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Supplementary Information for

Water-borne coatings that share the mechanism of action of oil-based coatings

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Table S1. Characterization of CO_2-responsive copolymers pDEAEMA-co-MMA and pDMAEMA-co-MMA

Copolymer composition	DEAEMA:MMA				DMAEMA:BMA
Predicted molar ratio	90:10	80:20	70:30	60:40	50:50
^{1}H NMR calculated ratio[a]	90:9	81:19	71:29	62:38	48:52
MMA (mL)	2.5	5	5	5	-
BMA (mL)	-	-	-	-	13
DEAEMA (mL)	42.3	37.6	21.9	14.1	-
DMAEMA (mL)	-	-		-	3.5
M_n (kDa)	46.6	64.3	69.5	49.1	43.1
Dispersity	1.8	1.7	2.4	1.8	1.4

[a] The molar ratios of monomers in copolymer were determined by ^{1}H NMR spectroscopy (Bruker Avance 500 MHz spectrometer). For example, the composition was calculated for 90:10 DEAEMA:MMA by comparing the integration of MMA methoxy group protons (3.6-3.5 ppm) with the DEAEMA methylene protons (2.6-2.5 ppm) on the terminal ethyl amine group (Fig S1)[1].

FTIR experimental methods

FTIR spectra were acquired during the drying process of pDEAEMA-co-MMA (80:20, 20 wt%) carbonated solutions using a Mettler Toledo ReactIR 15 system with MCT Detector using HappGenzel apodization; DiComp (Diamond) probe connected via AgX 9.5mm x 1.5m Fiber (Silver Halide); sampling 2500 to 650 cm^{-1} with a total of 128 scans and a 4 cm^{-1} resolution. ATR-FTIR measurements of dried pDEAEMA-co-MMA (80:20) powder and carbonated solution (20 wt%) were taken using an Bruker ALPHA FT-IR with an ATR module with a total of 64 scans and a resolution of 8 cm^{-1}.

The ReactIR provided a profile of the drying process of the film over 48 h (Fig S4). Using the ATR-FTIR, dry purified polymer powder, the carbonated polymer solution (20 wt%) and a dried sample of solution to solid polymer were obtained to assess the initial and final forms of the coating (Fig S5). Another ReactIR spectra was recorded to show DEAEMA in water as CO_2 was passed through the system to observe the bicarbonate peak at 820 cm^{-1} (Fig S6).[2]

