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Investigation of copolymer–micellar system $EO_{37}PO_{56}EO_{37}$ by low-frequency internal friction

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Abstract

The internal friction and relative modulus are measured for a copolymer–micellar system $EO_{37}PO_{56}EO_{37}$ at different concentrations. At concentration above ~21.5 wt%, we have evidenced the presence of two first-order phase transitions, corresponding to the sol–gel transition and the gel–sol transition, respectively. The former is related to the micelle crystallization, while the latter is due to the formation of worm-like micelles. It is found that the formation of crystalline phase strongly depends on the interpenetration and entanglement of the PEO chains. Our work confirms that internal friction technique is sensitive to structural changes of micellar systems.

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1. Introduction

Polyethylene oxide (PEO) and polypropylene oxide (PPO) triblock copolymers have been extensively studied because of their interesting self-assembling behavior in aqueous solution. The most attractive feature of PEO–PPO–PEO is the temperature-induced micellization [1–6]. At low polymer concentrations and low temperatures, the triblock copolymer in water exhibits a single-coil behavior; such polymers are often called unimers, where water is a good solvent for both PEO and PPO blocks. With increasing block copolymer concentration or temperature, the critical micelle concentration (CMC) or critical micelle temperature (CMT) can be observed, where the triblock copolymer chains form micelles with PPO blocks as the core and PEO blocks as the corona. At higher concentrations, the copolymer exhibits a sol–gel transition at low temperature and a gel–sol transition at higher temperature [7–12]. In the gel region, the micelles can form ordered phases, such as cubic, hexagonal and lamellar phases [8,9]. Because the hydrophilic/hydrophobic property of PEO–PPO–PEO copolymer can be altered by the variation of the total molecular weight and the composition, they are widely used in detergency, emulsification, drug delivery, cell therapy, tissue engineering, and separation media for the separation of small charged biomacromoleculars [13–16].

The nature of the sol–gel transition is ascribed to the micelle crystallization above a given critical value [9], the packing and crowding of micelles [17,18], and the formation of a percolated polymer network [11], while the gel–sol transition is believed to be the result of the breakage of micellar structure [18], the change of micelle shape which makes the volume fraction of micelle too low to form a gel structure [19,20], and the loss of bound solvent [11]. However, because the techniques to characterize copolymer–micellar systems are still limited, the dynamics of polymer chains in the micellar systems is not well understood.

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Internal friction technique has been widely used in solid-state physics and material science for its high sensitivity [21–24]. Recently, the internal friction technique has proven to be valid and sensitive for detecting structural changes and dynamics in liquid metals, polymers and biological matters [25–28]. Nevertheless, few works have yet been reported about using the internal friction method to study the structural changes in micellar systems. Compared with other techniques, internal friction can directly reflect the change of the microstructure due to the variation of the inter-micelle interaction. In the previous work [29], we applied the internal friction method to aqueous solutions of Pluronic PE10300 with a chemical composition of $EO_{17}PO_{56}EO_{17}$, and found that there exists a sol–gel transition and a gel–sol transition at high concentrations. The sol–gel transition is believed to be caused by micelle crystallization when the micellar volume fraction is above a critical value. However, the effect of the hydrophilic PEO blocks on the crystallization process is not clear yet. In the present work, another PEO–PPO–PEO triblock copolymer is used, which has the same size of PPO blocks as PE10300 but a larger PEO content than that of PE10300. We investigated the copolymer–micellar system as a function of temperature and concentration using the low-frequency internal friction technique. Compared with the internal friction results of PE10300 aqueous solutions, the influence of PEO blocks on the crystallization process could be understood.

2. Experiment

Our micellar system is made by dissolving a triblock copolymer Pluronic PE10500 (Aldrich), into deionized water at weight percentage (ϕ) <30.0 wt%. The copolymer has a nominal molecular weight of 6500, and a PEO content of 50 wt%. The chemical composition is $EO_{37}PO_{56}EO_{37}$.

