Supporting Information

Physical Gelation of AB-Alternating Copolymers Made of Vinyl Phenol and Maleimide Units: Cooperation between Precisely Incorporated Phenol and Long Alkyl Pendant Groups

Kana Nishimori,[1] Esther Cazares-Cortes,[2] Jean-Michel Guigner,[3] Francois Tournilhac,[2] and Makoto Ouchi[1]**

[1]Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Katsura Nishikyo-ku, Kyoto 615-8510, Japan

[2] Molecular, Macromolecular Chemistry, and Materials, CNRS, ESPCI-Paris, PSL Research University, 10 rue Vauquelin 75005 Paris, France

[3] Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie, Sorbonne Université, CNRS, UMR 7590, IRD, MNHN, 4 place Jussieu, F-75005 Paris, France

*Correspondence to: ouchi@living.polym.kyoto-u.ac.jp

*Correspondence to: francois.tournilhac@espci.fr

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Table S1. Characterization of Alternating Copolymers with tBOS and *N*-Alkylmaleimides Synthesized by Free Radical Copolymerization

Entry[a]	MI Derivatives	Conv.,%[b]		Composition Ratio[c]	M_n[d]	M_w/M_n[d]
		tBOS	MI	tBOS/MI	(GPC)	(GPC)
1	C18MI	97	98	49/51	190000	3.44
2	C12MI	98	99	49/51	91900	6.45
3	C8MI	96	100	49/51	154200	2.46
4	C2MI	93	99	50/50	75300	5.33

[a] Conditions: $[tBOS]_0/[MI]_0/[AIBN]_0 = 1000/1000/20$ mM in toluene at 60 ˚C (Entries 1-4).
[b] Conversions of tBOS and MI derivatives were determined by ^{1}H NMR.
[c] Composition Ratio of tBOS and MI derivatives was determined by ^{1}H NMR after purification.
[d] Determined by GPC in THF with PSt standard calibration (before deprotection reaction).

Table S2. Characterization of Alternating Copolymers with tBOS and *N*-Dodecylmaleimide (C12MI) Synthesized by RAFT Polymerization

Entry[a]	Conc., mM		Conv.,%[b]		DP[c]	Composition Ratio[d]	M_n[e]	M_w/M_n[e]
	tBOS	C12MI	tBOS	C12MI	(calcd.)	tBOS/C12MI	(GPC)	(GPC)
1	1000	1000	95	97	190	49/51	54300	1.32
2	1000	1000	94	96	95	48/52	31000	1.23
3	500	500	90	91	45	49/51	18700	1.20
4	300	300	96	99	29	48/52	12100	1.17
5	100	100	100	100	10	50/50	5100	1.11

[a] Conditions: $[CTA]_0/[AIBN]_0 = 5/1$ mM (Entry 1) and 10/1 mM (Entries 2-5) in toluene at 60 ˚C.
[b] Conversions of tBOS and C12MI were determined by ^{1}H NMR.
[c] The average DPs of tBOS and C12MI in copolymers were determined by monomer conversions.
[d] Composition Ratio of tBOS and C12MI was determined by ^{1}H NMR after purification.
[e] Determined by GPC in THF with PSt standard calibration (before deprotection reaction).

