

## SUPPORTING INFORMATION

### **Water-based acrylic coatings reinforced by PISA-derived fibres**

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## Experimental Part

**Materials.** Methacrylic acid (MAA, Acros, 99.5%), poly(ethylene oxide) methyl ether methacrylate (PEOMA, with 19 ethylene oxide units on average,  $M_n = 950 \text{ g}\cdot\text{mol}^{-1}$ , Aldrich), 4,4-azobis(4-cyanopentanoic acid) (ACPA, >98%, Fluka), sodium hydrogen carbonate ( $\text{NaHCO}_3$ , >99.7%, Aldrich), sodium 1-propanethiolate (Aldrich, 95%), carbon disulfide (Aldrich, 99%), and potassium hexaferrocyanide (Aldrich, 99%) were used as received. Styrene (S, 99%, Aldrich) was distilled at reduced pressure to remove the inhibitor. The RAFT agent 4-cyano-4-thiothiopropylsulfanylpentanoic acid (CTPPA) was obtained by reaction of ACPA with bis(propylsulfanylthiocarbonyl) disulfide synthesized in a first step, according to the literature.<sup>1,2</sup> Deionized water was used for all polymerizations.

Matrix **latex 1** was a statistical P(*n*BA-*co*-AA) copolymer latex and was kindly provided by the Dow Chemical Company, delivered as a latex emulsion with 54% solid content ( $D_z = 436 \text{ nm}$ ,  $\sigma = 0.07$ ). The relative amounts of *n*BA and AA were 98.1 wt% and 1.9 wt%, respectively. The mean molar mass was  $M_w = 1572 \text{ kg mol}^{-1}$ .<sup>3</sup> Matrix **latex 2** was a conventional P(*n*BA-*co*-AA) copolymer latex, synthesized in our lab using standard conditions (97.1 wt% *n*BA, 2.9 wt% AA, 1 wt% KPS, 4 wt% Brij L23, 62% solid content) and containing a typical important gel fraction of 55%. ( $T_g = -47.2^\circ\text{C}$ ,  $D_z = 406 \text{ nm}$ ,  $\sigma = 0.05$ )

**Synthesis of aqueous fibre dispersions by PISA (F1, F2).** The P(MAA-*co*-PEOMA)-*b*-PS core-shell fibre dispersions were synthesized, exclusively in water, according to previously established protocols.<sup>4,5</sup> The copolymers were synthesized in one single reactor, in two successive steps. The total synthesis took less than 6 h. Briefly, in the first, solution polymerization step, MAA (0.219 g, 2.55 mmol), PEOMA (1.182 g, 1.24 mmol), CTPPA (26 mg, 0.094 mmol), ACPA (5.1 mg, 0.018 mmol) and water (8.7 mL) were added into a 50 mL round-bottom septum-sealed flask with a magnetic bar. 1,3,5-Trioxane (37 mg) was also added into the flask as an internal reference for determination of the monomer conversion by  $^1\text{H}$  NMR. The solution was purged for 30 min with nitrogen, and then heated to  $80^\circ\text{C}$  in a thermostated oil bath under stirring at 375 rpm. After 120 min, the monomer conversion was close to 100% (determined by  $^1\text{H}$  NMR). The pH was then adjusted close to 5 by the addition of 0.5 mL 1N NaOH, and the second, emulsion polymerization, step started after the addition of styrene (2.926 g, 28 mmol), ACPA (5.3 mg, 0.019 mmol) previously dissolved with  $\text{NaHCO}_3$  (6.8 mg, 0.08 mmol) in 13.1 mL of water. The emulsion polymerization were performed at  $80^\circ\text{C}$  and finally quenched after 200 min by immersion of the flask in iced water. The conversion of styrene was determined by gravimetric analysis. Potentially remaining monomer was removed by air stripping.

The synthesis of the spherical core-shell particle aqueous dispersions (S1) was performed accordingly using a MAA/PEOMA molar ratio of 50/50 mol/mol instead of 67/33. The detailed experimental conditions are reported in Table SI-1.

