

Electronic Supplementary Information for:

**Thermoresponsive star-shaped polymer with
heteroarm type with methacrylates: Preparation
by living radical polymerization method and its
topological effect**

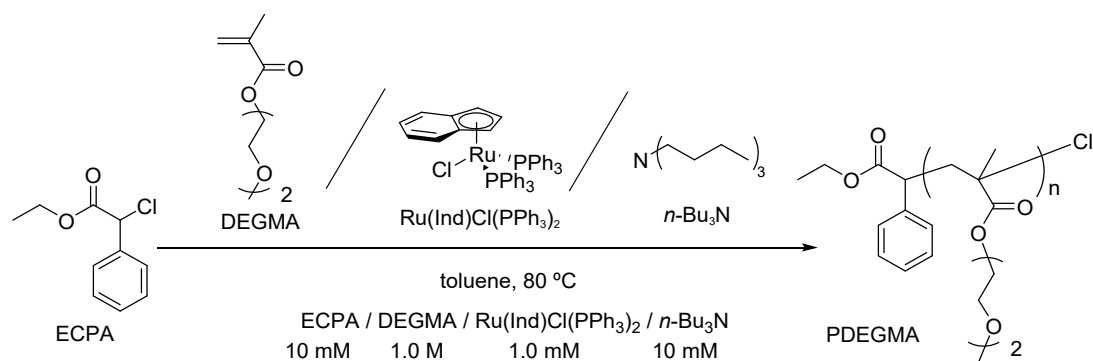
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The supporting information are composed of 10 schemes and 18 figures in 12 pages.



Scheme S1. Synthesis of PDEGMA by Ru-catalyzed living radical polymerization.

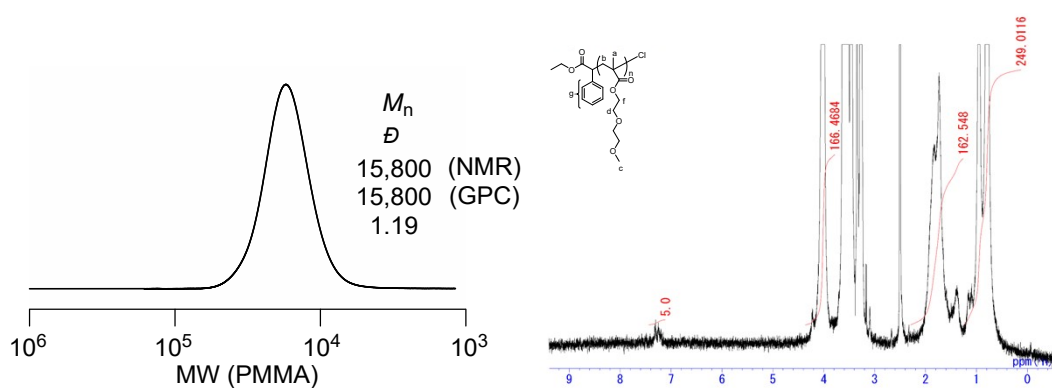


Figure S1. SEC curve (left) and ¹H NMR spectrum of PDEGMA in DMSO-d₆ (right).

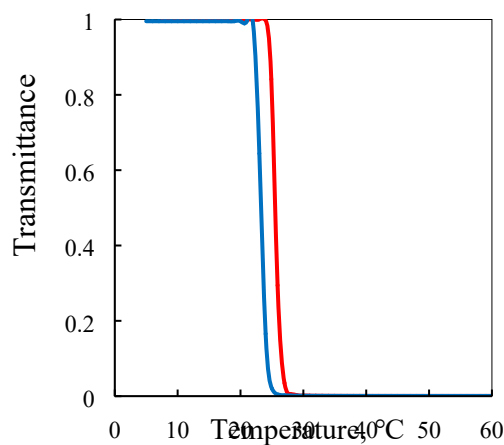
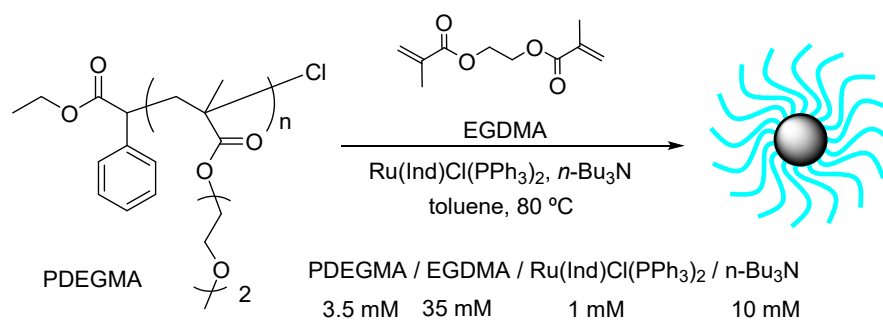


Figure S2. UV diagrams, traced by the transmittance with a 500 nm light beam, of 2 mg mL⁻¹ aqueous solution of PDEGMA: heating or cooling rate 1 °C min⁻¹, heating up (red) and cooling down (blue).



Scheme S2. Synthesis of star-shaped PDEGMA by Ru-catalyzed living radical polymerization.

