

## Supporting Information

### Hydrophobically Modified Complex Coacervates for Designing Aqueous Pressure-Sensitive Adhesives

Larissa van Westerveld,<sup>a</sup> Julien Es Sayed,<sup>a</sup> Marijn de Graaf,<sup>a</sup> Anton H. Hofman,<sup>\*a</sup> Marleen Kamperman,<sup>a</sup> and Daniele Parisi<sup>\*b</sup>

<sup>a</sup>Zernike Institute for Advanced Materials (ZIAM), University of Groningen, Nijenborgh 4, 9747 AG Groningen, the Netherlands.

<sup>b</sup>Engineering and Technology Institute Groningen (ENTEG), University of Groningen, Nijenborgh 4, 9747 AG Groningen, the Netherlands

\*Corresponding authors: Anton H. Hofman ([a.h.hofman@rug.nl](mailto:a.h.hofman@rug.nl)) and Daniele Parisi ([d.parisi@rug.nl](mailto:d.parisi@rug.nl))

#### Contents

<a href="#">Synthesis of 3-(isobutoxysulfonyl)propyl methacrylate (BSPMA)</a> .....	2
<a href="#">RAFT polymerization of BSPMA</a> .....	3
<a href="#">Quaternization of P4VP</a> .....	6
<a href="#">Time-salt superposition master curves: loss factor</a> .....	8
<a href="#">Probe tack test results</a> .....	9

## Synthesis of 3-(isobutoxysulfonyl)propyl methacrylate (BSPMA)

To start with, a 250 ml 2-neck flask was charged with 14.0 (57.0 mmol) grams of K-SPMA and all air and residual moisture were removed by applying 3 vacuum/argon cycles. The salt was then suspended in 40 ml anhydrous DMF and cooled to 0 °C using an ice bath. Meanwhile, 7.94 g (62.7 mmol; 1.10 eq.) oxalyl chloride was dissolved in 20 ml dichloromethane (DCM) and added dropwise with a glass Pasteur pipette to the suspension under an argon outflow. The suspension was left to stir for one hour. In a separate 250 ml 3-neck flask, a solution of 5.05 g (68.1 mmol; 1.20 eq.) isobutanol and 11.5 g (114 mmol; 2.00 eq.) TEA was prepared in 40 ml DCM under an argon outflow, and was subsequently cooled to 0 °C with an ice bath. After stirring for an hour, the SPMA-Cl suspension was allowed to slowly warm up to room temperature and carefully transferred to a dropping funnel. In the next 40 minutes the suspension was added dropwise to the isobutanol/TEA solution. The turbid yellowish solution was then stirred for one hour at 0 °C after which it was slowly warmed up to room temperature and stirred overnight. As soon as room temperature was reached, the argon inlet was closed. The next day, the reaction mixture was transferred to a separation funnel. After adding 300 ml water, the product was extracted by washing the aqueous fraction with 200 ml diethyl ether (3x). The combined organic fraction was washed once more with 200 ml fresh R.O. water in order to remove the majority of the DMF. Next, the organic fraction was dried over magnesium sulfate, filtered, and concentrated in vacuo using a rotary evaporator affording the crude product as a brown-orange oil (14.0 g). It was purified by silica gel column chromatography using a 1:4 ethyl acetate/hexane solution as eluent to give 12.4 g of BSPMA as a slightly yellow transparent oil (82% yield).

