve

A typical example of the swelling curve is shown in Fig. 2 for a selected sample (with less surface imperfections). In the vicinity of the phase transition point, the temperature change was carried out at one hour or longer interval (several hours after the transition starts). In this sample, the first collapsed phase emerges at 37.5°C at the edges (such as Fig. 1(a)), which develops with increasing the temperature, and the gel becomes the completely collapsed state at 39.7°C. Between both temperatures, the gel takes the phase coexistence, although it is not equilibrium; due to much longer relaxation time than the characteristic one in this tiny gel, it was difficult to obtain the equilibrium state within the laboratory time (several weeks). Note that the two-phase region depends on the sample, even if the gels were prepared at the same time. We believe that this is due to the initial treatment of dipping the gels into the aqueous sodium hydroxide and successively washing it by pure water. It is interesting to observe that the swollen diameter in the phase coexistence is evidently larger than the diameter just below the transition temperature; the swollen diameter increases slightly but discontinuously when the initial collapsed portion appears. We believe that not only the network collective diffusion but also the ion diffusion in the solvent should be both taken into accounts to explain this observation. We are currently investigating the origin of these unique properties, which will be published elsewhere.
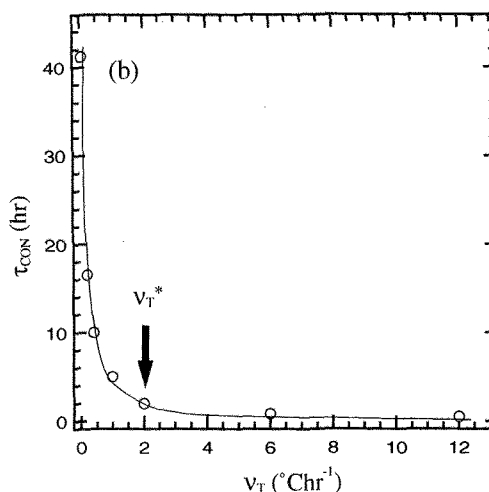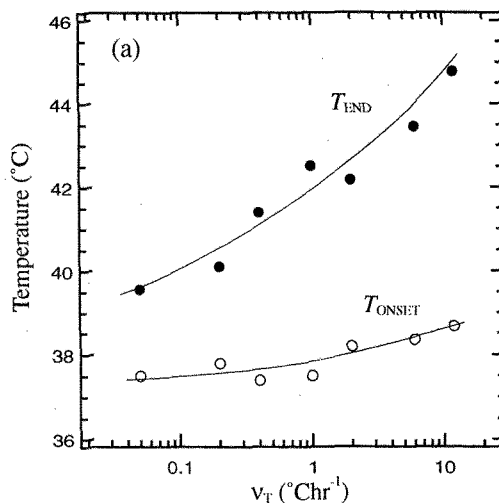

Fig. 3 (a) Characteristic temperatures, T_{ONSET} and T_{END}, and (b) time, τ_{CON} from onset to end of the swollen to collapsed phase transition as functions of v_T on the continuous heating processes. Lines added are to guide an eye. v_T^* indicates the threshold below which the phase coexistence (or linked-dumplings) can appear.

3.3 Characteristic Temperature of the Shrinking Phase Transition

Figure 3(a) shows the onset and the end temperatures of the phase transition on the continuous heating process with the constant v_T in the range between 0.05 and 12°Chr^{-1}. The onset temperature, T_{ONSET} is defined as the temperature where the collapsed portion appears at the corner of the edge (smaller v_T) or the shrinking pattern appears on the gel surface (larger v_T, described later); the end temperature, T_{END} is defined as the temperature where the gel length change stops. One can see that T_{ONSET} is just slightly increases with increasing v_T, while T_{END} largely increases. Figure 3(b) shows the time, τ_{CON} to complete the swollen to collapsed phase transition in the continuous heating process; $\tau_{CON} = (T_{END}-T_{ONSET}) / v_T$; τ_{CON} rapidly decreases with increasing v_T in the small v_T range, and becomes small in the larger v_T range than v_T^*.

3.4 Origin of the Characteristic Conformations

Figure 4 shows the characteristic conformations obtained at 38.5°C (same temperature) on the continuous

heating process with different v_Ts. The different patterns, phase coexistence (or linked-dumplings), grain pattern, and bubble pattern, can be attributed to the different phase-separation processes. The conformation change, categorized in four types, is shown in Fig. 5. When $v_T =$ $0.05°Chr^{-1}$, the collapsed portion, started at the corner of the edge, grows with time, then the phase coexistence appears. With increasing v_T, the number of locally collapsed portions increases, forming the linked-dumplings. In these cases, a small amount of nuclei can develop to form the phase coexistence. On the other hand, when v_T exceeds a threshold, v_T^* (around $2°Chr^{-1}$, marked in Fig. 3(b)), the phase transition exhibits two stages. At the first stage, the grain pattern appears on the entire surface, forming the macroscopic phase separation. This is because a lot of nuclei can appear and form the domain boundaries, which develop on the surface. At the second stage, if $v_T = 6°Chr^{-1}$, some collapsed patterns develop at the expense of the growth of the other patterns, hereafter the linked-dumplings appear. When $v_T = 12°Chr^{-1}$, the bubble pattern appears, shrinks with time, and finally disappears (not showing the linked-dumplings). We found that the shrinking pattern has a correlation with the phase transition velocity: when v_T exceeds v_T^*, τ_{CON} becomes very small (less than 1 hour, see Fig. 3(b)), which suggests that the grain pattern accelerates the shrinking phase transition.