**Film formation.** The acrylic latex (4.8 mL of latex at 23 wt%), or mixtures of latex with 5 or 10 wt% (with respect to the dried latex) of spheres or fibres, were dried in flat rectangular silicon molds (68 mm × 27.5 mm × 30 mm) for 7 days at ambient temperature and for further 12 h at room temperature under reduced pressure ( $10^{-2}$  mbar) at room temperature. For the mixtures of latex with fibres or spheres, the aqueous fibre (or sphere) dispersions were diluted with deionized water to 5 wt% and stirred for 7 days. The diluted sample was then added to the acrylic latex previously diluted to 25 wt%, and the mixture was stirred for 1 day before drying in the molds. For the mixtures realized at distinct pH (generally pH8 or pH12), both the latex and the aqueous fibre (or sphere) dispersion were individually adjusted to the desired pH (with NaOH 1M), before dilution, homogenization and mixing.

**Tensile tests.** Tensile rectangular specimens (20 mm × 5 mm × 0.5 mm) were cut from the dried films. Uniaxial tensile stress-strain measurements were carried out at 25°C using a standard tensile Instron machine (model 3343), equipped with a 10 N load cell. At least three replicate experiments were performed for each sample (strain rate =  $0.1 \text{ s}^{-1}$ ).

The force (F) and the elongation in the tensile direction (nominal strain,  $\epsilon_N = \Delta L/L_0$ ) were both recorded during the experiments. Nominal stress  $\sigma_N$  was defined as the tensile force per unit of initial area  $S_0$  (Eq. 1):

$$\sigma_N = \frac{F}{S_0} \quad \text{Equation 1}$$

**Creep experiments.** Tensile rectangular specimens (20 mm × 5 mm × 0.5 mm) were cut from dried films, powdered and fixed with adhesive tape to a charge of 10 g. The extension and rupture of the samples was recorded at regular time intervals.

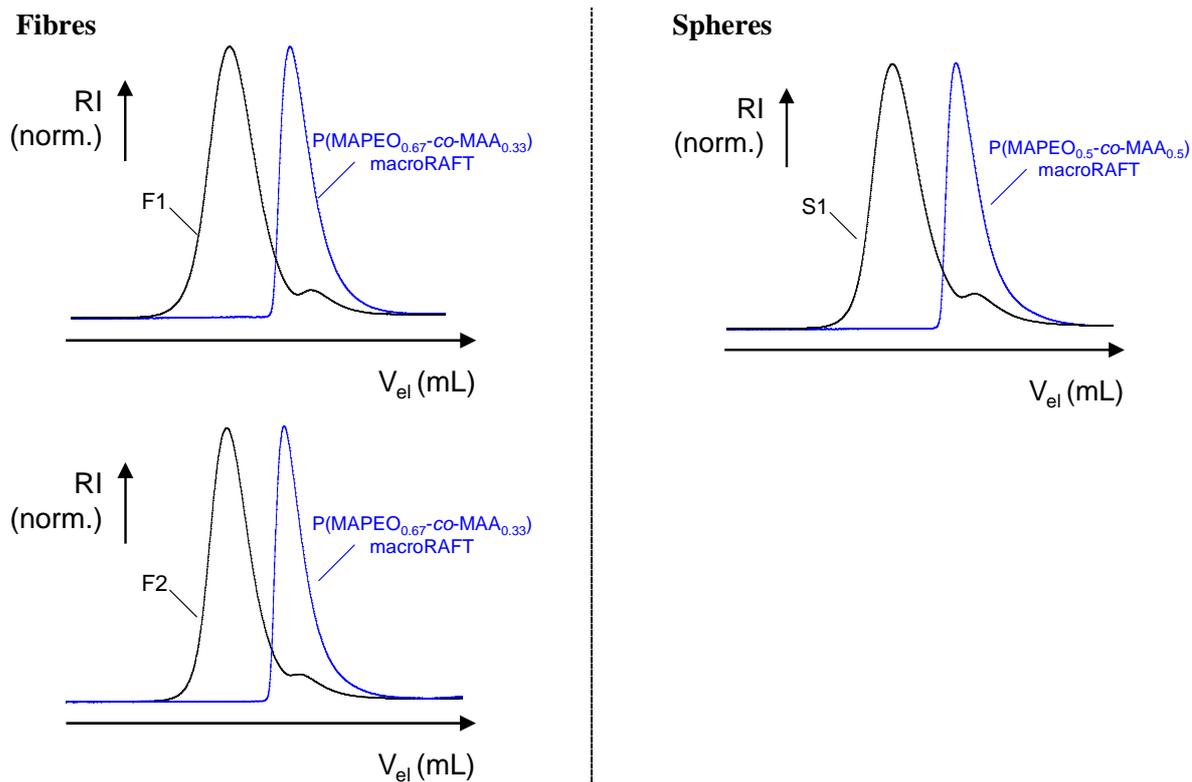
**NMR Spectroscopy.** Proton NMR spectra ( $^1\text{H}$  NMR) for determination of the MAA and PEOMA conversion were recorded in DMSO- $d_6$  solution at room temperature using a 300 MHz Bruker spectrometer in 5-mm diameter tubes.

