

Supplementary Information

Effect of Architecture on the Thermo-induced Phase Transition of Methacrylate-based Symmetric Pentablock Terpolymers

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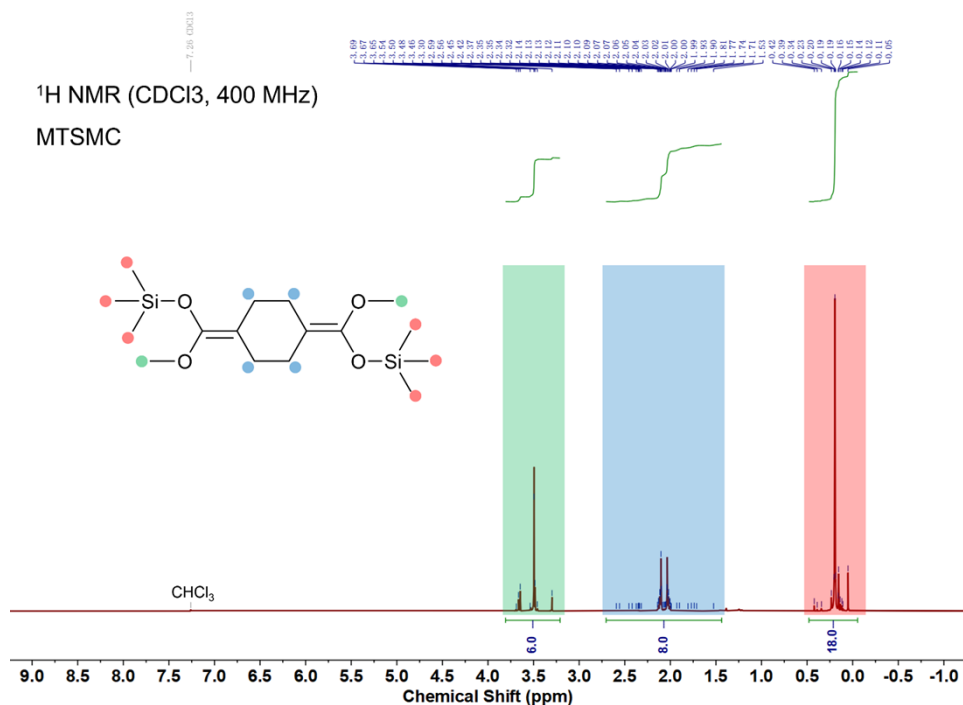


Figure S1. ¹H NMR spectrum of the obtained bifunctional initiator MTSMC (*Cis/trans* isomerism has been omitted). The spectrum was collected in CDCl₃ solution (TMS-free) at 25 °C with a scanning time of 16.

