

Influence of Different Inorganic Salts on Crystallization-driven Morphological Transformation of PCL-*b*-PEO Micelles in Aqueous Solutions*

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Abstract Different inorganic salts, including NaSCN, NaCl, MgCl₂ and Na₂SO₄, were added into the aqueous solution containing poly(ϵ -caprolactone)-*b*-poly(ethylene oxide) (PCL-*b*-PEO) semicrystalline micelles. The effects of inorganic salt on the micellar size and morphology were investigated with TEM and DLS. It is found that addition of NaSCN leads to increase of the micellar size, but the micelles remain to be spherical. By contrast, the other three inorganic salts can induce sphere-to-cylinder or sphere-to-lamella transformations of the PCL-*b*-PEO semicrystalline micelles. The alteration rate of the micellar size with the time after addition of the inorganic salts decreases in the following order: Na₂SO₄ > NaCl $\approx$ MgCl₂ > NaSCN. These results were interpreted in terms of the “salting-out” ability of the cations and anions. The anions SO₄²⁻ and Cl⁻ have a stronger “salting-out” ability, driving the morphological transformations of the micelles and leading to a rapid change in micellar size. By contrast, SCN⁻ has a weaker salting-out” ability. The cations Na⁺ and Mg²⁺ may associate with the PEO blocks, leading to a “salting-out” effect as well. However, the “salting-out” ability of cations is weaker than that of SO₄²⁻ and Cl⁻ anions, and the “salting-out” abilities of Na⁺ and Mg²⁺ are similar.

Keywords: Block copolymer; Crystallization; Inorganic salt; Micelle.

INTRODUCTION

Because of the good biocompatibility and biodegradability, the micelles of poly(ϵ -caprolactone)-*b*-poly(ethylene oxide) (PCL-*b*-PEO) block copolymers (BCPs) can be used as potential drug carriers for controlled release^[1]. The micellization behavior of PCL-*b*-PEO BCPs in aqueous solutions has been well studied^[2–5]. However, the next step toward practical application requires more controllable micellar morphology of PCL-*b*-PEO, which is key to the function of the micelles as drug carrier^[6, 7]. Moreover, understanding the morphological transformation induced by external stimuli, such as the components in the biological environment^[8, 9], is also important. Although drug loading can be carried out in a solution similar to the biological environment to avoid any change in the micellar morphology, studying the effect of the components in the biological environment on the micellar morphology of PCL-*b*-PEO is still necessary, since it can provide useful information for choice of PCL-*b*-PEO with a suitable chain structure.

In aqueous solutions, the PCL block in PCL-*b*-PEO is insoluble and may crystallize, thus semicrystalline micelles may be formed. Crystallization of the core-forming block can be utilized to regulate the size and shape of the semicrystalline micelles^[10–32]. In the PCL-*b*-PEO semicrystalline micelles, the soluble PEO blocks can be

* This work was financially supported by the National Natural Science Foundation of China (No. 21274130).

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Invited paper for the special issue of “Polymer Crystallization”

Received March 5, 2014; Revised April 24, 2014; Accepted May 9, 2014

doi: 10.1007/s10118-014-1512-z

viewed as grafting on the surface of PCL crystals. Our results showed that the morphology of semicrystalline micelles is related to the reduced tethering density of the corona ($\tilde{\sigma}$), which is defined as $\sigma\pi R_g^2$ (where σ is the tethered chain density and is equal to the reciprocal of the covered area of the soluble chains and R_g is the radius of gyration of a free soluble block having the same molecular weight at the same conditions)^[33]. The reduced tethering density is determined by the size of the soluble block and chain folds of the crystalline block. Therefore, the morphology of the crystalline micelles can be regulated by changing the chain length of each block, crystallization condition or conformation of the soluble block^[34–37].

In our previous work, we demonstrated that low concentration of NaCl could change the coil size of the PEO due to the “salting-out” effect and induce the sphere-to-cylinder or sphere-to-lamella transformation of the PCL-*b*-PEO micelles in aqueous solutions^[35]. The “salting-out” effect of inorganic salts is widely observed, especially in chemical and biological systems^[38–40]. However, it should be noted that the PCL-*b*-PEO micelles as drug carrier are mainly used in biofluids, where exist different sorts of inorganic salt. The “salting-out” abilities of different inorganic salts, such as the famous Hofmeister series^[41], are different. In the Hofmeister series, the “salting-out” ability of the anions decreases in the following order: $\text{CO}_3^{2-} > \text{SO}_4^{2-} > \text{S}_2\text{O}_3^{2-} > \text{H}_2\text{PO}_4^- > \text{F}^- > \text{Cl}^- > \text{Br}^- \approx \text{NO}_3^- > \text{I}^- > \text{ClO}_4^- > \text{SCN}^-$ ^[41]. The effect of inorganic salt on the chain conformation of homopolymers, such as poly(*N*-isopropylacrylamide) and PEO^[42–44], and micellization behavior of non-ionic BCPs has been widely reported^[45–47]. It is observed that inorganic salt may alter the critical micellization concentration, the critical micellization temperature, cloud point and sometimes micellar morphology, and so on. However, the effect of different inorganic salts on the morphology of semicrystalline micelles has not been reported yet. Herein we reported the effect of different Hofmeister ions on the micellar size and morphology of PCL-*b*-PEO in aqueous solutions at a concentration comparable to that in the biological environment.