## RAFT polymerization of BSPMA

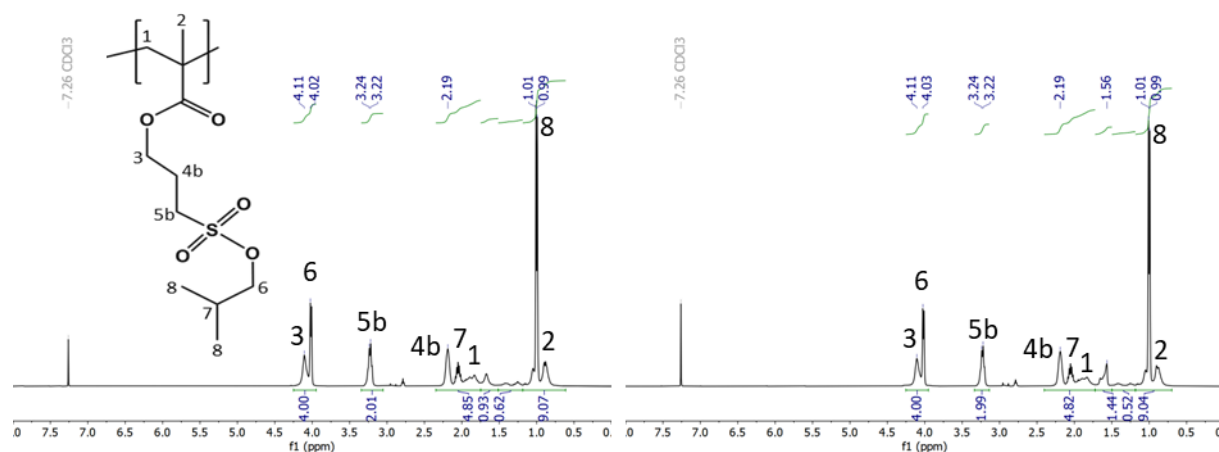
PBSPMA was synthesized by RAFT polymerization (Table S1). An example of the low molecular weight polymer (L-PBSPMA) is given below. For this polymer, 12.0 g BSPMA (45.4 mmol), 106 mg CTP (0.378 mmol; 0.00832 eq.) and 17 ml anhydrous DMF were added together in a 100 ml flask. Then, 6.2 mg (0.038 mmol; 0.00083 eq.) of AIBN was added via a stock solution in DMF (6.2 mg/ml). The solution was sparged with argon for one hour and afterwards the argon flow was closed and the reaction mixture was heated to 70 °C and stirred overnight. After 22 h, the polymerization was stopped by quenching the reaction mixture in an ice bath, subsequently it was diluted with 20 ml of acetone, and precipitated into 5:1 pentane/ethanol. The obtained sticky pink product was finally washed with a 2:1 pentane/ethanol solution. This precipitation procedure was repeated by re-dissolving the solid in 30 ml acetone. A pink powder was obtained for both L-PBSPMA (110 monomers, 83% yield) and H-PBSPMA (510 monomers, 84% yield) after drying the product in vacuo at room temperature overnight. NMR and GPC samples were analyzed to determine the monomer conversions and the lengths of the polymers (Fig. S1).

**Table S1.** Reaction conditions for the synthesis of L-PBSPMA and H-PBSPMA by RAFT. Concentrations of CTP and AIBN are in mM and the concentration of monomer is in M. Reaction times ( $t_r$ ) are in h and conversions were determined by  $^1\text{H-NMR}$  (%).  $M_{n,NMR}$  was calculated based on the reaction concentrations and the conversion. DP is based on  $M_{n,NMR}$  and the polydispersity  $\mathcal{D}$  was obtained by GPC (PMMA standards, conventional calibration).

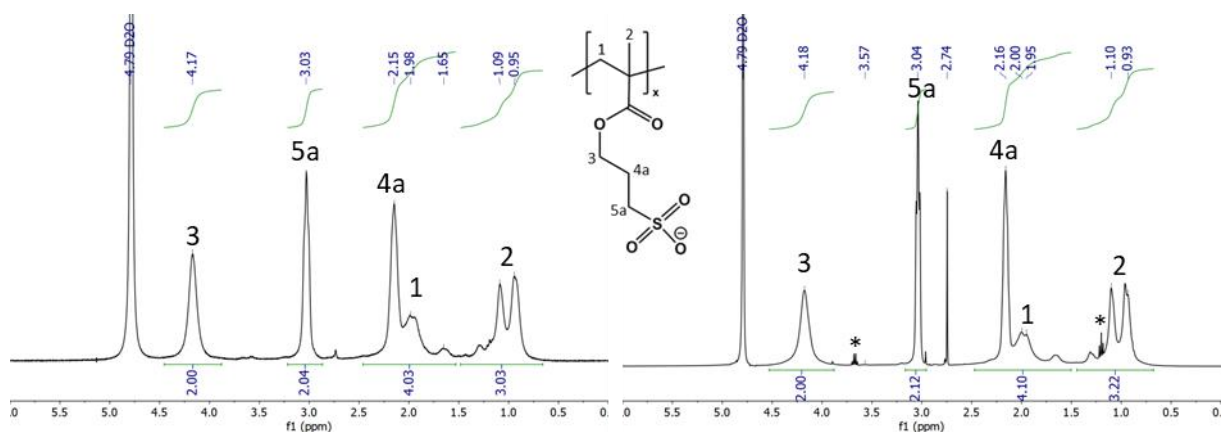
Polymer	[CTP] / (mM)	[AIBN] / (mM)	[AIBN]/[CTP]	[BSPMA] / (M)	$t_r$ / (h)	Conv. / (%)	$M_{n,NMR}$ / (kg/mol)	$M_{n,GPC}$ / (kg/mol)	DP	$\mathcal{D}$
L-PBSPMA	12.5	1.25	0.10	1.51	22	92	29.1	36.4	110	1.11
H-PBSPMA	3.56	0.71	0.20	1.97	22	93	135.8	121.8	514	1.36