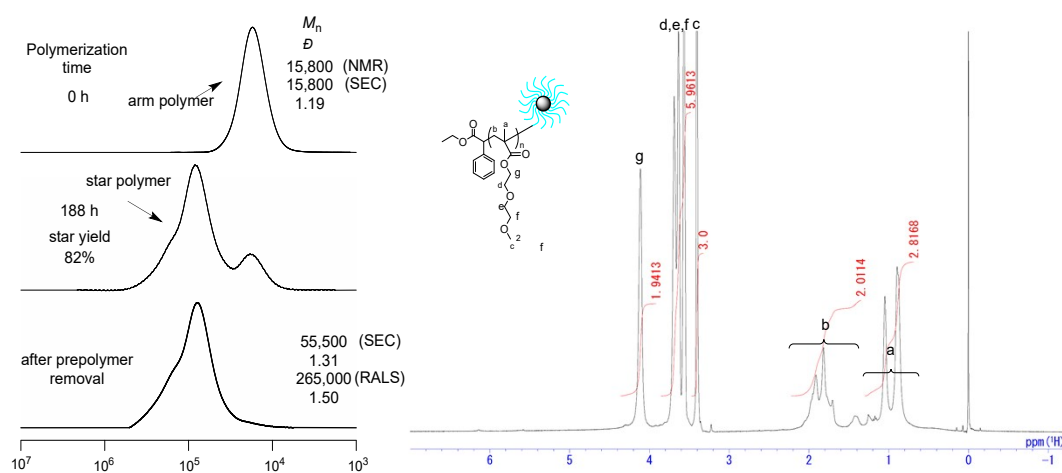
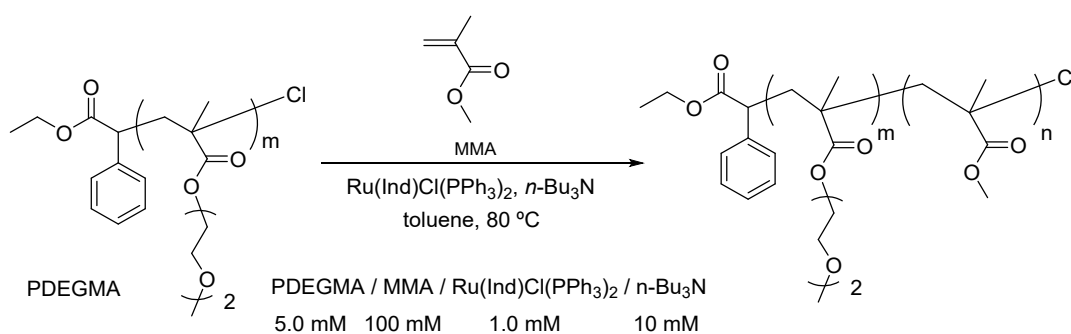


Figure S3. SEC curves (left) and ¹H NMR spectrum of star-shaped PDEGMA in CDCl₃ (right).



Scheme S3. Synthesis of PDEGMA-*b*-PMMA by Ru-catalyzed living radical polymerization.

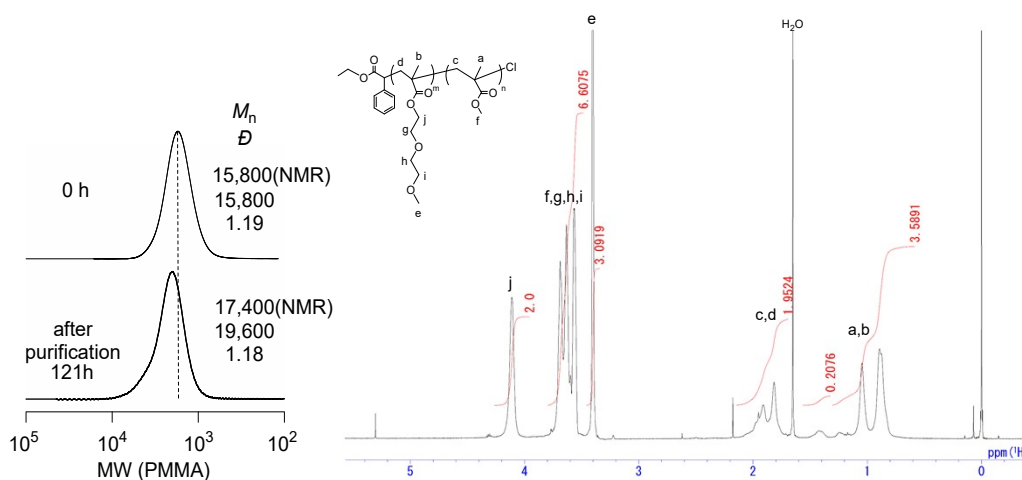


Figure S4. SEC curves (left) and ¹H NMR spectrum of PDEGMA-*b*-PMMA in CDCl₃ (right).

