PEO-PPO-PEO 삼중블록 공중합체의 구조와 물성에 대한 연구

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Structure-property relationship of PEO-PPO-PEO triblock copolymer

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Introduction

In the past decade, considerable effort has been made to understand the properties of PEO-PPO-PEO triblock copolymers which are widely used as a nonionic polymeric surfactant. These copolymers are commercially available as surfactants (Pluronics; BASF or Poloxamers; ICI). Aqueous solutions of poly (propylenne oxide) (PPO) exhibit dramatic temperature dependence. Below approximately 15℃, water is good solvent for PPO, whereas PPO at higher temperatures aggregates. Poly(ethylene · oxide) (PEO), on the other hand, is dominantly hydrophilic within the temperature range from 0 to 100℃. With blocks of PEO and blocks of PPO combined into single polymer chains, one can therefore expect amphiphilic characteristics with interesting aggregation phenomena.

Therefore a variety of techniques have been used to study the micelle formation, micelle structure, and gelation of PEO/PPO copolymer solutions. For example, small angle X-Ray scattering(SAXS), fluorescence, differential scanning calorimetry, static and dynamic light scattering, and rheological measurement. The motivations for these studies are application in emulsification, detergency, dispersion stabilization, controlled drug delivery, biotechnology, and so forth.

At temperature close to ambient it is well known that high-concentration polymer solutions exhibit a dramatic change in viscosity, revealing a "thermoreversible gelation". Several mechanisms of thermally reversible gelation have been proposed. The sol-to-gel transition has been explained in terms of intrinsic change in micellar properties or entropic change associated with locally ordered water molecules close to the PPO hydrophobic blocks. Mortensen et al.[1] systematically studied the micelle formation and gelation by using SANS with a shear cell and suggested that the mechanism of gelation is due to a "hard-sphere crystallization" as the micelle concentration approaches the critical volume fraction of 0.53. This implies that gels when the micelles are arranged in a close-packed (cubic) array of micelles. Glatter et al.[2] investigated the same system by using SAXS.

Prud'homme et al.[3] used rheometry together with SANS to examine the gelation and gel structure of Pluronic F127 in water. They observed that the transition between Newtonian and non-Newtonian behavior becomes more abrupt for higher solution concentrations. Hvidt et al.[4] observed more complicated rheology in solutions of $EO_{21}PO_{47}EO_{21}$. They observed soft gel and hard gel region using temperature sweep test.

But previous studies with rheometry, rheology was not used intensively to investigate the microstructure. The purpose of this work is to understand the relationship between structural changes and the rheological properties using various experiments. Specially, frequency sweep test and strain sweep test (LAOS) was conducted at different temperature. Frequency sweep test supplied more information of non-Newtonian behavior and microdomain structures. And LAOS test supplied more useful information.

Experimental Methods

Materials and sample preparation. In this study, commercial grade $EO_{100}PO_{65}EO_{100}$, Pluronic F127(BASF), was used without further purification. Pluronic F127 was selected because it has the lowest gelation concentration and the simplest phase behavior of the Pluronic series. The nominal molecular weight of this copolymer is 12600 and weight fraction of PEO in the triblock copolymer is approximately 70%. This sample was dissolved in dust-free purified water. To make samples homogeneous and transparent, the solution was rotated at 100rpm for about 30min at 90℃. Fig. 1 shows the phase diagram of F127 aqueous solution reported by K.W. Kwon et al[5]. Aqueous solutions of the $EO_{100}PO_{65}EO_{100}$ triblock copolymer at 20wt% were prepared. The solutions were stored below 5℃ for more than 1day.

Rheometry. Rheological measurements were carried out on a rheometer (RMS800 and ARES, Rheometrics) using a parallel plate fixture and cone-and-plate (cone angle 0.04 radians, gap 50㎛) with a diameter of 50mm and lower plate with a dam, and silicone oil was used to prevent water evaporation. Strain sweep test was carried out in the strain range from 0.01% to 100% at a fixed frequency of 1rad/s. Frequency sweep test was conducted in the range from 0.1 to 100rad/s at a fixed strain. Both strain and frequency sweep test were conducted at different temperature. Temperature sweep test was also conducted.

Results and Discussion

Temperature sweep test. Fig. 2 shows the results of the temperature sweep test for 20wt% solution. Temperature sweep test was carried out in the temperature range from 20℃ to 30℃ at a fixed frequency of 1rad/s. As a result, we observed sol-to-gel transition. In detail, we divided three regions. First region, in which both G′ and G″ have very low value, is sol region. Second region, where both G′ and G″ increase rapidly, is soft gel region. And third region, in which both G′ and G″ have very high value, is hard gel. But these definition is insufficient, so we make frequency and strain sweep tests at different temperatures.

