Electronic Supplementary Material (ESI) for Soft Matter.

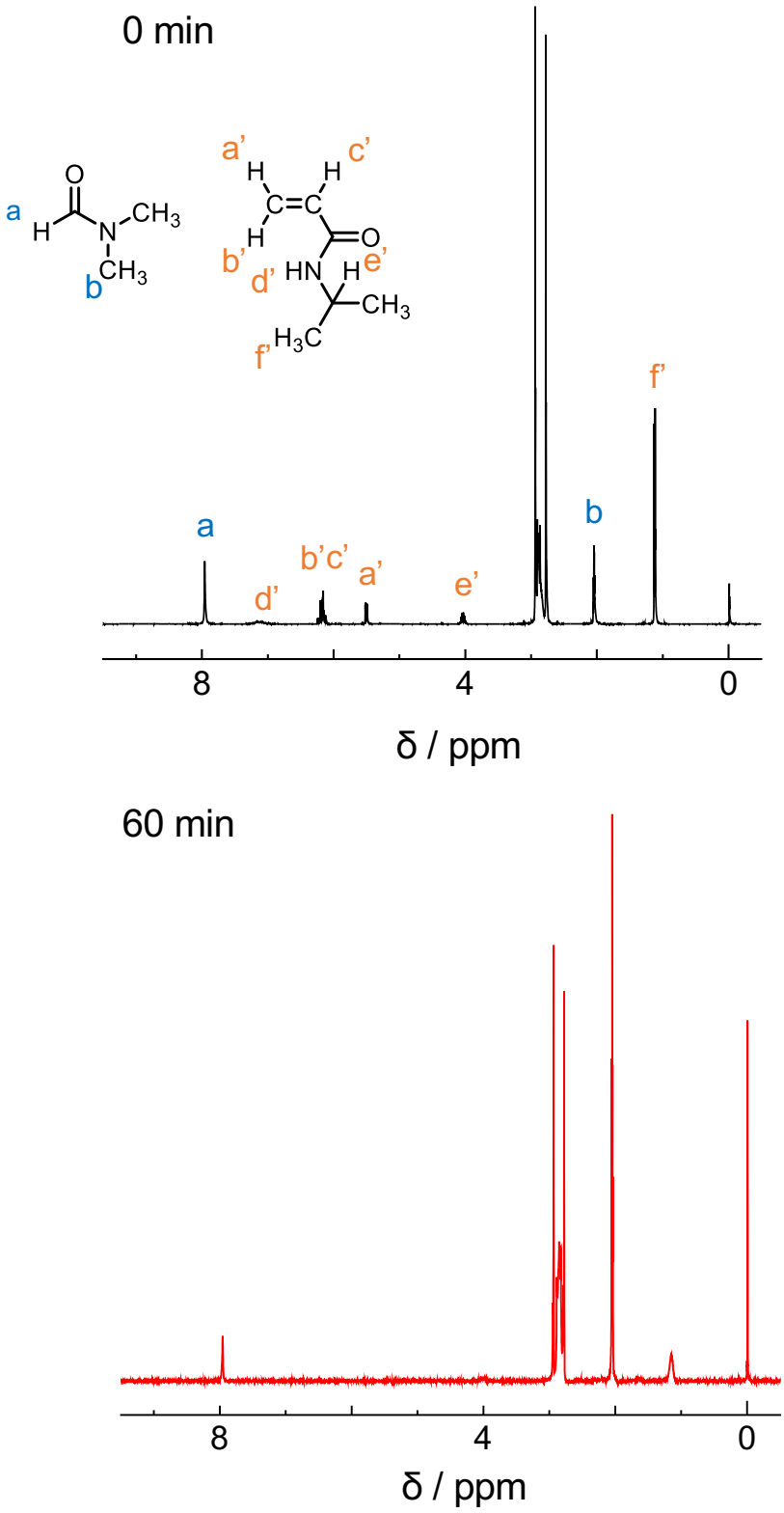


Figure S1. ^{1}H NMR spectra of the monomer solution (0 min) and the reaction solution sampled after 1 hour.

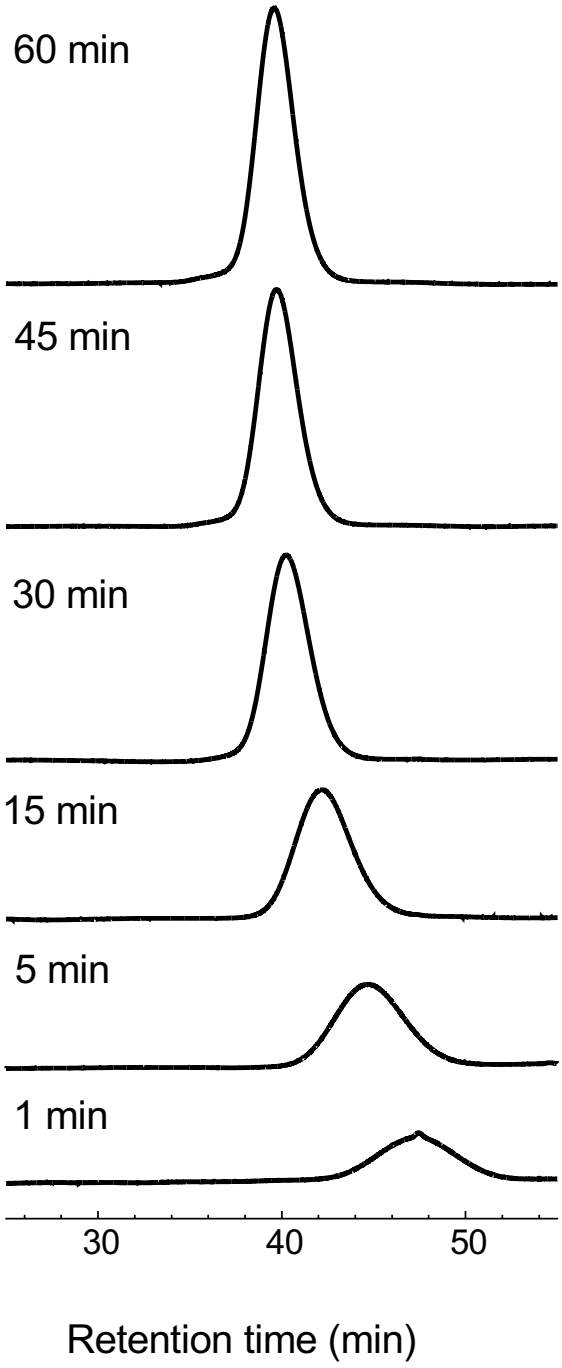


Figure S2. SEC curve with reaction time for tetrabranched PNIPA

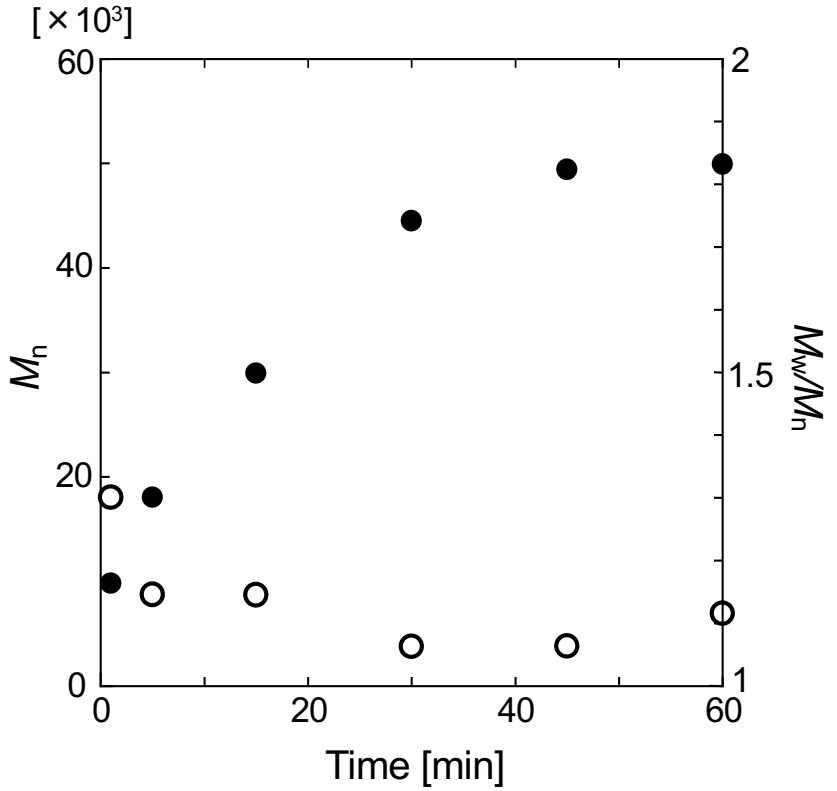


Figure S3. Number average molecular weight and molecular weight distribution calculated by SEC measurement versus reaction time for tetrabranched PNIPA

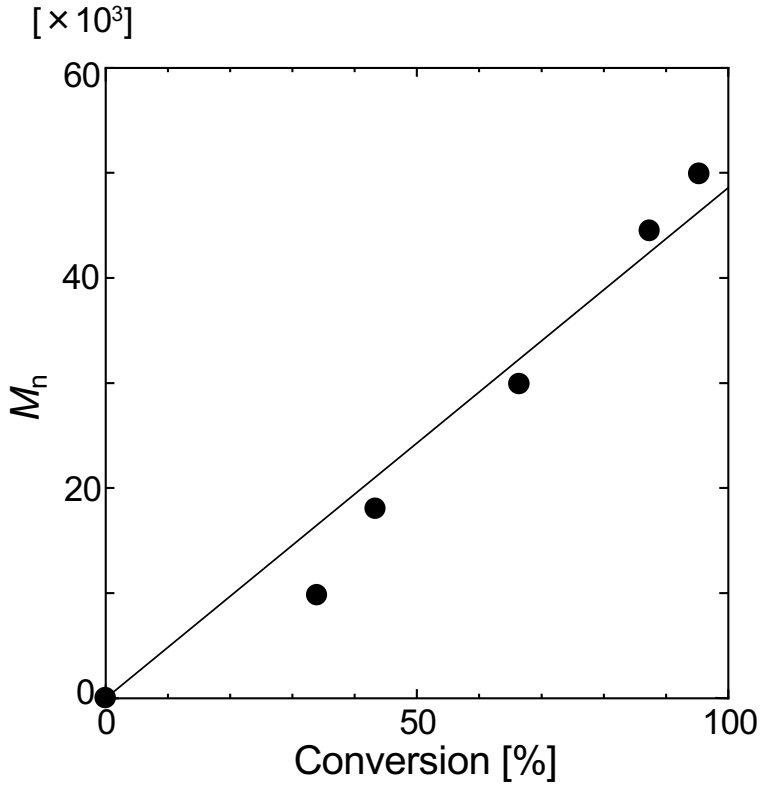


Figure S4. Number average molecular weight of tetrabranched PNIPA to monomer conversion ratio, calculated by SEC measurement

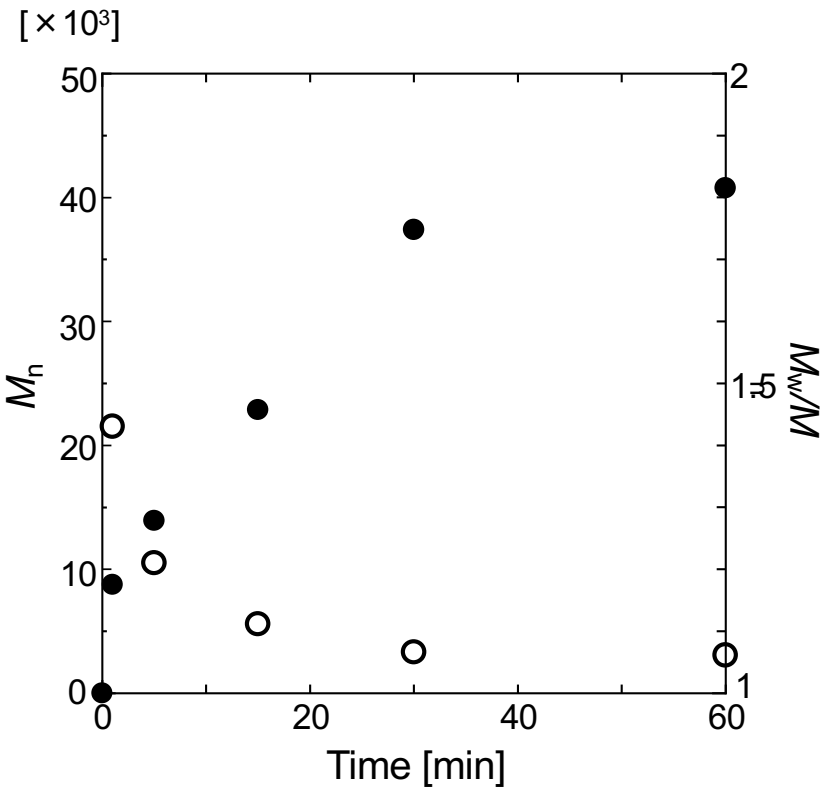


Figure S5. Number average molecular weight and molecular weight distribution of tetrabranched PNIPA portion calculated by SEC measurement versus reaction time for tetrabranched $PNIPA_{0.8}$-b-$PDMA_{0.2}$

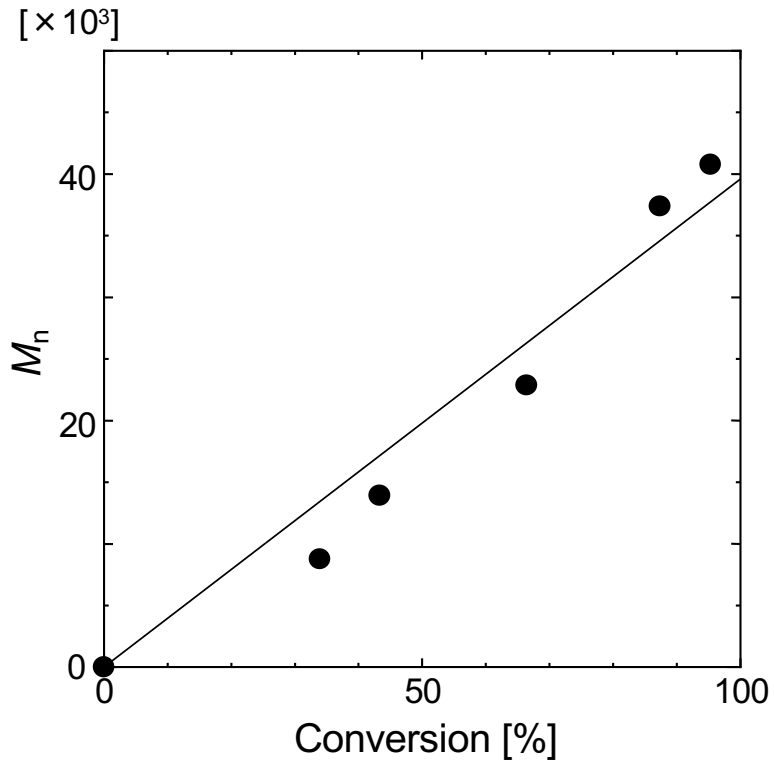


Figure S6. Number average molecular weight of tetrabranched PNIPA portion for tetrabranched $PNIPA_{0.8}$-b-$PDMA_{0.2}$ to monomer conversion ratio, calculated by SEC measurement

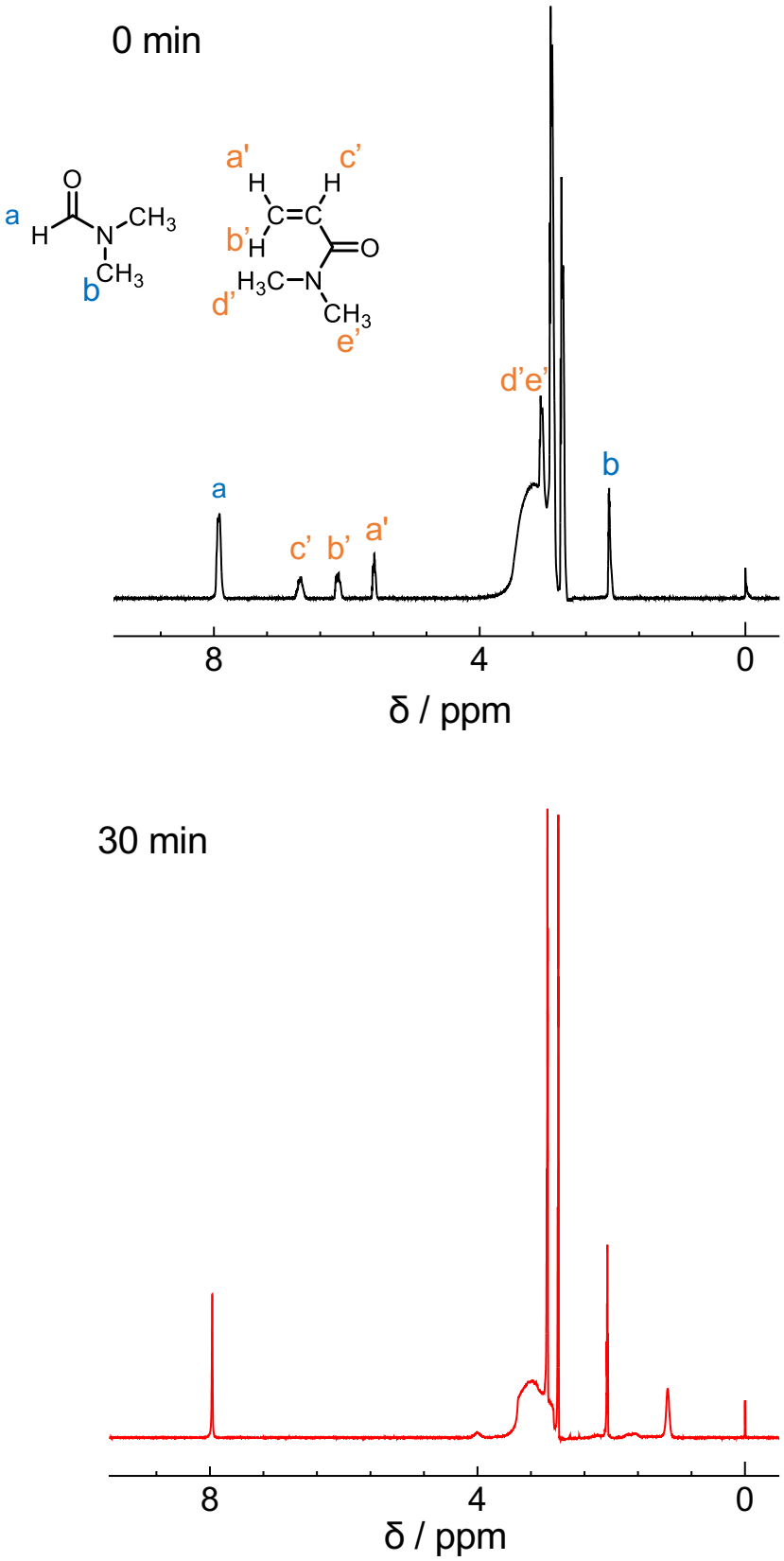


Figure S7. ^{1}H NMR spectra of DMA solution and the reaction solution sampled 30 min after the addition of DMA.

