

## Supporting Information

### **Waterborne polymers and coatings from bio-based butenolides**

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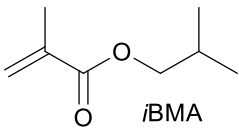

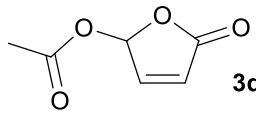

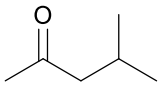

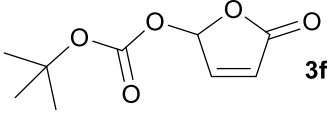

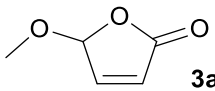

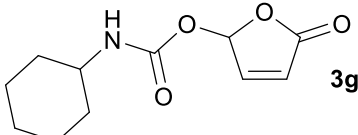

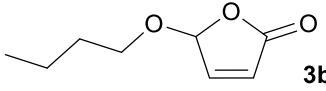

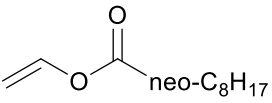

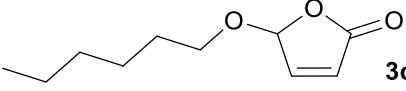

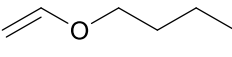

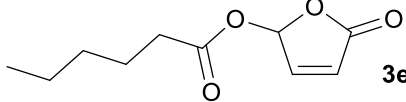

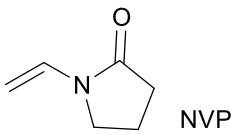

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## Extended results & discussion

### Solid content of monomers

The monomers used throughout our investigation were subjected to the analytical method to determine the solid content of the produced polymers (for method see page S27). As can be seen in Table 1, all monomers except 5-oxo-2,5-dihydrofuran-2-yl hexanoate (**3e**) and cyclohexyl carbamoyl butenolide (**3g**) evaporated under these conditions. Residual monomer present in the produced polymers was expected to evaporate from the sample using all monomers except **3e** and **3g**, allowing a rough estimate on monomer conversion (high / middle / low). For the hybrid dispersions using butenolide **3e** and **3g** assessment of monomer conversion using the solid content method was not feasible.

**Table 1:** Measured solid contents of the monomers (and M/BK) used throughout this investigation

Monomer	SC	Monomer	SC
 iBMA	 0.0%	 <b>3d</b>	 2.2%
 MiBK	 0.0%	 <b>3f</b>	 0.5%
 <b>3a</b>	 1.1%	 <b>3g</b>	 100%
 <b>3b</b>	 0.2%	 VeoVa 9	 0.0%
 <b>3c</b>	 0.3%	 BVE	 0.0%
 <b>3e</b>	 23.6%	 NVP	 0.0%

## Results with carboxy-, and carbamoy-butenolide

*tert*-Butyl carboxy butenolide (**3f**, R<sup>1</sup> = *t*BuO(CO)-) and cyclohexyl carbamoy butenolide (**3g**, R<sup>1</sup> = CyNH(CO)-) were evaluated in the PU hybrid dispersion synthesis. These butenolides are solids with melting points of 89 and 106°C respectively.<sup>1</sup> As anticipated, making the hybrid dispersions with solid butenolides was challenging using our described method in the section “Synthetic Procedures & Results” (page S36) since it relies on reducing the PU viscosity with monomers. Attempts to make homogeneous monomer solutions of **3f** or **3g** with VeoVa 9, BVE, or NVP prior to blending with PU only succeeded for **3f** and **3g** in combination with NVP as co-monomer (but required additional solvent and heating to 100°C). Adding the clear **3f** / NVP solution to the PU pre-polymer resulted in (part of) the butenolide to precipitated again. Eventually, only combination **3g** / NVP resulted in a homogeneous mixture with PU before emulsification, all other PU / monomer combinations were emulsified as heterogeneous mixtures resulting in (part of) the butenolide forming solid particles in the aqueous dispersions (see Figure 1A as example). Despite the synthetic challenges we managed to make the hybrid dispersions for all evaluated examples using **3f** and **3g** (see pages S54 – S59). During the radical polymerization process most solid butenolide particles gradually disappeared (Figure 1) resulting in small hybrid particles with a monomodal size distribution. Probably, mass transfer via the aqueous phase to the reaction loci (like in emulsion polymerization) is the cause of this phenomenon. For combination **3f** / BVE however, some solid particles remained next to the 34 nm hybrid particles.

Despite the successful preparation of the hybrid dispersions using solid butenolides, the measured solid content was often lower than expected. Probably this is not (only) related to incomplete polymerization of the butenolides but is (also) caused by monomer loss during transfer of the hot heterogeneous monomer blends.

All hybrid dispersions using carboxy butenolide **3f** built-up pressure during 1 month RT storage indicating the carbonate moiety (partially) hydrolyses resulting in CO<sub>2</sub> formation. The hybrid dispersion using **3f** + BVE was liquid after 1 month RT storage but opening triggered destabilization (see page S55). The dispersion using **3f** + NVP increased in particle size and viscosity during 1 month storage indicating that also this dispersion was not storage stable.

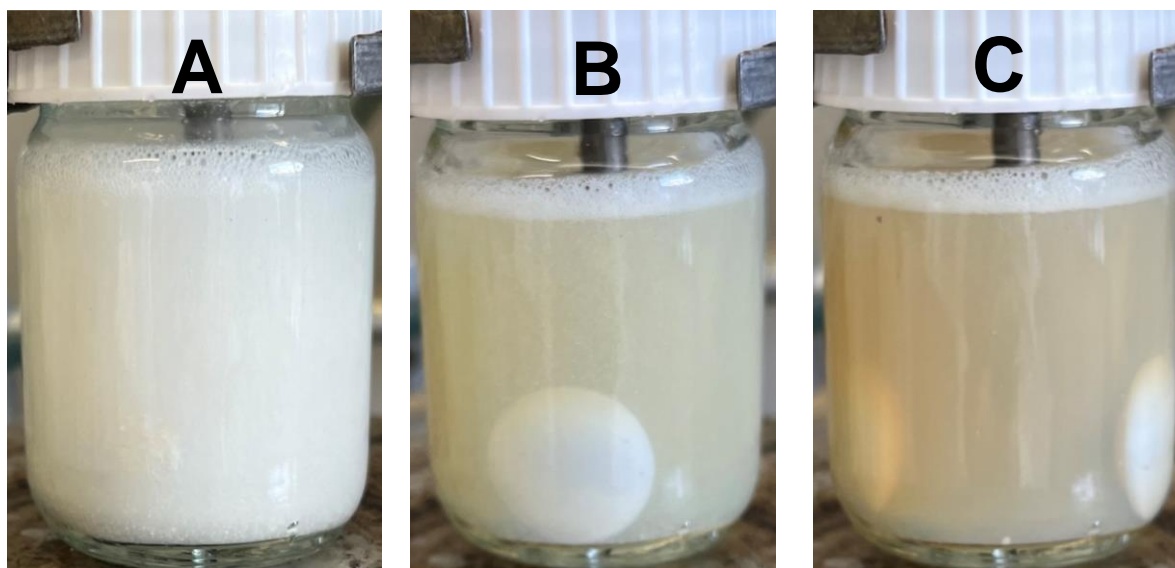


Figure 1: Gradual disappearance of solid particles during radical polymerization. Pictures correspond to hybrid dispersion using **3g** / BVE. A) before 1<sup>st</sup> radical polymerization, B) 30 min after 1<sup>st</sup> radical polymerization, C) 30 min after 2<sup>nd</sup> radical polymerization.

## Molecular weight distributions of dispersions

Molecular weight distribution (MWD) of the formed polymers were analysed after 1 month storage at room temperature storage using the method described on page S28. Detailed MWD plots can be found in the section “Synthetic Procedures & Results” (pages S37-S63), an overlay of 6 illustrative MWDs is provided in Figure 2. Since the hybrid dispersions contain two types of polymers, data interpretation was not trivial. Evidently, high Mw's ( $>150,000$  g/mol, against polystyrene standards) were measured for all hybrid dispersions, most often displaying a bimodal distribution at  $M_p \sim 1 \cdot 10^5$  &  $\sim 1 \cdot 10^{6.5}$  g/mol. Possibly, the bi-modal distribution originates from the two separate polymeric backbones dispersed in one particle, however, reference experiment 2 (having only polyurethane) also demonstrates a bimodal distribution (see page S38, and grey dashed distribution in Figure 2 underneath). The minor fraction at MW  $1 \cdot 10^{6.5}$  g/mol observed in the MWD of reference experiment 2 indicates other phenomena must attribute to the high MW fraction too (e.g. polymer entanglement).

Storage stability issues unfortunately only allowed the MWD analysis of the hybrid dispersions using **3a** and **3d** in combination with butyl vinyl ether. Clearly the  $1 \cdot 10^{6.5}$  g/mol fraction for these polymer mixtures is absent (orange and red distribution in Figure 2, respectively) resulting in lower Mw's ( $<200,000$  g/mol) for these materials compared to all other hybrid dispersions ( $>300,000$  g/mol).

Further analysis of MWDs is a topic of current investigations using fractionation followed by qualitative analysis of the polymers.

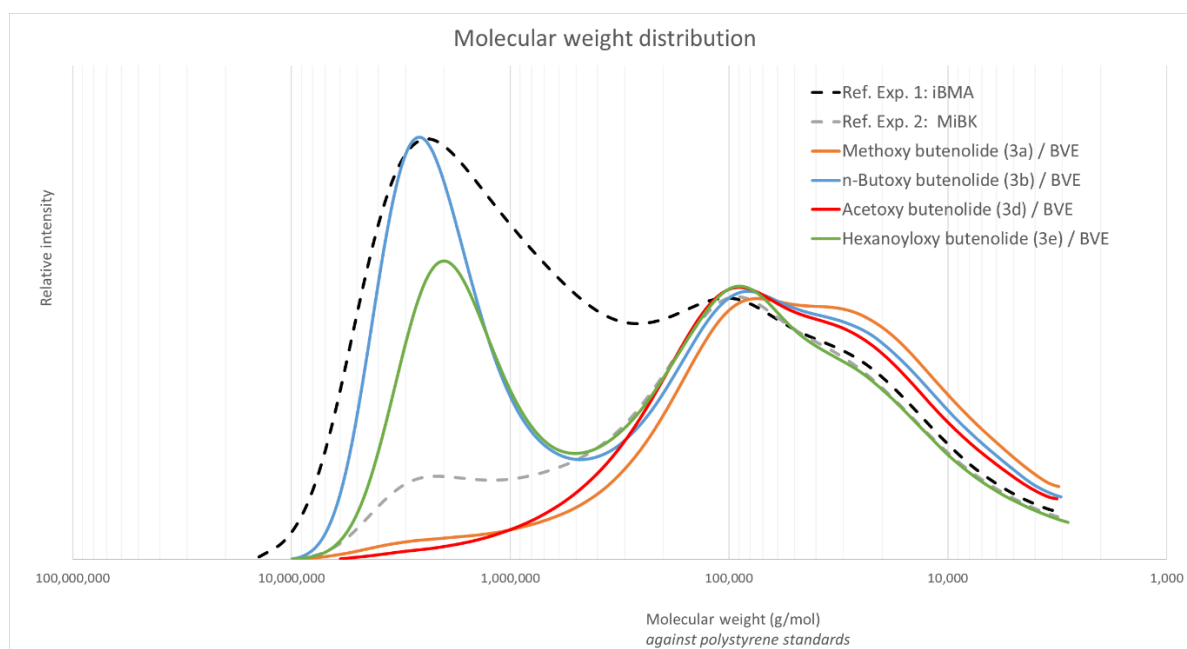


Figure 2: Illustrative examples of measured molecular weight distributions. Intensities normalized at  $M_p 1 \cdot 10^5$  g/mol.

## (Scanning) Transmission Electron Microscopy ((S)TEM)

The solvent free hybrid dispersions have been analyzed using (S)TEM techniques to elucidate the morphology of the dispersed particles and the corresponding films derived from them. TEM imaging of the solvent free 60/40 PU/poly-butenolide dispersion particles as such resulted in poor contrast (Figure 3). The contrast in TEM imaging could be increased by phosphotungstic acid (PTA) staining and best results were obtained by high-angle annular dark-field (HAADF)-STEM in combination with PTA staining. All three solvent free hybrid dispersions were analyzed using this imaging technique (Figure 3 - Figure 5). It can be clearly seen that the dispersion particles form clusters (often seen for polyurethane/polyacrylic hybrid dispersions too).<sup>2</sup> The average particle diameter increased with increasing poly-butenolide content (27, 34, and 50 nm respectively, based on 30 measurements). The particle sizes by STEM (*in vacuo*) were slightly smaller than measured with DLS (*aqueous*) but follow the same trend. The dispersion particles display most staining at the edges (see Figure 6 for EDX analysis) which suggests a core-shell particle morphology (poly-butenolide rich core and polyurethane rich shell). The core/shell morphology was most pronounced for the hybrid dispersion containing 60 wt% poly-butenolide (Figure 5). Measuring the core radius (19.16 nm) and shell thickness (5.77 nm average) for this dispersion resulted in the calculation of a core/shell volume ratio of 45/55 which is different from the designed poly-butenolide / PU mass ratio (60/40). Although care should be taken applying these calculations (due to unknown polymer densities and possible particle deformation during the measurement), most likely the polymers do not phase separate completely and some intermixing between the polymers occurs.

TEM imaging of unstained films again resulted in poor contrast (Figure 7 - Figure 9). The contrast could be increased by HAADF-STEM imaging, and best results were again obtained after PTA staining in combination with HAADF-STEM imaging. All three films displayed a honeycomb like pattern of unstained (poly-butenolide rich) domains in a stained (polyurethane rich) continuous phase. The dimensions of the unstained domains in the films corresponded well to the unstained domains in the original hybrid particles confirming the core/shell particle morphology. In the films, the honeycomb structure may appear a bit stretched due to sample preparation using the cryo-ultramicrotome.

Figure 3: (S)TEM images for solvent free 60/40 PU/poly-butenolide dispersion using *n*-butoxy butenolide (3b) + NVP

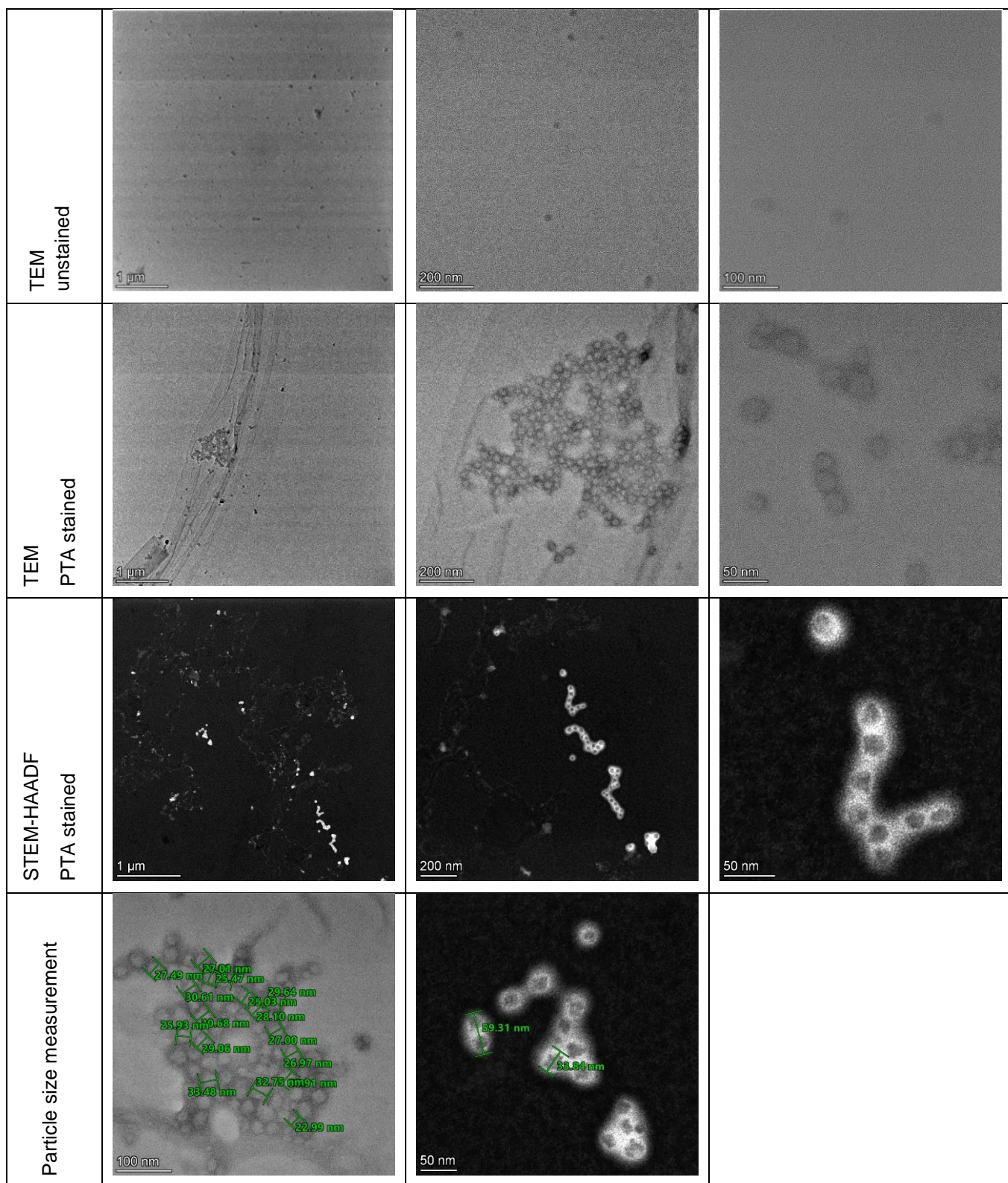




Figure 4: (S)TEM images for solvent free 50/50 PU/poly-butenolide dispersion using *n*-butoxy butenolide (3b) + NVP

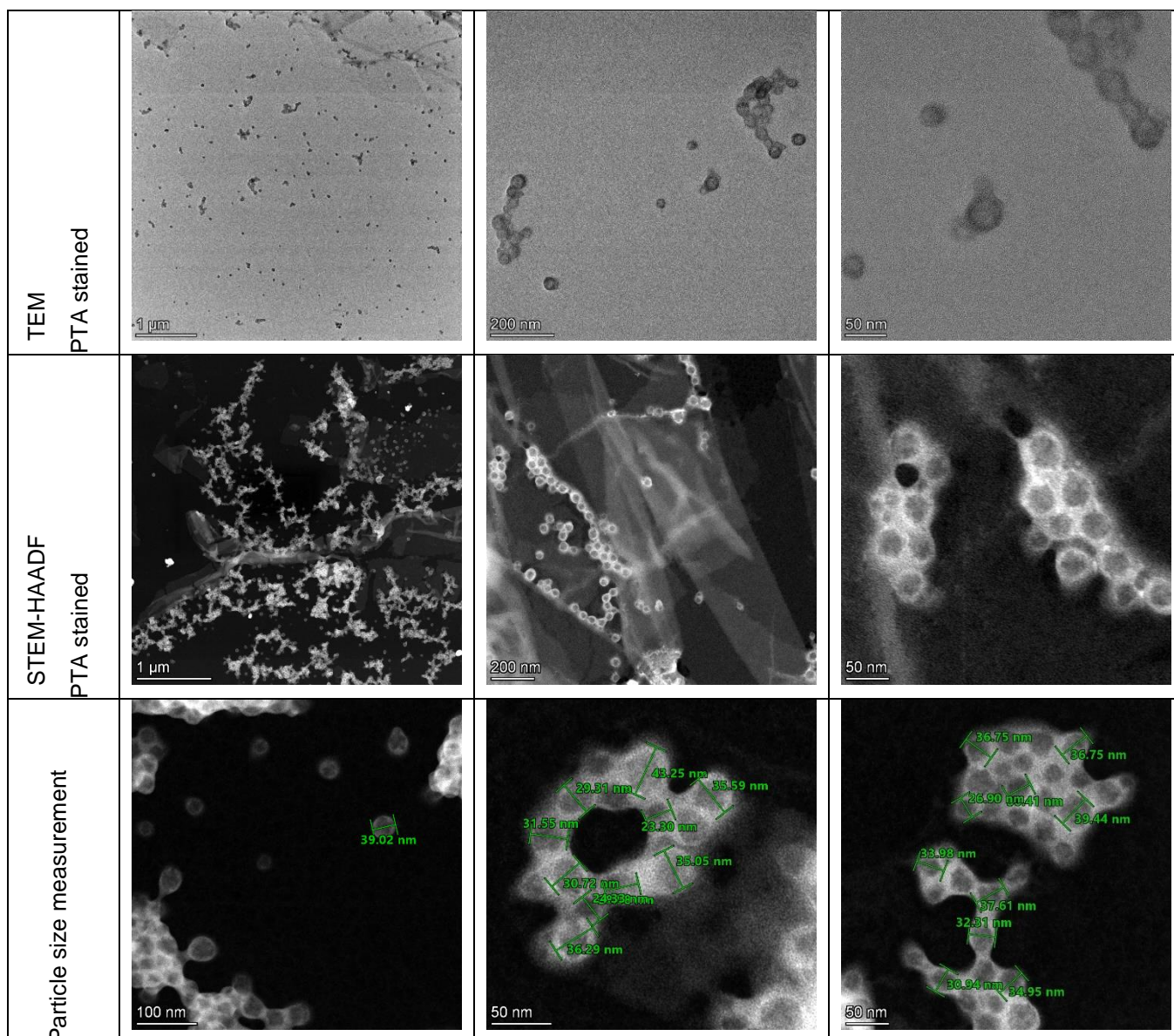


Figure 5: (S)TEM images for solvent free 40/60 PU/poly-butenolide dispersion using *n*-butoxy butenolide (3b) + NVP