Internal friction measurements were performed on a developed torsion pendulum using a forced-vibration method at constant excitation strain amplitude 2×10^{-5}. The mixture was held between two cylinders. The inner cylinder was immersed into the solution, while the outer was fixed and surrounded by a water bath so that the temperature could be controlled within $\pm0.5\,^{\circ}C$. The details of the device can be found elsewhere [26]. According to this technique, the internal friction (Q^{-1}) is determined by a direct measurement of the phase angle (δ), by which the strain lags behind the stress. Meanwhile, the relative modulus (G) was calculated from the ratio between the stress and strain. The temperature was typically increased in steps of 1 °C with 2 min equilibration time at each temperature.

3. Results and discussion

The concentration of PEO–PPO–PEO used in the present work is above CMC [30] and so we deal with micelles in the measurements. Fig. 1(a), (b) presents the anelastic spectra (internal friction Q^{-1} and relative modulus G) obtained on heating, for 23.7 wt% PEO–PPO–PEO aqueous solution at different vibration frequencies. The mixture exhibits two overlapping internal friction peaks (P1 and P2) at about 25 and 48 °C, respectively (see arrows in Fig. 1(a)). Note that the positions of the P1 and P2 peaks do not depend on the vibration frequency, and the magnitudes decrease as the frequency is increased from 0.5 to 7.0 Hz, implying that the P1 and P2 peaks are associated with the first-order phase transitions rather than dynamic relaxations [31]. Accompanied with the occurrence of P1 and P2 peaks, the relative modulus G shows a rapid increase and an abrupt drop during the transitions (see Fig. 1(b)). As discussed in the previous work [29], these two processes can be attributed to the sol–gel transition and the gel–sol transition, respectively. The similar phenomenon has been observed in 15 wt% $EO_{100}PO_{65}EO_{100}/D_2O$ solution [11]. Here, these two dissipation peaks appear as the internal friction manifestation of these two transitions. Moreover, they are both first order in nature.

The sol–gel transition may be due to the micelle crystallization [9,19,20,32,33]. The micellar volume fraction increases with increasing temperature and copolymer concentration. The most important inter-micelle interaction

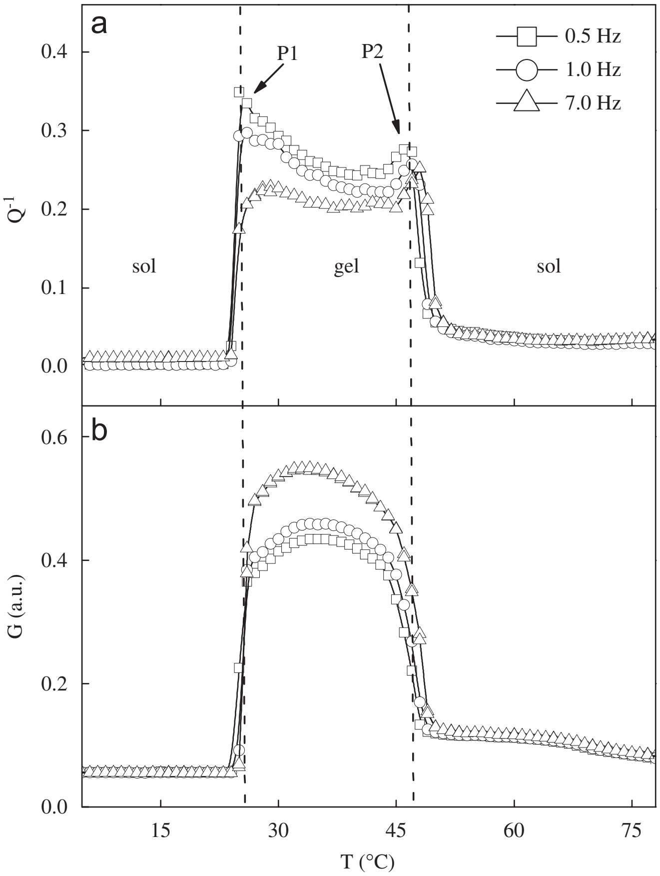

Fig. 1. Anelastic spectra (internal friction Q^{-1} and relative modulus G) of 23.7 wt% PEO–PPO–PEO aqueous solution, where the vibration frequency $f = 0.5$ Hz (□), 1.0 Hz (○), and 7.0 Hz (△).