Supplementary Information

Thermoresponsive Property of Poly(*N*-isopropyl,*N*-methylacrylamide) and its Statistical and Block Copolymers with Poly(*N*,*N*-dimethylacrylamide) Prepared by

B(C₆F₅)₃-Catalyzed Group Transfer Polymerization

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1. Experimental Section

Materials

N, *N*-Dimethylacrylamide (DMAm) was purchased from Tokyo Kasei Kogyo Co., Ltd. (TCI) and used after distillation over CaH₂ under reduced pressure. Tris(pentafluorophenyl)borane (B(C₆F₅)₃) (TCI) and was used after the recrystallization from *n*-hexane at -30 °C. Acryloyl chloride (TCI) was used after distillation at 77 °C. Dichloromethane (CH₂Cl₂, >99.5%; Extra Dry, with molecular sieves, water <50 ppm) and tetrahydrofuran (THF, >99.5%; Extra Dry, with molecular sieves, water <50 ppm) were purchased from Energy Chemical Co., Ltd. All other reagents were used as received without further purification. The Spectra/Por® 6 Membrane (MWCO: 1000) was used for the dialysis.

Measurements

The ¹H and ¹³C NMR spectra were recorded using a Bruker AVANCE III HD 500. The mass spectrum LC-MS-ESI was measured by Waters Acquity Arc and Acuity QDa system using methanol as solvent. The polymerization solution was prepared in a MIKROUNA glove box equipped with a gas purification system (molecular sieves and copper catalyst) and a dry argon atmosphere (H₂O, O₂ <1 ppm). The moisture and oxygen contents in the glove box were monitored by a MK-XTR-100 and a MK-OX-SEN-1, respectively. The number-average molecular weight distributions (M_w/M_n s) of the polymers were measured using size exclusion chromatography (SEC) at 60 °C using an

Agilent High Performance Liquid Chromatography (1260 Infinity II) system in DMF containing lithium chloride (LiCl, 0.01 mol L⁻¹) at a flow rate of 1.0 mL min⁻¹. The matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) measurements were performed using an Applied Biosystems Voyager-DE STR-H mass spectrometer with a 25 kV acceleration voltage. The positive ions were detected in the reflector mode (25 kV). A nitrogen laser (337 nm, 3 ns pulse width, 106 - 107 W cm⁻²) operating at 3 Hz was used to produce the laser desorption, and the 200 shots were summed. The spectra were externally calibrated using a sample prepared from the narrow-dispersed polystyrene (Chemco Scientific Co., Ltd., $M_n = 3.6$ kg mol⁻¹, $M_{\rm w}/M_{\rm n} = 1.08, 30 \,\mu\text{L}, 10 \,\text{mg mL}^{-1}$ in THF), the matrix (1,8-dihydroxy-9-(10H)-anthracenone, 30 mg mL⁻¹, 100 μ L), and the cationizing agent (silver trifluoroacetate, 10 mg mL⁻¹, 15 μ L) with a linear calibration. Samples for the MALDI-TOF MS were prepared by mixing the polymer (1.5 mg mL⁻¹, 10 μ L), the matrix (*trans*-3-indoleacrylic acid, 10 mg mL⁻¹, 90 μ L), and the cationizing agent (sodium trifluoroacetate, 10 mg mL⁻¹, 10 μ L) in THF. The absolute molecular weight ($M_{n, MALS}$) were estimated by SEC in DMF containing 0.01 mol L⁻¹ of LiCl (1.0 mL min⁻¹) at 40 °C using a DAWN 8 multi-angle laser light scattering (MALS) instrument (Wyatt Technology, HELEOS®). The hydrodynamic radii $(R_{\rm h}s)$ of the obtained polymer in deionized water were analyzed using a dynamic light scattering (DLS) detector (Wyatt Technology, Dyna Pro Nanostar®). The cloud point measurements were performed on the ultraviolet-visible (UV-vis) spectra by passing through a 10-mm path-length cell using a Jasco V-770 spectrophotometer equipped with a temperature controller (Jasco CTU-100).