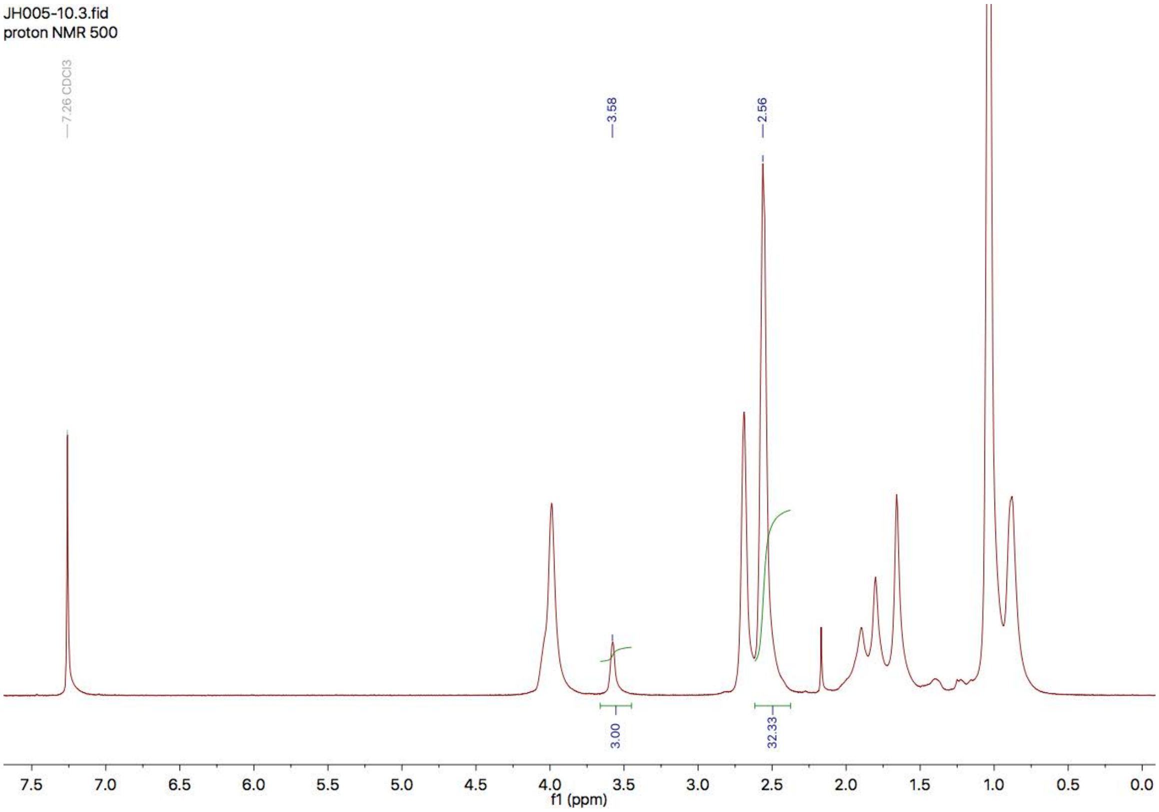


Figure S1. ^{1}H-NMR spectrum of purified 90:10 pDEAEMA-co-MMA. The polymer was precipitated from DMF in distilled water to remove residual monomer. Precipitation was repeated until no monomer was detected. Integrations of DEAEMA nitrogen bound methylene protons on the terminal diethylamine (2.6-2.5 ppm) and MMA methoxy protons (3.6-3.5 ppm) were used to determine the final composition of the copolymers.

