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Dynamics of PEO–PPO–PEO triblock copolymer in aqueous solutions investigated by internal friction

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Abstract

The dynamics of poly(ethylene oxide)-block-poly(propylene oxide)-block-poly(ethylene oxide) (PEO–PPO–PEO) in aqueous solutions in the range of the polymer concentration $\phi = 10.0\text{--}45.0$ wt% has been investigated by the tube inversion method and the internal friction technique. At $\phi \leq 31.0$ wt%, two internal friction peaks are observed with the characteristics of the first-order phase transition, corresponding to the opaque liquid-to-liquid transition and the phase separation. The opaque liquid-to-liquid transition is due to the sphere-to-rod transition in shape of the micelles, and the phase separation is caused by the destruction of core–shell structure. At $\phi \geq 32.0$ wt%, besides the internal friction peak associated with phase separation, two other peaks are observed, which correspond to the solution-to-gel (liquid-to-crystal) transition and gel-to-solution (crystal-to-liquid) transition, respectively. The former is due to the micelle crystallization, whereas the latter is the result of spherical micelles fusing into wormlike or rodlike micelles at elevated temperatures.

1. Introduction

Polyethylene oxide (PEO) and polypropylene oxide (PPO) block copolymers have attracted much attention in past years because of their applications in detergency, emulsification, dispersion stabilization, lubrication, foaming, drug solubilization and controlled release [1–4]. The most attractive property of PEO–PPO–PEO is the temperature induced micellization [5–10]. At low temperatures, PEO–PPO–PEO chains exist as unimers in a dilute aqueous solution. When the temperature reaches the so-called critical micellization temperature (CMT), the chains aggregate into micelles with PPO blocks as the core and PEO blocks as the corona. At high concentrations, PEO–PPO–PEO chains can form a gel or closely packed crystalline lattice structure [11–21]. Such a micellar crystal can be lamellar, hexagonal, face centered cubic (fcc), or body centered cubic (bcc), depending on the temperature, concentration, chemical composition and block length of the block copolymer.

Because the techniques to characterize concentrated polymer solutions are still limited, the dynamics of polymer chains in concentrated solutions is not well understood.

The internal friction technique has been widely used in studying crystal structures, defects and phase transition in metals [22–24] as well as dynamic relaxations in polymers [25–27]. Recently, it has proven to be valid and sensitive for detecting structural changes in liquid systems [28, 29]. In the present work, we have investigated PEO–PPO–PEO concentrated solutions as a function of temperature using the internal friction technique. Our aim is to understand the origin of the dynamics in PEO–PPO–PEO solution.

2. Materials and methods

PEO–PPO–PEO triblock copolymer (Pluronic PE10300) was purchased from Aldrich. Each PEO has 17 ethylene oxide (EO) units and the middle PPO block contains 56 propylene oxide (PO) units. The molecular weight (M_w) and polydispersity (M_w/M_n) of the copolymer are 4950 g mol^{-1} and 1.05, respectively. PEO–PPO–PEO aqueous solutions with different copolymer concentrations (ϕ) were prepared by dissolving the liquid copolymer in deionized water under stirring for 10 h at 10°C .

Internal friction measurements were performed on a developed torsion pendulum apparatus using the forced-vibration method. The mixture was held between two bell-like cups in a stainless-steel vessel. The inner cup was immersed in the mixture, and the outer cup was surrounded by a water bath so that the temperature could be controlled within $\pm 1^\circ\text{C}$. The details of the device can be found elsewhere [30]. The internal friction (Q^{-1}) was calculated by measuring the loss angle between applied stress and resulting strain. Meanwhile, the relative modulus (G) was calculated from the ratio between the stress and strain. The measurements were carried out with a torsion strain amplitude of 2×10^{-5} . The temperature was typically increased in steps of 1°C with 2 min equilibration time at each temperature.

In the tube inversion tests, 5.0 ml of water and PEO–PPO–PEO was mixed in a tube with a diameter of 10 mm. As temperature increased from 10 to 95°C , the changes of the mixture were observed. The mobility of the mixture was distinguished by inverting the tube for hours.

