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Micellar and surface properties of a poly(methyl methacrylate)–block–poly(*N*-isopropylacrylamide) copolymer in aqueous solution

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Abstract

Critical micelle concentrations (cmc) of aqueous solutions of poly(methyl methacrylate)–block–poly(*N*-isopropylacrylamide) were determined at several temperatures by surface tensiometry. Below the lower critical solution temperature (LCST), the low $\Delta_{\text{mic}}H^0$ determined can be assigned to the PMMA block being tightly coiled in the dispersed molecular state, so that the unfavorable interactions of hydrophobic entities with water are minimized. Above the LCST the cmc value was found to increase; an anomalous behavior that can be directly related to the micelle–globule transition of the hydrophilic block. Interestingly, above the LCST the surface tension of relatively concentrated solutions was found to depend weakly on temperature not following the usual strong decrease with temperature expected for aqueous solutions.

Keywords: Critical micelle concentration; Surface properties; Thermoresponsive aggregation

1. Introduction

The self assembly properties of aqueous solutions of poly(*N*-isopropylacrylamide) (PNIPAm) based systems have received substantial attention mainly due to their potential applications in a number of fields including the development of novel drug carriers [1–3], cell culture [4], smart hydrogels [5–9] and colloidal photonic crystals [10]. One of the most characteristic properties of PNIPAm is its multi responsive nature to external stimuli such as pH, ionic strength and temperature. In aqueous environment, PNIPAm exhibits a typical lower critical solution temperature (LCST) behavior, undergoing coil–globule transition [11] at 31 °C, e.g., near human body temperature. The incorporation of comonomers to the PNIPAm backbone can modify the LCST of the resulting copolymer [12,13].

Double hydrophilic PNIPAM/PEO [PEO = poly(ethylene oxide)] and PNIPAm/DMA [DMA = poly(*N*,*N*-dimethylacrylamide)] block copolymers with various architectures can self-organize in water to form PNIPAm core aggregates [3,14–19]. On the other hand, PNIPAm can be combined with highly hydrophobic blocks such as polystyrene [1] (PSt), poly(D,L-lactide) (PLA) [2], poly(butyl methacrylate) [12], polyphosphazene [13] (PPP), poly[*N*-(2-hydroxypropyl)methacrylamide)] (PHPMA) [20], poly(4-vinylpyridine) (P4VP) [21], poly(2-(diethylamino)ethyl methacrylate) (PDEA) [22]. These copolymers micellize in aqueous solutions to form PNIPAm corona particles; while syneresis takes place above the LCST. In certain double responsive systems, core–shell inversion can be achieved from PNIPAm–core to PNIPAm–corona particles and vice versa solely by modifying the external conditions (pH, temperature) [21–23].

The thermoresponsive aggregation of PMMA–*b*–PNIPAm [PMMA = poly(methyl methacrylate)] copolymers in aqueous solution has been recently investigated together with the formation of hydrogels at high concentrations [10]. In this report we focus on the surface properties, the critical micelle concentration (cmc) and the thermodynamics of micellization of

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a PMMA–*b*–PNIPAM copolymer synthesized by reversible addition fragmentation chain transfer (RAFT) polymerization.

2. Experimental

2.1. Material

RAFT polymerization was used to prepare the PMMA–*b*–PNIPAM copolymer considered here. The synthetic procedure followed and the characterization by ^{1}H and ^{13}C NMR and GPC (calibrated with poly(styrene) standards) has been reported in detail elsewhere [10]. The number average molecular weight (M_n) was determined to be $M_n = 21.2 \times 10^3$ g/mol, the weight percentage of PMMA $f_{\text{PMMA}} = 7.8$ and the polydispersity index (PDI) was $M_w/M_n = 1.21$. In a rough approximation each copolymer molecule consists of 16 repeating units of MMA and 170 NIPAm units.

2.2. Dynamic light scattering (DLS)

Dynamic light scattering (DLS) measurements were carried out on well filtered 0.5 wt% solutions by means of an ALV/CGS-3 Compact Goniometer System with ALV/LSE-5003 correlator using vertically polarized incident light of wavelength $\lambda = 632.8$ nm. Measurements were performed at angle $\theta = 90°$ to the incident beam and data were collected three times for 30 s. The correlation functions (DLS) were analyzed by the constrained regularized CONTIN method [24] to obtain distributions of decay rates (Γ), hence distributions of apparent mutual diffusion coefficient $D_{\text{app}} = \Gamma/q2$ [$q = (4\pi n/\lambda)\sin(\theta/2)$, where n is the refractive index of the solvent], and ultimately of apparent hydrodynamic radius of the particle via the Stokes–Einstein equation

$$r_{h,\text{app}} = kT/(6\pi\eta D_{\text{app}}), \tag{1}$$

where k is the Boltzmann constant and η is the viscosity of the solvent at temperature T.

