Supporting Information

Thermoresponsive functional polymers based on 2,6-diamino pyridine motif with tunable UCST behaviour in water/alcohol mixtures

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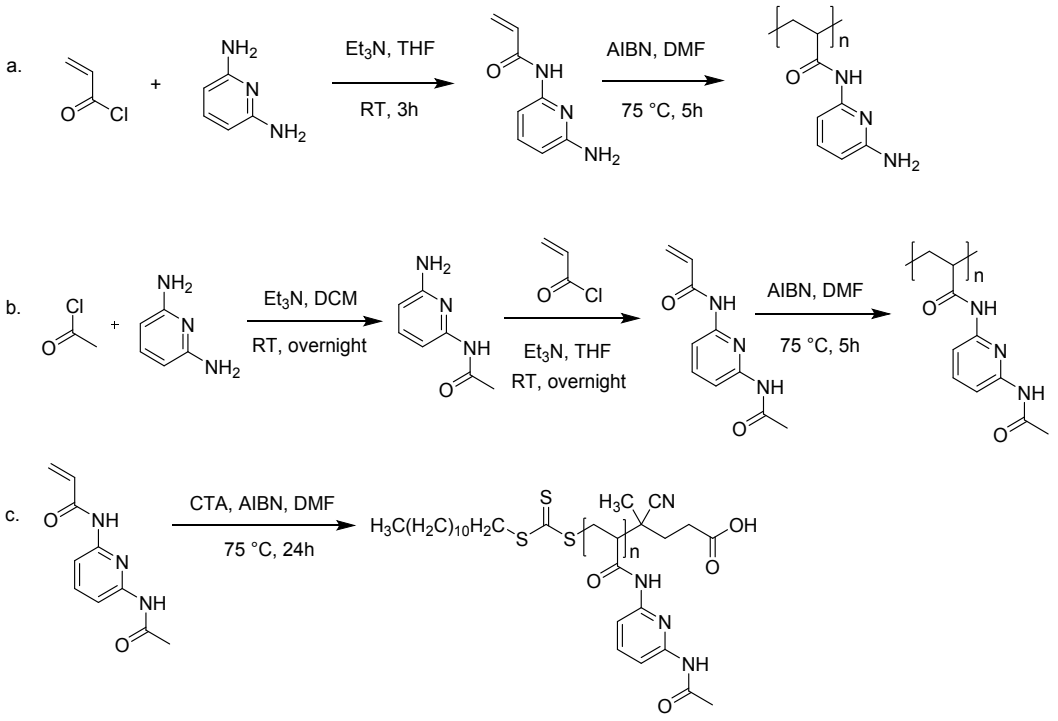
Synthesis of PNAPAAm and PNAcAPAAm:



Scheme S1. Synthesis procedure for (a) PNAPAAm and (b) PNAcAPAAm via free radical polymerization (FRP) and (c) synthesis of PNAcAPAAm via RAFT polymerization.

Table S1. Summary of the PNAPAAm and PNAcAPAAm synthesis.

Polymer type	Polymerization technique	Name of polymers	Monomer (mg)	AIBN (mg)	RAFT agent (mg)	DMF (mL)	Yield (%)
PNAPAAm	FRP	$PNAPAAm_{67}$	410	4.1	X	5.0	91
	FRP	$PNAPAAm_{87}$	410	2.6	X	5.0	88
PNAcAPAAm	FRP	$PNAcAPAAm_{54}$	510	8.2	X	5.0	93
	FRP	$PNAcAPAAm_{88}$	510	4.1	X	5.0	88
	FRP	$PNAcAPAAm_{597}$	510	2.6	X	5.0	91
	RAFT	$PNAcAPAAm_{29}$	255	1.0	10	4.3	60
	RFAT	$PNAcAPAAm_{41}$	508	1.0	10	8.6	63