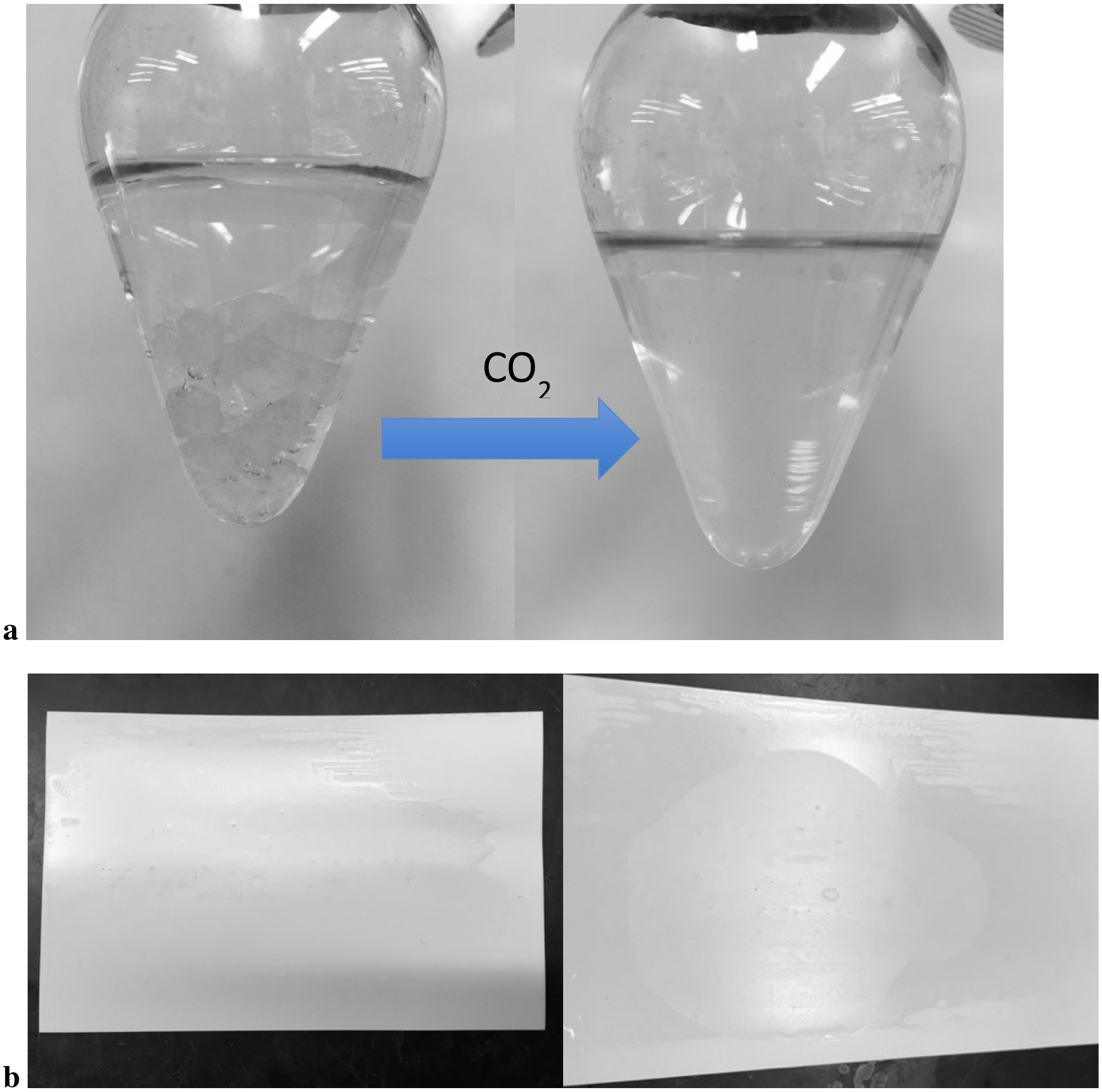


Figure S2. Homogeneous solution of pDEAEMA forming a continuous film. a, The hydrophobic pDEAEMA (2 g) is suspended in water (10 mL) (left) and remains undissolved until CO_2 is sparged through the water (6 hours). CO_2 sparging protonates the amine groups, yielding the hydrophilic form of pDEAEMA and a homogeneous solution of polymer (right) in carbonated water (20 wt%). **b,** When the 20 wt% solution of pDEAEMA was cast on a pre-primed aluminum sheet, the evaporation of CO_2 and water leads to a clear continuous coating of unprotonated (hydrophobic) pDEAEMA (left). This was then soaked (12 h) with distilled water. The coating showed swelling behavior once the water was removed (right). The coating returned to its initial unswollen state after drying for 24 h.

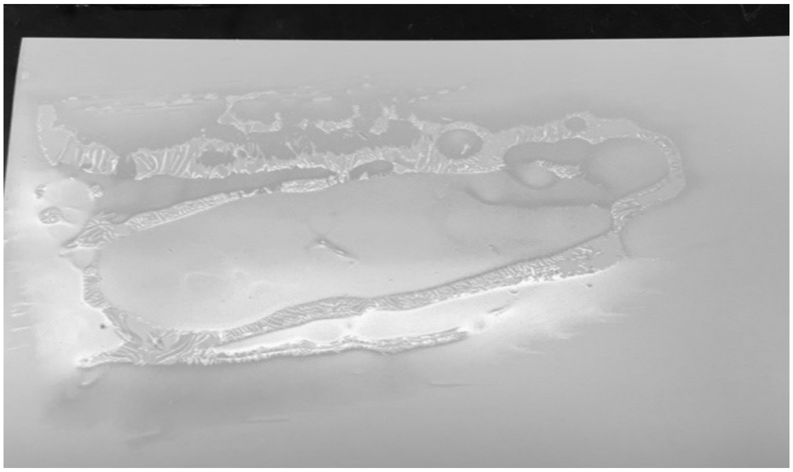


Figure S3. ptBAEMA coating. A 20 wt% solution of ptBAEMA cast on a pre-primed aluminum plate using a brush forms a relatively clear coating after the evaporation of water and CO_2 (dried at 23 ˚C for 24 h). However, the final coating is uneven and has rough brittle regions. The resulting ptBAEMA coating was partially soluble in water.

