Electronic Supplementary Material (ESI) for Polymer Chemistry.

Electronic Supplementary Information

Solvent-free, photoinduced block copolymer synthesis from polymerizable eutectics by simultaneous PET-RAFT and ring-opening polymerization in air

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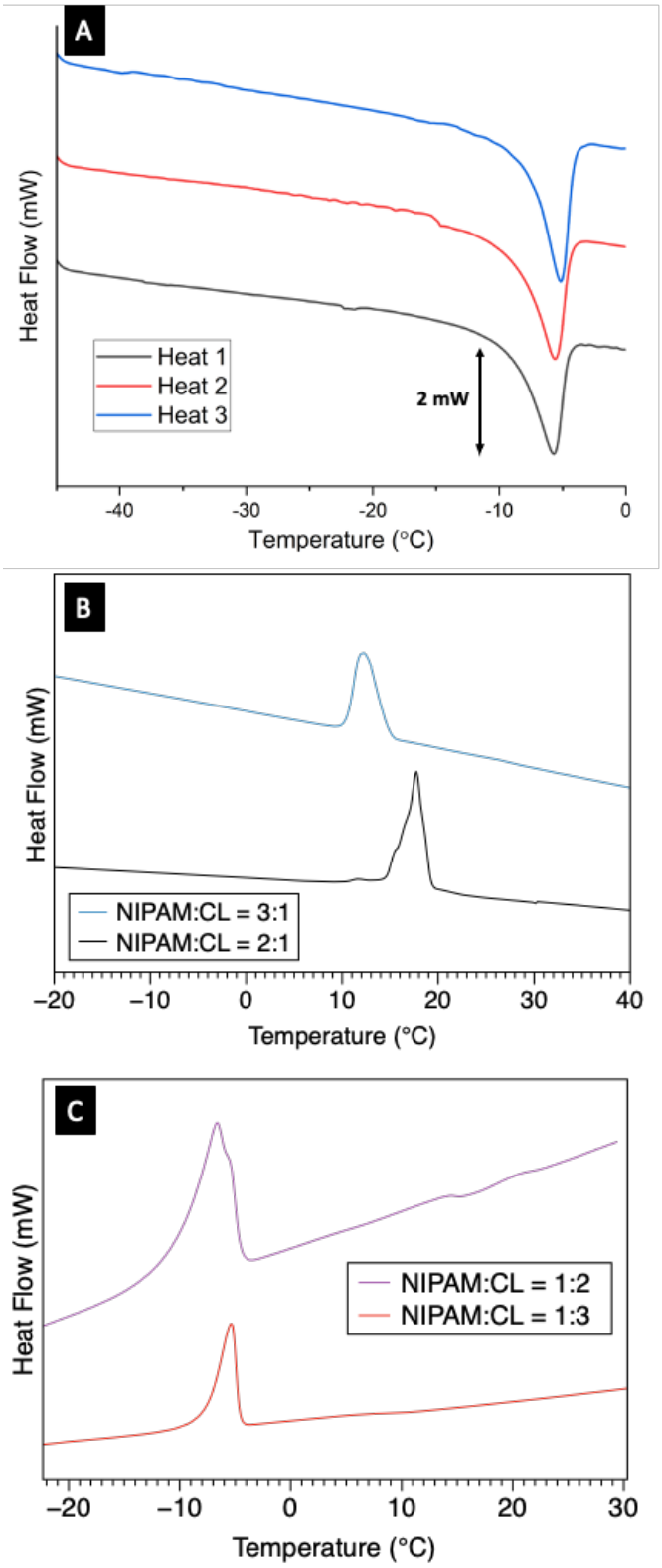

Fig S1. DSC thermograms of various mixtures prepared at different NIPAM:CL mole ratios. Shown are (A) heating thermograms of the 1:1 NIPAM:CL mixture (heating rate 2 °C min^{-1}), to accompany the data in Figure 1B and (B,C) cooling cycles of other NIPAM:CL mixtures (cooling rate 2 °C min^{-1}). Exothermic transitions are in the positive y direction; second loops shown in panels B and C. Data offset for clarity.