Characterization of the monomers

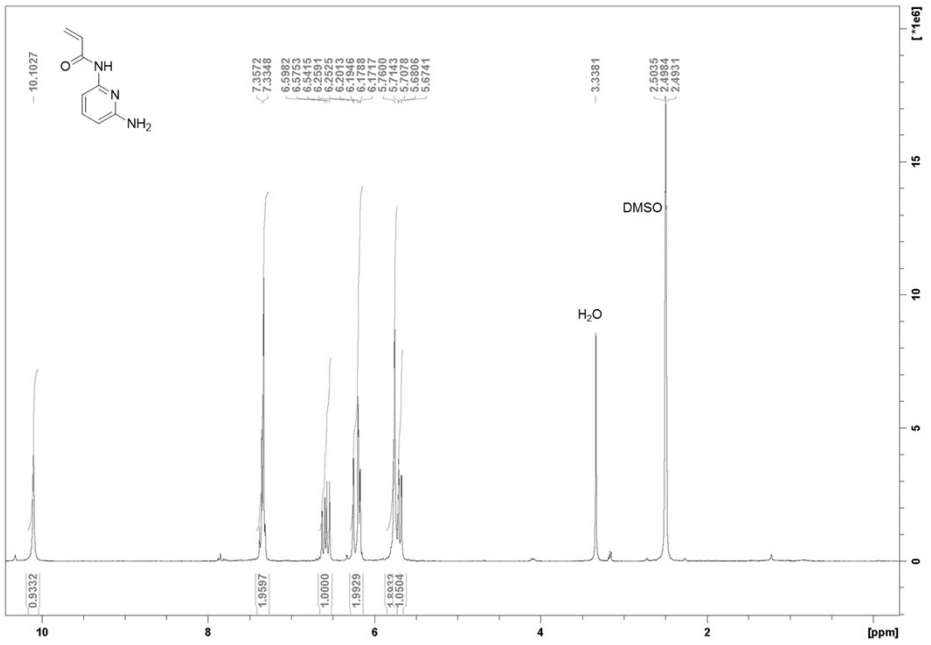


Fig. S1. ^{1}H-NMR spectrum of *N*-(6-aminopyridin-2-yl)acrylamide measured in DMSO-d6.

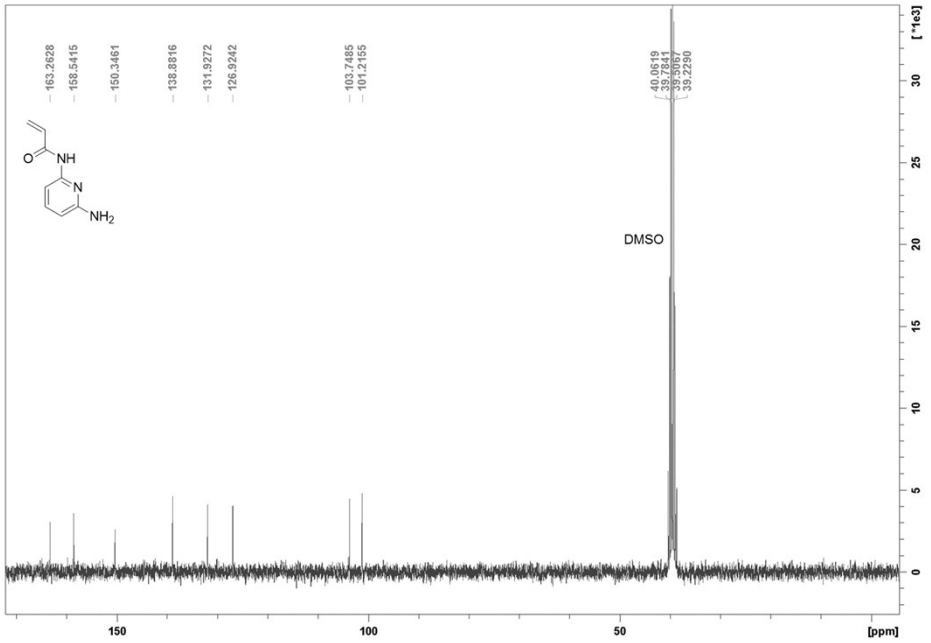


Fig. S2. ^{13}C-NMR spectrum of *N*-(6-aminopyridin-2-yl)acrylamide measured in DMSO-d6.

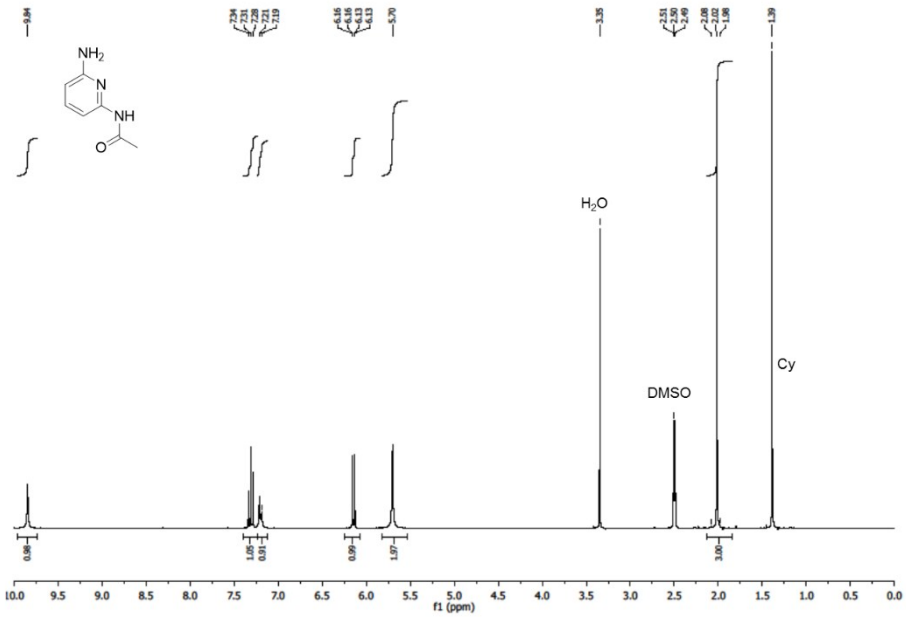


Fig. S3. ^{1}H-NMR spectrum of *N*-(6-aminopyridin-2-yl)acetamide measured in $CDCl_3$.