EXPERIMENTAL

Materials

Monomethoxyl poly(ethylene oxide) (PEO) with a number-average molecular weight of 2000 was purchased from ACROS. PEO was used after distillation with toluene to remove water. A PCL-*b*-PEO BCP, PCL₆₆-*b*-PEO₄₄ (the subscripts 66 and 44 being the polymerization degrees of the PCL and PEO blocks calculated from ¹H-NMR spectrum), with a narrow molecular-weight distribution ($M_w/M_n = 1.07$, measured by gel permeation chromatography) was synthesized according to our previous work^[48]. The analytic-reagent (AR) grade inorganic salts, NaSCN, Na₂SO₄, NaCl and MgCl₂, were used as received. Tetrahydrofuran (THF, AR grade with purity > 99.0%) was purchased from Sinopharm Chemical Reagent Co., Ltd., and refluxed with sodium flakes and distilled prior to use. Deionized water was distilled twice prior to use.

Preparation of the Micelles

PCL₆₆-*b*-PEO₄₄ was first dissolved in THF at a concentration of 0.5 mg/L, then the solution was dialyzed against twice-distilled water at 25 °C to obtain the neat micellar solution of PCL₆₆-*b*-PEO₄₄^[36]. Crystallinity of the PCL core in the PCL₆₆-*b*-PEO₄₄ micelles was also verified^[36]. Micellar solutions containing 0.1 mol/L inorganic salt were prepared by adding 0.5 mL aqueous solution of inorganic salts with a concentration of 1.0 mol/L to 4.5 mL of the neat micellar solution. Beyond such a salt concentration (0.1 mol/L), the micellar morphology is independent on the salt concentration. The solutions of inorganic salt were filtered with a polyvinylidene fluoride membrane with 0.22 μm pores prior to use.

Transmission Electron Microscopy (TEM)

TEM observation was performed using a JEOL JEM-1230 electron microscope operated at an acceleration voltage of 80 kV. The samples for TEM experiments were prepared by dropping 7 μL of the micelle solutions onto copper grids coated with carbon. The copper grids with coated polymer were then dried at atmospheric pressure and at room temperature. The grids were finally negatively stained with 2.0 wt% phosphotungstic acid (PTA) aqueous solution. The stained TEM samples were again allowed to dry in air before observation.

Fourier-Transform Infrared Measurements

Fourier-transform infrared (FTIR) spectra with a resolution of 2 cm^{-1} were recorded on a Thermo Fisher Scientific LLC Nicolet 6700 spectrometer. OPUS spectroscopic software was used for data analysis. PEO solid powder with a number-average molecular weight of 5000 was mixed with the aqueous solutions containing 0.1 mol/L inorganic salts to yield gel-like fluids. Deconvolution of the FTIR spectra was performed using OriginLab Origin software.

Dynamic Light Scattering (DLS)

The hydrodynamic diameter distributions of the micelles were determined by DLS using a Brookhaven Instrument BI-200SM with a laser wavelength of 636 nm at $25.0 \pm 0.05\text{ }^{\circ}\text{C}$. The detection angle was 90° .

The hydrodynamic diameter and size distribution of the scattering particles can be obtained by DLS analysis. DLS measures the normalized intensity-intensity time correlation function $g^{(2)}(t)$, which is related to the normalized electric field correlation function, $g^{(1)}(t)$, by the Siegert relation:

$$g^{(2)}(t) = 1 + \beta |g^{(1)}(t)|^2 \quad (1)$$

For a polydisperse system, $g^{(1)}(t)$ can be expressed as the Laplace transform of the distribution of relaxation rate (Γ), $G(\Gamma)$:

$$g^{(1)}(t) = \int_0^{\infty} G(\Gamma) \exp(-\Gamma t) d\Gamma \quad (2)$$

When the micelles in the solution are spherical, a second-order cumulant expansion can be used to fit the logarithm of $g^{(1)}(t)$, which is expressed as^[49]:

$$g^{(1)}(t) = A \exp(-\Gamma t) [1 + (1/2)\mu_2 t^2 + \dots] \quad (3)$$

where μ_2 is the second cumulant and μ_2/Γ^2 denotes the dispersion width of the particles, corresponding to the size distribution width of the particles.