2.3. Surface tension (γ)

Surface tension (γ) of aqueous solutions was measured by detachment of a platinum ring. Measurements were performed by means of two different devices; surface tensiometers Kruss, Model K8600 and model K-12. Both devices were well protected from vibrations and draughts and the temperature was controlled with an accuracy ±0.2 °C. The accuracy of the measurement was checked by frequent determinations of the surface tension of pure water. Copolymer solutions in deionized and doubly distilled water were made by dilution of a stock solution. Two different experimental protocols were used: (i) temperature ramps at a given concentration, with a temperature step of 5 °C and (ii) concentration sweeps at constant temperatures (5 and 25 °C). For the temperature ramp experiments, a new solution was first equilibrated at the lowest temperature (5 °C) for 24 h and then γ was measured every 1 h until consistent readings were obtained. Thereafter, the temperature was raised and the procedure was repeated. For the concentration sweep experiments, γ of the most concentrated solution was measured first and then diluted incrementally.

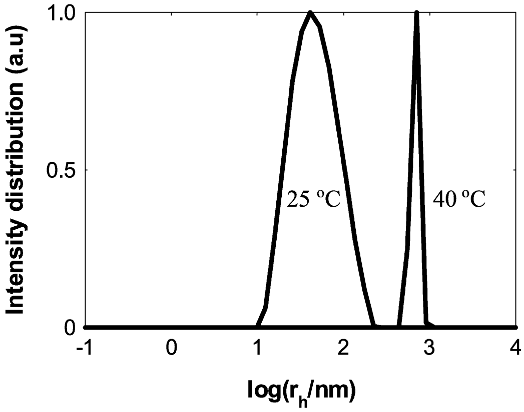

Fig. 1. Normalized intensity distribution of the logarithm of apparent hydrodynamic radius for 5 g/dm^3 aqueous solutions of PMMA–*b*–PNIPAm at temperatures indicated.

3. Results and discussion

3.1. Dynamic light scattering (DLS)

The formation of micelles in 5 g/dm^3 PMMA–*b*–PNIPAm aqueous solutions was checked by DLS. The intensity distribution of the logarithm of apparent hydrodynamic radius at two temperatures is shown in Fig. 1. The wide distribution of micellar size at 25 °C possibly indicates deviation to some extent from the closed association model. The apparent hydrodynamic radius (r_h) was found to be $r_h = 42$ nm at 25 °C, consistent with micelles with small cores and long coronal chains. A dramatic increase in particle dimensions was observed at 32 °C, i.e., at the LCST of PNIPAm. As demonstrated in Fig. 1, $r_h = 690$ nm at 40 °C. This behavior is typical for LCST polymers and the mechanism proposed is as follows [10,12,25,26]. At low temperatures strong H-bonding between the hydrophilic groups and surrounding water ensure good solubility of PNIPAm units. However, these H-bridges are broken at higher temperatures and aggregation occurs. In terms of thermodynamics it has been suggested that in cold solution hydrophilic group-water H-bonding overrides the energetic penalty arising from the exposure of hydrophobic entities to water, while in hot solution the gain in entropy associated with the release of structured water around the hydrophobic entities becomes the dominant factor, despite the reduced motional freedom of the hydrophilic parts. Above the LCST, deswelling of PNIPAM chains is observed, an effect that has been attributed to entropically driven enhanced association of the isopropyl groups that is accompanied by dehydration of the chains. In PNIPAm solutions two types of bound water have been recognized [6,27]; one around the isopropyl group and one around the amide group. Experimental evidence for this hypothesis has been reported by using temperature modulated differential scanning calorimetry (TMDSC) [27].