**SEC.** Size exclusion chromatography measurements in THF were performed at a flow rate of  $1 \text{ mL min}^{-1}$  with a Viscotek Tetra Detector Array (TDA, TriSEC Model 302), equipped with an integrated solvent and sample delivery module (GPCmax), a differential refractive index detector (RI), a right ( $90^\circ$ ) and a low ( $7^\circ$ ) angle light scattering (LS) detector (RALS/LALS), a four-capillary differential viscometer, and a diode array UV detector (Viscotek UV detector 2600). Toluene was used as a flow-rate marker. For analytical purposes, the carboxylic acid functions of the copolymers were transformed into methyl esters. Therefore, the copolymers were recovered by drying the aqueous dispersions. After dissolution in a THF/H<sub>2</sub>O mixture and acidification of the medium with a 1M HCl solution, they were methylated using an excess of trimethylsilyldiazomethane. Polymers were analyzed at a concentration of  $5 \text{ mg mL}^{-1}$  in THF after filtration through a  $0.45 \mu\text{m}$  pore size membrane.

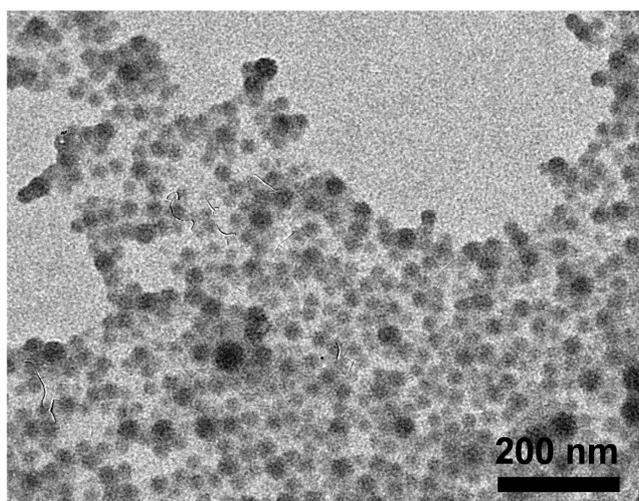
The separation was carried out on three PLgel Mixed C (7.5 mm × 300 mm, bead diameter: 5 μm), and a guard column (PL gel 5 μm). Columns and detectors were maintained at 40 °C. The OmniSEC 4.6 software was used for data acquisition and data analysis. The molar mass distribution (dispersity  $\mathcal{D} = M_w/M_n$ ) were derived from the RI signal by a calibration curve based on PS standards (from Polymer Standards Service). The number-average molar masses,  $M_{n,LS}$ , were calculated using the combined RALS/LALS, RI and viscosity signals. The refractive index increment for the copolymers was calculated according to  $dn/dc = w_x v_x + w_y v_y$ , where  $w_x$  is the weight fraction of P(MAA-co-PEOMA) (with  $v_x = 0.062 \text{ mL g}^{-1}$  for the macroRAFT agents with MAA/PEOMA= 50/50 (mol/mol) and  $v_x = 0.066 \text{ mL g}^{-1}$  for the macroRAFT agents with MAA/PEOMA= 67/33 (mol/mol), and  $v_y = 0.185 \text{ mL g}^{-1}$  for polystyrene, as reported previously<sup>4</sup>).

**Transmission electron microscopy (TEM).** Transmission electron microscopy (TEM) was performed on a JEOL JEM CX II UHR microscope operating at 100 keV and equipped with a Keen View CCD camera from Soft Imaging System (Olympus). The acquisition was done with the iTEM software from Soft Imaging System (Olympus). The samples (latex) were diluted in water to 0.05 wt% prior to analysis and then deposited on a carbon-coated copper grid.