On the other hand, for the systems exhibiting two relaxation modes (one fast relaxation mode and one slow relaxation mode), a stretched exponential function can be used to describe the electric field autocorrelation function^[50]:

$$g^{(1)}(t) = A \exp(-t/\tau_{\text{fast}}) + B \exp[-(t/\tau_{\text{slow}})^{\beta}] \quad (4)$$

where τ_{fast} and τ_{slow} represent the relaxation times of the fast and slow motions ($\tau = 1/\Gamma$), respectively, and the stretched exponent β ($0 < \beta < 1$) is inversely proportional to the distribution width of the decay time. A smaller value of β implies a wider distribution of the relaxation time. The pre-factors A and B are the amplitudes of the fast and slow relaxation modes, respectively, and the sum of A and B is close to 1.

RESULTS AND DISCUSSION

Morphological Transformations Induced by Inorganic Salts

In our previous work, we found that NaCl could induce the sphere-to-cylinder or sphere-to-lamella morphological transformation of PCL-*b*-PEO semicrystalline micelles^[35]. Besides NaCl, other inorganic salts, including NaSCN, Na₂SO₄ and MgCl₂, were also added into the aqueous solution of PCL₆₆-*b*-PEO₄₄, and the effect of different inorganic salts on the micellar morphology of PCL₆₆-*b*-PEO₄₄ was investigated in the present work. Figure 1 shows the TEM images of the PCL₆₆-*b*-PEO₄₄ micelles prepared from the neat aqueous solution containing no inorganic salt and the solutions in the presence of various inorganic salts (0.1 mol/L). It is observed that, the PCL₆₆-*b*-PEO₄₄ micelles in the neat aqueous solution are spherical with an average diameter of 41 nm (Fig. 1a). Noting that the observed white spheres correspond to the PCL core of the micelles, since the samples are negatively stained with PTA. After the addition of 0.1 mol/L NaSCN, the micelles remain spherical but the diameter becomes a little larger (60–70 nm) (Fig. 1b). A striped structure is observed for the PCL₆₆-*b*-

PEO₄₄ micelles when NaSCN is present in the solution. Such a structure can be attributed to intensified crystallization of the PCL block, which was also reported by Zhu *et al.* for the PCL-*b*-PEO micelles^[51]. When 0.1 mol/L NaCl or MgCl₂ is added into the PCL₆₆-*b*-PEO₄₄ aqueous solution, the micelles are a mixture of cylinders and lamellae (Figs. 1c and 1d). It seems that the lamellar micelles are formed due to growth on the one side of the cylindrical micelles. The light-white region belongs to the added inorganic salts. Most of the micelles become lamellar with irregular shapes after addition of 0.1 mol/L Na₂SO₄ (Fig. 1e). As a result, NaCl, MgCl₂ or Na₂SO₄ can trigger the “sphere-to-cylinder” or “sphere-to-lamella” morphological transformations of the PCL₆₆-*b*-PEO₄₄ semicrystalline micelles. Since cylinder is considered to be a transition morphology between sphere and lamella^[52], we believe that the effect of Na₂SO₄ on micellar morphology is stronger than that of NaCl and MgCl₂.