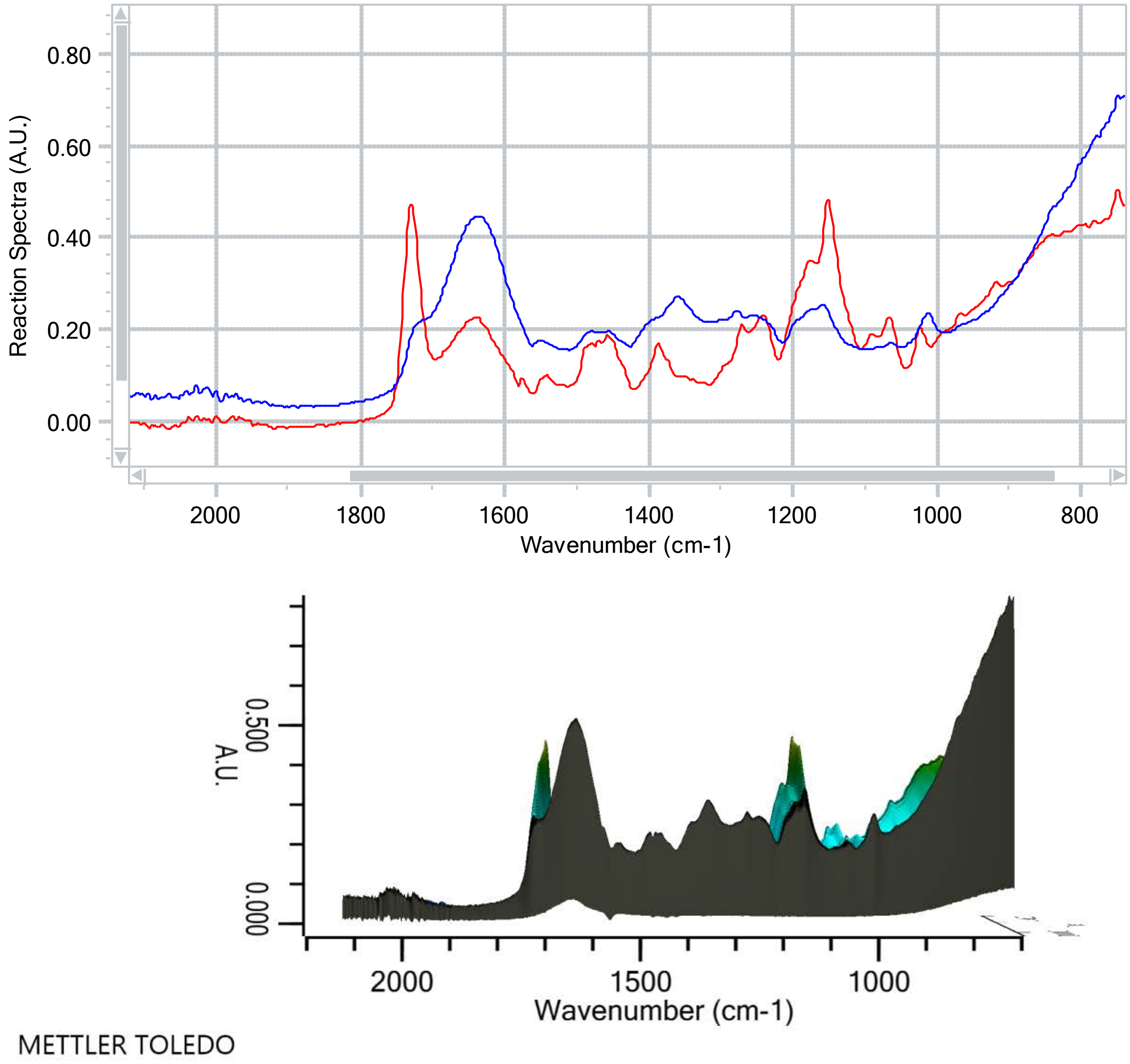
