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Effects of thiocyanate anions on switching and structure of poly(N-isopropylacrylamide) brushes*

Xin-Jun Zhao(赵新军)[1,2,†] and Zhi-Fu Gao(高志福)[3]

[1] *Xinjiang Laboratory of Phase Transitions and Microstructures of Condensed Matter Physics, Yili Normal University, Yining* 835000, *China*
[2] *Laboratory of Micro-Nano Electro Biosensors and Bionic Devices, Yili Normal University, Yining* 835000, *China*
[3] *Xinjiang Astronomical Observatory, Chinese Academy of Sciences, 150, Science* 1*-Street, Urumqi* 830011, *China*

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In this work, we investigate the effects of thiocyanate anions on the switching and the structure of poly (N-isopropylacrylamide) (PNIPAM) brushes using a molecular theory. Our model takes into consideration the PNIPAM–anion bonds, the electrostatic effects and their explicit coupling to the PNIPAM conformations. It is found that at low thiocyanate anion concentration, as the anion concentration of thiocyanate increases, thiocyanate anions are more associated with PNIPAM chains through the PNIPAM–anion bonds, which contributes to stronger electrostatic repulsion and leads to an increase of lower critical solution temperature (LCST). By analyzing the average volume fractions of PNIPAM brushes, it is found that the PNIPAM brush presents a plateau structure. Our results show that the thiocyanate anions promote phase segregation due to the PNIPAM–anion bonds and the electrostatic effect. According to our model, the reduction of LCST can be explained as follows: at high thiocyanate anion concentration, with the increase of thiocyanate concentration, more ion bindings occurring between thiocyanate anions and PNIPAM chains will result in the increase of the hydrophobicity of PNIPAM chains; when the increase of electrostatic repulsion is insufficient to overcome the hydrophobic interaction of PNIPAM chains, it will lead to the reduction of brush height and LCST at high thiocyanate anion concentration. Our theoretical results are consistent with the experimental observations, and provide a fundamental understanding of the effects of thiocyanate on the LCST of PNIPAM brushes.

Keywords: molecular theory, PNIPAM brushes, effect of thiocyanate anions

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1. Introduction

The design of stimulus responsive polymer brush has emerged as one of the most innovations in vitro and in vivo applications. As a prototype of thermally responsive polymer, Poly (N-isopropylacrylamide) (PNIPAM) has been studied extensively.[1–10] PNIPAM is particularly promising in the design of thermosensitive materials.[11–13]

It is well-established that the lower critical solution temperature (LCST) of PNIPAM is strongly affected by the addition of salt. The decrease in the LCST of PNIPAM brushes follows the Hofmeister series (Hofmeister effect).[14–18] Despite considerable efforts,[17–19] the underlying cause of this effect is still far from being understood because of the complexity of ion-specific interactions. Heyda *et al.*[20] performed a detailed study of the collapse transition occurring at the LCST of the PNIPAM induced by salts. The observed behavior of the LCST can be understood from a change of the interaction parameter of salt concentration between salts and polymers.

By applying neutron reflectometry, Murdoch *et al.*[21] investigated the influence of anion identity and temperature on the internal nanostructure of PNIPAM brushes. They found that both anionic properties and ionic strength influence the qualitative features of the profile. Experimental studies[16,18,21] show that anions can bind directly to the PNIPAM chain, while the change of LCST results from the concentration and anion identity. In experiments,[18,21,22] both the concentration and identity of anion shift the LCST of PNIPAM in solution, with thiocyanate anions raising the LCST of PNIPAM at low thiocyanate anion concentration.

Recently, the thermoresponse of PNIPAM brushes tethered on silica particles has been studied experimentally.[23] The experiment produced a number of interesting and unexpected results: (i) the conformation and structure of a PNIPAM brush is observed to vary as a function of specific ion effect; (ii) the thiocyanate anions (SCN) increase the LCST below 500 mM, though at 1000 mM the LCST is reduced. Although the influence of specific anions on the thermal response of PNIPAM brushes has been widely studied,[17–23] it is still unclear why the thiocyanate anions increase the LCST below 500 mM and reduce the LCST at 1000 mM. It is suggested that the thiocyanate anions may directly bind to the PNIPAM amide group. The thiocyanate anions have the ability to electrochemically stabilize brushes.[16,21,22] An interesting question arises: how do thiocyanate anions modulate the thermal response of PNIPAM brushes through an elec-

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†Corresponding author. E-mail: zhaoxinjunzxj@163.com

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trostatic effect? To answer this question, it is necessary to include more molecular details to appropriately describe the thiocyanate anion effects on the switching and structure of PNIPAM brushes. In this work, motivated by some intriguing experimental results,[21–23] a molecular theory[24–26] aiming at investigating the effects of thiocyanate anions on PNIPAM brush, the switches and structures is proposed. Our theory model takes PNIPAM–anion bonds and electrostatic effects into consideration, and we introduce the formation of PNIPAM–anion bonds following the ideas of Tamai, Dormidontova, Ren,[27–29] Zhang and Okur.[16,19] To explore how the PNIPAM–anion bonds and electrostatic effects influence the conformations and thermoresponse of PNIPAM brushes, we devote our efforts to expounding the mechanism of the influence of thiocyanate anions on the switching and structure of PNIPAM brushes and proposing a new design strategy for the PNIPAM brushes.