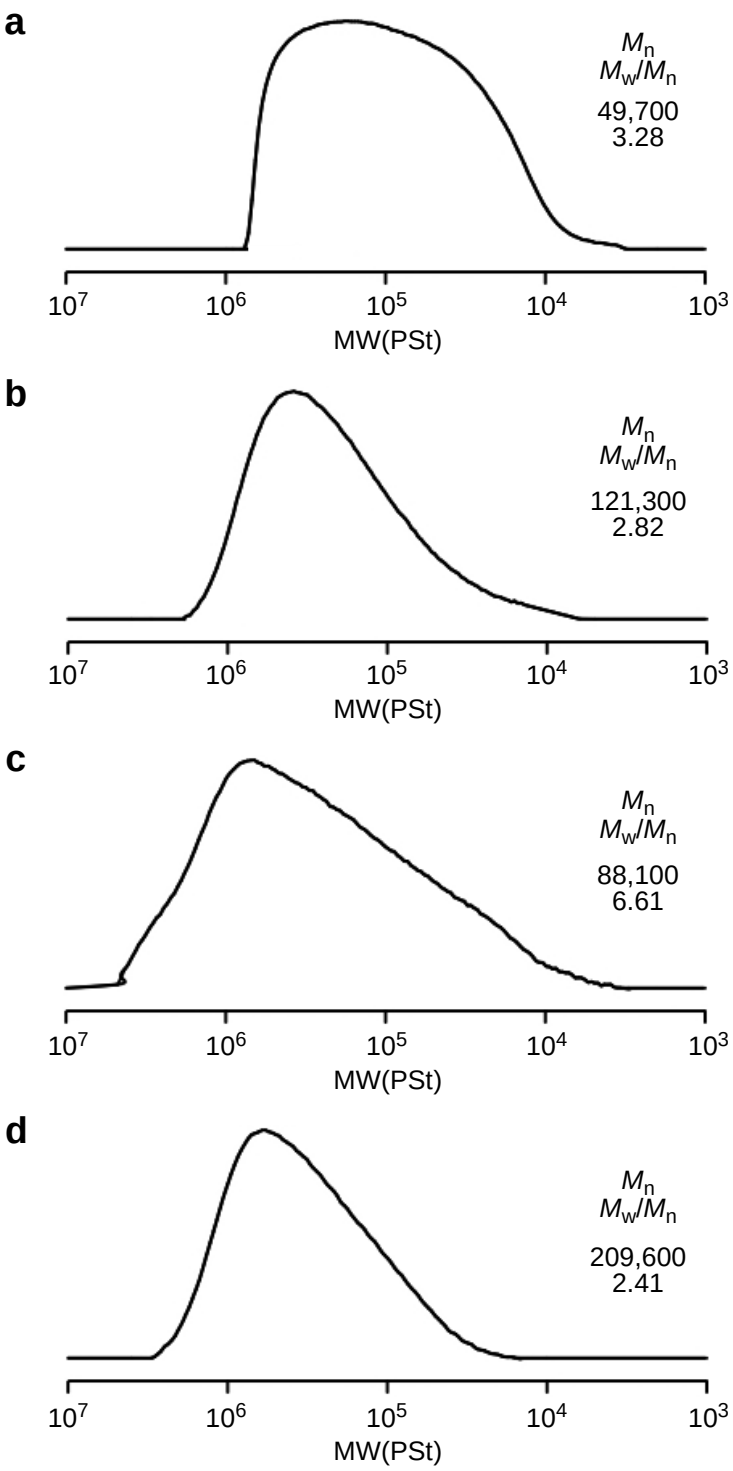

Figure S1. SEC curves of (a) **Alt-C2**, (b) **Alt-C8**, (c) **Alt-C12** and (d) **Alt-C18** in THF.