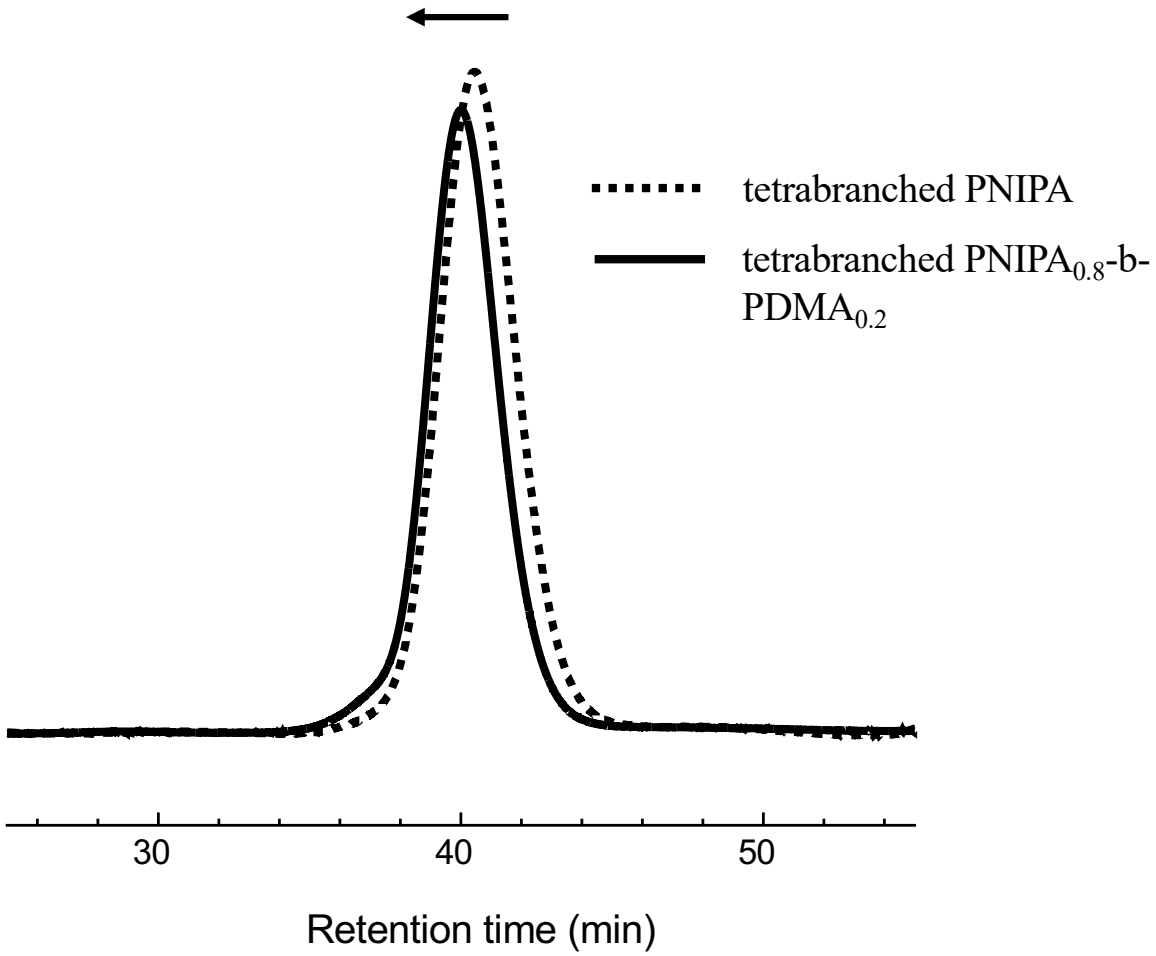


Figure S8. SEC curves of tetrabranched PNIPA (60 min after starting the polymerization of NIPA) obtained in the results shown in Fig. S5 and S6 and tetrabranched $PNIPA_{0.8}$-b-$PDMA_{0.2}$ obtained by subsequent reaction with DMA (30 min after the addition of DMA)

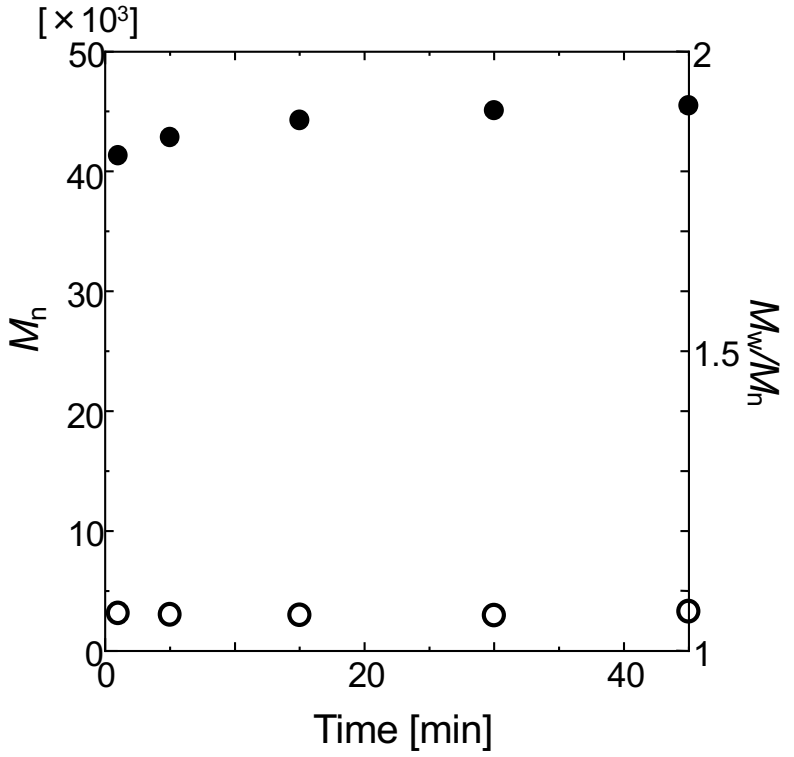


Figure S9. Number average molecular weight and molecular weight distribution calculated from SEC measurement versus reaction time (tetrabranched $PNIPA_{0.8}$-b-$PDMA_{0.2}$)

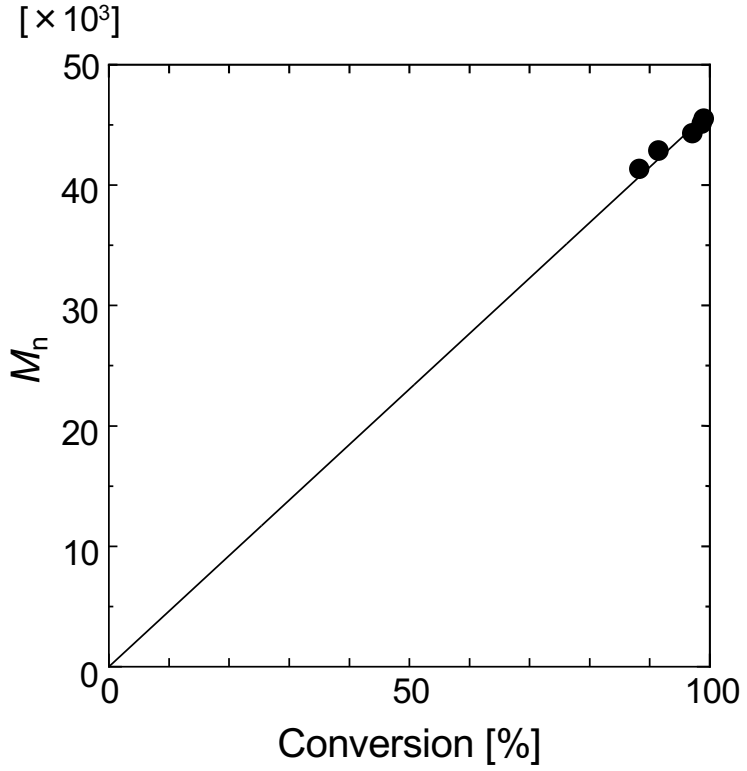
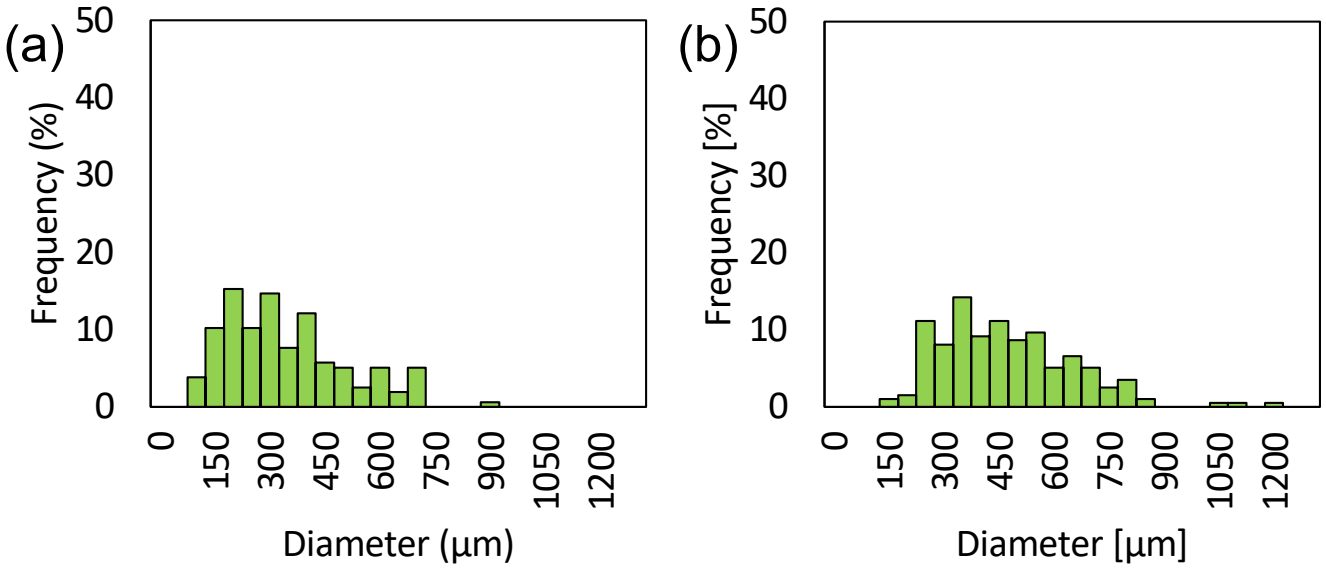
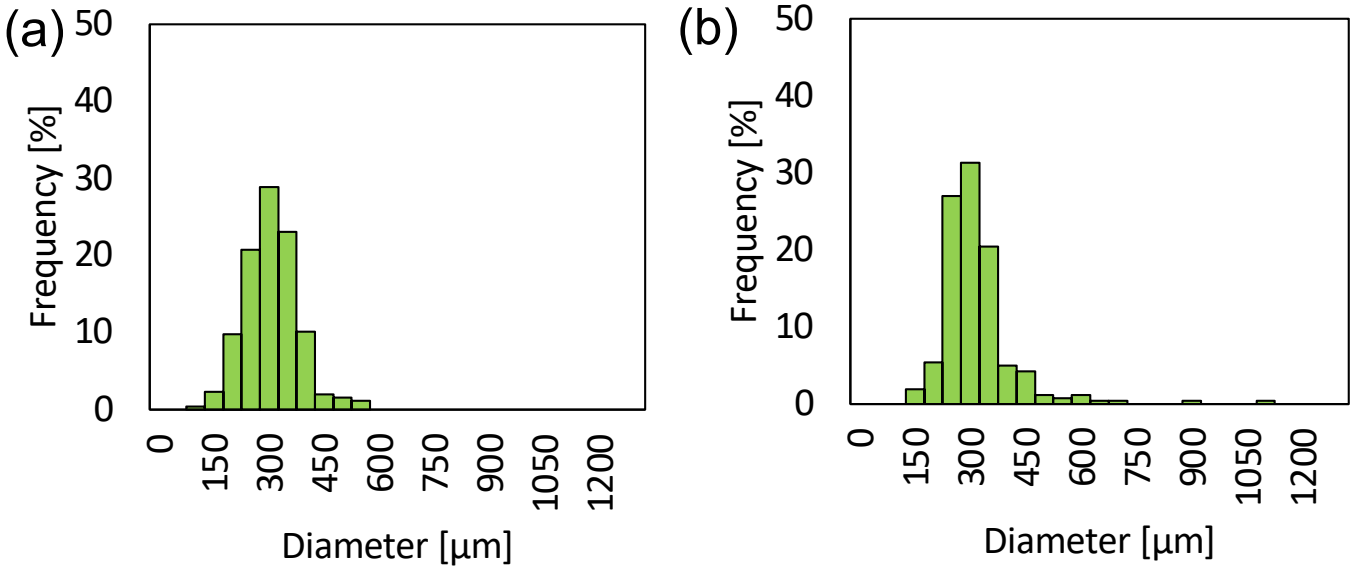


Figure S10. Number average molecular weight to monomer conversion ratio, calculated by SEC measurement (tetrabranched $PNIPA_{0.8}$-b-$PDMA_{0.2}$)



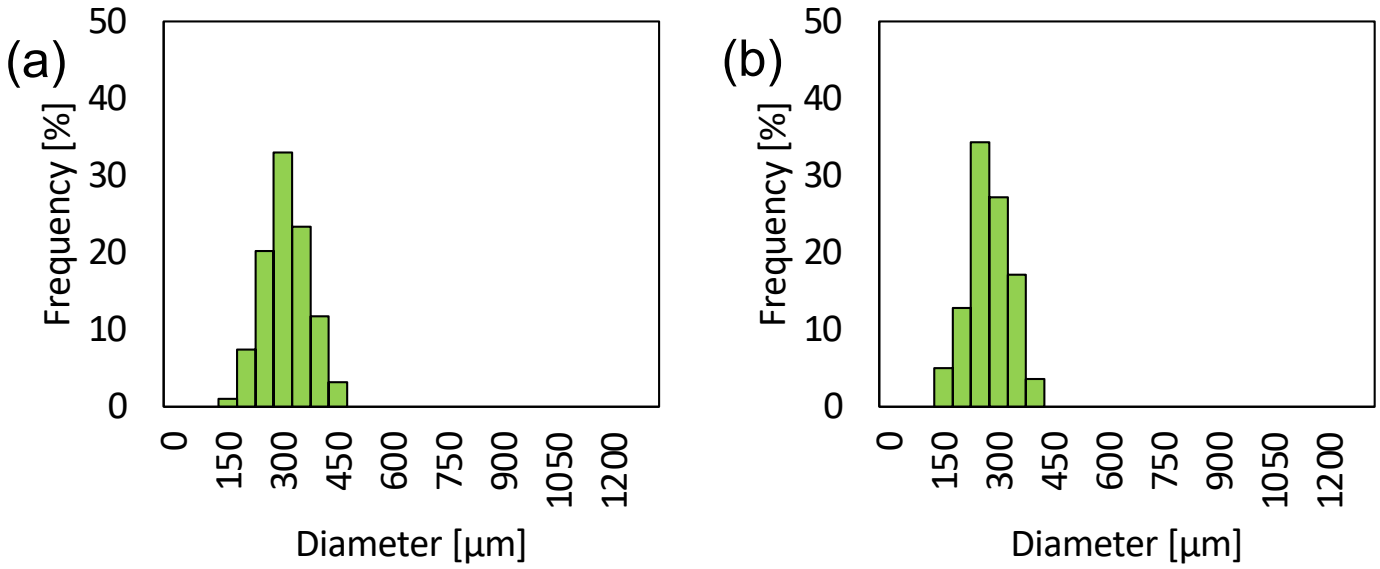
	In oil phase	In water phase
Average [μm]	320	446.9
Max [μm]	877.5	1178.4
Min [μm]	80.5	100.9
CV [%]	52.7	40.4

Figure S11. Particle size distribution of PNIPA gel at 20° C.



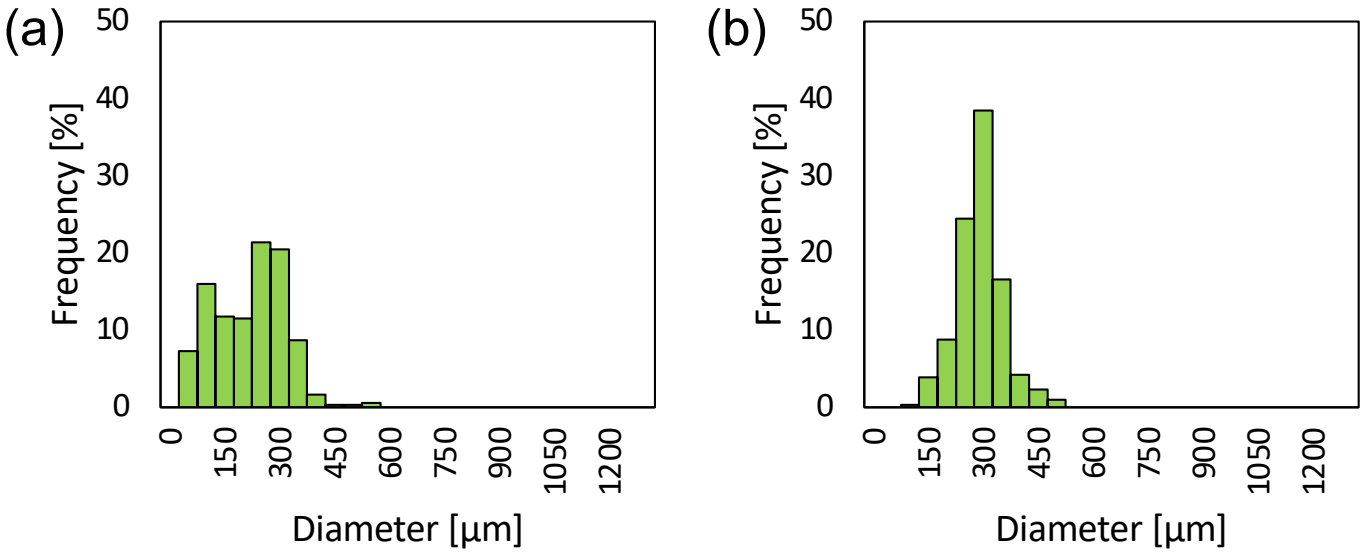
	In oil phase	In water phase
Average [μm]	281.5	290.5
Max [μm]	281.5	1094.0
Min [μm]	83.3	121.7
CV [%]	25.9	34.7

Figure S12. Particle size distribution of $PNIPA_{0.9}$ -b-$PDMA_{0.1}$ gel at 20° C.



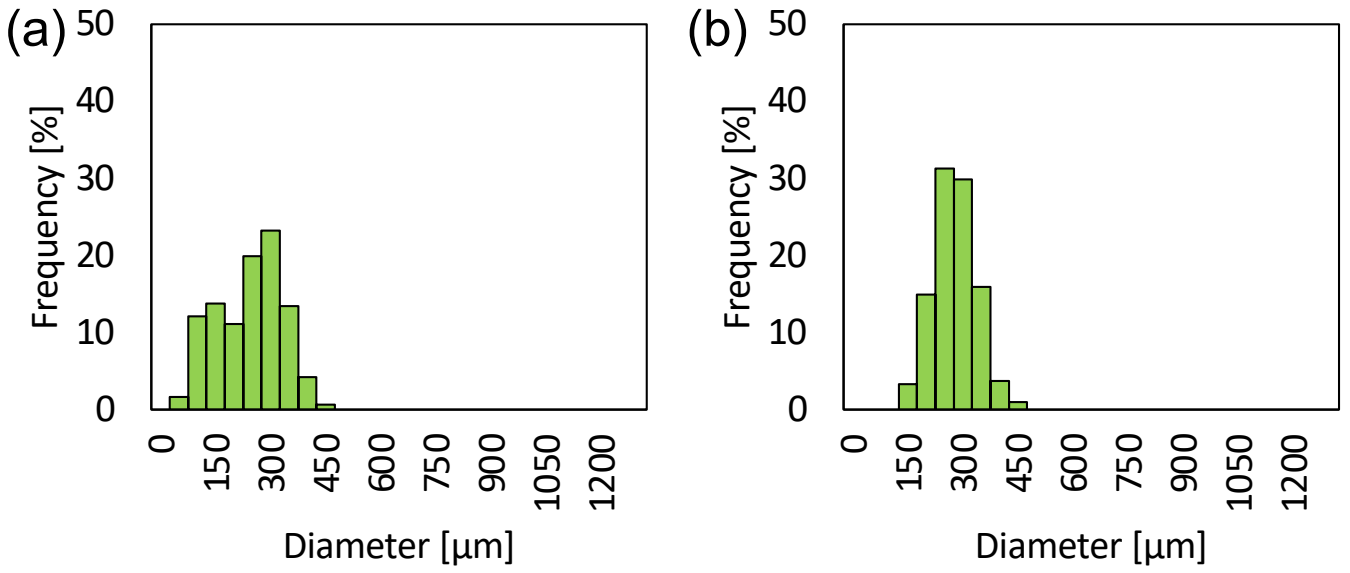
	In oil phase	In water phase
Average [μm]	250	282.8
Max [μm]	373.3	441.8
Min [μm]	109.9	105.0
CV [%]	22.3	22.3

Figure S13. Particle size distribution of $PNIPA_{0.8}$ -b-$PDMA_{0.2}$ gel at 20° C.