3. Results and discussion

The concentration of PEO–PPO–PEO used in the present work is above the critical micelle concentration (CMC) [6]. Figure 1 shows the phase diagram of PEO–PPO–PEO aqueous solutions from tube inversion test. At $\phi \leq 31.0 \text{ wt}\%$ and $T < 41^\circ\text{C}$, the mixture is transparent and mobile, but it turns turbid at $T > 41^\circ\text{C}$, indicating the appearance of a liquid-to-liquid transition. This is because spherical micelles develop into wormlike or rodlike structure at elevated temperatures [14, 15, 20, 31, 32]. Such rodlike micelles are anisotropic and scatter light. In the range $32.0 \text{ wt}\% \leq \phi \leq 45.0 \text{ wt}\%$, as temperature increases, the transparent mobile solution first transits into transparent gel then to a turbid and mobile solution. The transition from solution to transparent gel (solution to gel) shows a strong ϕ dependence. When ϕ increases from 32.0 to 45.0 wt%, the transition temperature gradually shifts from 28 to 15°C . The micellar volume fraction increases with increasing temperature and copolymer concentration. When the micellar volume fraction is above 0.53, a critical value for hard-sphere interaction, the copolymer solution undergoes a first-order crystallization transition and the gel structure is formed [11, 12, 14, 15].

The transition from transparent gel to turbid solution is located at the temperature range $38\text{--}44^\circ\text{C}$. The transition does not have concentration dependence, indicating that is thermodynamically controlled. At elevated temperatures, PEO chains become more

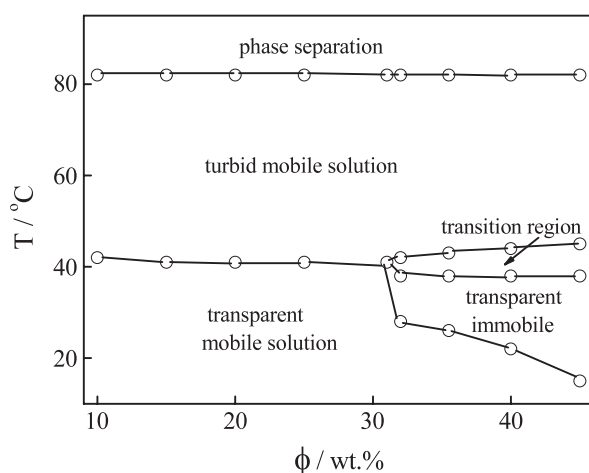


Figure 1. Phase diagram of the PEO–PPO–PEO aqueous solutions by a test inverting method.

hydrophobic and dehydrated. The aggregation and interpenetration of PEO chains in different micelles leads the coronas of the micelles to fuse and overlap each other. As a result, prolate ellipsoid or rodlike micelles are formed, leading inter-micelle interaction and occupied volume of micelles to decrease [13, 15, 31]. This is responsible for the gel-to-solution transition. Clearly, the temperature dependence indicates that the transition in the range 38–44 °C is dynamic in nature. Note that PEO chains should not entangle since their molecular weight is far below the entanglement molecular weight ($\sim 1600 \text{ g mol}^{-1}$) [33]. The gel turns into turbid mobile solution at a temperature above ~ 44 °C. A similar phenomenon has been observed in PEG–PLGA–PEG [34], PEG–PCL–PEG [35] and other systems [36–38]. In the present study, PEO chains are hydrophobic at a temperature of about 83 °C, and they probably interact and interpenetrate the hydrophobic PPO core. As a result, the core–shell structure is destroyed and the phase separation occurs.

The temperature dependences of the internal friction (Q^{-1}) and relative modulus (G) are shown in figure 2, where $\phi = 22.0 \text{ wt}\%$. The mixture exhibits two internal friction peaks at ~ 41 and ~ 83 °C, respectively. Meanwhile, the modulus shows two peaks there, indicating the occurrence of phase transition or relaxation. It is known that Q^{-1} is related to the energy dissipation of the material. The material with a higher damping capability displays a larger Q^{-1} value [23]. On the other hand, G reflects the micelle–micelle and micelle–water interactions. Note that the positions of the internal friction peaks do not depend on the frequency, implying that the peaks are associated with the first-order phase transitions instead of dynamic relaxations [39]. In comparison with figure 1, we know that the internal friction peak at ~ 41 °C corresponds to the sphere-to-rod transition, whereas the peak at 83 °C is due to the destruction of core–shell structure. Note that the concentration 22.0 wt% is so high that a crystalline structure of hard spheres is formed.

Figure 3 shows the temperature dependence of internal friction Q^{-1} and relative modulus G of PEO–PPO–PEO/water mixture as a function of frequency f , where $\phi = 35.5 \text{ wt}\%$. In comparison with the results in figure 1, as the temperature increases, the polymer solution is a transparent solution, transparent gel and turbid solution in regions I, II and III, respectively. In region IV, phase separation occurs. Besides the internal friction peak at ~ 83 °C corresponding to the phase separation, we can observe two other overlapping peaks located at ~ 30 and