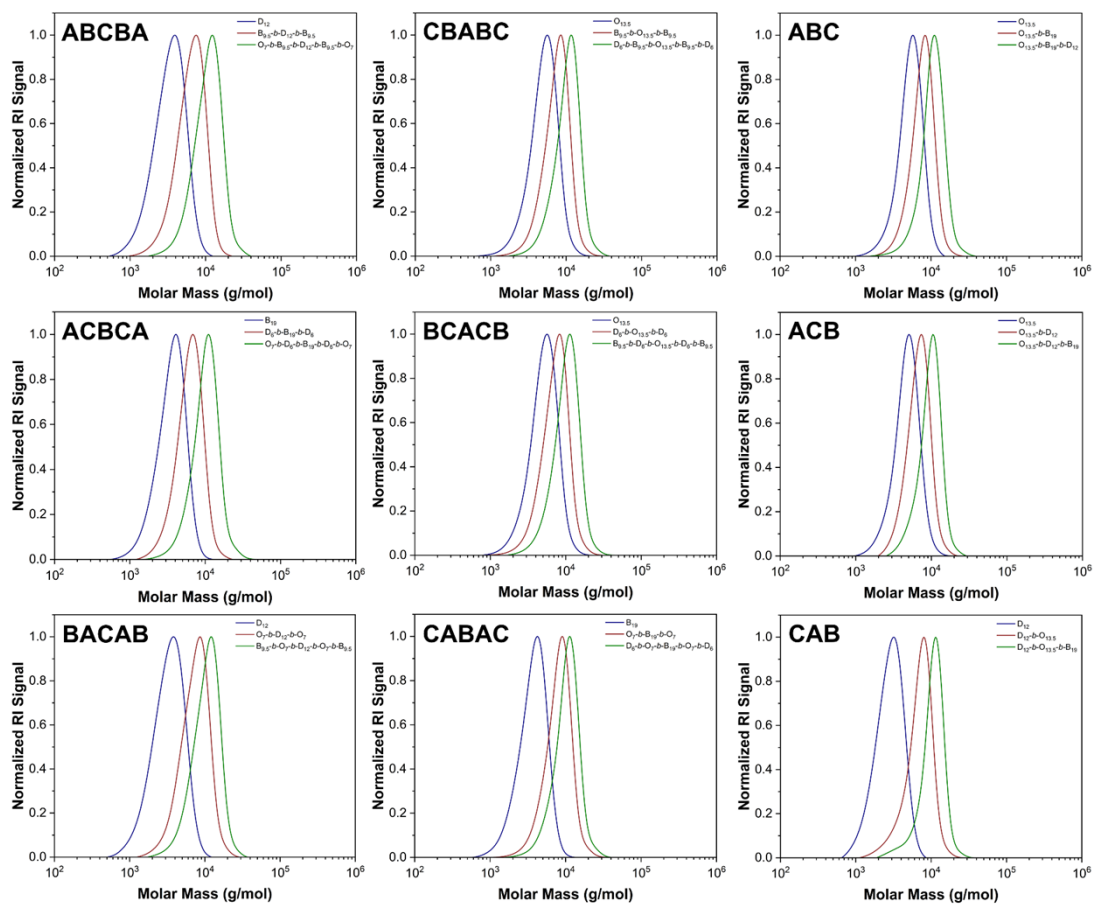


Figure S2. GPC traces of the obtained terpolymers with the respective precursors in THF-Et₃N (95-5 vol%) mixture.

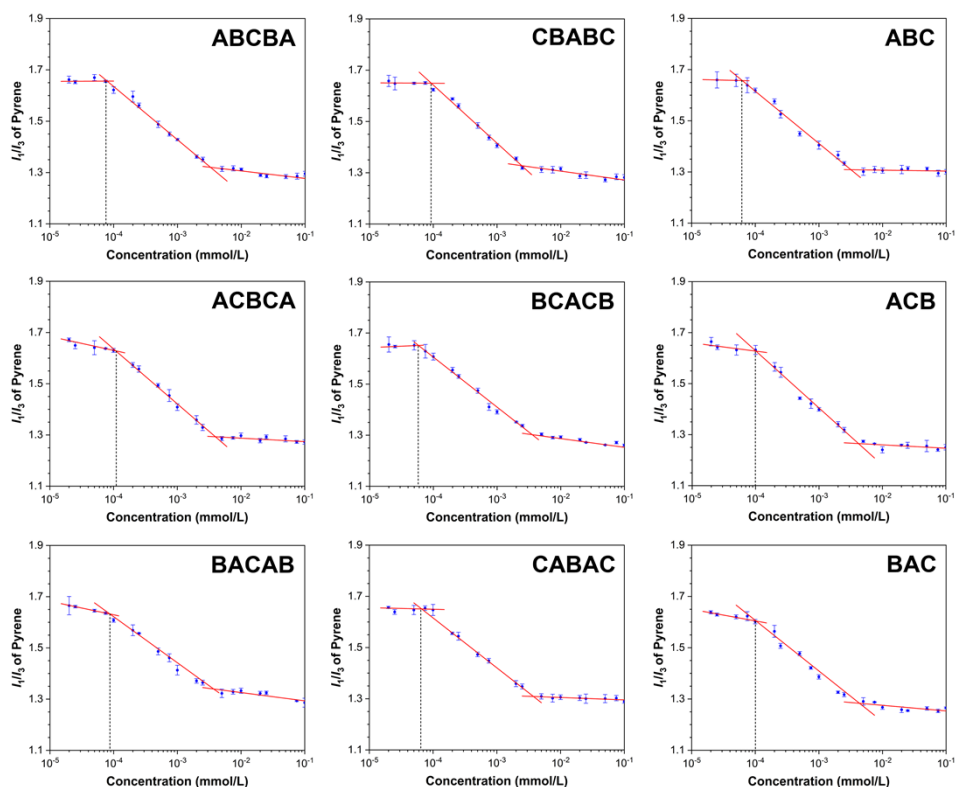


Figure S3. I_1/I_3 of pyrene-concentration relationships of the terpolymers in DI water at 25 °C. The excitation wavelength was 334 nm.

