Electronic Supplementary Information (ESI)

Free-standing thermo-responsive nanoporous membranes from high molecular weight PS-PNIPAM block copolymers synthesized *via* RAFT polymerization

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Table S1. Synthesis conditions and characterization results for PS macro-RAFT agents.

PS	CTA	$[M]_o$	$[M]_o/[CTA]_o$	$[CTA]_o/[I]_o$	*t* (h)	$\bar{M}_n$ GPC (kDa)	PDI GPC	Yield (%)
PS-1	BDAT	2.2	3142	0.875	48	57	1.42	23
PS-2	BDAT	2.6	2500	10.1	72	124	1.35	11
PS-3	BDAT	4.8	1915	3.5	24	87	1.30	13
PS-4	BDAT	6.4	1915	3.5	24	101	1.28	15
PS-5	BDAT	6.4	2867	7	24	162	1.28	15
PS-6	BDAT	6.4	2867	10	24	165	1.26	11
PS-7	BDAT	6.4	1915	10	24	110	1.26	15
PS-8	BDAT	7.68	1915	10	24	110	1.22	20
PS-9	**BDAT**	**8.04**	**1915**	**10**	**24**	**92**	**1.21**	**16**
PS-10	BDAT	Bulk	1915	10	24	45	1.27	4

Table S2. Synthesis conditions and characterization results for PNIPAM macro-RAFT agents.

PNIPAM	CTA	$[M]_o$	$[M]_o/[CTA]_o$	$[CTA]_o/[I]_o$	*t* (h)	$\bar{M}_n$ GPC (kDa)	PDI GPC	Yield (%)
PN-1	BDAT	1.77	260	5	48	41	1.15	82
PN-2	BDAT	1.18	216	10	24	33	1.13	83
PN-3	DTMA	1.77	216	10	4	41	1.04	84
PN-4	DTMA	1.18	162	10	3	35	1.03	77
PN-5	DTMA	1.18	145	10	4	25	1.10	81