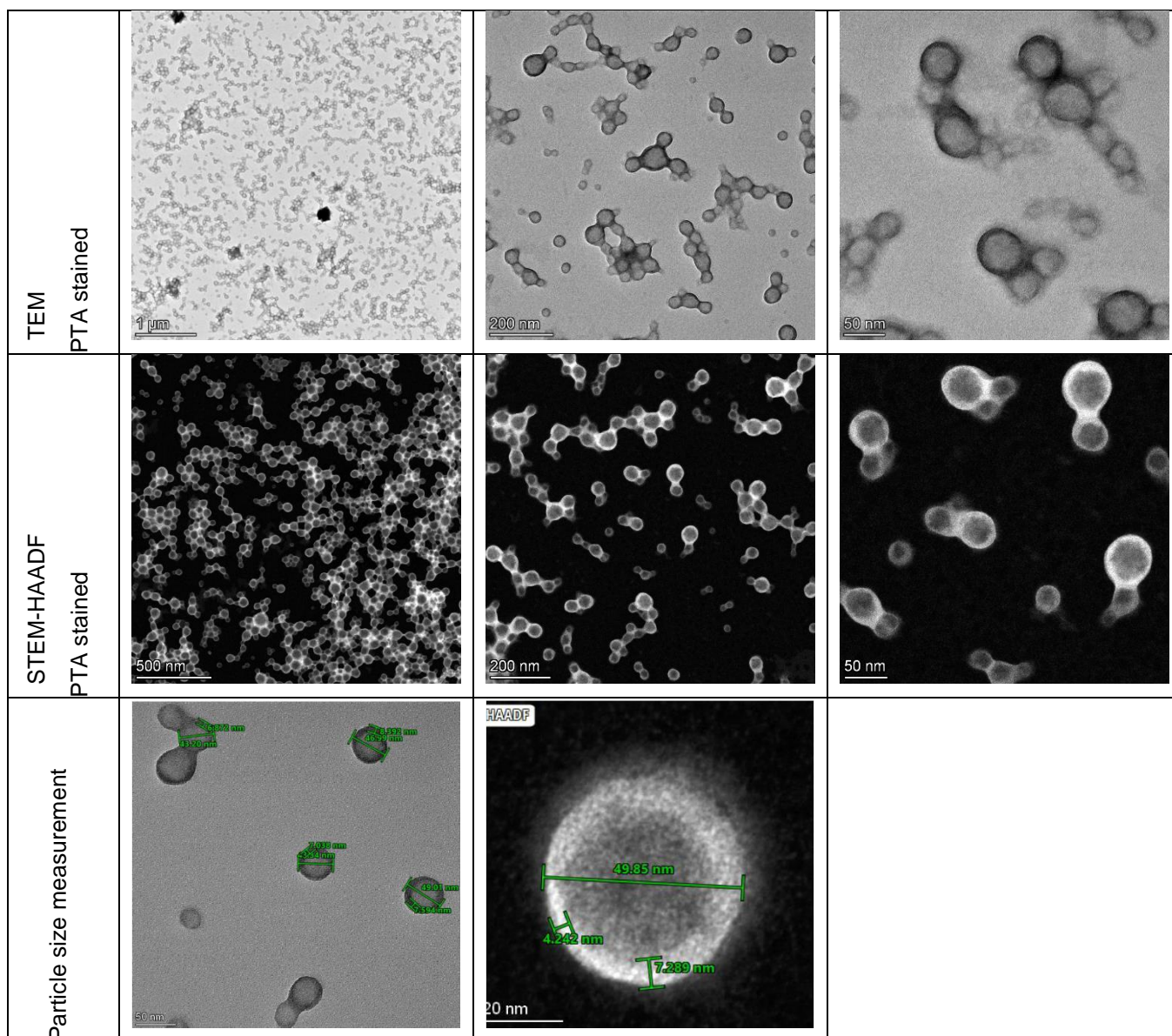


Figure 6: STEM-EDX analysis for solvent free hybrid dispersions

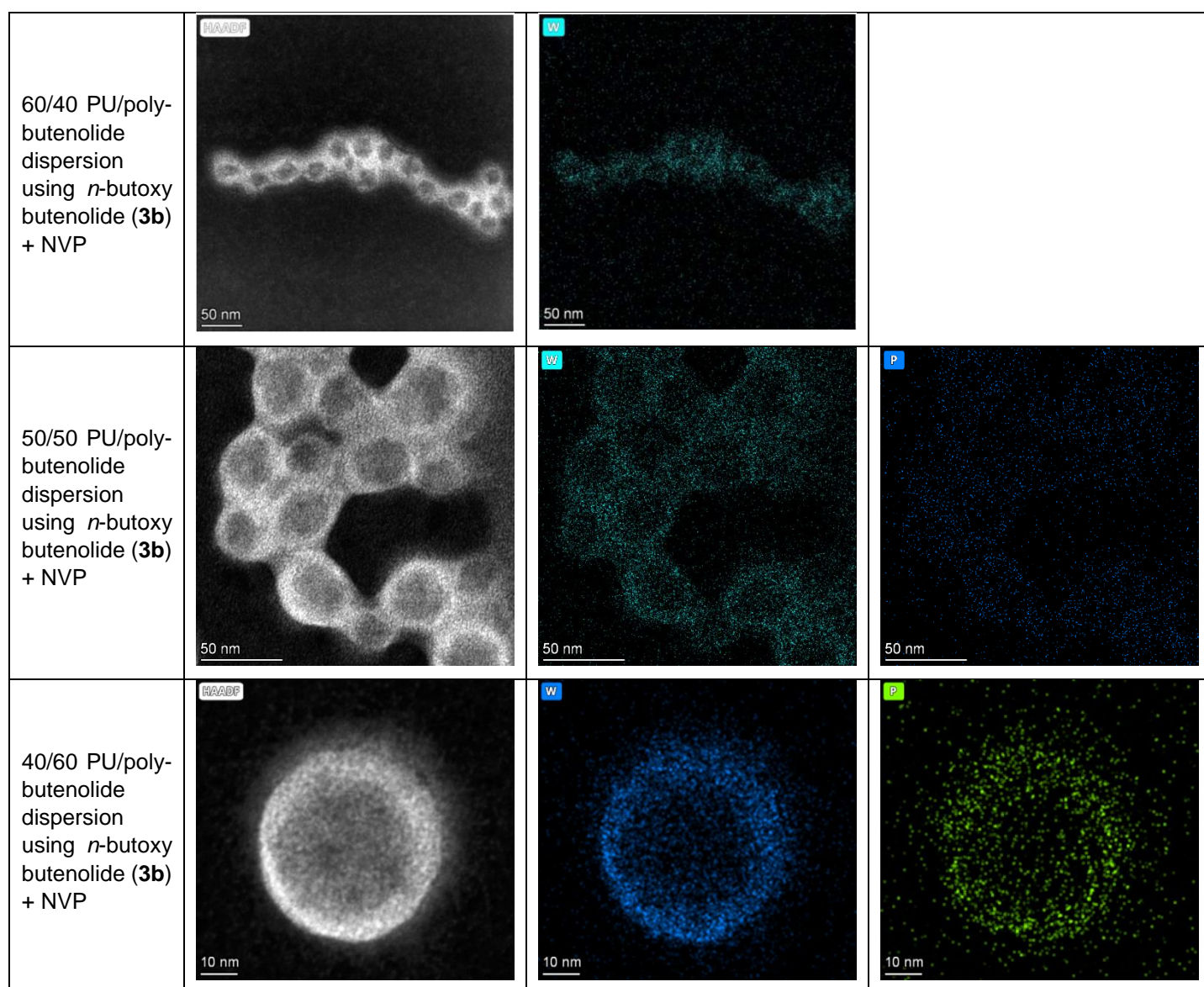
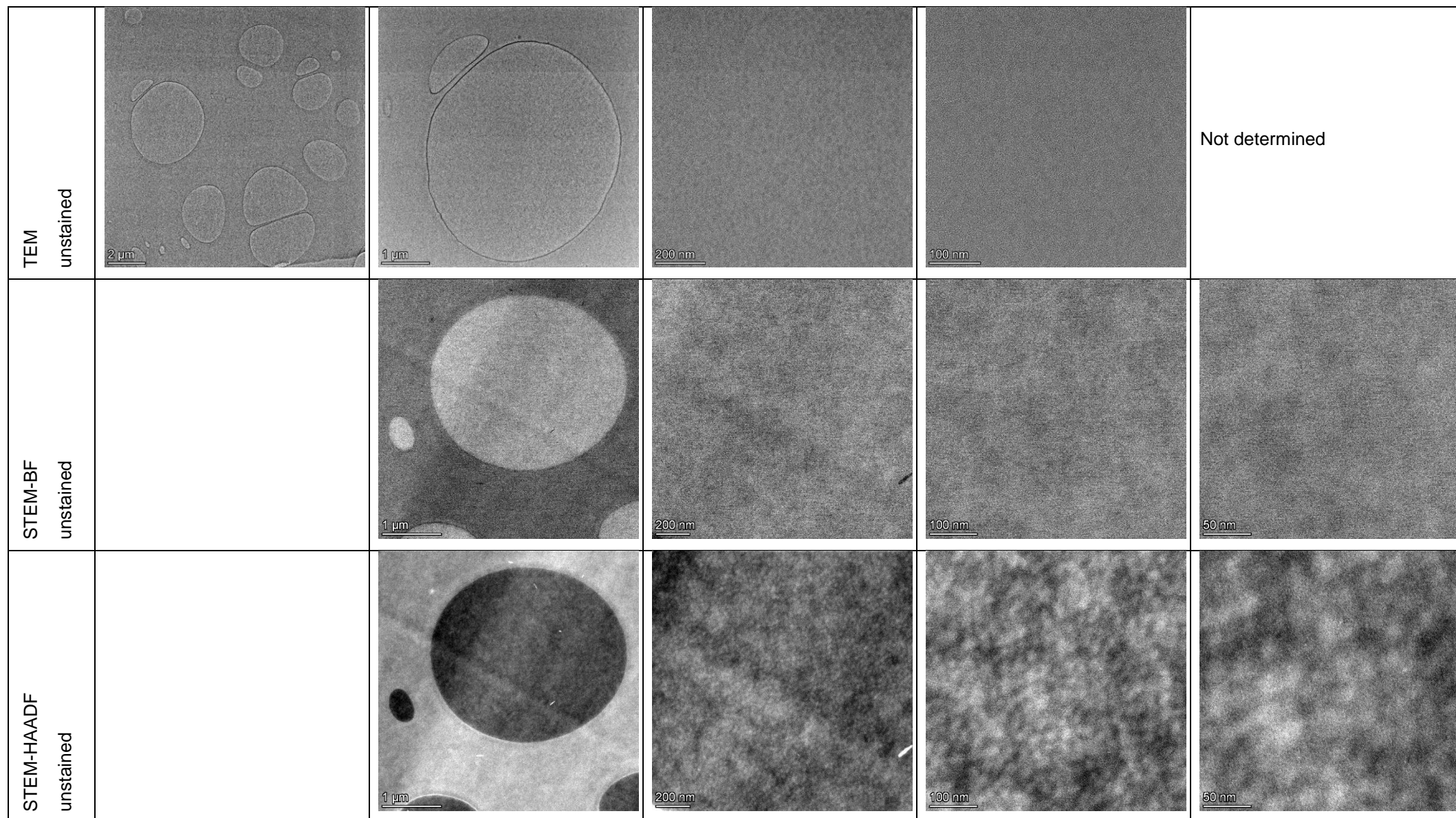


Figure 7: (S)TEM images for coating film derived from solvent free 60/40 PU/poly-butenolide dispersion using *n*-butoxy butenolide (**3b**) + NVP



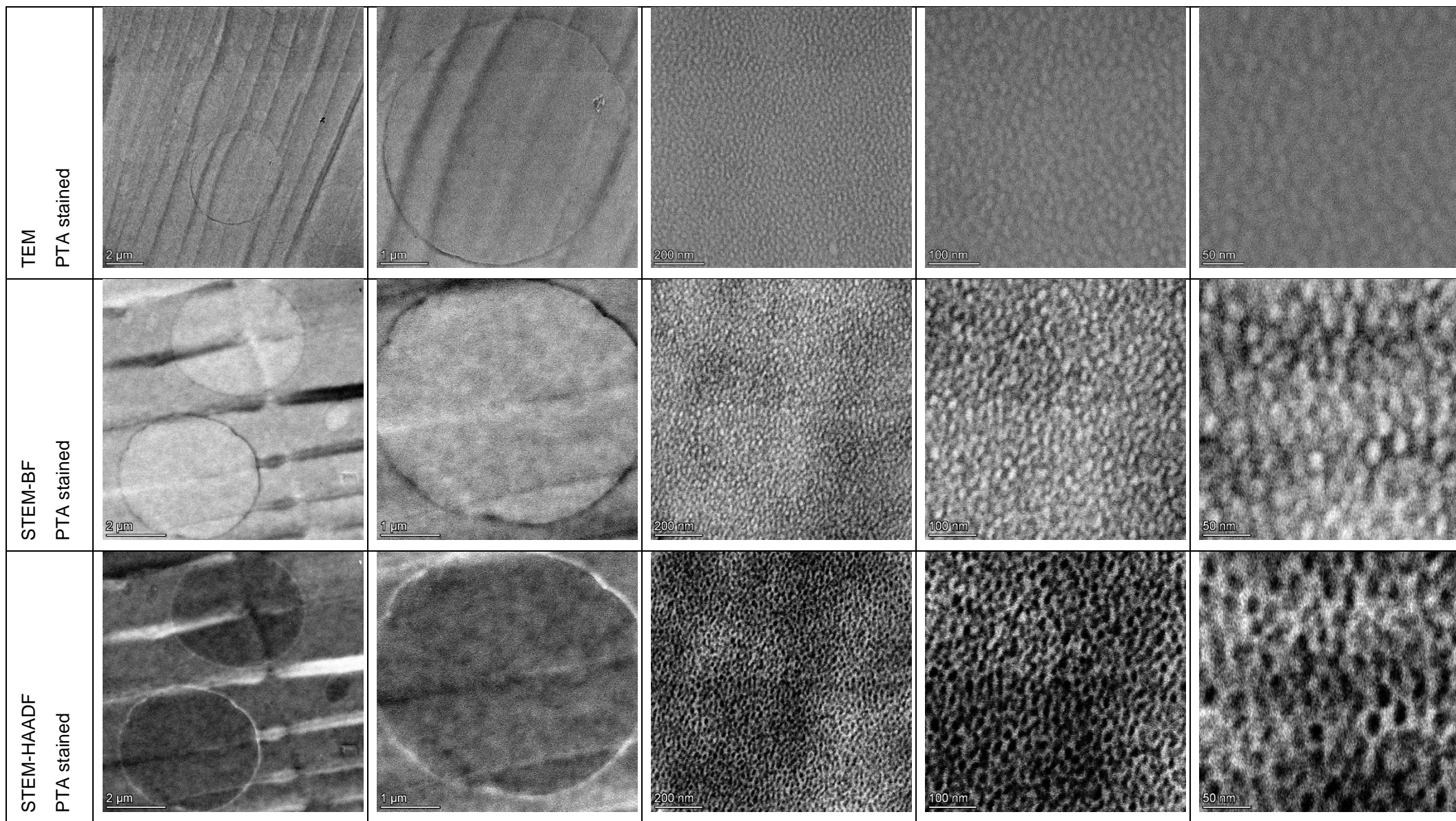
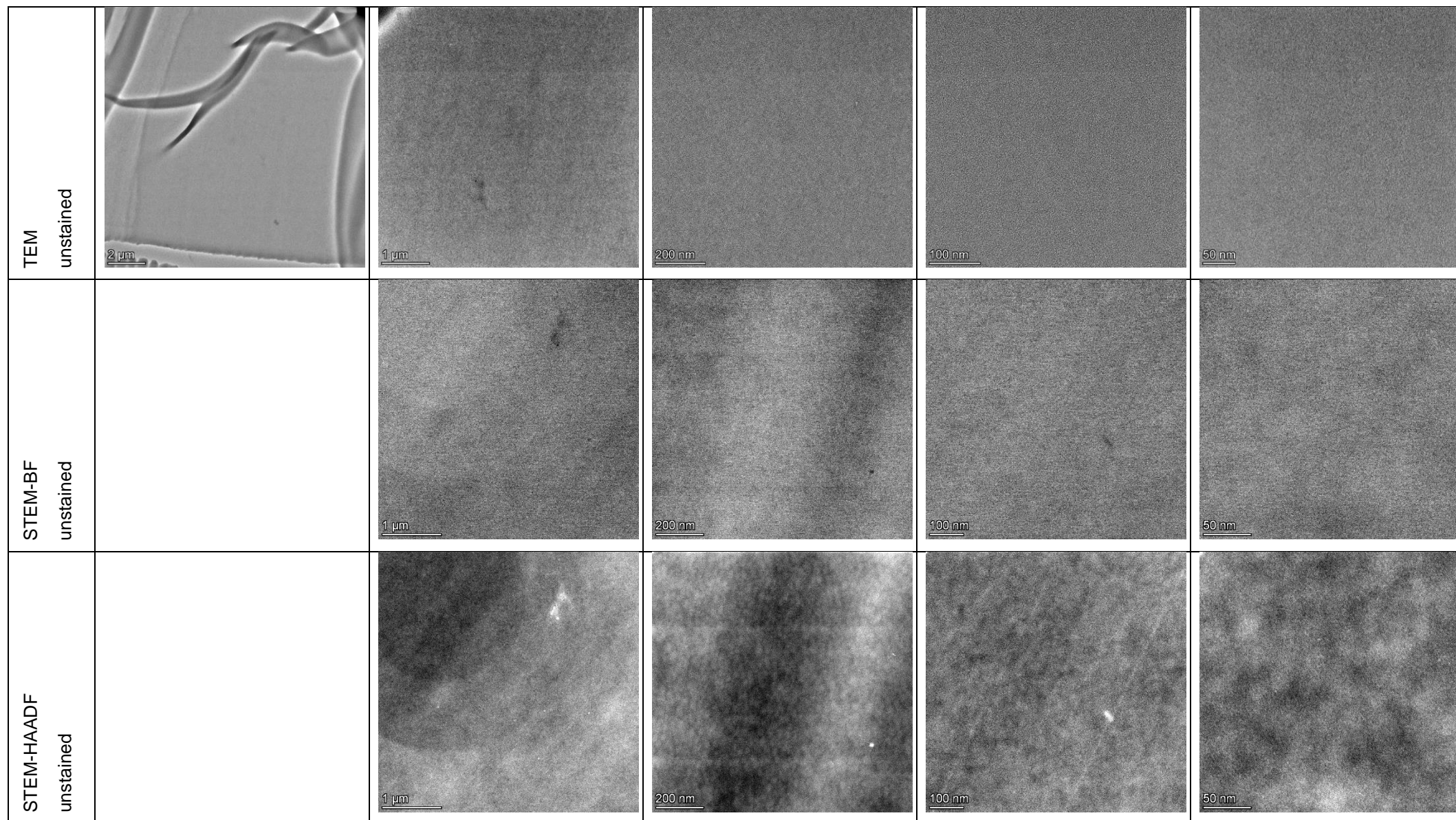


Figure 8: (S)TEM images for coating film derived from solvent free 50/50 PU/poly-butenolide dispersion using *n*-butoxy butenolide (**3b**) + NVP



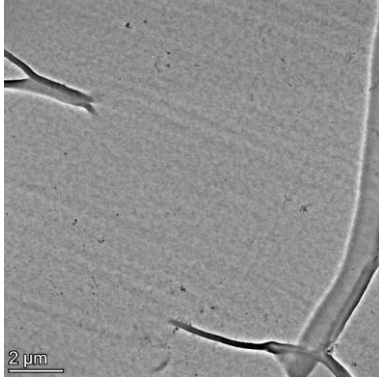
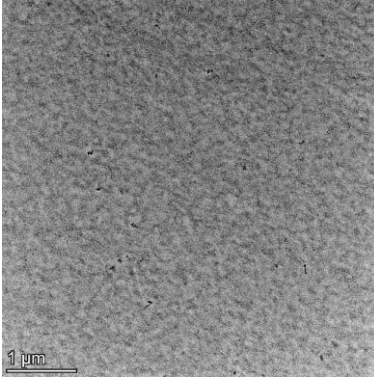
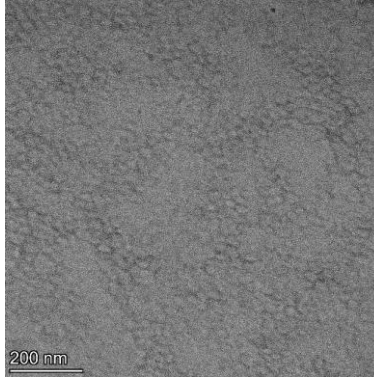
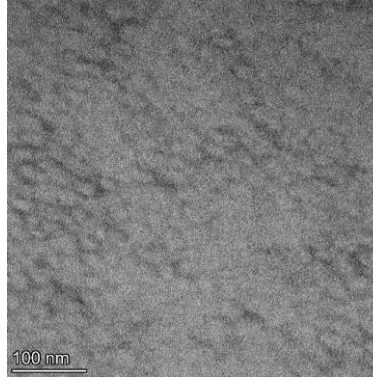

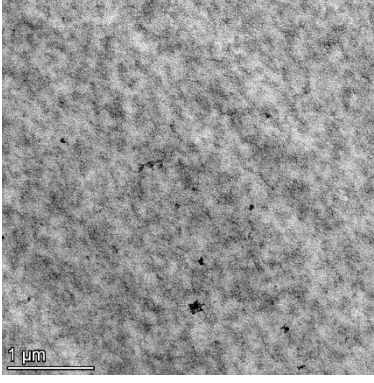
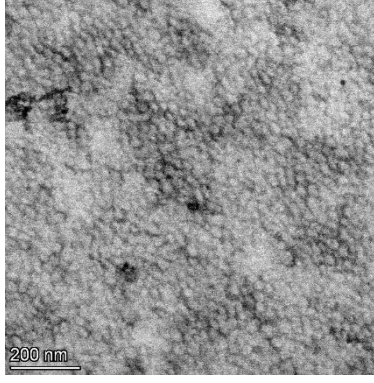
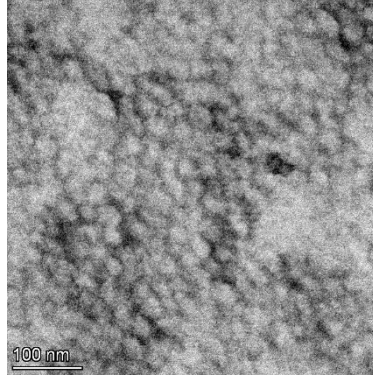
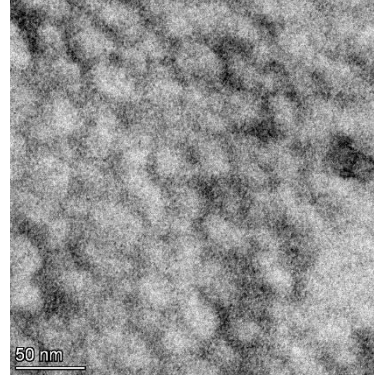

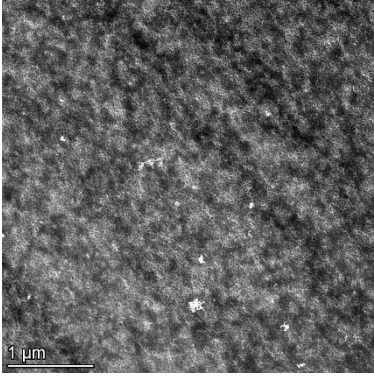
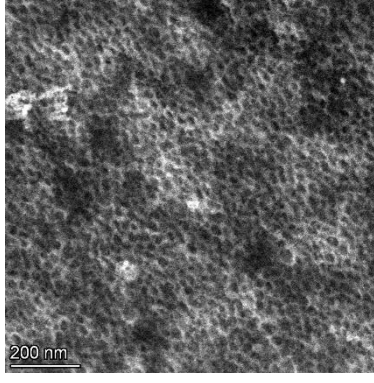
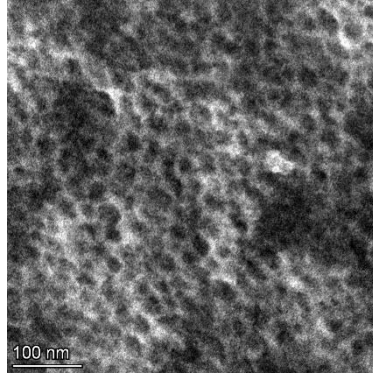
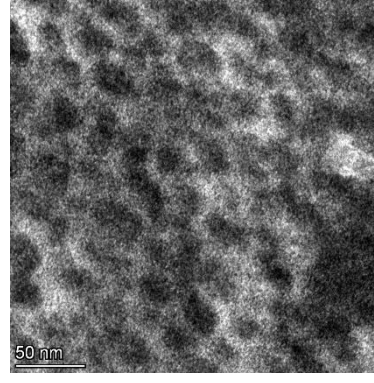
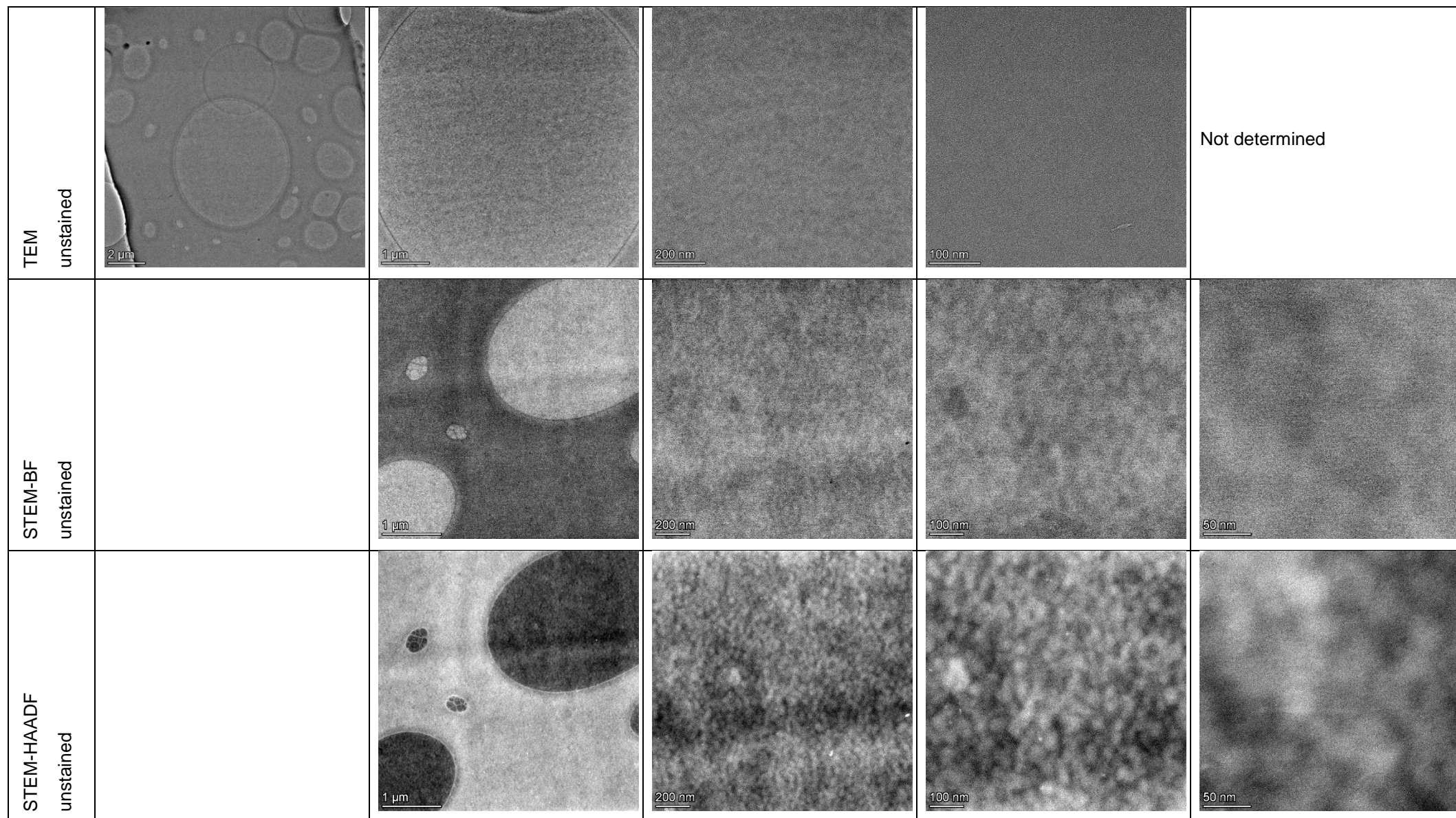
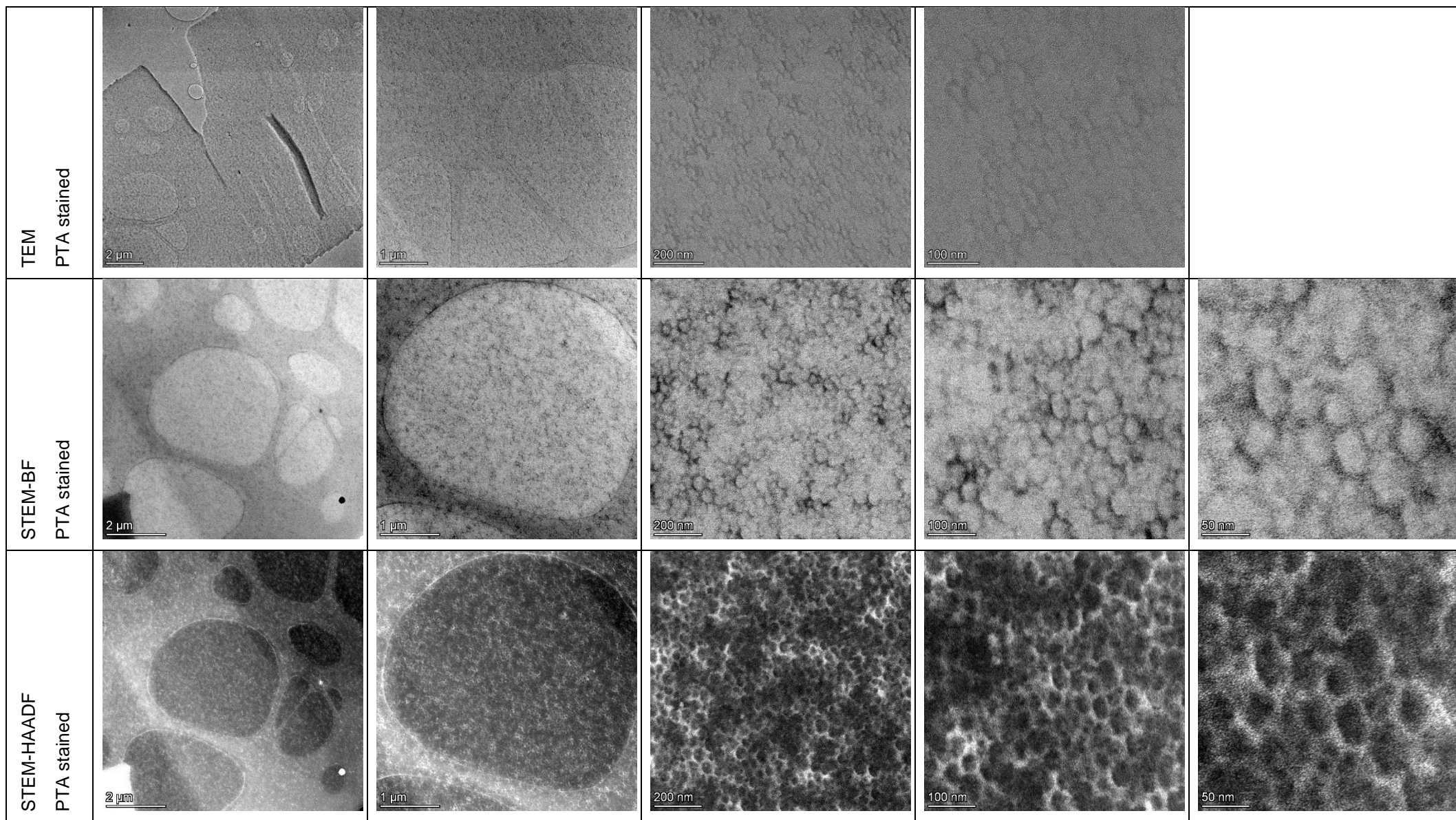
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<p>STEM-HAADF PTA stained</p>					