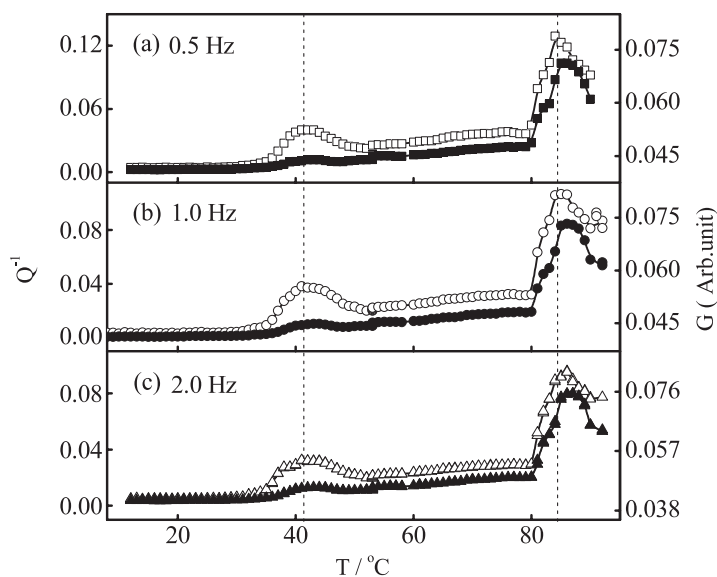


Figure 2. The internal friction–temperature (Q^{-1} – T) and relative modulus–temperature (G – T) curves of PEO–PPO–PEO aqueous solution, where $\phi = 22.0$ wt%, and $f = 0.5$ Hz (\square), 1.0 Hz (\circ) and 2.0 Hz (\triangle). The open and solid symbols are for the internal friction Q^{-1} and relative modulus G , respectively.

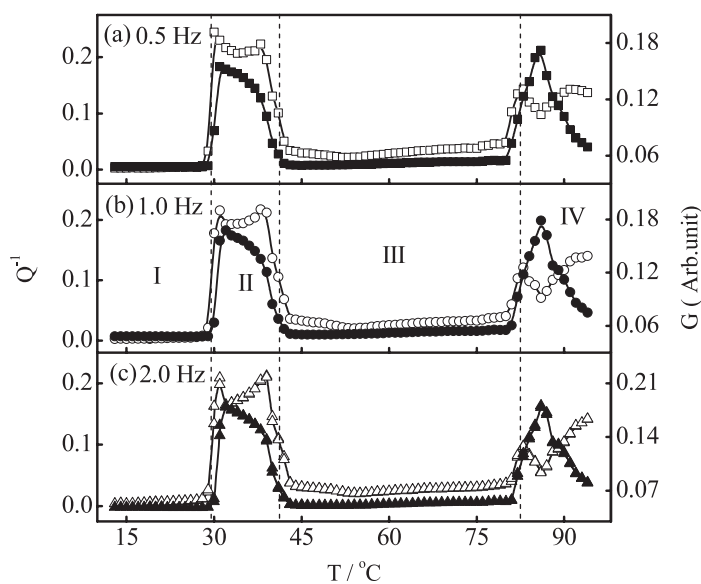


Figure 3. Temperature dependence of the internal friction Q^{-1} and relative modulus G of PEO–PPO–PEO aqueous solution, where $\phi = 35.5$ wt%, and $f = 0.5$ Hz (\square), 1.0 Hz (\circ) and 2.0 Hz (\triangle). The open and solid symbols are for the internal friction Q^{-1} and relative modulus G , respectively. (I) Transparent solution; (II) transparent gel formation; (III) turbid solution formation; (IV) phase separation.

~ 38 °C. Both of them are independent of frequency, suggesting that the mixture undergoes two first-order phase transitions at ~ 30 and ~ 38 °C, respectively. They are attributed to the

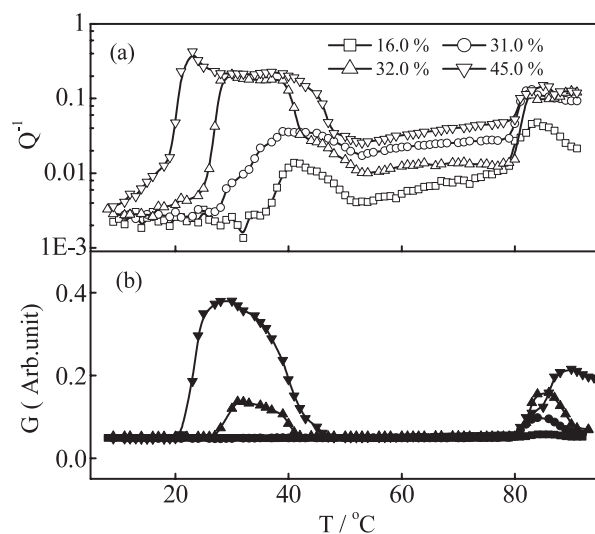


Figure 4. Concentration (ϕ) dependence of PEO–PPO–PEO on the internal friction Q^{-1} (a) and relative modulus G (b) at $f = 0.8$ Hz, where $\phi = 16.0$ wt% (\square), 31.0 wt% (\circ), 32.0 wt% (\triangle) and 45.0 wt% (∇). The open and solid symbols are for the internal friction Q^{-1} and relative modulus G , respectively.

solution-to-gel transition (liquid-to-crystal transition) and the gel-to-solution transition (crystal-to-liquid transition), respectively (figure 1).