The rest of this article is organized as follows. In Section 2, the molecular theoretical model is described. In Section 3, we give the results and discuss the PNIPAM–anion bonds, their electrostatic effects and their explicit coupling with the PNIPAM conformations. Finally, in Section 4 some conclusions are drawn from the present study.

2. Molecular theoretical model

Figure 1 shows the interaction between a PNIPAM brush and thiocyanate ions by forming PNIPAM–anion bonds in potassium thiocyanate solution.

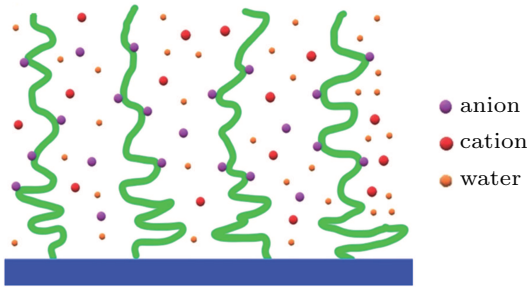


Fig. 1. Schematic diagram of proposed equilibrium interaction between PNIPAM brush and thiocyanate ions by forming PNIPAM–anion bonds in potassium thiocyanate solution.

We consider the size, shape, and conformation of each PNIPAM molecular type with an explicit inclusion of the PNIPAM–anion bonds. To build a PNIPAM brush system, we assume that the PNIPAM chains immersed in a sodium halide solution are homogeneously grafted onto the substrate surface, defined as the x–y plane at $z = 0$. The PNIPAM brush system contains $N_{\rm P}$ PNIPAM chains are tethered onto the substrate surface, which can be allowed only in the $z \geq 0$ half-space. The number of tethered chains per unit area is given as $\sigma = N_{\rm p}/A$. Each PNIPAM chain has N segments, and each segment has a volume of $v_{\rm p} = 0.16\ {\rm nm}^3$. The numbers of water molecules and anions are denoted as $N_{\rm w}$ and $N_{\rm a}$, respectively. For simplicity, we assume that the water molecules, anions (thiocyanate anions) and cations (K^+) possess the same volume of $v = 0.03\ {\rm nm}^3$, and the only inhomogeneous direction is the one perpendicular to the substrate surface, namely the z direction. The free energy per unit area of the PNIPAM brush system in a potassium thiocyanate solution has the following form:

$$\frac{\beta F}{A} = -\frac{S_{\rm p}}{k_{\rm B}A} - \frac{\sum S_i}{k_{\rm B}A} + \frac{\beta F_{\int}}{A} + \frac{\beta F_{\rm assoc}}{A} + \frac{\beta U_{\rm rep}}{A} + \frac{\beta F_{\rm e}}{A} + \frac{\beta}{A}\int [\mu_+\rho_+(z) + \mu_-\rho_-(z)]\,{\rm d}z. \tag{1}$$

The first term on the right-hang side of Eq. (1) refers to the conformational entropy of PNIPAM chains, and is given by

$$-\frac{S_{\rm p}}{k_{\rm B}A} = \sigma\sum_{\alpha} P(\alpha)\ln P(\alpha), \tag{2}$$

where $P(\alpha)$ is the probability distribution function of finding a single PNIPAM chain in the conformation α. Given a probability distribution function, we can calculate any average thermodynamical structural quantity for polymers.[26–28] The PNIPAM volume fraction profile is determined by

$$\langle\phi_{\rm p}(z)\rangle\,{\rm d}z = \sigma\sum_{\alpha} P(\alpha)v_{\rm p}(z;\alpha)\,{\rm d}z, \tag{3}$$

where $v_{\rm p}(z;\alpha)$ denotes the volume contributed by one PNIPAM chain in the conformation α between z and $z + {\rm d}z$ of the brush. The second term on the right-hand side of Eq. (1) describes the translational entropy of water molecules, anions and cations in the system,

$$\frac{-\sum S_i}{k_{\rm B}A} = \int \sum_{i={\rm w},-,+} \rho_i(z)[\ln(\rho_i(z)v_i) - 1]\,{\rm d}z, \tag{4}$$

where $\rho_i(z)$ ($i = {\rm w}, -, +$) denotes the local particle number density of the i-th species (the signs of "w", "−", and "+" are for water molecules, anions, and cations, respectively), and v_i denotes the volume of the corresponding molecule. The local volume fraction of water molecules, anions and cations are given by $\phi_i(z) = \rho_i(z)v_i$ ($i = {\rm w}, -, +$).

The third term on the right-hand side of Eq. (1) describes the effective intermolecular interaction of PNIPAM in the solution, and is expressed as

$$\frac{\beta F_{\rm int}}{A} = \frac{\chi_{\rm pw}}{v_{\rm w}}\int \langle\phi_{\rm p}(z)\rangle\phi_{\rm w}(z)\,{\rm d}z + \frac{\chi_{\rm p-}}{v_{\rm w}}\int \langle\phi_{\rm p}(z)\rangle\phi_{-}(z)\,{\rm d}z, \tag{5}$$

where the Flory interaction parameters $\chi_{\rm pw}$ and $\chi_{\rm p-}$ measure the strengths of the PNIPAM–water and PNIPAM–anion effective interactions, respectively. We consider the form of the Flory interaction parameter $\chi_{\rm pw} = A + B/T (B > 0)$, because the PNIPAM-water, hydrogen and hydrophobic interactions have been described by Refs. [28] and [29] The temperature dependence of $\chi_{\rm p-}$ obeys a standard form of $\chi_{\rm p-} =$

$A' + B'/T$. To capture the main quantitative features observed in Refs. [21] and [22], we take the following values: $A = -135$, $B = 165$, $A' = -105$, and $B' = 95$.