Frequency sweep test. Fig. 3 shows the results of frequency sweep test for 20wt% solution at different temperatures. Frequency sweep test was carried out in the frequency range from 0.1 to 100rad/s at a fixed strain 3%. In fig. 3, the slope of G′ curves at low frequency region has different value. As temperature increases, the slope of G′ approach zero. Kossuth et al.[6] have observed the slope of G′ about microdomain structure in block copolymer melts, they pointed out that the slope of G′ at cubic phase is zero. Although block copolymer solutions are different from block copolymer melts, and the slope of G′ at 30℃ is 0, we concluded that block copolymer microdomain structure is alike cubic shape.

From previous section, gels form when the micelles are arranged in a close-packed (cubic) array of micelles. We observed this cubic array of micelles with frequency sweep data.

Strain sweep test. In general, strain sweep test is performed to find out the linear viscoelastic region before the frequency sweep test. And many rheologists have not concerned about nonlinear behavior after critical strain point which distinguishes linear from nonlinear region. But in our previous study[7], we observed that the results in the nonlinear region at strain sweep test are very different and the reason is originated by different microstructure. And we divided the strain sweep results into 4 types. Pluronic F127 20wt% solution has different microstructures according to temperature, so that strain sweep(LAOS) results will show different types. Fig. 4, 5, 6 show the results of strain sweep test at different temperatures. We selected three temperatures region to compare the results of LAOS test.

Fig. 4 shows newtonian behavior at sol temperature region. Fig. 5 shows type IV (both G′ and G" increase and decrease) at soft gel temperature region . Fig. 6 shows type III (G′ decreases and G" increases and decrease) at hard gel temperature region. In reference, high concentration emulsion or suspension system sometimes show type III behavior. Namely, spherical micelles has microstructure of a close packed (cubic) array in water as a high concentration emulsion or suspension at hard gel region.

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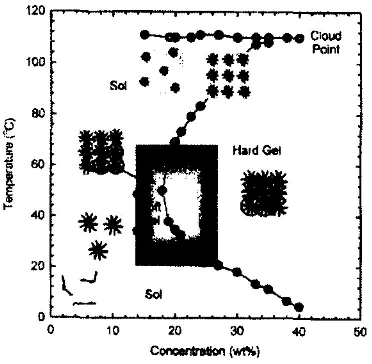

Fig. 1 Phase diagram of F127 in water

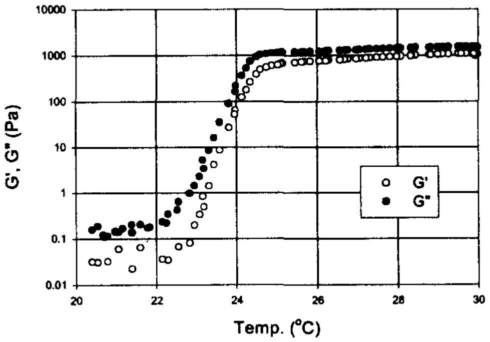

Fig. 2 Temperature sweep test of F127 20wt% solution from 20℃ to 30℃

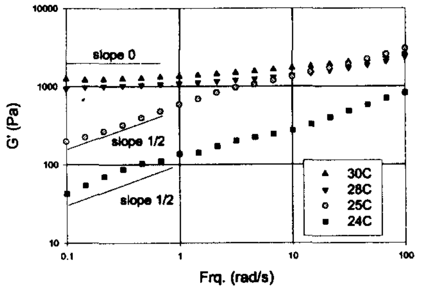

Fig. 3 Frequency sweep test of F127 20wt% at different temperature.

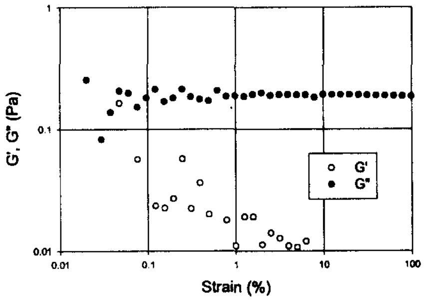

Fig. 4 Strain sweep test of F127 20wt% solution at 23℃

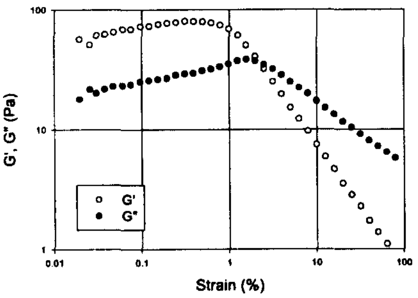

Fig. 5 Strain sweep test of F127 20wt% solution at 25℃

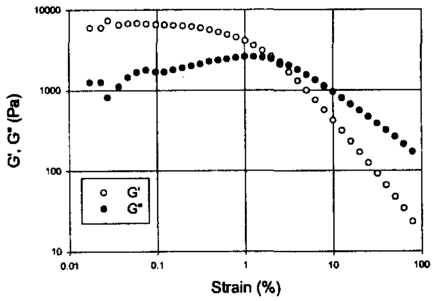

Fig. 6 Strain sweep test of F127 20wt% solution at 27℃