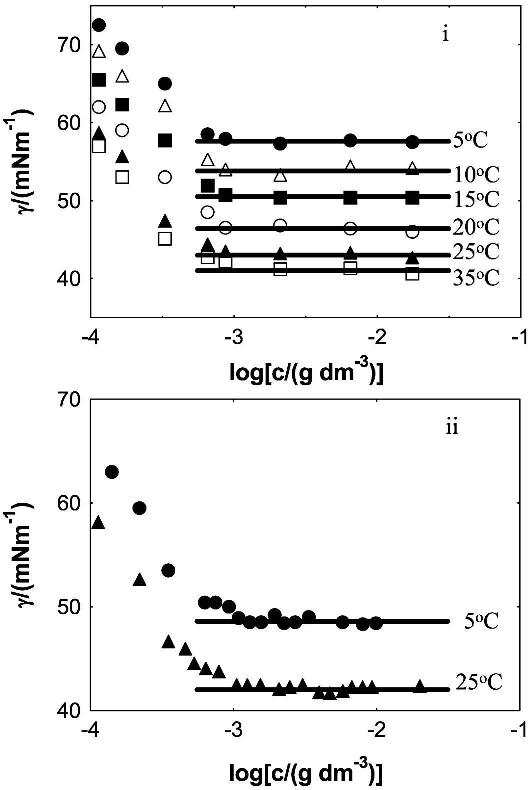

Fig. 2. Surface tension (γ) versus concentration for aqueous solutions of PMMA–*b*–PNIPAm block copolymer at several temperatures. (i) Data obtained from temperatures ramps at constant concentration. The data points have been shifted by 8, 6, 4, 2 mN/m units on the ordinate scale for 5, 10, 15, 20 °C, respectively. (ii) Data obtained from concentration sweeps at constant temperature.

3.2. Surface properties below LCST

Plots of surface tension against logarithm of concentration for aqueous solutions of block copolymer PMMA–*b*–PNIPAm are shown in Fig. 2. The critical micelle concentration (cmc) was assigned to the concentration at which surface tension reached a steady value. At each temperature, the horizontal lines shown in Fig. 2 correspond to the average γ value above cmc (γ_{cmc}). The data plotted in Fig. 2i were collected following a temperature ramp protocol at a given concentration, while data plotted in Fig. 2ii were collected following a concentration sweep protocol at a given temperature. Regardless of the specific experimental protocol followed, it can be seen that cmc values do not change with temperature in the range 5–25 °C. The cmc value determined is 8.7×10^{-4} g/dm^3. This value is comparable with cmc $= 10^{-3}$ g/dm^3 reported for PNIPAM–PSt [1] and considerably lower than cmc $= 18.7 \times 10^{-3}$ g/dm^3 reported for (PNIPAM–*g*–polyphosphazene) [13] particles.

The standard enthalpy of micellization $\Delta_{\mathrm{mic}}H^0$ is given by

$$\Delta_{\mathrm{mic}}H^0 = -RT\,\mathrm{d}\ln(\mathrm{cmc})/\mathrm{d}(1/T) \tag{2}$$

calculated from cmc values reported above is $\Delta_{\mathrm{mic}}H^0 \approx 0$ kJ/mol. This low $\Delta_{\mathrm{mic}}H^0$ can be assigned to the PMMA block being tightly coiled in the dispersed molecular state, so that the unfavorable interactions of hydrophobic entities with water are minimized [28,29].

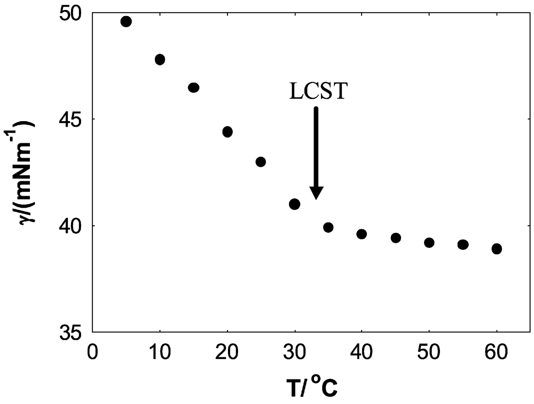

Fig. 3. Surface tension (γ) versus temperature of aqueous solutions of 0.02 g/dm^3 PMMA–*b*–PNIPAm block copolymer.

