

Electronic Supplementary Information

Characterization of gelable PS-PAPTES diblock copolymer micelles before and after hydrolysis-condensation by SAXS and SANS

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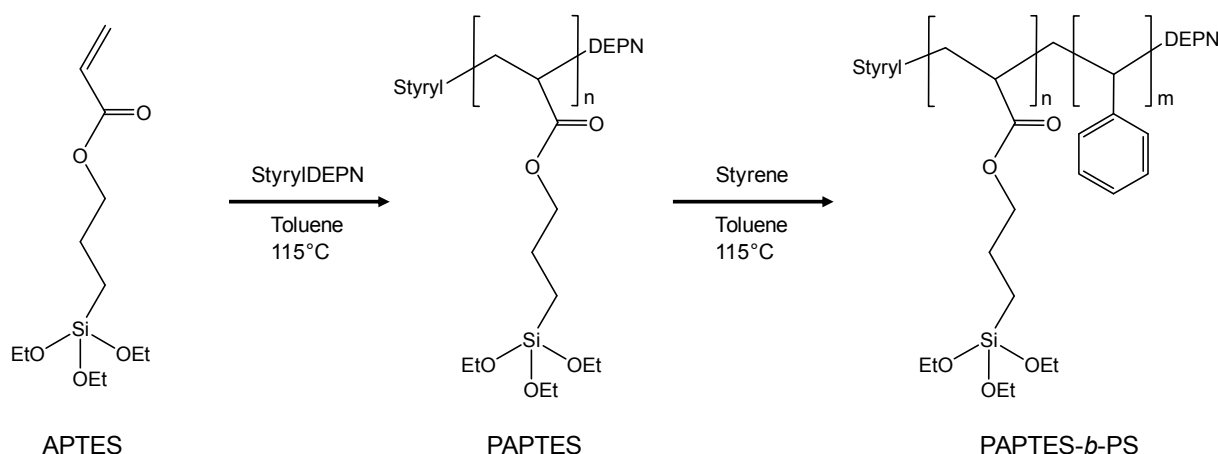
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Synthesis of PS and PAPTES-based diblock copolymers

PAPTES and PS homopolymers were used as macroinitiators for the synthesis of diblock copolymers by Nitroxide Mediated Polymerization as described in previous studies¹⁻² (Scheme S1).



Scheme S1: Synthesis of PAPTES-PS block copolymers by NMP from PAPTES-DEPN macroinitiator

Using this procedure, well-defined PAPTES-b-PS and PS-b-PAPTES diblock copolymers with various chain lengths and compositions were successfully obtained from PAPTES₉₁-DEPN, PAPTES₁₁₃-DEPN and PS₂₇₂-DEPN macroinitiators, respectively (**Table S1**).

Table S1: Molecular parameters of a series of PS-PAPTES diblock copolymers obtained by NMP at 115°C using respectively PAPTES₉₁-DEPN, PAPTES₁₁₃ - DEPN and PS₂₇₂-DEPN as macroinitiators. Detailed polymerization conditions are available in the literature¹⁻².

Sample	Time (h)	Conversion ^a (%)	M _{n,theo} ^b (g.mol ⁻¹)	M _{n,SEC} (g.mol ⁻¹)	M _w /M _n	dn/dc ^c (mL.g ⁻¹)
PAPTES ₉₁ -PS ₃₄	0.25	4.3	28740	31070	1.44	0.065
PAPTES ₉₁ -PS ₁₇₅	1	21.9	43380	45830	1.37	0.110
PAPTES ₉₁ -PS ₃₁₇	2.5	39.6	58110	57250	1.40	0.130
PAPTES ₁₁₃ -PS ₄₈₉	10	61.1	82050	84940	1.33	0.122
PS ₂₇₂ -PAPTES ₁₃₀	16	26.1	64300	59990	1.18	0.100
PS ₂₇₂ -PAPTES ₂₂₄	32	44.9	90250	83310	1.21	0.077
PS ₂₇₂ -PAPTES ₂₉₀	64	58.1	108470	101250	1.30	0.064
PS ₂₇₂ -PAPTES ₃₃₆	128	67.2	121000	110800	1.32	0.056

^aCalculated by ¹H NMR. ^bM_{n,theo} = [M]₀/[I]₀ x Conversion x M(monomer). ^cDetermined by interferometric refractometry.

References

- 1 Gamys CG.; Beyou, E. and Bourgeat-Lami, E., *J. Polym. Sci., PartA : Polym. Chem.*, 2010, **48**, 784.
- 2 Gamys CG.; Beyou, E.; Bourgeat-Lami, E., David, L. and Alcouffe, P. *J. Polym. Sci., PartA : Polym. Chem.*, 2011, **49**, 4193.