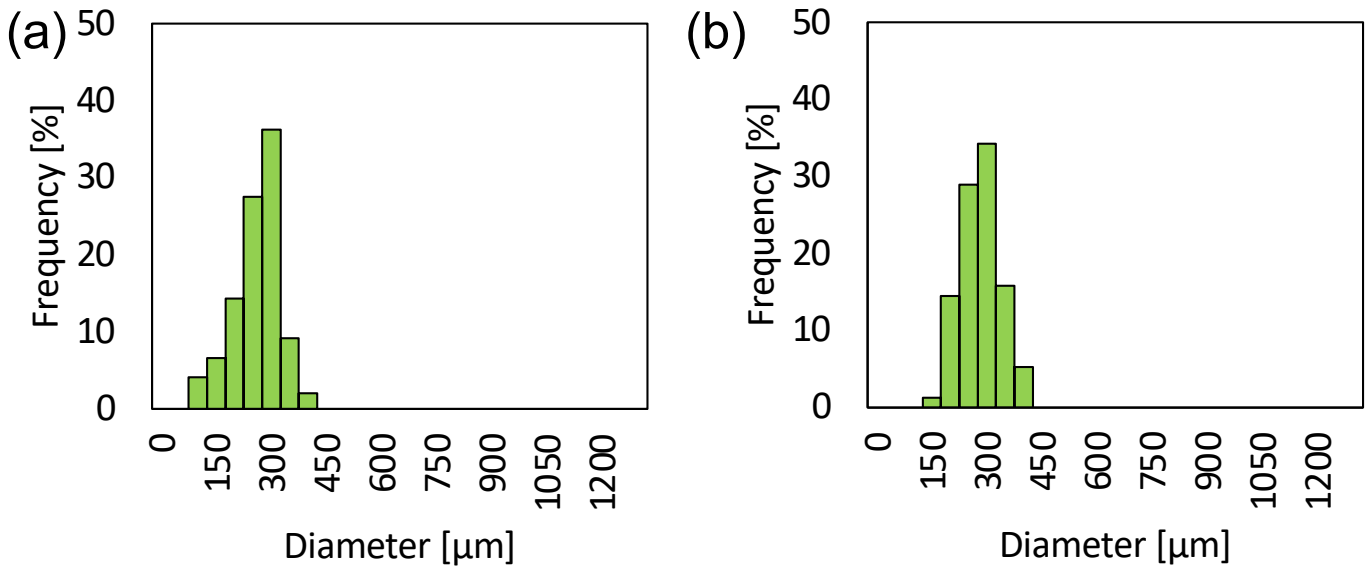
	In oil phase	In water phase
Average [μm]	250	282.8
Max [μm]	548.2	493.3
Min [μm]	20.1	92.8
CV [%]	49.2	23.9

Figure S14. Particle size distribution of $PNIPA_{0.7}$ -b-$PDMA_{0.3}$ gel at 20° C.



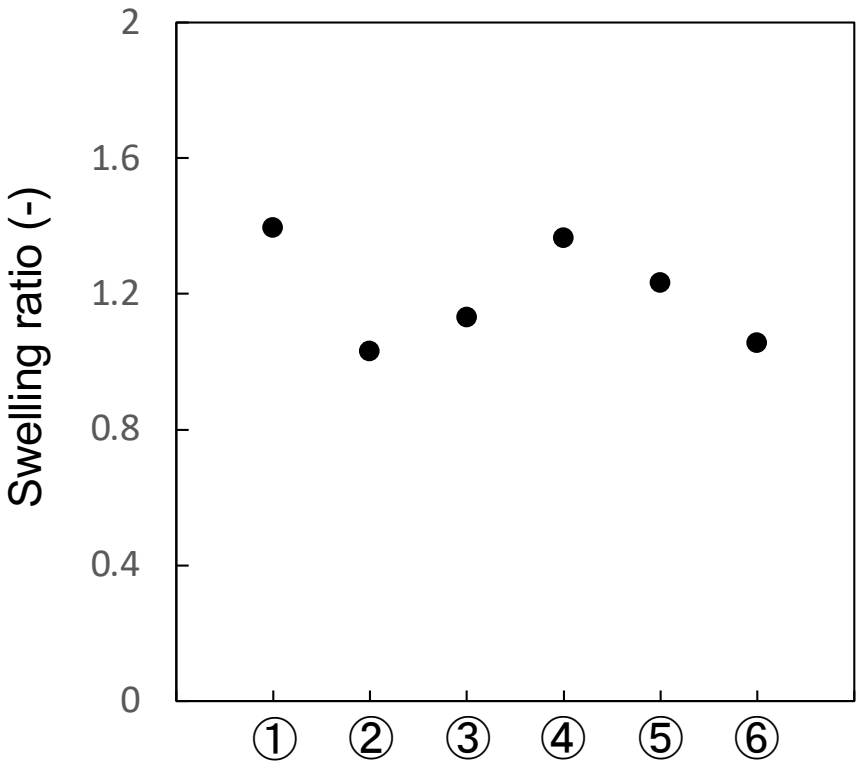
	In oil phase	In water phase
Average [μm]	200.5	247.5
Max [μm]	400.6	404.9
Min [μm]	37.5	102.1
CV [%]	46.4	23.5

Figure S15. Particle size distribution of $PNIPA_{0.8}$-r-$PDMA_{0.2}$ gel at 20° C.



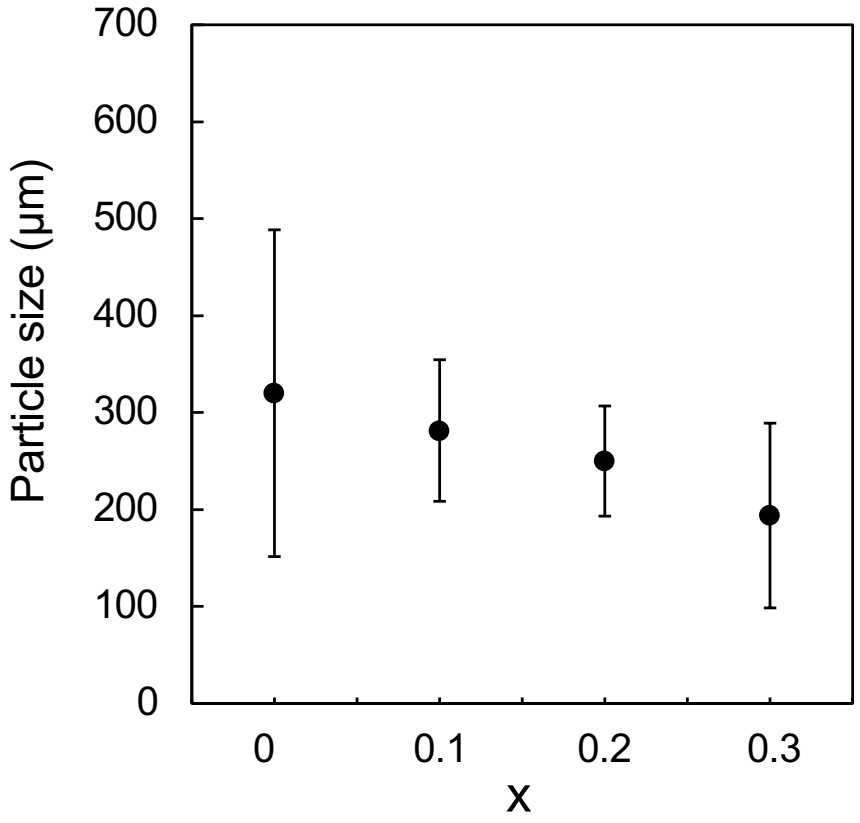
	In oil phase	In water phase
Average [μm]	242.4	256.0
Max [μm]	373.3	399.0
Min [μm]	118.2	142.2
CV [%]	21.2	20.8

Figure S16. Particle size distribution of conventional gel at 20° C.



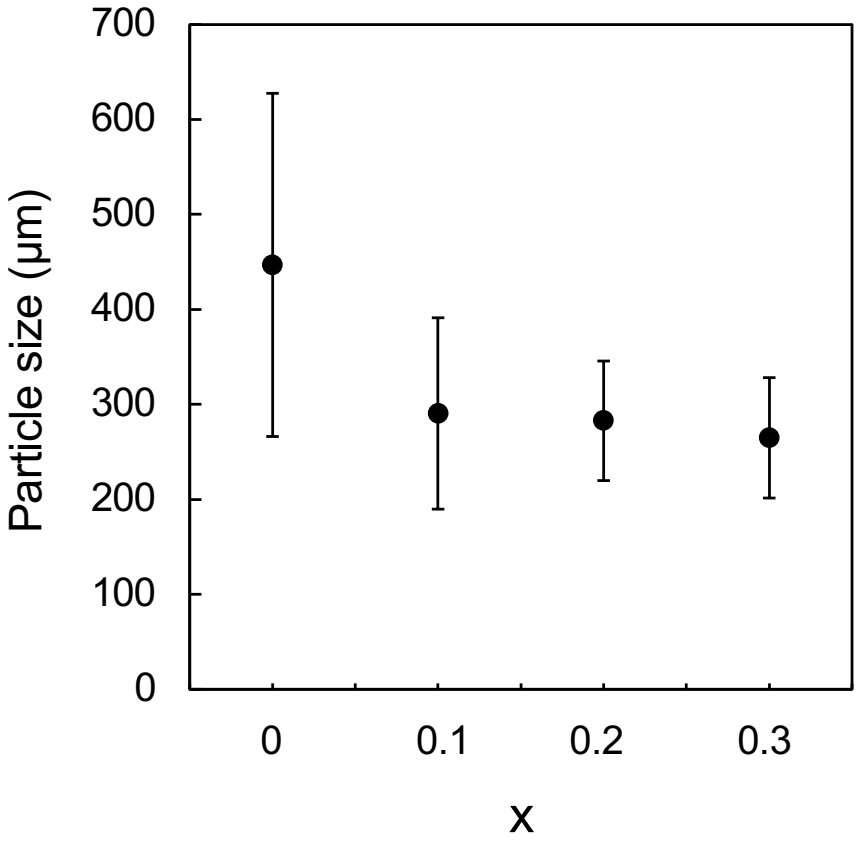
	Swelling ratio [-]
① PNIPA	1.40
② $PNIPA_{0.9}$-b-$PDMA_{0.1}$	1.03
③ $PNIPA_{0.8}$-b-$PDMA_{0.2}$	1.13
④ $PNIPA_{0.7}$-b-$PDMA_{0.3}$	1.37
⑤ $PNIPA_{0.8}$-r-$PDMA_{0.2}$	1.23
⑥ PNIPA (conventional)	1.06

Figure S17. Swelling ratio of each gel



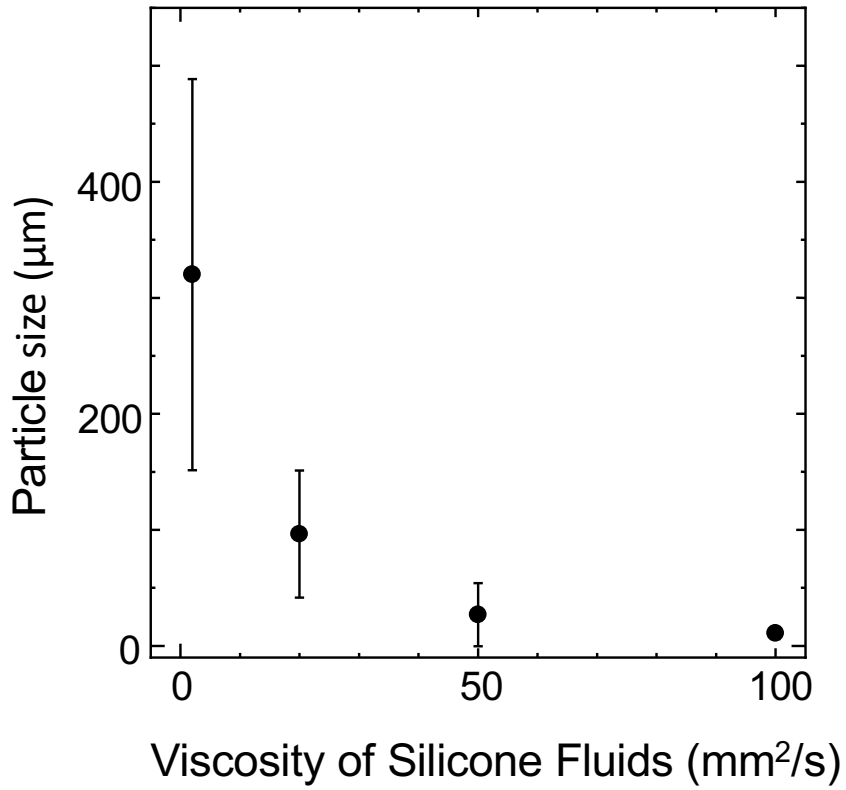
x	average [μm]	max [μm]	min [μm]	CV [-]
0 (PNIPA)	320	877.5	80.5	52.7
0.1 ($PNIPA_{0.9}$-b-$PDMA_{0.1}$)	281.5	534.8	83.3	25.9
0.2 ($PNIPA_{0.8}$-b-$PDMA_{0.2}$)	250.7	373.3	109.9	22.7
0.3 ($PNIPA_{0.7}$-b-$PDMA_{0.3}$)	193.8	548.2	20.1	49.2

Figure S18. Particle size of the gel in the oil phase at 20° C in the conditioned state.



x	average [μm]	max [μm]	min [μm]	CV [-]
0 (PNIPA)	446.9	1178.4	100.9	40.4
0.1 ($PNIPA_{0.9}$-b-$PDMA_{0.1}$)	290.5	1094.0	121.7	34.7
0.2 ($PNIPA_{0.8}$-b-$PDMA_{0.2}$)	282.8	441.8	105.0	22.3
0.3 ($PNIPA_{0.7}$-b-$PDMA_{0.3}$)	264.8	493.3	92.8	23.9

Figure S19. Particle size of gel in equilibrium swelling state when dispersed at 20° C in water.



Viscosity [mm^2/s]	average [μm]	max [μm]	min [μm]	CV
2	320.0	877.5	80.5	52.7
20	96.4	346.5	21.8	56.9
50	26.8	170.0	6.0	101.5
100	10.8	39.1	3.1	45.4

Figure S20. Particle size of PNIPA gel against viscosity of silicone fluid

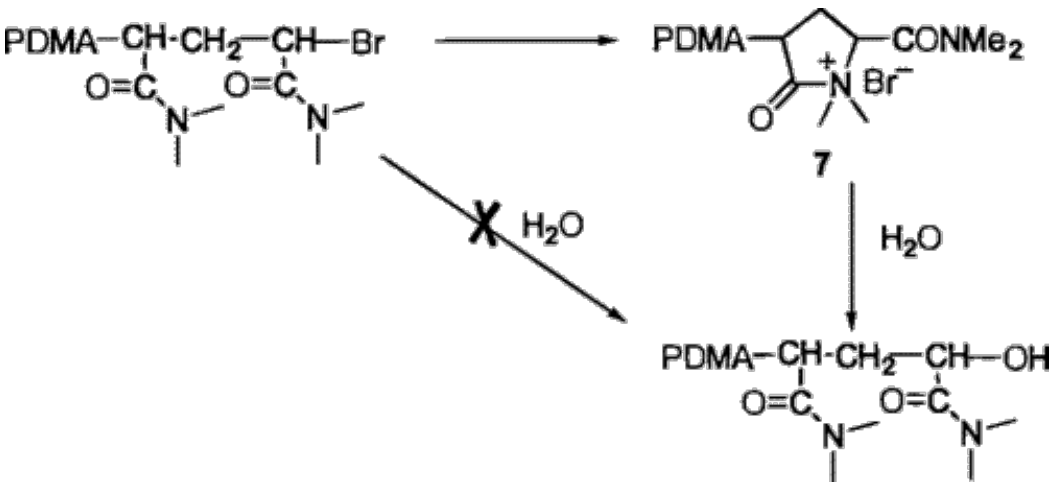


Figure S21. The bromine-terminated PDMA chain goes through a cyclic intermediate, which is hydrolyzed to become hydroxyl-terminated.

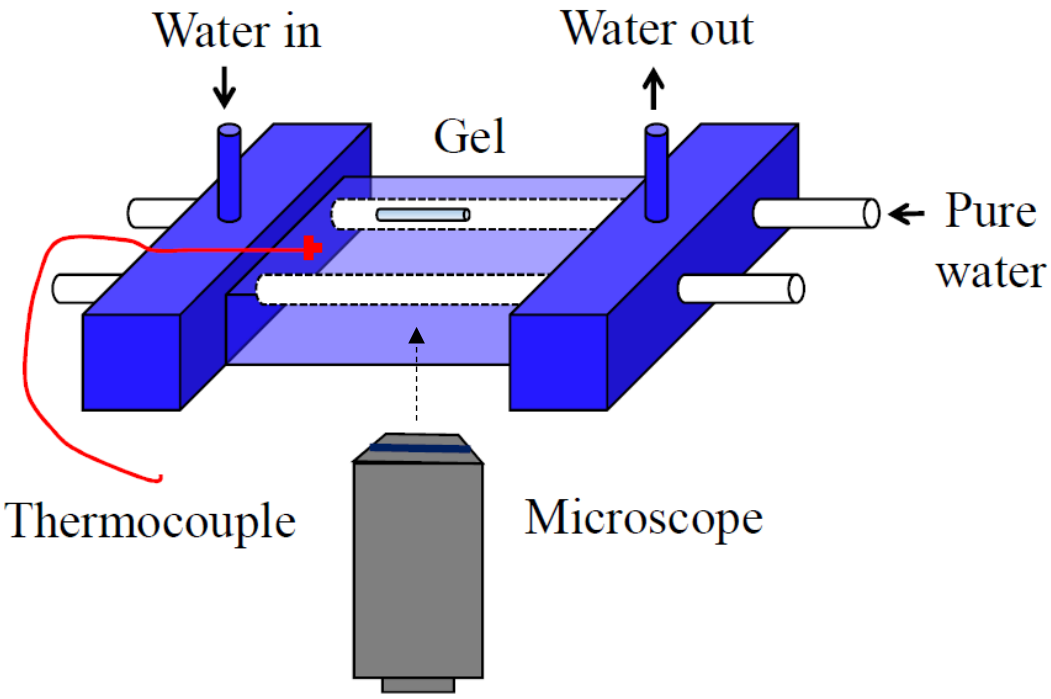


Figure S22. Illustration of equipment for swelling measurement of spherical gels

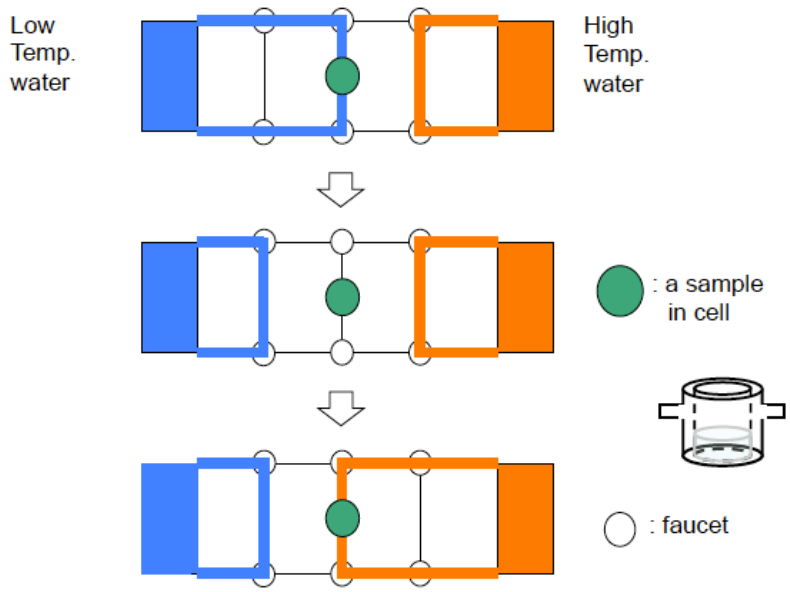


Figure S23. Circuit for temperature jump

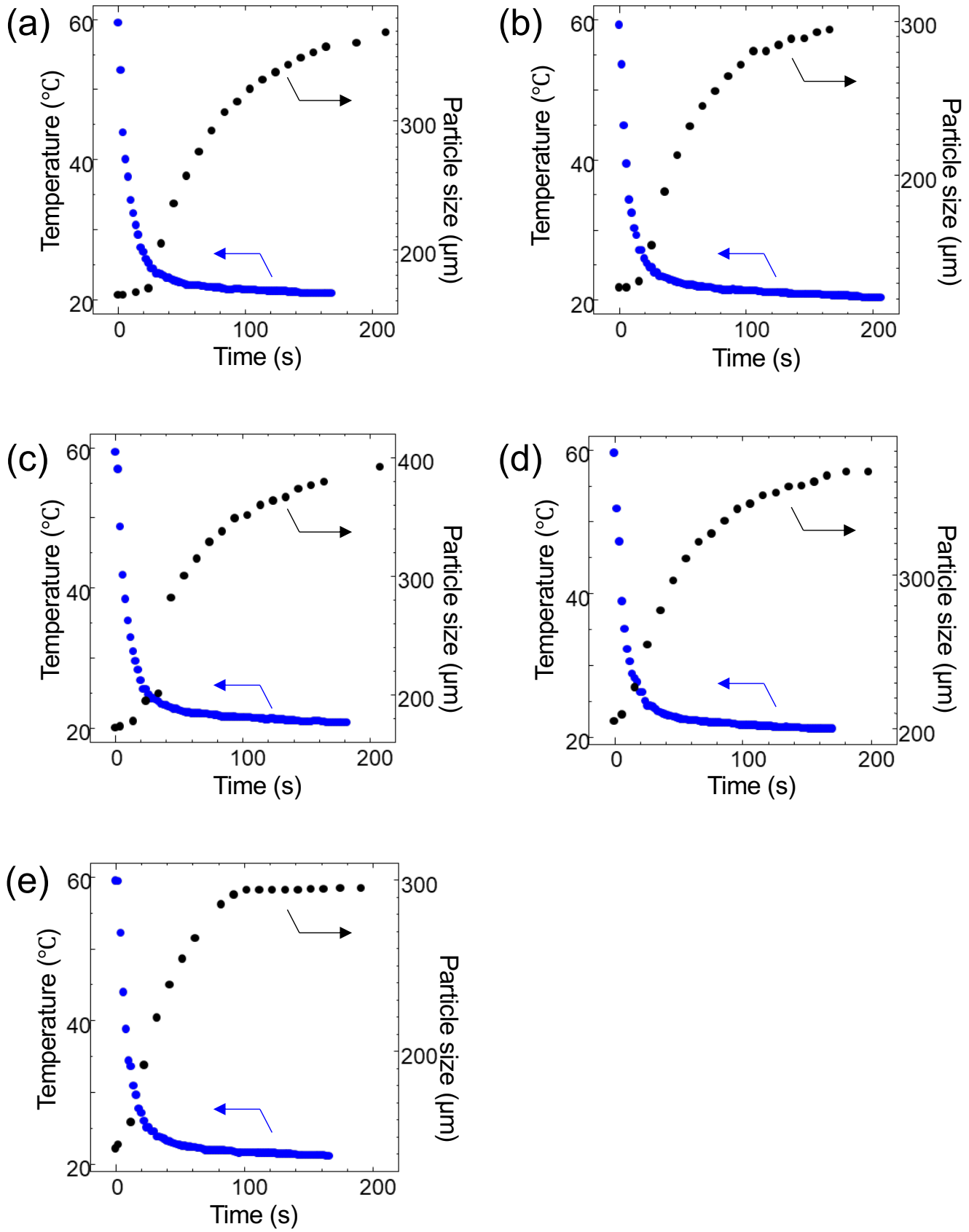


Figure S24. Variation of diameter and temperature with time during a temperature jump from 60°C to 20°C. (a) PNIPA gel (b) $PNIPA_{0.9}$-b-$PDMA_{0.1}$ gel (c) $PNIPA_{0.8}$-b-$PDMA_{0.2}$ gel (d) $PNIPA_{0.7}$-b-$PDMA_{0.3}$ gel (e) $PNIPA_{0.8}$-r-$PDMA_{0.2}$ gel