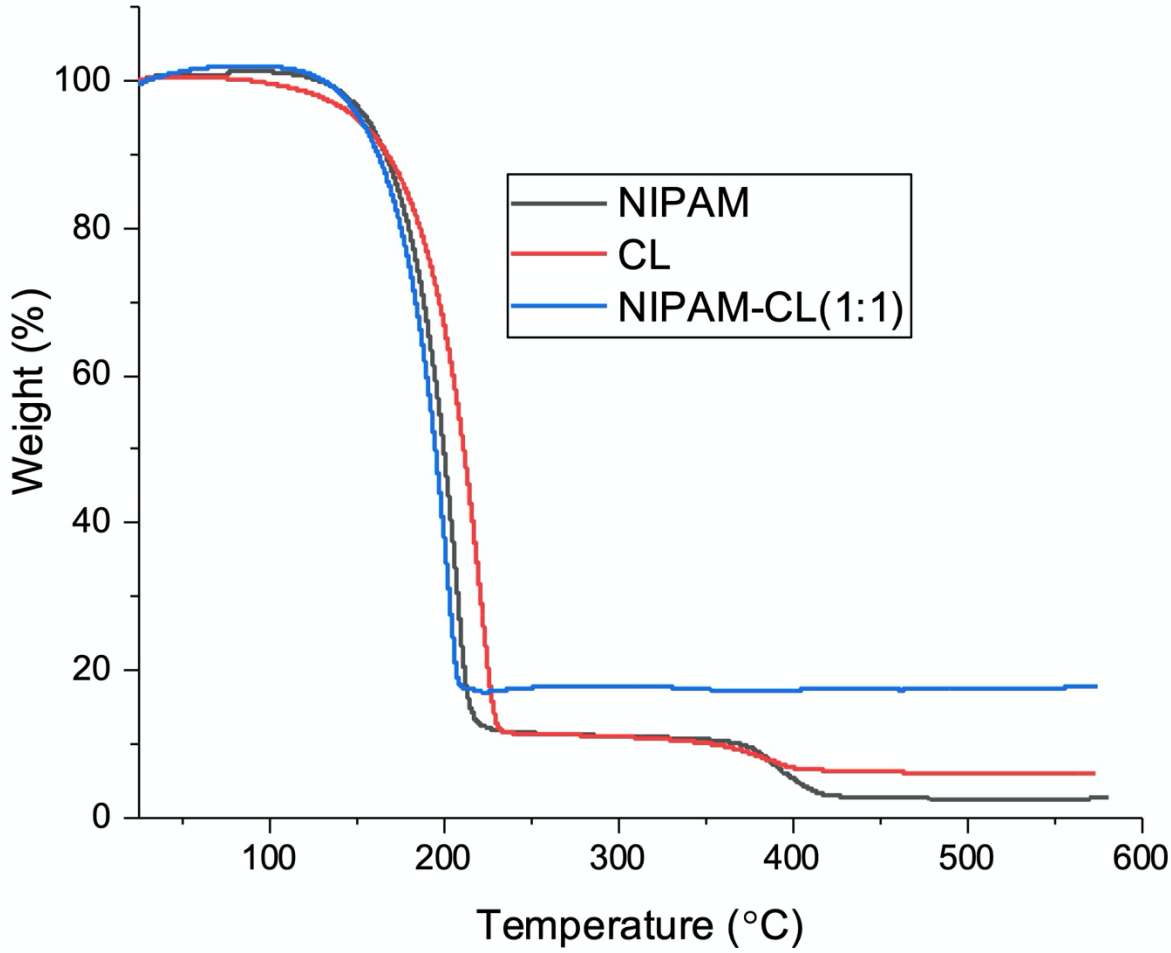

Fig S2. TGA analysis of 1:1 NIPAM:CL eutectic (blue), NIPAM (black) and CL (red). Heating rate was 10 °C min^{-1} in a nitrogen atmosphere.