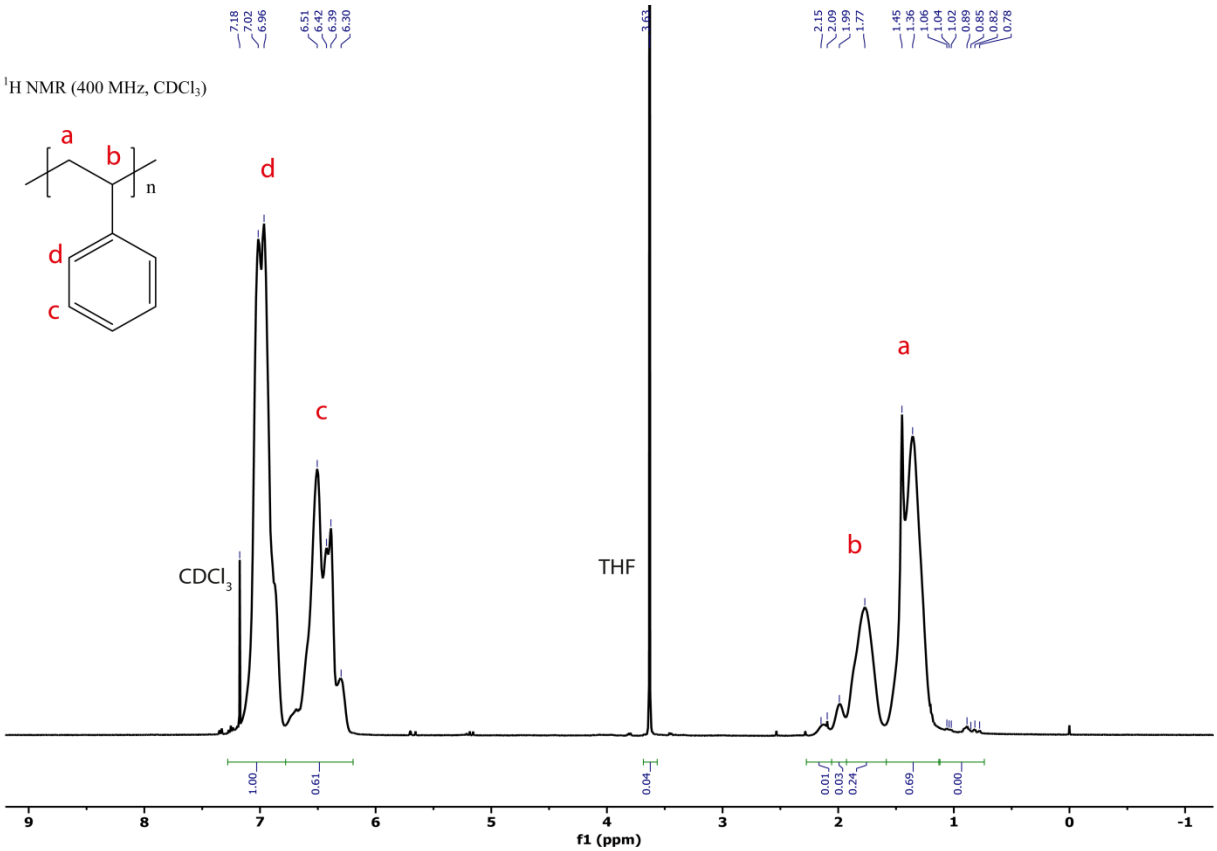

Figure S1. ^{1}H-NMR spectrum of PS macro-RAFT agent (PS-1).

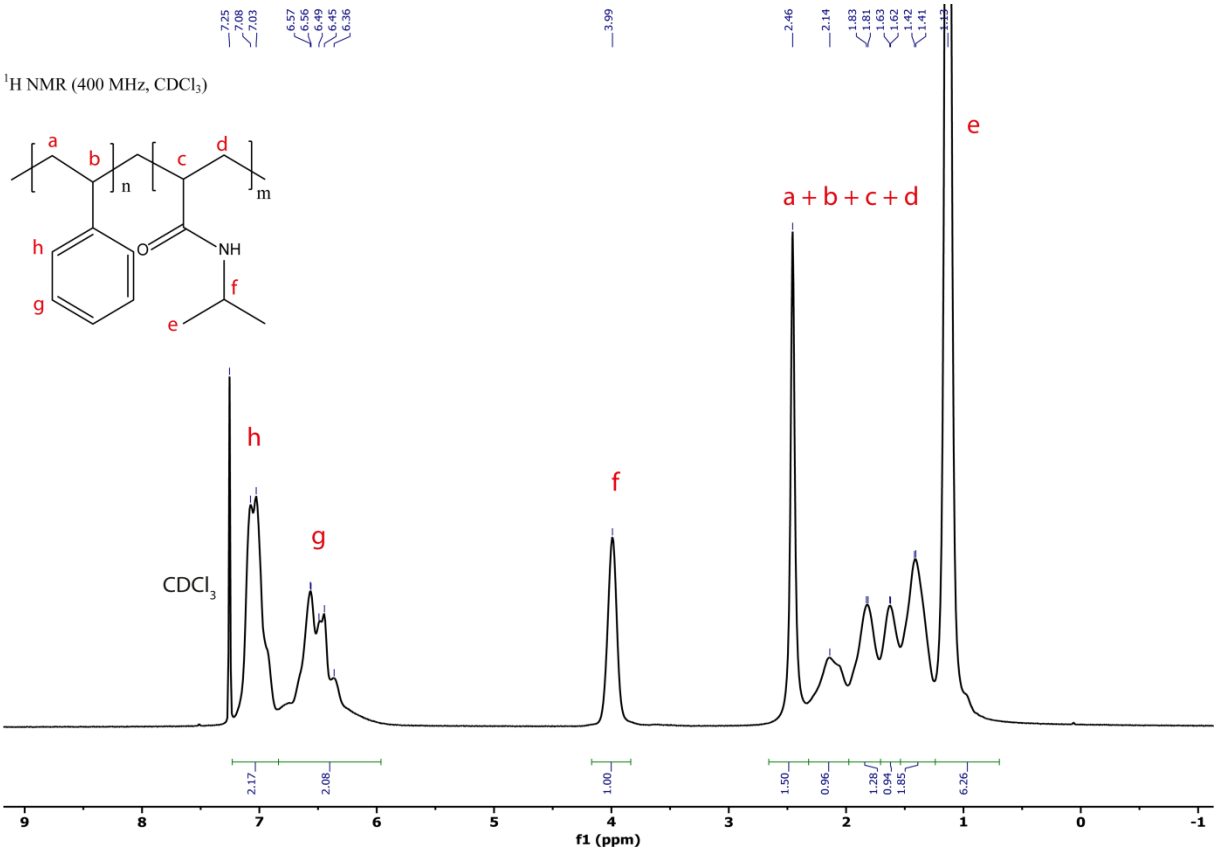

Figure S2. ^{1}H-NMR spectrum of PS-*b*-PNIPAM-*b*-PS copolymer (CP-1).