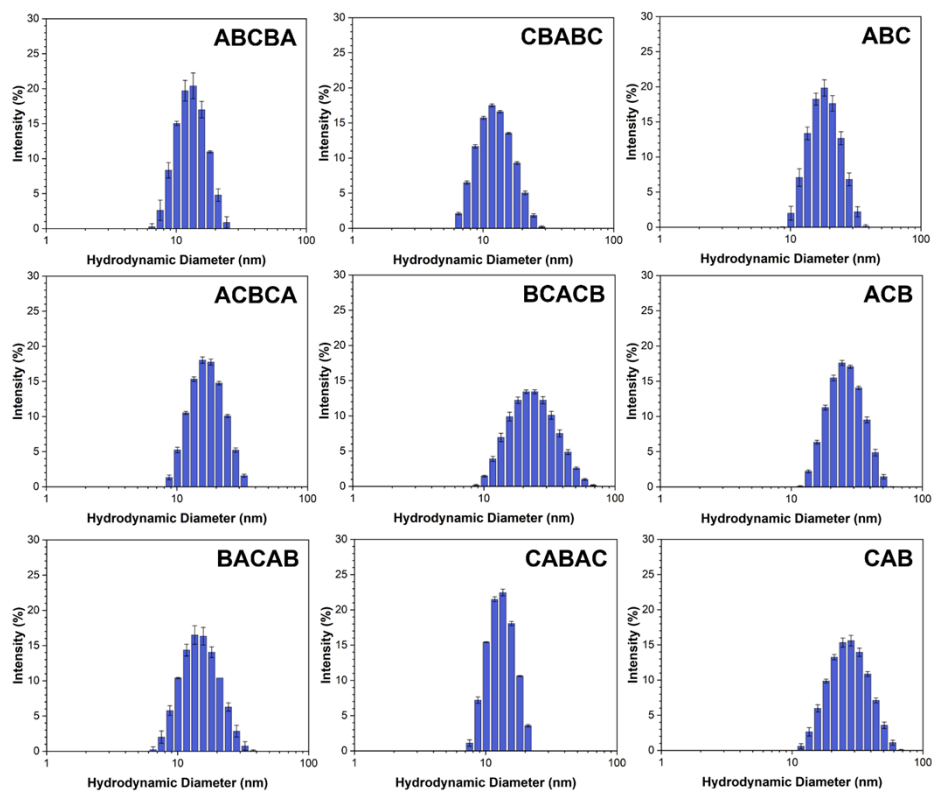


Figure S4. DLS histograms of the overall intensity-based d_h distribution of the 1 wt% H₂O solution of the terpolymers at 25 °C.