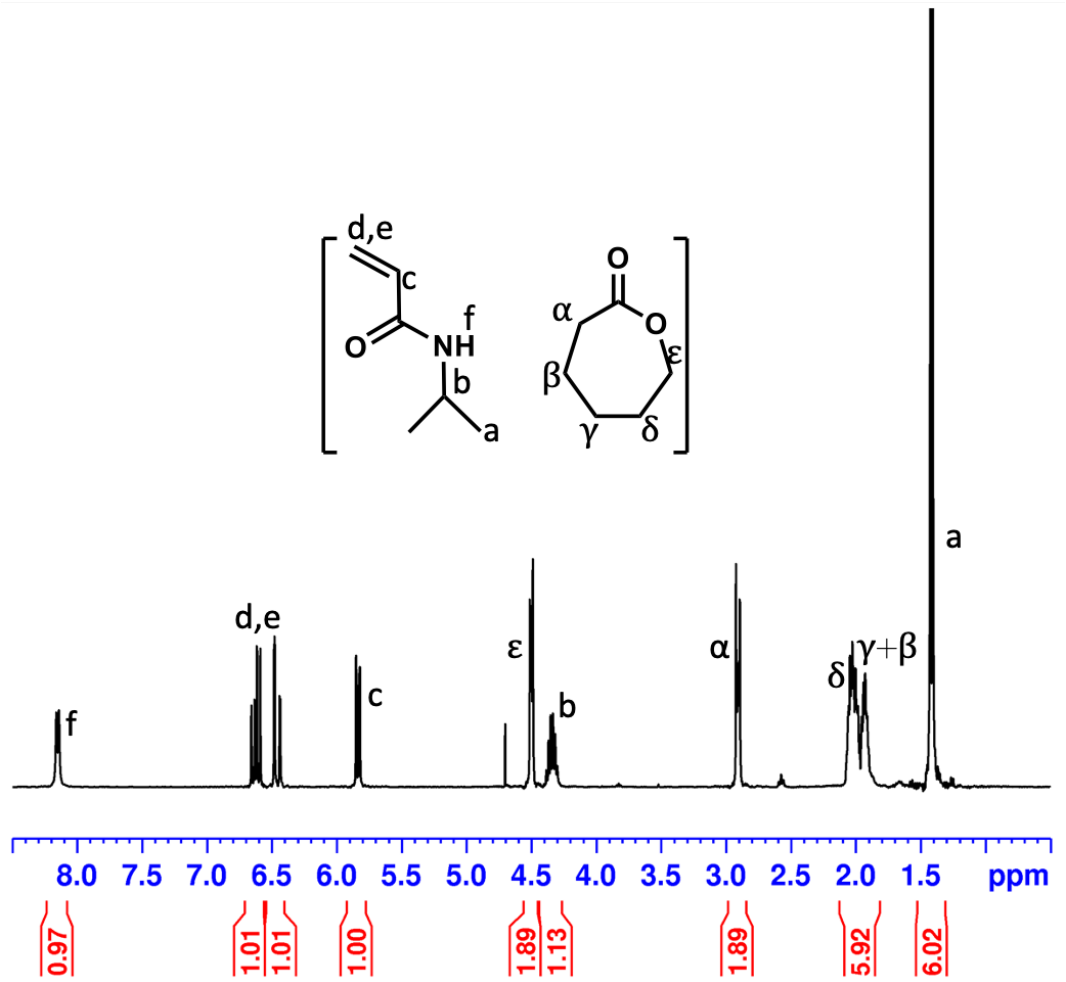

Fig S3. ^{1}H NMR spectrum of 1:1 NIPAM:CL eutectic. The spectrum was acquired by placing D_2O in a sealed capillary tube within the NMR sample tube to lock and shim the sample; spectrum was indirectly referenced to sodium trimethylsilylpropanesulfonate.