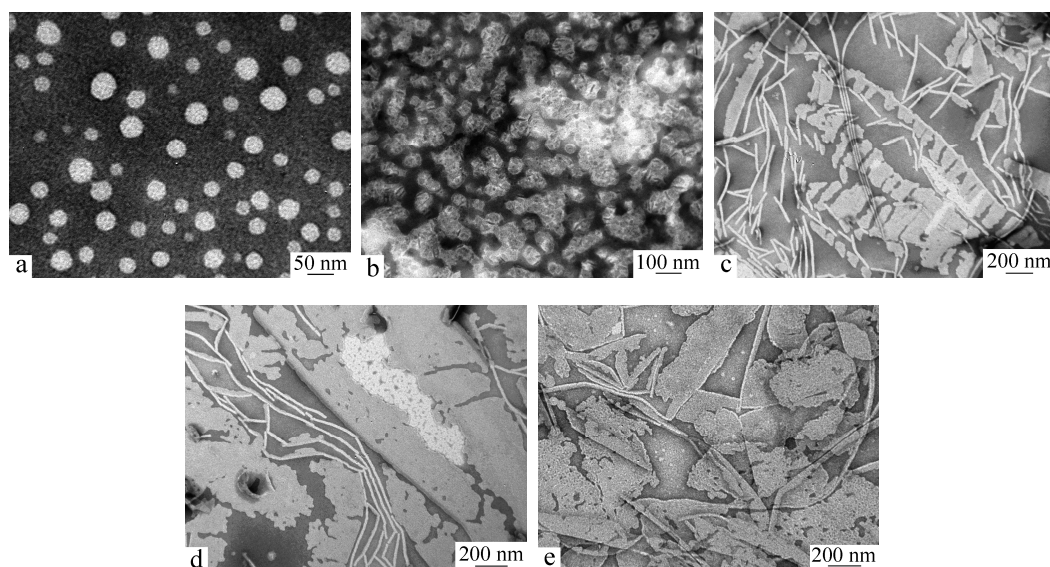


Fig. 1 TEM images of the PCL₆₆-*b*-PEO₄₄ micelles prepared from the neat aqueous solution (a) and from the solutions containing 0.1 mol/L inorganic salts: NaSCN (b), NaCl (c), MgCl₂ (d) and Na₂SO₄ (e)

The neat PCL₆₆-*b*-PEO₄₄ micellar solution and the micellar solutions containing 0.1 mol/L inorganic salts were characterized with DLS as well. Figure 2 shows the auto-correlation functions of different micellar solutions at the scattering angle of 90°. One can see that addition of inorganic salts slows down the decay of the intensity of scattering light. This means that the apparent hydrodynamic radius of the scattering particles becomes larger. However, we notice that the effects of different inorganic salts are different. The intensity of scattering light for different micellar solutions decays in the following order: Na₂SO₄ > NaCl ≈ MgCl₂ > NaSCN. Such an order is in accordance with that in the Hofmeister series^[39]. Additionally, the effect of anions is much more prominent than that of cations, since there is no significant difference for the micellar solutions containing MgCl₂ and NaCl.

The DLS data were further analyzed by fitting the intensity auto-correlation functions, $g^{(1)}(t)$. Since the neat PCL₆₆-*b*-PEO₄₄ micellar solution and the micellar solution containing 0.1 mol/L NaSCN exhibit a single exponential decay, the intensity auto-correlation functions of these two solutions are fitted with Eq. (3). By contrast, the micellar solutions containing 0.1 mol/L NaCl, MgCl₂ and Na₂SO₄ exhibit a double exponential decay and the intensity auto-correlation functions are fitted with Eq. (4). The parameters obtained by fitting are summarized in Table 1. We can see that the relaxation rate of the micelles in the NaSCN solution is smaller, as compared with that in the neat aqueous solution. This is consistent with the larger micellar size in the NaSCN solution (Figs. 1a and 1b). For the micellar solutions containing MgCl₂, NaCl and Na₂SO₄, the relaxation rate of the fast motion corresponding to the cylindrical micelles decreases gradually, while the relaxation rate of the slow motion resulting from the lamellar micelles barely changes with the inorganic salt added. The proportion of

the slow motion ($B/(A + B)$) increases gradually when the added salt changes from MgCl_2 to NaCl and then to Na_2SO_4 , implying that the micelles of larger size, *i.e.* lamellar micelles, becomes more and more. The value of $1/\gamma$, which represents the polydispersity of particle size, also increases from 5.6 for MgCl_2 to 6.7 for NaCl and to 11.2 for Na_2SO_4 , indicating that the micelles in the Na_2SO_4 solution have a broader polydispersity in the micellar size than those in NaCl and MgCl_2 solutions.

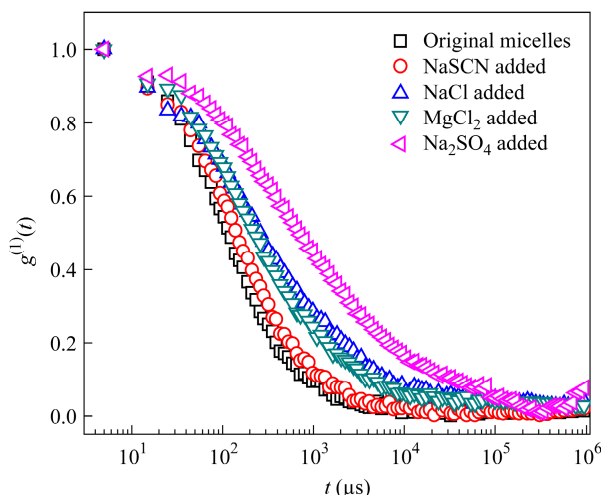


Fig. 2 The DLS auto-correlation functions, $g^{(1)}(t)$, of the neat $\text{PCL}_{66}\text{-}b\text{-PEO}_{44}$ solution and the micellar solutions containing 0.1 mol/L Na_2SO_4 , NaCl , MgCl_2 and NaSCN

Table 1. Parameters obtained by fitting the intensity correlation functions of different $\text{PCL}_{66}\text{-}b\text{-PEO}_{44}$ micellar solutions