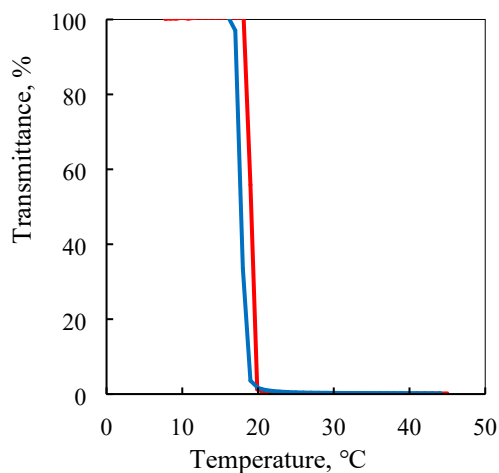
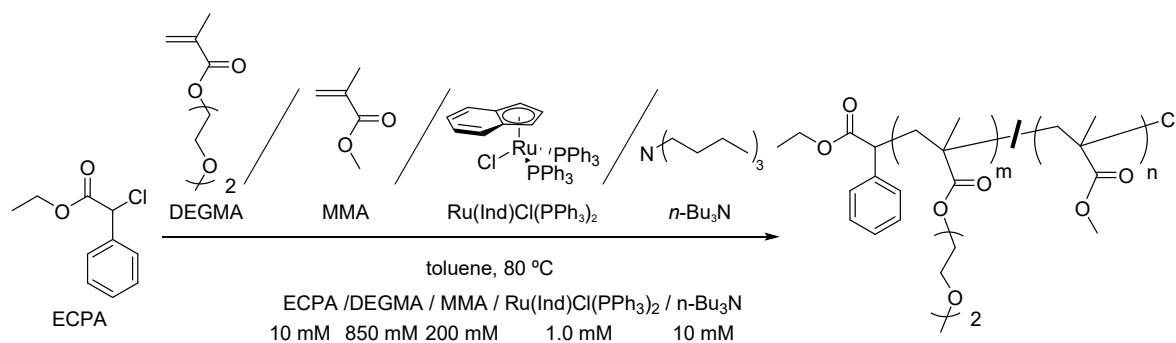


Figure S5. UV diagrams, traced by the transmittance with a 500 nm light beam, of 2 mg mL⁻¹ aqueous solution of PDEGMA-*b*-PMMA: heating or cooling rate 1 °C min⁻¹, heating up (red) and cooling down (blue).



Scheme S4. Synthesis of P(DEGMA-*stat*-MMA) by Ru-catalyzed living radical polymerization.

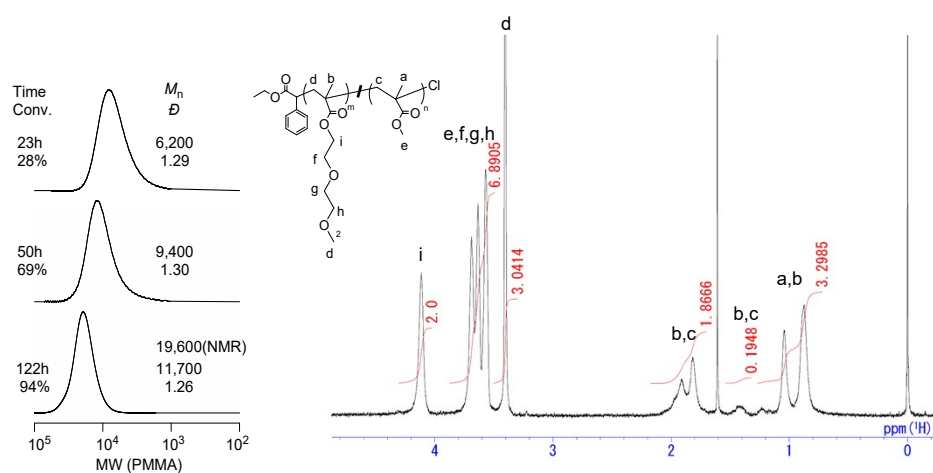


Figure S6. SEC curves (left) and ¹H NMR spectrum of P(DEGMA-*stat*-MMA) in CDCl₃ (right).

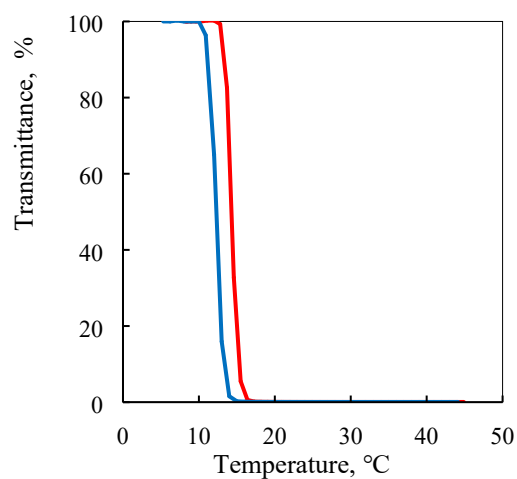
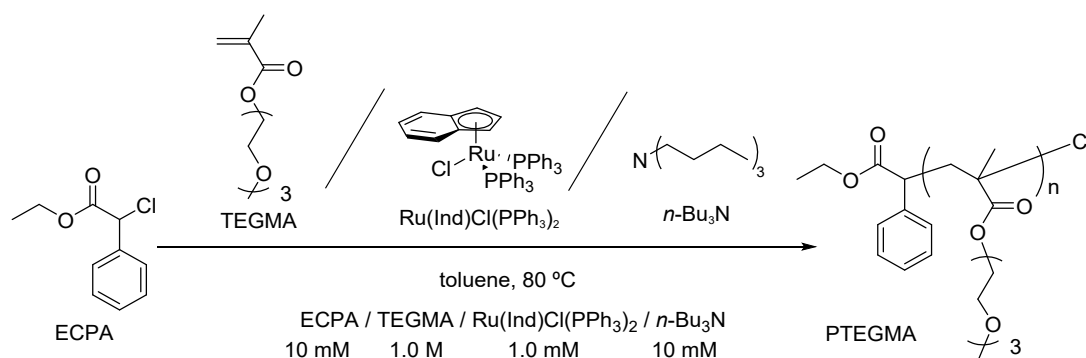


Figure S7. UV diagrams, traced by the transmittance with a 500 nm light beam, of 2 mg mL⁻¹ aqueous solution of P(DEGMA-*stat*-MMA): heating or cooling rate 1 °C min⁻¹, heating up (red) and cooling down (blue).