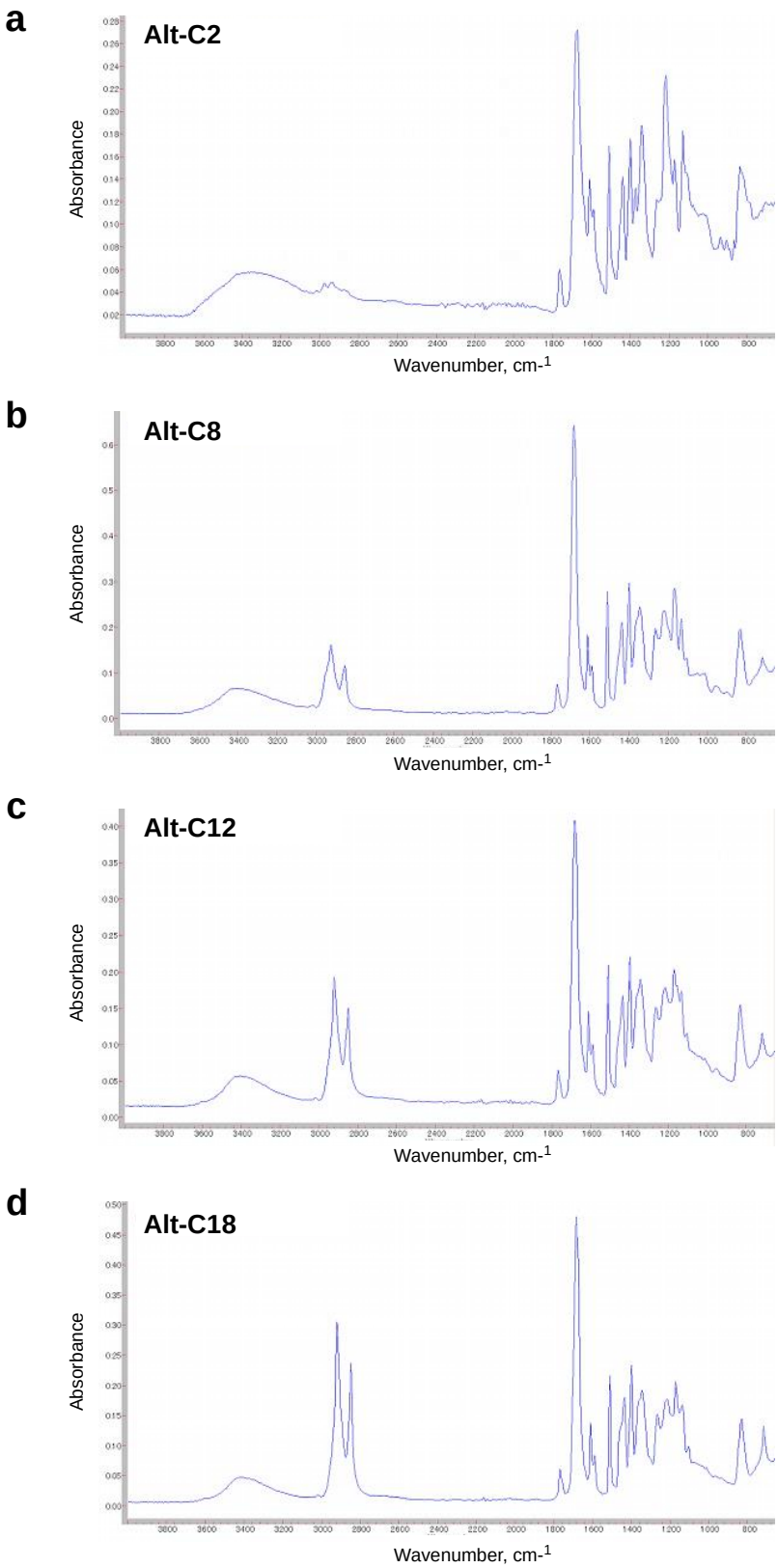

Figure S2. FT-IR spectra of (a) **Alt-C2**, (b) **Alt-C8**, (c) **Alt-C12** and (d) **Alt-C18**.

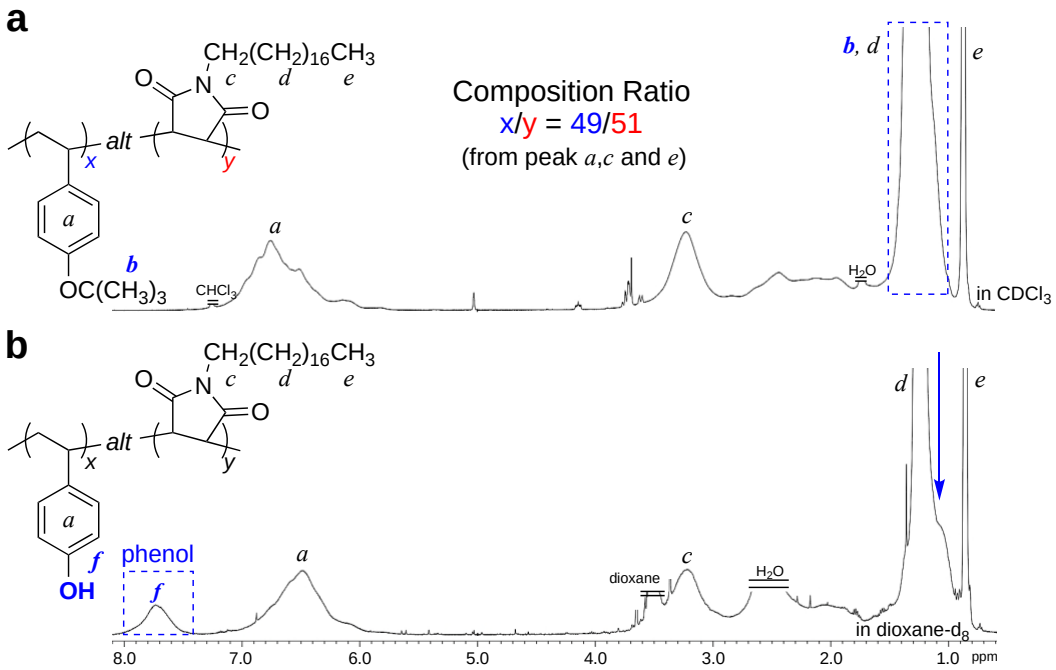

Figure S3. ^{1}H NMR spectra of the copolymer with tBOS and C18MI (a, $CDCl_3$) and the copolymer after deprotection reaction (b, 1,4-dioxane-d_8).