The fourth term on the right-hand side of Eq. (1) describes the contribution from the formation of the PNIPAM–anion bonds. When the potassium thiocyanate is added, other bonds including the amide–anion (PNIPAM–anion) and ion–ion bonds should be considered. As reported in previous studies,[16,19,24] thiocyanate anions can be combined directly with polyamide. The ion–ion pairs do not contribute to donors/acceptors, but only to the excluded volume interactions. Thus, in the potassium thiocyanate solution the PNIPAM–anion bonds should be considered, and the ion–ion bonds should be ignored. According to Ref. [29], the contribution to the free energy arising from the formation of the PNIPAM–anion bonds can be written as

$$\begin{aligned}\frac{\beta F_{\text{assoc}}}{A} &= \int \rho_{\text{p}}(z)[x_{\text{p}}(z)\ln x_{\text{p}}(z) + (1-x_{\text{p}}(z)) \\ &\quad \times \ln(1-x_{\text{p}}(z)) - x_{\text{p}}(z)\beta F_{\text{p}}]\,\text{d}z \\ &\quad + \int \rho_{-}(z)\left[1 - x_{\text{p}}(z)\frac{\rho_{\text{p}}(z)}{\rho_{-}(z)}\right] \\ &\quad \times \ln\left[1 - x_{\text{p}}(z)\frac{\rho_{\text{p}}(z)}{\rho_{-}(z)}\right]\text{d}z \\ &\quad - \int \rho_{\text{p}}(z)\ln[\frac{\rho_{-}(z)v_{-}}{e}]\,\text{d}z, \end{aligned} \tag{6}$$

where F_{p} is the free energy gain from the single PNIPAM–anion bond formation, which includes the energetic gain and entropic loss: $-\beta F_{\text{p}} = \beta E_{\text{p}} - \Delta S_{\text{p}}$,[29] E_{p} is the binding energy of a donor-acceptor pair, and ΔS_{p} is the entropic loss. However, the corresponding experimental data of the binding energy and entropic loss have not been found yet. Thus, we choose $E_{\text{p}}/k_{\text{B}} = 1485$ K for the binding energy, and $\Delta S_{\text{p}} = -27$ (J·K^{-1}·mol^{-1}) for the entropic loss, both of which are consistent with the experimental observations.[21,22] It is worth noting that the PNIPAM–anion bonds depend on the free energy, F_{p}, which determines the formation of PNIPAM–anion bonds at a fixed temperature. In Eq. (6), the variable $x_{\text{p}}(z)$ is the local fraction of the PNIPAM–anion bonds, defined as

$$x_{\text{p}}(z) = \frac{n_{\text{p}}(z)}{N_{\text{p}}(z)N}, \tag{7}$$

where $n_{\text{p}}(z)$ and $N_{\text{p}}(z)$ are the number of position-dependent PNIPAM–anion bonds and the number of PNIPAM chains, respectively. When the PNIPAM–anion bonds between PNIPAM molecules and anions are formed, with the increase of thiocyanate anion concentration, the formation of the PNIPAM–anion bonds is more favorable, which makes the PNIPAM chains charged (as shown in Fig. 1(a)). That is to say, the fraction of charged PNIPAM segments increases with the increase of a variable $x_{\text{p}}(z)$. By combining the PNIPAM–anion bonds, it is necessary to introduce an effective interaction parameter χ_{eff}, given by

$$\chi_{\text{eff}} = \chi_{\text{p}-} - \left[x_0\frac{v_{-}}{v_{\text{p}}} + x_0^2\left(\frac{v_{-}}{v_{\text{p}}}\right)^2\right], \tag{8}$$

where x_0 describes the association between the PNIPAM–anion bonds.[28] We will assume that x_0 is proportional to thiocyanate anion concentration and $x_0 = k_0 C/T$. To capture main qualitative features observed in PNIPAM brushes,[21,22] the corresponding proportional parameter is taken as $k_0 = 0.55$, and another important parameter $\chi_{\text{p}-}$ can be replaced by χ_{eff}. The fifth term on the right-hand side of Eq. (1) represents the repulsive interaction of the system, which is given by

$$\frac{\beta U_{\text{rep}}}{A} = \int \beta\pi(z)[\langle\phi_{\text{p}}(z)\rangle + \sum_{i=\text{w},-,+}\rho_i(z)v_i]\,\text{d}z. \tag{9}$$

Here $\pi(z)$ is the position-dependent repulsive interaction field, which is determined by the packing constraints,

$$\langle\phi_{\text{p}}(z)\rangle + \sum_{i=\text{w},-,+}\rho_i(z)\,v_i = 1. \tag{10}$$