Scheme S5. Synthesis of PTEGMA by Ru-catalyzed living radical polymerization.

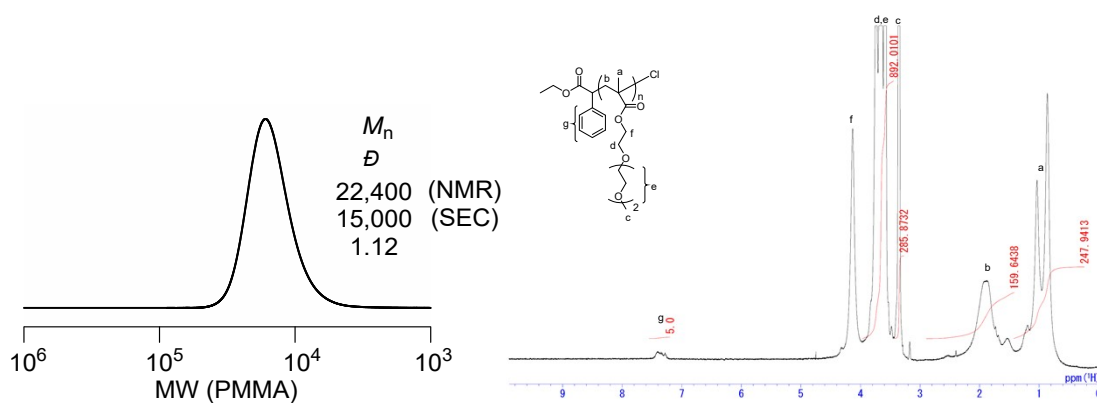


Figure S8. SEC curve (left) and ^1H NMR spectrum of PTEGMA in D_2O (right, water signal removal).

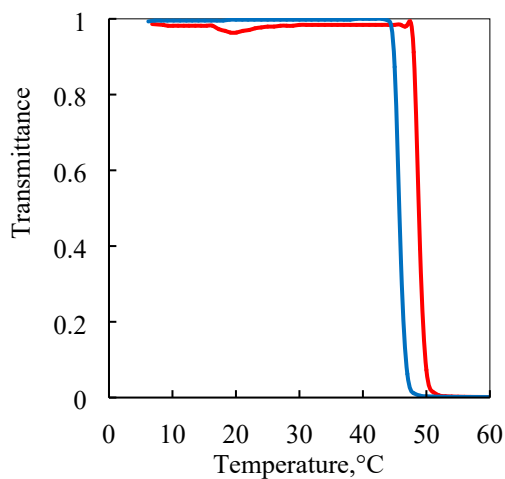
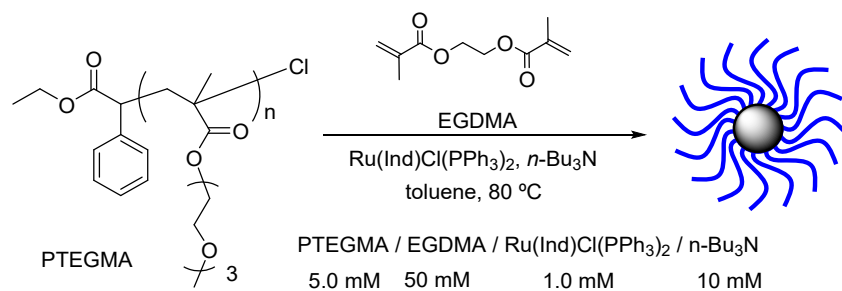


Figure S9. UV diagrams, traced by the transmittance with a 500 nm light beam, of 2 mg mL^{-1} aqueous solution of PTEGMA: heating or cooling rate $1 \text{ }^\circ\text{C min}^{-1}$, heating up (red) and cooling down (blue).



Scheme S6. Synthesis of star-shaped PTEGMA by Ru-catalyzed living radical polymerization.