In the present open system, the shrinking phase transition is considered as the phase separation and its relaxation to the collapsed state during the entire volume shrinkage;[4] the phase separation is accompanied by the total increase of the mean network density. The kinetic properties can be determined not only by the phase-separated networks but also by the collective polymer diffusion in water solvent.[4] When v_T is small enough, the network phase-separation progresses by the nucleation mechanism, resulting in the phase coexistence or linked-dumplings: the number of locally collapsed portions (linkages between dumplings) increases one by one with increasing v_T. The phase separation completes before the temperature exceeds the spinodal line. On the other hand, when v_T becomes large enough, the gel is expected to come into the unstable region before the completion of phase separation through the nucleation mechanism. According to our previous study for the isothermal process after the steplike temperature jump,[6] the phase transition comes into the unstable region when the final temperature exceeds the spinodal line (about $12°C$ higher than T_{ONSET}), and the opaque phase was observed. Although the maximum T_{END} in the present experiment is expected to be below the spinodal temperature, this evidence does not confirm that all of the phase separations complete in the metastable region (does not deny that the gel could come into the unstable region). This is because the total volume decreases (the mean network density increases), which could force the gel into the unstable region even below the spinodal temperature. From the present experiment, the critical v_T could not be determined, where the gel enters the unstable region before the completion of the nucleation-assisted phase-separation. We believe that all the shrinking phase transitions in the present experiments are dominant by the nucleation mechanism even at the maximum v_T, since τ_{CON} is monotonically decreases and the opaque phase could not be observed even in the maximum v_T. The phase separation by the spinodal decomposition, even if the temperature crosses the
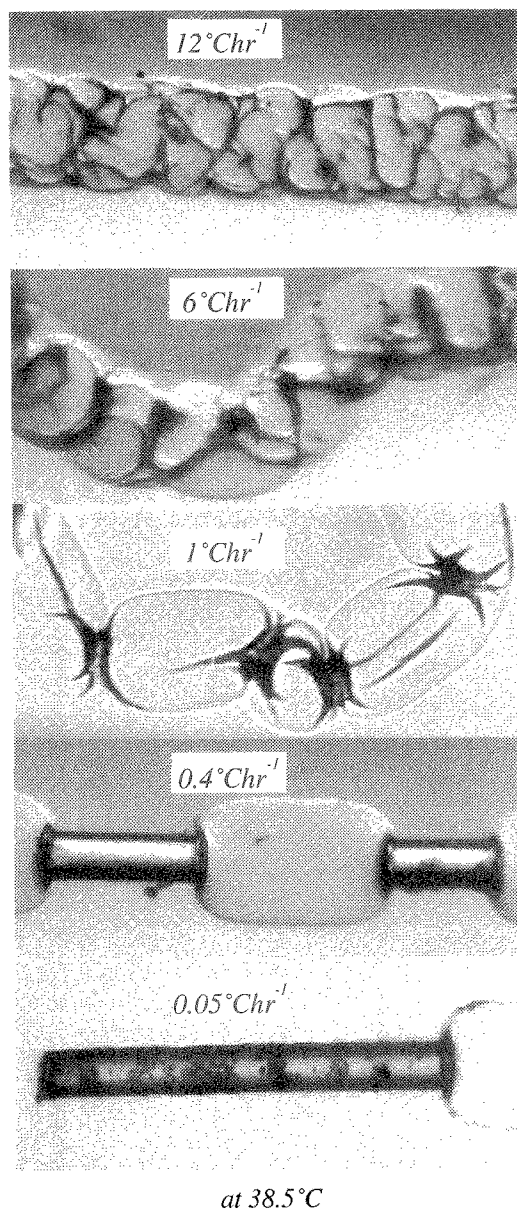

at 38.5°C

Fig. 4 Pictures of the shrinking phase transition at 38.5 °C on the continuous heating processes with different v_Ts. The collapsed diameters are in 70 ± 2 μm.

spinodal line, could not form the macroscopic opaque phase. If we can continuously increase the temperature with much faster, the macroscopic opaque phase could be observed before the phase transition completes.