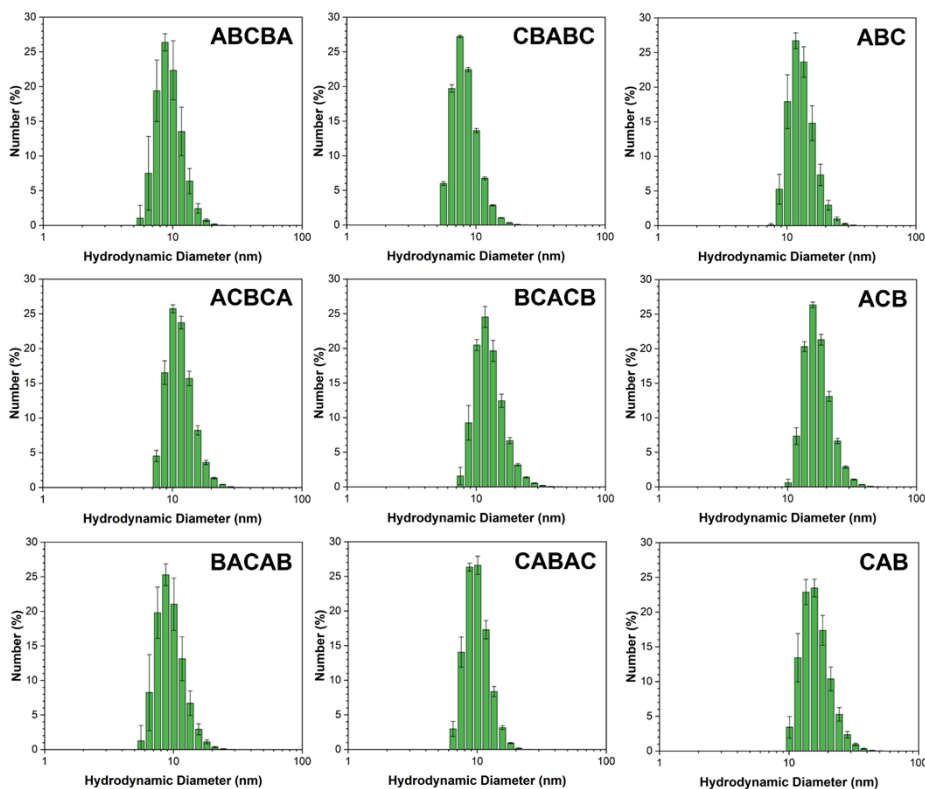


Figure S5. DLS histograms of the overall number-based d_h distribution of the 1 wt% H₂O solution of the terpolymers at 25 °C.

Group	Triblocks	Pentablocks	
I	ABC 200 nm Size by TEM: 14 ± 2 nm by DLS: 13 ± 3 nm	ABCBA 200 nm Size by TEM: 12 ± 2 nm by DLS: 10 ± 3 nm	CBABC 200 nm Size by TEM: 15 ± 2 nm by DLS: 8 ± 2 nm
II	ACB 200 nm Size by TEM: 16 ± 3 nm by DLS: 17 ± 4 nm	ACBCA 200 nm Size by TEM: 13 ± 3 nm by DLS: 12 ± 3 nm	BCACB 200 nm Size by TEM: 14 ± 2 nm by DLS: 13 ± 4 nm
III	CAB 200 nm Size by TEM: 15 ± 4 nm by DLS: 17 ± 5 nm	CABAC 200 nm Size by TEM: 13 ± 2 nm by DLS: 10 ± 2 nm	BACAB 200 nm Size by TEM: 12 ± 2 nm by DLS: 10 ± 3 nm

Figure S6. Representative TEM micrographs of the polymeric micelles at 1 wt% in DI water at 25 °C. Samples were negatively stained by 2 wt% uranyl acetate before observation. “Size by DLS” here is the number-averaged d_h .