Synthesis of N-isopropyl, N-methylacrylamide (*i*PMAm). solution of То а N-isopropylmethylamine (25.0 mL, 0.24 mol) and triethylamine (60 mL, 0.43 mol) in dry THF (500 mL) in an ice bath, acryloyl chloride (30 mL, 0.36 mol) was dropwise added. After stirring for 15 h at room temperature (25°C), the precipitated ammonium salt was removed by suction filtration, the filtrate was concentrated, and the residue was dissolved in CH₂Cl₂, washed by a dilute HCl solution (0.1 mol L⁻¹) and brine, and dried using anhydrous sodium sulfate. After removing sodium sulfate and CH₂Cl₂, the residue was distilled under reduced pressure in the presence of a small amount of CaH₂ to afford *i*PMAm as a colorless liquid. Yield, 23.7 g (77.8%); b.p., 65 °C (0.04 mmHg). Anal. Calcd. for C7H13NO (127.19): C, 66.11; H, 10.30; N, 11.01; O, 12.58. Found. C 66.15; H 10.27; O 12.56; N 11.02. LC-MS-ESI (m/z) $[M + H]^+$ calculated for $[C_7H_{13}NO+H]^+$ 128.19, found 128.04. *cis-i*PMAm conformer, ¹H NMR (500 MHz, CDCl₃, δ): 1.20 - 1.21 (d, 6H, J = 6.63 Hz, -NCH(CH₃)₂), 2.85 (s, 3H, -NCH₃), 4.18 - 4.23 (m, 1H, -NCH(CH₃)₂), 5.63 - 5.68 (m, 1H, -CH=CH), 6.23 - 6.32 (m, 1H, -CH=CH), 6.53 - 6.63 (m, 1H, -CH=CH₂). ¹³C NMR (125 MHz, CDCl₃, δ): 22.07 (-NCH(CH₃)₂), 33.96 (-NCH₃), 51.65 (-NCH(CH₃)₂), 126.76 (-CH=CH₂), 128.53 (-CH=CH₂), 166.60 (-NCOCH=).

*trans-i*PMAm conformer, ¹H NMR (500 MHz, CDCl₃, δ): 1.12 - 1.13 (d, 6H, J = 6.63 Hz,

-NCH(CH₃)₂), 2.89 (s, 3H, -NCH₃), 4.90 - 4.94 (m, 1H, -NCH(CH₃)₂), 5.63 - 5.68 (m, 1H, -CH=CH), 6.23 - 6.32 (m, 1H, -CH=CH), 6.53 - 6.63 (m, 1H, -CH=CH₂). ¹³C NMR (125 MHz, CDCl₃, δ): 20.40 (-NCH(CH₃)₂), 35.45 (-NCH₃), 49.57 (-NCH(CH₃)₂), 127.40 (-CH=CH₂), 128.73 (-CH=CH₂), 166.00 (-NCOCH=).

Synthesis of poly(*N*-isopropyl,*N*-methylacrylamide)s (*PiPMAm*₃). In a glove box, to a solution of *i*PMAm (145 µL, 1.0 mmol) and SKA^{Et} (40 µL, 0.02 mmol; 0.50 mol L⁻¹ CH₂Cl₂) in CH₂Cl₂ (0.96 mL) in a test tube, a stock solution of B(C₆F₅)₃ (40 µL, 2.0 µmol; 0.05 mol L⁻¹ in CH₂Cl₂) was added. The polymerization was quenched by adding a small amount of a 2-PrOH/pyridine mixture to the polymerization solution. Aliquots were removed from the reaction mixture to determine the conversion of *i*PMAm using ¹H NMR measurements. The polymer product was purified by dialysis against methanol using a cellophane tube, after which the product was lyophilized to give *PiPMAm*₅₀ as a white solid. Yield, 124.2 mg (97.8 %); $M_{n,MALS}$, 6.7 kg mol⁻¹; M_w/M_n , 1.09.

Synthesis of statistical copolymers (P*i*PMAm_x-*stat*-PDMAm_y). In a glove box, *i*PMAm (260 μ L, 1.8 mmol), DMAm (22 μ L, 0.2 mmol), SKA^{Et} (40 μ L, 20.0 μ mol; 0.50 mol L⁻¹ CH₂Cl₂), and CH₂Cl₂ (1.62 mL) were added to a test tube, followed by the addition of the B(C₆F₅)₃ stock solution in CH₂Cl₂ (80 μ L, 4.0 μ mol; 0.05 mol L⁻¹). The polymerization was quenched, the monomer conversions were confirmed, and the polymer purification was carried out similar to that for P*i*PMAm to give P*i*PMAm₉₀-*stat*-PDMAm₁₀ as a white solid. Yield, 245.4 mg (98.7 %); *M*_{n,MALS},

13.1 kg mol⁻¹; $M_{\rm w}/M_{\rm n}$, 1.09.

