

수용성 블록공중합체의 졸-겔 전이 변화 연구

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Rheological Characterization of the Sol-to-Gel Transition of Water Soluble Triblock Copolymers

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Introduction

Block copolymers having hydrophilic chains such as PEO covalently connected to hydrophobic chains such as PPO, PBO, and PLGA can form micelles[1,2] in water when their solution concentration exceeds a critical micelle concentration (cmc)[3,4,5] or solution temperature is increased above the critical micelle temperature (cmt)[3,5,6] due to their self-assembling nature. It is also known that aqueous solution of these block copolymers undergoes the sol-to-gel transition at high concentration. The gels derived from these block copolymers are physical gels formed through non-covalent associations and the gels turn into sols again when temperature is lowered below the gelation temperature; in other words, thermoreversible gelation[5,7]. Typical water soluble amphiphilic block copolymer is PEO-PPO-PEO (Pluronic®; BASF or Poloxamers®; ICI). This copolymer is commercially available as surfactants and widely used for emulsification, detergency, dispersion stabilization and so forth[8]. It is well known by small-angle neutron scattering (SANS) experiments that the gel of PEO₁₀₀PPO₆₅PEO₁₀₀ (Pluronic F127) consists of close-packed (cubic) array of micelles[7,9] and the gel transition is due to the hard-sphere crystallization when micelle concentration reaches a critical volume fraction of 0.53[10]. There are many factors affecting the formation of gels: molecular architecture, degree of hydrophilicity (or hydrophobicity), ratio of hydrophilic and hydrophobic blocks, molecular weight, solvency, and additives.

PEO-PLGA-PEO is another class of water soluble amphiphilic block copolymers. Moreover, because PEO-PLGA-PEO is nontoxic and biodegradable, this block copolymer can be used in drug delivery system (DDS) taking advantage of the sol-to-gel transition. However, the gelation mechanism of the PEO-PLGA-PEO in water is not investigated in detail because this triblock copolymer is a recently discovered material. In present study, we investigated the gelation mechanism in aqueous solution of PEO-PLGA-PEO triblock copolymer using tube inversion method (TIM), small-angle light scattering (SALS), and rheological measurements and compared with the gelation mechanism of PEO-PPO-PEO block copolymers.

Experimental

A commercial grade of PEO₁₀₀PPO₆₅PEO₁₀₀, Pluronic F127, was kindly donated by BASF and used without further purification. The nominal molecular weight is 12.6K in total and the weight fraction of PEO is approximately 70 %.

PEO-PLGA-PEOs were synthesized by ring opening polymerization in our laboratory. The molecular weights and DLLA/GA ratios in the PLGA block were summarized in Table 1.

Tube inversion method (TIM) was employed to determine the sol-gel boundaries. Vials with a 13 mm diameter were used and the vials sealed with Teflon film were placed in a

water bath which can control temperature with an accuracy of 0.01 °C. To ensure equilibrium, the equilibration time for more than 10 min was allowed for each temperature and measurements were carried out every 0.5 °C from 1 °C to 90 °C. The change from a mobile to an immobile state was determined by inverting the tube. Hard gel was defined as immobile for a long time while soft gel was defined as a detection of any slow movement of a meniscus over a period of 1 min. Sol was defined to flow massively to the bottom of a tube within 1 min upon inversion.

Small-angle light scattering (SALS) was used to detect turbidity in aqueous solutions of PEO-PLGA-PEO and to measure q_{\max} and Λ_m (correlation length) as a function of time. Home-made SALS is equipped with a He-Ne laser of $\lambda = 632.8$ nm and a rotating photodiode.

Rheometer RMS-800 (Rheometrics, Inc.) in conical-cylinder geometry (cup diameter, 52 mm; bob diameter, 50 mm; bob length, 20 mm) was used to measure the storage modulus G' of solutions as a function of temperature. Strain was fixed at 2.7 % which was small enough to ensure linear viscoelasticity.