**Table S2.** Ratios of polymer and NaI for obtaining different degrees of deprotection on the PBSPMA polymers.

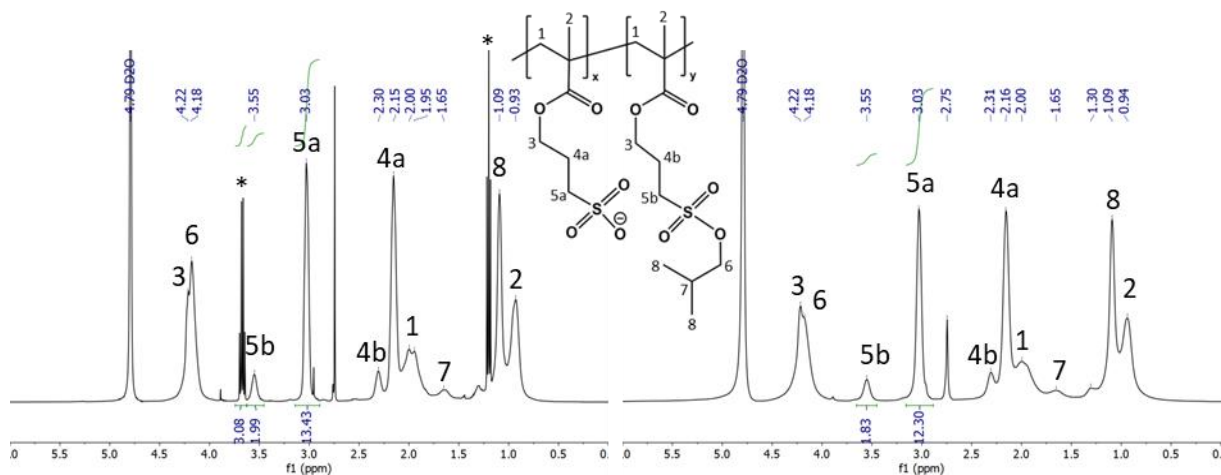
Polymer	100%	86-87%	73-74%	60-61%
	(3.00 eq. NaI)	(1.50 eq NaI)	(1.13 eq NaI)	(0.75 eq NaI)
L/x	1.00 g (3.80 mmol)	1.61 g (6.08 mmol)	2.01 g (7.58 mmol)	3.01 g (11.4 mmol)
NaI	1.71 g (11.4 mmol)	1.36 g (9.08 mmol)	1.28 g (8.51 mmol)	1.28 g (8.52 mmol)
H/x	1.11 g (4.19 mmol)	1.61 g (6.10 mmol)	2.01 g (7.60 mmol)	2.50 g (9.47 mmol)
NaI	1.87 g (12.5 mmol)	1.36 g (9.09 mmol)	1.28 g (8.51 mmol)	1.07 g (7.12 mmol)