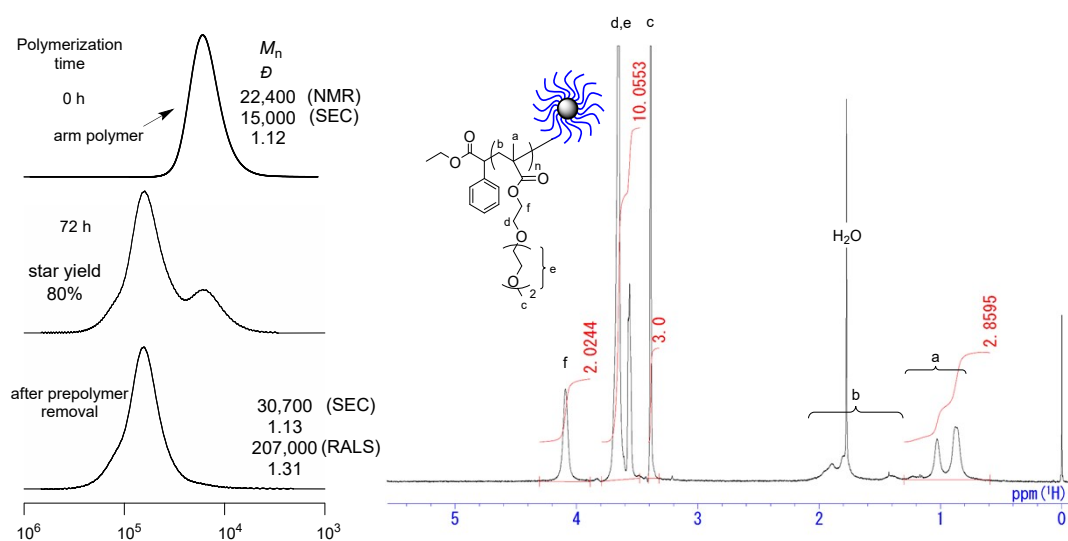


Figure S10. SEC curves (left) and (B) ¹H NMR spectrum of star-shaped PTEGMA in CDCl₃ (right).

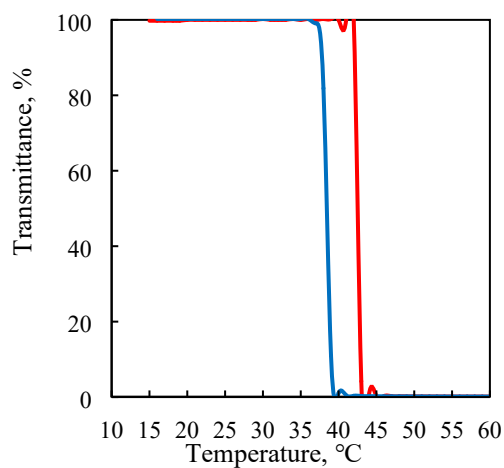
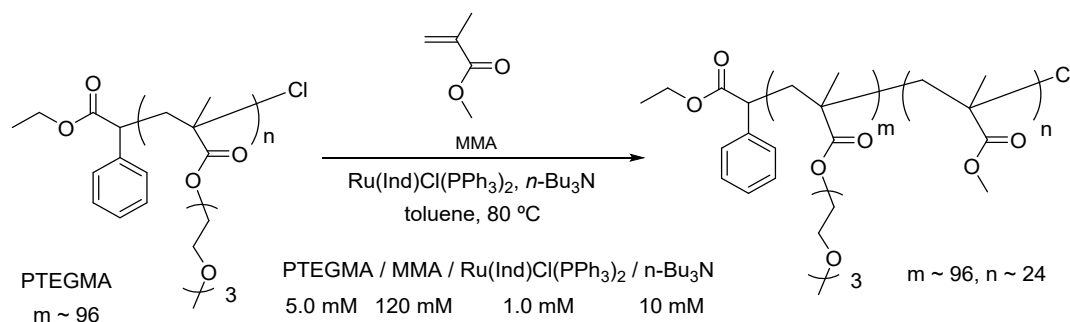


Figure S11. UV diagrams, traced by the transmittance with a 500 nm light beam, of 2 mg mL⁻¹ aqueous solution of star-shaped PTEGMA: heating or cooling rate 1 °C min⁻¹, heating up (red) and cooling down (blue).



Scheme S7. Synthesis of PTEGMA-*b*-PMMA by Ru-catalyzed living radical polymerization.

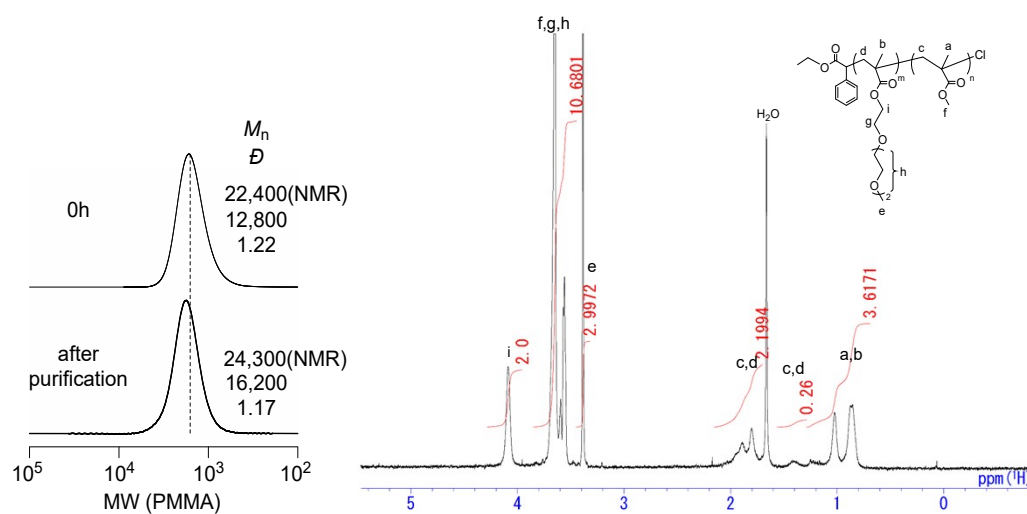


Figure S12. SEC curves (left) and ¹H NMR spectrum of PTEGMA-*b*-PMMA in CDCl₃ (right).