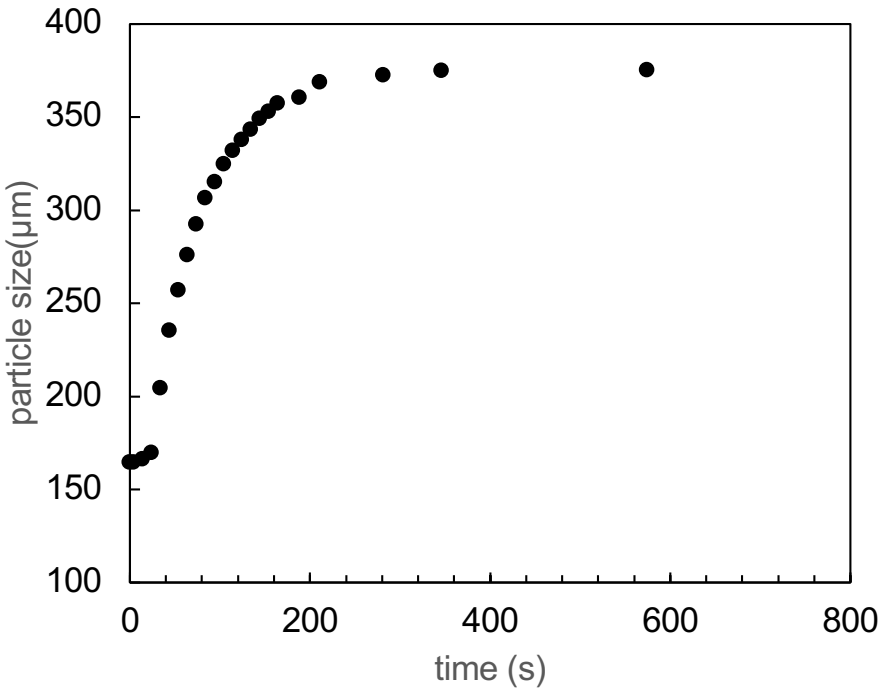


Figure S25. Diameter change of PNIPA gel up to equilibrium swelling state in a temperature jump from 60℃ to 20 ℃

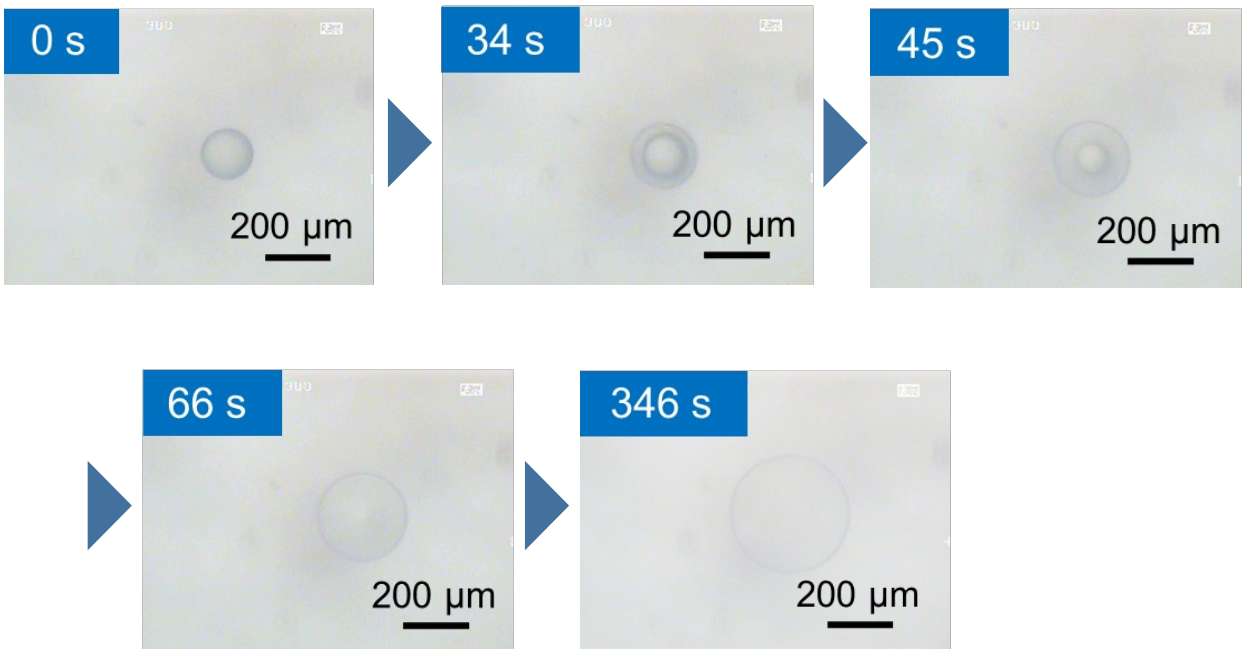


Figure S26. Optical microscopy images of PNIPA gel in a temperature jump from 60℃ to 20 ℃

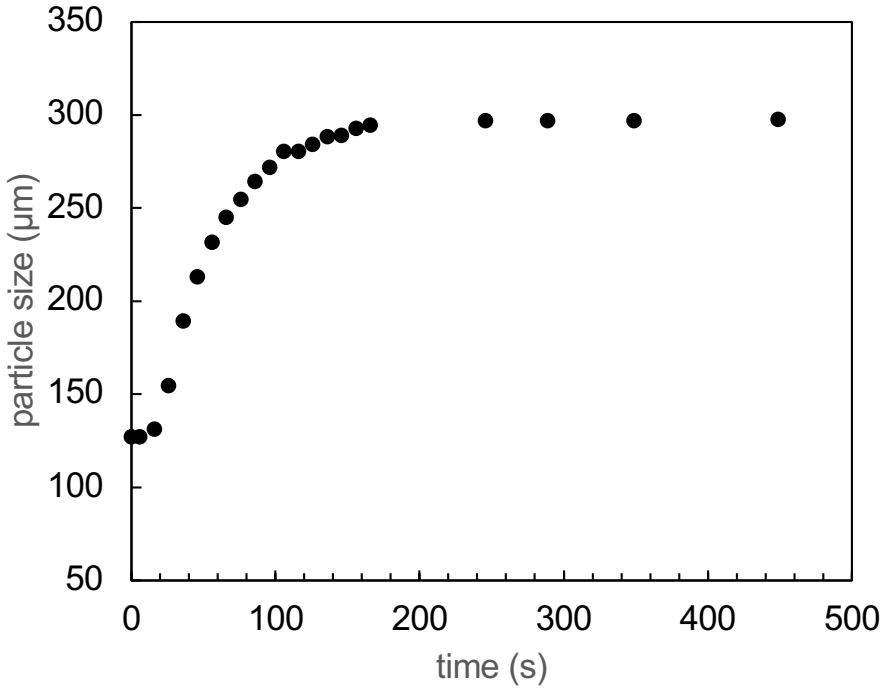


Figure S27. Diameter change of $PNIPA_{0.9}$-b-$PDMA_{0.1}$ gel up to equilibrium swelling state in a temperature jump from 60°C to 20 °C

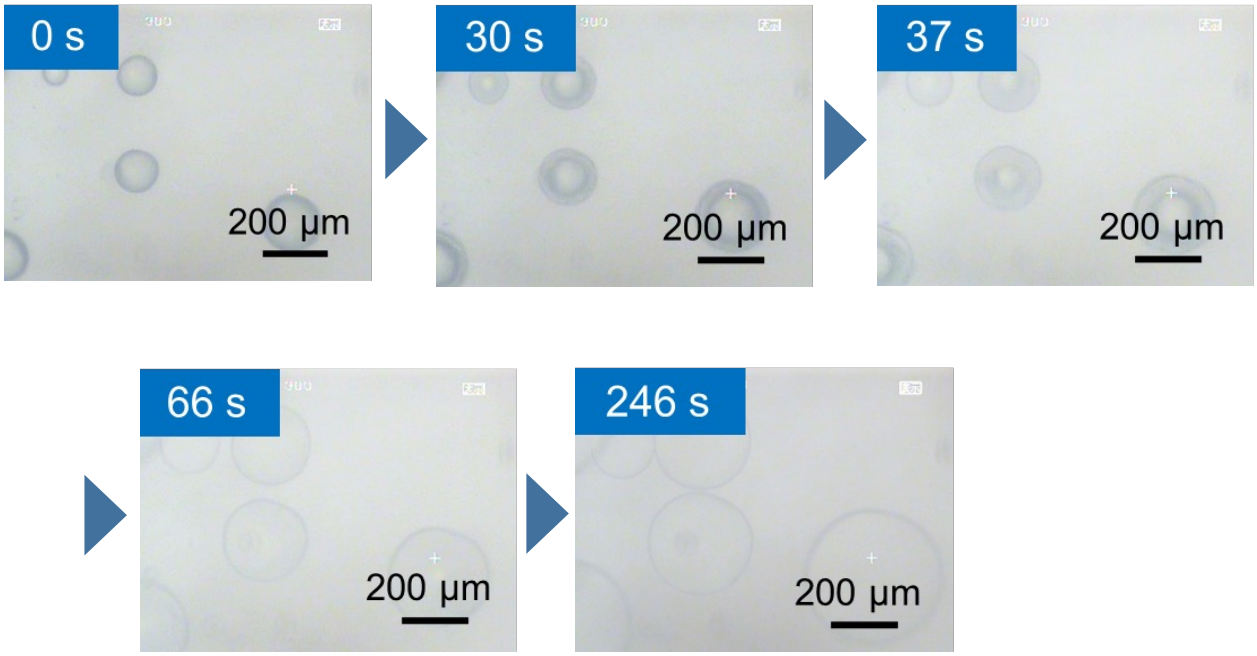


Figure S28. Optical microscopy images of $PNIPA_{0.9}$-b-$PDMA_{0.1}$ gel in a temperature jump from 60°C to 20 °C

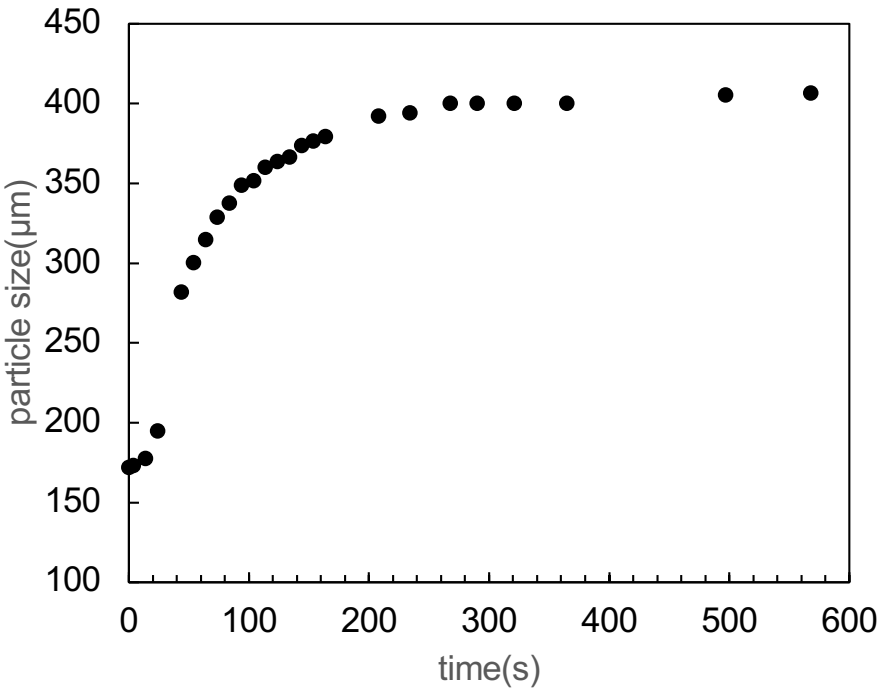


Figure S29. Diameter change of $PNIPA_{0.8}$-b-$PDMA_{0.2}$ gel up to equilibrium swelling state in a temperature jump from 60°C to 20 °C

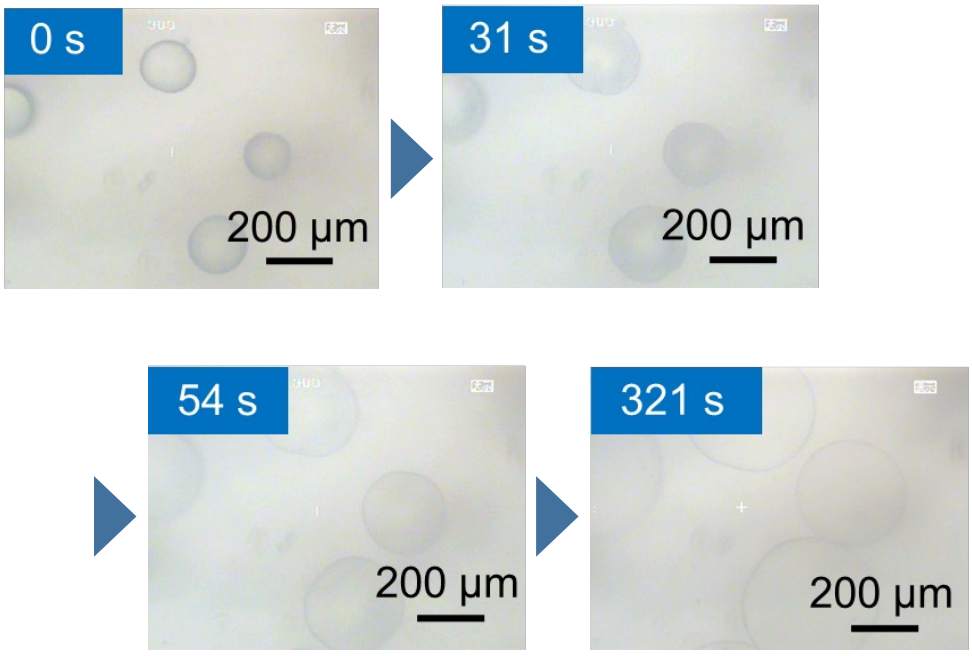


Figure S30. Optical microscopy images of $PNIPA_{0.8}$-b-$PDMA_{0.2}$ gel in a temperature jump from 60°C to 20 °C

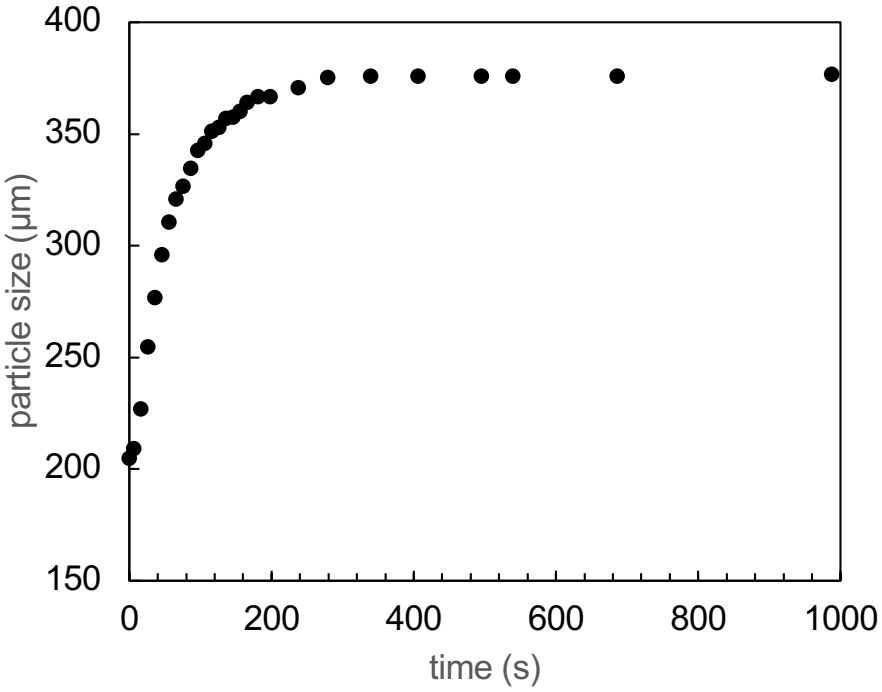


Figure S31. Diameter change of $PNIPA_{0.7}$-b-$PDMA_{0.3}$ gel up to equilibrium swelling state in a temperature jump from 60°C to 20 °C

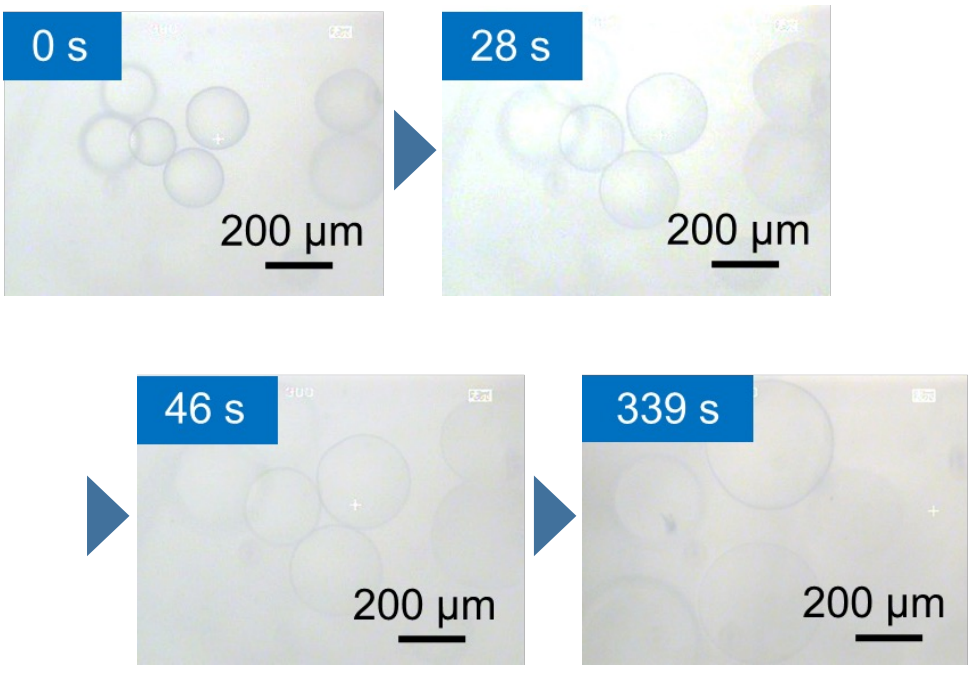


Figure S32. Optical microscopy images of $PNIPA_{0.7}$-b-$PDMA_{0.3}$ gel in a temperature jump from 60°C to 20 °C