The last term of Eq. (1) is the electrostatic contribution to the free energy,

$$\begin{aligned}\frac{\beta F_{\text{e}}}{A} &= \int\left[\langle\rho_{\text{q}}(z)\rangle\beta\psi(z) - \frac{1}{2}\beta\varepsilon\left(\frac{\partial\psi}{\partial z}\right)^2\right. \\ &\quad \left. + \lambda\langle\rho_{\text{q}}(z)\rangle\right]\text{d}z, \end{aligned} \tag{11}$$

where ε is the dielectric constant of the solution, $\psi(z)$ is the strongly coupled electrostatic potential, and $\langle\rho_{\text{q}}(z)\rangle$ is the total average charge density, and thus we have

$$\langle\rho_{\text{q}}(z)\rangle = x_{\text{p}}(z)\frac{\langle\phi_{\text{p}}(z)\rangle}{v_{\text{p}}}q_{\text{p}} + \sum_{\gamma=-,+}\rho_\gamma(z)q_\gamma, \tag{12}$$

where the quantity $q_{\text{p}} = -e$ represents the charge associated with polymer chains by the PNIPAM–anion bonds, while $q_\gamma = \mp e$ ($\gamma = -,+$) denote the charge of anions and cations, respectively. We require the system to be globally electroneutral, that is

$$\int\langle\rho_{\text{q}}(z)\rangle\,\text{d}z = 0. \tag{13}$$

The quantity of μ_{-} and μ_{+} in the sixth term of Eq. (1) represents the chemical potential of anions and cations, respectively. Minimization of the free energy with respect to $P(\alpha)$ yields

$$\begin{aligned}P(\alpha) &= \frac{1}{Q}\exp\left\{-\frac{\chi_{\text{pw}}}{v_{\text{w}}}\int\phi_{\text{w}}(z)n(\alpha;z)v_{\text{p}}\,\text{d}z\right. \\ &\quad -\frac{\chi_{\text{eff}}}{v_{-}}\int\phi_{-}(z)n(\alpha;z)v_{\text{p}}\,\text{d}z \\ &\quad -\int n(\alpha;z)\ln(1-x_{\text{p}}(z))\,\text{d}z - \beta\int\pi(z)n(\alpha;z)v_{\text{p}}\,\text{d}z \\ &\quad \left.-\beta\int\psi(z)q_{\text{p}}n(\alpha;z)\,\text{d}z\right\}, \end{aligned} \tag{14}$$

where Q is a normalization constant ensuring that $\sum_\alpha P_i(\alpha) = 1$, and $n_i(\alpha;z)$ is the number of monomers in unit volume for a chain in the conformation α. The volume fraction of water molecules, $\phi_w(z)$, is related to the repulsive interaction field $\pi(z)$, and is written as

$$\phi_w(z) = \exp[-\beta\pi(z)v_w], \tag{15}$$

while the volume fraction of anions and cations, associated with both the field $\pi(z)$ and the potential $\psi(z)$, are determined by

$$\phi_-(z) = \phi_{\text{bulk},-}\exp\left[-\beta\pi(z)v_- - \ln(1-x_p(z)) - \ln\left(1-\frac{x_p(z)}{\rho_-(z)}\right)+\beta\psi(z)e\right], \tag{16}$$

and

$$\phi_+(z) = \phi_{\text{bulk},+}\exp[-\beta\pi(z)v_+ - \beta\psi(z)e], \tag{17}$$

respectively. The bulk values of ions can be obtained from their concentrations $\phi_{\text{bulk},\mp} = c_\mp N_a v_\mp$. The quantity $x_p(z)$ is given by

$$x_p(z) = \exp(\beta F_p + \beta\psi(z)e)(1-x_p(z))(1-\phi_p(z)) \times\left(1-x_p(z)\frac{\rho_p(z)}{\rho_-(z)}\right). \tag{18}$$

According to this equation, the average fraction of different bonds related to the species densities offers donors or acceptors. Therefore, the densities of different species for PNIPAM–potassium thiocyanate solutions and the average fraction of PNIPAM–anion bonds are non-linearly coupled. For the electrostatic potential, we obtain a generalized Poisson–Boltzmann equation

$$\frac{\partial^2\psi}{\partial z^2} = -\frac{1}{\varepsilon}\langle\rho_q(z)\rangle, \tag{19}$$

where $\langle\rho_q(z)\rangle$ is given by Eq. (3), and the density and PDF depend on the strongly coupled electrostatic potential $\psi(z)$ and the field $\pi(z)$. The unknowns in equations above are the position-dependent PNIPAM–anion bond $x_p(z)$, the potential $\psi(z)$ and the field $\pi(z)$. These quantities are obtained by substituting Eqs. (14)–(19) into the packing constraints of Eq. (10) and Eq. (13). A detailed numerical methodology can be found in Refs. [24], [26], and [29].

3. Results and discussion

In this section, we present some representative results of thiocyanate anions and electrostatic effects on the switching and structure of PNIPAM brushes. To begin, we analyze the heights of the grafted PNIPAM brushes, which is a function of temperature, at different thiocyanate anion concentrations.