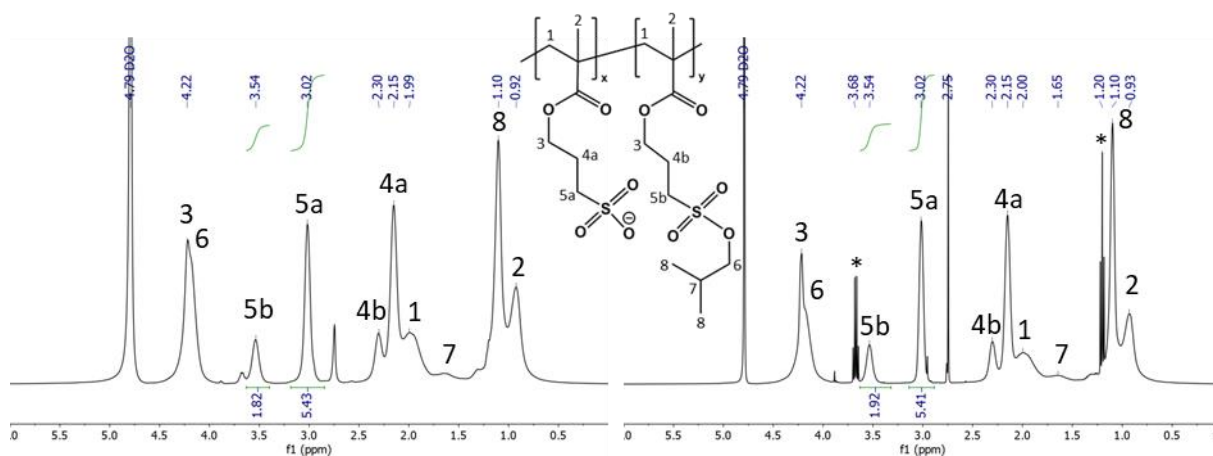
**Fig. S1.** <sup>1</sup>H-NMR spectra of RAFT synthesized L-PBSPMA (left) and H-PBSPMA (right) in deuterated chloroform.



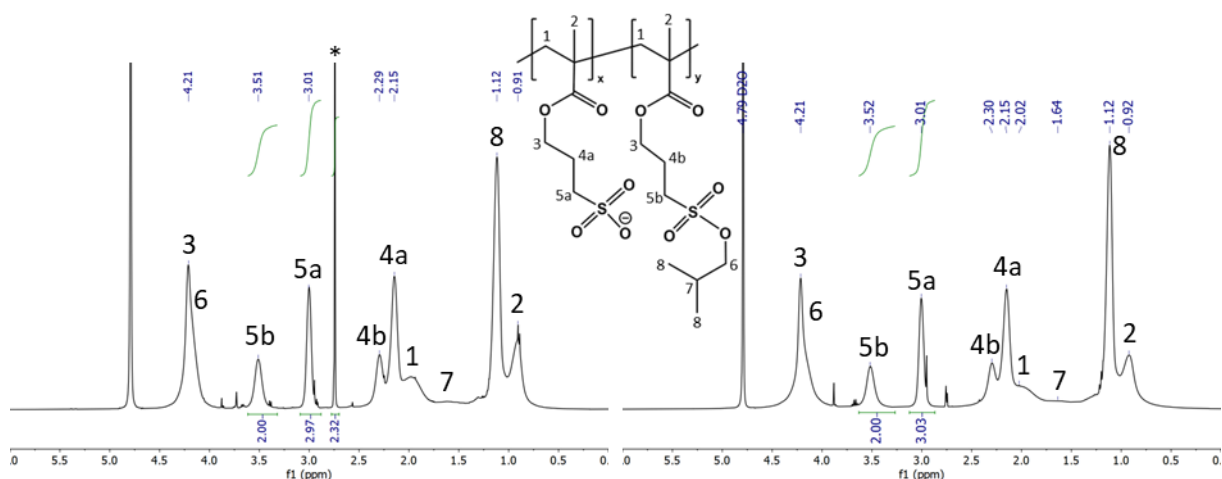
**Fig. S2:**  $^1\text{H-NMR}$  spectra of deprotected L/100 (left) and H/100 (right) in  $\text{D}_2\text{O}$ . The asterisks indicate residual ethanol from the precipitation.



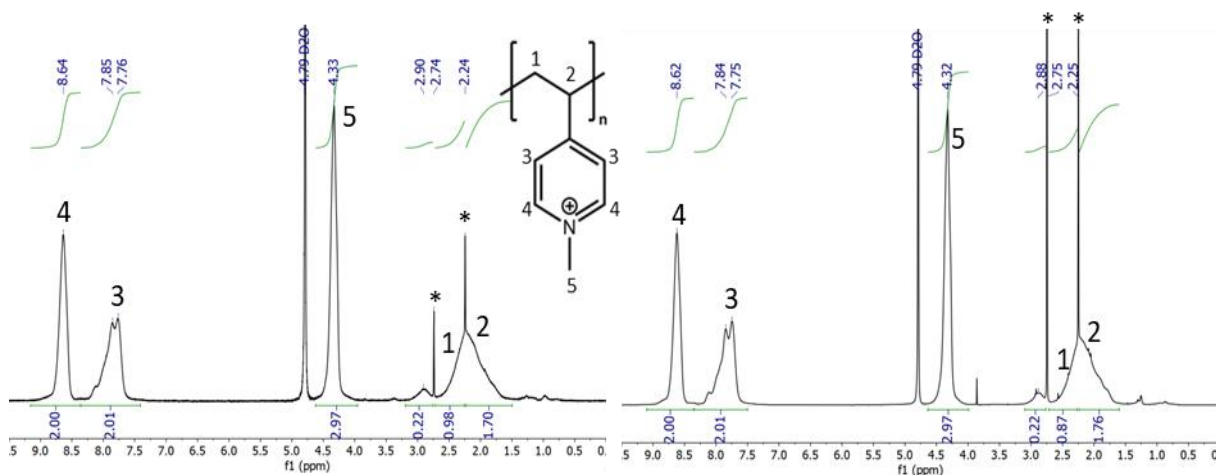
**Fig. S3:**  $^1\text{H-NMR}$  spectra of partially deprotected L/87 (left) and H/86 (right) in  $\text{D}_2\text{O}$ . The asterisks indicate residual ethanol from the precipitation.