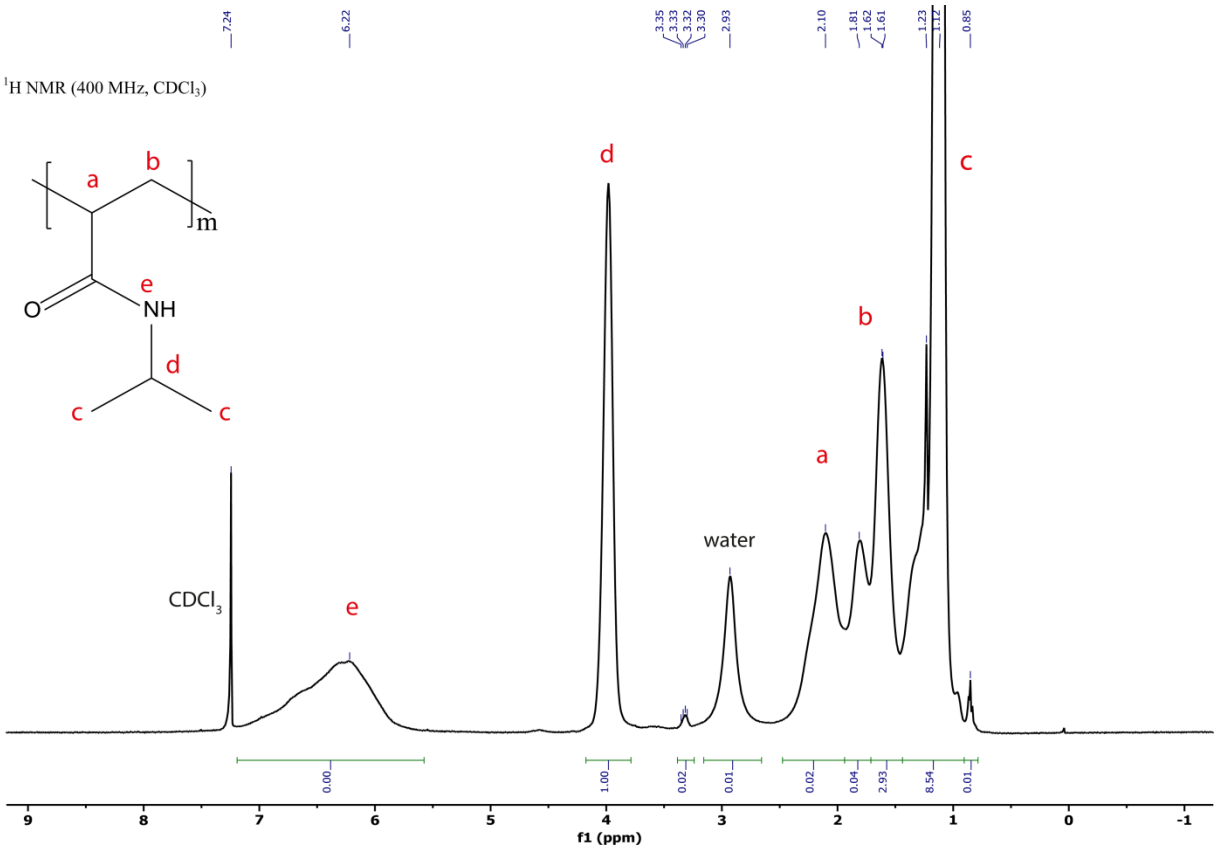

Figure S3. ^{1}H-NMR spectrum of PNIPAM macro-RAFT agent (PN-5).