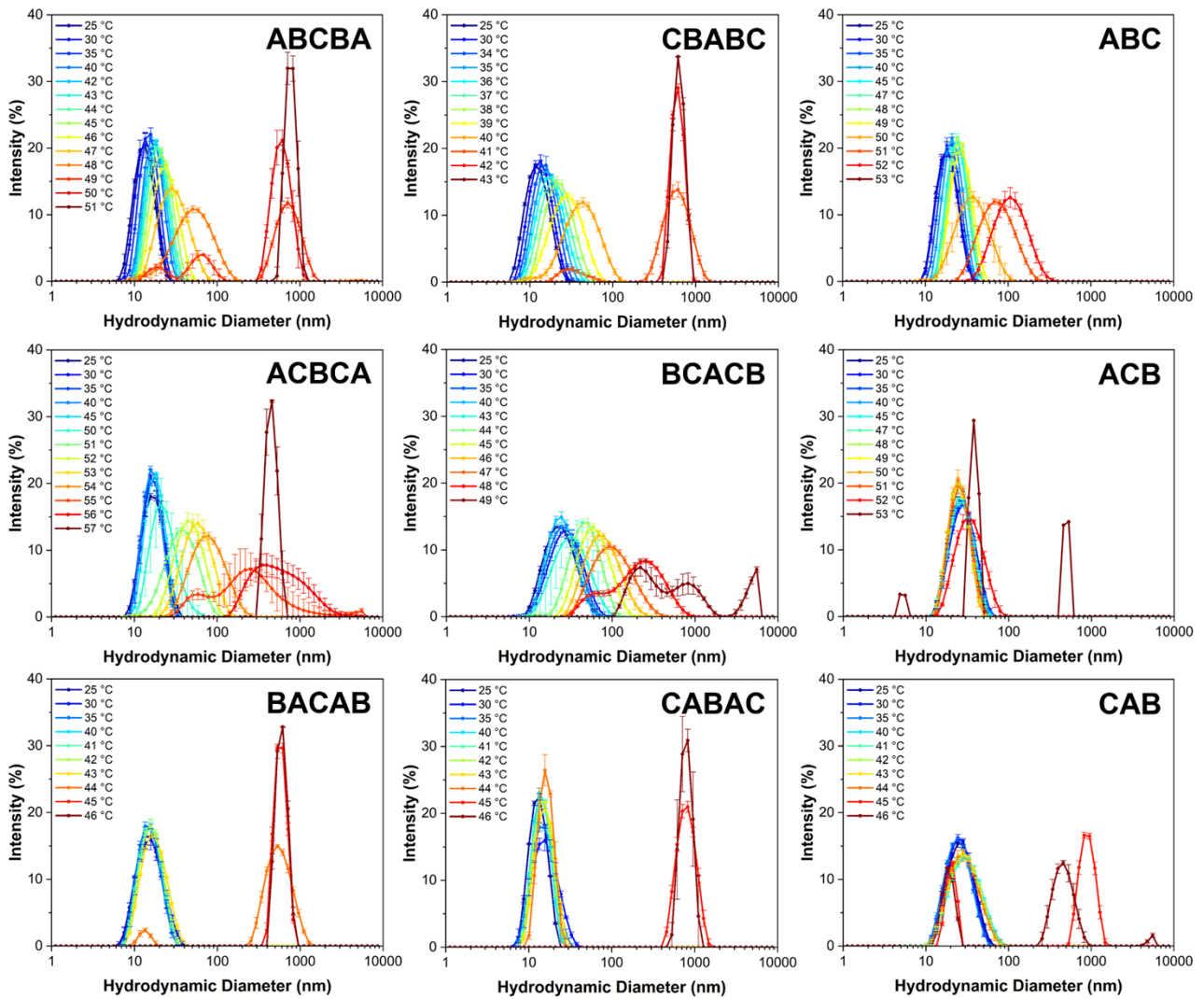


Figure S7. The DLS curves of overall intensity-averaged d_h distributions of the terpolymers in 1 wt% H₂O solution in various temperatures.

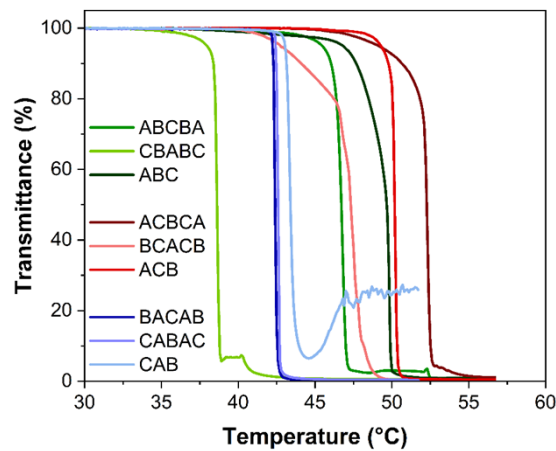


Figure S8. Transmittance-temperature dependence of the terpolymers in 1 wt% D₂O solution.

Table S1. T_{cp} of the terpolymers in 1 wt% D₂O solution.

Group	Architecture	T_{cp} (± 1 °C)
I	ABCBA	47
	CBABC	39
	ABC	50
II	ACBCA	52
	BCACB	47
	ACB	50
III	BACAB	42
	CABAC	43
	CAB	43