It should be noted that the surface nucleation at the initial stage of the phase transition has an important role in determining the surface patterns and the phase transition velocity. This is because the locally collapsed skin layer is subject to stress by proximity to the core portion, which takes a maximum at the boundary between the dense surface and dilute core portion. This inhomogeneous shrinking results in the local modification of the phase transition temperature of the swollen state in the vicinity of the interface. In order to verify these considerations, not only the macroscopic observations but also the microscopic network structure in the same sample are desirable. This is a subject for future investigations.
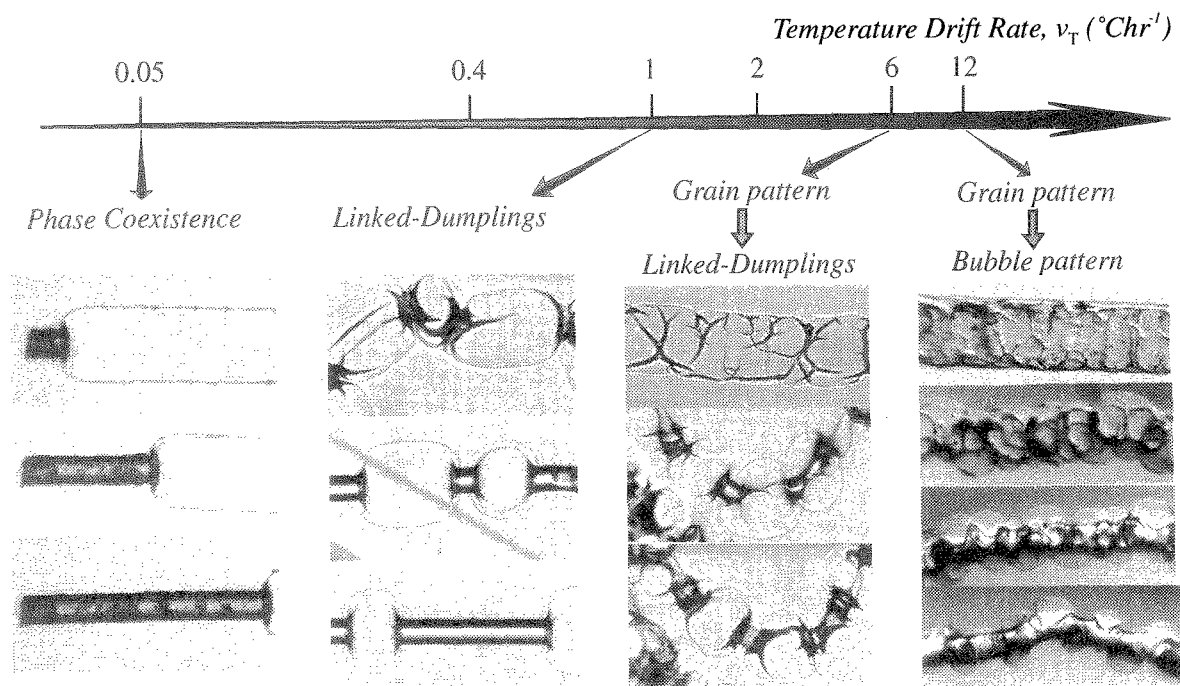
Temperature Drift Rate, v_T *(°Chr^{-1})*

Fig. 5 Summary of the relationship between the characteristic conformation and v_T on the continuous heating processes.

4. CONCLUSION

We have investigated the conformation changes during the shrinking phase transition of the slightly ionized poly(N-isopropylacrylamide) gels. The experimental results can be summarized in Fig. 5. The shrinking phase transition starts at the surface, and the characteristic conformations can be determined by the nucleation and the spinodal decomposition in the smaller and the larger temperature drift rate, respectively. Three characteristic patterns, the phase coexistence (or linked-dumplings), the grain pattern, and the bubble pattern were observed. Shrinking pattern has a strong correlation with the phase transition velocity. The condition for the appearance of the phase coexistence was determined on the continuous heating process.

REFERENCES

[1] See for instance, *The Polymer Networks Group Series*, Vol.1; K. te Nijenhuis, W. J. Mijs (eds.) (John Wiley & Sons Ltd., Chichester, 1998).

[2] K. Dusek and D. Patterson, *J. Polym. Sci.*, Part A-2, **6**, 1209 (1968).

[3] T. Tanaka, *Phys. Rev. Lett.*, **40**, 820 (1978).

[4] S. Hirotsu, *Phase Transitions*, **47**, 183 (1994).

[5] A. Suzuki, S. Yoshikawa and G. Bai, *J. Chem. Phys.*, **111**, 360 (1999).

[6] G. Bai and A. Suzuki, *J. Chem. Phys.*, **111**, 10338 (1999).

[7] S. Hirotsu, *J. Chem. Phys.*, **88**, 427 (1988).

[8] E. S. Matsuo and T. Tanaka, *J. Chem. Phys.*, **89**, 1695 (1988).