The height of the grafted PNIPAM brush is defined as $H = \int\langle\phi_p(z)\rangle z\,dz/\int\langle\phi_p(z)\rangle\,dz$, which measures the stretch of the grafted PNIPAM chain. Figure 2 shows the plots of temperature-dependent height of the grafted PNIPAM brushes. As shown in Fig. 2, the height decreases with the increase of temperature in pure water, in each of 10-mM, 100-mM, 250-mM potassium thiocyanate solutions, respectively, indicating that the grafted PNIPAM brushes collapse as temperature increases, and the LCST at $H \approx 12$ nm is available. The LCST shifts from ~ 33 °C in the 10-mM potassium thiocyanate solution to ~ 35 °C in the 250-mM potassium thiocyanate solution, which are consistent with the experimental results.[22] In previous experiments,[21,22] it was reported that the PNIPAM chains did collapse rapidly with the increase of temperature, revealing the anion-dependent behavior of thiocyanates. It is obvious that the collapse and expansion thickness of the PNIPAM brushes are affected by the added thiocyanate anions. Interestingly, the presence of the added thiocyanate anions did not appear to change the rate of the hydration transition.[21] The thiocyanate anions were found to be directly associated with the amide group of PNIPAM by PNIPAM–anion bonds.[16,22,23] Because of different concentrations of thiocyanates associated with the formation of a single PNIPAM–anion bond, the direct contact of thiocyanate anions and PNIPAM chains in the brush can result in electrostatic repulsion between the inside and the adjacent chains and lead to the observed thiocyanate anion concentrations dependent on the switching of the brush.

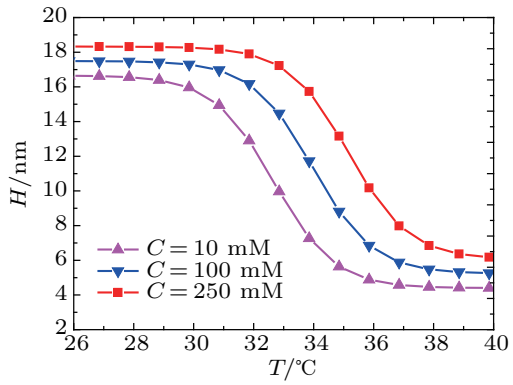


Fig. 2. Plots of height of grafted PNIPAM brush *versus* temperature at three different thiocyanate anion concentrations. Molecular weight of polymer chains is $M_w = 22500\ \text{g}\cdot\text{mol}^{-1}$, and the surface coverage is $\sigma = 0.5\ \text{nm}^{-2}$.

It is worth stressing here that the molecular weight ($M_w = 22500$ g/mol) chosen here is smaller than the experimental results ($M_w > 90000$ g/mol),[22] due to the limitation of theoretical calculations. The experiments[30,31] also demonstrated that the LCST of PNIPAM is independent of molecular weight. The molecular weight chosen here is thus sufficient to describe the shift of LCST of PNIPAM brushes in the potassium thiocyanate solution, which helps us to understand its physical origin. To better understand the origin of this behavior,

we calculate the electrostatic potential $\beta\psi(z)$ and make plots of $\beta\psi(z)$ *versus* z (the distance from the surface) at different thiocyanate anion concentrations under a given temperature as shown in Fig. 3.

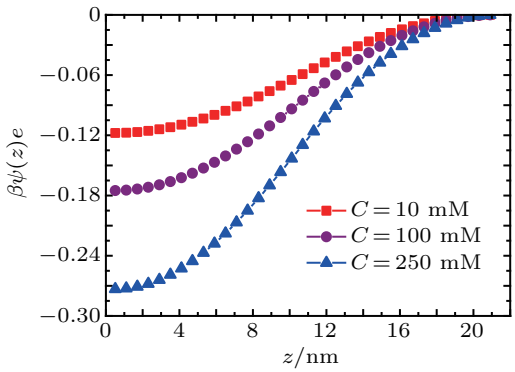


Fig. 3. Plots of electrostatic potential *versus* distance from the surface at different thiocyanate anion concentrations under given temperature of $T = 34$ °C. Remaining parameters are the same as those in Fig. 2.

The electrostatic potential of the complex is negative and decreases as the concentration of thiocyanate anion increases. The negative electrostatic potential in the PNIPAM brush implies an electrostatic repulsion between the negatively charged PNIPAM segments. The insertion of charged monomers into a varying electrostatic potential is thus energetically unfavorable. With the increase of thiocyanate anion concentration, the bounding degree of PNIPAM–anion bonds increases significantly, and the PNIPAM becomes more negatively charged. The electrostatic repulsions will overcome the elastic energy of PNIPAM, causing the polymer chain to stretch.

From Fig. 3, the electrostatic potential shows a tendency to decrease as thiocyanate anion concentration increases. In a low salt concentration region, with the increase of thiocyanate anion concentration, the thiocyanate anions and PNIPAM chains are more associated through PNIPAM–anion bonds, which will result in larger magnitude of the electrostatic potential in the brush layer, and contribute to a stronger electrostatic repulsion, making the polymer chain stretch.