Inorganic salt	Γ or $\Gamma_{\text{fast}}/10^3 \times \text{s}^{-1}$	$\Gamma_{\text{slow}}/10^3 \times \text{s}^{-1}$	$B/(A + B)/\%$	$1/\gamma$
—	5.78	—	—	—
NaSCN	4.43	—	—	—
MgCl_2	4.48	0.98	27	5.6
NaCl	4.03	0.98	33	6.7
Na_2SO_4	3.33	0.96	44	11.2

Kinetics for Transformation of Micellar Morphology

The TEM and DLS characterizations show that addition of inorganic salts may result in change of micellar size or transformation of micellar morphology for the $\text{PCL}_{66}\text{-}b\text{-PEO}_{44}$ semicrystalline micelles. Considering the different “salting-out” abilities of various inorganic salts, the rate of change in micellar size or morphological transformation may vary with the inorganic salt added. As a result, the micellar size after addition of inorganic salt was monitored with DLS. Figure 3 shows the distributions of the apparent micellar size (D_h^{app}) of $\text{PCL}_{66}\text{-}b\text{-PEO}_{44}$ at different times after adding the inorganic salt. It should be noted that, the DLS data are usually analyzed with CONTIN method, which can give a bimodal distribution for the solutions containing micelles of different shapes. However, the DLS data were analyzed with the quadratic method in the present work, since it gives a unimodal log-normal distribution and information of the average micellar size. It should also be pointed out that, D_h^{app} only provides an overview of the micellar size, but cannot be correlated with the real size of anisotropic cylindrical and lamellar micelles.