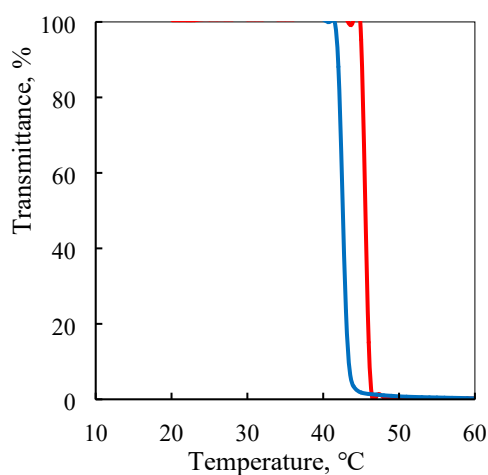
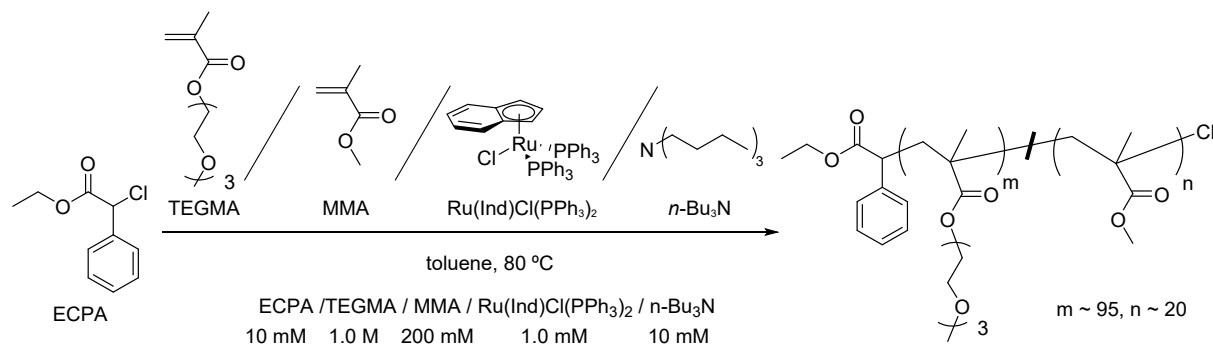


Figure S13. UV diagrams, traced by the transmittance with a 500 nm light beam, of 2 mg mL⁻¹ aqueous solution of PTEGMA-*b*-PMMA: heating or cooling rate 1 °C min⁻¹, heating up (red) and cooling down (blue).



Scheme S8. Synthesis of P(TEGMA-*stat*-MMA) by Ru-catalyzed living radical polymerization.

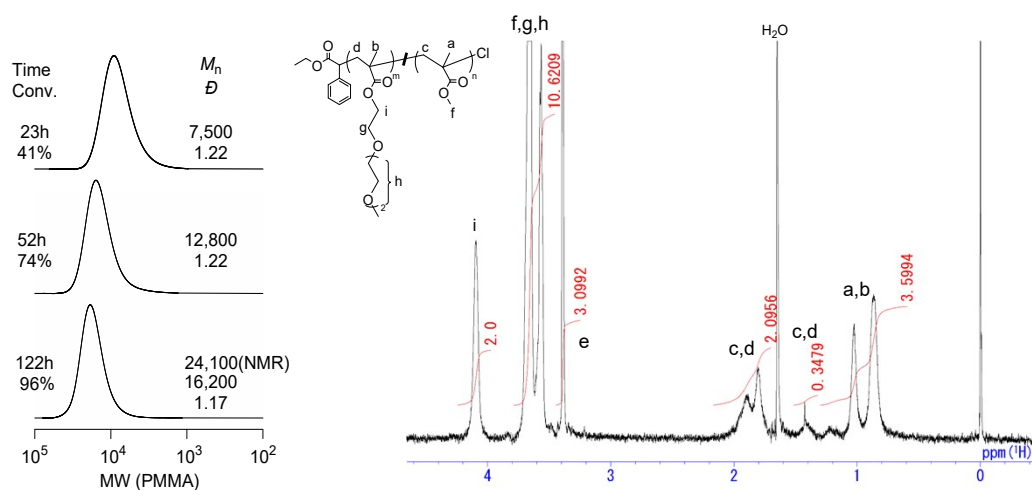


Figure S14. SEC curves (left) and ¹H NMR spectrum of P(TEGMA-*stat*-MMA) in CDCl₃ (right).