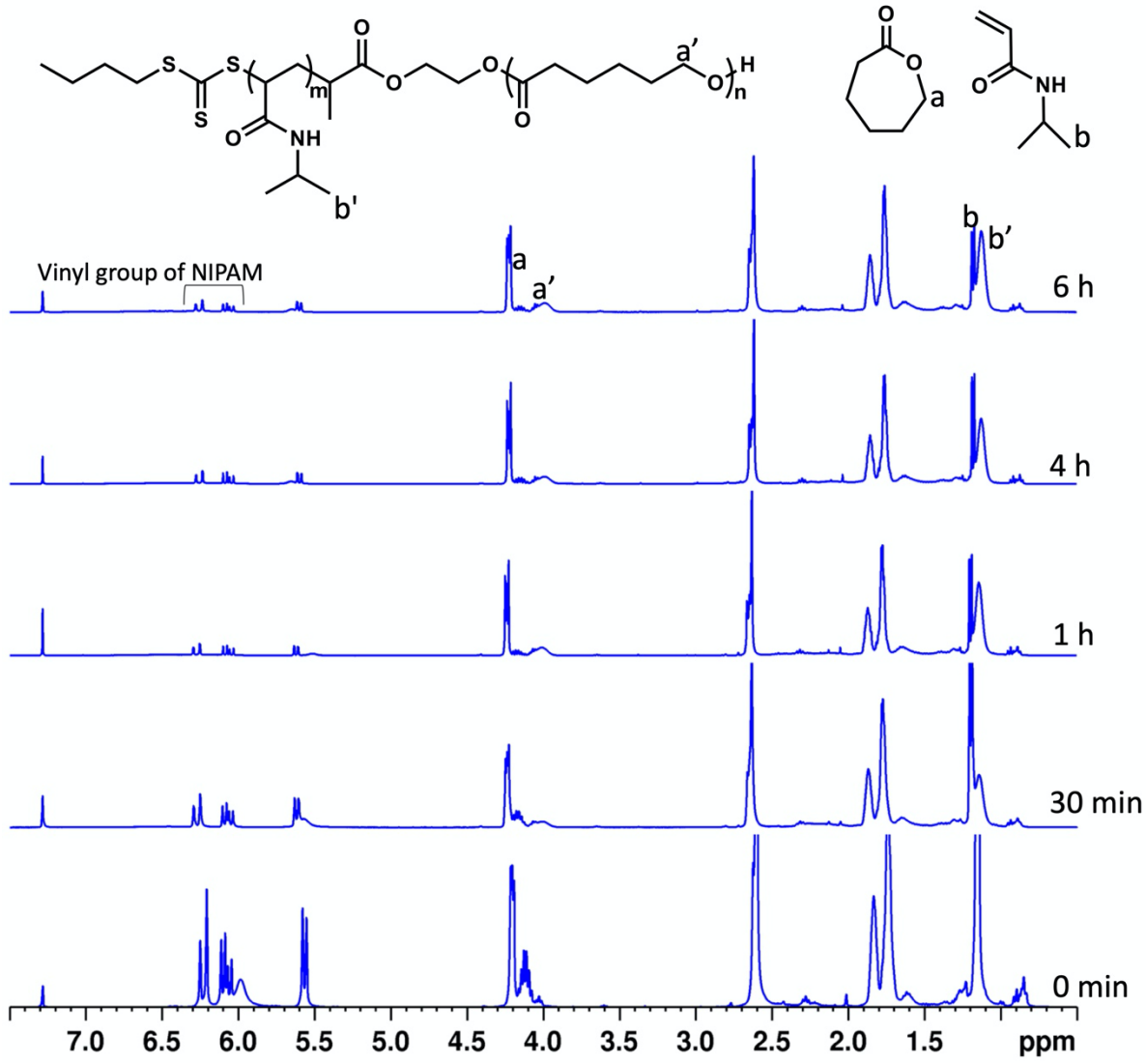

Fig S4. ^{1}H NMR spectra of the 1:1 NIPAM:CL eutectic in $CDCl_3$ performed at the specified time intervals during the simultaneous PET-RAFT and ROP polymerisation to prepare PNIPAM-b-PCL block copolymers.

Theoretical molar masses were calculated by the equation:

$$M_{n,theo} = MW_{HCTA} + \alpha^1 \times DP_{NIPAM} \times MW_{NIPAM} + \alpha^2 \times DP_{CL} \times MW_{CL}$$

where α^1 and α^2 represent the fractional conversion of NIPAM and CL. DP_{NIPAM} and DP_{CL} represent the targeted degree of polymerization of NIPAM and CL respectively, in this case 60 units each.