Results and Discussion

In aqueous solutions of PEO₁₀₀-PPO₆₅-PEO₁₀₀ triblock copolymer, hard gels were observed above a copolymer concentration of 16 wt% within a temperature window of 10-90 °C and this result is in agreement with other previously reported results[1,5,11]. For a copolymer concentration of 15-19 wt%, a soft gel was detected in the peripheral region of the hard gel by the tube inversion method (TIM) as shown in Fig.1. For a 20 wt% aqueous solution of PEO₁₀₀-PPO₆₅-PEO₁₀₀ triblock copolymer, rheological properties such as storage modulus G' , loss modulus G'' , complex viscosity η^* , and $\tan \delta$ are measured as a function of temperature with a heating rate of 1 °C/min (Fig. 2). In the concentration of 20 wt%, aqueous solution of PEO₁₀₀-PPO₆₅-PEO₁₀₀ triblock copolymer undergoes sol-to-hard gel-to-sol transitions by increasing temperature as shown in Fig. 1. The crossover point, $G' \approx G''$, has been proposed as a criterion[12] for the sol-to-gel transition and this criterion has been discussed in other previous studies. In our work, the abrupt change in the modulus was defined as the sol-to-gel transition[13] in aqueous solution of PEO₁₀₀-PPO₆₅-PEO₁₀₀ triblock copolymer and this criterion is in accord with the result made by TIM.

Phase diagram of PEO-PLGA-PEO (750-3.6K-750) in water is represented in Fig. 3. Compared with the aqueous solution of PEO₁₀₀-PPO₆₅-PEO₁₀₀, the aqueous solution of PEO-PLGA-PEO (750-3.6K-750) has a narrow temperature window for gelation. Moreover, turbidity is observed in aqueous solutions of PEO-PLGA-PEO (750-3.6K-750) and it is interesting to note that the turbidity depends only on temperature not on concentration. As noticed from Fig. 3, turbidity increases in the temperature region from <1> to <2> and again decreases from <2> to <3>, indicating that points <2> have the highest degrees of turbidity. In the temperature region from <3> to <4> turbidity is almost constant and the massive collapse of copolymers is observed above <4>. It is believed that the extensive aggregation of micelles causes turbidity in the aqueous solutions of PEO-PLGA-PEO (750-3.6K-750). The aggregation of micelles is observed in time-resolved SALS experiment. As shown in Fig. 4, q_{\max} [$q = (4\pi n/\lambda)\sin(\theta/2)$] decreases and correlation length Λ_m , defined as $\Lambda_m = 2\pi/q_{\max}$, increases, implying that the micelles aggregate one another as time progresses. From the rheological measurement of aqueous solutions of PEO-PLGA-PEO (750-3.6K-750) we also noted that the storage modulus G' has a different temperature behavior compared with the storage modulus G' of aqueous solutions of PEO₁₀₀-PPO₆₅-PEO₁₀₀. No abrupt changes in the storage modulus G' are observed at the sol-to-hard gel transition and the gradual decrease of G' as a function of temperature shows that the aggregation of micelles is disrupted for a small shear by increasing temperature. It is interesting to note that the temperature at the local

maximum G' corresponds to the temperature of the highest degree of turbidity as shown in Fig. 5. From the rheological measurements, the distinction between the hard gel and the soft gel, however, seems to depend only on the absolute value of G' .

Unlike PEO₁₀₀-PPO₆₅-PEO₁₀₀, the micelles of PEO-PLGA-PEO (750-3.6K-750) in aqueous solution can not pack through entanglement of the PEO corona due to short PEO chains because the entanglement molecular weight (M_e) of PEO is about 1600. We conclude at this point that the gelation observed for the aqueous solutions of PEO-PLGA-PEO (750-3.6K-750) is believed to be mainly because of the massive aggregation of micelles caused by hydrophobic interaction.