Synthesis of diblock copolymers (*PiPMAm_x-b-PDMAm_y*). In a glove box, *iPMAm* (260 µL, 1.8 mmol), SKA^{Et} (40 µL, 0.02 mmol; 0.50 mol L⁻¹ in CH₂Cl₂), and CH₂Cl₂ (1.42 mL) were added to a test tube. A stock solution of B(C₆F₅)₃ (80 µL, 4.0 µmol; 0.05 mol L⁻¹ CH₂Cl₂) was then added to start the polymerization. After quantitatively consuming *i*PMAm for the polymerization time of 1.5 h, DMAm (22 µL, 0.2 mmol) was further added to the polymerization mixture to continue the block copolymerization for 0.5 h. For the first and second polymerizations, the complete conversions of *i*PMAm and DMAm were confirmed based on the ¹H NMR measurements. The polymerization was quenched and the polymer purification was carried out similar to P*i*PMAm to give P*i*PMAm₉₀-*b*-PDMAm₁₀ as a white solid. Yield, 243 mg (97.9 %); $M_{n,MALS}$, 13.2 kg mol⁻¹; M_w/M_n , 1.08.

Synthesis of triblock copolymers (P*i*PMAm_{x/2}-*b*-PDMAm_y-*b*-P*i*PMAm_{x/2} and PDMAm_{y/2}-*b*-P*i*PMAm_x-*b*-PDMAm_{x/2}). In a glove box, *i*PMAm (28 μ L, 0.1 mmol), SKA^{Et} (40 μ L, 0.02 mmol; 0.50 mol L⁻¹ in CH₂Cl₂), and CH₂Cl₂ (50 μ L) were added to a test tube. A stock solution of B(C₆F₅)₃ (80 μ L, 4.0 μ mol; 0.05 mol L⁻¹ CH₂Cl₂) was then added to start the polymerization. After quantitatively consuming *i*PMAm for the polymerization time of 0.5 h, DMAm (176 μ L, 1.6 mmol) and CH₂Cl₂ (1.13 mL) were further added to the polymerization mixture to continue the diblock copolymerization for 1 h. After complete consumption of DMAm, *i*PMAm (28 μ L, 100

µmol) was further added to the polymerization mixture to continue the triblock copolymerization for 0.5 h. For each polymerization step, the quantitative conversions of *i*PMAm and DMAm were confirmed based on the ¹H NMR measurements. The polymerization was quenched and the polymer purification carried similar for **PiPMAm** out that give was to to PiPMAm₁₀-b-PDMAm₈₀-b-PiPMAm₁₀ as a white solid. Yield, 180 mg (97.9 %); $M_{n,MALS}$, 11.4 kg mol^{-1} ; M_w/M_n , 1.12.

Determination of monomer reactivity ratios for the statistical copolymerization of *i***PMAm and DMAm**. The monomer reactivity ratios for *i*PMAm and DMAm, r_{iPMAm} and r_{DMAm} , respectively, were determined using the Kelen-Tüdös method (see Supporting Information).

Determination of the cloud point (T_c). An aqueous solution of the polymer (1 wt%) was sonicated for several minutes, and the resulting clear solution was then transferred to a 10 mm quartz cell. The transmittance of the aqueous solution at 500 nm was recorded by a UV-vis spectrophotometer equipped with a temperature controller. The solution was heated at the heating rate of 1.0 °C min⁻¹. **Determination of hydrodynamic radius** (R_h). A sonicated aqueous solution of the polymer (1 wt%) was filtrated into glass cells using a 0.45 µm PTFE filter. The relaxation-time (τ) distribution and particle size distribution were obtained by the CONTIN analysis of the autocorrelation function. The apparent diffusion coefficients *D* were calculated using the following equation:

$$\left.\frac{\Gamma}{q^2}\right|_{q\to 0} = D$$

where Γ is the relaxation frequency ($\Gamma = \tau^{-1}$) and q is the wavevector defined by the following equation:

$$q = \frac{4\pi n}{\lambda} \sin\left(\frac{\theta}{2}\right)$$

where λ is the wavelength of the laser beam (532 nm), θ is the scattering angle, and *n* is the refractive index of the media. Consequently, the hydrodynamic radius (*R*_h) was calculated from the Stokes-Einstein relation as follows:

$$R_{\rm h} = \frac{k_{\rm B}T}{6\pi\eta\Gamma}q^2 = \frac{k_{\rm B}T}{6\pi\eta D}$$

where $k_{\rm B}$ is the Boltzmann constant, *T* is the temperature, and η is the viscosity of the medium.