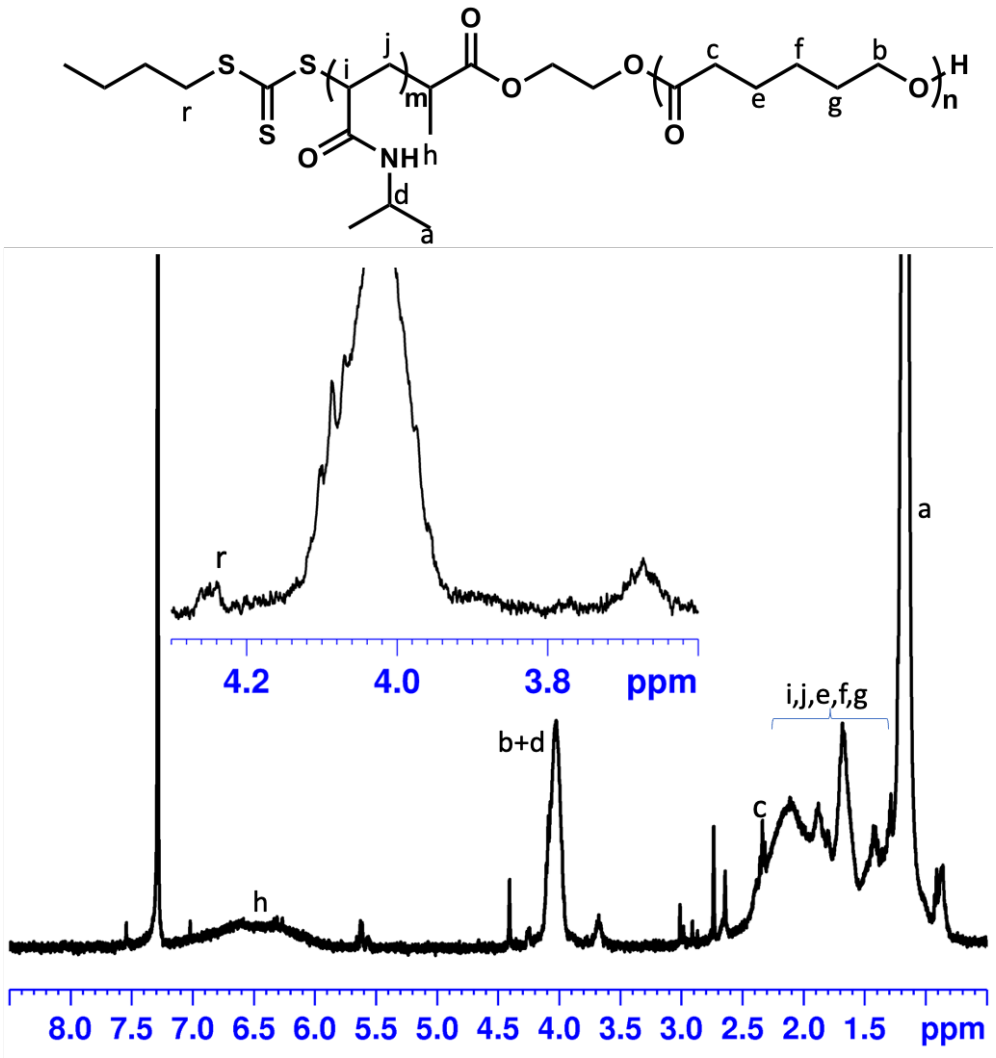

Fig S5. ^{1}H NMR spectrum of PNIPAM-b-PCL copolymer in $CDCl_3$.

The peak at δ_H 4.05 ppm is assigned to the OCH_2 in PCL and the isopropyl proton in PNIPAM. Characteristic peaks of the methyl group and N–H of NIPAM at δ_H 1.11 and 6.5 ppm are clearly observable in addition to PCL and PNIPAM backbone peaks. Integration of methylene group of HEBCP at δ_H 3.38ppm relative to the integration of peaks at δ_H 4.05 and 6.50 ppm indicated that PNIPAM-*b*-PCL contained 52 repeating units of NIPAM and 28 repeating units of CL.

The molar mass of the block copolymer was calculated as 9392 Da via the equation

$M_{n,NMR} = MW_{HCTA} + m \times MW_{NIPAM} + n \times MW_{CL}$

where m,n are the number of repeating units of NIPAM and CL respectively.