The fraction of PNIPAM–anion bonds depends on the thiocyanate anion concentration. Figure 4 shows that the fraction of PNIPAM–anion bonds first increases slightly, and then increases abruptly with the increase of thiocyanate anion concentration, implying that the PNIPAM chain switching depends on the thiocyanate anion concentration. The main reasons for these changes are explained as follows. The initial increase in thiocyanate anion concentration is linked to the formation of PNIPAM–anion bonds, and thiocyanate anions are bound up with PNIPAM chains through PNIPAM–anion bonds. The local fraction density of PNIPAM–anion bonds in PNIPAM brushes increases with thiocyanate anion concentration increasing. This in turn increases the probability of PNIPAM–anion bonding. The increase of PNIPAM–anion bonds leads to the adsorption of thiocyanate anion into the PNIPAM chains, where electrostatic repulsion within brushes is produced. With the increase in the thiocyanate anion concentration, the increase of the PNIPAM–anion bonds leads to a gain in free energy, which is balanced by the loss of conformational entropy of the chain (due to the stretch of the chain) and the increase of intermolecular repulsion. The stretch of PNIPAM further enhances the PNIPAM–anion bonding association. According to this analysis, the larger value of $x_{\mathrm{p}}(z)$ will be expected. As thiocyanate anion concentration increases, there are more thiocyanate anions that can be adsorbed into the grafted chains, and the mole fraction of thiocyanate anions adsorbed within brushes will increase, which implies that the thermoresponse of PNIPAM brushes will be modulated by the thiocyanate anion concentration.

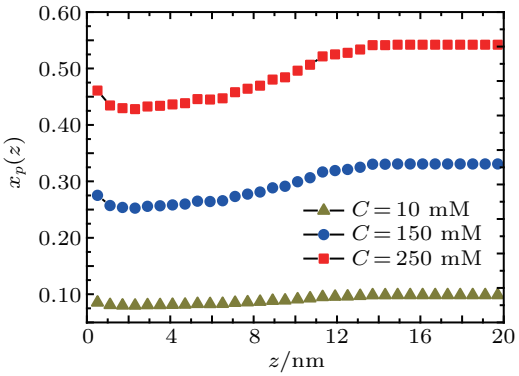


Fig. 4. Plots of local fraction of PNIPAM–anion at different thiocyanate anion concentrations under given temperature of $T = 34$ °C. Remaining parameters are the same as those in Fig. 2.

Our predictions can be verified by recent experiments.[21,22] The thermoresponse of PNIPAM brushes regulated by thiocyanate anions is the direct consequence of the adsorption–desorption equilibrium of thiocyanate anions within the brushes. Murdoch *et al.*[21] and Humphreys *et al.*[22] also noted that thiocyanate anions have specific effects on the internal structure of PNIPAM brushes.

Figure 5 shows the distribution of tethered PNIPAM segments near the critical temperature. The volume fractions of PNIPAM brushes for two different thiocyanate anion concentrations are presented in Figs. 5(a) and 5(b), respectively. An interesting result in Fig. 5 is a plateau of volume fractions (at $z = 8$ nm for $C = 100$ mM and $C = 250$ mM, respectively), which corresponds to a collapsed structure including a distance from the substrate surface. At the same temperature, the addition of thiocyanate anion can result in relatively swollen structure. In Fig. 5, a relatively swollen phase is present at a temperature as low as 32 °C in the 250-mM potassium thiocyanate, while it is only present at 30 °C in the 100-mM potassium thiocyanate. The vertical phase separation occurs at 34 °C in the 250-mM potassium thiocyanate. However, there is a dense interior layer near the substrate followed by a dilute tail at 32 °C in the 100-mM potassium thiocyanate, which means that a vertical phase separation occurs. This matches

previous studies on ellipsometry.[22] The profiles corresponding to $T = 34$ °C in Fig. 5(b) are different from those corresponding to other temperatures in Fig. 5(a). This result indicates that thiocyanate anions promote the phase segregation of PNIPAM brushes, due to the PNIPAM–anion bonds and electrostatic effect. This effect could be caused by the increase in the fraction of charged PNIPAM segments. Clearly, the nanostructure of these brushes is affected by the thiocyanate anion concentration. The transition of LCST in PNIPAM brushes can be caused by the limited concentration of thiocyanate anion, which can be seen from the increase of the thickness of the first moment as shown in Fig. 2. The plateau value of brush thickness is seen in Fig. 2. At low temperatures, it is suggested that the total transition occurs within a certain range of temperature, because the capacity of thiocyanate to bind directly with the monomer results in electrostatic stabilization of the collapsed brushes. This is similar to the vertical phase segregation induced by dipolar interactions.[32]

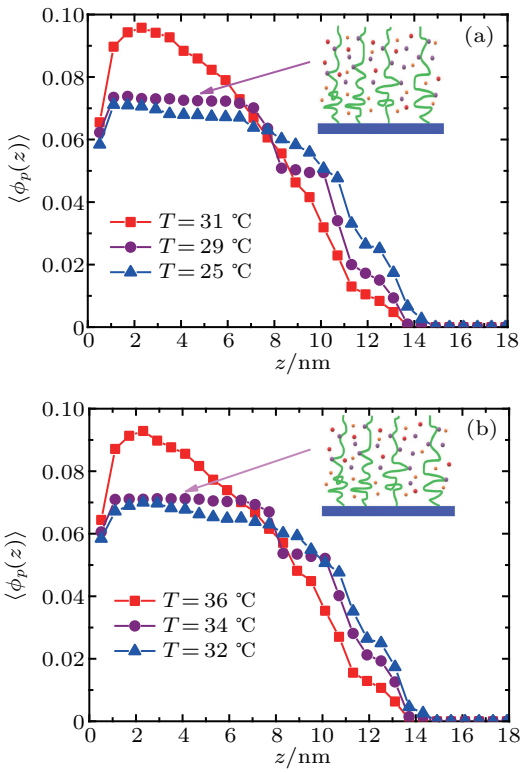


Fig. 5. Plots of average volume fraction of the grafted chains *versus* distance from surface for thiocyanate anion concentration: (a) $C = 100$ mM and (b) $C = 250$ mM. Remaining parameters are the same as those in Fig. 2.