Figure 9: (S)TEM images for coating film derived from solvent free 60/40 PU/poly-butenolide dispersion using *n*-butoxy butenolide (**3b**) + NVP







## Coating performance

All dispersions that passed 1 month RT storage stability were formulated to a coating and applied on glass panels (methods on page S28). After 7 days physical drying, basic coating properties have been measured, all results are summarized in Table 2. It should be noted that we deliberately evaluated the dispersions as clearcoats using as little coating-additives as possible. This way the differences in measured properties were solely due to the differences in the polymer design. The properties of coatings can be further optimized by addition of other coating constituents (*i.e.* coalescing agents, additives, and pigments). Lastly, the coating properties can be changed by altering the polyurethane design in the hybrid dispersion, these optimizations were beyond the scope of this research.

As can be seen in Table 2, most dispersions formed clear colourless films. The hybrid dispersions consisting of **3a** / BVE and **3d** / BVE had a slightly brown colour which is probably caused by their poorer storage stability. Despite all coatings were applied using the same method, the measured dry layer thicknesses range from 16 to 39  $\mu\text{m}$ . This can be explained by differences in solid content of the dispersions (*e.g.* the solid content of the material used in Ref. Exp. 2 is lower due to the presence of MIBK), also the rheological properties of the applied waterborne coatings have an influence on the applied wet layer thickness. Especially for methyl ethyl ketone (MEK) double rub resistance measurements, the dry layer thickness is known to have a significant influence, nevertheless, trends can be observed in the measured values.

### *Alkoxy butenolides (3a – 3c)*

The hybrid dispersions synthesized using alkoxy butenolides demonstrated MEK double rub resistances in the same order of magnitude in reference experiment 1 (using iBMA). Water resistance properties were generally equal to the iBMA reference as well, except for combination **3a** / BVE which demonstrated poor water resistance. Most likely, poly-butenolide combination **3a** / BVE has an inherently higher hydrophilicity but the lower molecular weight observed for this material may have a contribution to the lower water resistance too.

As expected, softer coatings were obtained with increasing alkoxy chain length on the butenolide moiety (comparison of entry 3, 5, and 8). The co-monomer used in the butenolide polymer also had a significant contribution to hardness, with NVP providing the hardest coatings.

### *Acyloxy butenolides (3d – 3e)*

Acetoxy-butenolide (**3d**) provided similar film appearance and MEK resistance as methoxy-butenolide (**3a**). Water resistance, however, was better indicating the resulting coating is more hydrophobic. The MEK resistance was greatly improved by using 5-oxo-2,5-dihydrofuran-2-yl hexanoate (**3e**), the combination **3e** / NVP even provided 160 MEK double rubs which is considered outstanding for a physically drying coating. The water resistance remained on an acceptable level, some micro blistering was observed but the coating demonstrated full recovery within 24h.

### *tert-butyl carbonoxy butenolide (3f) and cyclohexyl carbamoxo butenolide (3g)*

Although the synthesis of the hybrid dispersions using **3f** and **3g** was not ideal (see extended discussion on page S5) the derived coatings generally demonstrated high MEK resistances (> 80 double rubs) and high hardnesses. Water resistances, unfortunately, were very poor leading to full delamination of all 5 evaluated coating within 3 h water spot exposure.

### *Solvent free hybrid dispersions with increasing poly-butenolide ratio*

By comparing entry 6 with entry 19 in Table 2 it can be concluded that removing the solvent from the hybrid dispersion increased the MEK resistance of the resulting coating while the observed water resistance and coating hardness were similar. Increasing the **3b** / NVP wt ratio in the hybrid dispersion clearly increased the hardness of the obtained coating but the water resistance was reduced. Whether the reduced water resistance was caused by an increased hydrophilicity of the coating or due to inferior film formation (coalescence) we cannot conclude at this stage. No clear trend in MEK resistance could be observed when increasing the poly-butenolide ratio.

### Glass transition temperature ( $T_g$ )

Next to the coating evaluation tests described above, the influence of the poly-butenolide constituent on the coating glass transition temperature was investigated. Unfortunately, the glass transitions were often difficult to observe and only minor differences in differential scanning calorimetry (DSC) curves could be observed between the coatings. The presence of multiple polymeric phases in the coating which may be (partially) intermixed makes data interpretation difficult. In general, the following observations were made:

- I. Low temperature  $T_g$ : Most coatings display a  $T_g$  at  $-66^\circ\text{C}$  to  $-35^\circ\text{C}$  which most likely originates from the soft-block constituent in the PU (reported  $T_g$  for PTMEG1000:  $-77^\circ\text{C}$ ).<sup>i</sup> The difference in the measured low temperature  $T_g$  between the coatings was probably caused by intermixing of the PU soft-block segment with the PU hard-block segment and/or intermixing with the poly-butenolide phase.
- II. Room temperature  $T_g$ : All coatings display a  $T_g$  around RT ( $16 - 22^\circ\text{C}$ ). The origin of this  $T_g$  was unclear but since reference experiment 2 contains this  $T_g$ , the PU constituent must have a contribution to it. Besides the PU design, the synthesis of the hybrid dispersions at  $\sim\text{RT}$  and/or the drying of the coating at RT may have an origin in the observation of this  $T_g$ .
- III. RT- $100^\circ\text{C}$   $T_g$ : Some coatings display a third  $T_g$  in the RT- $100^\circ\text{C}$  window which was likely related to the poly-butenolide constituent. A  $T_g$  of  $77^\circ\text{C}$  was observed for the coating derived from the methoxy butenolide (**3a**) / BVE hybrid dispersion. The *n*-butoxy butenolide (**3b**) equivalent demonstrates a  $T_g$  at  $47^\circ\text{C}$  while for the *n*-hexyloxy (**3c**) analogue this  $T_g$  probably overlaps the RT  $T_g$  (at  $19^\circ\text{C}$ ).<sup>ii</sup> This reduction in  $T_g$  corresponds to the previously observed reduced hardness upon increasing the alkoxy chain length on the butenolide monomer (see page S18). Lastly, also the coating derived from the **3e** / BVE hybrid dispersion demonstrates a  $T_g$  at  $51^\circ\text{C}$  and for the coatings derived from **3f** and **3g** a  $T_g$  at  $60-64^\circ\text{C}$  could be measured, for the last two butenolides we expected  $T_g$ 's  $> 100^\circ\text{C}$ ,<sup>5</sup> the change in experimental method for their production (and reduced storage stability) may have an origin in the observation  $T_g$  at  $60-64^\circ\text{C}$ .

Interestingly, the RT- $100^\circ\text{C}$   $T_g$  was often only observed when (some butenolides monomers were polymerized) using BVE as co-monomer. Probably, their VeoVa 9 and NVP analogues (using the same butenolide monomer) have  $T_g$ 's above  $100^\circ\text{C}$ .<sup>iii</sup> Unfortunately, running the DSC measurements above  $100^\circ\text{C}$  resulted in discoloration of the samples indicating (part of) the polymeric mixture decomposes and no reliable results can be obtained.

The coating derived from the  $\beta$ BMA reference experiment also did not display a clear  $T_g$  for poly- $\beta$ BMA (literature value:  $53^\circ\text{C}$ ), instead a minor signal can be observed at  $66^\circ\text{C}$  which was probably caused by intermixing with the PU hard-block segment.

Gravimetric analysis before and after the DSC measurement indicated only very minor weight losses. In general, films derived from NVP containing hybrid dispersions display highest weight losses which was probably caused by their hygroscopic character.

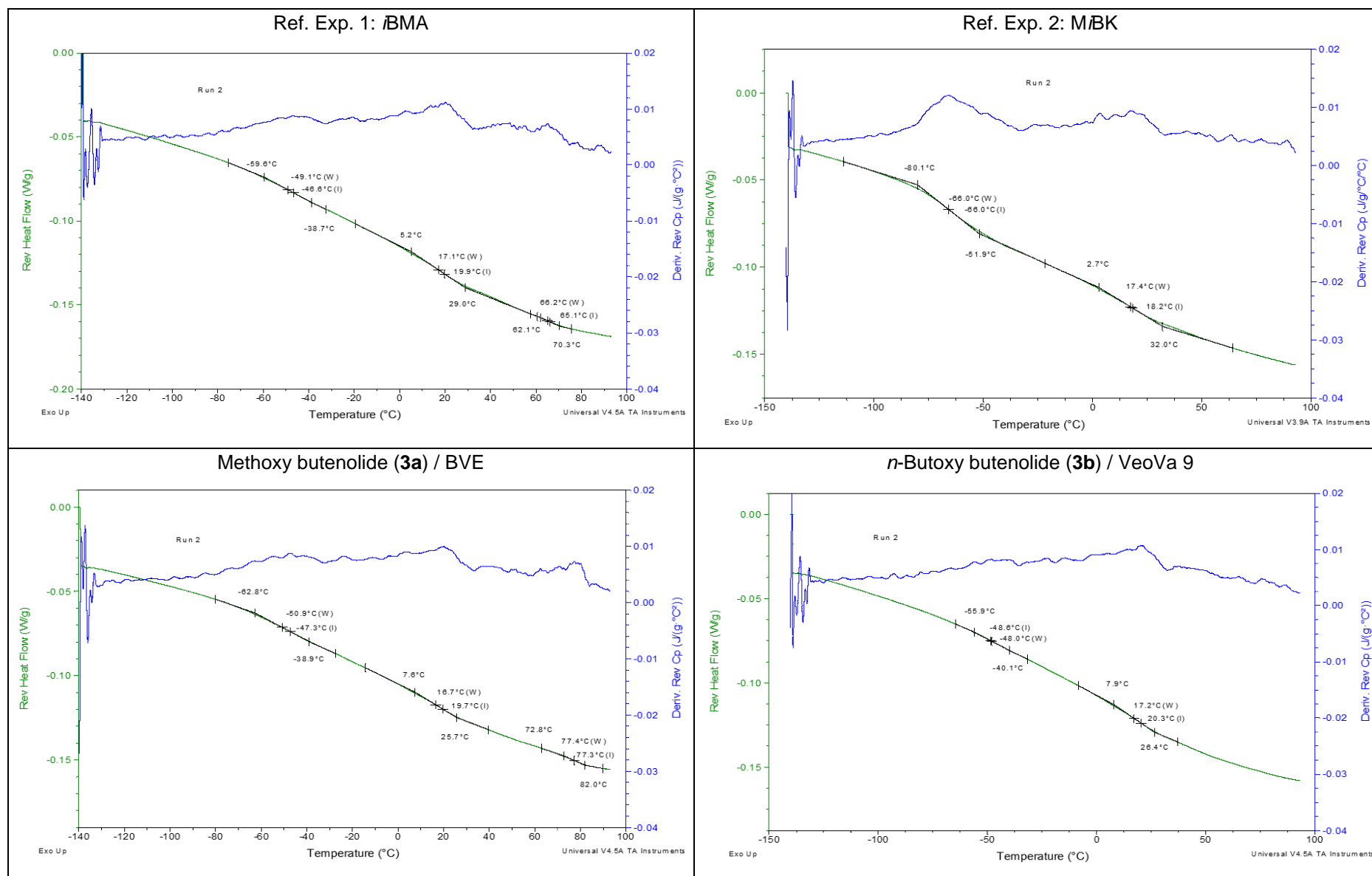
- 
- i In the PU only coating (reference experiment 2) the low temperature  $T_g$  is found at lowest value and is most pronounced, which supports the conclusion that indeed this  $T_g$  corresponds to the PTMEG soft-block phase.
  - ii The coating derived from the **3c** / BVE hybrid dispersion displays the most pronounced  $T_g$  around RT of all studied coatings.
  - iii Homopolymer  $T_g$ 's of the used co-monomers increase in the order BVE  $<$  VeoVa 9  $<$  NVP ( $-55^\circ\text{C}$ ,  $70^\circ\text{C}$ , and  $>110^\circ\text{C}$  respectively).

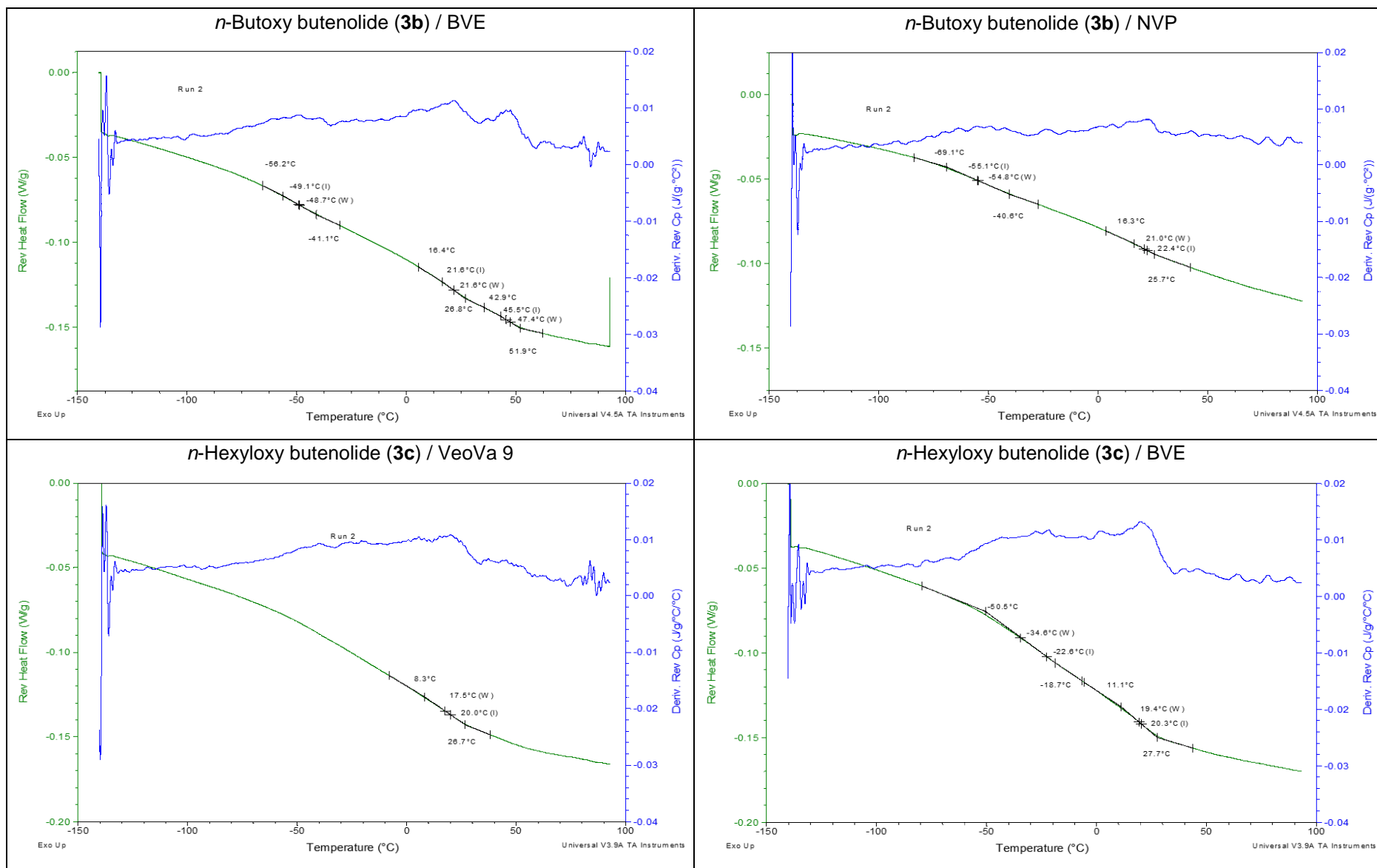
Table 2: Physical coating properties of evaluated dispersions

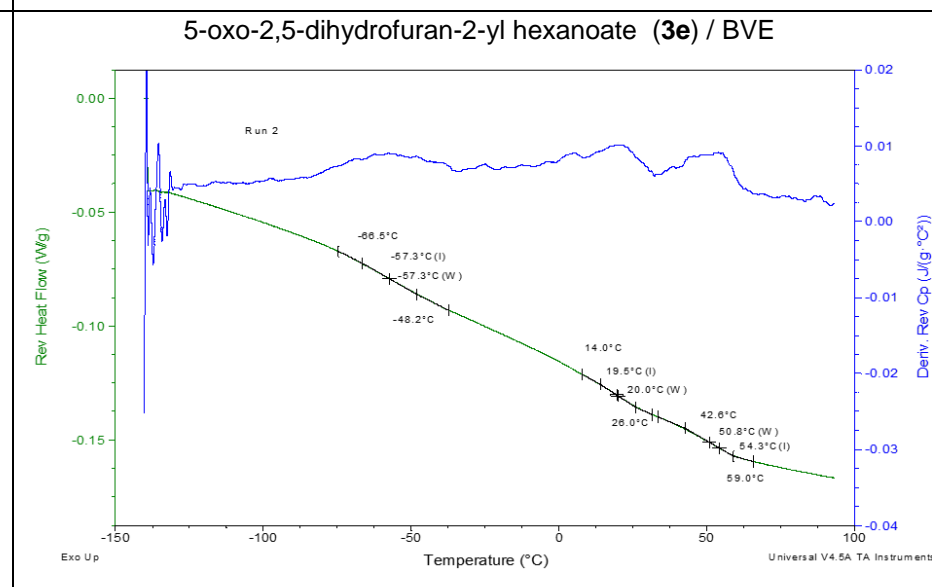
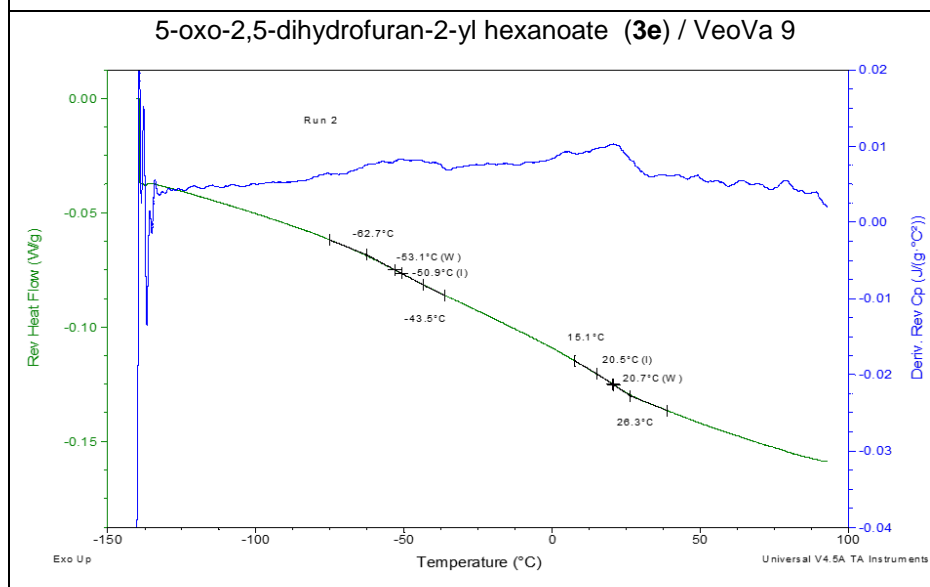
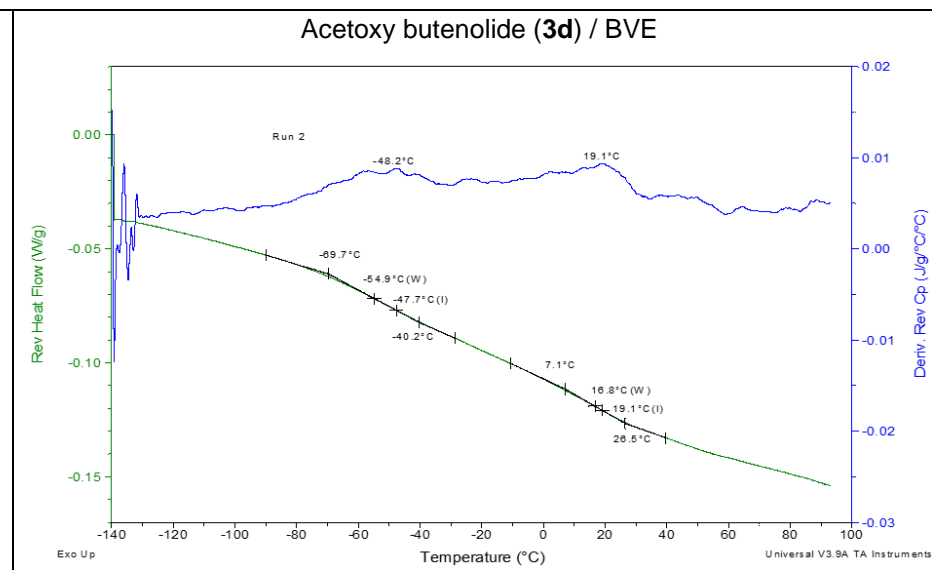
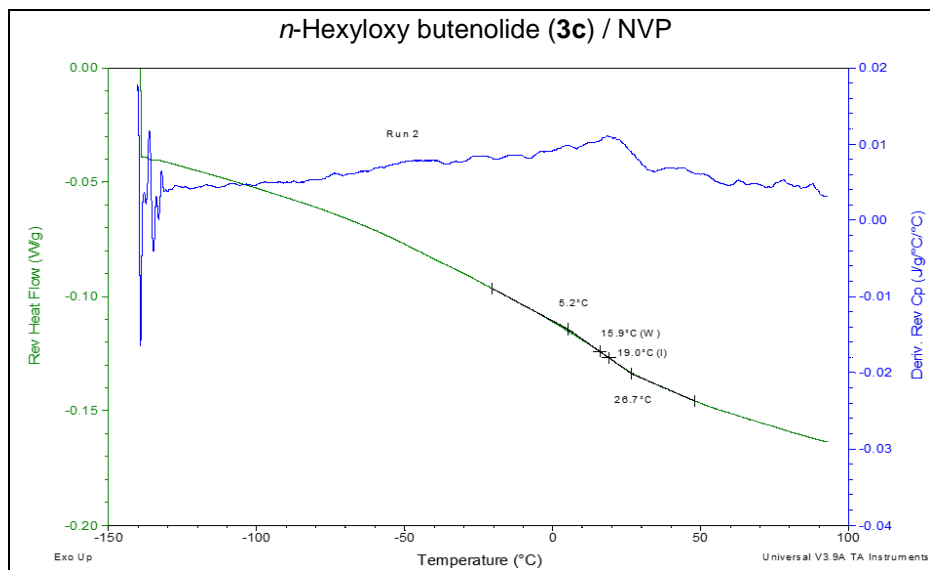
Entry	Hybrid dispersion	Appearance	Dry layer thickness	MEK dr resistance	Water resistance <sup>[i]</sup>				Knoop hardness (kg/mm <sup>2</sup> & st.dev.)	DSC			
					1h	3h	6h	+24h		Tg (W) (2 <sup>nd</sup> )	Δwt		
1	Ref. Exp. 1: /BMA	Clear film	28 μm	50	5	5	4	5	0.47 ± 0.01	-49	17	66	-0.4%
2	Ref. Exp. 2: /MBK	Clear film	16 μm	30	5	1	n.d.	1	0.54 ± 0.01	-66	17	-	-0.3%
3	<b>3a</b> / BVE	Clear film (slightly brown)	16 μm	50	3	1	n.d.	5	0.52 ± 0.02	-51	17	77	-0.5%
4	<b>3b</b> / VeoVa 9	Clear film	22 μm	30	5	4	4	5	0.40 ± 0.01	-48	17	-	-0.4%
5	<b>3b</b> / BVE	Clear film	21 μm	40	4	4	4	5	0.38 ± 0.01	-49	22	47	-0.2%
6	<b>3b</b> / NVP	Clear film	31 μm	50	5	4	4	5	1.62 ± 0.04	-55	21	-	-1.0%
7	<b>3c</b> / VeoVa 9	Clear film	24 μm	60	5	5	4	5	0.25 ± 0.01	-	18	-	-0.8%
8	<b>3c</b> / BVE	Clear film	25 μm	30	5	5	4	5	0.09 ± 0.01	-35	19	-	-0.2%
9	<b>3c</b> / NVP	Clear film	33 μm	80	5	5	4	5	0.62 ± 0.01	-	16	-	-0.5%
10	<b>3d</b> / BVE	Clear film (slightly brown)	21 μm	40	5	4	4	5	0.72 ± 0.04	-55	17	-	-0.6%
11	<b>3e</b> / VeoVa 9	Clear film	25 μm	100	5	3	3	5	0.75 ± 0.03	-53	21	-	-0.4%
12	<b>3e</b> / BVE	Clear film	19 μm	110	5	4	4	5	0.78 ± 0.05	-57	20	51	-0.3%
13	<b>3e</b> / NVP	Clear film	28 μm	160	5	3	3	5	1.78 ± 0.02	-59	21	-	-0.9%
14	<b>3f</b> / VeoVa 9	Clear film	36 μm	80	5	1	n.d.	5	1.23 ± 0.06	-	19	60	-0.1%
15	<b>3f</b> / NVP	Clear film	26 μm	160	1	n.d.	n.d.	1	3.69 ± 0.03	-58	20	63	-0.6%
16	<b>3g</b> / VeoVa 9	Clear film	36 μm	100	5	1	n.d.	5	2.08 ± 0.04	-	21	62	-0.3%
17	<b>3g</b> / BVE	Clear film	30 μm	140	5	1	n.d.	5	3.64 ± 0.03	-	21	64	-0.3%
18	<b>3g</b> / NVP	Clear film	31 μm	80	3	1	n.d.	5	5.51 ± 0.08	-61	22	62	-0.4%
19	60/40 PU / <b>3b</b> + NVP	Clear film	39 μm	100	4	4	4	5	1.83 ± 0.04	-57	20	-	-0.7%
20	50/50 PU / <b>3b</b> + NVP	Clear film	36 μm	110	4	3	2	5	3.02 ± 0.04	-57	19	-	-1.1%
21	40/60 PU / <b>3b</b> + NVP	Clear film	29 μm	70	4	1	n.d.	5	4.70 ± 0.68	-49	21	-	-1.3%