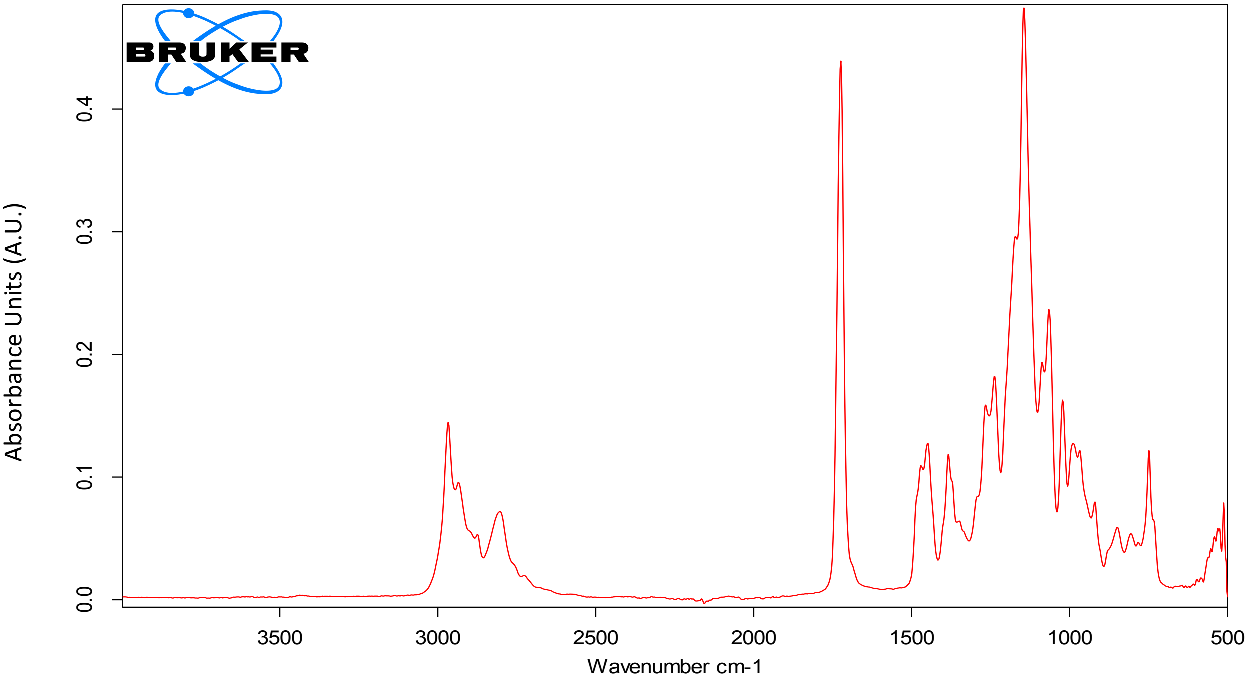