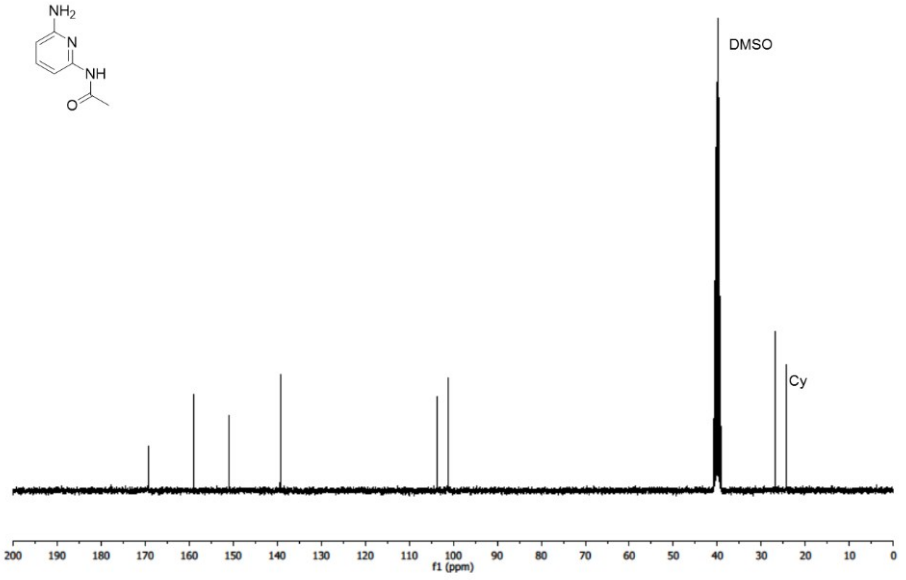


Fig. S4. ^{13}C-NMR spectrum of *N*-(6-aminopyridin-2-yl)acetamide measured in DMSO-d6.

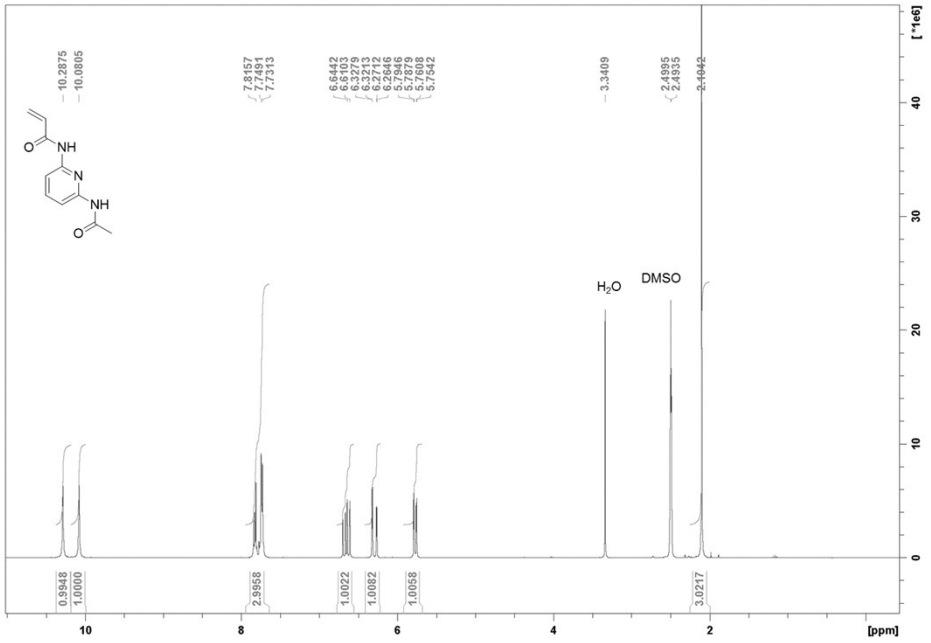


Fig. S5. ^{1}H-NMR spectrum of *N*-(6-acetamidopyridin-2-yl)acrylamide measured in DMSO-d6.

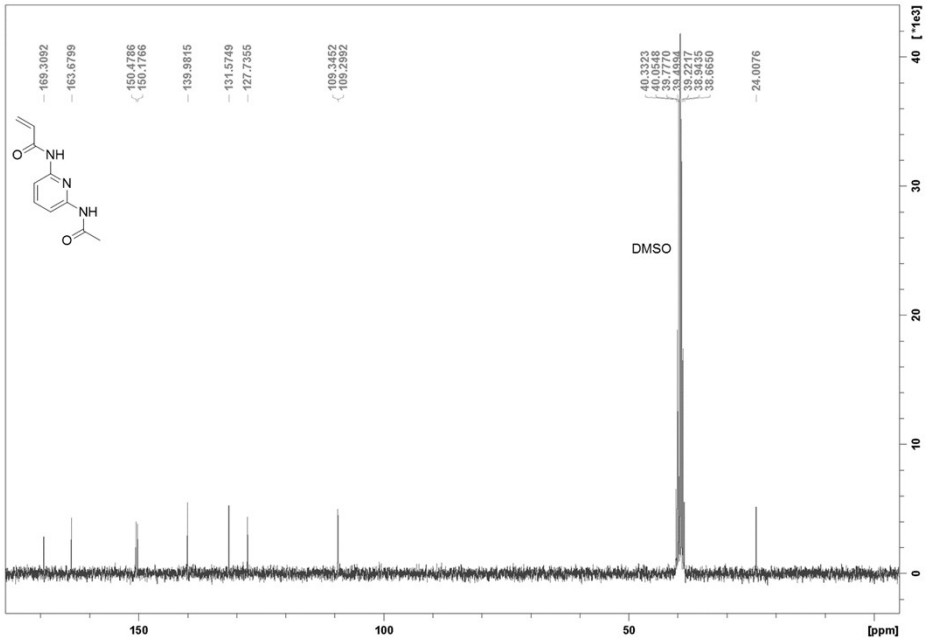


Fig. S6. ^{13}C-NMR spectrum of *N*-(6-acetamidopyridin-2-yl)acrylamide measured in DMSO-d6.