[i] 5 = no defects, 4 = matting / ring visible, 3 = micro blisters, 2 = macro blisters, 1 = wrinkling / delamination

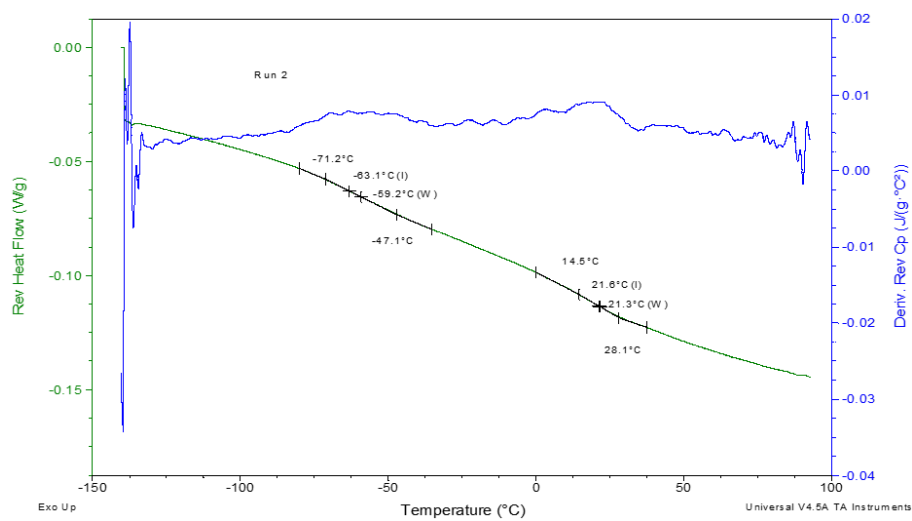
Table 3: DSC analysis of coating films derived from the PU hybrid dispersions.



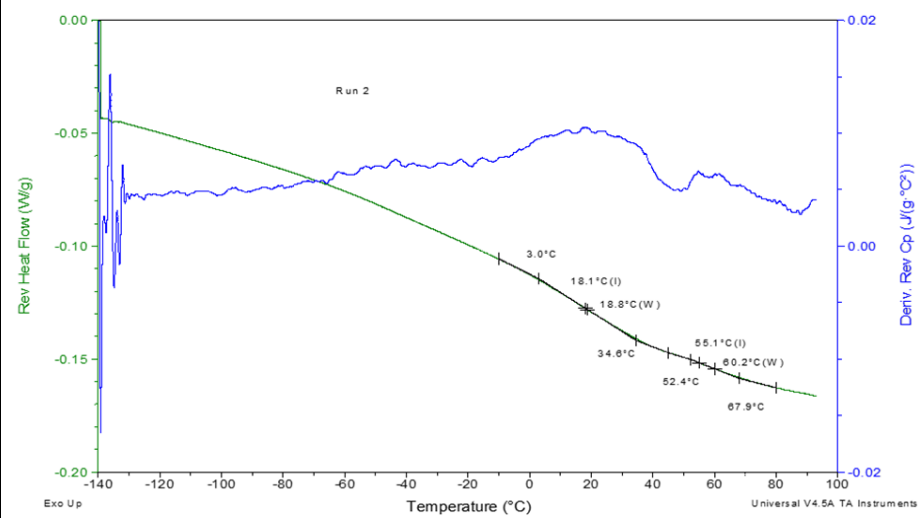




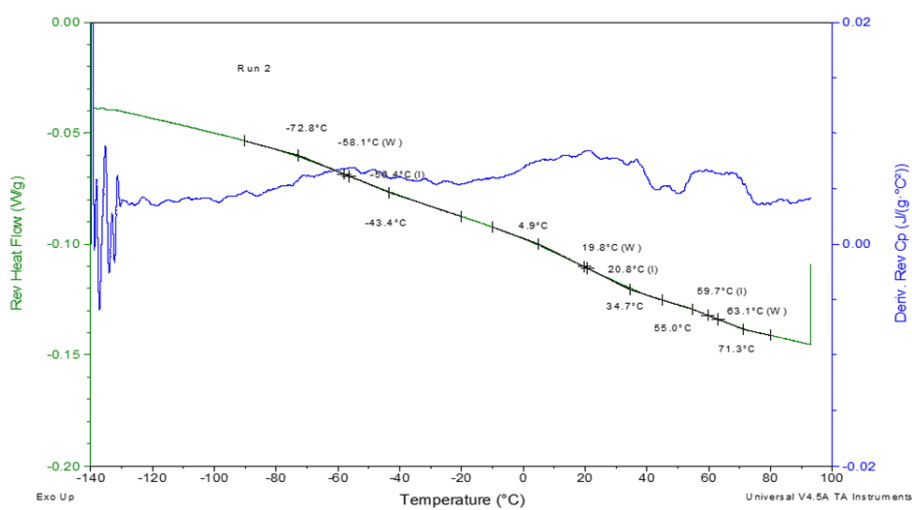
5-oxo-2,5-dihydrofuran-2-yl hexanoate (**3e**) / NVP



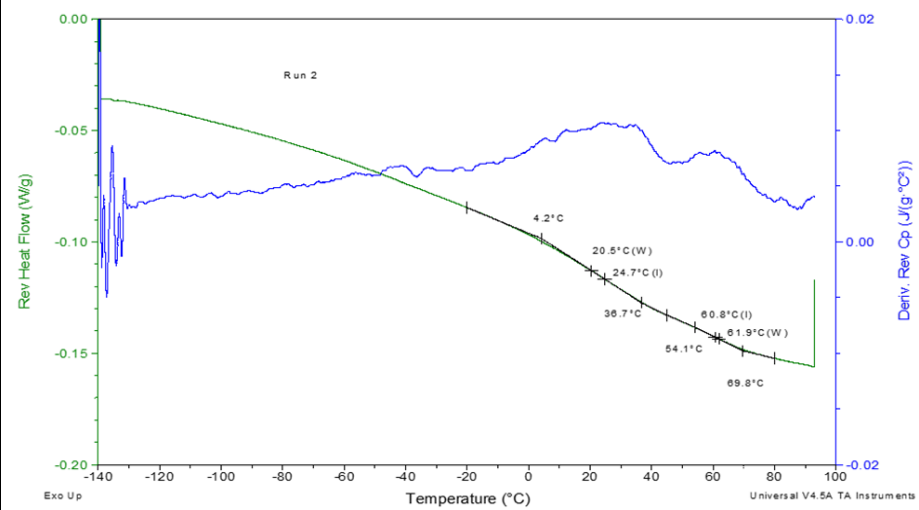
*t*-Butyl carboxy butenolide (**3f**) / VeoVa 9



*t*-Butyl carboxy butenolide (**3f**) / NVP

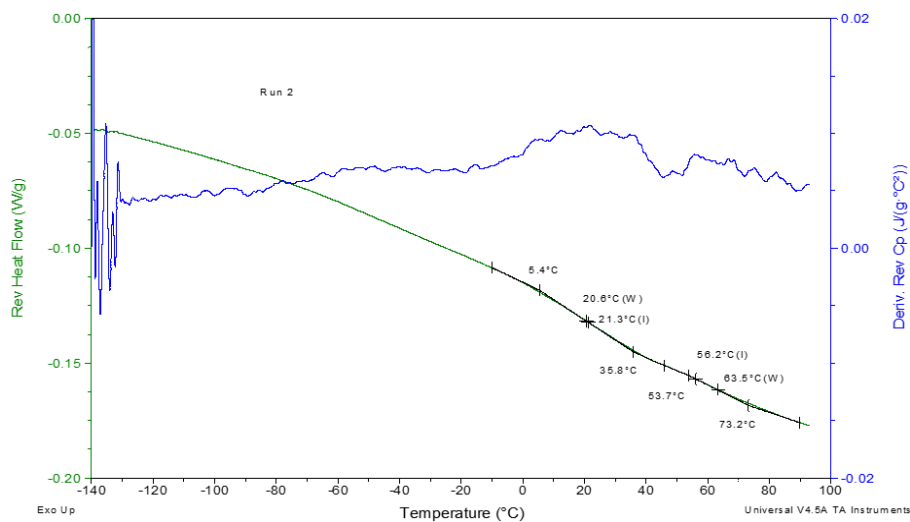


Cyclohexyl carboxy butenolide (**3g**) / VeoVa 9

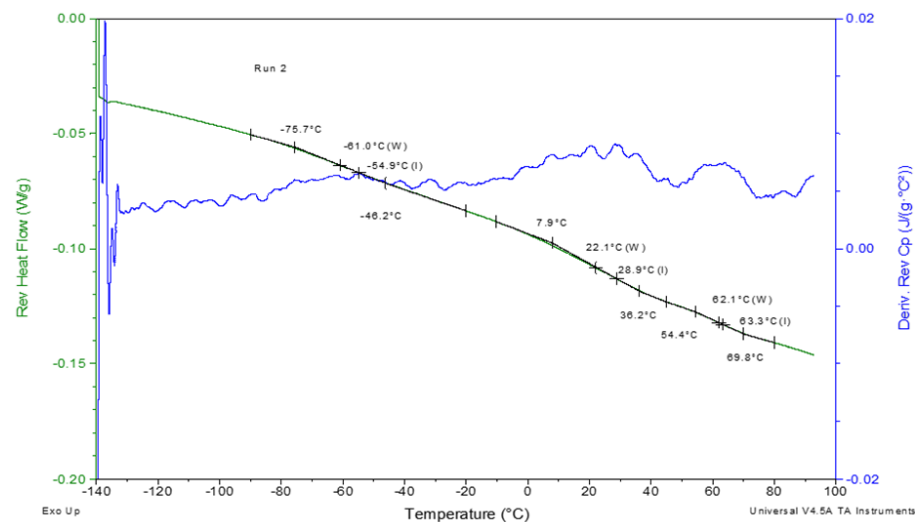




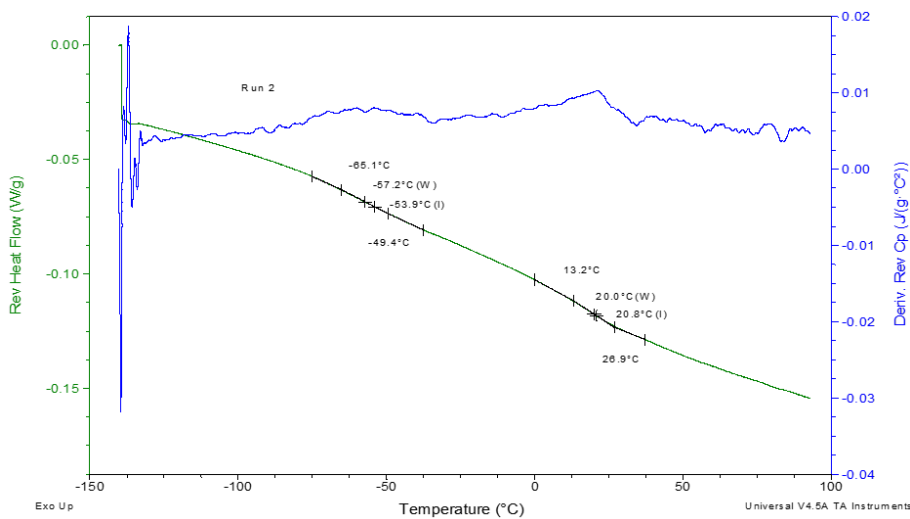
Cyclohexyl carbamoxy butenolide (**3g**) / BVE



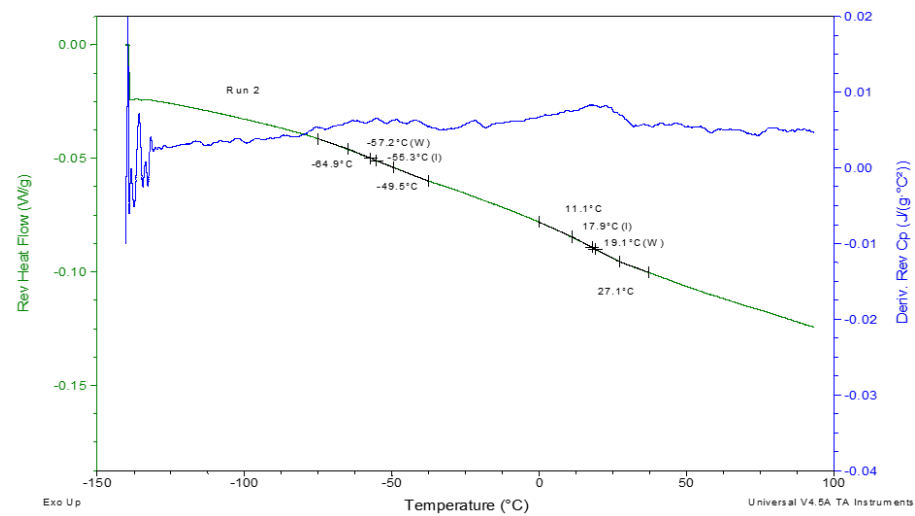
Cyclohexyl carbamoxy butenolide (**3g**) / NVP



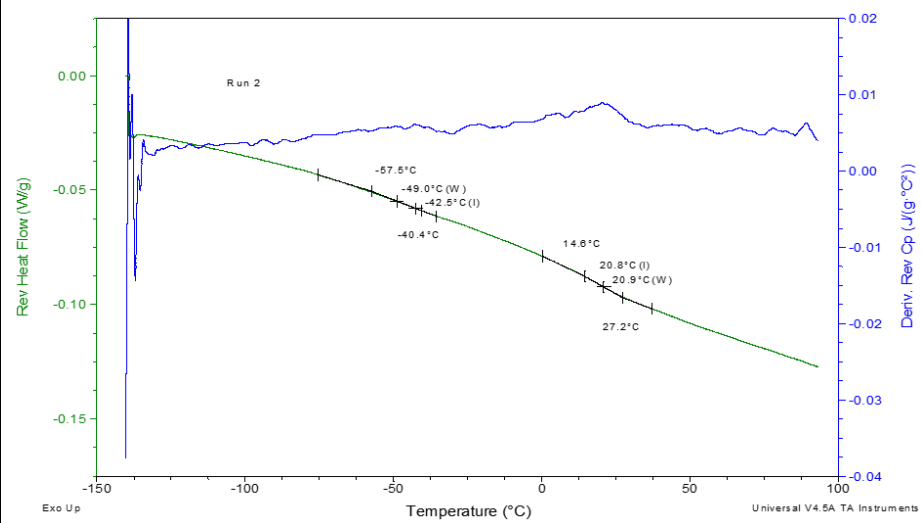
Solvent free 60/40 PU / *n*-butoxy butenolide (**3b**) + NVP



Solvent free 50/50 PU / *n*-butoxy butenolide (**3b**) + NVP



Solvent free 40/60 PU / *n*-butoxy butenolide (**3b**) + NVP



## Materials

Hydroxy butenolide (**2**) was synthesized at 100 g scale via continuous flow photooxygenation using our previously described modular flow photoreactor.<sup>3</sup> Methoxy butenolide (**3a**) and *n*-hexyloxy butenolide (**3c**) were synthesized according to Hermens *et al.*<sup>4</sup> Acetoxy butenolide (**3d**), *tert*-butyl carbonoxy butenolide (**3f**) and cyclohexyl carbamoxy butenolide (**3g**) were synthesized according to Lepage *et al.*<sup>5</sup> *n*-Butoxy butenolide (**3b**) and *n*-5-oxo-2,5-dihydrofuran-2-yl hexanoate (**3e**) were synthesized according to the methods described on page S30 and S33, respectively.

Vinyl ester of versatic acid 9 (Veova 9) was acquired from Hexion Inc. Polystyrene standards for GPC calibration was purchased from Agilent. BYK-346 was purchased from Altana AG. All other raw materials was purchased from Merck KGaA.

Dipropylene glycol dimethyl ether (DPGDME) was dried over 3Å molecular sieves for > 24 h prior to use, all other commercial raw materials were used as received.

## Experimental methods

### Analytical Methods

The following methods were used for analysis of the synthesized monomers and polyurethane / poly-butenolide hybrid dispersions.

#### *Nuclear Magnetic Resonance (NMR)*

Nuclear Magnetic Resonance spectra were measured with an Agilent Technologies 400-MR (400/54 Premium Shielded) spectrometer (400 MHz). All spectra were measured at room temperature (22–24 °C). Chemical shifts for the specific NMR spectra were reported relative to the residual solvent peak [in ppm; CDCl<sub>3</sub>: δ<sub>H</sub> = 7.26; CDCl<sub>3</sub>: δ<sub>C</sub> = 77.16]. The multiplicities of the signals are denoted by *s* (singlet), *d* (doublet), *t* (triplet), *q* (quartet), *m* (multiplet), *br s* (broad signal), *app* (apparent). All <sup>13</sup>C-NMR spectra are <sup>1</sup>H-broadband decoupled.

#### *High Resolution Mass Spectrometry (HR-MS)*

High-resolution mass spectrometric measurements were performed using a Thermo Scientific LTQ OrbitrapXL spectrometer with ESI ionization. The molecule-ion (as sodium adduct, M+Na<sup>+</sup>) is given in *m/z*-units.

#### *Solid Content (SC)*

Solid contents of monomers and PU / poly-butenolide hybrid dispersions were measured in accordance to ISO 3251. A 1.0 gram sample was placed in a 20 mL aluminium weighing dish and heated for 1 h at 125°C in a ventilated oven. The remaining mass was determined gravimetrically and the fraction remaining (solids) according to the original sample size was calculated as percentage. The average of duplicate measurements is reported.

#### *pH*

pH's of the PU / poly-butenolide hybrid dispersions were measured using a Mettler Toledo FiveGo™ pH / mV portable meter fitted with a Mettler-Toledo InLab® Routine Pro pH electrode. Hamilton DuraCal pH buffer solutions (pH 4.01 / 7.00 / 10.01) were used for calibration.

#### *Particle size (d<sub>43</sub>)*

PU / poly-butenolide hybrid dispersion particle sizes were measured by dynamic light scattering using a Malvern Panalytical Zetasizer Nano ZS. Samples were diluted using demineralized water and measured at 25°C in disposable polystyrene macro cuvettes (2.5 – 4.5 mL, 10 mm path length). 15 consecutive measurements were performed using a polymer refractive index of 1.59 and absorption of 0.010. The modelled volume-weighted mean particle diameter (*d*<sub>43</sub>) is reported.

### *Molecular Weight Distribution (MWD)*

Molecular weight distributions of the PU / poly-butenolide hybrid dispersions were determined by gel permeation chromatography using a Waters Alliance e2695 separations module + Waters 2414 refractive index detector. Separation was accomplished using a PLgel MIXED-A (7.5 x 300 mm, 20  $\mu$ m) column in combination with THF/water/AcOH/LiBr (96.4/3.0/0.5/0.1 wt ratio) as eluent. Sample solutions were prepared at 4 mg polymer per mL eluent and were filtered over 0.45  $\mu$ m PTFE syringe filters prior to measuring. The chromatograms were recorded by injecting 50.0  $\mu$ L sample solution, at a flow rate of 1.0 mL/min and a temperature of 40  $^{\circ}$ C (both column and detector). The chromatograms were converted to molecular weight distributions using polystyrene standards (at peak molecular weights (Mp): 6,850,000; 3,950,000; 2,250,000; 735,500; 330,000; 193,000; 72,450; 22,000; 9,200; 2,960; and 580 g/mol) for calibration.

### *(Scanning) Transmission Electron Microscope ((S)TEM)*

(S)TEM imaging was performed using a Thermo Talos F200X FEG-TEM (200kV). TEM images are recorded at 5 nA using a bright field (BF) detector. STEM was performed at 250 pA using a BF-detector, a high-angle annular dark-field (HAADF) detector, and an energy-dispersive X-ray spectroscopy (EDX) detector (SuperX EDX).

The hybrid dispersion particles were analyzed by diluting the dispersions 30x followed by dropcasting on carbon film copper grid (200 mesh) and leaving them to dry for 18h at RT. For unstained analysis the dispersions were diluted with demineralize water. For stained analysis, the dispersions were diluted with 0.4 wt% aqueous phosphotungstic acid (PTA).

Paint films were analyzed by producing, applying, and drying the corresponding coatings as described in below chapter with the only exception that isopropyl alcohol cleaned polypropylene panels were used as substrate. After drying, a small section of the coating was removed from the substrate and 50-70 nm coupes were made using a cryo-ultramicrotome (Leica UC7) at -50 $^{\circ}$ C followed by wet collection of the coupes in DMSO/water (1/1, m/m). The coupes were measured using holey carbon film copper grid (300 mesh) or carbon film copper grid (200 mesh) as support. The coupes were measured as such and after PTA staining (by exposing the coupe to 2.0 wt% PTA (aq) for 5 min followed by thorough rinsing).