2. ¹H NMR spectra of P*i*PMAm₂₅, P*i*PMAm₅₀-*stat*-PDMAm₅₀, P*i*PMAm₅₀-*b*-PDMAm₅₀, P*i*PMAm₂₀-*b*-PDMAm₆₀-*b*-P*i*PMAm₂₀, and PDMAm₃₀-*b*-P*i*PMAm₄₀-*b*-PDMAm₃₀



Figure S1. The ¹H NMR spectrum of P*i*PMAm₂₅ (run 1) measured in CDCl₃.



Figure S2. The ¹H NMR spectrum of PiPMAm₅₀-stat-PDMAm₅₀ (run 12) measured in CDCl₃.



Figure S3. The ¹H NMR spectrum of PiPMAm₅₀-b-PDMAm₅₀ (run 21) measured in CDCl₃.



Figure S4. The ¹H NMR spectra of P*i*PMAm₂₀-*b*-PDMAm₆₀-*b*-P*i*PMAm₂₀ (run 27, upper) and PDMAm₃₀-*b*-P*i*PMAm₄₀-*b*-PDMAm₃₀ (run 32, lower) measured in CDCl₃.



Figure S5. Expanded ¹H NMR spectra of the methylene signals for P*i*PMAm and PDEAm measured in CDCl₃ at 50 °C.

3. Statistical GTcoP of *i*PMAm and DMAm using SKA^{Et}

The monomer reactivity ratios of r_{iPMAm} and r_{DMAm} were determined using the Kelen-Tüdös equation of $\eta = \left(r_1 + \frac{r_2}{\alpha}\right)\xi - \frac{r_2}{\alpha}$, where $\eta = \frac{G}{\alpha + F}$; $\xi = \frac{F}{\alpha + F}$, $G = \frac{x(y-1)}{y}$; $F = \frac{x^2}{y}$, and $x = \frac{M_1}{M_2}$; $y = \frac{m_1}{m_2}$. F_i and F_2 are the mole fraction of *i*PMAm and DMAm, respectively, in the monomer feed. M_1 and M_2 are the mole fraction of *i*PMAm and DMAm, respectively, in the residual monomer mixture. m_1 and m_2 are the mole fraction of *i*PMAm and DMAm units, respectively, in the copolymer. $\alpha = \sqrt{F_m F_M}$ is an appropriately chosen constant to obtain a uniform spread of the data ($\alpha > 0$). F_m and F_M , the lowest and highest values from experimental data. The monomer reactivity ratios of r_{iPMAm} and r_{DMAm} were determined as 0.93 and 8.34, respectively, by calculation using the least-squares technique.

F_1	M_1 b	conv. %	$m_1 b$	ξ	η
0.1	0.10	23.78	0.02	0.10	-0.27
0.2	0.21	20.75	0.05	0.21	-0.20
0.3	0.30	19.92	0.09	0.31	-0.02
0.4	0.42	20.81	0.13	0.41	0.06
0.5	0.51	18.46	0.18	0.50	0.19
0.6	0.61	21.23	0.26	0.59	0.41
0.7	0.72	19.54	0.37	0.69	0.50
0.8	0.81	19.93	0.51	0.79	0.67
0.9	0.90	19.62	0.70	0.90	0.75

Table S1. Statistical GTcoP of *i*PMAm with DMAm^a

^{*a*} [SKA^{Et}]₀/[B(C₆F₅)₃]₀ = 1 / 0.2; solvent, CH₂Cl₂; temperature, 25 °C. ^{*b*} Determined by ¹H NMR in CDCl₃.



Figure S6. The equation obtained by fitting ξ and η .



Figure S7. SEC(RI) traces of statistical copolymers of P*i*PMAm-*stat*-PDMAm. (eluent, DMF containing 0.01 mol L⁻¹ of LiCl; flow rate, 1 mL min⁻¹).