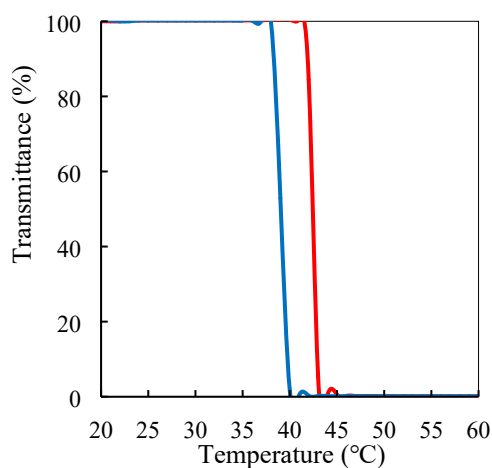
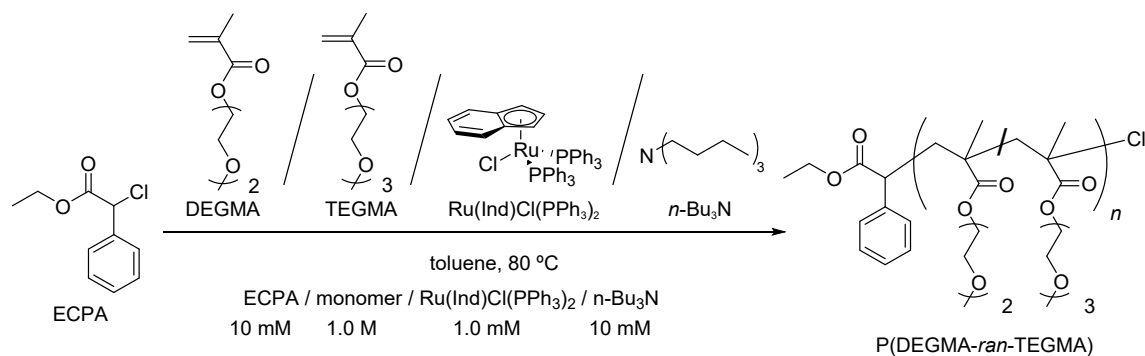


Figure S15. UV diagrams, traced by the transmittance with a 500 nm light beam, of 2 mg mL⁻¹ aqueous solution of P(TEGMA-*stat*-MMA): heating or cooling rate 1 °C min⁻¹, heating up (red) and cooling

down (bule).



Scheme S9. Synthesis of P(DEGMA-*stat*-TEGMA) by Ru-catalyzed living radical polymerization.

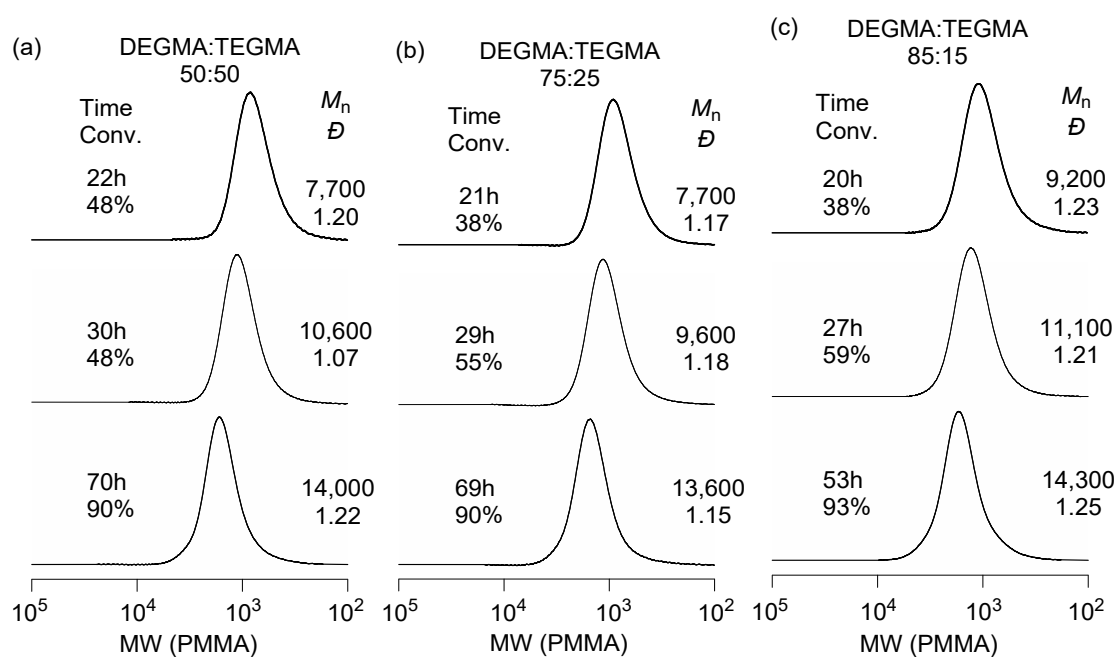


Figure S16. SEC curves of P(TEGMA-*stat*-MMA) with different DEGMA:TEGMA ratio. DEGMA:TEGMA = (a) 50:50, (b) 75:25, (c) 85:15.