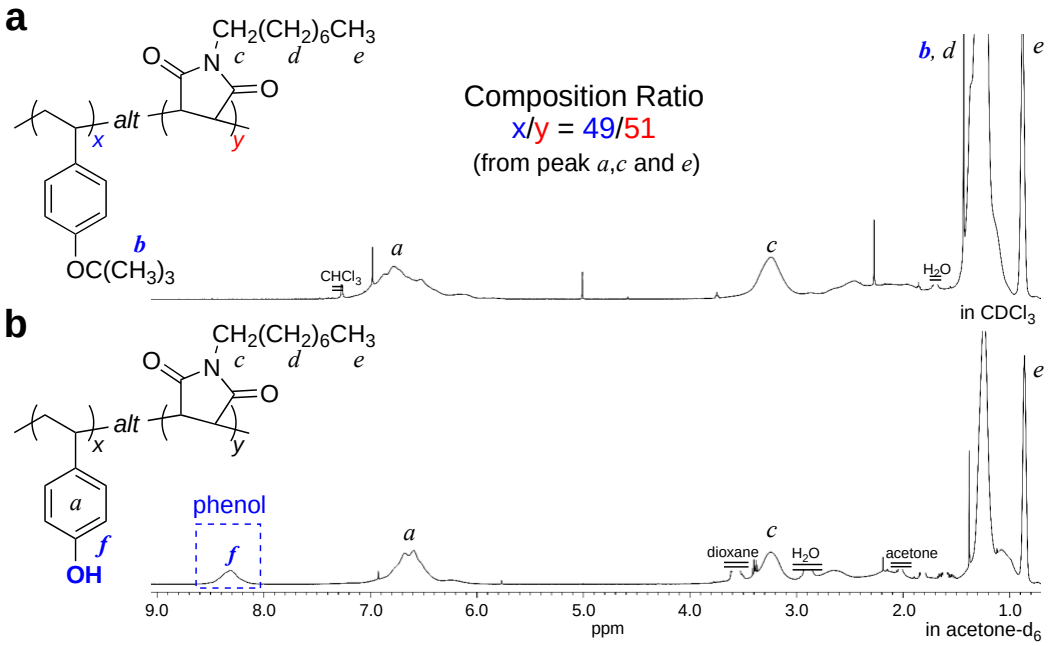

Figure S4. ^{1}H NMR spectra of the copolymer with tBOS and C8MI (a, $CDCl_3$) and the copolymer after deprotection reaction (b, acetone-d_6).

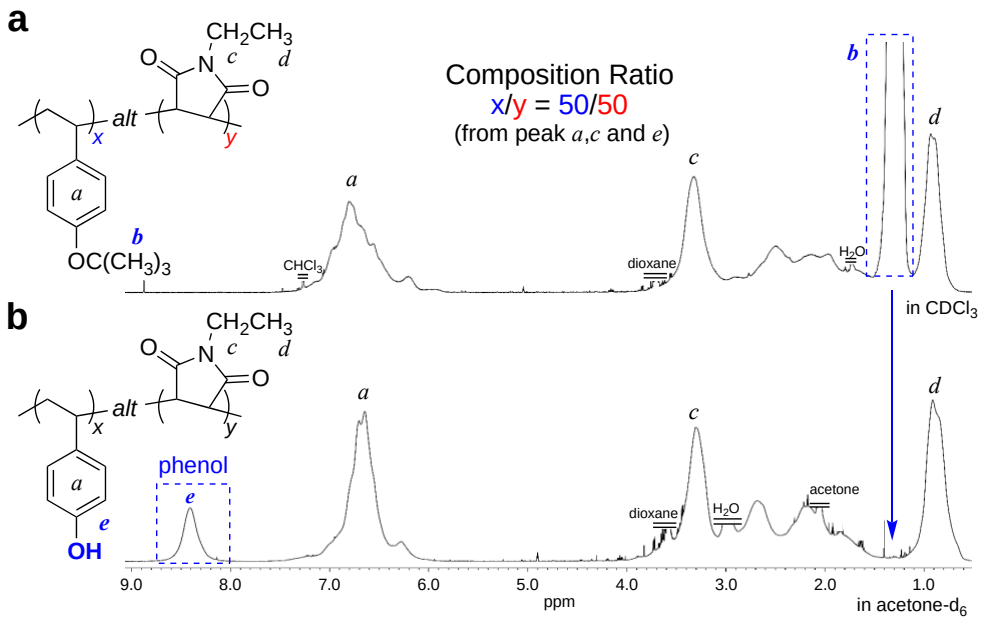

Figure S5. ^{1}H NMR spectra of the copolymer with tBOS and C2MI (a, $CDCl_3$) and the copolymer after deprotection reaction (b, acetone-d_6).