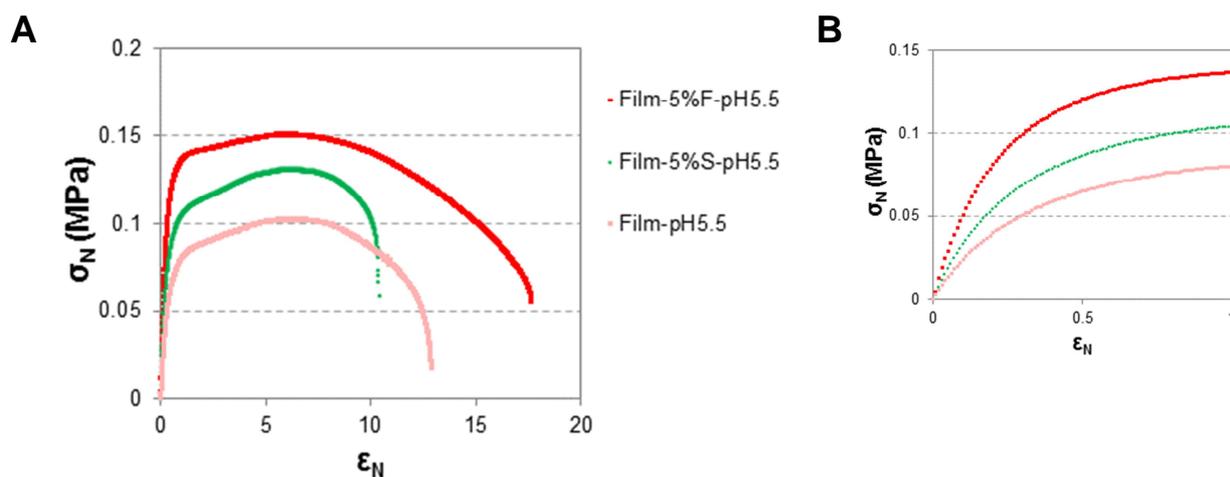




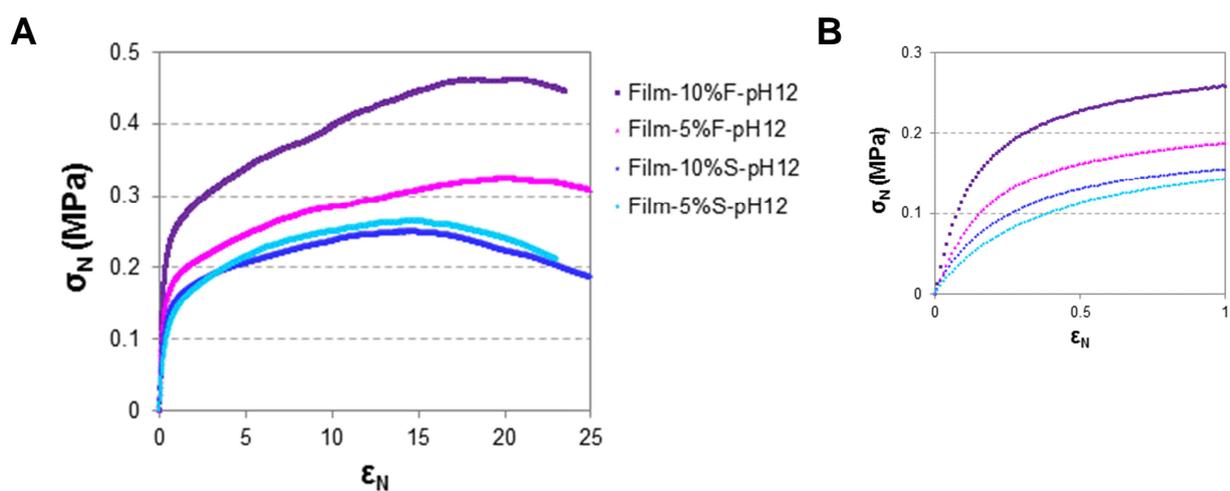
**Figure SI-1.** Overlays of the size exclusion chromatograms of the **P(MAA-co-PEOMA) macroRAFT** agents and the resulting diblock copolymers **P(MAA-co-PEOMA)-b-PS** (F1, F2 and S1).