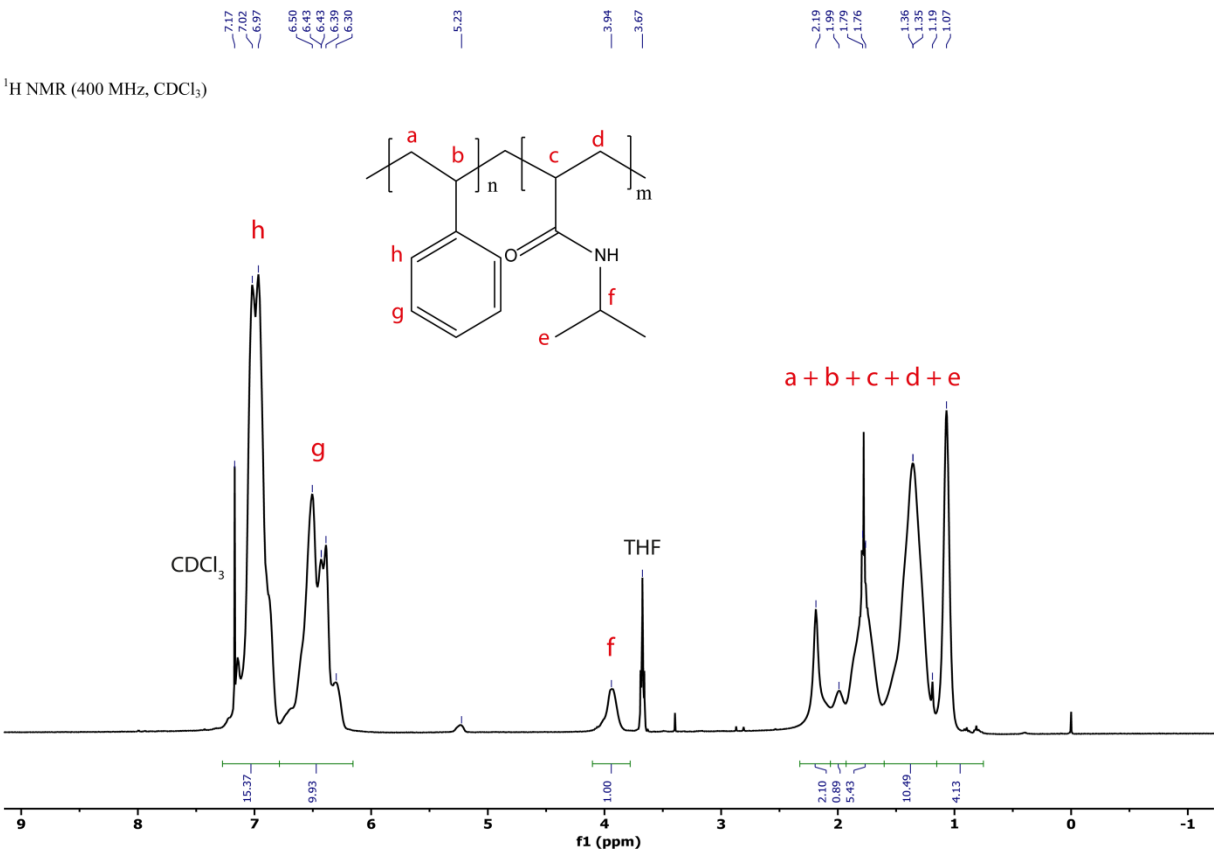

Figure S4. ^{1}H-NMR spectrum of PS-*b*-PNIPAM copolymer (CN-3).

Calculation of Hansen solubility parameters

To compare the selectivity of the used solvents for the blocks of the copolymer, we calculated the Flory interaction parameters (χ) using Hansen solubility parameters. χ parameters were calculated using Equation 1 and 2.[1]

$$A_{1,2} = [(\delta_{D2} - \delta_{D1})^2 + 0.25(\delta_{P2} - \delta_{P1})^2 + 0.25(\delta_{H2} - \delta_{H1})^2] \quad (1)$$

In Equation 1, δ_D, δ_P and δ_H are Hansen solubility parameters for dispersive, polar and hydrogen bonding contributions of the two blocks of the BCP, respectively.[1, 2] Subscript 1 stands for the solvent and 2 for the polymer block.

$$\chi_{12} = VA_{1,2}/RT \quad (2)$$

In Equation 2, *V*, *R* and *T* correspond to the molar volume of the solvent, the ideal gas constant and the absolute temperature, respectively. Although some of the calculated χ values were significantly higher than experimental values reported in the literature, for our experiments it was sufficient to compare the selectivity of the solvents between the blocks.

References

1. Hansen, C. M., *Hansen Solubility Parameters: A User's Handbook*. CRC Press: U.S.A, 2000.

2. Ahmad, H. Solubility Parameter of Acrylamide Series Polymers through Its Components and Group Contribution Technique. *Journal of Macromolecular Science: Part A - Chemistry* **1982,** 17 (4), 585-600 DOI: 10.1080/00222338208062410.