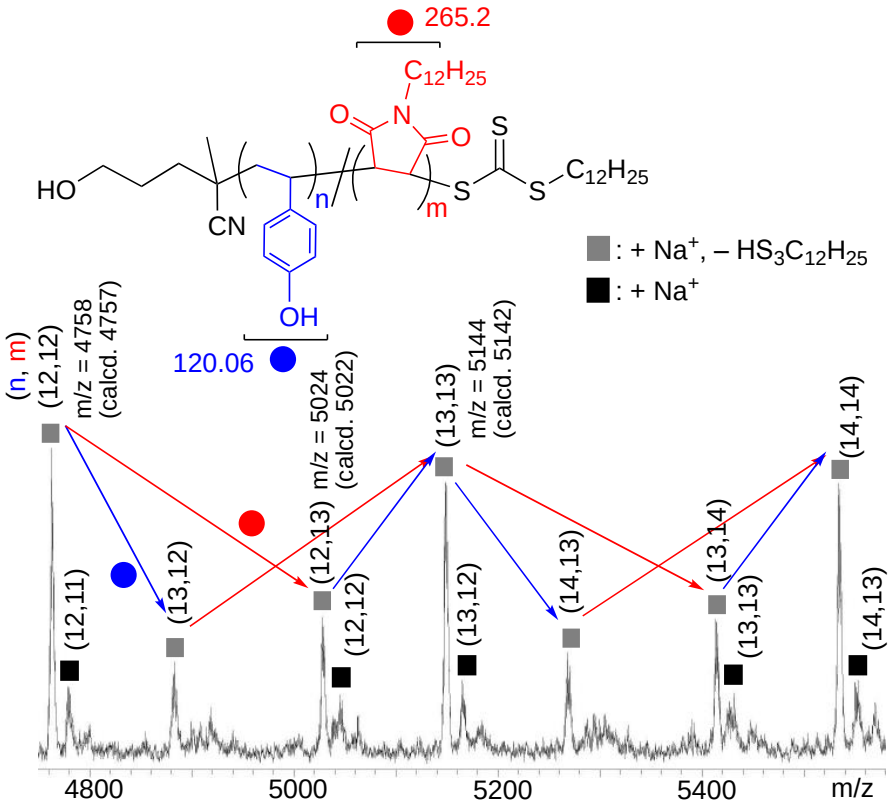

Figure S6. MALDI-TOF-MS spectrum of **Alt-C12** (M_n = 18200, M_w/M_n = 1.22) synthesized by RAFT copolymerization.

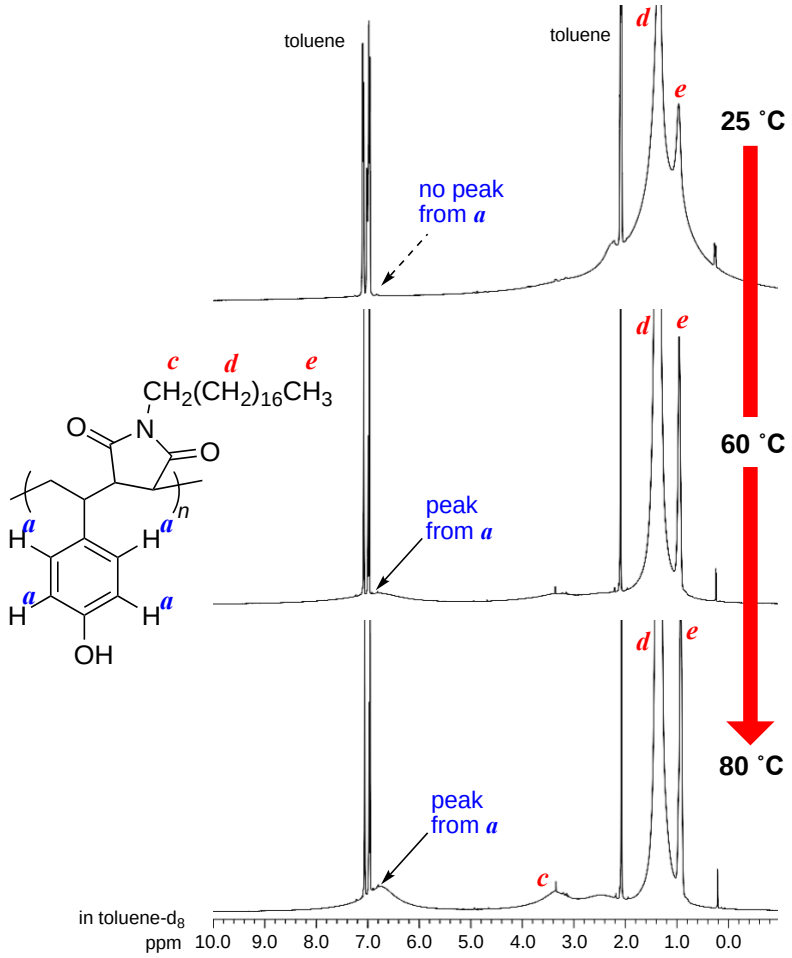

Figure S7. ^{1}H NMR spectra of 5wt% **Alt-C18** gel in tolunene-d_8 at 25 ˚C, 60 ˚C and 80 ˚C.

Table S3. Viscosity of the Solution of **Alt-C12** in Toluene (5wt%) After Addition of Pyridine in Comparison with the Solution in THF (5wt%)

Angle (°)	Viscosity (mPa·s)	
	In Toluene After Addition of Pyridine[a]	**In THF**
20	8.35	10.19
25	8.29	10.17
30	8.26	10.22
35	8.29	10.25
40	8.33	10.32
45	8.36	10.39
50	8.41	10.44
55	8.44	10.50
60	8.48	10.53
65	8.46	10.51
70	8.36	10.40
Average	**8.37**	**10.36**

[a] The amount of pyridine added in toluene solution was 2 equimolar with phenol groups in the solution.