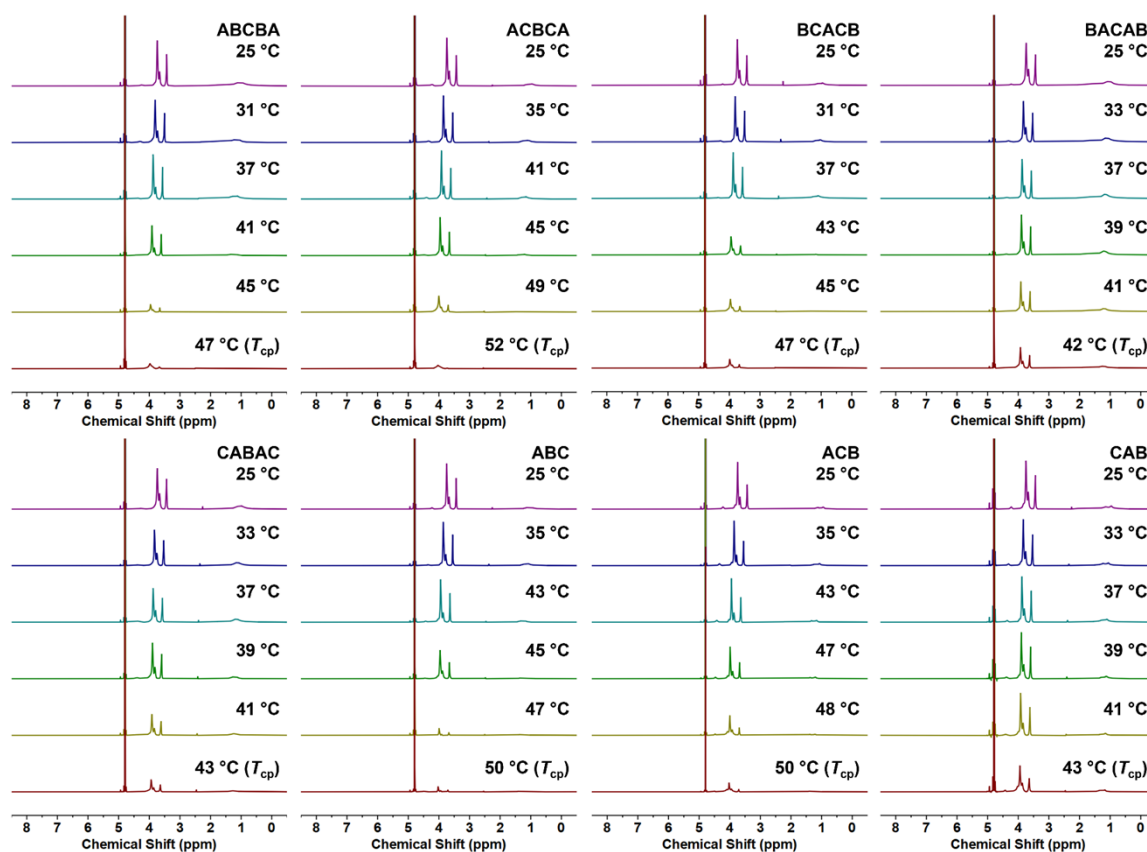


Figure S9. VT-¹H NMR of the terpolymers at 1 wt% in D₂O, collected with 16 scans and a relaxation time of 10 seconds. Top row from left to right: ABCBA, ACBCA, BCACB, and BACAB; bottom row from left to right: CABAC, ABC, ACB, and CAB.