## Storage stability of hybrid dispersions

1 day after the synthesis of the PU / poly-butenolide hybrid dispersion the solid content, pH, and particle size were measured. The dispersions were stored in a dark cabinet at room temperature for 1 month followed by re-measuring these properties. In addition, photographs of the hybrid dispersions were taken on the day of synthesis, after 1 day, and after 1 month storage for a visual comparison (photographs are not color corrected). For the dispersions that were 1 month RT stable (still dispersions), the molecular weight distribution is determined, and coatings were formulated for physical property evaluation.

## Coating formulation, application & drying

The hybrid dispersions that passed 1 month RT storage were formulated to clearcoats by addition of 1 wt% BYK-346 on resin solids (addition of 0.04 g BYK-346 to 15.0 g dispersion). The mixture was stirred for 10 min using a magnetic stirrer bar at 300 rpm followed by overnight storage. The next day, 200  $\mu$ m wet films were applied on isopropyl alcohol degreased glass panels and the coatings were dried horizontally for 1 h followed by 7 days vertical drying in a fume hood under ambient conditions.

## Coating film properties

After 7 days vertical drying the resulting coatings were evaluated on the following physical coating properties.

### *Dry layer thickness (DFT)*

The dry layer thickness (according to ISO 2808) of the coatings were measured using the Heidenhain VRZ 402 apparatus calibrated with calibration foil. A spot (10 mm diameter) of coating was removed from the glass substrate. The measuring probe was placed on the bare substrate and the measured

value was tared, next, three layer thickness measurements were performed. This procedure was performed at three different locations on the substrate (9 measurements in total), the average value is reported.

#### *Solvent resistance (MEK dr resistance)*

Methyl ethyl ketone double rub (MEK dr) resistances were measured by rubbing the coating back and forth (5 cm) with a cloth soaked in 2-butanone (MEK) applying 10 N downward pressure. The number of double rubs (= 1x forth and 1x back) until the coating fails (dissolution) were counted with a maximum of 200 double rubs. When the coating withstands >200 double rubs, the film appearance is described (e.g. dulling, staining, or any other change in appearance).

#### *Water resistance*

Water resistance (according to ISO 2812-4:2007 part 4) were measured by placing a droplet of demineralized water on the coating and covering it with a watch glass. After 60 min, the water droplet was wiped off and the effect on the coating was determined visually on a scale of 5 to 1:

- 5 = no defects
- 4 = matting / ring visible
- 3 = micro blisters
- 2 = macro blisters
- 1 = wrinkling / delamination

After the 60 min inspection, a new droplet was placed on the same location. The inspection was repeated after a total of 3 h and 6 h water exposure. After the 6 h inspection, the coating was left exposed to air, after 24 h a final inspection was performed to judge if the coating recovers.

#### *Hardness (Knoop)*

Knoop hardness's (related to ASTM D1474, method A) were measured using the Fischerscope HM 2000 Xyp equipment calibrated using poly(methyl methacrylate) (PMMA). The indentation hardness was determined by measuring the indentation depth after applying a 98 mN (10 gram) load for 18 sec using a diamond pyramidal shaped indenter (longitudinal angles: 172°30' and transverse angles: 130°) to the dried coating. Five consecutive measurements on different predefined spots were performed making sure the indentation depth does not exceed 75% of the coating thickness. The Knoop hardness was calculated by:

$$H_k = \frac{P}{C \times d^2}$$

Where:

- $H_k$  = Knoop hardness in kg/mm<sup>2</sup>.
- $P$  = load applied on the indenter in kg.
- $C$  = indenter correction constant: 65.438.
- $d$  = indentation depth in mm.

#### *Glass transition temperature (Tg)*

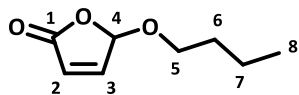
Tg's were measured by Differential Scanning Calorimetry (DSC) using TA Instruments DSC Q2000 equipment. A DSC cup, filled with 6 +/- 1 mg dry coating sample, and an empty DSC reference cup were heated in the differential scanning calorimeter in a modulated way (+/- 1°C every 40 sec) from -140°C to 100°C at 5°C/min in two consecutive runs using helium (50 mL/min) as purge gas. The Tg was calculated both at the point of inflection (Tg(I)) and by half width (Tg(W)) using the reversing heat flow curve, the Tg(W) in the second run was reported.

Potential loss of volatiles over the two consecutive DSC runs were determined gravimetrically.

## Synthetic Procedures & Results

### Butenolide synthesis

*n*-Butoxy butenolide (**3b**):



5-butoxyfuran-2(5H)-one

Chemical Formula: C<sub>8</sub>H<sub>12</sub>O<sub>3</sub>

Exact Mass: 156,08

Molecular Weight: 156,18

Hydroxy butenolide (**2**) (5 g, 50 mmol, 1 eq.) was dissolved in *n*-butanol (20 mL, 2.5 M) and heated at reflux for 4 h. The conversion was followed by <sup>1</sup>H-NMR until all substrate was consumed. The solvent was evaporated *in vacuo* and the crude was purified by column chromatography (silica gel, *n*-pentane : ethyl acetate / 90:10) yielding pure **3b** (5.8 g, 37 mmol, 74%) as a colorless oil.

<sup>1</sup>H-NMR (400 MHz, Chloroform-d) δ 7.20 (d, J = 5.7 Hz, 1H, H-3), 6.21 (d, J = 5.7 Hz, 1H, H-2), 5.91 (s, 1H, H-4), 3.86 (dt, J = 9.3, 6.5 Hz, 1H, H-5), 3.67 (dt, J = 9.3, 6.7 Hz, 1H, H-5), 1.61 (m, 2H, H-6), 1.37 (m, 2H, H-7), 0.92 (t, J=7.1 Hz, 2H, H-8).

<sup>13</sup>C-NMR (101 MHz, Chloroform-d) δ 170.68 (C-1) 150.48 (C-3), 125.11 (C-2), 103.52 (C-4), 70.46 (C-5), 31.60 (C-6), 19.17 (C-7), 13.85 (C-8).

HRMS ESI pos [M+Na<sup>+</sup>] calc. for C<sub>8</sub>H<sub>12</sub>O<sub>3</sub>Na<sup>+</sup>: 179.0679, found: 179.0678.

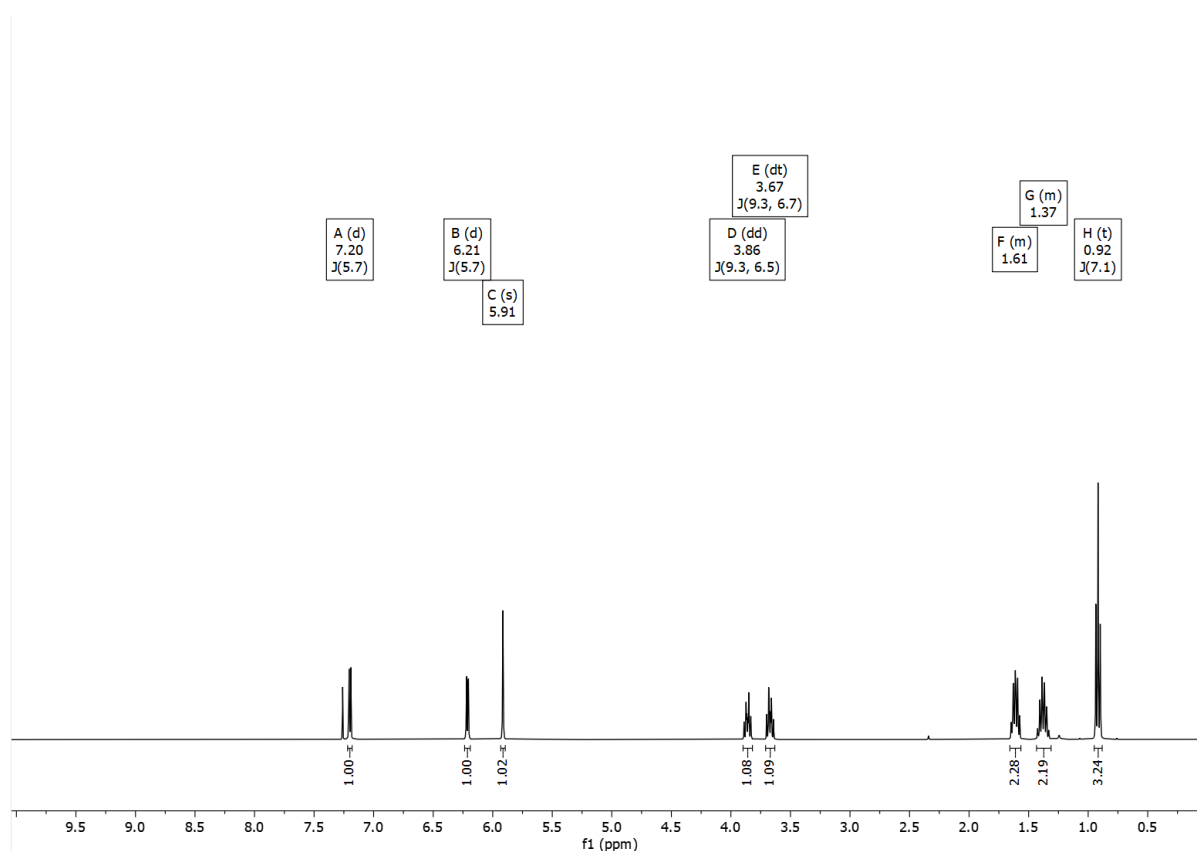
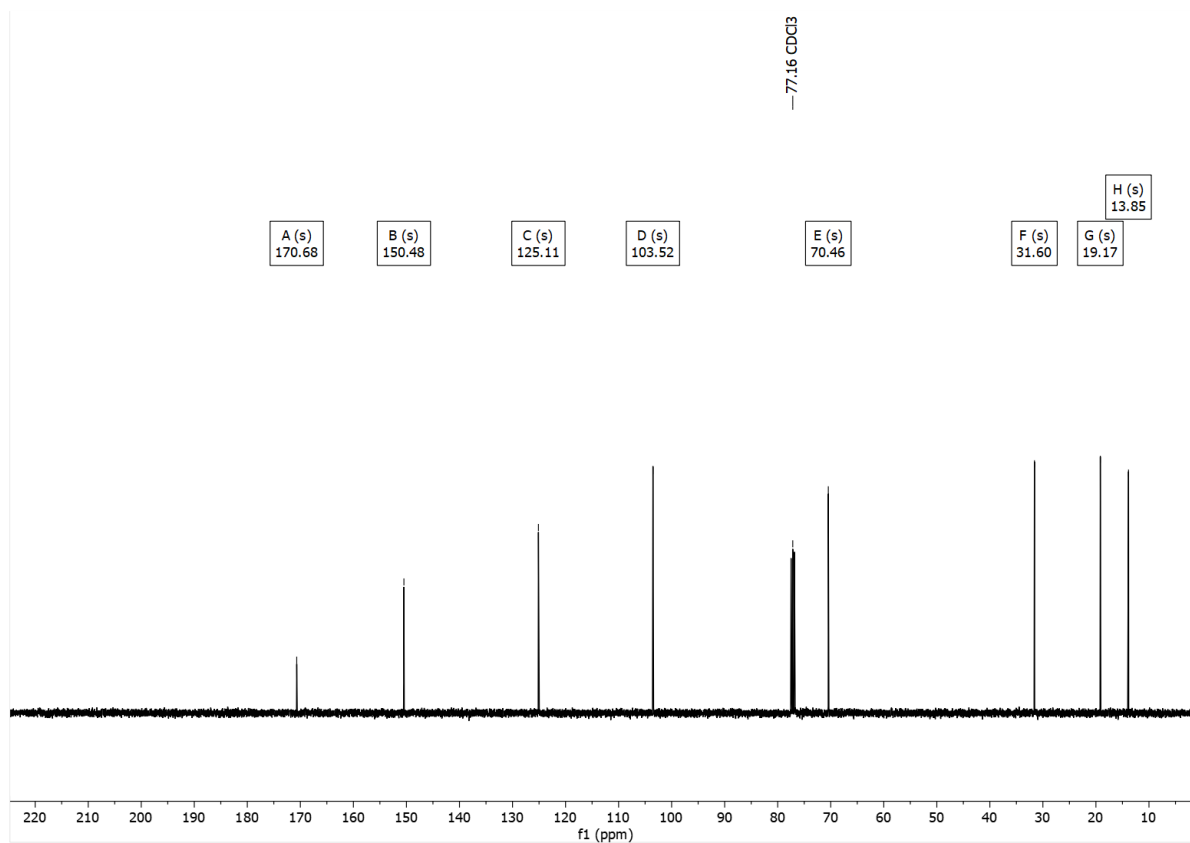
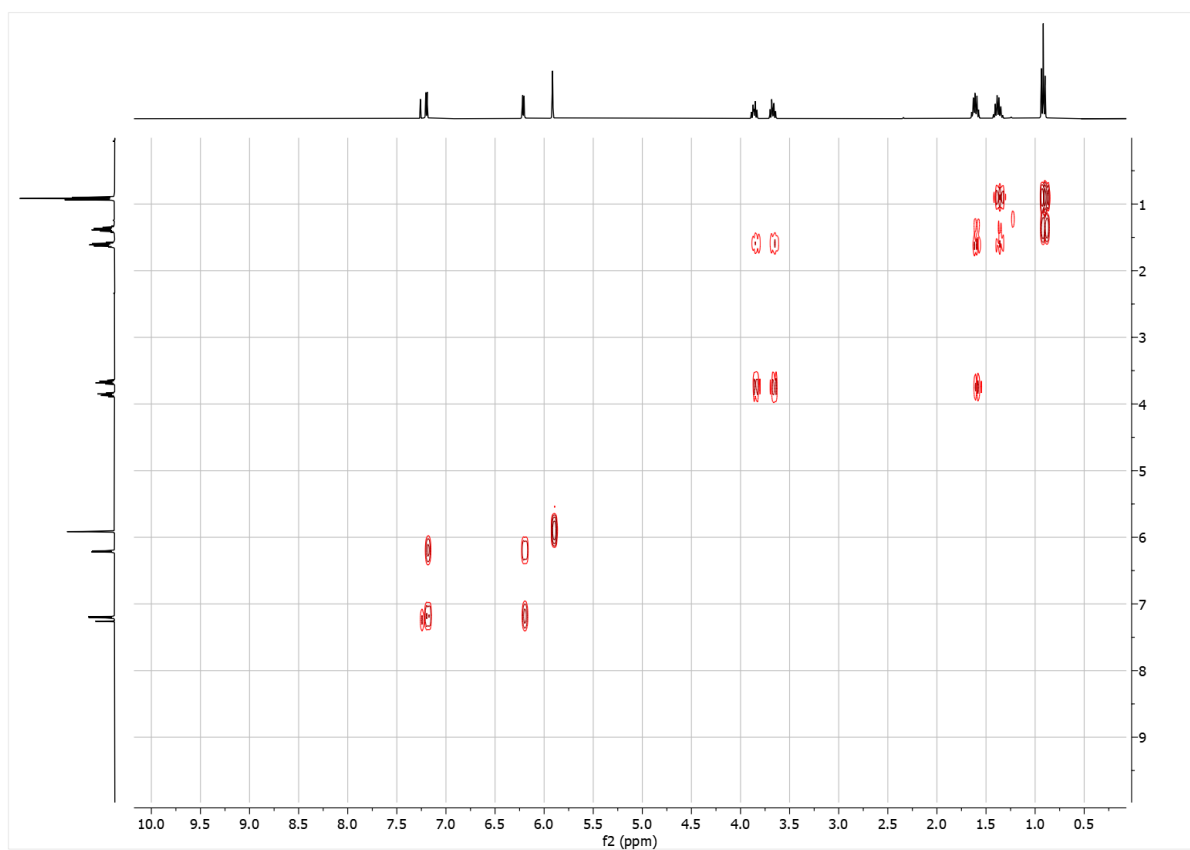


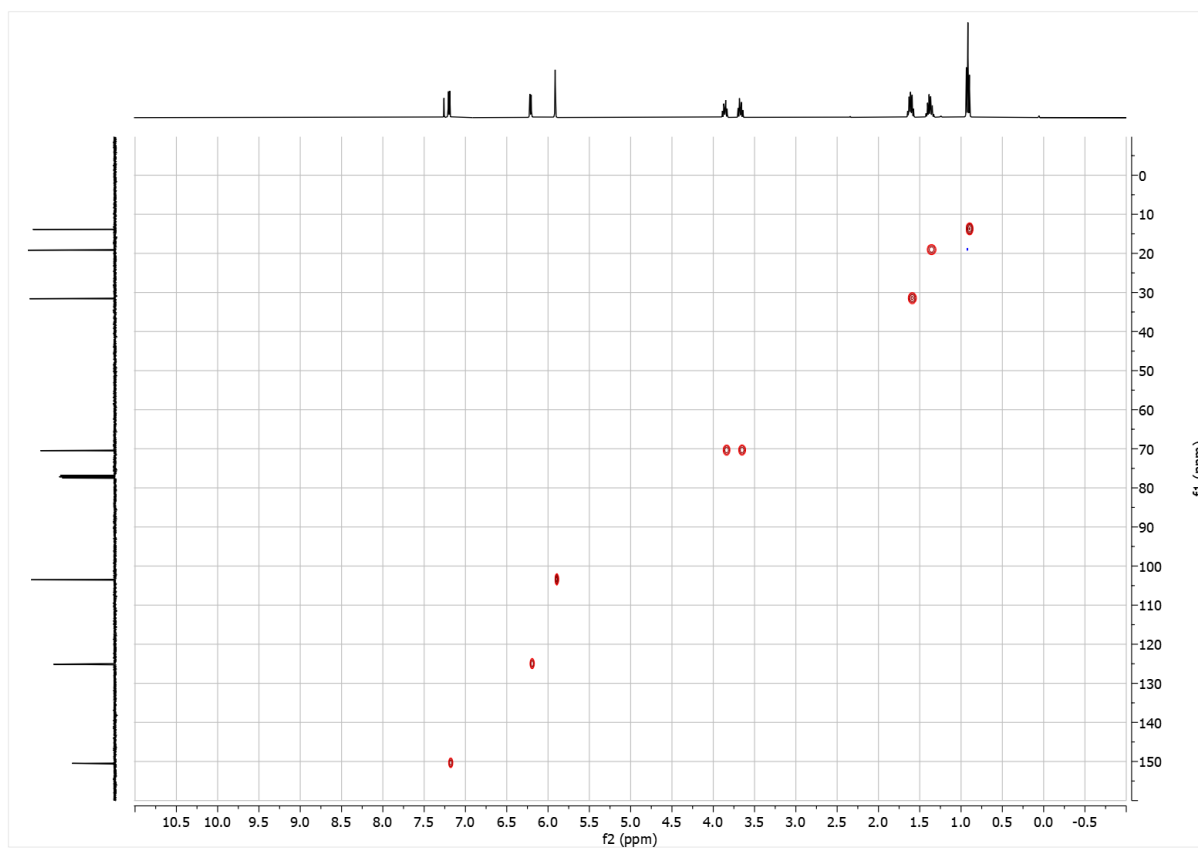
Figure 10: <sup>1</sup>H NMR spectrum *n*-butoxy butenolide (**3b**)



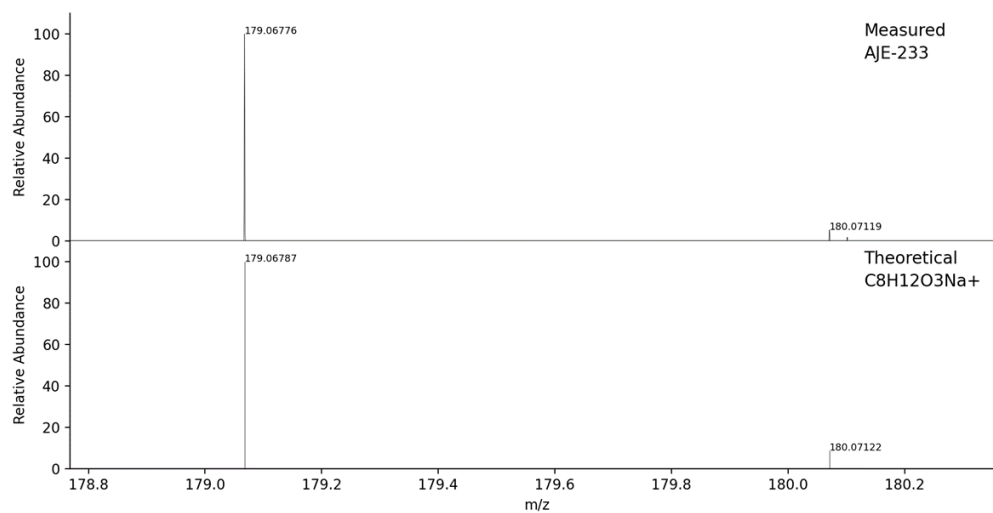
**Figure 11:**  $^{13}\text{C}$  NMR spectrum *n*-butoxy butenolide (3b)



**Figure 12:** COSY NMR spectrum *n*-butoxy butenolide (3b)



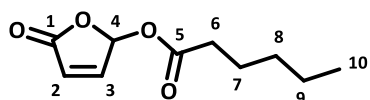
**Figure 13:** HSQC NMR spectrum *n*-butoxy butenolide (**3b**)



**Figure 14:** HRMS analysis of *n*-butoxy butenolide (**3b**)



5-Oxo-2,5-dihydrofuran-2-yl hexanoate (**3e**):



5-oxo-2,5-dihydrofuran-2-yl hexanoate

Chemical Formula: C<sub>10</sub>H<sub>14</sub>O<sub>4</sub>

Exact Mass: 198,09

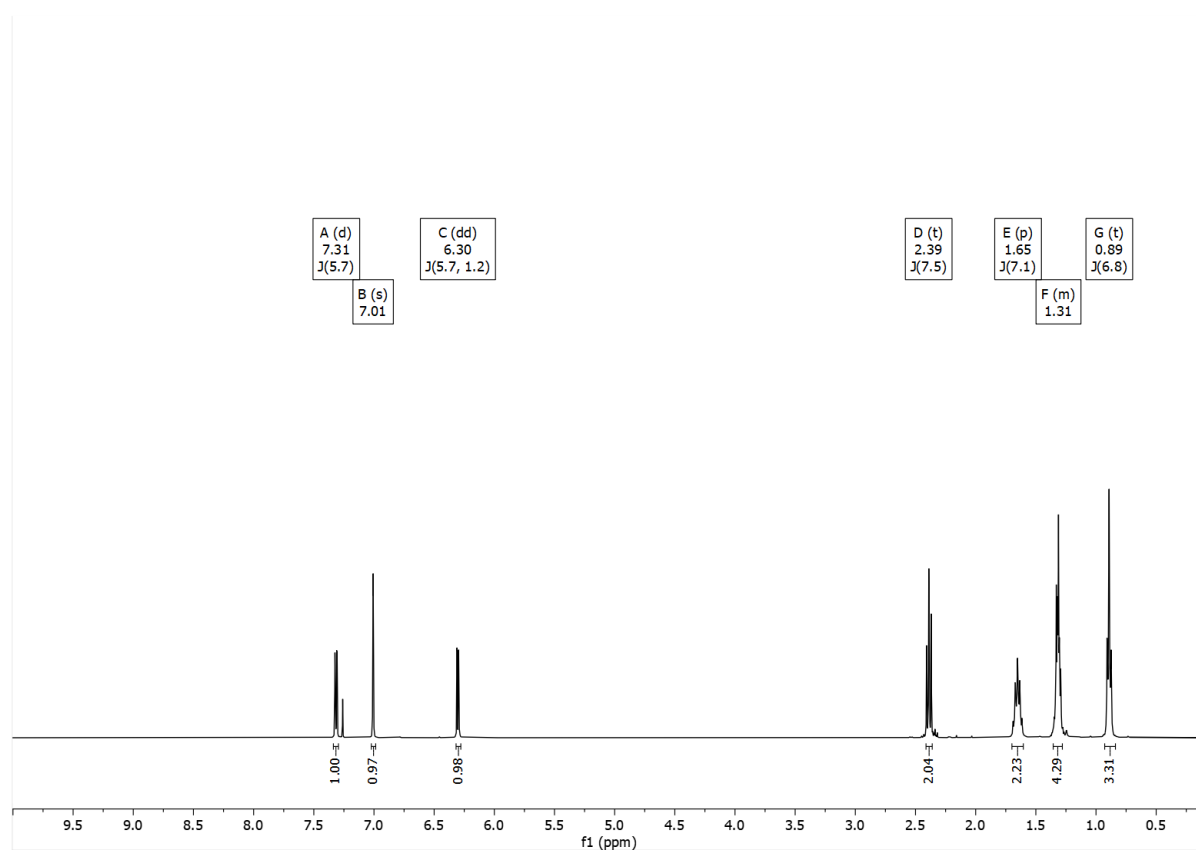
Molecular Weight: 198,22

Hydroxy butenolide (**2**) (5.0 g, 50 mmol, 1 eq.) was dissolved in DCM (80 mL, 0.63 M) in a flask under nitrogen atmosphere and was subsequently cooled in an ice bath. Hexanoic anhydride (10.7 g, 50 mmol, 1 eq.) was added, followed by *N,N*-dimethylaminopyridine (0.3 g, 2.5 mmol, 0.05 eq.). The mixture was stirred for 2 h and then allowed to warm up to room temperature. After quenching by methanol (2 eq.) and stirring for 10 min, the mixture was concentrated *in vacuo*. The crude compound was purified by column chromatography (silica gel, *n*-pentane : ethyl acetate / 85:15) to afford pure **3e** (7.5 g, 38 mmol, 76%) as a colorless oil.