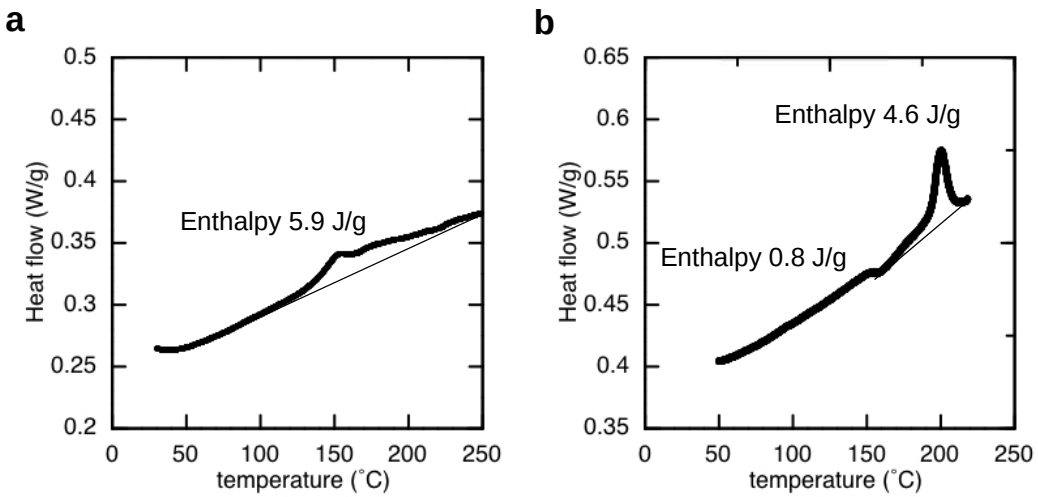

Figure S8. DSC thermograms recorded at 2nd heating process for bulk samples of (a) **Alt-C12** and (b) **Alt-C18**. Temperature program: 1st heating at 10 ˚C/min from 20 ˚C to 250 ˚C; 5 min holding at 250 ˚C; 1st cooling at 10 ˚C/min from 250 ˚C to 20 ˚C; 2nd heating at 10 ˚C/min from 20 ˚C to 250 ˚C.

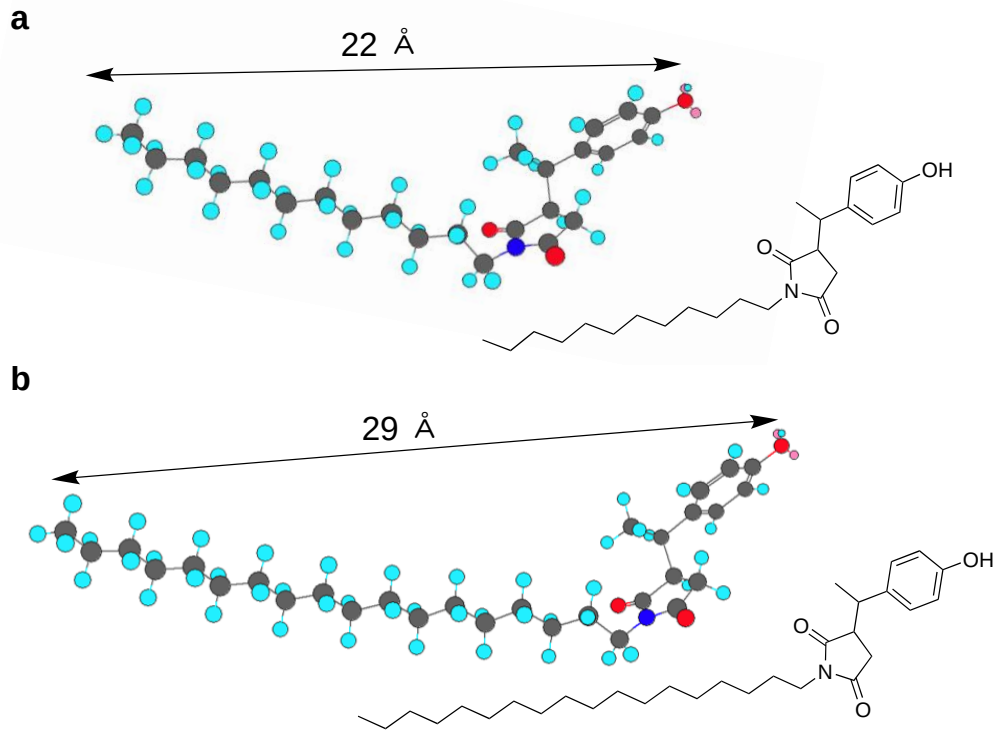

Figure S9. Chem3D Molecular models of dimers of 4-vinylphenol and *N*-alkylmaleimide (a, C12MI; b, C18MI) with alkyl chains in the fully extended conformation.