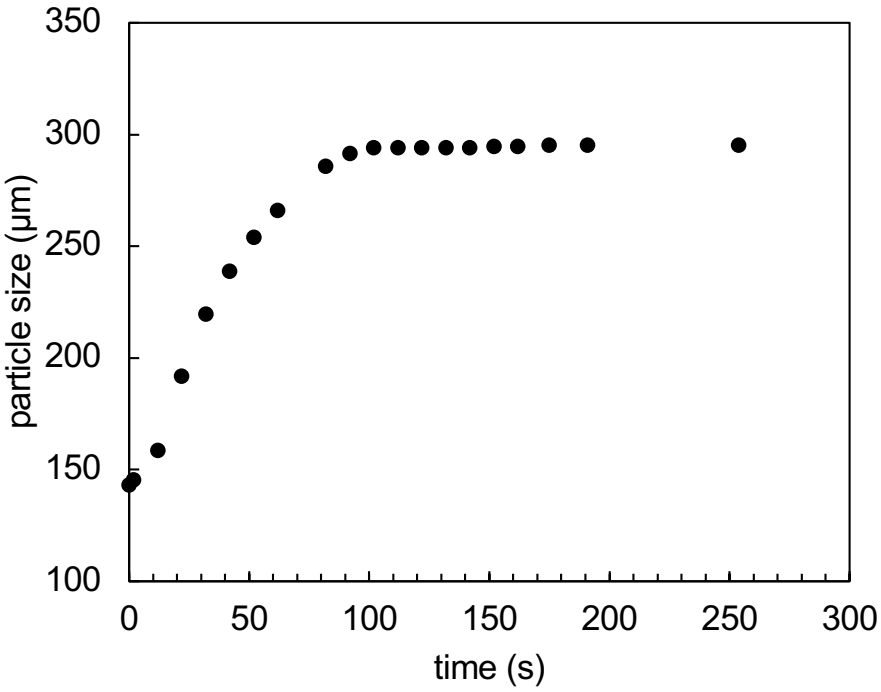


Figure S33. Diameter change of $PNIPA_{0.8}$-r-$PDMA_{0.2}$ gel up to equilibrium swelling state in a temperature jump from 60°C to 20 °C

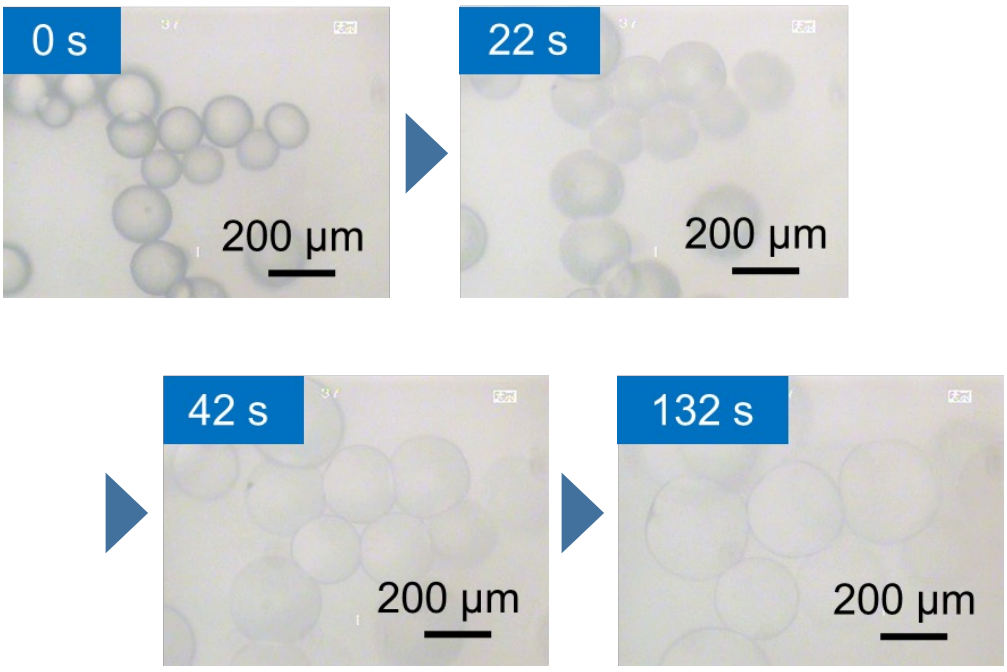


Figure S34. Optical microscopy images of $PNIPA_{0.8}$-r-$PDMA_{0.2}$ gel in a temperature jump from 60°C to 20 °C

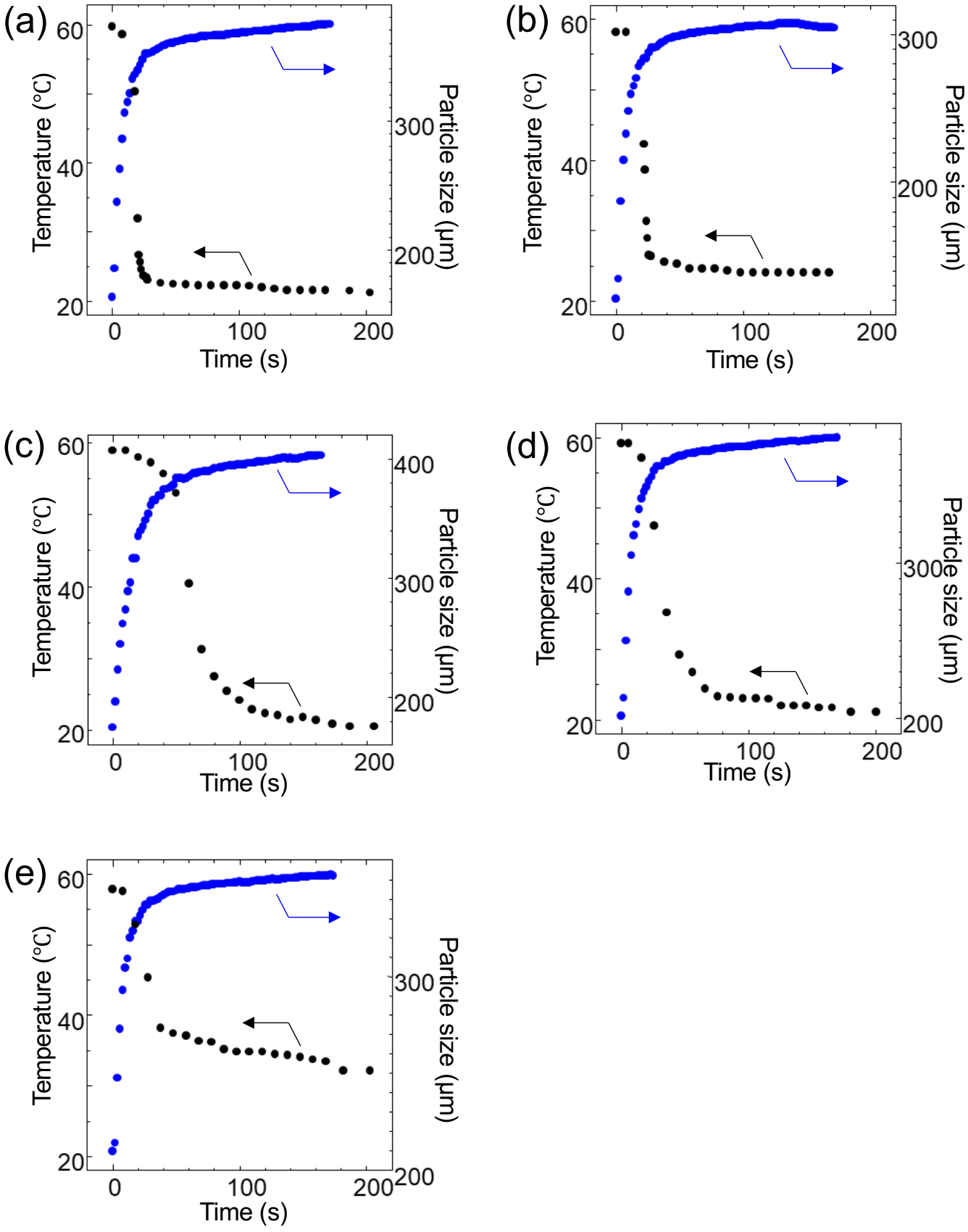


Figure S35. Variation of diameter and temperature with time during a temperature jump from 20°C to 60°C (a) PNIPA gel (b) $PNIPA_{0.9}$-b-$PDMA_{0.1}$ gel (c) $PNIPA_{0.8}$-b-$PDMA_{0.2}$ gel (d) $PNIPA_{0.7}$-b-$PDMA_{0.3}$ gel (e) $PNIPA_{0.8}$-r-$PDMA_{0.2}$ gel

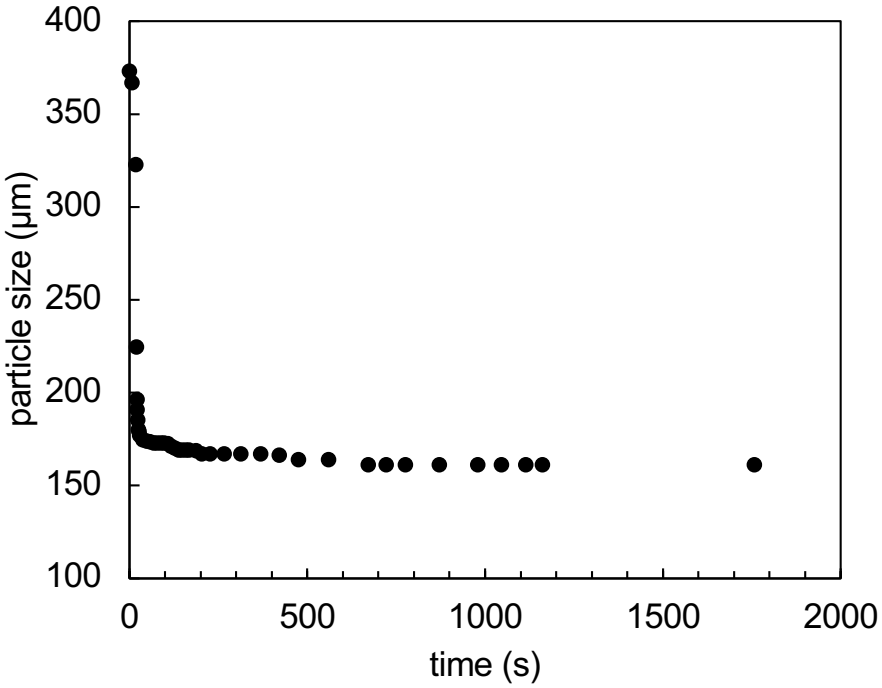


Figure S36. Diameter change of PNIPA gel up to equilibrium swelling state in a temperature jump from 20°C to 60 °C

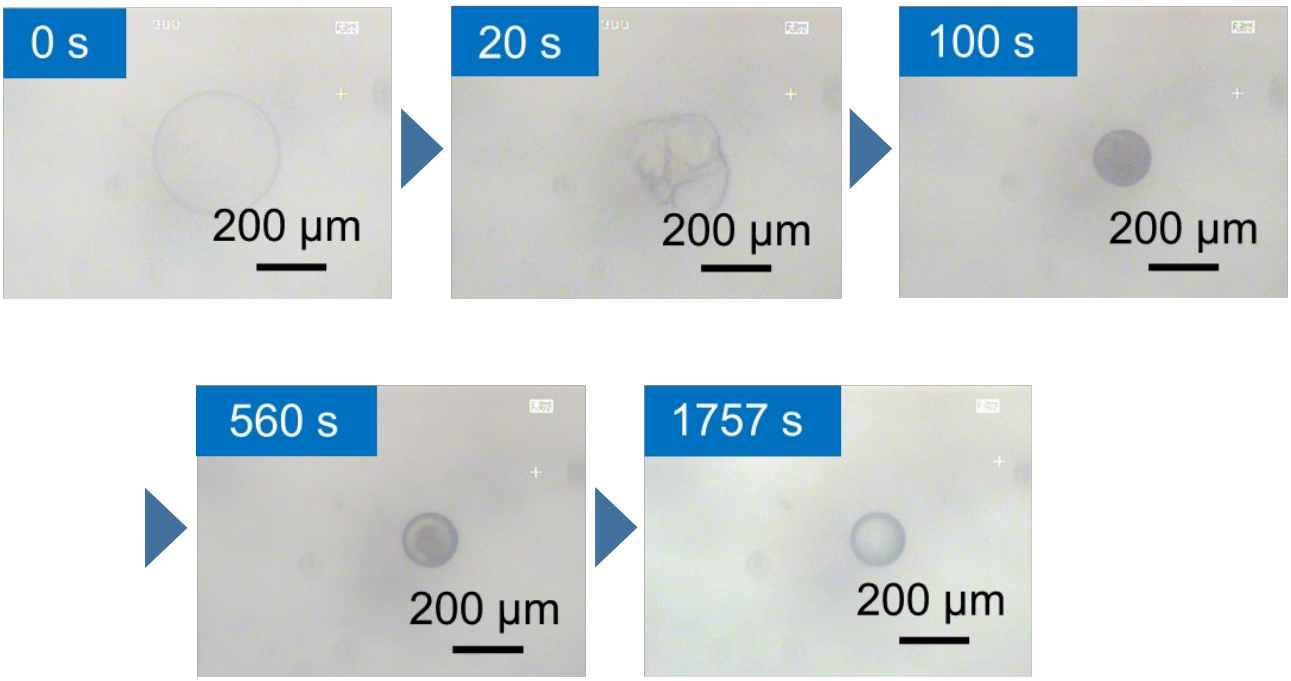


Figure S37. Optical microscopy images of PNIPA gel in a temperature jump from 20°C to 60 °C

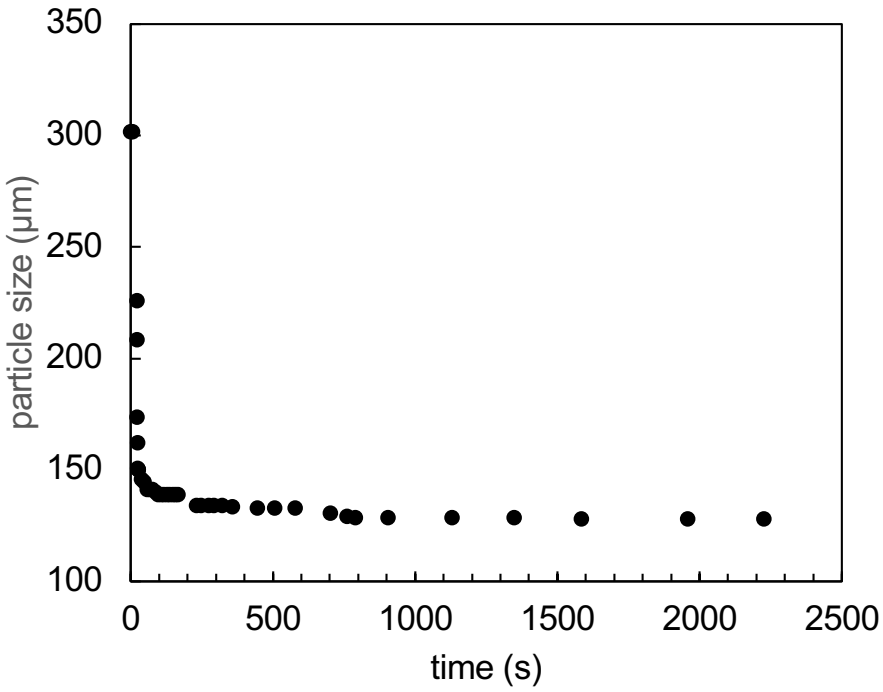


Figure S38. Diameter change of $PNIPA_{0.9}$-b-$PDMA_{0.1}$ gel up to equilibrium swelling state in a temperature jump from 20°C to 60 °C

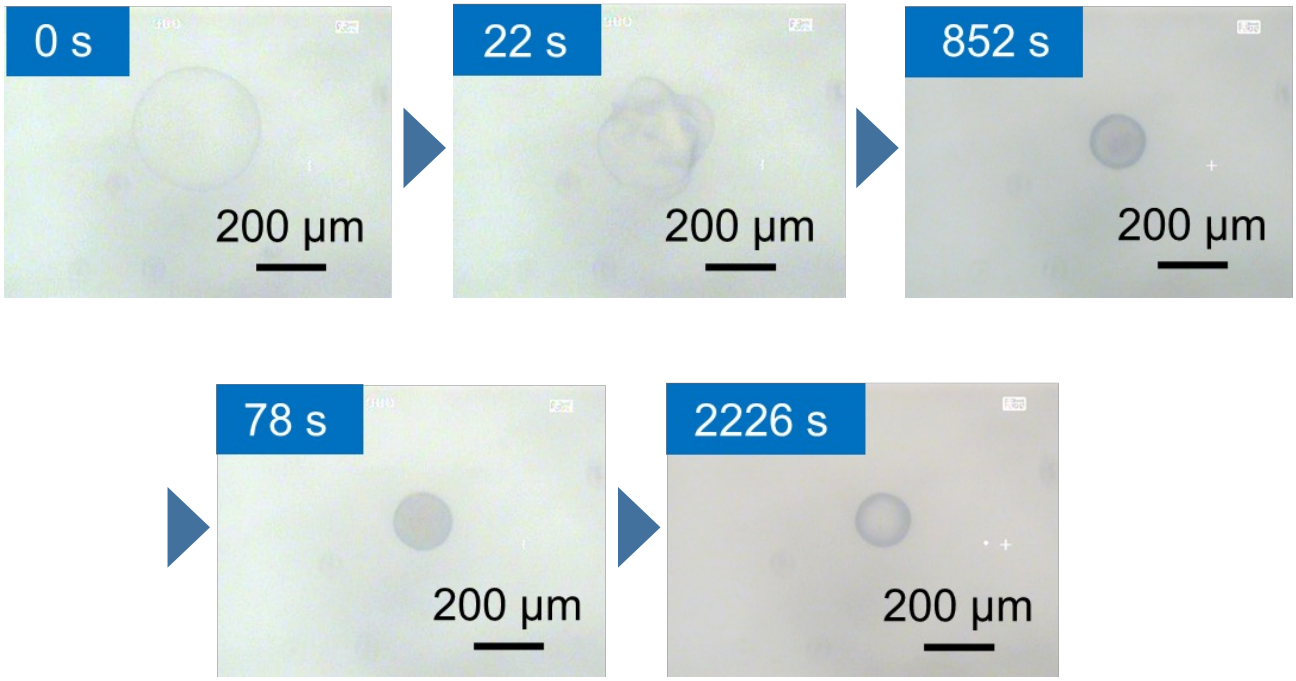


Figure S39. Optical microscopy images of $PNIPA_{0.9}$-b-$PDMA_{0.1}$ gel in a temperature jump from 20°C to 60 °C

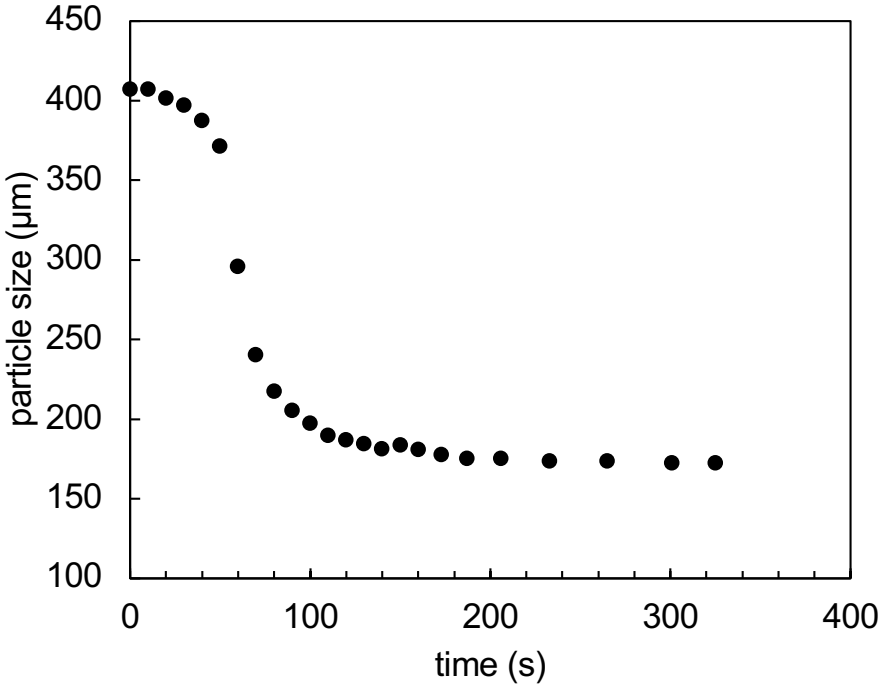


Figure S40. Diameter change of $PNIPA_{0.8}$-b-$PDMA_{0.2}$ gel up to equilibrium swelling state in a temperature jump from 20°C to 60 °C