The overall $\Delta_{\mathrm{mic}}H^0$ can be deconvoluted as follows [29,30]:

$$\Delta_{\mathrm{mic}}H^0 = \Delta_{\mathrm{mic}}H^0_{\mathrm{HP}} + \Delta_{\mathrm{mic}}H^0_S + \Delta_{\mathrm{mic}}H^0_D + \Delta_{\mathrm{mic}}H^0_E, \tag{3}$$

where $\Delta_{\mathrm{mic}}H^0_{\mathrm{HP}}$ is related to the hydrophobic effect, $\Delta_{\mathrm{mic}}H^0_S$ to the formation of core–corona interface, $\Delta_{\mathrm{mic}}H^0_D$ to dispersion (van der Waals) interactions between the hydrophobic units in the core and $\Delta_{\mathrm{mic}}H^0_E$ is associated with transfer of the hydrophilic block to the more concentrated environment of the micellar corona and, thus, reflects the reverse enthalpy of dilution of PNIPAm, and has a low and positive value. $\Delta_{\mathrm{mic}}H^0_S$ is also likely to be small and positive. However, given that micellization enhances the interactions between the hydrophobic entities in the micellar core, $\Delta_{\mathrm{mic}}H^0_D$ should have a negative value. Therefore, the low $\Delta_{\mathrm{mic}}H^0$ value reflects a balance between the contributions of hydrophobic and dispersion interactions.

3.3. Surface properties above LCST

Approaching the LCST two interesting effects in the behavior of PNIPAm–*b*–PMMA micellar behavior were observed; First, the cmc values, determined in a similar manner as above, were found to slightly increase with temperature rather than decrease as expected for a LCST system (see data for 35 °C in Fig. 2i). Secondly, the surface tension of relatively concentrated solutions ($c = 0.02$ g/dm^3) was found to depend weakly on temperature (Fig. 3); not showing the usual strong decrease with temperature expected for aqueous solutions. Both these observations are consistent with the fact that PMAA–*b*–PNIPAm solutions are partially phase separated at elevated temperatures. At low T the system can be described by an equilibrium between two species: unimers and micelles, whereas at high T unimers, micelles and phase-separated particles coexist in the system. The development of phase-separated particles introduces an additional component to the unimer–micelle equilibrium, resulting in a decrease in actual concentration of dispersed unimers and, thus, displacing the cmc to higher concentrations.

Moreover, the insensitivity of γ observed within the range 35–60 °C (at concentrations well above the apparent cmc) can be viewed as an interplay between the tendency of aqueous solutions to lower their γ with temperature (through weakening of the H-bonding) and the tendency of PMAA–*b*–PNIPAm to undergo phase separation; a mechanism that removes amphiphilic molecules from the air/solution interface (by lowering the unimer concentration in solution) and, thus, enhances γ. The weak dependence of γ over the wide temperature range 30–60 °C is a unique property of the system considered here, that has to our knowledge not been reported for any other related colloidal solution.

Although the exact pattern of cmc(T) and $\gamma(T)$ plots reported here is rather unique, values of cmc that are independent of temperature has been reported in other systems [28,29,31,32]. In each case the behavior has been assigned to collapse of hydrophobic coils, i.e., to the formation of monomolecular micelles. It has been supported that the dominant underlying mechanism is thermodynamic in origin rather than kinetic [33]. The anomalous trends observed at high temperatures for PMMA–*b*–PNIPAm copolymer can be directly related to LCST of the hydrophilic block and the introduction of phase-separated particles as an additional component to the unimer–micelle equilibrium at high temperatures.

4. Conclusions

Measurement of cmc values of a poly(methyl methacrylate)–block–poly(N-isopropylacrylamide) copolymer in aqueous solution within the temperature range 5–25 °C by surface tensiometry, reveals a case of almost athermal micellization. This behavior can be assigned to the PMMA block being tightly coiled in the dispersed molecular state (monomolecular micelle), so that the interactions of the hydrophobic units with water are minimized. At the LCST (32 °C), the polymer conformation undergoes a micelle–globule transition, giving rise to aggregates with $r_h = 690$ nm, as probed by dynamic light scattering. This effect is directly reflected as a break point in surface tension (γ) versus temperature (T) curve. Above the LCST, the cmc was found to increase rather than decrease, that also points to the dramatic conformational changes of the hydrophilic block that take place at elevated temperatures. Moreover, the weak dependence of γ over the temperature range 30–60 °C observed for the system is a unique property that has not been reported so far in any related study. These anomalous trends can be attributed to the development of phase-separated particles as an additional component to the unimer–micelle equilibrium at high temperatures.