Characterization of the polymers

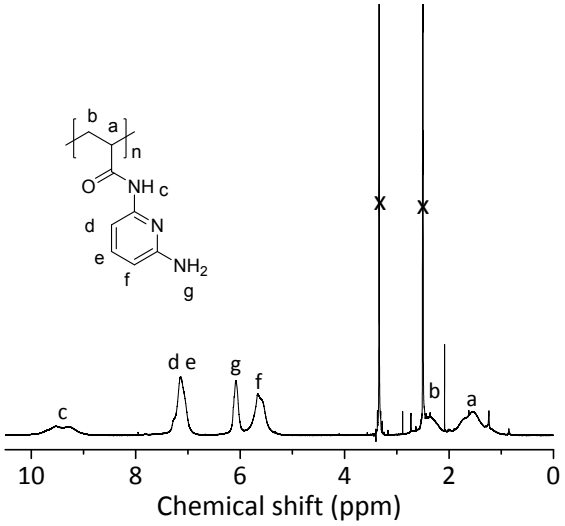


Fig. S7. ^{1}H-NMR spectrum of poly(*N*-(6-aminopyridin-2-yl)acrylamide) (PNAPAAm) measured in DMSO-d6.

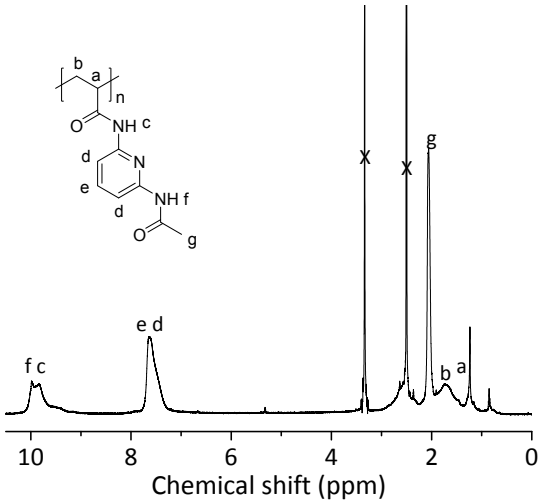


Fig. S8. ^{1}H-NMR spectrum of poly(*N*-(6-acetamidopyridin-2-yl)acrylamide) (PNAcAPAAm) measured in DMSO-d6.

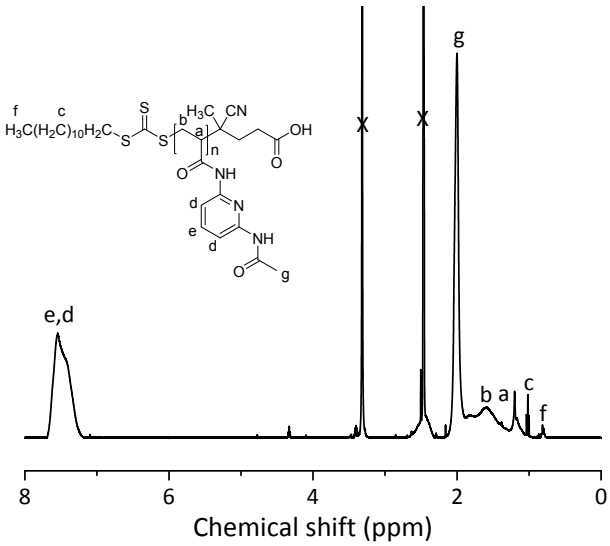


Fig. S9. ^{1}H-NMR spectrum of poly(*N*-(6-acetamidopyridin-2-yl)acrylamide) (PNAcAPAAm) via RAFT polymerization measured in DMSO-d6.

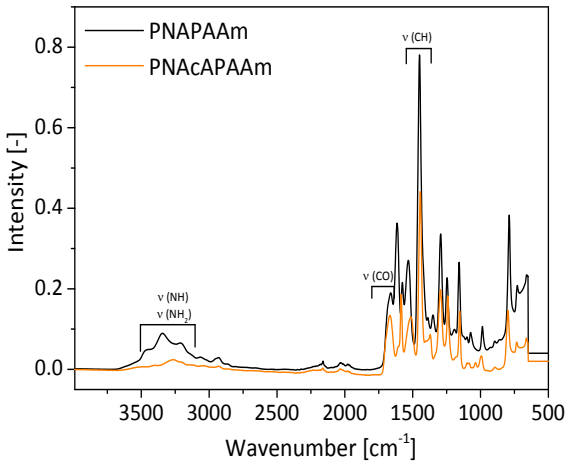


Fig. S10. ATR-FTIR measurements of the poly(*N*-(6-aminopyridin-2-yl)acrylamide) (PNAPAAm) and poly(*N*-(6-acetamidopyridin-2-yl)acrylamide) (PNAcAPAAm).