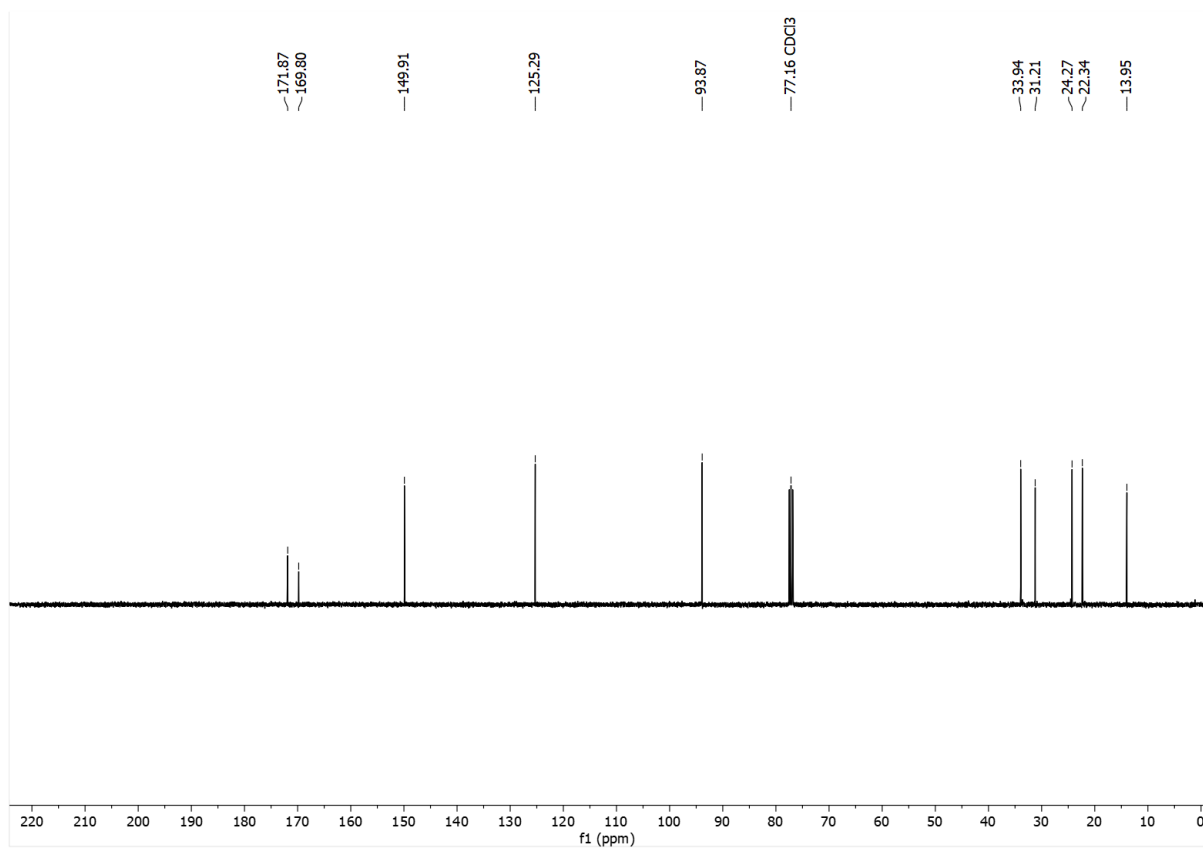
<sup>1</sup>H-NMR (400 MHz, Chloroform-d) δ 7.32 (d, J = 5.7 Hz, 1H, H-3), 7.01 (s, 1H, H-4), 6.31 (dd, J = 5.7 Hz, 12 Hz, 1H, H-2), 2.39 (t, J = 7.5 Hz, 2H, H-6), 1.65 (p, J = 7.1 Hz, 2H, H-7), 1.31 (m, 4H, H-8 and H-9), 0.89 (t, J = 6.8 Hz, 3H, H-10).

<sup>13</sup>C-NMR (101 MHz, Chloroform-d) δ 171.87 (C-5), 169.80 (C-1), 149.91 (C-3), 125.29 (C-2), 93.87 (C-4), 33.94 (C-6), 31.21 (C-8), 24.27 (C-7), 22.34 (C-9), 13.95 (C-10).

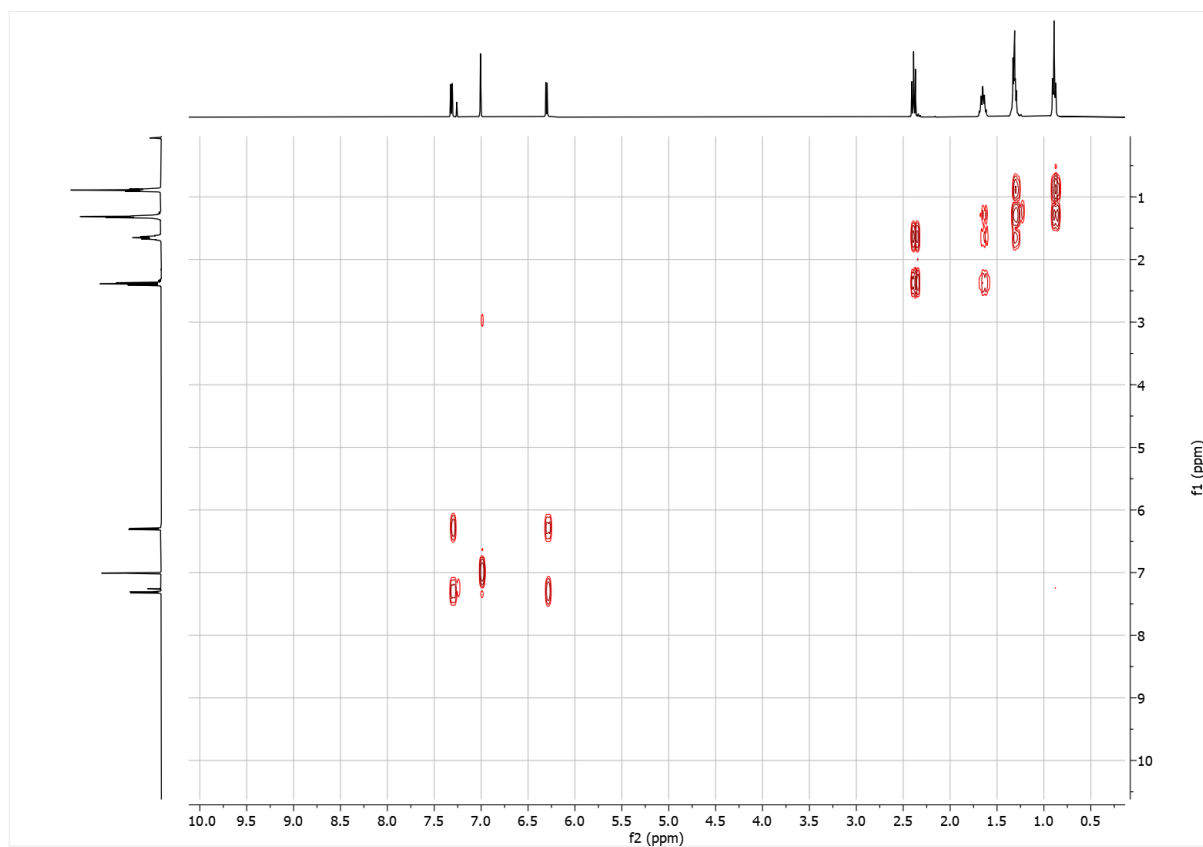
HRMS ESI pos [M+Na<sup>+</sup>] calc. for C<sub>10</sub>H<sub>14</sub>O<sub>4</sub>Na<sup>+</sup>: 221.0784, found: 221.0786.



**Figure 15:** <sup>1</sup>H NMR spectrum 5-oxo-2,5-dihydrofuran-2-yl hexanoate 5-oxo-2,5-dihydrofuran-2-yl hexanoate (**3e**)

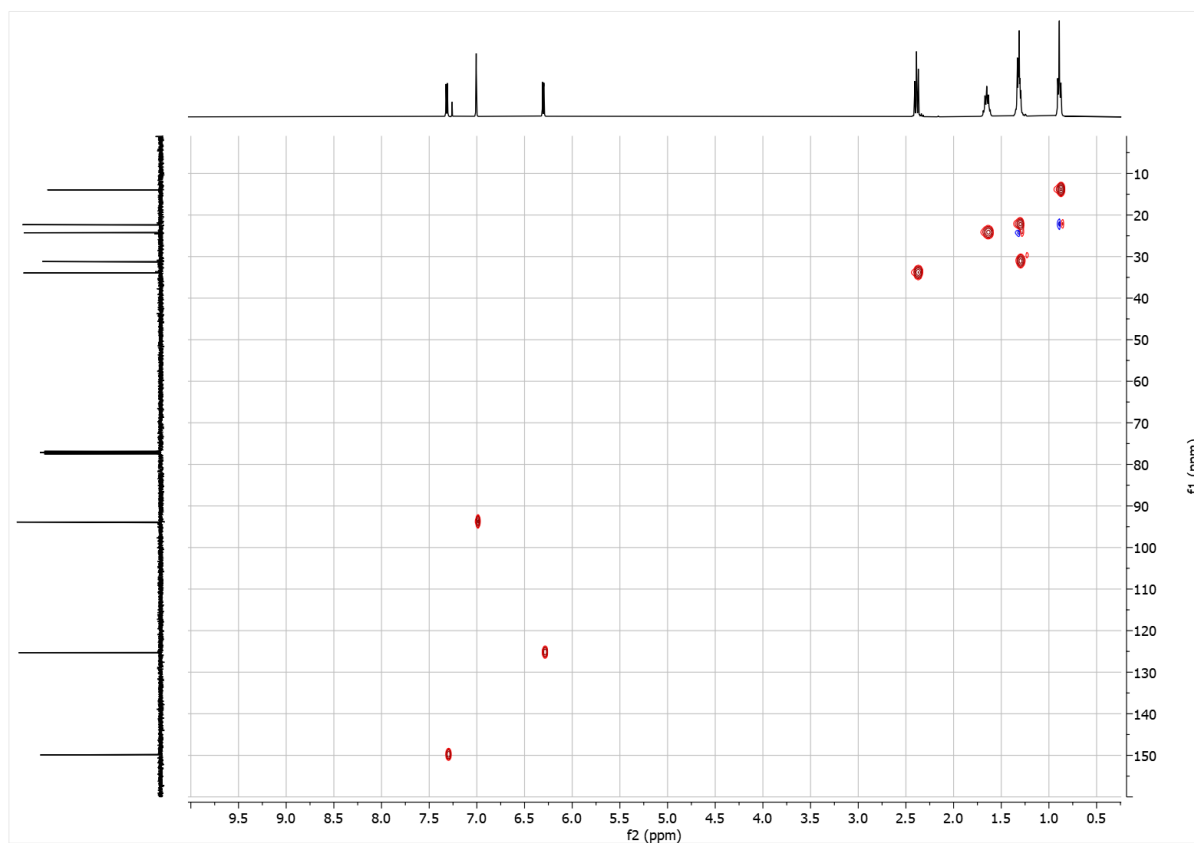


**Figure 16:** <sup>13</sup>C NMR spectrum 5-oxo-2,5-dihydrofuran-2-yl hexanoate 5-oxo-2,5-dihydrofuran-2-yl hexanoate (**3e**)

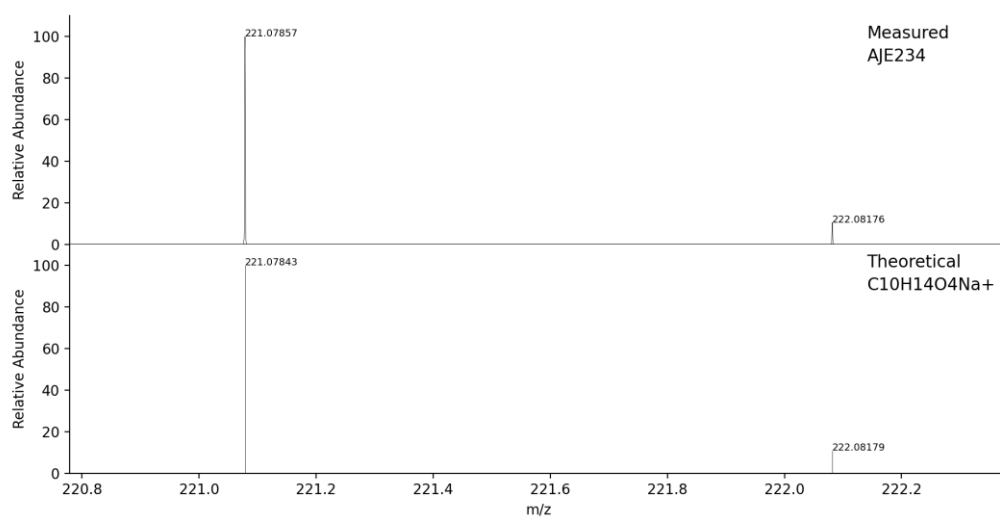


**Figure 17:** COSY NMR spectrum 5-oxo-2,5-dihydrofuran-2-yl hexanoate 5-oxo-2,5-dihydrofuran-2-yl

hexanoate (**3e**)



**Figure 18:** HSQC NMR spectrum 5-oxo-2,5-dihydrofuran-2-yl hexanoate 5-oxo-2,5-dihydrofuran-2-yl hexanoate (**3e**)



**Figure 19:** HRMS analysis of 5-oxo-2,5-dihydrofuran-2-yl hexanoate 5-oxo-2,5-dihydrofuran-2-yl hexanoate (**3e**)

## 60/40 wt ratio, solvent containing PU / poly-butenolide hybrid dispersions

All solvent containing PU / poly-butenolide hybrid dispersions were made using the synthetic procedure described underneath. The synthesized PU pre-polymer was stored for maximum one night. This enabled the synthesis of all three hybrid dispersions using one butenolide entry with consistent PU quality in one day.

### *Synthetic procedure*

130.0 g (130.0 mmol) PTMEG, Mn 1000 (**7**), 13.64 g (101.9 mmol) DMPA (**6**), and 75.88 g (341.4 mmol) IPDI (**8**) were charged in a reactor and heated under N<sub>2</sub> atmosphere using 85°C oil. After the reaction exotherm (92-93°C), the temperature of the heating oil was gradually increased to 100°C. The batch is reacted for 4 h followed by 54.9 g DPGDME addition and cooling. At 70°C, the 80% SC PU solution (**9**) was transferred to a 250 mL glass jar, the NCO% was measured by Bu<sub>2</sub>NH back titration (3.04 – 3.21% NCO = 104 – 102% conversion), and the pre-polymer was stored overnight.




The next day, 12.5 g viscous PU-solution (**9**) was transferred to a 50 mL vial using a spatula and blended with 6.67 g monomer mixture (using the monomer weights listed in the paragraphs below) providing a 60/40 PU/ vinyl-monomer wt ratio). 0.47 g (4.7 mmol) TEA (= 100% neutralization of the PU carboxylic acid groups) was added followed by manual mixing for 5 min used a spatula. Next, 12.6 g of above neutralized PU / monomer solution (at room temperature) was added to 26.0 g demineralized and deoxidized (by 5 min N<sub>2</sub> bubbling) water (at room temperature) while applying stirring using a “dumbbell shaped” magnetic stirring bar at 500 rpm (see reactor set-up on the right). 0.67 g 20 wt% (2.2 mmol) EDA (aq) was added dropwise as chain extender for the NCO groups (70 mol% chain extension of residual isocyanate groups). The free radical polymerization of the butenolide co-monomer mixture was initiated by addition of 0.05 g, 70 wt%, (0.4 mmol) *t*BuOOH (aq) and a freshly prepared solution of 22 mg (0.1 mmol) sodium ascorbate + 0.26 mg (9.4·10<sup>-4</sup> mmol) FeSO<sub>4</sub>·7H<sub>2</sub>O dissolved in 0.22 mL water. The reaction exotherm was recorded and an additional portion of the radical initiator redox couple was added as mob-up 30 min after the first addition. 30 min after the mob-up, the reactor lid was replaced by a conventional screwcap and the dispersion was stored in the glass jar in which it was synthesized.

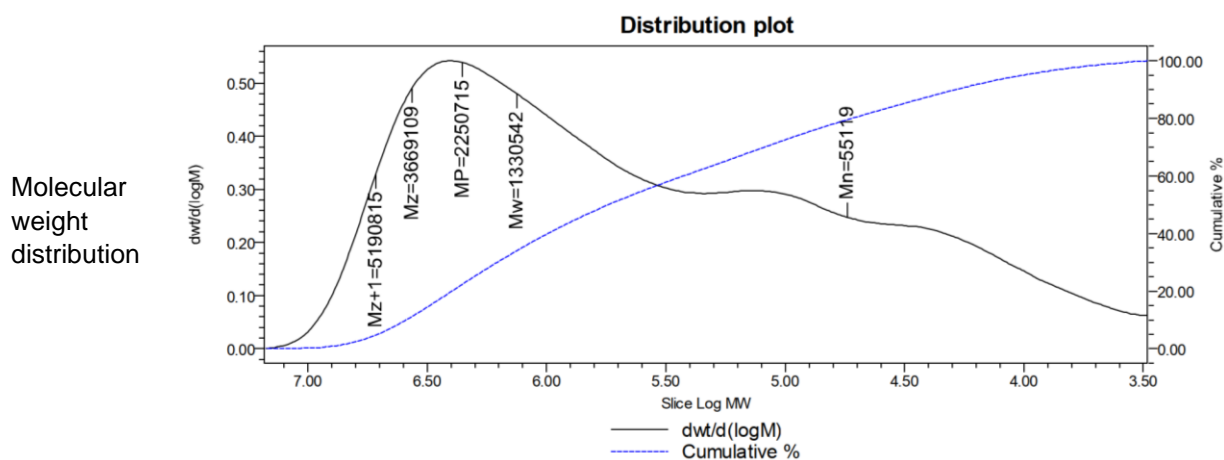


The used amounts of butenolide- and co-monomer as well as the measured reaction exotherms and final properties of the produced polymer dispersions are listed in the following paragraphs.

Reference experiment 1, using *i*BMA




The synthetic procedure on page S36 was followed using 6.67 g (46.9 mmol) *i*BMA. During the first radical initiation phase an exotherm of +7.9°C was observed over 5 min (peak temperature reached), no exotherm was observed in the second radical initiation phase.

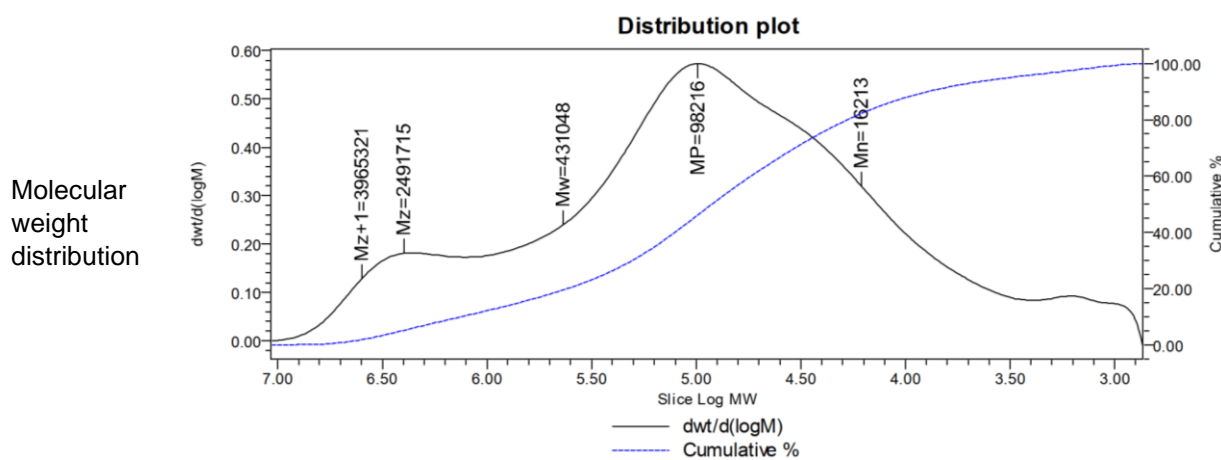
	Day 0	1 day RT storage	1 month RT storage
Appearance			
Measured properties	Not determined	SC: 27.3% pH: 7.7 $d_{43}$ : 50 nm	SC: 27.3% pH: 7.1 $d_{43}$ : 49 nm



Reference experiment 2, using MiBK




The synthetic procedure on page S36 was followed using 6.67 g MBK. Like expected, no exotherms were observed during both radical initiation phases.

	Day 0	1 day RT storage	1 month RT storage
Appearance			
Measured properties	Not determined	SC: 16.7% pH: 8.1 $d_{43}$ : 44 nm	SC: 16.8% pH: 7.6 $d_{43}$ : 75 nm



*PU/poly-butenolide dispersion using methoxy butenolide (3a) + VeoVa 9*

The synthetic procedure on page S36 was followed using 2.55 g (22.3 mmol) **3a** and 4.12 g (22.4 mmol) VeoVa 9. During the first radical initiation phase an exotherm of +2.3°C was observed over 30 min, in the second radical initiation phase +0.8°C exotherm over 30 min was observed.




	Day 0	1 day RT storage	1 month RT storage
Appearance			
Measured properties	Not determined	SC: 26.3% pH: 6.5 $d_{43}$ : 77 nm	Not determined, <i>gelled between 3 and 6 days storage</i>

Molecular weight distribution

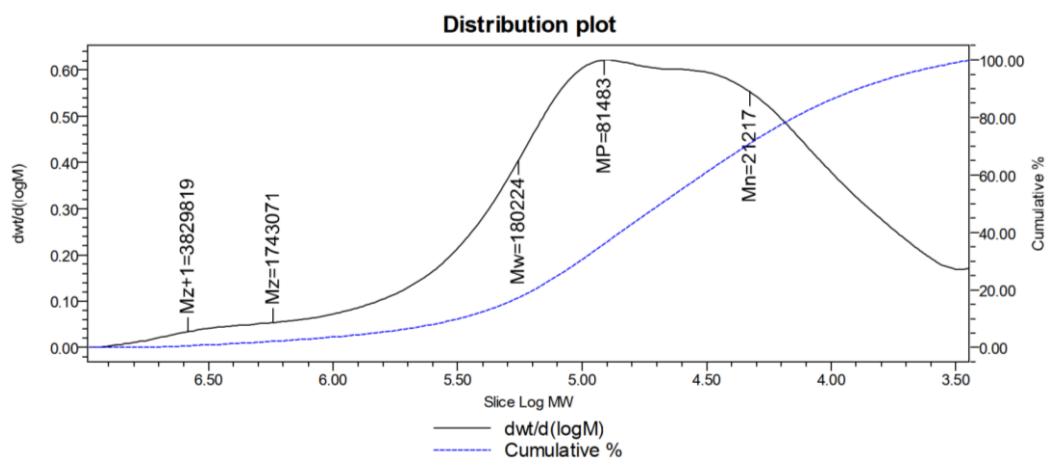
*"not measured due to sample instability"*

*PU/poly-butenolide dispersion using methoxy butenolide (3a) + BVE*

The synthetic procedure on page S36 was followed using 3.55 g (31.1 mmol) **3a** and 3.12 g (31.1 mmol) BVE. During the first radical initiation phase an exotherm of +3.9°C was observed over 30 min, in the second radical initiation phase +0.5°C exotherm over 30 min was observed.

	Day 0	1 day RT storage	1 month RT storage
Appearance			
Measured properties	Not determined	SC: 25.7% pH: 6.6 $d_{43}$ : 138 nm	SC: 25.5% pH: 6.6 $d_{43}$ : 164 nm




Molecular weight distribution





*PU/poly-butenolide dispersion using methoxy butenolide (3a) + NVP*

The synthetic procedure on page S36 was followed using 3.38 g (29.6 mmol) **3a** and 3.29 g (29.6 mmol) NVP. During the first radical initiation phase an exotherm of only +0.1°C in the first min was observed, in the second radical initiation phase +0.4°C exotherm over 30 min was observed. A viscosity increased after overnight storage was observed.