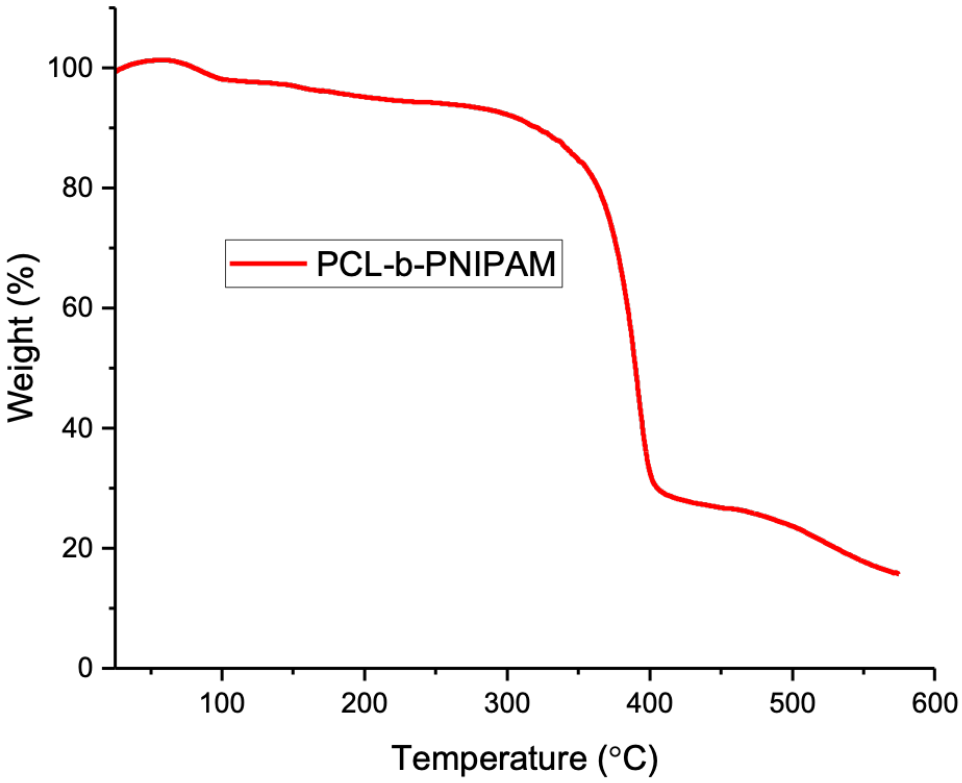

Fig S6. TGA of PNIPAM-b-PCL copolymer, performed at 10 °C min^{-1} in a nitrogen atmosphere.