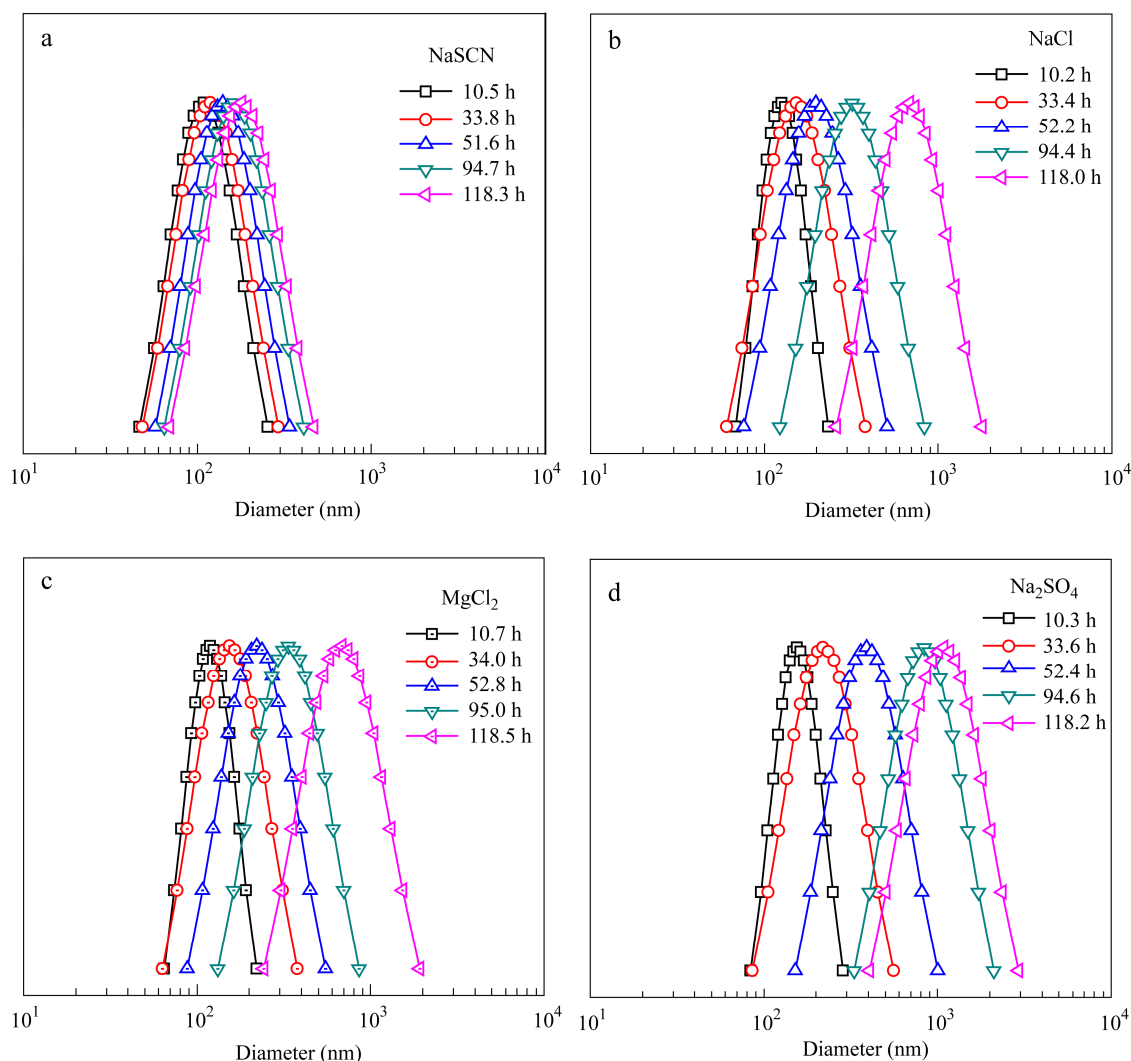


Fig. 3 Distributions of the apparent hydrodynamic diameters for the PCL₆₆-*b*-PEO₄₄ micelles in the aqueous solution at different times after addition of 0.1 mol/L inorganic salts: (a) NaSCN, (b) NaCl, (c) MgCl₂ and (d) Na₂SO₄

One can see that all inorganic salts cause increase in the average micellar size. However, at the same time scale (118 h), addition of NaSCN leads to the change of the micellar size from ~100 nm to ~180 nm. By contrast, after addition of Na₂SO₄ the micellar size changes to ~1000 nm. This shows that Na₂SO₄ causes a more rapid change of the micellar size than other inorganic salts. In order to compare the effects of different inorganic salts more clearly, the average values of D_h^{app} are further plotted versus time, as shown in Fig. 4. It is observed that, the size of the PCL₆₆-*b*-PEO₄₄ micelles in the neat aqueous solution hardly changes with time, showing the stability of the micelles. After addition of various inorganic salts, the micellar size changes gradually with time. The order for the alteration rate of the micellar size is the following: Na₂SO₄ > NaCl $\approx$ MgCl₂ > NaSCN, which is also consistent with the “salting-out” ability in the Hofmeister series.

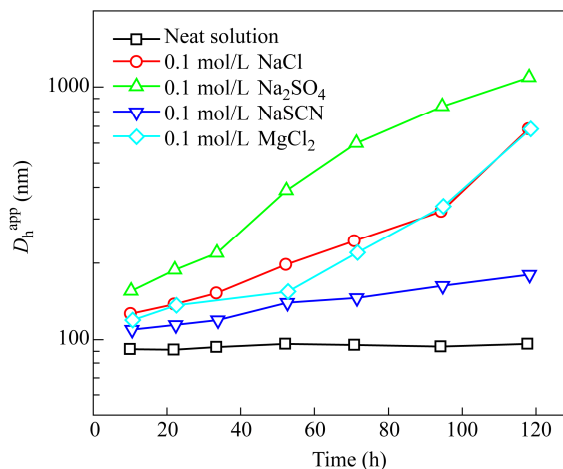


Fig. 4 Change of the apparent hydrodynamic diameter with time for the PCL₆₆-*b*-PEO₄₄ micelles in the neat aqueous solution and the solutions containing 0.1 mol/L NaSCN, NaCl, MgCl₂ and Na₂SO₄, respectively

“Salting-out” Ability of Different Inorganic Salts

The above results show that the size and morphology of the PCL₆₆-*b*-PEO₄₄ micelles in aqueous solutions vary with the inorganic salt added. The micellar size becomes slightly larger but the micellar shape remains to be spherical after addition of 0.1 mol/L NaSCN. NaCl leads to a mixture of cylindrical and lamellar micelles, while Na₂SO₄ results in predominant lamellar micelles. MgCl₂ exerts an effect similar to NaCl, showing that there is no significant difference between the cations of the inorganic salts. Because the ability of the inorganic salts affecting the micellar size and morphological transformation quite agrees with the sequence in the Hofmeister series, we interpret these results based on the “salting-out” ability of inorganic salts.