The experiment performed by Humphreys *et al.*[23] demonstrated that the LCST of PNIPAM brushes is reduced when the thiocyanate anion concentration is at 1000 mM.

At higher thiocyanate anion concentrations, a quantitative comparison of these profiles can be made by considering the average brush thickness, and the LCST shifts from ~ 32.5 °C in the 600-mM potassium thiocyanate solution to ~ 28.5 °C in the 1000-mM potassium thiocyanate solution as shown in Fig. 6. This is different from the behavior of PNIPAM brushes with lower thiocyanate anion concentration as demonstrated in Fig. 2. The main reason for the change in Fig. 2 is as follows. At the initial stage, lower thiocyanate anion concentrations are related to the formation of PNIPAM–anion bonds, and the thiocyanate anions are bound up in the PMIPAM through PNIPAM–anion bonds, then the increased PNIPAM–anion bonds lead to electrostatic repulsion along the chains, and the LCST and height of brushes increase when the thiocyanate anion concentration increases (see Fig. 2).

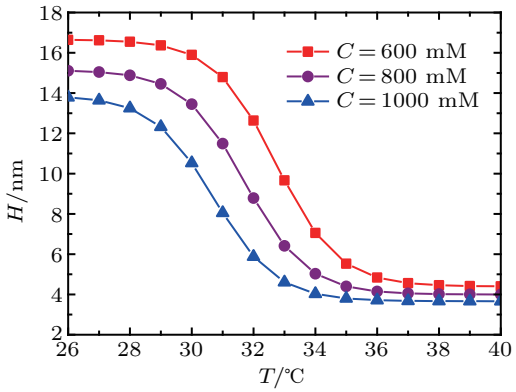


Fig. 6. Plots of height of the grafted PNIPAM brushes *versus* temperature at different thiocyanate anion concentrations. Remaining parameters are the same as those in Fig. 2.

For both cases of 800-mM and 1000-mM thiocyanates, the temperatures, at which the plateau thickness is reached (at high or low T), are much higher than the LCST value observed in Fig. 2. For the highest thiocyanate concentration, the transition near the plateau is broader and more gradual than that for the lower thiocyanate anion concentration. This proves that the behavior of thiocyanate anions at higher thiocyanate anion concentration is different from that at lower thiocyanate anion concentration, due to their different mechanisms.

It is worth mentioning here that the potassium thiocyanate should be added to the bulk solution, whether the thiocyanate anion increases or decreases. The increase and decrease of the thiocyanate anion are accompanied with an increase in concentration of K^+ cations considered as counterions in this study. The counterions will generate entropic pressure, which can induce the collapse of PNIPAM brushes. The counterion-mediated attractive interactions along a single chain can also cause the chain concentration to collapse. As the relative thiocyanate anion concentration exceeds $C = 500$ mM, the PNIPAM–anion bonds are filled. As the thiocyanate anion concentration increases, the electrostatic screening within the brush and counterion-mediated attractive interactions along the chain will be caused, and thus the brush height and LCST will be reduced. This indicates that the ability to form the PNIPAM–anion bonds would be affected, leading to the electrostatic screening caused by a high potassium thiocyanate concentration, and PNIPAM brush will collapse slightly as

thiocyanate anion concentration increases. By comparing Fig. 2 with Fig. 6, we find that thiocyanate anions have a significant effect on the temperature switching between collapsed and swollen profile. To understand the origin of this behavior, we investigate the variation in PNIPAM–anion bond fraction at higher thiocyanate anion concentration.

Diagrams of local fraction of PNIPAM–anion bonds as a function of the distance from the surface at higher thiocyanate anion concentrations are given in Fig. 7. We can see that the average fraction of PNIPAM–anion bonds increases slightly with thiocyanate anion concentration increasing. As the salt concentration increases, more thiocyanate anion counterions will bind to the PNIPAM chains through the PNIPAM–anion bonds, thus increasing the PNIPAM–anion bonds as the thiocyanate anion concentration increases. As the thiocyanate anion concentration exceeds 50 mM, the increase of the PNIPAM–anion bonds leads to the gain in free energy. The additional free energy loss further hinders PNIPAM–anion association. A small increase in the local fraction of PNIPAM–anion bonds found in thiocyanate anion $C = 1000$ mM strongly suggests that the PNIPAM–anion bonds have been filled.