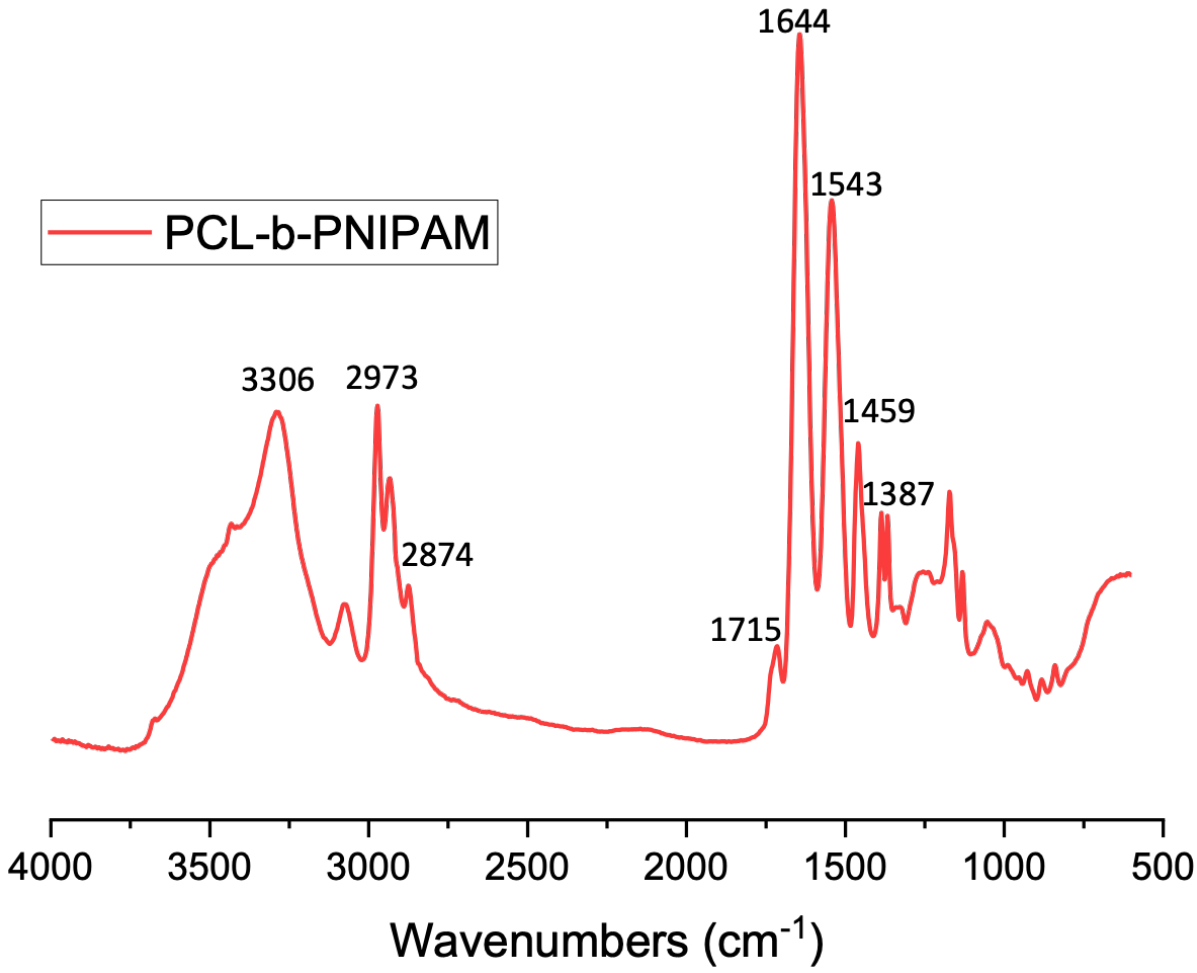

Fig S7. ATR-IR spectrum of PNIPAM-b-PCL.