We first evaluate the “salting-out” ability of different inorganic salts using FTIR. Figure 5 shows the FTIR spectra of the mixtures of PEO homopolymer ($M_n = 5000$), water and different inorganic salts. The absorptions in the range from 1200 cm⁻¹ to 1000 cm⁻¹ are investigated, in which the spectra are deconvoluted into five bands. The absorption band around 1086 cm⁻¹ is produced by hydrogen-bonded (H-bonded) C—O—C, whereas the band located at 1108 cm⁻¹ corresponds to free C—O—C^[53]. The height ratios of the free C—O—C over the H-bonded C—O—C (H_f/H_h) for different mixtures are illustrated in Fig. 6. One can see from Fig. 6 that, the value of H_f/H_h becomes larger after addition of inorganic salts and it increases in the following order for the mixtures containing different inorganic salts: Na₂SO₄ > NaCl ≈ MgCl₂ > NaSCN. This means that more H-bonds between PEO and water molecules are formed in the neat aqueous solution of PEO. After addition of inorganic salts, H-bonds become fewer. The number of H-bond in the mixture of PEO/water/Na₂SO₄ is the smallest, whereas the H-bonds are least affected by NaSCN. The effect of inorganic salts on H-bond formation is related to their “salting-out” ability. The ions can be viewed as spheres with point charges on the surface^[38]. When the diameter of the spheres is larger, the distance between point charges and H₂O molecules is longer, thus the interaction between the ions and H₂O molecules is weaker. If the interaction between the ions and H₂O molecules is weaker than that between different H₂O molecules, the ions are named as structural breakers (or chaotropes). The ions on the right side of Cl⁻ in the Hofmeister series, such as SCN⁻, are structural breakers. By contrast, the ions on the left side of Cl⁻ in the Hofmeister series, such as SO₄²⁻, are named as structural makers (or kosmotropes), which are inclined to form hydrogen bonds with H₂O molecules, and reduce water solubility of organic solutes (“salting-out” effect). Since the anions tend to interact with water molecules, the H-bonds formed between PEO and water molecules become fewer. On the other hand, although SCN⁻ is an anion of structural breaker, the value of H_f/H_h of the PEO/water/NaSCN mixture is still slightly larger than that of the PEO/water mixture. This may be attributed to association of the cations, Na⁺ ions, with the PEO blocks, which is widely recognized^[54, 55]. The association between the Na⁺ ions and PEO can also weaken the formation of

H-bond between PEO and water to some extent, but the effect of Na^+ is not so strong as that of the anions. Because the values of H_f/H_h for the PEO/water/ NaCl and PEO/water/ MgCl_2 mixtures are similar, we tentatively draw the conclusion that different cations have no big difference in the “salting-out” ability.

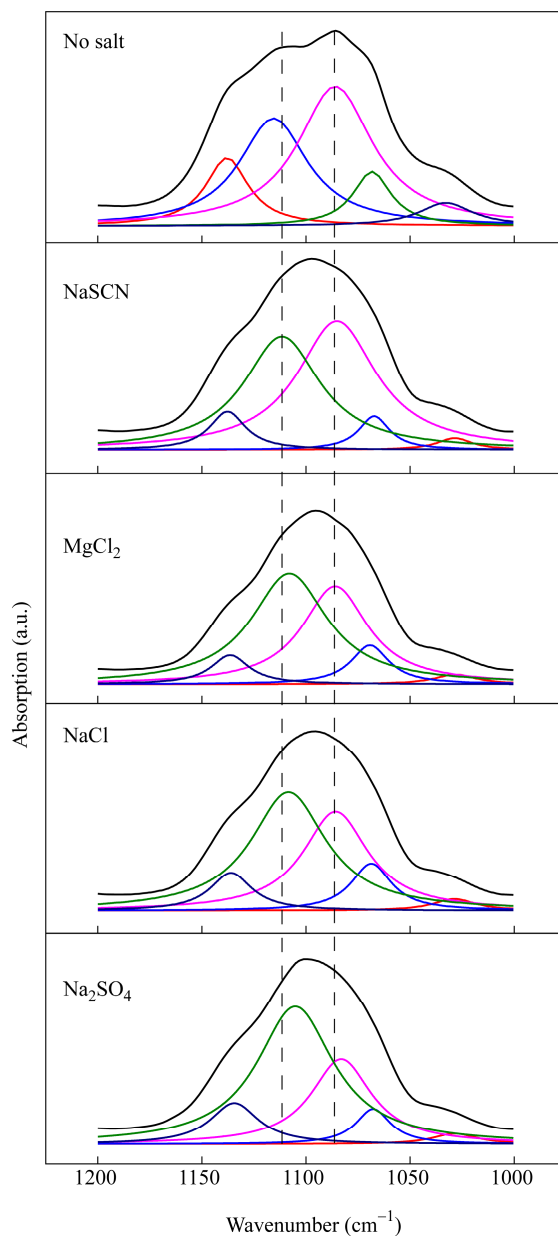


Fig. 5 FTIR spectra for the mixtures of PEO homopolymer and water with different inorganic salts

The FTIR result shows that the ability of different inorganic salts to hinder formation of H-bond decreases in the order: $\text{Na}_2\text{SO}_4 > \text{NaCl} > \text{MgCl}_2 > \text{NaSCN}$, in which the order of the anions is similar to that in the Hofmeister series. Since formation of H-bond is an indication of hydration of PEO, inorganic salts can alter the solvation degree and thus conformation of PEO in the aqueous solution. When more H-bonds (a smaller H_f/H_h) are formed between PEO and water molecules, PEO is highly solvated and has a larger coil size, *i.e.* the radius of gyration (R_g).