	Day 0	1 day RT storage	1 month RT storage
Appearance			
Measured properties	Not determined	SC: % SC pH: 6.4 $d_{43}$ : 260 nm <sup>[a]</sup>	Not determined, <i>gelled between 1 and 3 days storage</i>




Molecular weight distribution

*“not measured due to sample instability”*

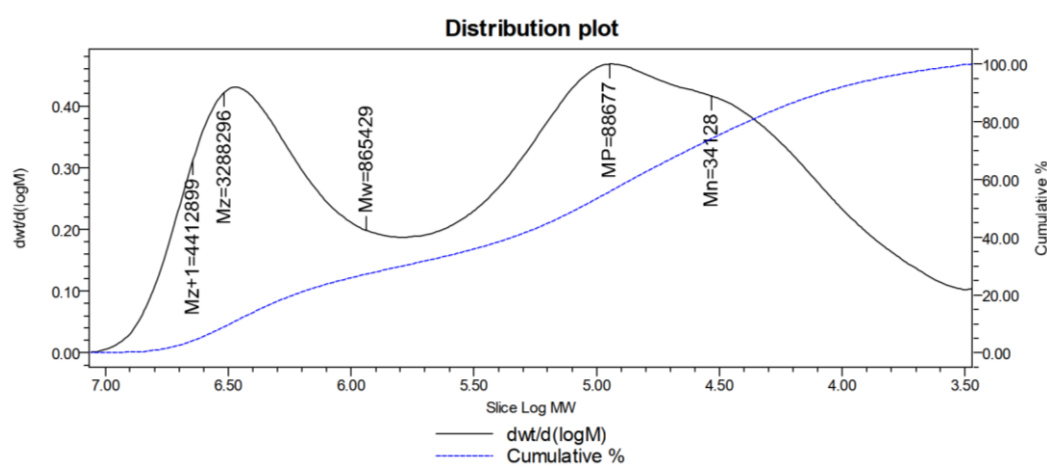
[a] Bimodal particle size distribution, 44 nm (33 vol%) + 363 nm (67 vol%).

*PU/poly-butenolide dispersion using n-butoxy butenolide (3b) + VeoVa 9*

The synthetic procedure on page S36 was followed using 3.06 g (19.6 mmol) **3b** and 3.61 g (19.6 mmol) VeoVa 9. During the first radical initiation phase an exotherm of +1.0°C was observed over 30 min, in the second radical initiation phase +1.4°C exotherm over 30 min was observed.




	Day 0	1 day RT storage	1 month RT storage
Appearance			
Measured properties	Not determined	SC: 27.6% pH: 7.5 $d_{43}$ : 99 nm	SC: 27.4% pH: 7.2 $d_{43}$ : 89 nm

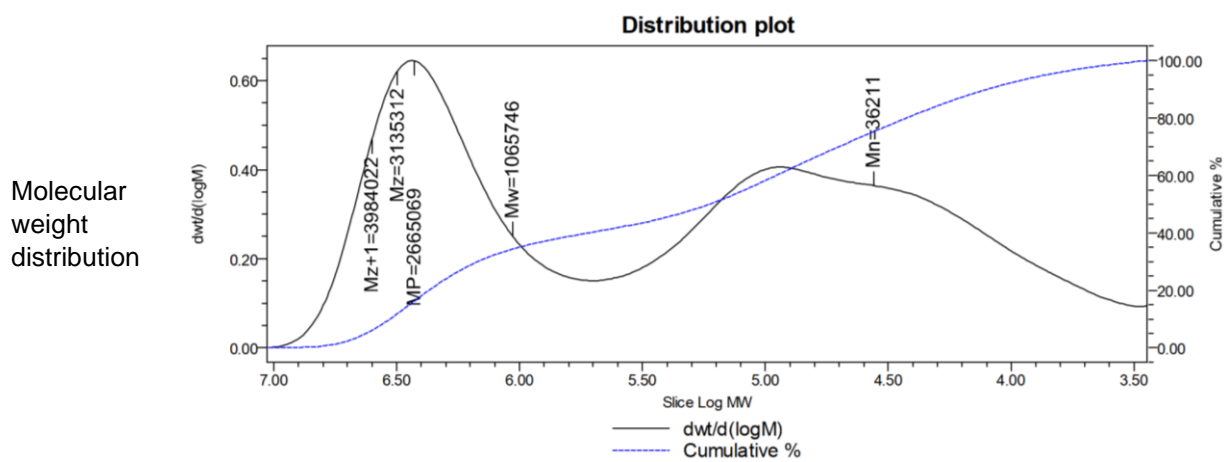
Molecular weight distribution



*PU/poly-butenolide dispersion using n-butoxy butenolide (3b) + BVE*




The synthetic procedure on page S36 was followed using 4.06 g (26.0 mmol) **3b** and 2.61 g (26.0 mmol) BVE. During the first radical initiation phase an exotherm of +3.6°C was observed over 30 min, in the second radical initiation phase +0.8°C exotherm over 30 min was observed.

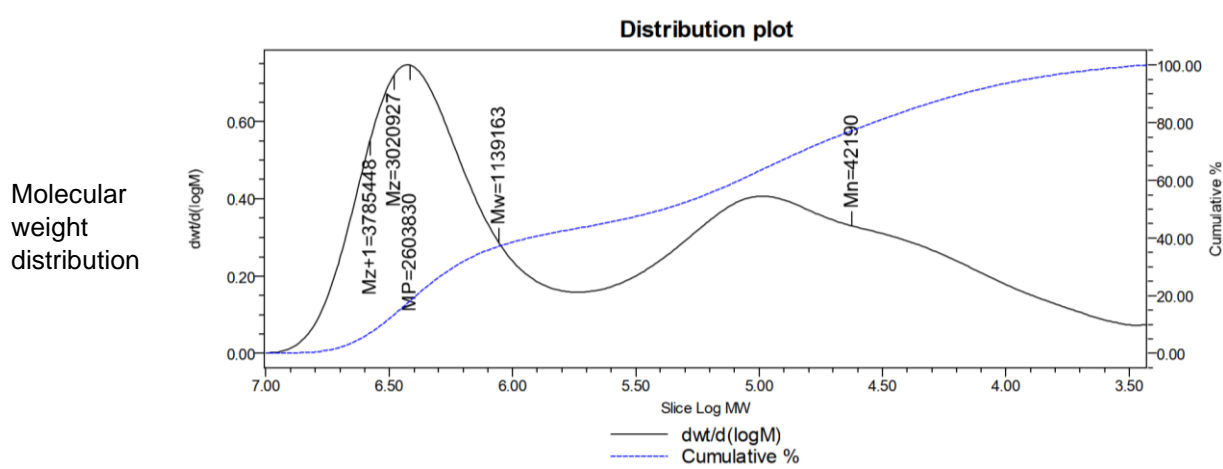
	Day 0	1 day RT storage	1 month RT storage
Appearance			
Measured properties	Not determined	SC: 27.0% pH: 7.7 $d_{43}$ : 86 nm	SC: 27.0% pH: 7.2 $d_{43}$ : 75 nm



*PU/poly-butenolide dispersion using n-butoxy butenolide (3b) + NVP*




The synthetic procedure on page S36 was followed using 3.90 g (25.0 mmol) **3b** and 2.77 g (24.9 mmol) NVP. During the first radical initiation phase an exotherm of +5.6°C was observed over 20 min (peak temperature reached), no exotherm was observed in the second radical initiation phase.

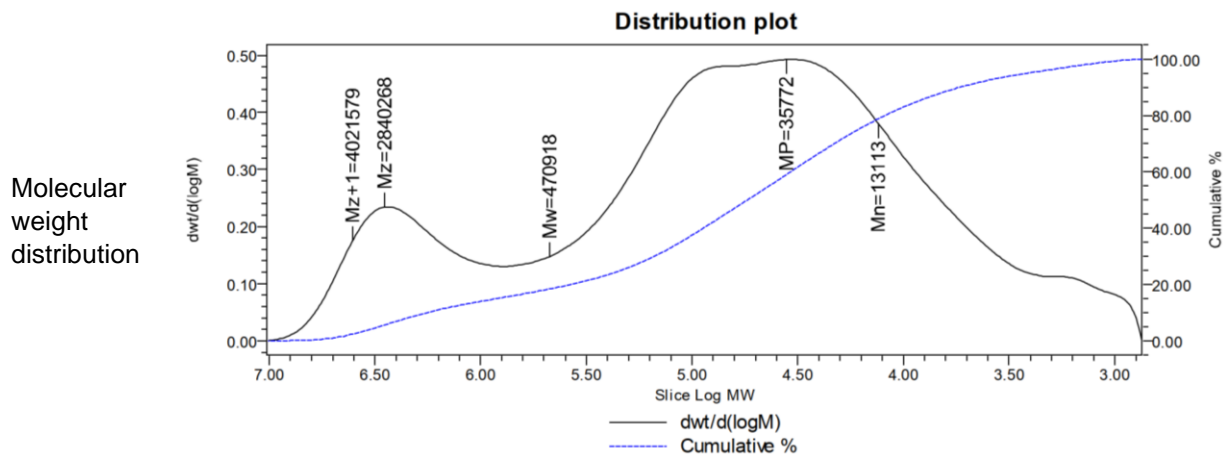
	Day 0	1 day RT storage	1 month RT storage
Appearance			
Measured properties	Not determined	SC: 27.8% SC pH: 7.3 $d_{43}$ : 30 nm	SC: 27.6% SC pH: 7.1 $d_{43}$ : 37 nm



*PU/poly-butenolide dispersion using n-hexyloxy butenolide (3c) + VeoVa 9*




The synthetic procedure on page S36 was followed using 3.34 g (18.1 mmol) **3c** and 3.34 g (18.1 mmol) VeoVa 9. During the first radical initiation phase an exotherm of +0.9°C was observed over 30 min, in the second radical initiation phase +0.9°C exotherm over 25 min (peak temperature reached) was observed.

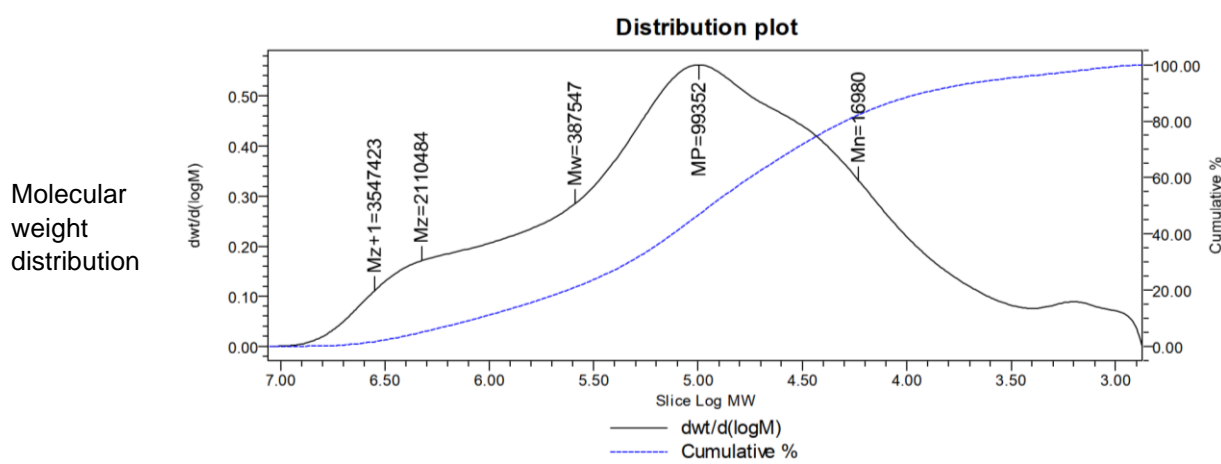
	Day 0	1 day RT storage	1 month RT storage
Appearance			
Measured properties	Not determined	SC: 27.2% pH: 7.5 $d_{43}$ : 64 nm	SC: 27.2% pH: 7.0 $d_{43}$ : 59 nm



*PU/poly-butenolide dispersion using n-hexyloxy butenolide (3c) + BVE*




The synthetic procedure on page S36 was followed using 4.32 g (23.5 mmol) **3c** and 2.35 g (23.5 mmol) BVE. During the first radical initiation phase an exotherm of +1.4°C was observed over 30 min, in the second radical initiation phase +1.6°C exotherm over 30 min was observed.

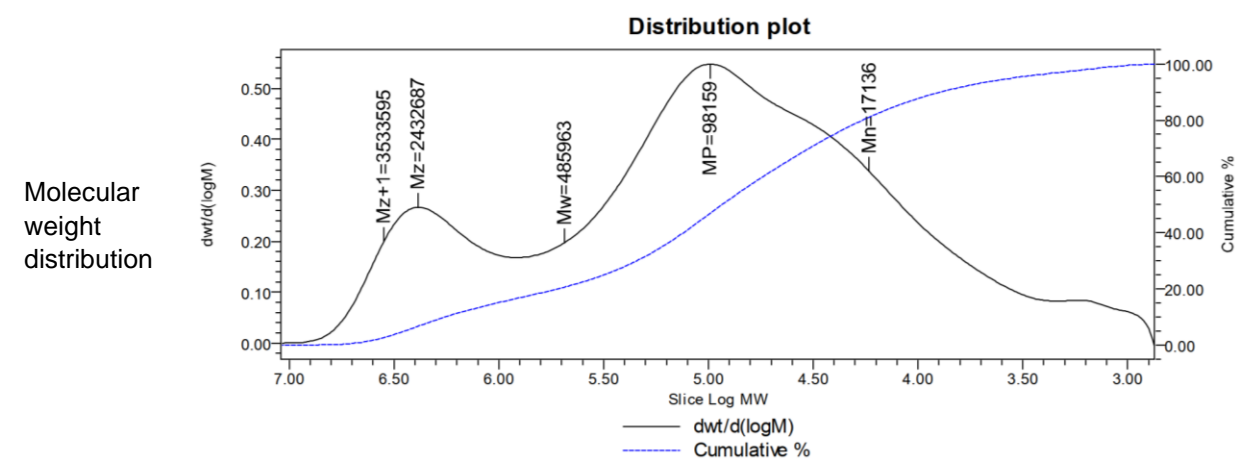
	Day 0	1 day RT storage	1 month RT storage
Appearance			
Measured properties	Not determined	SC: 26.8% pH: 7.5 $d_{43}$ : 65 nm	SC: 26.7% pH: 7.0 $d_{43}$ : 53 nm



*PU/poly-butenolide dispersion using n-hexyloxy butenolide (3c) + NVP*




The synthetic procedure on page S36 was followed using 4.16 g (22.6 mmol) **3c** and 2.51 g (22.6 mmol) NVP. During the first radical initiation phase an exotherm of +4.4°C was observed over 20 min (peak temperature reached), no exotherm was observed in the second radical initiation phase.

	Day 0	1 day RT storage	1 month RT storage
Appearance			
Measured properties	Not determined	SC: 27.1% pH: 7.5 $d_{43}$ : 37 nm	SC: 27.2% pH: 7.3 $d_{43}$ : 37 nm



*PU/poly-butenolide dispersion using acetoxy butenolide (3d) + VeoVa 9*

The synthetic procedure on page S36 was followed using 2.90 g (20.4 mmol) **3d** and 3.77 g (20.5 mmol) VeoVa 9. During the first radical initiation phase an exotherm of +2.9°C was observed over 15 min (peak temperature reached), in the second radical initiation phase +0.4°C exotherm over 10 min was observed (peak temperature reached).




	Day 0	1 day RT storage	1 month RT storage
Appearance			
Measured properties	Not determined	Not determined, <i>gelled overnight</i>	Not determined

Molecular weight distribution *"not measured due to sample instability"*

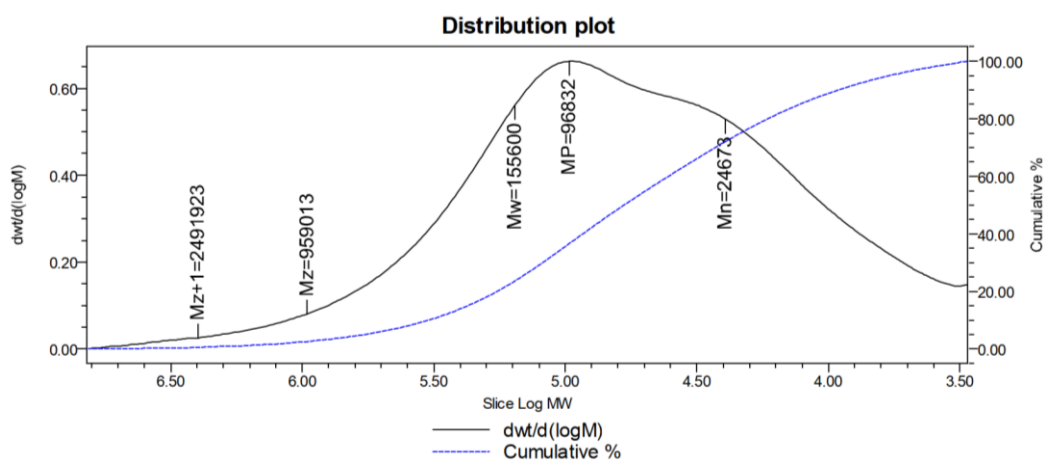


*PU/poly-butenolide dispersion using acetoxy butenolide (3d) + BVE*

The synthetic procedure on page S36 was followed using 3.91 g (27.5 mmol) **3d** and 2.76 g (27.5 mmol) BVE. During the first radical initiation phase an exotherm of +6.3°C was observed over 5 min (peak temperature reached), no exotherm was observed in the second radical initiation phase.




	Day 0	1 day RT storage	1 month RT storage
Appearance			
Measured properties	Not determined	SC: 26.3% pH: 6.5 $d_{43}$ : 137 nm	SC: 26.2% pH: 6.6 $d_{43}$ : 286 nm

Molecular weight distribution



*PU/poly-butenolide dispersion using acetoxy butenolide (3d) + NVP*




The synthetic procedure on page S36 was followed using 3.74 g (26.3 mmol) **3d** and 2.93 g (26.4 mmol) NVP. During the first radical initiation phase an exotherm of only +0.1°C was observed in the first min, in the second radical initiation phase +0.4°C exotherm over 15 min (peak temperature reached) was observed.

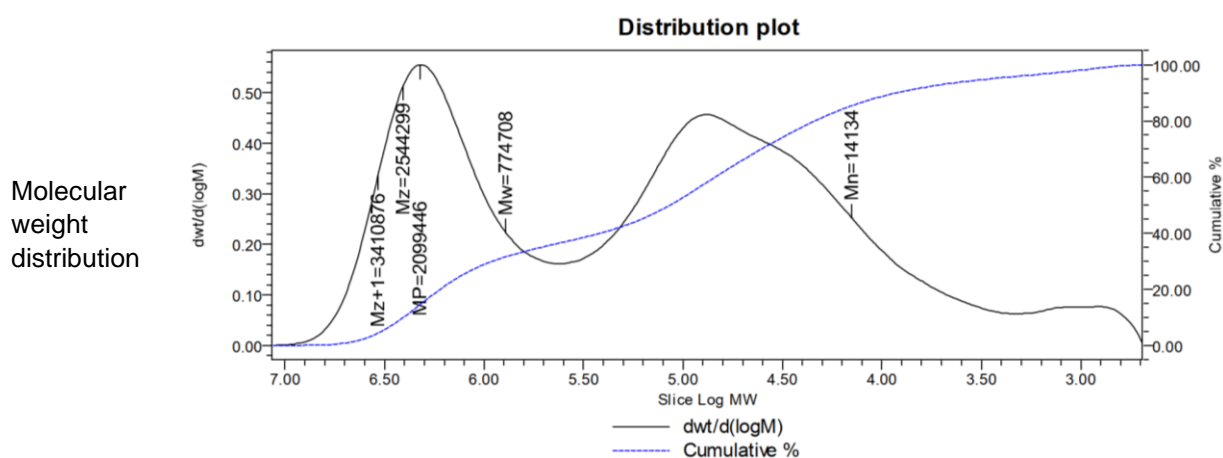
	Day 0	1 day RT storage	1 month RT storage
Appearance			
Measured properties	Not determined	Not determined, <i>gelled overnight</i>	Not determined

Molecular weight distribution  
*"not measured due to sample instability"*

*PU/poly-butenolide dispersion using 5-oxo-2,5-dihydrofuran-2-yl hexanoate (3e) + VeoVa 9*




The synthetic procedure on page S36 was followed using 3.45 g (17.4 mmol) **3e** and 3.22 g (17.5 mmol) VeoVa 9. During the first radical initiation phase an exotherm of +2.1°C was observed over 30 min, in the second radical initiation phase +0.5°C exotherm over 7 min (peak temperature reached) was observed.

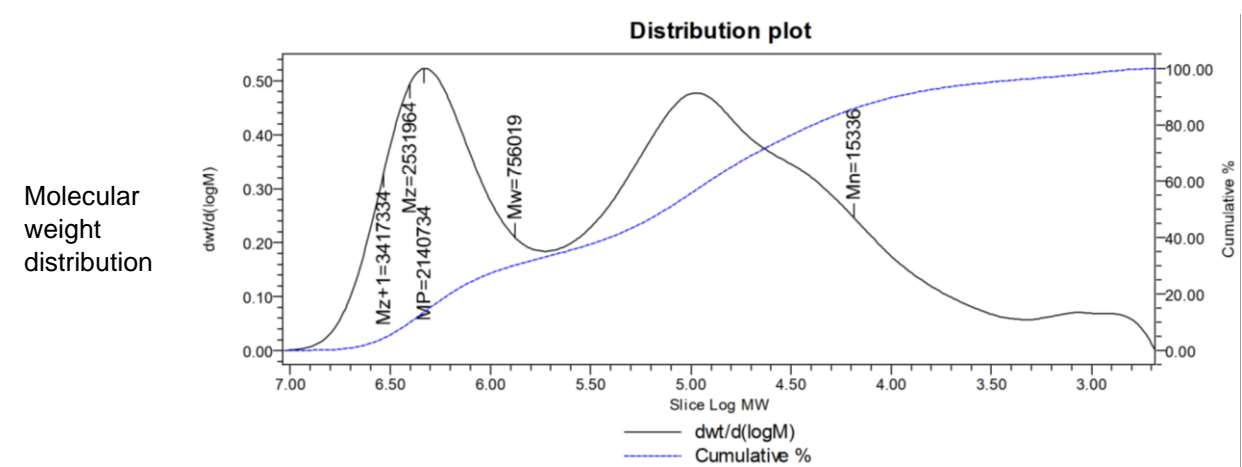
	Day 0	1 day RT storage	1 month RT storage
Appearance			
Measured properties	Not determined	SC: 27.0% pH: 7.2 $d_{43}$ : 75 nm	SC: 26.9% pH: 7.1 $d_{43}$ : 79 nm



*PU/poly-butenolide dispersion using 5-oxo-2,5-dihydrofuran-2-yl hexanoate (3e) + BVE*




The synthetic procedure on page S36 was followed using 4.43 g (22.4 mmol) **3e** and 2.24 g (22.4 mmol) BVE. During the first radical initiation phase an exotherm of +5.3°C was observed over 11 min (peak temperature reached), no exotherm was observed in the second radical initiation phase.

	Day 0	1 day RT storage	1 month RT storage
Appearance			
Measured properties	Not determined	SC: 26.8% pH: 7.2 $d_{43}$ : 62 nm	SC: 26.7% pH: 7.1 $d_{43}$ : 68 nm

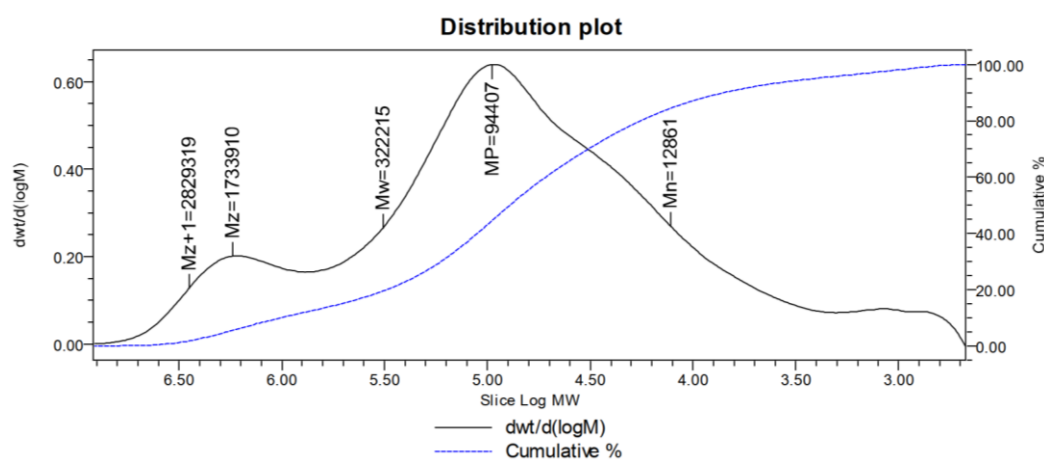


*PU/poly-butenolide dispersion using 5-oxo-2,5-dihydrofuran-2-yl hexanoate (3e) + NVP*

The synthetic procedure on page S36 was followed using 4.27 g (21.5 mmol) **3e** and 2.40 g (21.6 mmol) NVP. During the first radical initiation phase an exotherm of +7.1°C was observed over 4 min (peak temperature reached), no exotherm in the second radical initiation phase was observed.