**Fig. S4:**  $^1\text{H-NMR}$  spectra of partially deprotected L/74 (left) and H/73 (right) in  $\text{D}_2\text{O}$ . The asterisks indicate residual ethanol from the precipitation.



**Fig. S5.**  $^1\text{H-NMR}$  spectra of partially deprotected L/61 (left) and H/60 (right) in  $\text{D}_2\text{O}$ . The asterisk indicates residual DMSO from the reaction mixture.

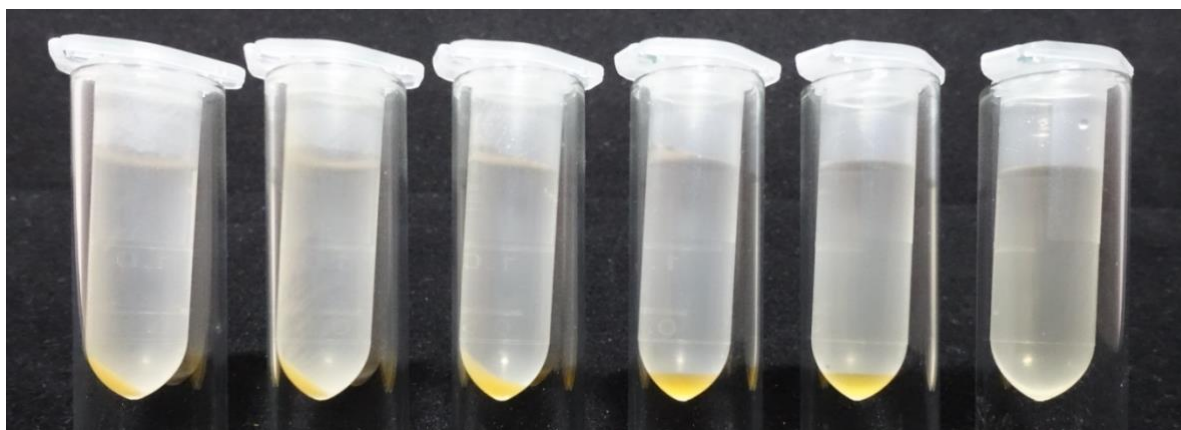


**Fig. S6.**  $^1\text{H-NMR}$  spectra of quaternized L-QP4VP (left) and H-QP4VP (right) in  $\text{D}_2\text{O}$ . The asterisk at 2.24 ppm highlights residual acetone from precipitation and the asterisk at 2.74 ppm indicates residual DMSO from the reaction mixture.

