
**Surface Phase Separation and Morphology of Stimuli Responsive Complex Micelles**

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**Synthesis and characterization of block copolymer PEG$_{114}$-b-P4VP$_{58}$ and PNIPAM$_{93}$-b-P4VP$_{58}$.**

**Materials.** Polyethylene glycol methyl ether (CH$_3$O-PEG$_{114}$-OH, $M_n \sim 5000$ and the polydispersity index, PDI = 1.05) was purchased from Fluka. The monomer 4-vinyl pyridine (Acros Organics, 95%) was purified by vacuum distillation. N-isopropylacrylamide (NIPAM, Acros Organics, 99%) was purified by recrystallization in a benzene/n-hexane mixture and dried in vacuum. CuCl was purchased from Aldrich and purified according to ref.$^{[1]}$ Tris[2-(dimethylamino)ethyl]amine (Me$_6$TREN) was synthesized from tris(2- aminoethyl)amine (Aldrich, 95) according to ref.$^{[2]}$ 1-Chlorophenylethane (1-PECl, Acros Organics) and all the other regents were used as received.

**Synthesis of PEG$_{114}$-b-P4VP$_{58}$.** The macroinitiator PEG$_{114}$-Br was synthesized and purified according to ref.$^{[3]}$ PEG$_{114}$-b-P4VP$_{58}$ was synthesized by atom transfer radical polymerization (ATRP) of 4-vinyl pyridine with PEG$_{114}$-Br as macroinitiator. The typical polymerization procedure to synthesize PEG$_{114}$-b-P4VP$_{58}$ was introduced as follows. 5.0 g macroinitiator of PEG$_{114}$-Br was added to a reaction flask and 10 ml solvent mixture of butanone and 2-propanol (1:1, v:v) was added. The sample was first stirred with ultrasonic and then degassed under nitrogen
purge. Subsequently, the CuCl and Me₆TREN catalysts were introduced into the reaction flask. At last, 5.0 g 4-vinyl pyridine was added into the flask and degassed under nitrogen purge. Polymerization was performed at 40°C for 10 hours. The block copolymer PEG₁₁₄-b-P₄VP₅₈ was purified by first passing through an Al₂O₃ column to remove the copper catalyst and then deposited in cold ether. The powder of PEG₁₁₄-b-P₄VP₅₈ was dried in vacuum at room temperature.

**Synthesis of PNIPAM₉₃-b-P₄VP₅₈.** Macroinitiator PNIPAM-Cl was synthesized by ATRP of N-isopropylacrylamide using PECI as initiator and CuCl/Me₆TREN as catalyst. The detailed process is introduced as follows. 0.16 g CuCl and 0.38 g Me₆TREN were introduced into the reaction flask and then 10 ml toluene was added. The sample was first stirred with ultrasonic and then degassed under nitrogen purge. Subsequently, 10g N-isopropylacrylamide and 0.117g PECI were introduced into the flask and degassed under nitrogen purge again. Polymerization was performed at 40 °C for 10 hours and monomer conversion in 24 hours is about 70%. The PNIPAM-Cl was purified by passing through a Al₂O₃ Column to remove the copper catalyst and then the sample was deposited in a toluene/n-hexane mixture (3:7, v:v). The precipitate of PNIPAM-Cl was then filtered under vacuum and dried in vacuum at room temperature.

PNIPAM-b-P₄VP was synthesized by ATRP of 4-vinyl pyridine using PNIPAM-Cl as macroinitiator and CuCl/ Me₆TREN as catalyst. The procedure is similar to that of synthesizing PEG₁₁₄-b-P₄VP₅₈ from PEG₁₁₄-Br except using mixture of butanone and 2-propanol (7:3, v:v) as the solvent for polymerization and toluene as the precipitator for the block copolymer.

**Gel permeation chromatography (GPC) analysis.** Gel permeation chromatography (GPC) was measured on a Waters 600E system by using narrowly distributed polystyrene for calibration. PNIPAM₉₃-Cl was characterized by using tetrahydrofuran as eluent with \( M_n = 1.05 \times 10^4 \) g/mol and PDI = 1.26. The \( M_n \) and PDI of PEG-Br were same as for PEG as received. Block copolymer PEG₁₁₄-b-P₄VP₅₈ and PNIPAM₉₃-b-P₄VP₅₈ were characterized by the same GPC system as above except using CHCl₃ as eluent. The PDIs of PEG₁₁₄-b-P₄VP₅₈ and PNIPAM₉₃-b-P₄VP₅₈ are 1.28 and 1.21 respectively.
**1H NMR characterization.** 1H NMR spectra were recorded on a Varian UNITY-plus 400 spectrometer. Chemical shifts are given in ppm relative to TMS. The 1HNMR spectra of PEG_{114}-Br in D_{2}O and PEG_{114}-b-P4VP_{58} in CDCl_3 were shown in Figure S1. The composition of PEG_{114}-b-P4VP_{58} is determined by the ratio of the total area of peaks c and d to peak a.