	Day 0	1 day RT storage	1 month RT storage
Appearance			
Measured properties	Not determined	SC: 27.3% pH: 7.1 $d_{43}$ : 40 nm	SC: 27.2% pH: 6.9 $d_{43}$ : 44 nm


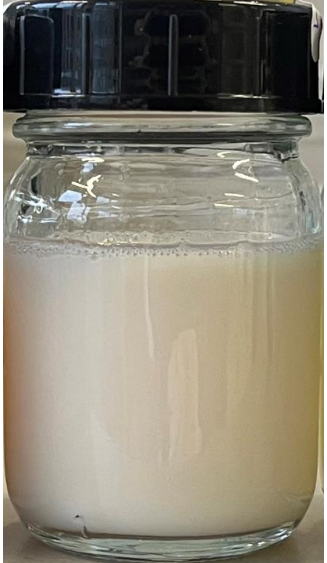

Molecular weight distribution

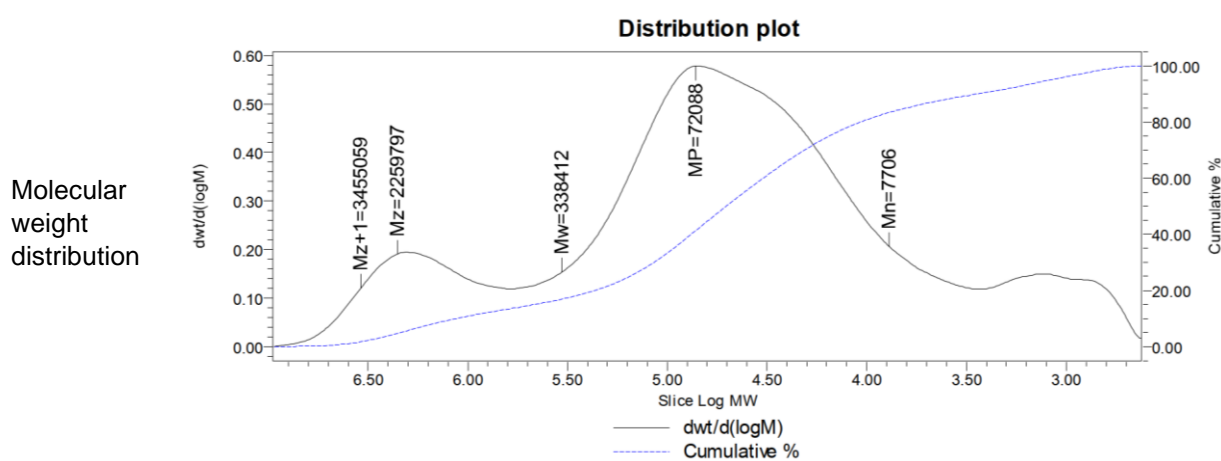


*PU/poly-butenolide dispersion using t-butyl carboxy butenolide (3f) + VeoVa 9*

The synthetic procedure on page S36 was followed using 3.47 g (17.3 mmol) **3f** and 3.20 g (17.4 mmol) VeoVa 9. An attempt was made to first blend **3f** and VeoVa 9 using 1.0 g DPGDME and heating in a 100°C oil bath, unfortunately, **3f** did not dissolve fully. The heterogeneous monomer mix was added to the PU and further processed as described in the synthetic procedure. To compensate for the additional DPGDME used in the process, 14.2 g PU / monomer / DPGDME was emulsified (11.5 g PU + monomer) resulting in a theoretical solid content of 28.2% after radical polymerization. During the first radical initiation phase an exotherm of +1.8°C was observed over 30 min, in the second radical initiation phase +0.4°C exotherm over 7 min (peak temperature reached) was observed.

Pressure build-up was observed upon opening after 1 month RT storage, probably CO<sub>2</sub> formation due to partial hydrolysis.

	Day 0	1 day RT storage	1 month RT storage
Appearance			
Measured properties	Not determined	SC: 26.8% pH: 7.0 <i>d</i> <sub>43</sub> : 102 nm	26.8% SC pH: 6.7 <i>d</i> <sub>43</sub> : 128 nm






*PU/poly-butenolide dispersion using t-butyl carbonoxy butenolide (3f) + BVE*

The synthetic procedure on page S36 was followed using 4.45 g (22.2 mmol) **3f** and 2.22 g (22.2 mmol) BVE. An attempt was made to first blend **3f** and BVE using 1.0 g DPGDME and heating in a 100°C oil bath, unfortunately, **3f** did not dissolve fully. The heterogeneous monomer mix was added to the PU and further processed as described in the synthetic procedure. To compensate for the additional DPGDME used in the process, 14.0 g PU / monomer / DPGDME was emulsified (11.3 g PU + monomer) resulting in a theoretical solid content of 27.9% after radical polymerization. During the first radical initiation phase an exotherm of +1.4°C was observed over 30 min, no exotherm in the second radical initiation phase was observed.

A close inspection indicated the presence of a minor amount solid particles in the final dispersion, probably these originate from incomplete mass transfer of solid **3f** particles to the reaction loci during radical polymerization (see Figure 1 on page S5).

Pressure build-up was observed upon opening after 1 month RT storage, probably CO<sub>2</sub> formation due to partial hydrolysis. Opening of the container triggered destabilization of the dispersion.




	Day 0	1 day RT storage	1 month RT storage
Appearance			
Measured properties	Not determined	SC: 23.9% pH: 6.7 <i>d</i> <sub>43</sub> : 34 nm	Not determined

Molecular weight distribution "not measured due to sample instability"

*PU/poly-butenolide dispersion using t-butyl carbonoxy butenolide (3f) + NVP*

The synthetic procedure on page S36 was followed using 4.29 g (21.4 mmol) **3f** and 2.38 g (21.4 mmol) NVP. **3f** and NVP were first mixed using 0.5 g DPGDME and heating in a 100°C oil bath. Unfortunately, addition of the homogeneous monomer solution to PU resulted in (partial) precipitation of **3f**, emulsification of the heterogeneous mixture was proceeded as described in the synthetic procedure. To compensate for the additional DPGDME used in the process, 13.5 g PU / monomer / DPGDME was emulsified (11.2 g PU + monomer) resulting in a theoretical solid content of 28.0% after radical polymerization. During the first radical initiation phase an exotherm of +2.5°C was observed over 30 min, in the second radical initiation phase +0.4°C exotherm over 5 min (peak temperature reached) was observed.

Pressure build-up was observed upon opening after 1 month RT storage, probably CO<sub>2</sub> formation due to partial hydrolysis. A viscosity increase was also observed during 1 month RT storage.

	Day 0	1 day RT storage	1 month RT storage
Appearance			
Measured properties	Not determined	SC: 25.6% pH: 6.9 <i>d</i> <sub>43</sub> : 32 nm	25.7% SC pH: 6.4 <i>d</i> <sub>43</sub> : 140 nm




Molecular weight distribution

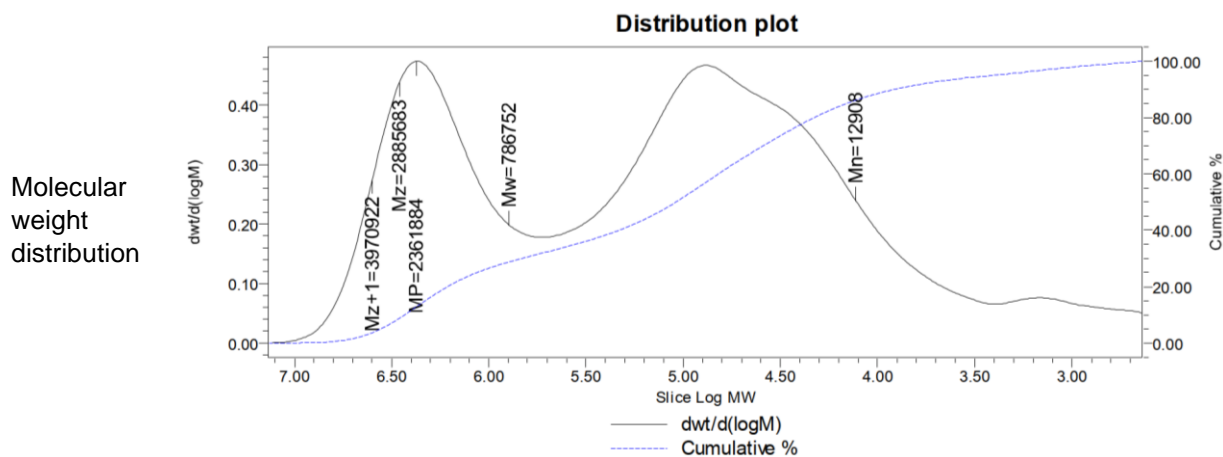
*Not analyzed, polymer did not dissolve in eluent.*



*PU/poly-butenolide dispersion using cyclohexyl carbamoy butenolide (3g) + VeoVa 9*




The synthetic procedure on page S36 was followed using 3.67 g (16.3 mmol) **3g** and 3.00 g (16.3 mmol) VeoVa 9. An attempt was made to first blend **3g** and VeoVa 9 using 2.0 g DPGDME and heating in a 100°C oil bath, unfortunately, **3g** did not dissolve fully. The heterogeneous monomer mix was added to the PU and further processed as described in the synthetic procedure. To compensate for the additional DPGDME used in the process, 13.6 g PU / monomer / DPGDME was emulsified (10.5 g PU + monomer) resulting in a theoretical solid content of 26.2% after radical polymerization. During the first radical initiation phase an exotherm of +1.7°C was observed over 20 min (peak temperature reached), no exotherm in the second radical initiation phase was observed.

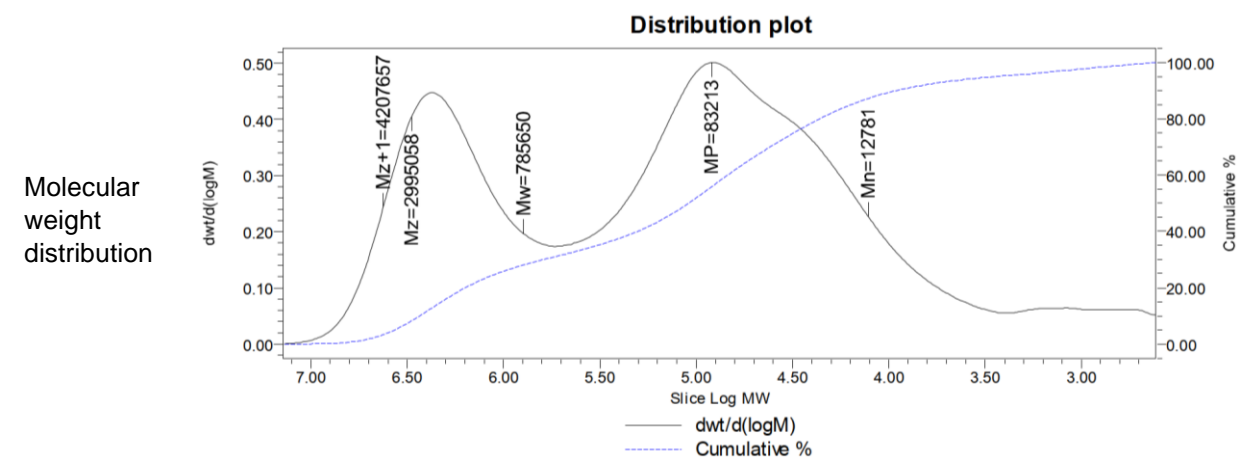
	Day 0	1 day RT storage	1 month RT storage
Appearance			
Measured properties	Not determined	SC: 26.3% pH: 6.9 $d_{43}$ : 42 nm	26.2% SC pH: 7.0 $d_{43}$ : 50 nm



*PU/poly-butenolide dispersion using cyclohexyl carbamoxy butenolide (3g) + BVE*




The synthetic procedure on page S36 was followed using 4.62 g (20.5 mmol) **3g** and 2.05 g (20.5 mmol) BVE. An attempt was made to first blend **3g** and BVE using 2.0 g DPGDME and heating in a 100°C oil bath, unfortunately, **3g** did not dissolve fully. The heterogeneous monomer mix was added to the PU and further processed as described in the synthetic procedure. To compensate for the additional DPGDME used in the process, 14.2 g PU / monomer / DPGDME was emulsified (11.0 g PU + monomer) resulting in a theoretical solid content of 27.0% after radical polymerization. During the first radical initiation phase an exotherm of +2.6°C was observed over 16 min (peak temperature reached), no exotherm in the second radical initiation phase was observed.

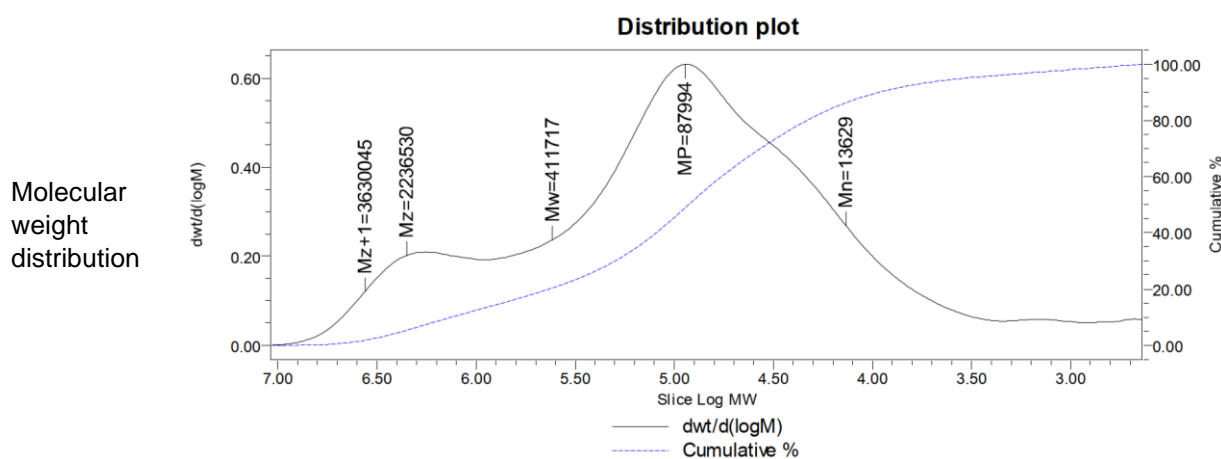
	Day 0	1 day RT storage	1 month RT storage
Appearance			
Measured properties	Not determined	SC: 26.1% pH: 7.1 $d_{43}$ : 49 nm	26.0% SC pH: 7.1 $d_{43}$ : 54 nm



*PU/poly-butenolide dispersion using cyclohexyl carbamoxy butenolide (3g) + NVP*

The synthetic procedure on page S36 was followed using 4.47 g (19.8 mmol) **3g** and 2.20 g (19.8 mmol) NVP. **3g** and NVP were first mixed using 1.0 g DPGDME and heating in a 100°C oil bath. Upon addition of the monomer solution to PU a homogeneous solution was obtained, emulsification was proceeded as described in the synthetic procedure. To compensate for the additional DPGDME used in the process, 13.3 g PU / monomer / DPGDME was emulsified (10.8 g PU + monomer) resulting in a theoretical solid content of 27.1% after radical polymerization. During the first radical initiation phase an exotherm of +3.7°C was observed over 6 min (peak temperature reached), no exotherm in the second radical initiation phase was observed.

	Day 0	1 day RT storage	1 month RT storage
Appearance			
Measured properties	Not determined	SC: 27.0% pH: 6.9 $d_{43}$ : 36 nm	27.0% SC pH: 7.1 $d_{43}$ : 65 nm



## Solvent-free PU / poly-butenolide hybrid dispersions

All solvent-free PU / poly-butenolide hybrid dispersions were made using the synthetic procedure described underneath. The synthesized PU pre-polymer was stored for one night. This enabled the synthesis of three solvent free hybrid dispersions with consistent PU quality the next day.

### *Synthetic procedure*

130.0 g (130.0 mmol) PTMEG, Mn 1000 (**7**), 13.64 g (101.9 mmol) DMPA (**6**), and 75.88 g (341.4 mmol) IPDI (**8**) were charged in a reactor and heated under N<sub>2</sub> atmosphere using 85°C oil. After the reaction exotherm (93°C), the temperature of the heating oil was gradually increased to 100°C. The batch was reacted for 4 h followed by 54.9 g (494 mmol) NVP addition and cooling. At 70°C, the 80 wt% PU in NVP solution was transferred to a 250 mL glass jar, the NCO% was measured by Bu<sub>2</sub>NH back titration (3.08% NCO = 104% conversion), and the pre-polymer was stored overnight.




The next day, part of the viscous PU-solution was transferred to a 50 mL vial using a spatula and blended with additional NVP and *n*-butoxy butenolide (**3b**) (using the monomer weights listed in the paragraphs below). TEA (100 mol% according to the PU carboxylic acid groups) was added followed by manual mixing for 5 min used a spatula. Next 12.6 g of above neutralized PU / monomer solution (at room temperature) was added to 26.0 g demineralized and deoxidized (by 5 min N<sub>2</sub> bubbling) water (at room temperature) while applying stirring using a “dumbbell shaped” magnetic stirring bar at 500 rpm (see reactor set-up on the right). 20 wt% EDA (aq) was added dropwise as chain extender for the NCO groups (70 mol% chain extension of residual isocyanate groups). The free radical polymerization of **3b** + NVP was initiated by addition of 0.05 g, 70 wt%, (0.4 mmol) *t*BuOOH (aq) and a freshly prepared solution of 22 mg (0.1 mmol) sodium ascorbate + 0.26 mg (9.4·10<sup>-4</sup> mmol) FeSO<sub>4</sub>·7H<sub>2</sub>O dissolved in 0.22 mL water. The reaction exotherm was recorded and an additional portion of the radical initiator redox couple was added as mob-up 30 min after the first addition. 30 min after the mob-up, the reactor lid was replaced by a conventional screwcap and the dispersion was stored in the glass jar in which it was synthesized.

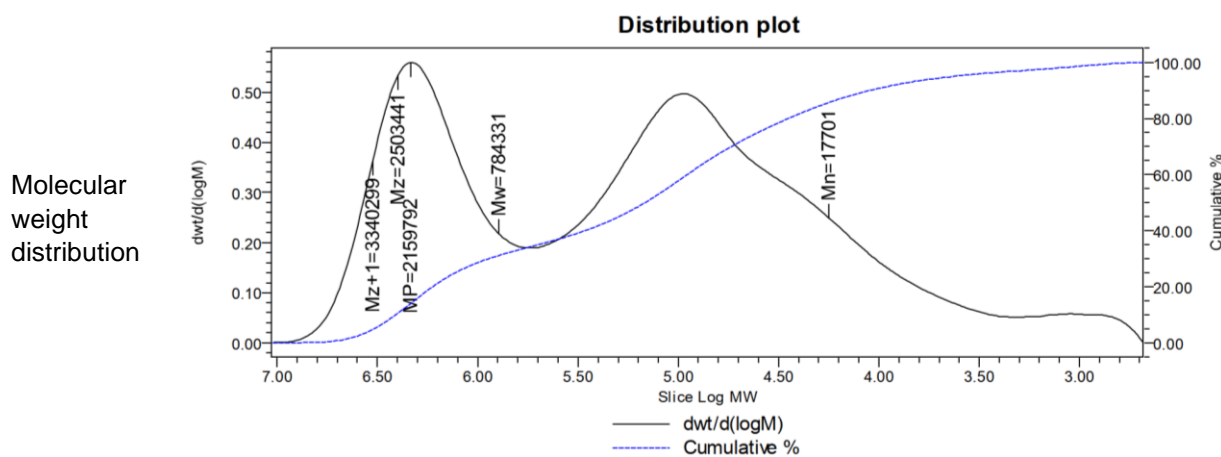


The used amounts PU-solution, **3b**, NVP, TEA, and 20 wt% EDA (aq) as well as the measured reaction exotherms and final properties of the produced polymer dispersions are listed in underneath paragraphs.

60/40 PU/poly-butenolide dispersion using *n*-butoxy butenolide (**3b**) + NVP




The synthetic procedure on page S60 was followed using 12.5 g viscous PU solution (= 10.0 g PU + 2.5 g (22.5 mmol) NVP), 0.28 g (2.5 mmol) additional NVP, 3.89 g (24.9 mmol) **3b**, 0.47 g (4.7 mmol) TEA and 0.67 g 20 wt% (2.2 mmol) EDA (aq). During the first radical initiation phase an exotherm of +5.3°C was observed over 30 min, in the second radical initiation phase +0.1°C exotherm over 3 min was observed (peak temperature reached).

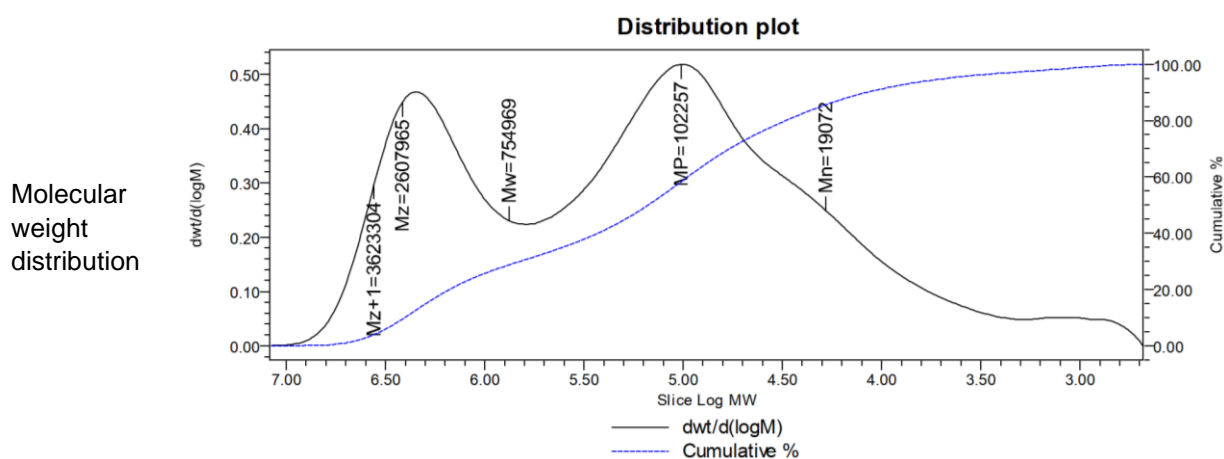
	Day 0	1 day RT storage	1 month RT storage
Appearance			
Measured properties	Not determined	SC: 31.1% pH: 7.1 $d_{43}$ : 42 nm	SC: 31.4% pH: 6.8 $d_{43}$ : 40 nm



50/50 PU/poly-butenolide dispersion using *n*-butoxy butenolide (**3b**) + NVP




The synthetic procedure on page S60 was followed using 12.5 g viscous PU solution (= 10.0 g PU + 2.5 g (22.5 mmol) NVP), 1.66 g (14.9 mmol) additional NVP, 5.84 g (37.4 mmol) **3b**, 0.47 g (4.7 mmol) TEA and 0.56 g 20 wt% (1.8 mmol) EDA (aq). During the first radical initiation phase an exotherm of +6.3°C was observed over 30 min, in the second radical initiation phase +0.6°C exotherm over 5 min was observed (peak temperature reached).

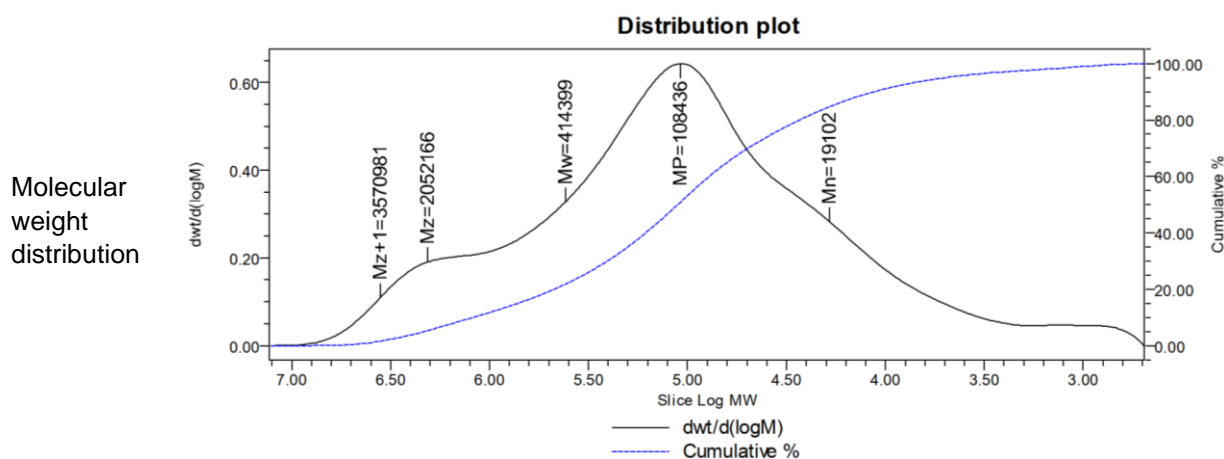
	Day 0	1 day RT storage	1 month RT storage
Appearance			
Measured properties	Not determined	SC: 31.4% pH: 7.0 $d_{43}$ : 41 nm	SC: 31.4% pH: 6.8 $d_{43}$ : 48 nm



40/60 PU/poly-butenolide dispersion using *n*-butoxy butenolide (**3b**) + NVP

The synthetic procedure on page S60 was followed using 10.0 g viscous PU solution (= 8.0 g PU + 2.0 g (18.0 mmol) NVP), 2.99 g (26.9 mmol) additional NVP, 7.01 g (44.9 mmol) **3b**, 0.38 g (3.8 mmol) TEA and 0.45 g 20 wt% (1.5 mmol) EDA (aq). During the first radical initiation phase an exotherm of +6.9°C was observed over 30 min, in the second radical initiation phase +2.4°C exotherm over 7 min was observed (peak temperature reached).

	Day 0	1 day RT storage	1 month RT storage
Appearance			
Measured properties	Not determined	SC: 31.3% pH: 7.0 $d_{43}$ : 67 nm	SC: 31.5% pH: 6.6 $d_{43}$ : 69 nm



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