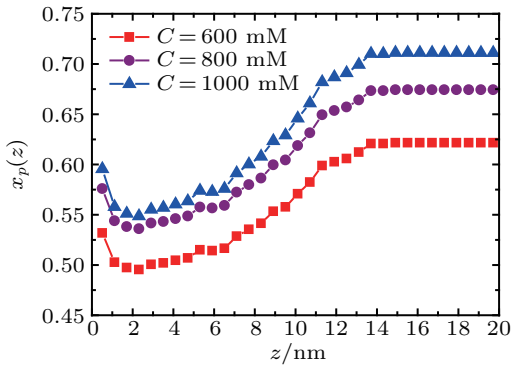


Fig. 7. Plots of local fraction of PNIPAM–anion bonds *versus* distance from surface at different thiocyanate anion concentrations under temperature of $T = 32$ °C. Remaining parameters are the same as those in Fig. 2.

To clarify the charge behavior of PNIPAM brushes at higher thiocyanate anion concentrations, we calculate the values of electrostatic potentials inside the PNIPAM brushes with different thiocyanate anion concentrations as shown in Fig. 8. It should be stressed that all the charged species in the solution contribute to electrostatic potentials. The electrostatic potential of the complex displays both negative and positive value. In the high thiocyanate anion concentration region, with the increase of thiocyanate concentration, the PNIPAM–anion bonds have been filled, which will result in smaller increase in the electrostatic potential within the brush. Thiocyanate anion is highly polarisable and weakly hydrated.[21] Theoretical studies[32] have revealed that the hydration is changed by forming the PNIPAM–anion bonds. Since more ion bindings occur between the thiocyanate anions and the amide moieties along the PNIPAM chains, the presence of thiocyanate can change the rate of the hydration transition, which will result in increasing the hydrophobicity of the PNIPAM chains. Consequently, the electrostatic repulsion is insufficient to overcome the hydrophobic interaction of PNIPAM chains. This leads to a decrease of the brush height and LCST at higher thiocyanate anion concentrations. The temperature response of the PNIPAM brushes is weakened with the increase of thiocyanate anion concentration. This behavior is qualitatively consistent with the experimental observations made by Humphreys *et al.*,[23] which showed that the LCST is reduced ($\Delta T \approx -1$ °C) at $C = 1000$ mM. However, we cannot make a quantitative comparison between our results and the experiments. The PNIPAMs that are tethered to different curvatures or planar surfaces exhibit qualitatively similar behaviors, but their behaviors may differ in quantity.

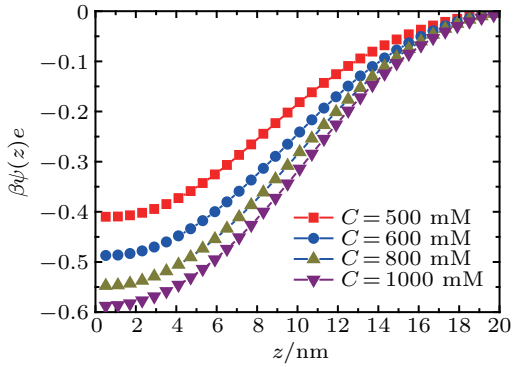


Fig. 8. Plots of electrostatic potential *versus* distance from surface for different thiocyanate anion concentrations at a temperature of $T = 32$ °C. Remaining parameters are the same as those in Fig. 2.

4. Summary and conclusions

In this work, we have employed a molecular theory to study the effect of thiocyanate anions on the switching and structure of PNIPAM brushes. In our model, we take into consideration the PNIPAM–anion bonds and electrostatic effects, and their explicit coupling to the PNIPAM conformations. We first investigate the switching behavior of PNIPAM brushes as a function of temperature at low thiocyanate anion concentrations. Our results show that the LCST shifts from ~ 33 °C in a 10-mM potassium thiocyanate solution to ~ 35 °C in a 250-mM potassium thiocyanate solution. Then, we explore the electrostatic potential and the distribution of local fraction of PNIPAM–anion bonds, and find that as the thiocyanate anion concentration increases, more thiocyanate anions are linked to the PNIPAM chains by PNIPAM–anion bonds, which contributes to a stronger electrostatic repulsion and leads to an increased LCST. Finally, by analyzing the distribution of PNIPAM segments near the critical temperature, we find a structure of plateau shown in the tethered PNIPAM segments, indicating that the thiocyanate anion promotes the phase segregation due to the PNIPAM–anion bonds and electrostatic effects.

The experimental investigations suggest that thiocyanate anions (SCN^-) reduce the LCST at 1000 mM.[18,21] According to our model, the reduced LCST at 1000 mM can be a direct consequence of the increasing hydrophobicity of PNIPAM chains together with filled PNIPAM–anion bonds. In particular, the experimental and theoretical studies[16,32] revealed that hydration is changed by the addition of salt ions.

It is worth mentioning that in the present model, we only consider the PNIPAM–anion bonds and electrostatic effects on the shift of solubility of PNIPAM brushes in potassium thiocyanate solutions. However, in reality, there are additional bonds (including ion–ion bonds) and additional interaction between K^+ and amide.[19] Earlier researchers also suggested that the anions play a critical role in the conformational transitions for the LCST of PNIPAM.[16,33–37] Therefore, we believe that the specific thiocyanate anion effect on the LCST behavior of PNIPAM brushes in the potassium thiocyanate solution is captured by our approach to considering the PNIPAM–anion bonds and electrostatic effects. Our theoretical results accord well with the experimental observations,[21,22] suggesting that the PNIPAM–anion bonds and electrostatic effects may become key elements inducing the shift of LCST of PNIPAM by thiocyanate anions.

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