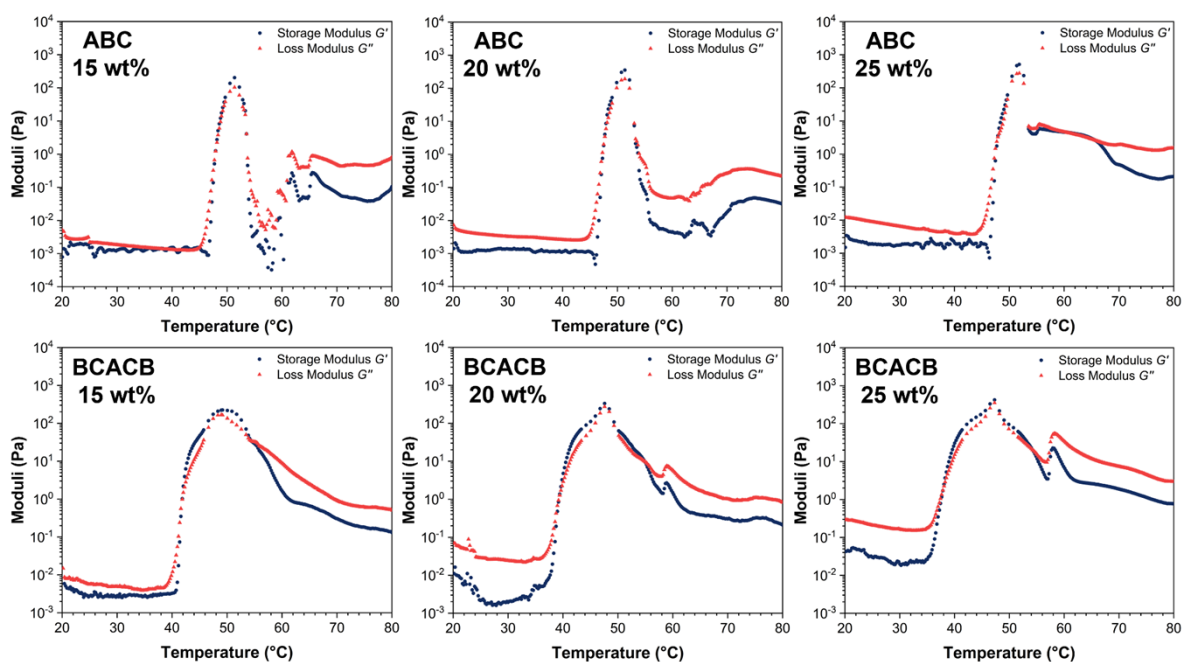


Figure S10. Typical temperature-moduli relationship of ABC and BCACB at gellable concentrations in PBS, obtained under an angular frequency of 1.0 rad/s, a strain of 1.0%, and a heating rate of 1 °C/min.

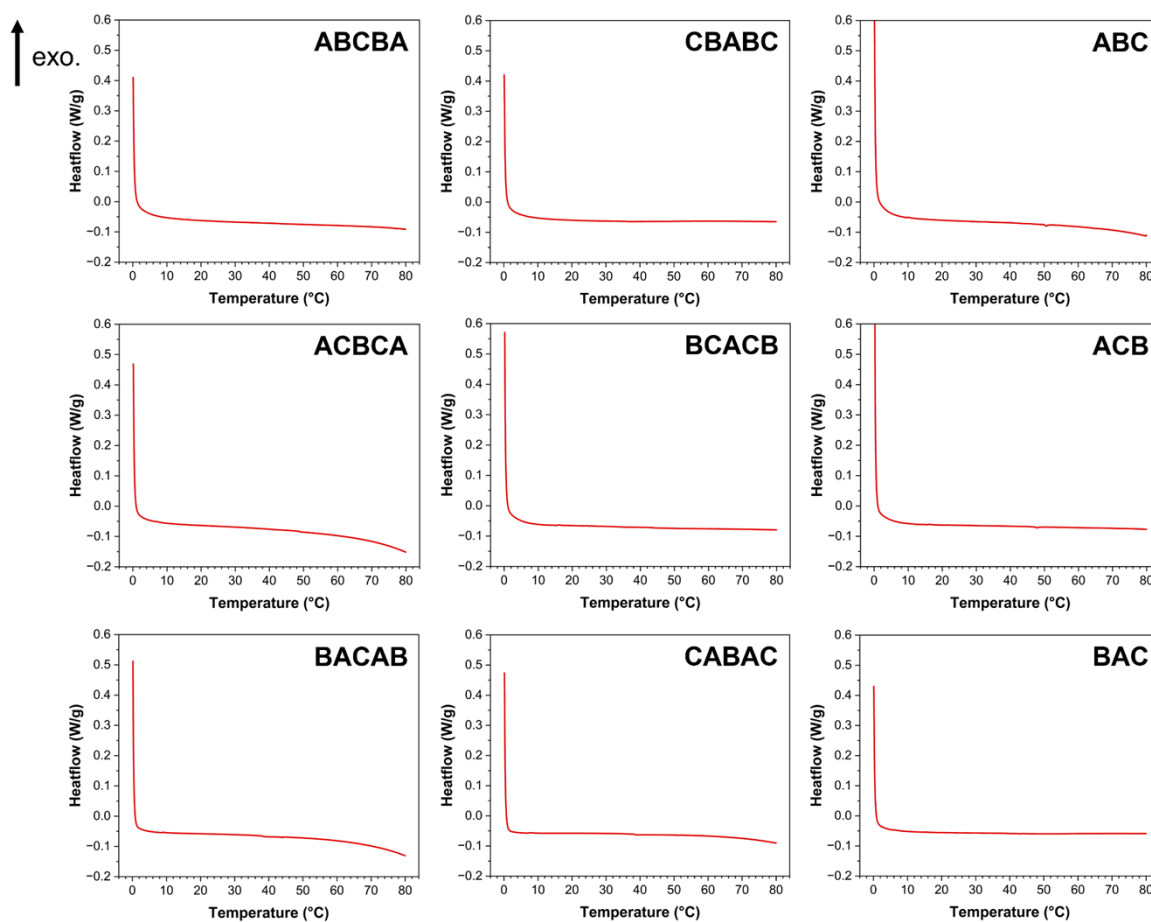


Figure S11. DSC thermograms of the polymer solutions at 25 wt% in PBS (pH = 7.4, 1 \times). The characterisations were performed under constant nitrogen flow (10 mL/min) and the heating rate was 1.0 °C/min.