Supporting Information

Micellization and Phase Separation in Aqueous Solutions of Thermosensitive Block Copolymer Poly(*N*-isopropylacrylamide)-*b*-poly(*N*-vinyl-2-pyrrolidone) upon Heating

Chen Kuang,[1] Shin-ichi Yusa,[2] and Takahiro Sato[1,*]

[1] Department of Macromolecular Science, Osaka University, 1-1 Machikaneyama-cho, Toyonaka, Osaka 560-0043, Japan

[2] Department of Applied Chemistry, Graduate School of Engineering, University of Hyogo, 2167 Shosha, Himeji, Hyogo 671-2280, Japan

[*] Corresponding authors. E-mail addresses: tsato@chem.sci.osaka-u.ac.jp

Fitting Parameters Obtained from SAXS Profiles. The following Tables list fitting parameters obtained by fitting experimental SAXS profiles for three PNIPAM-*b*-PNVP samples in water at different temperatures by the theoretical scattering function explained in the text (eqs 12-21). For the single chain, the effective bond length b for PNIPAM may be underestimated by the chain thickness effect on the scattering function.[1-3] The second virial coefficient A_2 was chosen to be 1×10^{-4}, 2×10^{-5}, and 0 cm^3mol/g^2 for $PNIPAM_{60}$-*b*-$PNVP_{368}$, $PNIPAM_{31}$-*b*-$PNVP_{120}$, and $PNIPAM_{100}$-*b*-$PNVP_{218}$, respectively.

Table S1. Values of fitting parameters for the single chain, micelle, and polydisperse spheres determined by fits of eqs 12-21 to the experimental SAXS scattering profiles for (a) $PNIPAM_{60}$-*b*-$PNVP_{368}$, (b) $PNIPAM_{31}$-*b*-$PNVP_{120}$, and (c) $PNIPAM_{100}$-*b*-$PNVP_{218}$.

(a) $PNIPAM_{60}$-*b*-$PNVP_{368}$ ($x = 0.14$)

	25 °C	35 °C	45 °C	55 °C	65 °C	73 °C
w_{chain} [a]	0.999	0.999_5	0.987	0.875	0.71	0.66
b_{PNVP}/nm [b]	0.67	0.67	0.67	0.67	0.67	0.67
b_{PNIPAM}/nm [b]	0.1	0.1	0.1	0.1	0.1	0.1
w_{mic} [a]	0	0	0.01	0.12	0.29	0.34
m_{mic} [c]	–	–	90	90	90	90
c_{core} / g cm^{-3} [d]	–	–	1.0	1.0	1.0	1.0
b_{corona}/nm [b]	–	–	0.7	0.7	0.7	0.7
$(\sigma/\text{nm})^2$ [e]	–	–	7	7	7	7
w_{sph} [a]	0.001	0.0005	0.0028	0.005	0	0
$m_{w,sph}$ [c]	4000	4000	4000	4000	–	–
$Đ$ [f]	10	10	10	10	–	–
c_{in} / g cm^{-3} [d]	1.0	1.0	1.0	1.0	–	–

[a] Weight fractions of the isolated chain, spherical micelle, and polydisperse sphere. [b] Effective monomer unit lengths of the PNVP block chain, the PNIPAM block chain, and coronal (PNVP) chain. [c] Aggregation number of the spherical micelle and the weight average aggregation number of the polydisperse sphere. [d] Polymer mass concentrations inside the hydrophobic core of the micelle and the polydisperse sphere. [e] Width of the core-corona interface. [f] Dispersity index for the aggregation number of the polydisperse sphere.

(b) PNIPAM$_{31}$-*b*-PNVP$_{120}$ (x = 0.205)

	25 °C	35 °C	45 °C	55 °C	65 °C	73 °C
w_{chain}	0.997	0.986	0.983_5	0.979_5	0.967_5	0.924
b_{PNVP}/nm	0.67	0.67	0.67	0.67	0.67	0.68
b_{PNIPAM}/nm	0.2	0.2	0.2	0.2	0.2	0.2
w_{mic}	0	0.0095	0.0095	0.01	0.018	0.060
m_{mic}	–	100	100	100	110	110
c_{core} / g cm^{-3}	–	1.0	1.0	1.0	1.0	1.0
b_{corona}/nm	–	0.67	0.67	0.67	0.67	0.67
$(\sigma/\text{nm})^2$	–	3	3	3	3	2
w_{sph}	0.0033	0.0045	0.007	0.0105	0.0145	0.016
$m_{w,sph}$	4×10^4	5×10^4	5×10^4	5×10^4	5×10^4	3.5×10^4
$Đ$	1×10^4	1×10^4	1×10^4	1×10^4	1×10^4	1×10^4
c_{in} / g cm^{-3}	1.05	0.6	0.6	0.5	0.5	0.65

(c) PNIPAM$_{100}$-*b*-PNVP$_{218}$ (x = 0.31)

	25 °C [4]	40 °C	60 °C
w_{chain}	1.0	0.895	0.55
b_{PNVP}/nm	0.65	0.90	0.95
b_{PNIPAM}/nm	0.25	0.50	0.50
w_{mic}	0	0.005	0.15
m_{mic}	–	8	10
c_{core} / g cm^{-3}	–	1.0	1.0
b_{corona}/nm	–	0.60	0.58
$(\sigma/\text{nm})^2$	–	0.5	1.0
w_{sph}	6×10^{-5} *	0.10	0.30
$m_{w,sph}$	7700 *	2.4×10^4	4300
$Đ$	–	2	6
c_{in} / g cm^{-3}	–	0.40	0.50

* Fitted by the randomly branching chain of tri-functional monomers.[4]

REFERENCES

1. Hickl, P.; Ballauff, M.; Scherf, U.; Müllen, K.; Lindner, P. Characterization of a Ladder Polymer by Small-Angle X-ray and Neutron Scattering. *Macromolecules* **1997**, *30*, 273-279.
2. Terao, T.; Mizuno, K.; Murashima, M.; Kita, Y.; Hongo, C.; Okuyama, K.; Norisuye, T.; Bächinger, H. P. Chain Dimensions and Hydration Behavior of Collagen Model Peptides in

Aqueous Solution: [Glycyl-4(R)-hydroxyprolyl-4(R)-hydroxyproline]$_n$, [Glycylprolyl-4(R)-hydroxyproline]$_n$, and Some Related Model Peptides. *Macromolecules* **2008**, *41*, 7203-7210.

3. Arakawa, S.; Terao, K.; Kitamura, S.; Sato, T. Conformational Change of an Amylose Derivative in Chiral Solvents: Amylose Tris(*n*-butylcarbamate) in Ethyl Lactates. *Polym. Chem.* **2012**, *3*, 472-478.
4. Sato, T.; Tanaka, K.; Toyokura, A.; Mori, R.; Takahashi, R.; Terao, K.; Yusa, S. Self-Association of a Thermosensitive Amphiphilic Block Copolymer Poly(*N*-isopropylacrylamide)-*b*-Poly(*N*-vinyl-2-pyrrolidone) in Aqueous Solution upon Heating. *Macromolecules* **2013**, *46*, 226-235.