Figure S4. ReactIR ATR-FT-IR spectra of 81:19 pDEAEMA-co-MMA. FT-IR spectra of the carbonated polymer solution were recorded on the ReactIR over 48 h to observe changes as the carbonated solution dries into a coating (top). The red line is the spectrum of the dissolved polymer in carbonated water (20 wt%) at t = 0 and the blue line is the spectrum of the dried polymer at t = 48 h. A reaction profile of the drying process is below where the start of the drying process is at the front and the reaction proceeds towards the back of the reaction profile. The presence of the bicarbonate stretch (820 cm^{-1}) is difficult to observe during the drying process because of the overwhelming water signal.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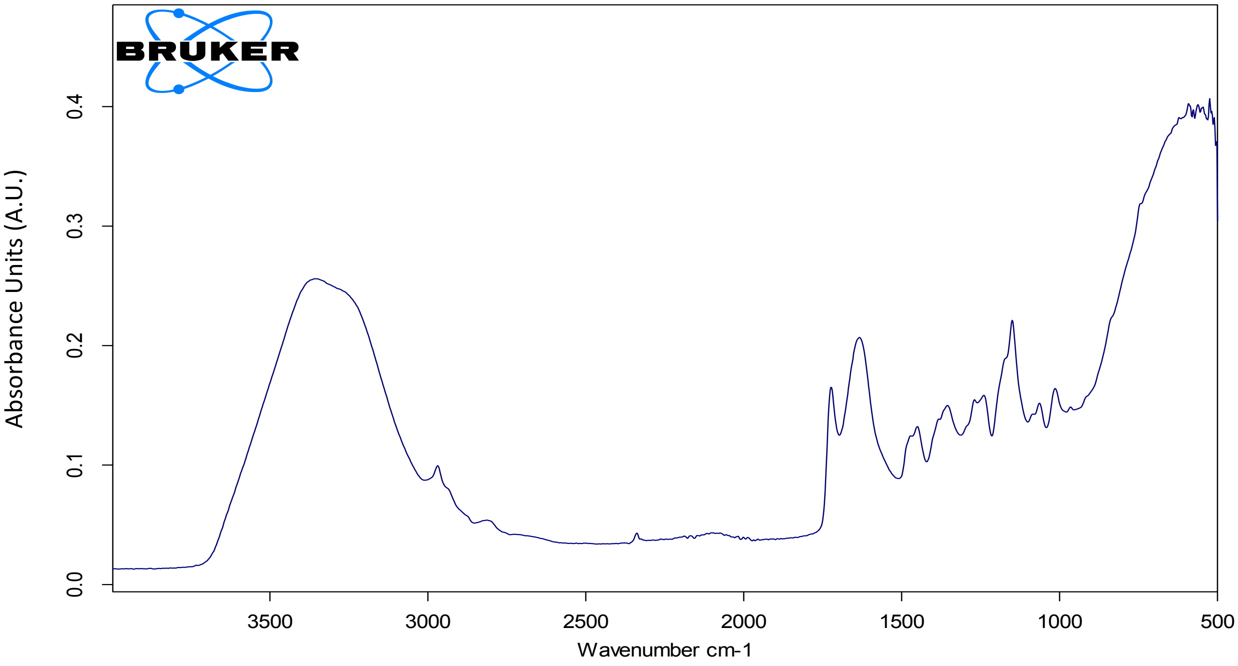
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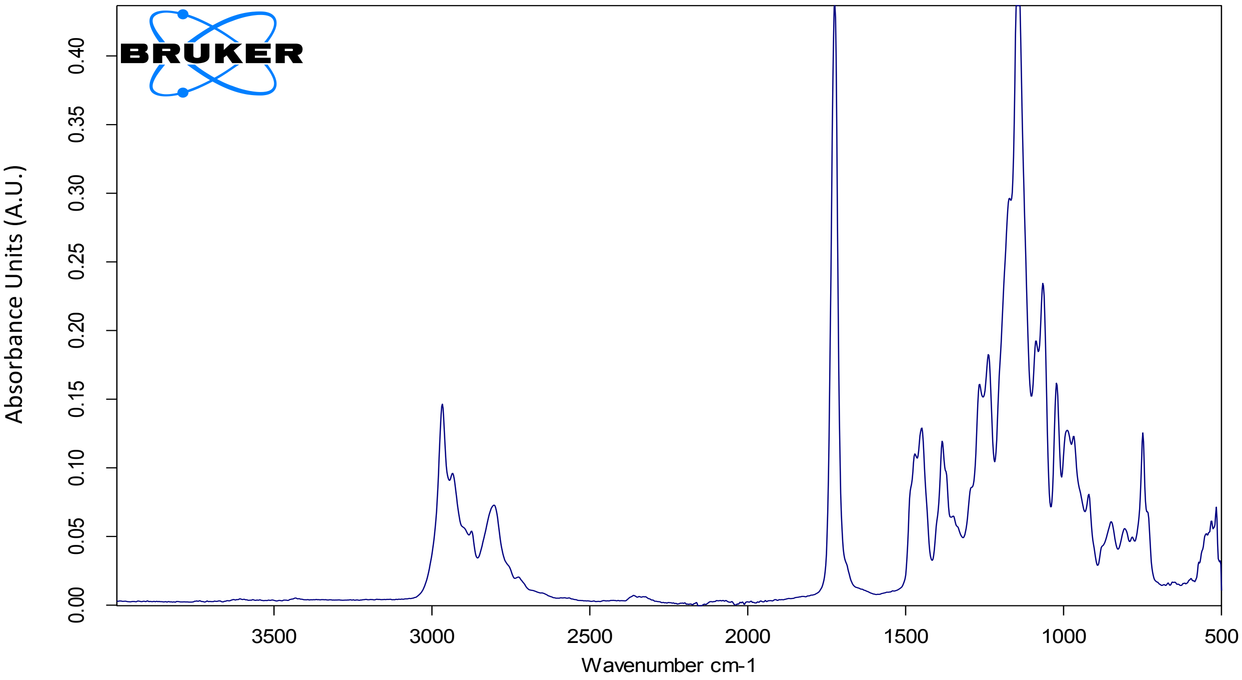