## Quaternization of P4VP

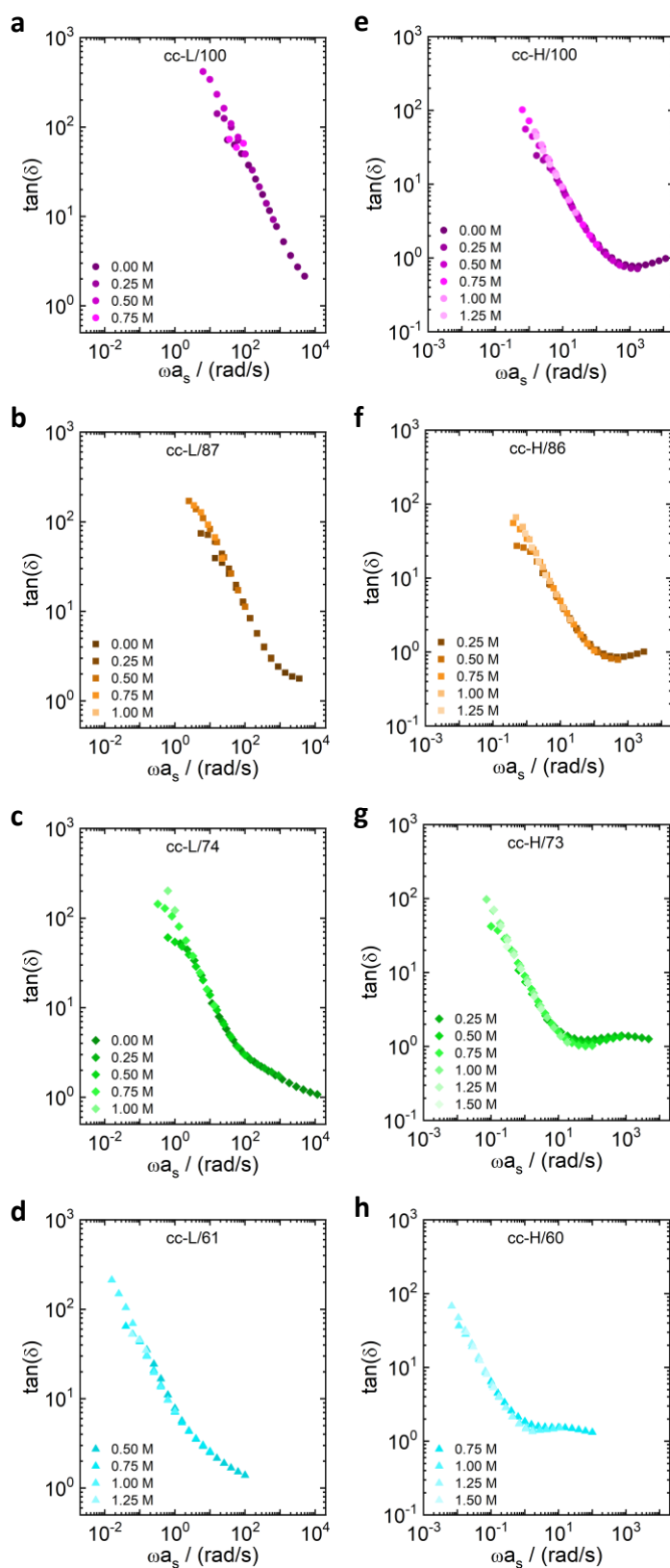
Two polymer lengths were used in order to match the lengths of the PBSPMA polymers. For the low molecular weight sample 2.0 g (19 mmol 4VP units) P4VP was dissolved in 20 ml DMSO in a round-bottom flask and 5.43 g (38.3 mmol; 2.00 eq.) MeI was added dropwise to the solution. For the high molecular weight 1.82 g (17.1 mmol 4VP units) P4VP was dissolved in 18 ml DMSO and 4.86 g (34.2 mmol; 2.00 eq.) MeI was added dropwise. The solution gradually

changed colour from transparent bright yellow to turbid orange/dark yellow. The solution was stirred for 4 hours at room temperature and was then precipitated into 300 ml acetone. The precipitate was filtered and washed with acetone until the filtrate became colourless. The precipitate was dried overnight in a vacuum oven at 40 °C. For the low and high molecular weight 4.51 g (DQ > 98%, yield 96%) and 4.19 g (DQ > 98%, yield 98%) QP4VP were obtained as ochre coloured powders, respectively.



**Fig. S7.** Example of the determination of the salt resistance of cc-L/74. Salt concentrations from left to right: 0.25 M, 0.50 M, 0.75 M, 1.00 M, 1.25 M and 1.35 M.