![Figure S1. 1H NMR Spectra of (I) PEG_{114}-Br in D_{2}O and (II) PEG_{114}-b-P4VP_{58} in CDCl_3.](image1)

The 1H NMR spectra of PNIPAM_{93}-Cl and PNIPAM_{93}-b-P4VP_{58} in CDCl_3 were also recorded using the same spectrometer, as shown in Figure S2. The composition of PNIPAM_{93}-b-P4VP_{58} is determined by the ratio of the total area of peaks e and f to peak c.

![Figure S2. 1H NMR Spectra of (I) PNIPAM_{93}-Cl and (II) PNIPAM_{93}-b-P4VP_{58} in CDCl_3.](image2)
**1H NMR analysis of the complex micelles.**

The micelle solution in D$_2$O for $^1$H NMR analysis was similarly prepared as described in the Experimental Section except that the solution of micelles in D$_2$O was not dialyzed against D$_2$O, because it is very expensive to do this experiment. In fact, both the dialyzed and non-dialyzed complex micelle solutions were characterized by DLS and SLS. No marked difference in the parameters of $D_h$, $R_g$ and $R_g/R_h$ of the complex micelles was observed between the dialyzed and non-dialyzed micelle solutions, which indicate that removing the Na$^+$ and SO$_4^{2-}$ in the micelle solutions by dialyzing them against water don’t have remarkable influence on properties of the complex micelles. We think that the $^1$H NMR analysis on the non-dialyzed solutions of complex micelles in D$_2$O can be used to demonstrate the behavior of the dialyzed solutions of complex micelles in H$_2$O.

$^1$H NMR spectra of the sample with the $W_{\text{PEG}} = 0.41$ recorded in D$_2$O at different temperatures and pH values, as shown in Figure S3, were further used to investigate the structure of the complex micelles. In curve I, all of the characteristic signals due to PEG, P4VP and PNIPAM blocks are evident, which means these three blocks are completely water-soluble at pH 2 and 25 in aqueous solution. After addition of Na$_2$SO$_4$ and basification, the peaks d and e due to P4VP blocks disappear in curve II, suggesting they form the immobile and non-solvated micellar cores. The disappearance of peaks f and g due to PNIPAM blocks in curve III indicates the desolvation and collapse of the PNIPAM chains at 50. The shifting of the peak c due to PEG chains in curve III to lower field may be attributed to the thermo-effect on the H-bonds between PEG and D$_2$O.
Figure S3. $^1$H NMR spectra of the sample with $W_{\text{PEG}} = 0.41$ in D$_2$O (I) as true solution at pH 2 and 25 , (II) (PNIPAM/PEG)-P4VP complex micelles at pH 9 and 25 , and (III) (PNIPAM/PEG)-P4VP complex micelles at pH 9 and 50.

**The detailed operation for the controlled acidification of the complex micelles.**

The samples for controlled acidification were first prepared by filtering about 1 mL of the aqueous solution with a 0.2 µm Gelman filter into a clean scintillation vial and bathed at 50 for about two hours, and then characterized by DLS and SLS to obtain $D_h$ and $R_g$ before acidification. At the same time, a given volume of dilute aqueous HCl solution with pH 2 was filtered with a 0.2 µm Gelman filter into a clean vial and bathed at 50 as stock solution. Subsequently, 0.2 mL aqueous HCl solution was quickly pipetted into the scintillation vial with a pre-heated tip and the scintillation vial was stirred for less than 10 seconds and then put into the sample cell for monitoring and characterization by laser light scattering.

**Figures for the angular dependence of the translational diffusion coefficient $D_t$ of the micellar systems involved in this communication.**
Figure S4. Angular dependence of the translational diffusion coefficient $D_t$ of the complex micelles with $W_{\text{PEG}}=0.41$ under different conditions.

Figure S5. Angular dependence of the translational diffusion coefficient $D_t$ of the complex micelles with $W_{\text{PEG}}=0.41$ at 50 °C.
Figure S6. Angular dependence of the translational diffusion coefficient $D_t$ of the complex micelles with $W_{\text{PEG}}=0.58$ at 50 °C.

References