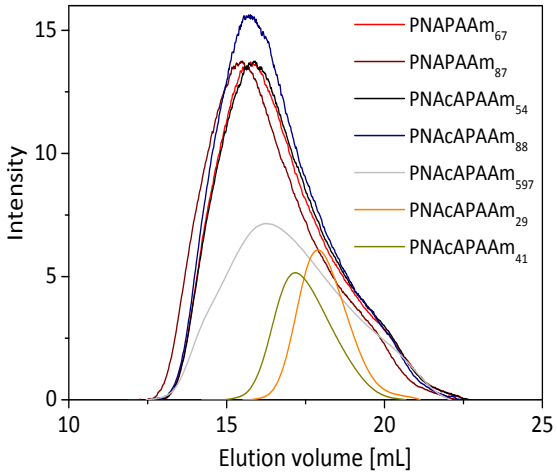


Fig. S11. GPC traces of PNAPAAm and PNAcAPAAm with different molecular weights.

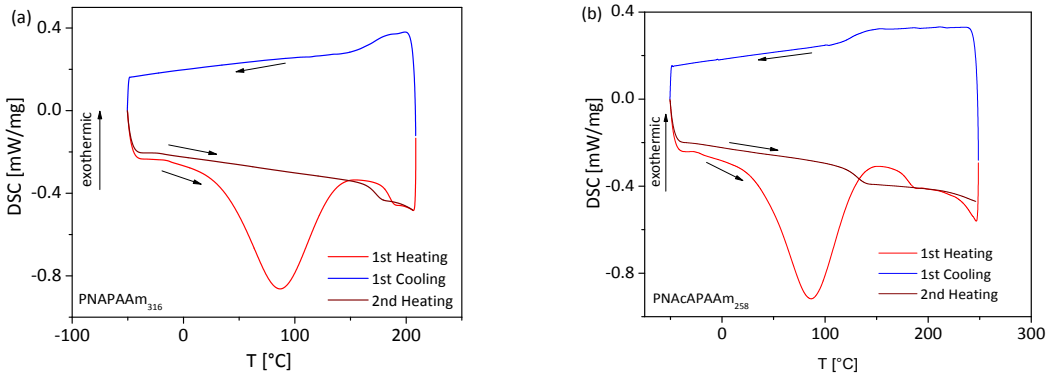


Fig. S12. DSC curves for (a) $PNAPAAm_{87}$ and (b) $PNAcAPAAm_{88}$.

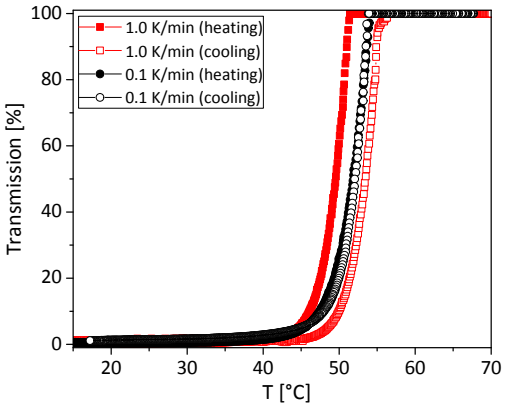


Fig. S13. Turbidity vs. temperature plot for $PNAcAPAAm_{88}$ solution in water/EtOH mixture (50% v/v) at a fixed polymer concentration of 1 mg/mL. The measurements were done at two different temperature gradients of 1 K/min (red squares) and 0.1 K/min (black circles). No hysteresis was observed at temperature gradient of 0.1 K/min, whereas around 2-3°C of hysteresis were observed at temperature gradient of 1 K/min.

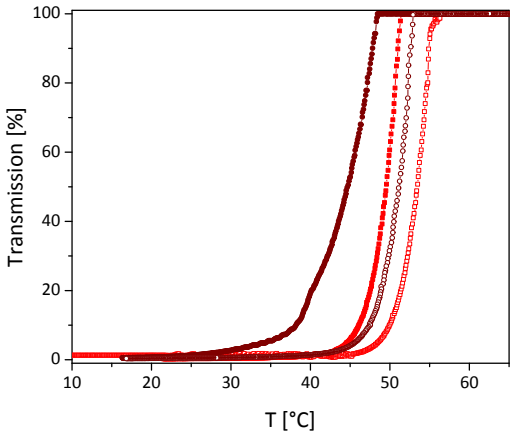


Fig. S14. Turbidity vs. temperature plot for PNAcAPAAm$_{88}$ solution in water/EtOH mixture (50% v/v) at a fixed polymer concentration of 1 mg/mL. The measurements were done by keeping the polymer solution at 70 °C for an extended time of around 2h (wine circles) and without keeping polymer solution at higher temperature (red squares) before measurements. Open symbols for cooling and solid filled symbols for heating run. The temperature gradient was 1 K/min for both measurements.