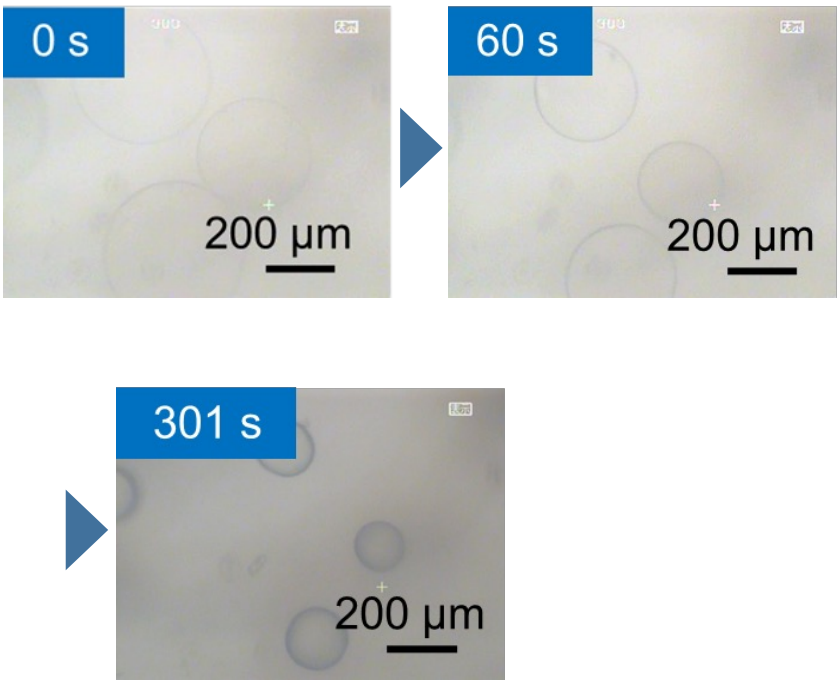


Figure S41. Optical microscopy images of $PNIPA_{0.8}$-b-$PDMA_{0.2}$ gel in a temperature jump from 20°C to 60 °C

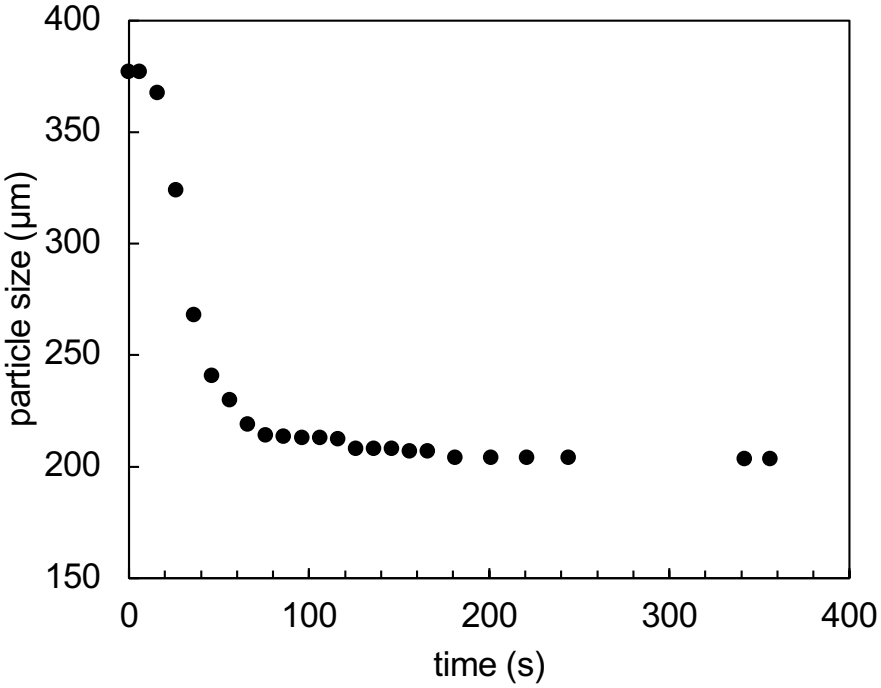


Figure S42. Diameter change of $PNIPA_{0.7}$-b-$PDMA_{0.3}$ gel up to equilibrium swelling state in a temperature jump from 20°C to 60 °C

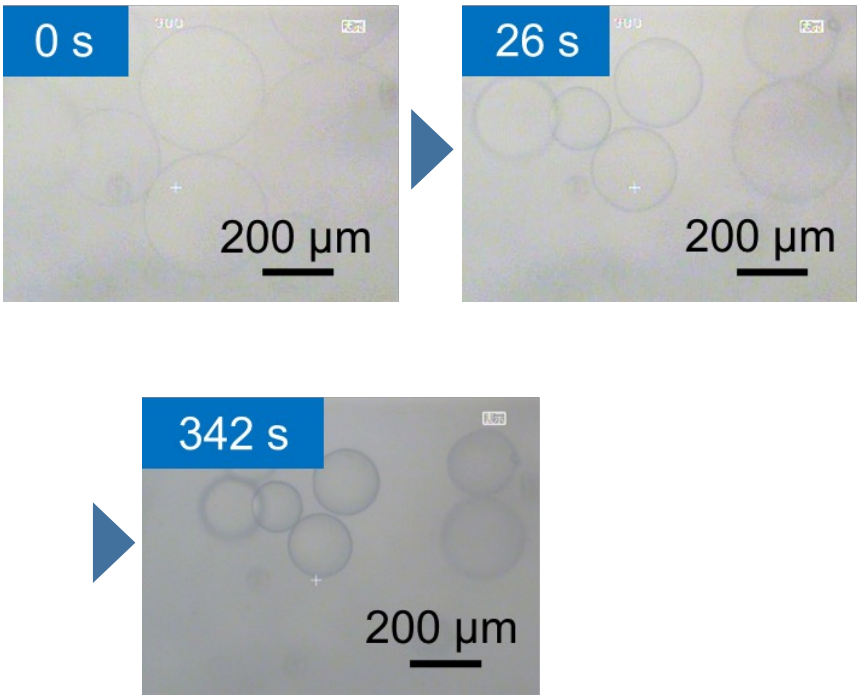


Figure S43. Optical microscopy images of $PNIPA_{0.7}$-b-$PDMA_{0.3}$ gel in a temperature jump from 20°C to 60 °C

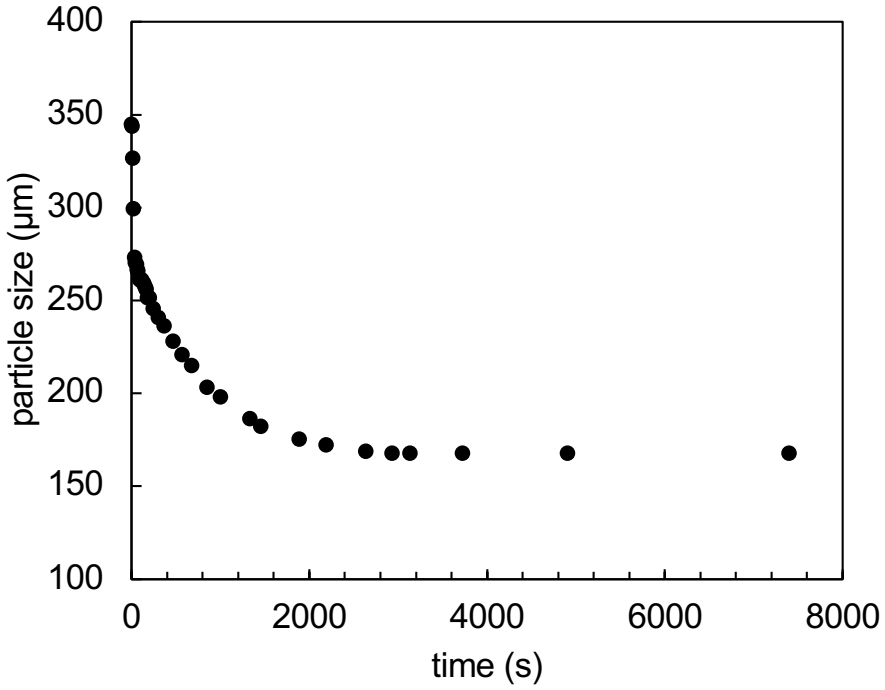


Figure S44. Diameter change of $PNIPA_{0.8}$-r-$PDMA_{0.2}$ gel up to equilibrium swelling state in a temperature jump from 20°C to 60 °C

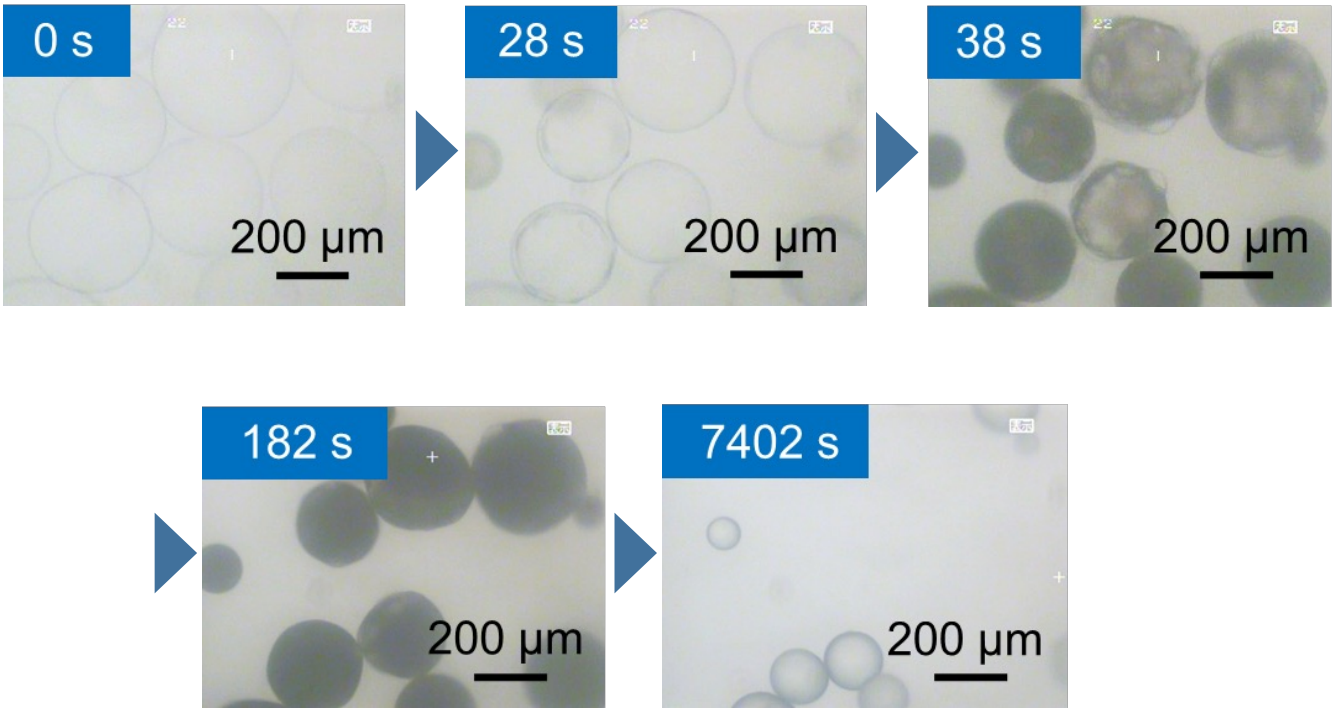


Figure S45. Optical microscopy images of $PNIPA_{0.8}$-r-$PDMA_{0.2}$ gel in a temperature jump from 20°C to 60 °C

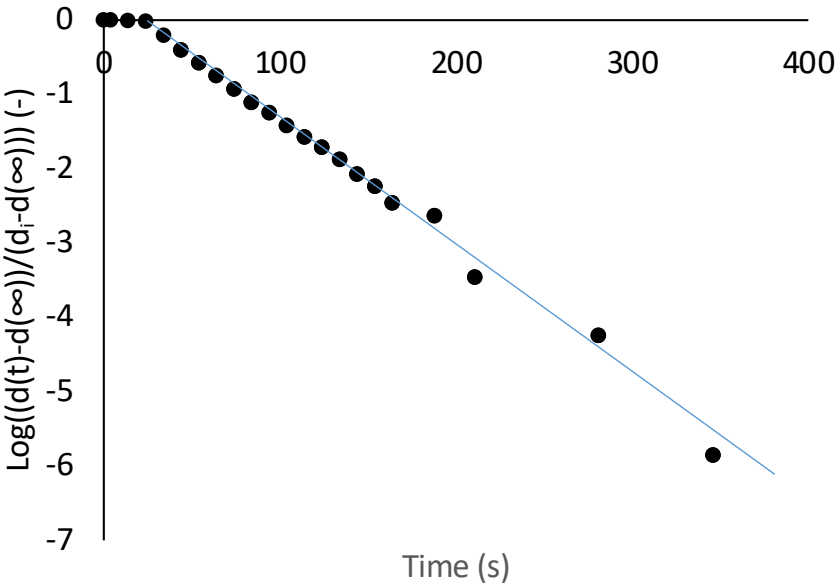
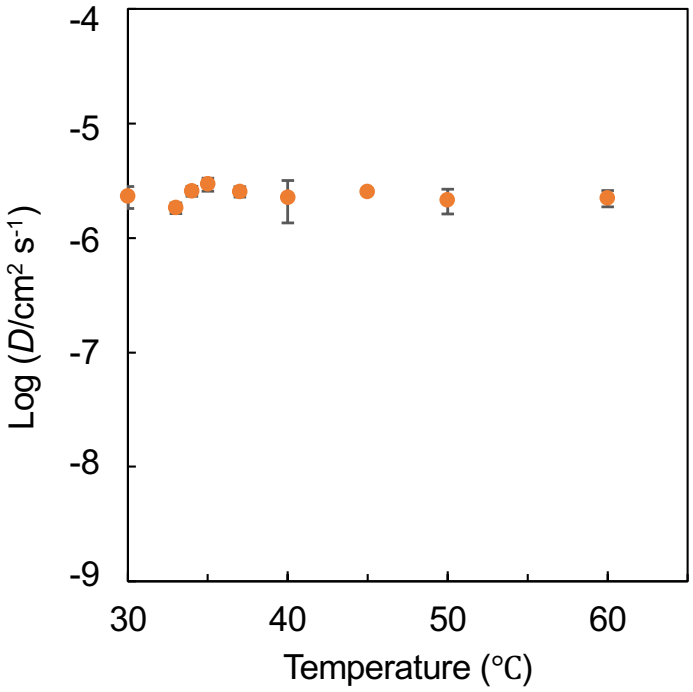


Figure S46. The result of substituting the diameter change with time into the swelling equation when the initial temperature is 60°C (PNIPA gel)



Temperature [℃]	$D_{average}$ [cm^2/s]
30	2.31×10^{-6}
33	1.82×10^{-6}
34	2.56×10^{-6}
35	2.94×10^{-6}
37	2.53×10^{-6}
40	2.26×10^{-6}
45	2.53×10^{-6}
50	2.14×10^{-6}
60	2.23×10^{-6}

Figure S47 Cooperative diffusion coefficient at various initial temperatures (PNIPA gel)

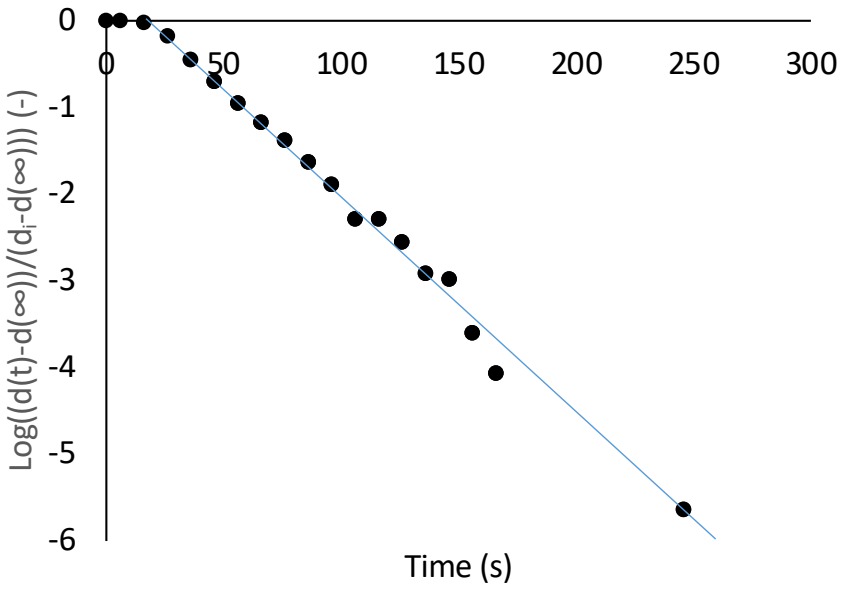
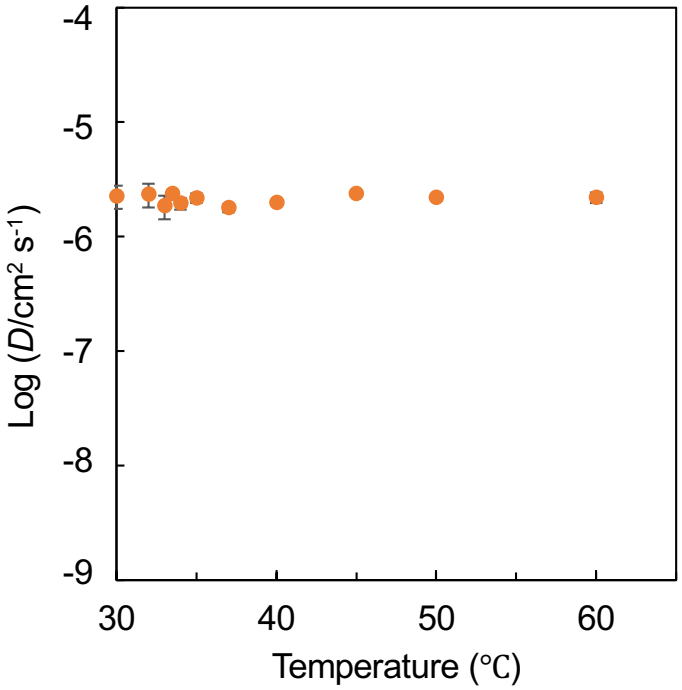
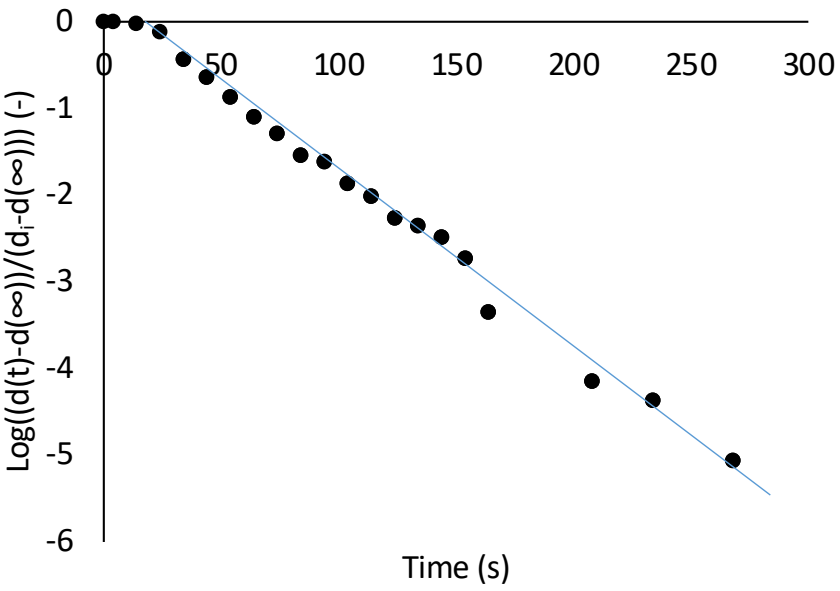


Figure S48. The result of substituting the diameter change with time into the swelling equation when the initial temperature is 60°C ($PNIPA_{0.9}$-b-$PDMA_{0.1}$ gel)

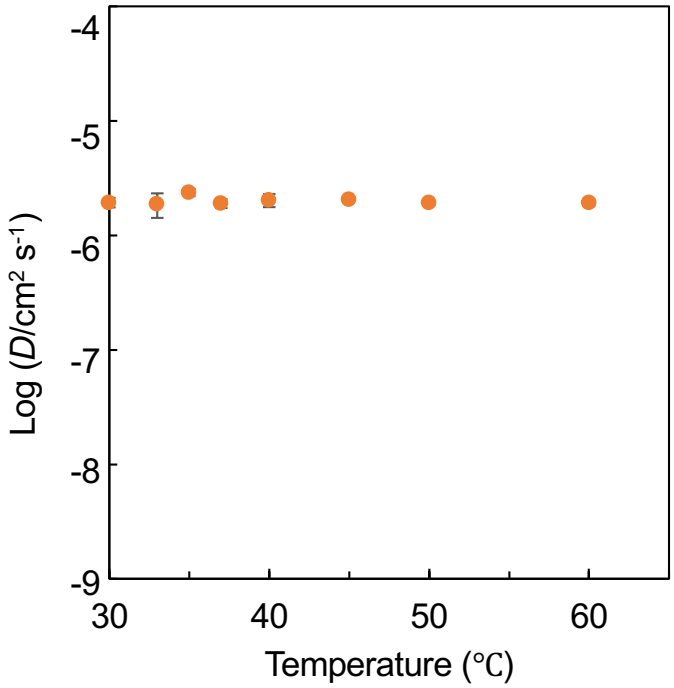


Temperature [℃]	$D_{average}$ [cm^2/s]
30	2.27×10^{-6}
32	2.35×10^{-6}
33	1.85×10^{-6}
33.5	2.38×10^{-6}
34	1.95×10^{-6}
35	2.18×10^{-6}
37	1.78×10^{-6}
40	1.97×10^{-6}
45	2.39×10^{-6}
50	2.2×10^{-6}
60	2.2×10^{-6}