4. Cloud point (*T*_c), hydrodynamic radius (*R*_h), and aggregate size distribution (ASD) for *PiPMAm-stat-PDMAm*, *PiPMAm-b-PDMAm*, *PiPMAm-b-PDMAm-b-PiPMAm*, and *PDMAm-b-PiPMAm-b-PDMAm*

Table S2. Cloud point (T_c) , hydrodynamic radius (R_h) , and aggregate size distribution (ASD) for

1-	$T_{\rm c} ^{\circ}{\rm C}$ —	$R_{\rm h}{}^a$ nm (ASD b)			
sample		20 °C	60 °C	90 °C	
PiPMAm90-stat-PDMAm10	30.4	2.8 (0.308)	1620.2 (0.374)	-	
PiPMAm ₈₀ -stat-PDMAm ₂₀	40.7	2.4 (0.244)	1524.6 (0.445)	-	
PiPMAm70-stat-PDMAm30	50.5	2.9 (0.369)	1859.9 (0.319)	-	
PiPMAm60-stat-PDMAm40	60.0	2.7 (0.308)	-	1448.7 (0.397)	
PiPMAm50-stat-PDMAm50	70.7	2.2 (0.283)	-	1789.6 (0.461)	
PiPMAm40-stat-PDMAm60	80.8	2.3 (0.215)	-	1887.1 (0.496)	
PiPMAm ₃₀ -stat-PDMAm ₇₀	90.1	2.5 (0.233)	-	617.9 (0.347)	
PiPMAm ₂₀ -stat-PDMAm ₈₀	-	2.1 (0.271)	-	10.1 (0.313)	
PiPMAm ₁₀ -stat-PDMAm ₉₀	-	2.6 (0.256)	-	8.3 (0.293)	

PiPMAm-stat-PDMAm

^a Calculated based on CONTIN analysis. ^b Calculated based on cumulant analysis.

1	E oc	$R_{ m h}$ a nm	$R_{\rm h}$ ^{<i>a</i>} nm (ASD ^{<i>b</i>})		
sample	T_{c} °C —	15 °C	45 °C		
PiPMAm ₉₀ -b-PDMAm ₁₀	18.8	3.4 (0.373)	656.5 (0.111)		
PiPMAm ₈₀ -b-PDMAm ₂₀	22.1	3.5 (0.249)	593.7 (0.173)		
PiPMAm ₇₀ -b-PDMAm ₃₀	25.9	2.9 (0.279)	603.9 (0.128)		
PiPMAm ₆₀ -b-PDMAm ₄₀	29.8	2.0 (0.284)	572.3 (0.125)		
PiPMAm ₅₀ -b-PDMAm ₅₀	34.1	3.1 (0.301)	554.7 (0.102)		
PiPMAm ₄₀ -b-PDMAm ₆₀	40.0	2.8 (0.413)	571.8 (0.084)		
PiPMAm ₃₀ -b-PDMAm ₇₀	46.2	3.6 (0.308)	278.1 (0.534) ^c		
PiPMAm ₂₀ -b-PDMAm ₈₀	-	3.9 (0.324)	128.9 (0.467) ^c		
PiPMAm ₁₀ -b-PDMAm ₉₀	-	3.1 (0.363)	10.9 (0.412) ^c		
P <i>i</i> PMAm ₁₀ - <i>b</i> -PDMAm ₈₀ - <i>b</i> -P <i>i</i> PMAm ₁₀	35.2	2.7 (0.255)	804.1 (0.153)		
PiPMAm ₂₀ -b-PDMAm ₆₀ -b-PiPMAm ₂₀	32.4	2.3 (0.337)	940.3 (0.176)		
PiPMAm ₃₀ -b-PDMAm ₄₀ -b-PiPMAm ₃₀	25.0	2.9 (0.251)	1047.6 (0.134)		
PiPMAm ₄₀ -b-PDMAm ₂₀ -b-PiPMAm ₄₀	19.9	3.4 (0.269)	1237.5 (0.181)		
PDMAm ₁₀ - <i>b</i> -P <i>i</i> PMAm ₈₀ - <i>b</i> -PDMAm ₁₀	22.3	3.0 (0.301)	1383.4 (0.103)		
PDMAm ₂₀ -b-PiPMAm ₆₀ -b-PDMAm ₂₀	25.4	2.8 (0.312)	1008.9 (0.146)		
PDMAm ₃₀ -b-PiPMAm ₄₀ -b-PDMAm ₃₀	31.2	2.5 (0.298)	527.5 (0.197)		
PDMAm ₄₀ -b-PiPMAm ₂₀ -b-PDMAm ₄₀	-	3.4 (0.286)	9.6 (0.265)		

Table S3. Cloud point (T_c) , hydrodynamic radius (R_h) , and aggregate size distribution (ASD) for

PiPMAm-b-PDMAm, PiPMAm-b-PDMAm-b-PiPMAm, and PDMAm-b-PiPMAm-b-PDMAm

^a Calculated based on CONTIN analysis. ^b Calculated based on cumulant analysis. ^c Measured at 60 °C.