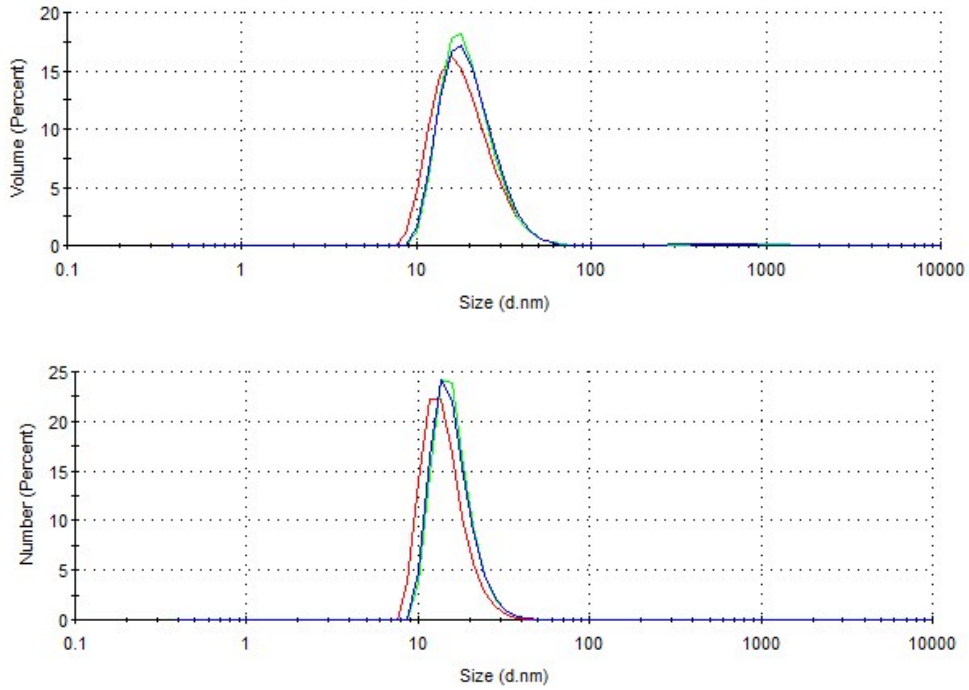


Fig. S15. Volume and number distribution of sizes in three consecutive runs for PNAcPAAm$_{88}$ in water/ethanol mixture (50% v/v) at fixed polymer concentration of 1 mg/mL. The temperature was fixed at 5 °C (below phase transition temperature). Red, green and blue line representing 1st, 2nd and 3rd measurements, respectively.

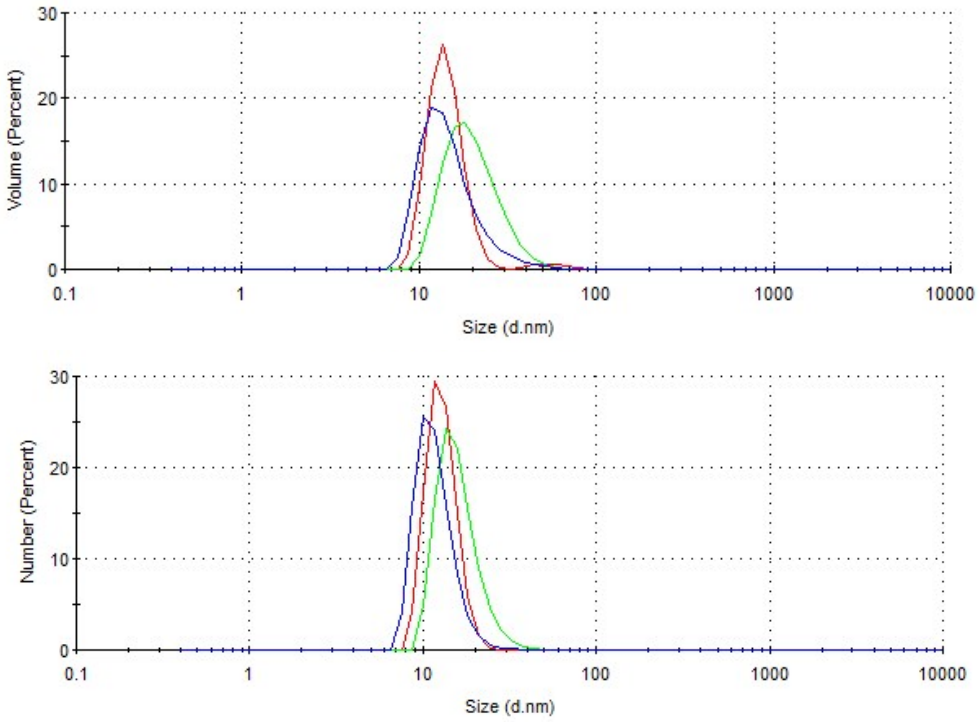


Fig. S16. Volume and number distribution of sizes of PNAcAPAAm$_{88}$ in different alcohol/water (60% v/v in alcohol) mixtures at fixed polymer concentration of 1 mg/mL above the phase transition temperature (65°C). Blue, red and green line representing water/MeOH, water/EtOH and water/*i*PrOH mixtures, respectively.