Figure S49. Cooperative diffusion coefficient at various initial temperatures ($PNIPA_{0.9}$-b-$PDMA_{0.1}$ gel)



FigureS50. The result of substituting the diameter change with time into the swelling equation when the initial temperature is 60℃ ($PNIPA_{0.8}$-b-$PDMA_{0.2}$ gel)



Temperature [℃]	$D_{average}$ [cm^2/s]
30	1.94×10^{-6}
33	1.87×10^{-6}
35	2.37×10^{-6}
37	1.9×10^{-6}
40	2.03×10^{-6}
45	2.07×10^{-6}
50	1.93×10^{-6}
60	1.93×10^{-6}

Figure S51. Cooperative diffusion coefficient at various initial temperatures ($PNIPA_{0.8}$-b-$PDMA_{0.2}$ gel)

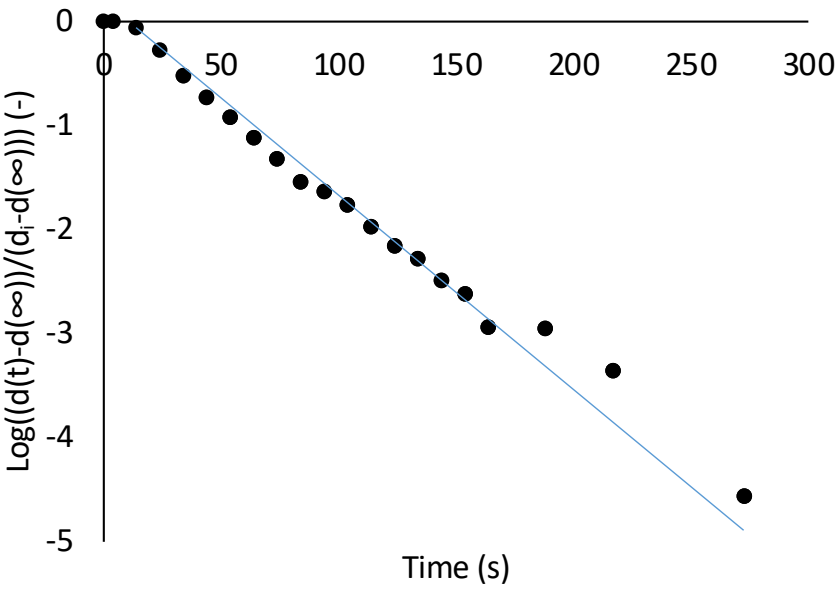
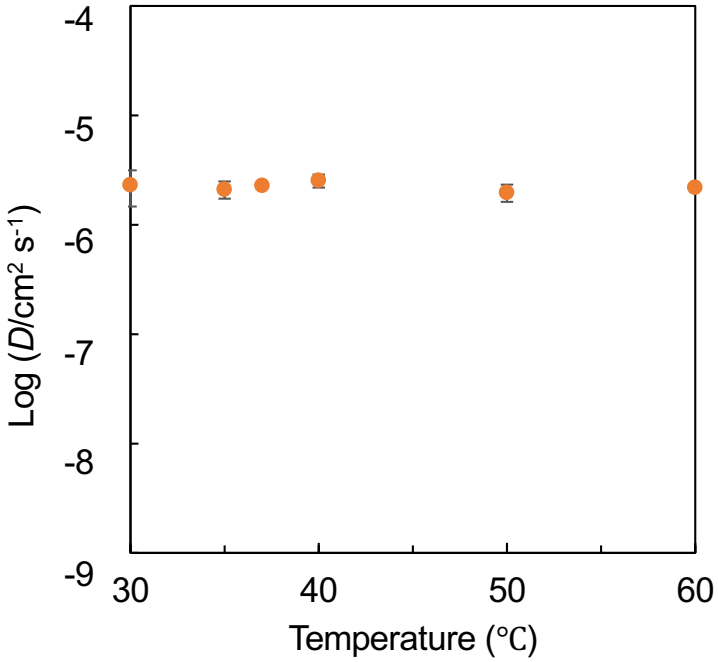


Figure S52. The result of substituting the diameter change with time into the swelling equation when the initial temperature is 60°C ($PNIPA_{0.7}$-b-$PDMA_{0.3}$ gel)



Temperature [℃]	$D_{average}$ [cm^2/s]
30	2.31×10^{-6}
35	2.11×10^{-6}
37	2.28×10^{-6}
40	2.53×10^{-6}
50	1.97×10^{-6}
60	2.18×10^{-6}

Figure S53. Cooperative diffusion coefficient at various initial temperatures ($PNIPA_{0.7}$-b-$PDMA_{0.3}$ gel)

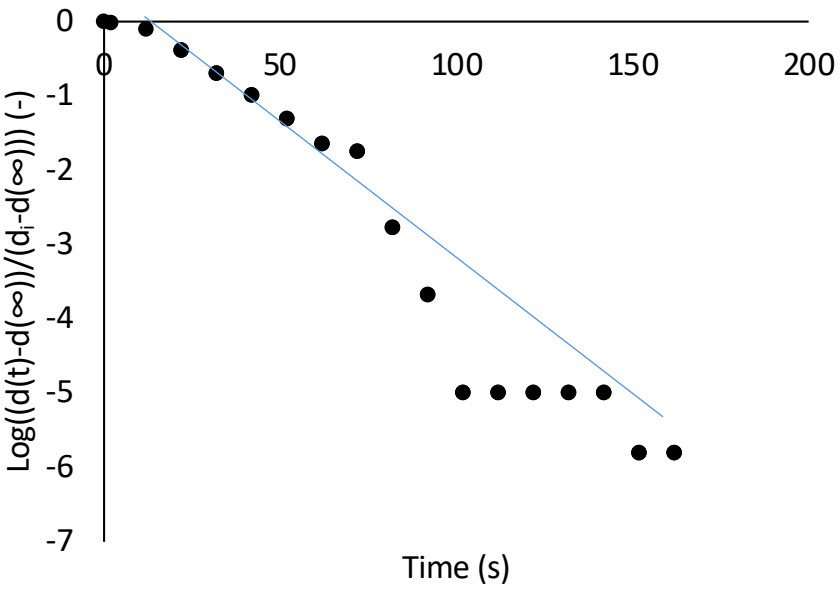
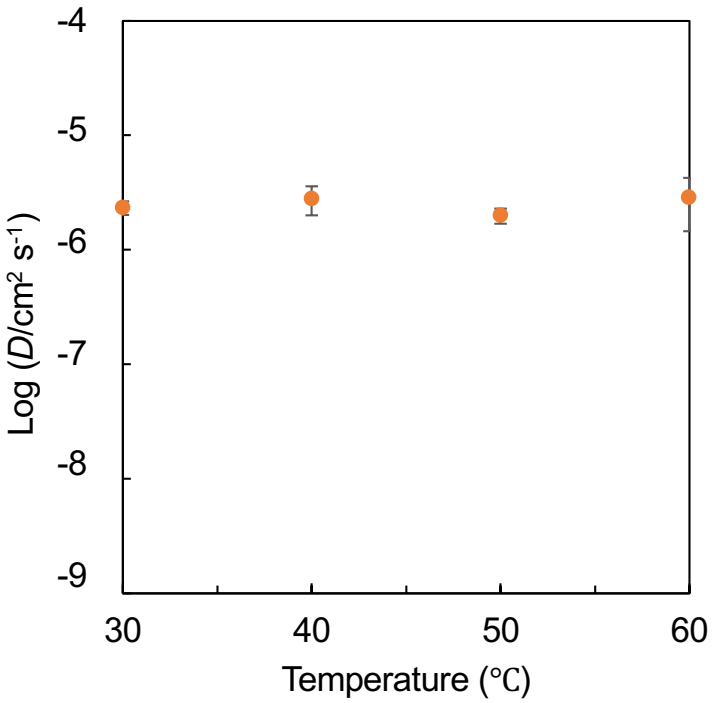


Figure S54. The result of substituting the diameter change with time into the swelling equation when the initial temperature is 60°C ($PNIPA_{0.8}$-r-$PDMA_{0.2}$ gel)



Temperature [℃]	$D_{average}$ [cm^2/s]
30	2.34×10^{-6}
40	2.80×10^{-6}
50	2.00×10^{-6}
60	2.86×10^{-6}

Figure S55. Cooperative diffusion coefficient at various initial temperatures ($PNIPA_{0.8}$-r-$PDMA_{0.2}$ gel)

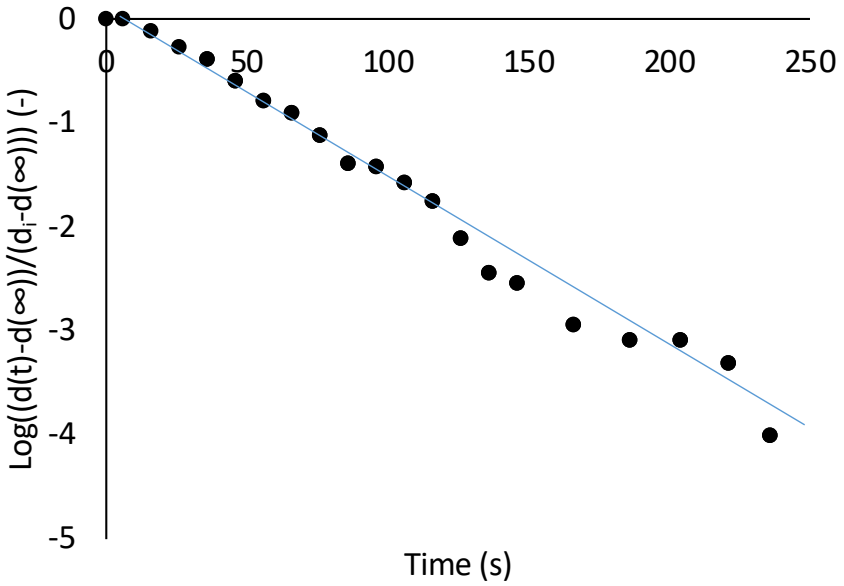


Figure S56. The result of substituting the diameter change with time into the swelling equation when the final temperature is 30°C (PNIPA gel)

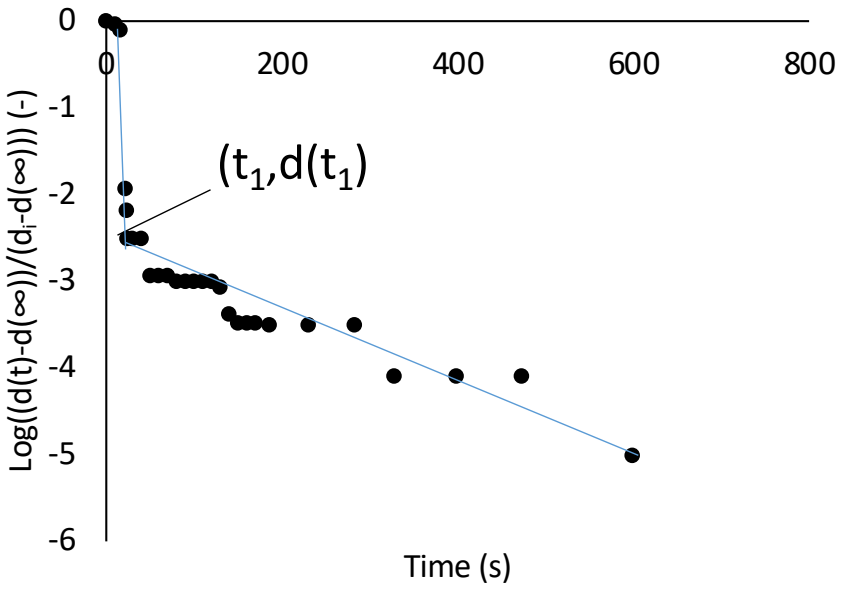
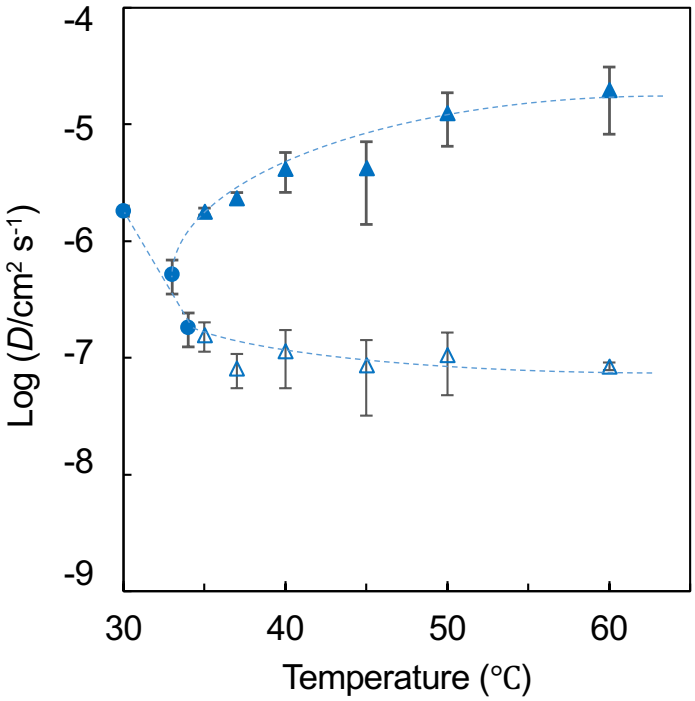


Figure S57. The result of substituting the diameter change with time into the swelling equation when the final temperature is 60°C (PNIPA gel)



Temperature [℃]	$D_{average}$ [cm²/s]	$D_{average}$ [cm²/s]	
		Stage 1	Stage 2
30	1.82×10^{-6}		
33	5.2×10^{-7}		
34	1.83×10^{-7}		
35		1.80×10^{-6}	1.57×10^{-7}
37		2.34×10^{-6}	8.14×10^{-8}
40		4.18×10^{-6}	1.14×10^{-7}
45		4.25×10^{-6}	8.70×10^{-8}
50		1.26×10^{-5}	1.06×10^{-7}
60		1.97×10^{-5}	8.48×10^{-8}

Figure S58. Cooperative diffusion coefficient at various final temperatures (PNIPA gel)

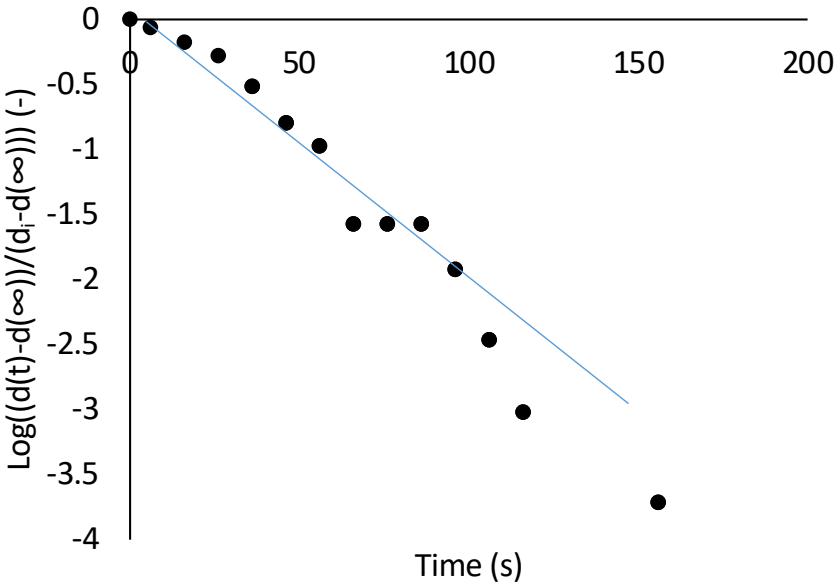


Figure S59. The result of substituting the diameter change with time into the swelling equation when the final temperature is 30°C ($PNIPA_{0.9}$-b-$PDMA_{0.1}$ gel)

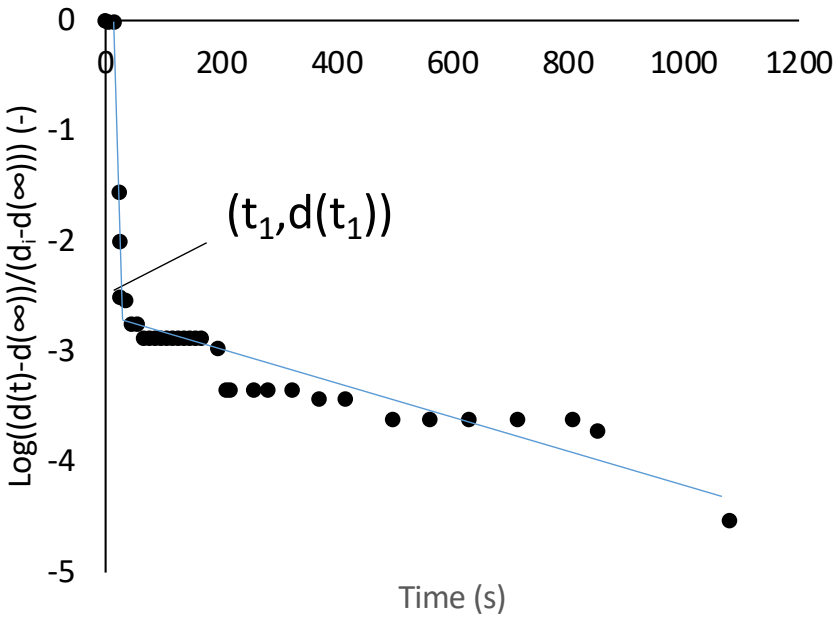
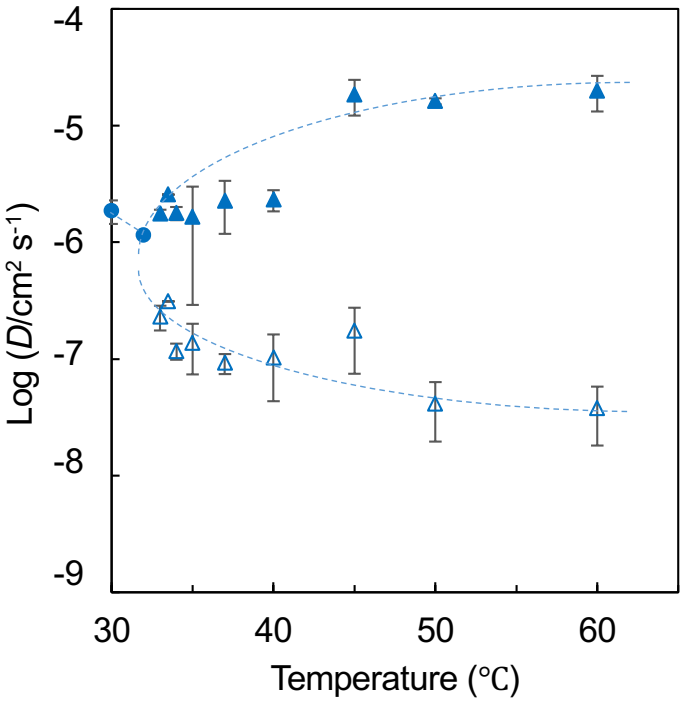


Figure S60. The result of substituting the diameter change with time into the swelling equation when the final temperature is 60°C ($PNIPA_{0.9}$-b-$PDMA_{0.1}$ gel)



Temperature [°C]	$D_{average}$ [cm²/s]	$D_{average}$ [cm²/s]	
		Stage 1	Stage 2
30	1.86×10^{-6}		
32	1.15×10^{-6}		
33		1.75×10^{-6}	2.31×10^{-7}
33.5		2.56×10^{-6}	3.11×10^{-7}
34		1.78×10^{-6}	1.17×10^{-7}
35		1.64×10^{-6}	1.37×10^{-7}
37		2.27×10^{-6}	9.21×10^{-8}
40		2.32×10^{-6}	1.03×10^{-7}
45		1.84×10^{-5}	1.75×10^{-7}
50		1.62×10^{-5}	4.14×10^{-8}
60		1.99×10^{-5}	3.80×10^{-8}

Figure S61. Cooperative diffusion coefficient at various final temperatures ($PNIPA_{0.9}$-b-$PDMA_{0.1}$ gel)