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Table 1. Molecular weight of PEO-PLGA-PEO triblock copolymers used in present study

Block Copolymer	¹ H-NMR		GPC		
	M _n	DLA/GA (mole ratio)	M _n	M _w	PDI
PEO-PLGA-PEO	810-3620-810	80/20	5530	8060	1.46
	1940-2150-1940	79/21	7550	9690	1.28

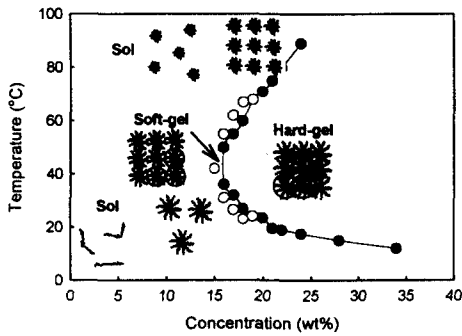


Figure 1. Phase diagram of PEO₁₀₀-PPO₆₅-PEO₁₀₀ in water.

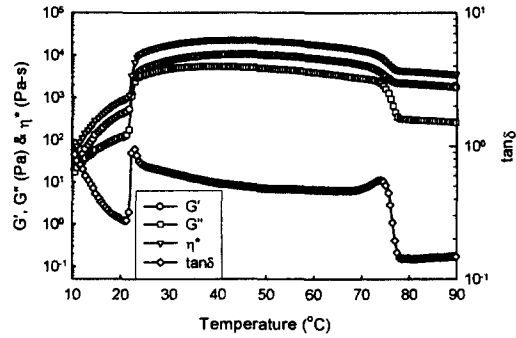


Figure 2. Plots of G', G'', η*, and tanδ as a function of temperature for an aqueous solution of PEO₁₀₀-PPO₆₅-PEO₁₀₀ in water.

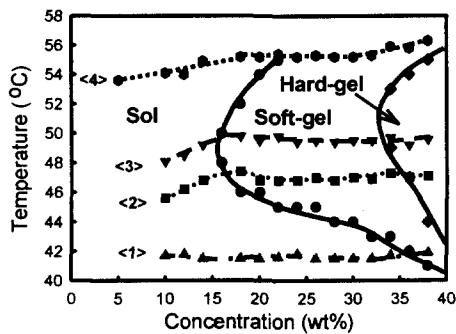


Figure 3. Phase diagram of PEO-PLGA-PEO (750-3.6K-750) in water including turbidity data.

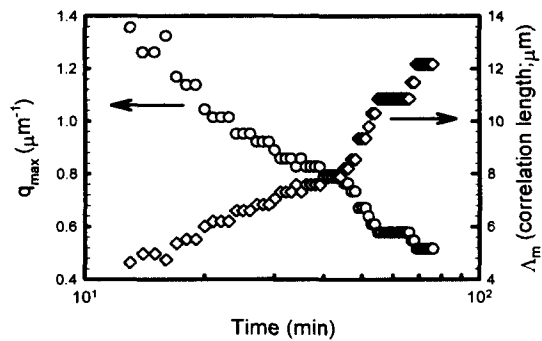


Figure 4. q_{max} and Λ_m as a function of time measured from time-resolved SALS experiment for an aqueous solution of PEO-PLGA-PEO (750-3.6K-750). Concentration = 36 wt%, temperature = 47°C, and data was measured per 1 min.

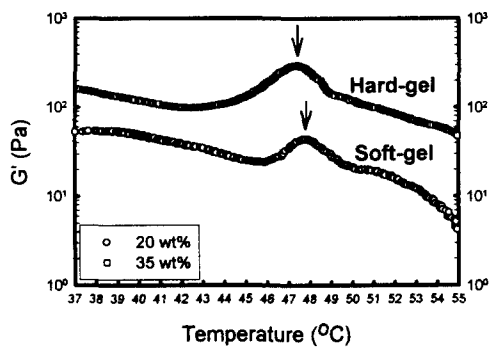


Figure 5. Change of G' as a function of temperature in aqueous solutions of PEO-PLGA-PEO (750-3.6K-750).