References

[1] S. Cammas, K. Suzuki, C. Sone, Y. Sakurai, K. Kataoka, T. Okano, J. Controlled Release 48 (1997) 157.
[2] F. Kohori, K. Sakai, T. Aoyagi, M. Yokoyama, T. Sakurai, T. Okano, J. Controlled Release 55 (1998) 87.
[3] S. Qin, Y. Geng, D.E. Discher, S. Yang, Adv. Mater. 18 (2006) 2905.
[4] T. Okano, N. Yamada, M. Okuhara, H. Sakai, Y. Sakurai, Biomaterials 16 (1995) 297.
[5] P.W. Zhu, D.H. Napper, Macromolecules 32 (1999) 2068.
[6] V.Y. Grinberg, A.S. Dubovik, D.V. Kuznetsov, N.V. Grinberg, A.Y. Grosberg, T. Tanaka, Macromolecules 33 (2000) 8685.
[7] C. Li, Y. Tang, S.P. Armes, C.J. Morris, S.F. Rose, A.W. Lloyd, A.L. Lewis, Biomacromolecules 6 (2005) 994.
[8] C. Li, N.J. Buurma, I. Haq, C. Turner, S.P. Armes, V. Castelletto, I.W. Hamley, A.L. Lewis, Langmuir 21 (2005) 11026.
[9] J. Zhang, L.-Y. Chu, Y.K. Li, Y.M. Lee, Polymer 48 (2007) 1718.
[10] T. Tang, V. Castelletto, P. Parras, I.W. Hamley, S.M. King, D. Roy, S. Perrier, R. Hoogenboom, U.S. Schubert, Macromol. Chem. Phys. 207 (2006) 1718.
[11] C. Wu, X. Wang, Phys. Rev. Lett. 80 (1998) 4092.
[12] H. Feil, Y.H. Bae, J. Feijen, S.W. Kim, Macromolecules 26 (1993) 2496.
[13] J.X. Zhang, L.Y. Qiu, K.J. Zhu, Y. Jin, Macromol. Rapid. Commun. 25 (2004) 1563.
[14] M.D.C. Topp, P.J. Dijkstra, H. Talsma, J. Feijen, Macromolecules 30 (1997) 8518.
[15] J. Virtanen, S. Holappa, H. Lemmetyinen, H. Tenhu, Macromolecules 35 (2002) 4763.
[16] W. Zhang, L. Shi, K. Wu, Y. An, Macromolecules 38 (2005) 5743.
[17] B. Liu, S. Perrier, J. Polym. Sci. Part A Polym. Chem. 43 (2005) 3643.
[18] A.J. Convertime, B.A. Lokitz, Y. Vasileva, L.J. Myrick, C.W. Scales, A.B. Lowe, C.L. McCormick, Macromolecules 39 (2006) 1724.
[19] Y. Li, B.S. Lokitz, C.L. McCormick, Macromolecules 39 (2006) 81.
[20] C. Konak, D. Oupicky, V. Chytry, K. Ulbrich, Macromolecules 33 (2000) 5318.
[21] Y. Xu, L. Shi, R. Ma, W. Zhang, Y. An, X.X. Zhu, Polymer 48 (2007) 1711.
[22] Z. Ge, Y. Cai, J. Yin, Z. Zhu, J. Rao, S. Liu, Langmuir 23 (2007) 1114.
[23] C.M. Schilli, M. Zhang, E. Rizzardo, S.H. Thang, Y.K. Chong, K. Edwards, G. Karlsson, A.H.E. Muller, Macromolecules 37 (2004) 7861.
[24] S.W. Provencher, Makromol. Chem. 180 (1979) 201.
[25] F.M. Winnik, Macromolecules 23 (1990) 233.
[26] T. Tokuhiro, T. Amiya, A. Mamada, T. Tanaka, Macromolecules 24 (1991) 2936.
[27] E.C. Cho, J. Lee, K. Cho, Macromolecules 36 (2003) 9929.
[28] A. Kelarakis, V. Havredaki, G.-E. Yu, L. Derici, C. Booth, Macromolecules 31 (1998) 944.
[29] A. Kelarakis, V. Havredaki, C.J. Rekatas, C. Booth, Phys. Chem. Chem. Phys. 3 (2001) 5550.
[30] J.M. del Rio, M.N. Jones, J. Phys. Chem. B 105 (2001) 1200.
[31] M. Crothers, D. Attwood, J.H. Collett, Z. Yang, C. Booth, P. Tabaoka, V. Mosquera, N.M.P.S. Ricardo, L. Martini, Langmuir 18 (2002) 8685.
[32] P. Taboada, G. Velasquez, S. Barbosa, Z. Yang, S.K. Nixon, Z. Zhou, F. Heatley, M. Ashford, V. Mosquera, D. Atwood, C. Booth, Langmuir 22 (2006) 7465.
[33] D. Attwood, C. Booth, S.G. Yeates, C. Chaibundit, N.M.P.S. Ricardo, Int. J. Pharm. 345 (2007) 35.