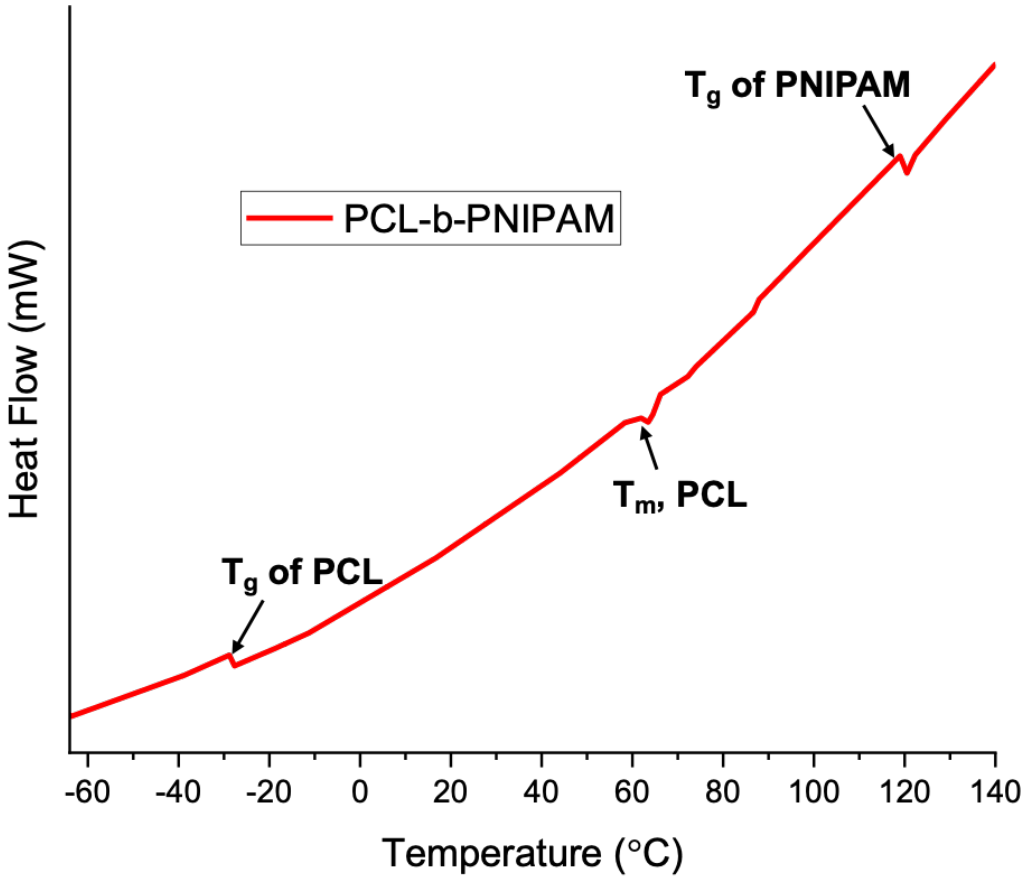

Fig S8. DSC trace of PNIPAM-b-PCL, collected at a heating rate of 2 °C min^{-1}

DSC analysis of the block copolymer reported in the manuscript exhibits a melting point at 63 °C, attributed to the PCL block. Glass transitions were observed at – 30 °C and 122 °C respectively.

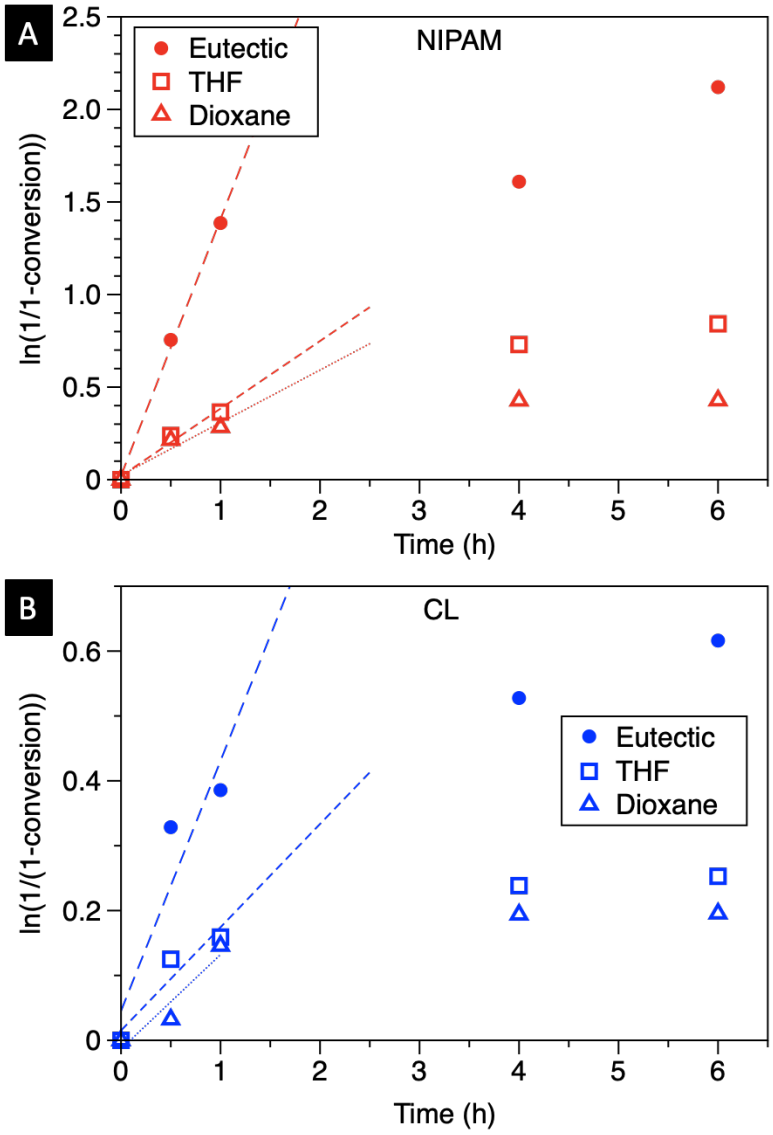

Fig S9. Semi-logarithmic plots to determine the pseudo-first order polymerization rate k_p^{app} for both (A) NIPAM and (B) CL in a 1:1 eutectic (filled circles), THF (open squares) and 1,4-dioxane (open triangles).

Table S1. Pseudo-first order rate coefficient for the rate of polymerization of both NIPAM and CL within the first hour of polymerization (based on the linear fits in the above figure).

System	**NIPAM k_p^{app} (h^{-1})**	**CL k_p^{app} (h^{-1})**
Eutectic	1.39 ± 0.07	0.39 ± 0.16
THF	0.37 ± 0.06	0.16 ± 0.05
1,4-dioxane	0.28 ± 0.08	0.15 ± 0.05