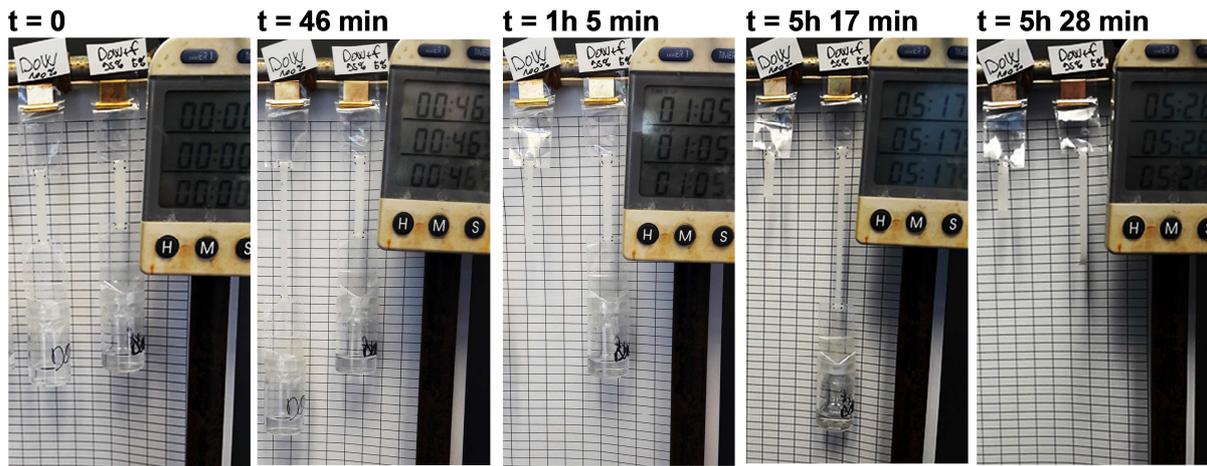
**Figure SI-2.** TEM micrograph of spheres S1.



**Figure SI-3.** (A) Stress-strain curves for Film-pH5.5, Film5%S-pH5.5 and Film5%F-pH5.5 (prepared with 5 wt% additive at pH 5.5). (B) Enlargement of the low strain region.



**Figure SI-4.** (A) Stress-strain curves for films prepared at pH 12, incorporating either spheres of fibres at 5 or 10 wt%, (B) Enlargement of the low strain region.



**Figure SI-5.** Creep tests. Powdered films prepared at pH 5.5, load = 10 g, on the left side in the pictures: Film-pH5.5, on the right side in the pictures: Film5%F-pH5.5 (specimen: 20 mm × 5 mm × 0.5 mm)

## Tables

**Table SI-1. Synthesis conditions and characterization of aqueous fibre and sphere dispersions obtained by PISA in two successive polymerization steps.**

*1<sup>st</sup> step: Synthesis of macroRAFT agents (P(MAA<sub>0.67</sub>-co-PEOMA<sub>0.33</sub>), for fibre dispersions and P(MAA<sub>0.5</sub>-co-PEOMA<sub>0.5</sub>) for sphere dispersions) via solution polymerization at 80 °C using ACPA as an initiator*

entry	[MAA] <sub>0</sub> /mol L <sup>-1</sup>	[PEOMA] <sub>0</sub> /mol L <sup>-1</sup>	[CTPPA] <sub>0</sub> /mol L <sup>-1</sup>	[CTPPA] <sub>0</sub> / [ACPA] <sub>0</sub>	[monomers] <sub>0</sub> / [CTPPA] <sub>0</sub>	Conv. /%	$M_{n,th}$ <sup>a</sup> /kg mol <sup>-1</sup>	$M_{n,LS}$ <sup>b</sup> /kg mol <sup>-1</sup>	$\bar{D}^{PS}$
<b>M-S1</b>	0.20	0.20	0.013	5	30	97	16	25	1.12
<b>M-F1</b>	0.25	0.12	0.009	5	40	99	15	22	1.12
<b>M-F2</b>	0.40	0.20	0.014	5	42	97	16	25	1.11

<sup>a</sup>Theoretical number-average molar mass:  $M_{n,th} = [m_0(\text{MAA}) + m_0(\text{PEOMA})] \times \text{conv.}/100 / n_0(\text{CTPPA}) + \text{MM}(\text{CTPPA})$ , <sup>b</sup> experimental number-average molar mass using  $dn/dc([MAA]/[PEOMA] = 50/50) = 0.066$ ,  $dn/dc([MAA]/[PEOMA] = 67/33) = 0.062$ , recalculated to the non-methylated mass values