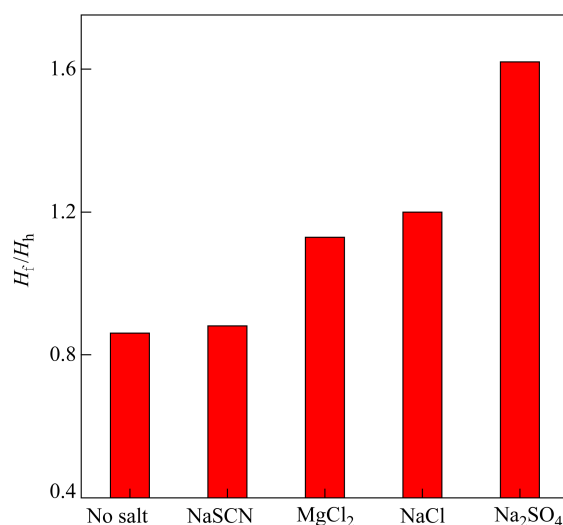


Fig. 6 Height ratios of the IR bands corresponding to free and hydrogen-bonded C—O—C in the mixtures of PEO and water with different inorganic salts

The PCL₆₆-*b*-PEO₄₄ micelles in the aqueous solution are semicrystalline. The morphology of semicrystalline micelles of BCPs is strongly dependent on the reduced tethering density ($\tilde{\sigma} = \sigma \pi R_g^2$)^[33]. A larger value of $\tilde{\sigma}$ means that the soluble blocks are crowded on the surfaces of the semicrystalline core and then tend to bend to the lateral surfaces of the crystals. We have demonstrated that, even after semicrystalline cylindrical micelles of BCPs are formed, growth of the micelles can still take place by the end-to-end coupling of different micelles^[56]. If the lateral surfaces of the semicrystalline cores are covered by the soluble blocks due to over-crowding, growth of the semicrystalline micelles may be hindered and the original micellar shape is retained. Otherwise, if the soluble blocks become less crowded, growth of the semicrystalline micelles may be triggered.

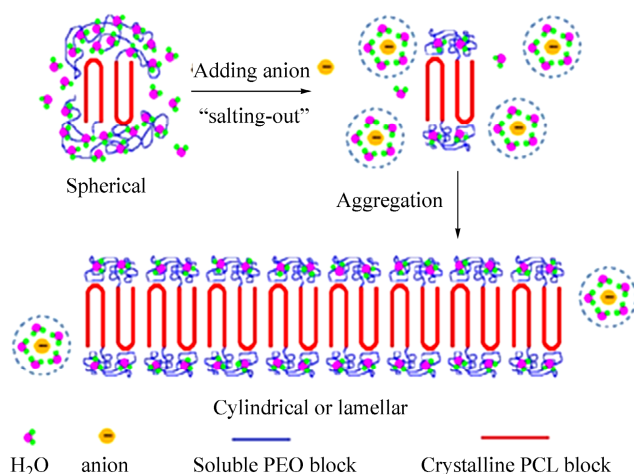


Fig. 7 Schematic mechanism for the morphological transformation of the semicrystalline PCL-*b*-PEO micelles induced by inorganic salts

Since inorganic salts can affect the solvation degree and R_g of PEO in the aqueous solution *via* the “salting-out” effect, growth of the PCL₆₆-*b*-PEO₄₄ semicrystalline micelles may take place after addition of inorganic salts. The largest H_f/H_h indicates that R_g of PEO in the Na₂SO₄ aqueous solution is the smallest. Therefore, growth of the PCL₆₆-*b*-PEO₄₄ semicrystalline micelles proceeds more easily, and it can occur simultaneously on

four different lateral surfaces of PCL crystals to form lamellar micelles. By contrast, the smaller H_l/H_h in the NaSCN solution implies that growth of the semicrystalline micelles can hardly take place. One-dimensional growth of the semicrystalline micelles on two lateral surfaces along the same direction is observed when the reduced tethering density is intermediate, such as in the NaCl and MgCl_2 aqueous solutions. The possible mechanism for the morphological transformations induced by inorganic salts is schematically illustrated in Fig. 7, which is the modification of the model we proposed previously^[35].

CONCLUSIONS

The ability of different inorganic salts driving the morphological transformation and alteration in size of the PCL₆₆-*b*-PEO₄₄ semicrystalline micelles in the aqueous solution decreases in the following order: $\text{Na}_2\text{SO}_4 > \text{NaCl} \approx \text{MgCl}_2 > \text{NaSCN}$. Such an order is in accordance with that of the anions in the Hofmeister series. The morphological transformation and size change of the micelles can be explained in terms of the “salting-out” ability of different inorganic salts. The SO_4^{2-} and Cl^- anions can dehydrate the soluble PEO blocks and lead to a smaller coil size, which drives the transformation of the micellar morphology. On the other hand, the cations may also associate with the PEO blocks, but the “salting-out” ability of the cations is relatively weak and there is no obvious difference for different cations.

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