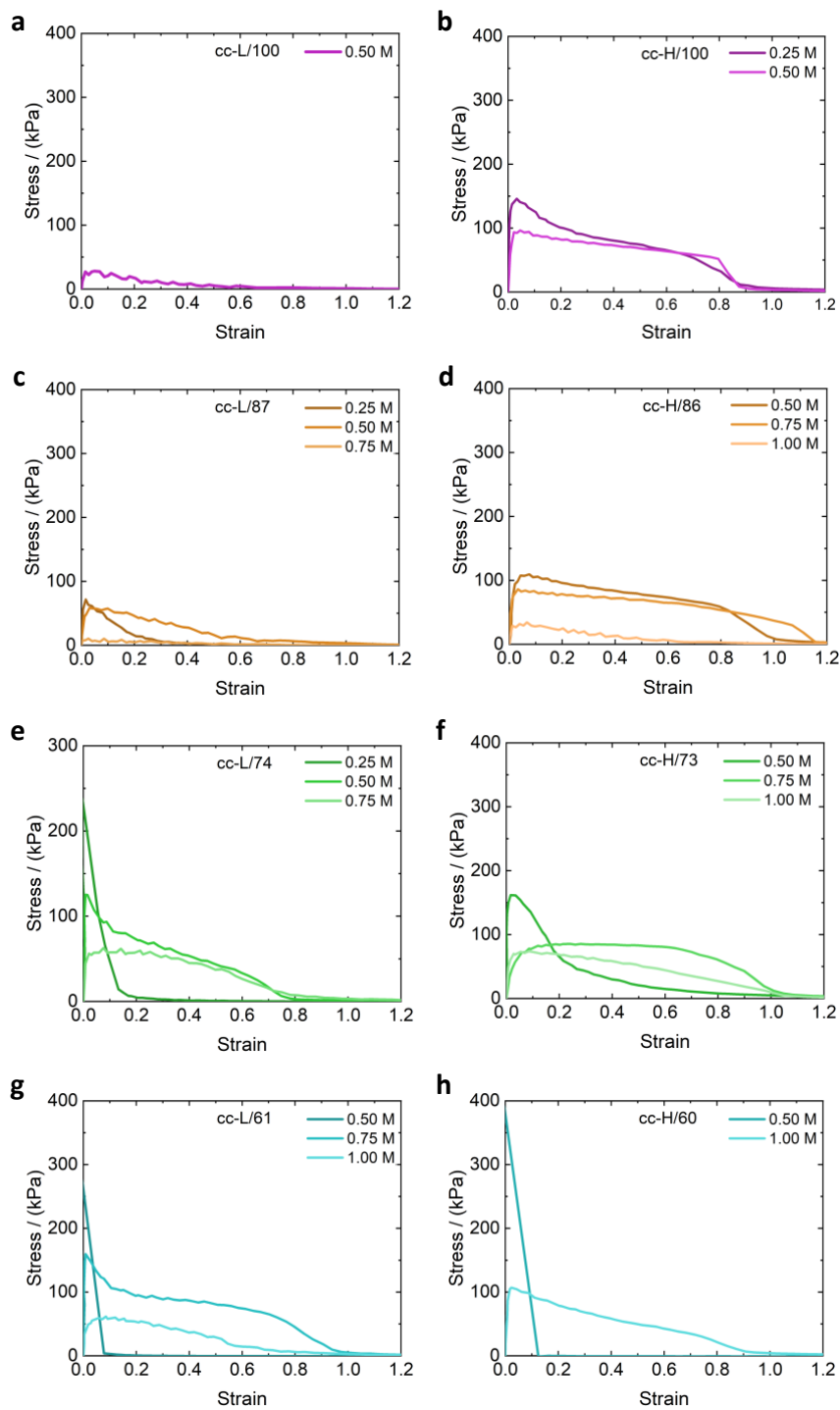
## Time-salt superposition master curves: loss factor



**Fig. S8.** Horizontally shifted  $\tan(\delta)$  for L-PBSPMA (left column) and H-PBSPMA (right column) for a) cc-L/100, b) cc-H/100, c) cc-L/87, d) cc-H/86, e) cc-L/74, f) cc-H/73, g) cc-L/61 and h) cc-H/60.



## Probe tack test results



**Fig. S9.** Representative probe tack curves for each hydrophobicity degree at various salt concentrations: a) cc-L/100, b) cc-H/100, c) cc-L/87, d) cc-H/86, e) cc-L/74, f) cc-H/73, g) cc-L/61 and h) cc-H/60.

**Movies 1-4** are representative videos of the probe tack experiments for all measured salt and hydrophobicity combinations.

**Movie 1:** cc-L/100 and cc-H/100 performed at various salt concentrations.

**Movie 2:** cc-L/87 and cc-H/86 performed at various salt concentrations.

**Movie 3:** cc-L/74 and cc-H/73 performed at various salt concentrations.

**Movie 4:** cc-L/61 and cc-H/60 performed at various salt concentrations.