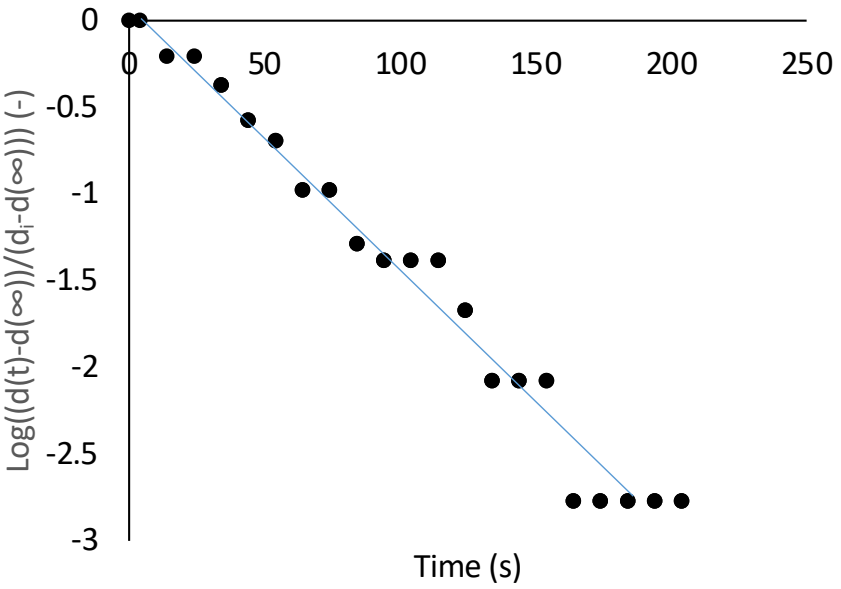


Figure S62. The result of substituting the diameter change with time into the swelling equation when the final temperature is 30°C ($PNIPA_{0.8}$-b-$PDMA_{0.2}$ gel)

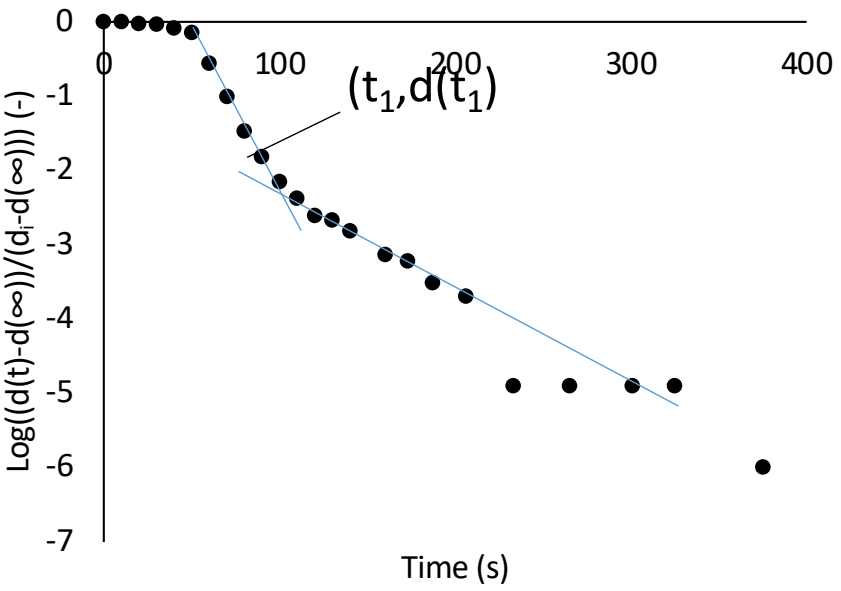
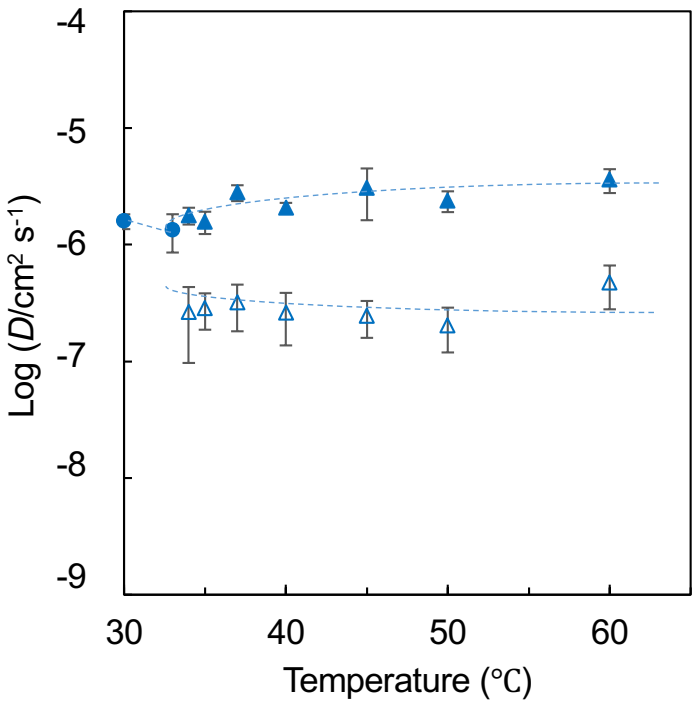


Figure S63. The result of substituting the diameter change with time into the swelling equation when the final temperature is 60°C ($PNIPA_{0.8}$-b-$PDMA_{0.2}$ gel)



Temperature [℃]	$D_{average}$ [cm²/s]	$D_{average}$ [cm²/s]	
		Stage 1	Stage 2
30	1.59×10^{-6}		
33	1.34×10^{-6}		
34		1.78×10^{-6}	2.65×10^{-7}
35		1.58×10^{-6}	2.85×10^{-7}
37		2.8×10^{-6}	3.18×10^{-7}
40		2.08×10^{-6}	2.62×10^{-7}
45		3.06×10^{-6}	2.44×10^{-7}
50		2.38×10^{-6}	2.04×10^{-7}
60		3.6×10^{-6}	4.71×10^{-7}

Figure S64. Cooperative diffusion coefficient at various final temperatures ($PNIPA_{0.8}$-b-$PDMA_{0.2}$ gel)

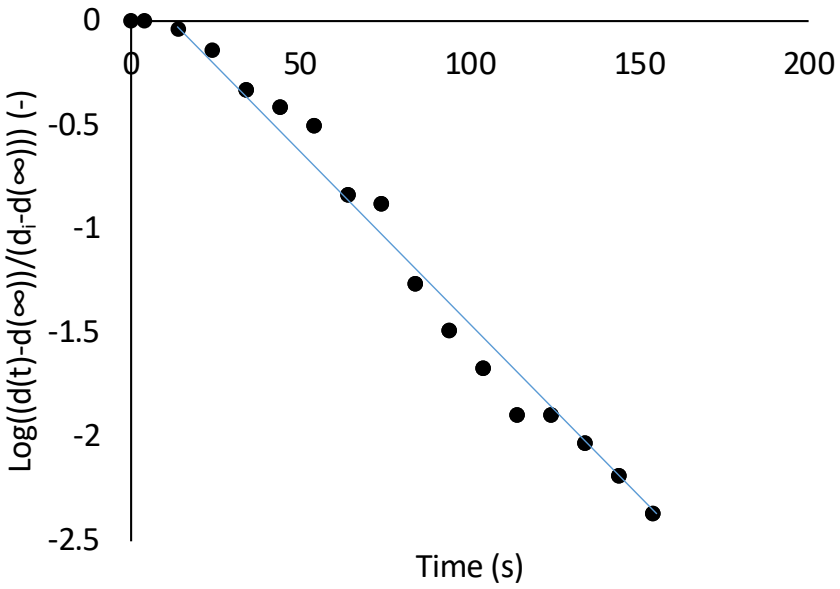


Figure S65. The result of substituting the diameter change with time into the swelling equation when the final temperature is 30°C ($PNIPA_{0.7}$-b-$PDMA_{0.3}$ gel)

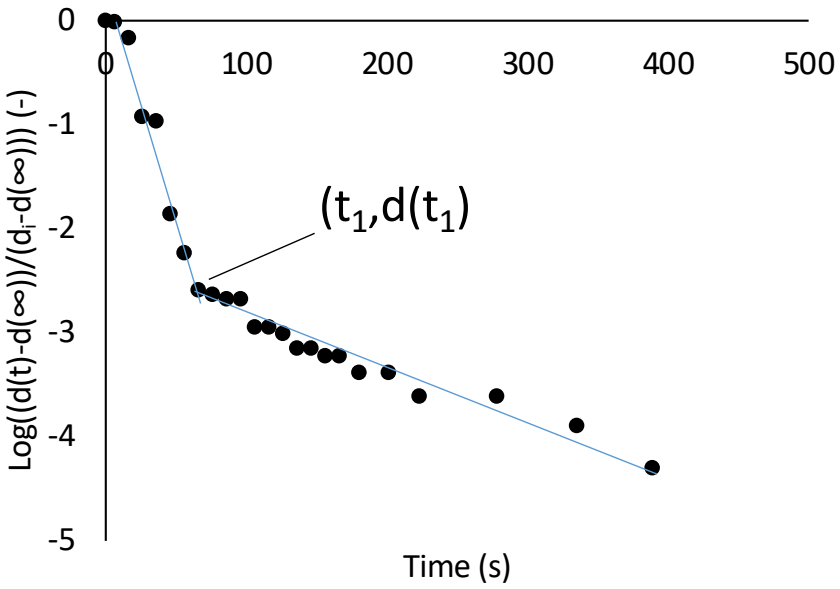
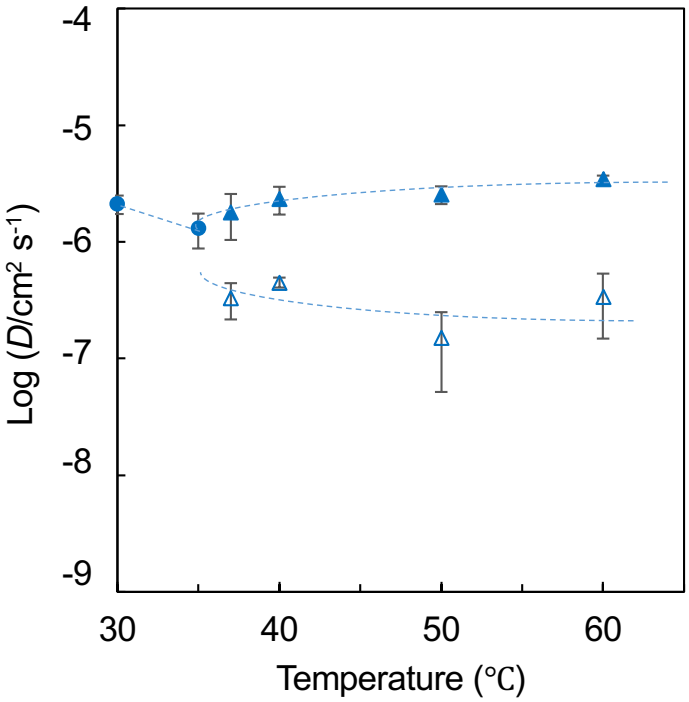


Figure S66. The result of substituting the diameter change with time into the swelling equation when the final temperature is 60°C ($PNIPA_{0.7}$-b-$PDMA_{0.3}$ gel)



Temperature [℃]	$D_{average}$ [cm^2/s]	$D_{average}$ [cm^2/s]	
		Stage 1	Stage 2
30	2.11×10^{-6}		
35	1.31×10^{-6}		
37		1.81×10^{-6}	3.29×10^{-7}
40		2.34×10^{-6}	4.50×10^{-7}
50		2.55×10^{-6}	1.51×10^{-7}
60		3.45×10^{-6}	3.41×10^{-7}

Figure S67. Cooperative diffusion coefficient at various final temperatures ($PNIPA_{0.7}$ -b-$PDMA_{0.3}$ gel)

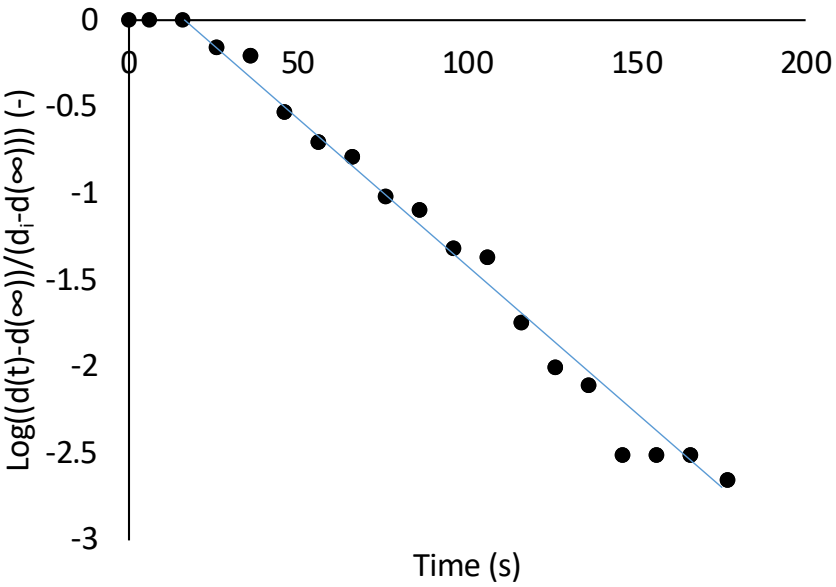


Figure S68. The result of substituting the diameter change with time into the swelling equation when the final temperature is 30°C ($PNIPA_{0.8}$-r-$PDMA_{0.2}$ gel)

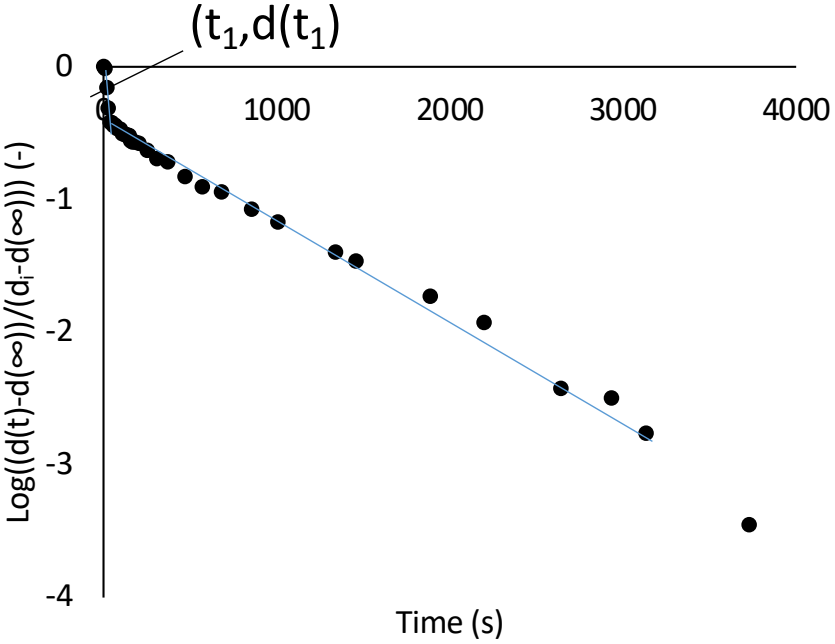
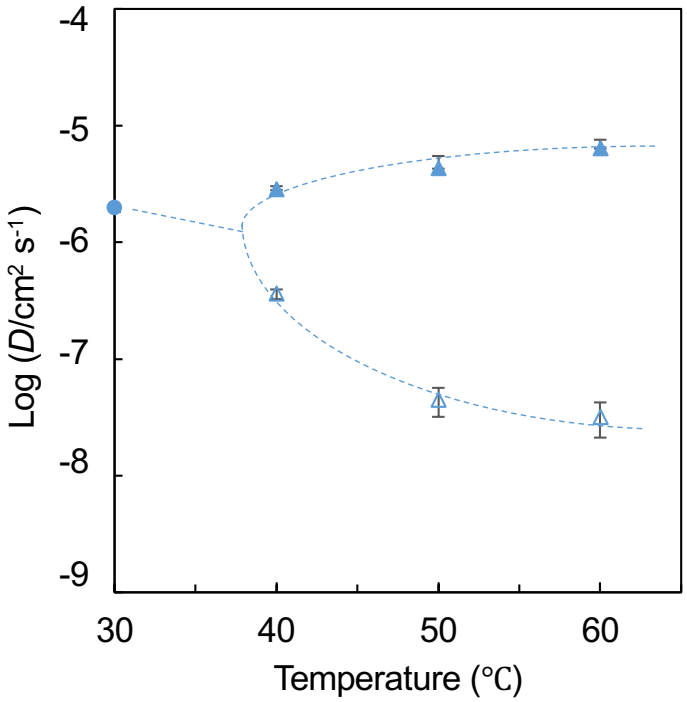


Figure S69. The result of substituting the diameter change with time into the swelling equation when the final temperature is 60°C ($PNIPA_{0.8}$-r-$PDMA_{0.2}$ gel)



Temperature [℃]	$D_{average}$ [cm^2/s]	$D_{average}$ [cm^2/s]	
		Stage 1	Stage 2
30	1.96×10^{-6}		
40		2.84×10^{-6}	3.60×10^{-7}
50		4.29×10^{-6}	4.42×10^{-8}
60		6.38×10^{-6}	3.18×10^{-8}

Figure S70. Cooperative diffusion coefficient at various final temperatures ($PNIPA_{0.8}$-r-$PDMA_{0.2}$ gel)

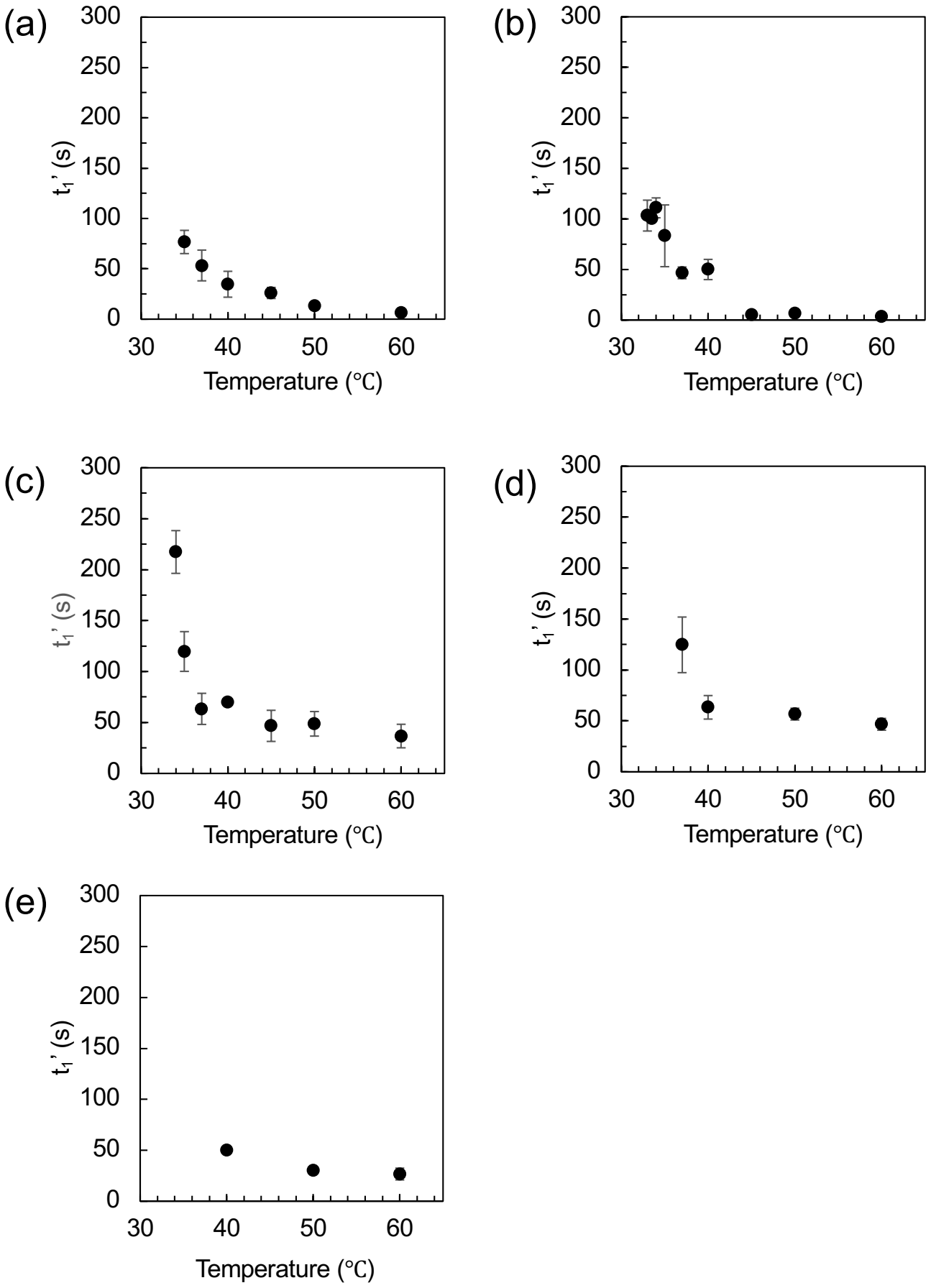


Figure S71. Change in t_1' (a) PNIPA gel (b) $PNIPA_{0.9}$-b-$PDMA_{0.1}$ gel (c) $PNIPA_{0.8}$-b-$PDMA_{0.2}$ gel (d) $PNIPA_{0.7}$ -b-$PDMA_{0.3}$ gel (e) $PNIPA_{0.8}$-r-$PDMA_{0.2}$ gel