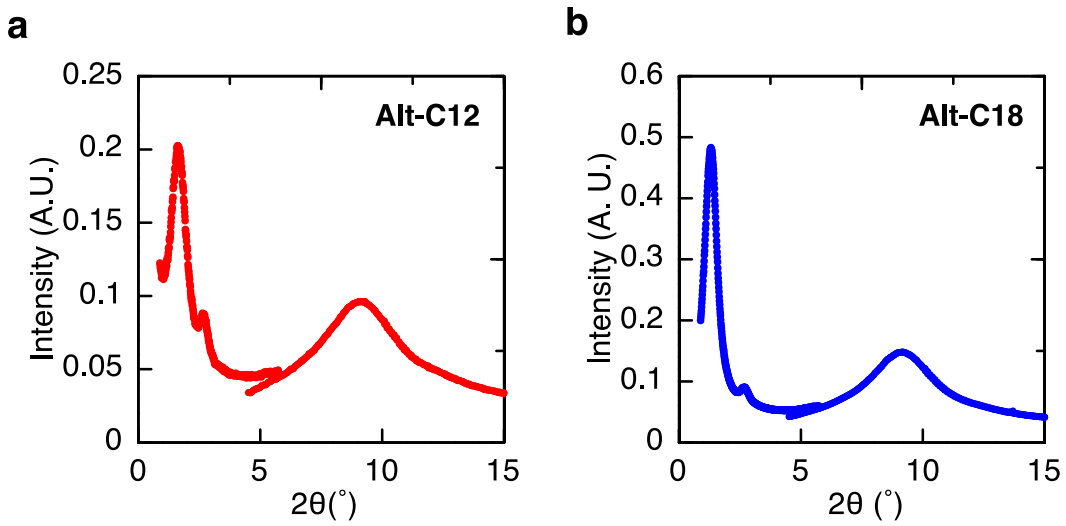

Figure S10. Wide angle X-ray diffraction patterns of freeze dried bulk **Alt-C12** (a) and **Alt-C18** (b). The peak arising at $2\theta = 2.7^{\circ}$ is due to Kapton windows.