Figure S5. ATR-FT-IR spectrum. Pure 81:19 pDEAEMA-co-MMA dry powder (top) and 81:19 pDEAEMA-co-MMA dissolved in carbonated water (20 wt%; middle). The 81:19 pDEAEMA-co-MMA dissolved in carbonated water was placed on the ATR and allowed to dry for 1 h (bottom). In the dry polymer powder and in the final coating, the there is a small bicarbonate stretch at 840 cm^{-1}.

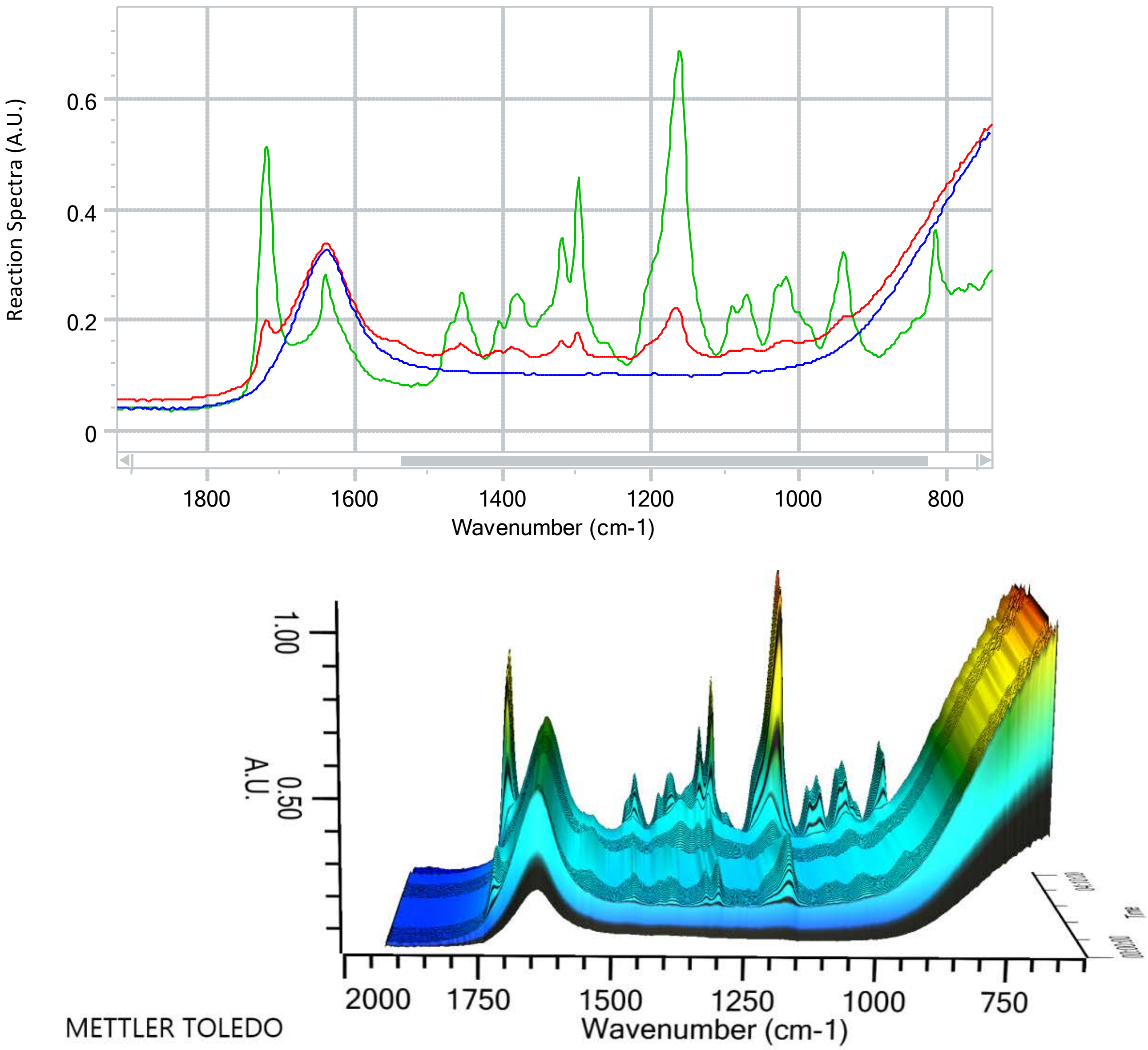


Figure S6. FT-IR spectra of DEAEMA in water. In the top image the reference spectra of water is shown (blue) and then the monomer is added (red). There is no presence of a bicarbonate peak around 840 cm^{-1}. With the addition of CO_2 through the solution, a bicarbonate peak forms around 820 cm^{-1} (green).