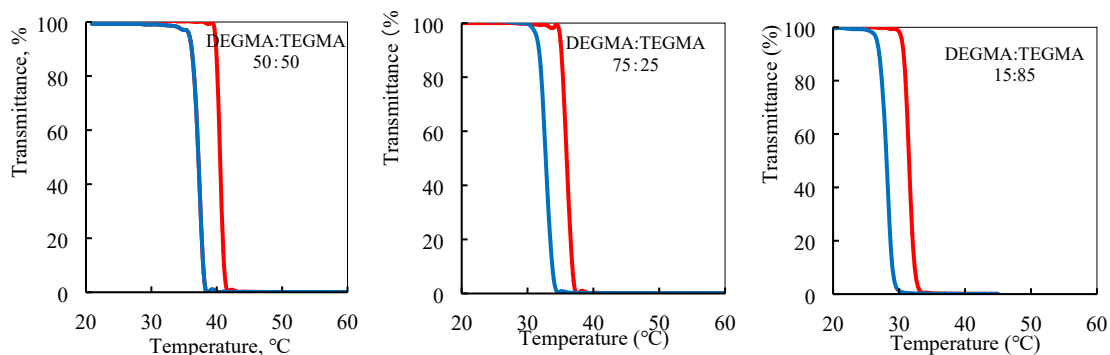
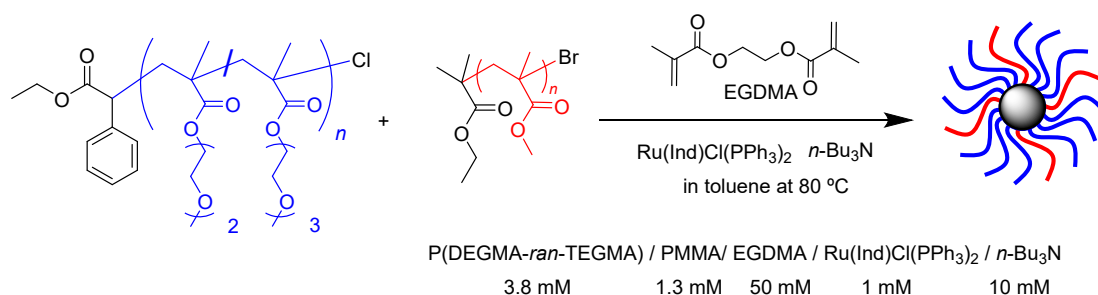


Figure S17. UV diagrams, traced by the transmittance with a 500 nm light beam, of 2 mg mL⁻¹ aqueous solution of P(DEGMA-*stat*-TEGMA) with different DEGMA:TEGMA ratio: heating or cooling rate 1 °C min⁻¹, heating up (red) and cooling down (blue). DEGMA:TEGMA = 50:50 (left), 75:25 (center), 85:15 (right).



Scheme S10. Synthesis of heteroarm star-shaped P(DEGMA-*stat*-TEGMA)/PMMA by Ru-catalyzed living radical polymerization.

Calculation of arm ratio and arm number of the heteroarm star-shaped P(DEGMA-*stat*-TEGMA)/PMMA

The molar ratio of DEGMA and TEGMA was determined from ¹H NMR spectrum of P(DEGMA-*stat*-TEGMA) in CDCl₃ by using the signal intensity ratio of the methylene ester group, the methylene ether group, and the methyl ether group of the side chain to be DEGMA:TEGMA = 83:17. The degree of polymerization (DP_n) of P(DEGMA-*stat*-TEGMA) was determined from ¹H NMR spectrum of P(DEGMA-*stat*-TEGMA) in DMSO-*d*₆ by using the signal intensity ratio of the phenyl group (5H) at the initiating end and the methylene ester group (2n H) to be 84, where n means DP_n . Thus, M_n of P(DEGMA-*stat*-TEGMA) was determined as 16,600 (= 84 × 188.2 × 0.83 + 84 × 232.3 × 0.17 + 198.7), which was close to the value obtained from SEC analysis. M_n of PMMA was obtained from

SEC analysis to be 8,200 and DP_n of PMMA was thus calculated to be 80.

Assuming the arm ratio of P(DEGMA-*stat*-TEGMA):PMMA is x:y, the signal intensity ratio of the methylene ester group (DEGMA/TEGMA) (signal f in Fig. 2), the methylene ether group (DEGMA/TEGMA) and methyl ester group (MMA) (signal e+i in Fig. 2), and the methyl ether group (DEGMA/TEGMA) (signal d in Fig. 2) is shown as

$$I_f : I_{e+i} : I_d = 84 \times 2 \times x : 84 \times (6 \times 0.83 + 10 \times 0.17) \times x + 80 \times 3 \times y : 3 \times x$$

, where I_f , I_{e+i} , and I_d means the intensities of signal f, e+i, and d, respectively.

From above equation, the arm ratio of P(DEGMA-*stat*-TEGMA):PMMA was determined as 73:27.

The arm number of the heteroarm star-shaped polymer was calculated as the following equation:

$$N_{arm} = \frac{M_{n(star)} - MW_{(EGDMA)} \times 10}{M_{n(P(DEGMA-stat-TEGMA))} \times 0.73 + M_{n(PMMA)} \times 0.27} = 8.7$$

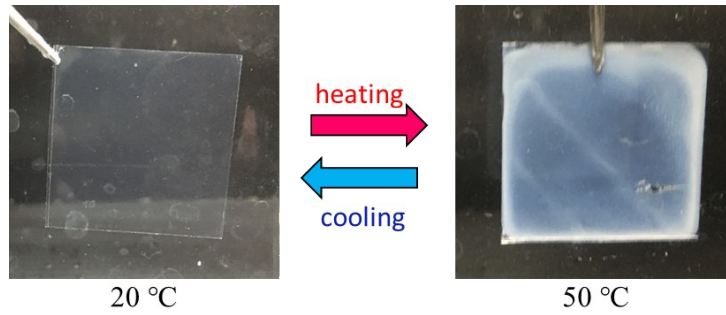


Figure S18. Photo images of reversible thermoresponsive behavior of heteroarm star-shaped P(DEGMA-*stat*-TEGMA)/PMMA-coated film in water at 20 and 50 °C.