*2<sup>nd</sup> step: Synthesis of aqueous fibre dispersions and spherical latexes via emulsion polymerization at 80 °C.<sup>a</sup>*

entry	Morpho- logy	[macro- RAFT] <sub>0</sub> /mmol L <sub>H20</sub> <sup>-1</sup>	[S] <sub>0</sub> /g mL <sub>H20</sub> <sup>-1</sup>	[S] <sub>0</sub> / [macro- RAFT] <sub>0</sub>	[ACPA] <sub>0</sub> /mmol L <sub>H20</sub> <sup>-1</sup>	Conv <sup>b</sup> / %	$M_{n,th}$ <sup>c</sup> /kg mol <sup>-1</sup>	$dn/dc$ <sup>d</sup> /mL g <sup>-1</sup>	$M_{n,LS}$ <sup>e</sup> /kg mol <sup>-1</sup>	$\bar{D}^{PS}$	$\tau_{\text{polymer/latex}}$	m(PS)/ m(macro- RAFT)	pH <sub>final</sub>
<b>S1</b>	<b>spheres</b>	6.7	0.21	300	1.3	> 85	47	0.139	58	1.32	22%	1.7	5.9
<b>F1</b>	<b>fibres</b>	4.2	0.13	300	0.8	> 86	46	0.142	53	1.15	15%	1.8	5.8
<b>F2</b>	<b>fibres</b>	6.9	0.21	300	1.4	> 84	47	0.141	63	1.29	22%	1.7	5.8

<sup>a</sup>RAFT/ACPA = 5, the macroRAFT was neutralized with 1M NaOH before the addition of styrene,  $n(\text{base})/n(\text{acide}) = 0.2$ , <sup>b</sup> the conversion of styrene determined by gravimetric analysis can be underestimated due to monomer evaporation during polymerization and sampling<sup>6</sup>, <sup>c</sup> theoretical number-average molar mass:  $M_{n,th} = [m_0(\text{MAA}) + m_0(\text{PEOMA}) + m_0(\text{S})] / n_0(\text{CTPPA}) + \text{MM}(\text{CTPPA})$ , <sup>d</sup>  $dn/dc$  were calculated as reported in the SI, <sup>e</sup>  $M_{n,LS}$  = experimental number-average molar mass using in line static light scattering (LS), recalculated to the non-methylated mass value

**Table SI-2.** Mechanical properties of series III Films' prepared from latex 2 at pH8<sup>a</sup>.

Entry	Film	Additive	wt%	$\sigma_{\max}^b$	$\epsilon_B^b$	E <sup>c</sup>	E/E <sub>0</sub> <sup>c</sup>
			additive	/MPa		/MPa	
<i>Series III prepared from P(nBA-co-AA) latex 2 at pH 8<sup>a</sup></i>							
9	<b>Film'-pH8</b>	-	-	0.14 ± 0.03 <sup>d</sup>	6.5 ± 0.8 <sup>d</sup>	0.28 ± 0.04 <sup>d</sup>	1.0
10	<b>Film'-5%S-pH8</b>	S1	5	0.10 ± 0.01	5.0 ± 0.2	0.40 ± 0.01	1.4
11	<b>Film'-10%S-pH8</b>	S1	10	0.12 ± 0.01	5.7 ± 0.3	0.79 ± 0.09	2.8
12	<b>Film'-5%F-pH8</b>	F2	5	0.11 ± 0.01	5.0 ± 0.7	0.65 ± 0.08	2.3
13	<b>Film'-10%F-pH8</b>	F2	10	0.12 ± 0.01	3.4 ± 1.1	1.45 ± 0.14	5.2

<sup>a</sup> pH of the latex or the latex mixture before film formation. It should be noted that the degree of ionization of the carboxylic acids, present in both the matrix and the shell of the additives, is comparable at pH8 and pH12.<sup>7</sup>

<sup>b</sup>  $\sigma_{\max}$  = maximum stress,  $\epsilon_B$  = strain at break =  $(L_B - L_0)/L_0$

<sup>c</sup> E = Young's modulus, E<sub>0</sub> = Young's modulus of the reference film prepared at the same pH without additive, <sup>d</sup> standard deviations on at least 3 samples

## References

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