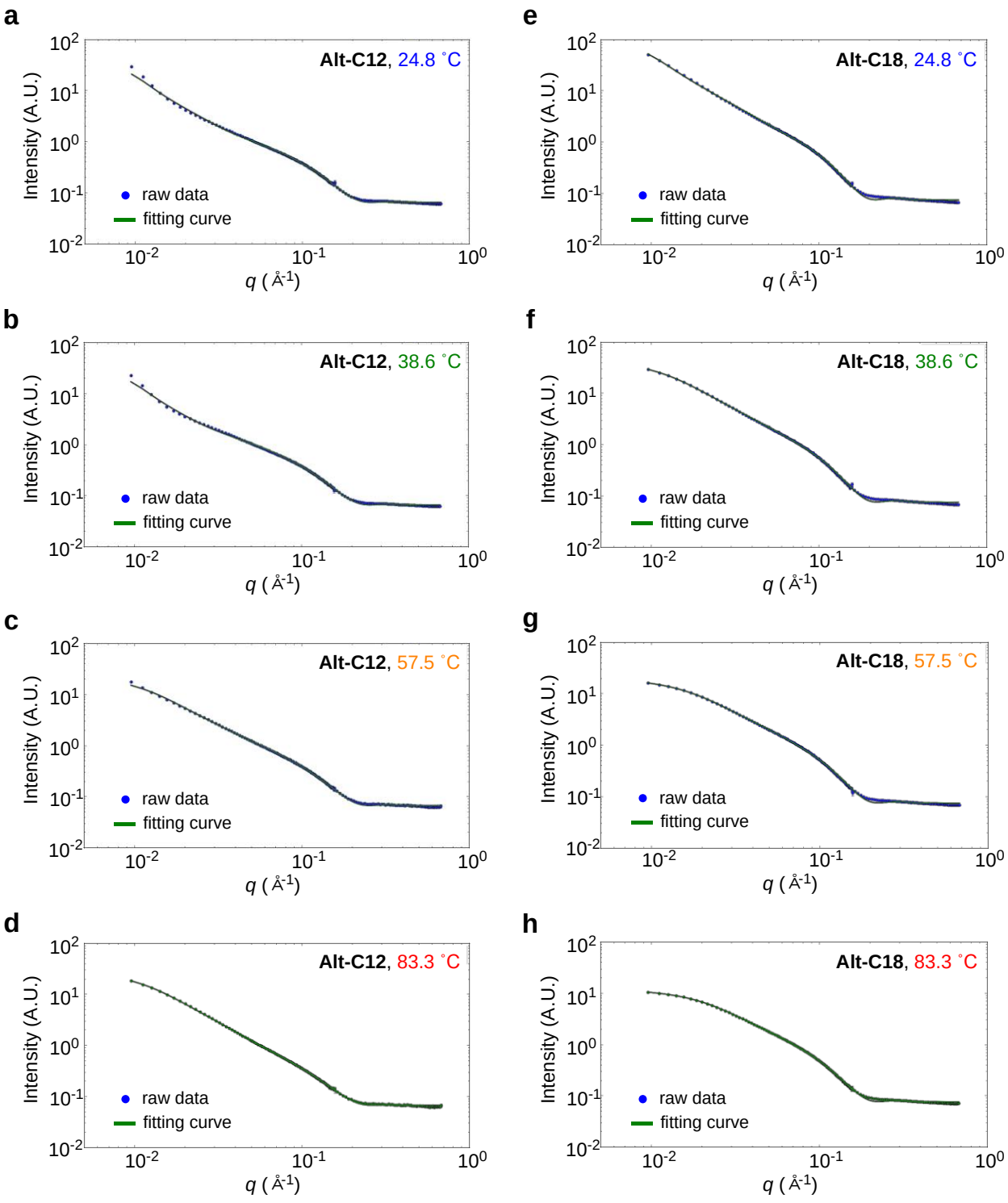

Figure S11. SANS data with fitting curves for **Alt-C12** (a-d) and **Alt-C18** (e-f).

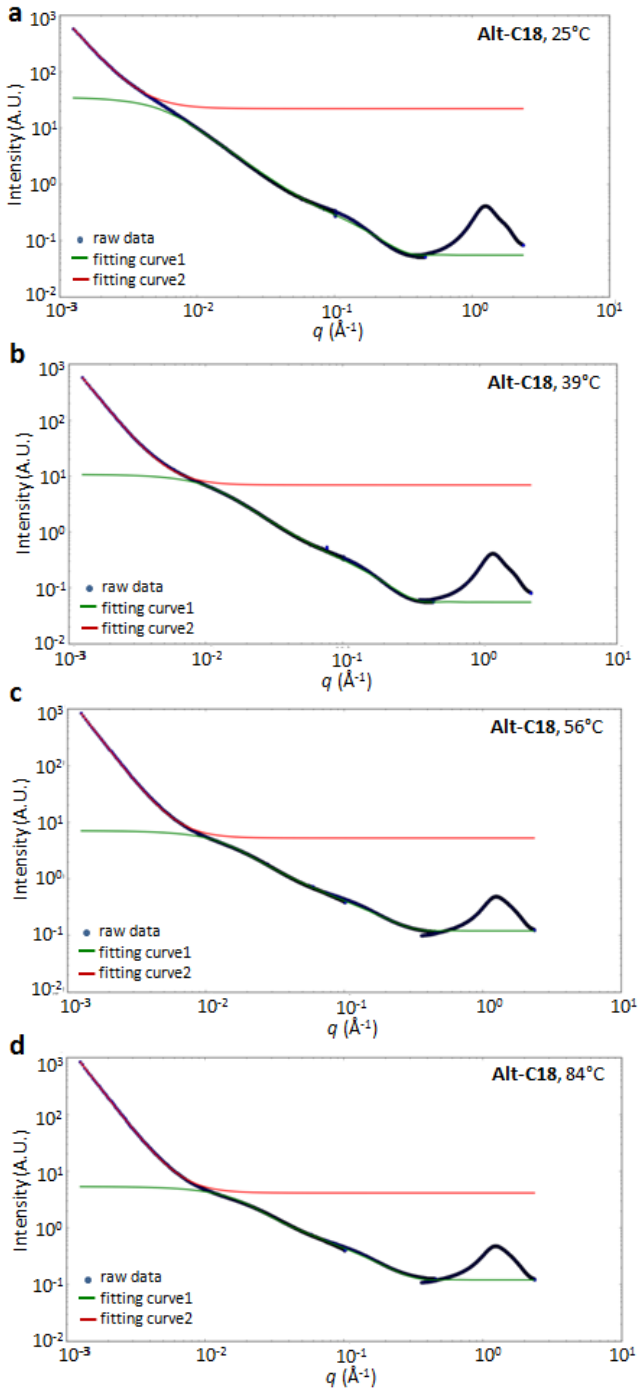

Figure S12. SAXS data with fitting curves for **Alt-C18** (a-d) at different temperatures. The fitting curve1 (green) correspond to a flexible cylinder model fitted from 0.01 to 0.5 $Å^{-1}$. The fitting curve2 (red) correspond to a shape unique power law model fitted from 0.001 to 0.01 $Å^{-1}$.

Table S4. Fitting Parameters from Modeling of SAXS Data Recorded at Various Temperatures of 5wt% **Alt-C18** Solutions in Toluene-d_8

Sample	flexible cylinder					power law	
	Temperature (°C)	Av. Radius (Å)	Kuhn length (Å)	Contour length (Å)	Background (cm^{-1})	power	Background (cm^{-1})
Alt-C18	84	8.48	140.4	429.0	0.12	3.19	4.11
	56	8.51	103.4	634.6	0.12	3.17	5.23
	39	8.50	76.0	1092.5	0.05	3.03	6.87
	25	8.50	58.3	4000.0	0.05	2.80	21.96