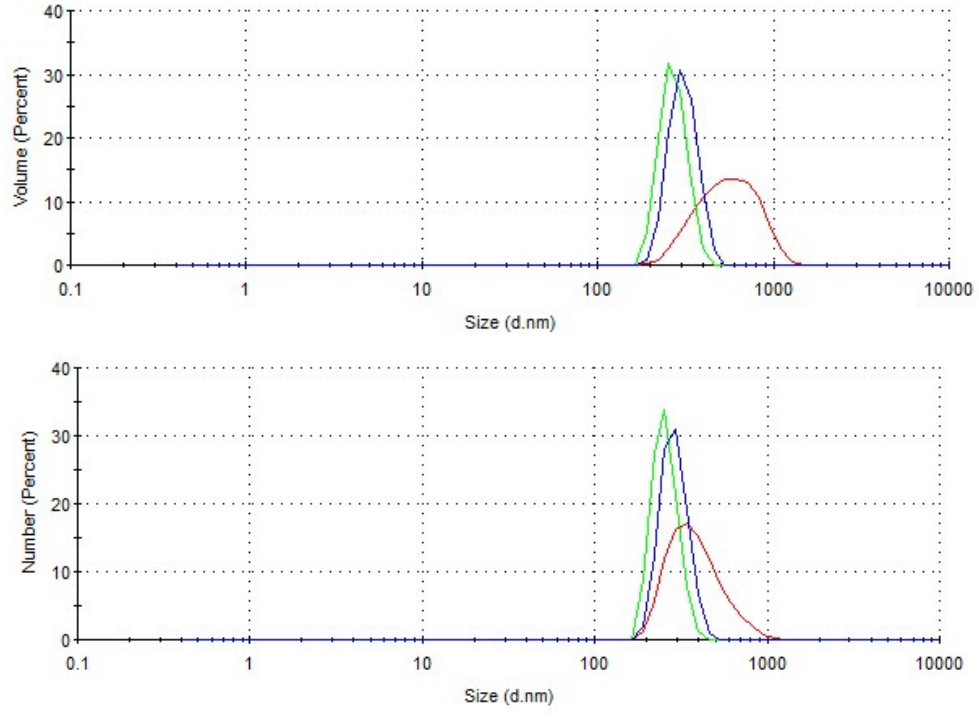


Fig. S17. Volume and number distribution of sizes of PNAcAPAAm$_{88}$ in different water/alcohol (60% v/v in alcohol) mixtures at fixed polymer concentration of 1 mg/mL below the phase transition temperature (5°C). Green, blue and red line represent for water/MeOH, water/EtOH and water/*i*PrOH mixtures, respectively.

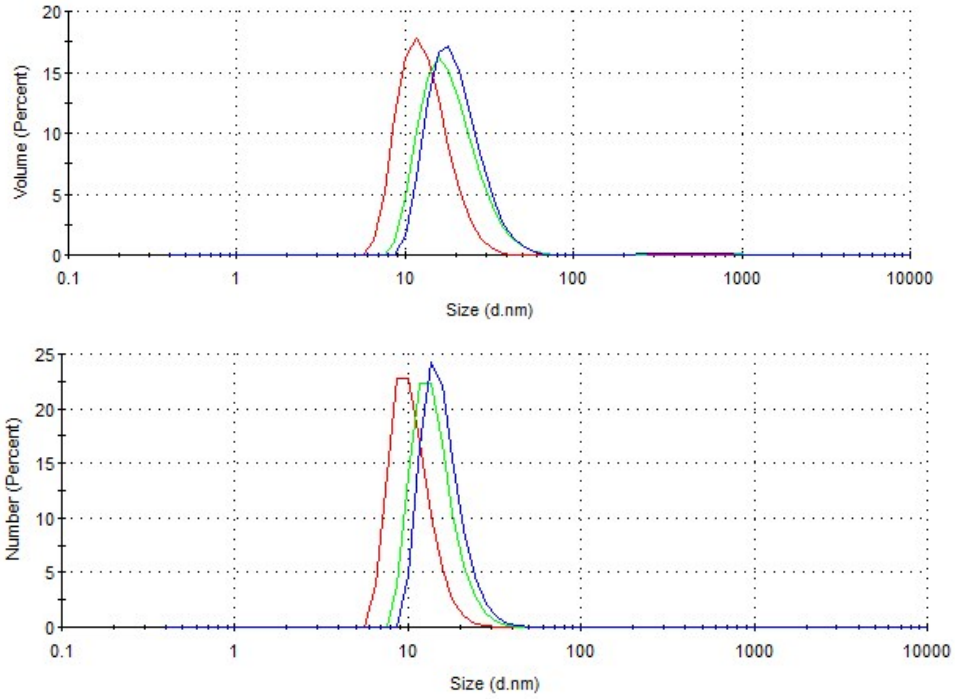


Fig. S18. Volume and number distribution of sizes of PNAcAPAAm$_{88}$ in different ethanol content in water at fixed polymer concentration of 1 mg/mL above the phase transition temperature (70°C). Blue, green and red line representing for 50, 60 and 70% v/v of EtOH in water, respectively.