The concentration also has an effect on the dynamics of the copolymer/water mixture. Figure 4 shows the effect of the concentration (ϕ) of PEO–PPO–PEO/water mixture on internal friction Q^{-1} and relative modulus G at $f = 0.8$ Hz, where $\phi = 16.0, 31.0, 32.0$ and 45.0 wt%, respectively. When $\phi \leq 31.0$ wt%, the mixture exhibits two internal friction peaks, located at ~ 41 and ~ 83 °C, respectively. They are attributed to sphere-to-rod transition [32] and phase separation, respectively (figure 1). At $\phi \geq 32.0$ wt%, besides the peak at ~ 83 °C, we can observe two overlapping peaks in the range of 23–42 °C. The peaks have strong ϕ dependence. Namely, increasing ϕ lowers the onset temperature and increases the degelation temperature. As mentioned above, the gel is formed when the micellar hard-sphere volume fraction reaches a value of 0.53 and the micelles close-pack in the bcc structure [11, 12, 14]. Here the critical gel concentration is about 32.0 wt%. On the other hand, figure 4 also shows the modulus peak becomes broader and higher with increasing ϕ , further indicating the increase of the gel region and the gel strength. This is understandable because the greater overlapping and interpenetration of micelles in the gel causes the modulus to increase.

Figure 5 shows the frequency dependence of internal friction at different temperatures, where $\phi = 40.0$ wt%. Q^{-1} exhibits a maximum at 21 °C and a minimum at 38 °C. Since the mixture is a stable liquid at 18 °C, Q^{-1} increases with the frequency f (figure 5(a)), which is in agreement with the results for liquid metals [40]. As temperature increases up to 21 °C, a turnover can be observed (figure 5(b)). It corresponds to the solution-to-gel transition (liquid-to-crystal transition). At 29 °C, the mixture becomes a transparent gel, so Q^{-1} decreases with increasing frequency f (figure 5(c)), indicating the gel exhibits viscoelastic behavior under thermal energy [41]; namely, individual microgels are physically close-packed. Therefore, they could follow the slow oscillation and slide with each other, just like a liquid, if vibration frequency is low. At 38 °C, the slope of the curve changes from negative to positive (figure 5(d)), corresponding to the gel-to-solution (crystal-to-liquid) transition.

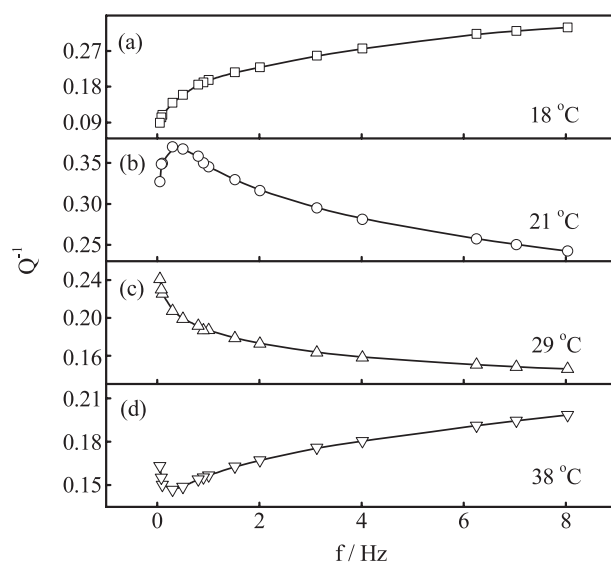


Figure 5. Frequency dependence of internal friction Q^{-1} of PEO-PPO-PEO aqueous solution, where $\phi = 40.0$ wt%, and $T = 18$ °C (\square), 21 °C (\circ), 29 °C (\triangle) and 38 °C (∇).

4. Conclusions

In summary, we have investigated the temperature and concentration effects on the dynamics of PEO-PPO-PEO aqueous solutions by the tube inversion method and the internal friction technique. The internal friction technique has proven to be sensitive to the structural transition in polymer solutions. The solution-to-gel transition is the result of micelle crystallization when concentration is above 32.0 wt%. The origins of the opaque liquid-to-liquid transition and the gel-to-solution transition are the formation of wormlike or rodlike micelles at elevated temperatures. At about 83 °C, the core-shell structure is destroyed. This is responsible for the phase separation.

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