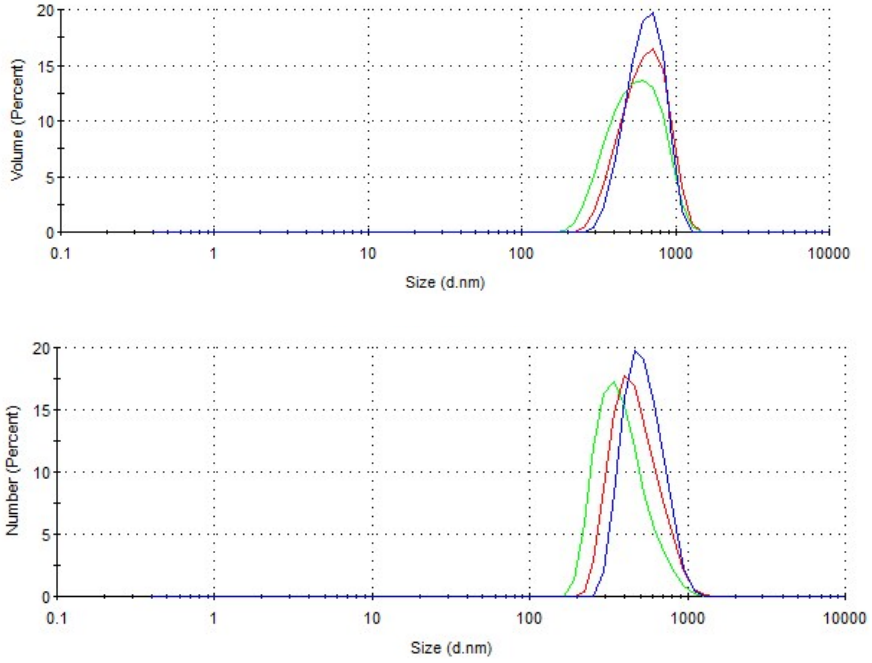


Fig. S19. Volume and number distribution of sizes of PNAcAPAAm$_{88}$ in different ethanol content in water at fixed polymer concentration of 1 mg/mL above the phase transition temperature (5°C). Blue, red and green line representing for 50, 60 and 70% v/v of EtOH in water, respectively.

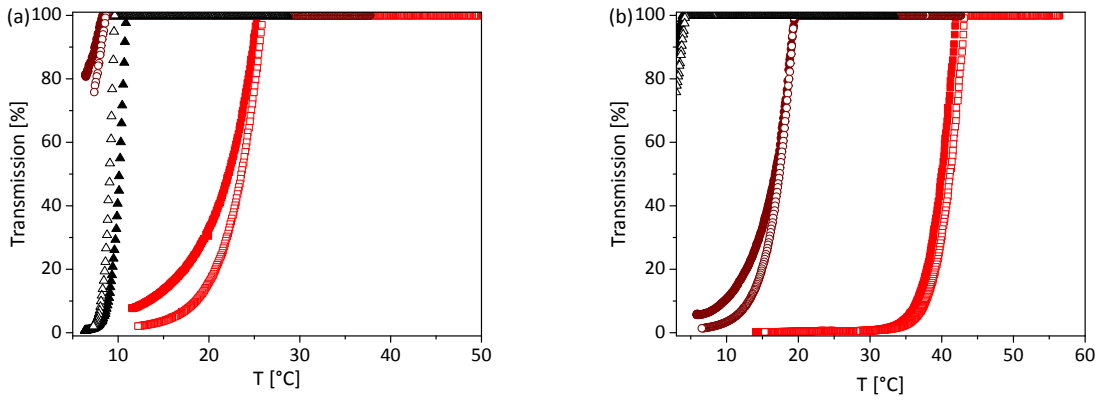


Figure S20. Transmittance versus temperature plots for PNAcAPAAm synthesized via RAFT polymerization with M_w (a) 8.0 KDa and (b) 12.2 KDa in water/alcohol mixtures at fixed polymer concentration of 1 mg/mL. Red squares for water/MeOH (60% v/v in alcohol) mixture, wine circles for water/EtOH (50% v/v) mixture and black triangles for water/*i*PrOH (50% v/v) mixture. Open symbols represent cooling run and solid filled symbols represent heating run. The obtained T_{CP} values are tabulated in table 1.

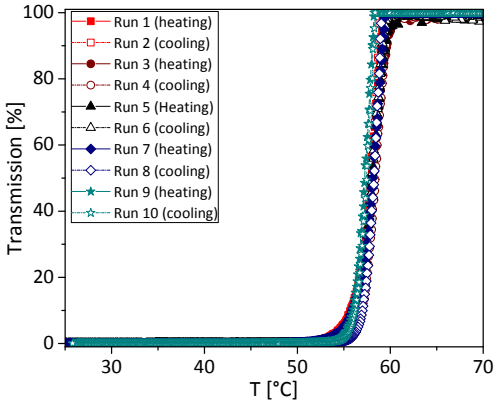


Fig. S21. Five consecutive turbidity curves (heating and subsequent cooling) of $pNAcAPAAm_{88}$ with constant polymer concentration of 5 mg/mL in water/EtOH mixtures (50% v/v). At high concentration the hysteresis is less than 1°C.