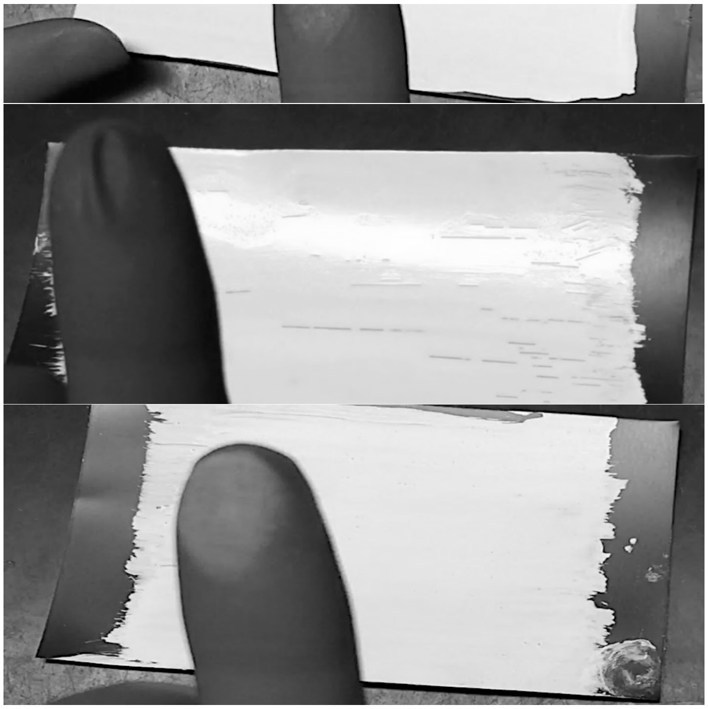
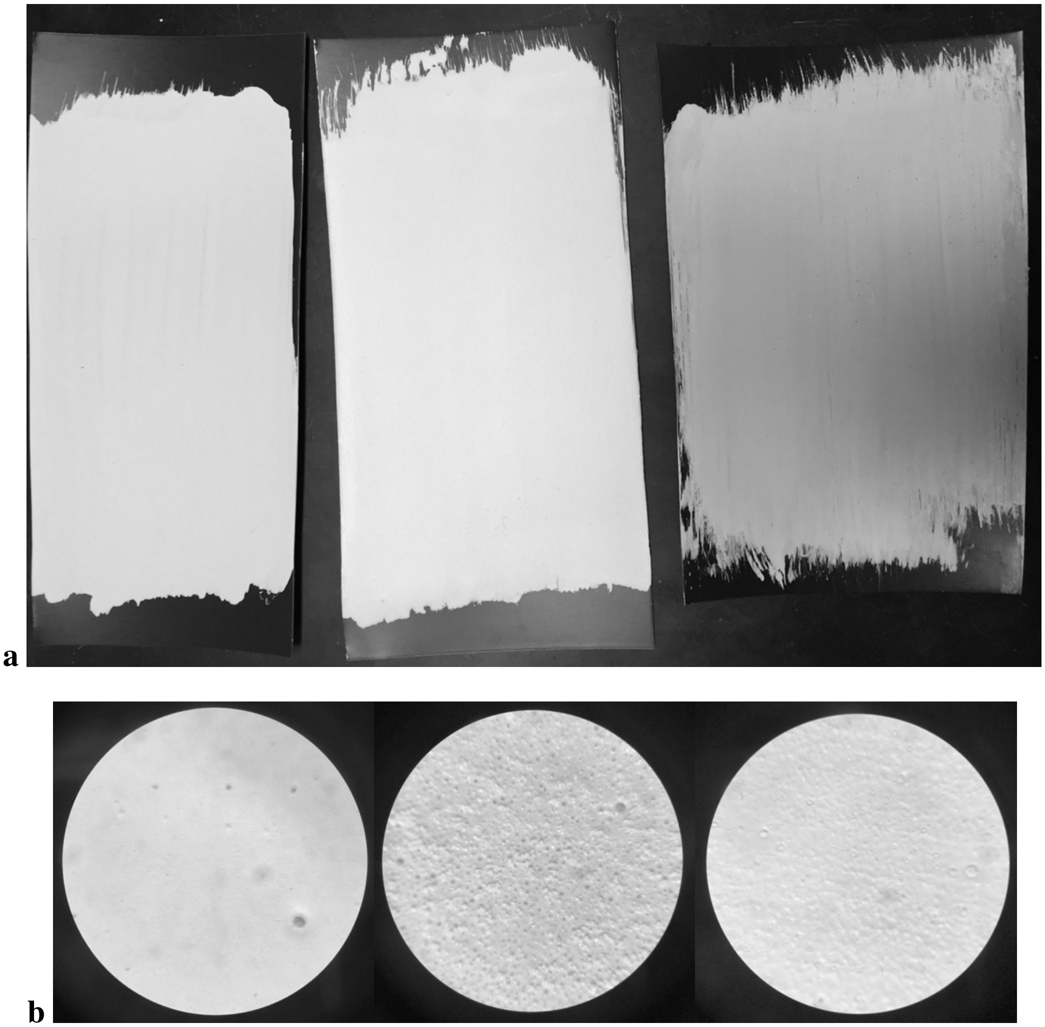


Figure S7. Chalking tests on CO_2-responsive polymers and commercial latex. Chalking tests were performed on each coating after it had dried at 5 ˚C for 24 h. Commercial latex (top), 80:20 p(DEAEMA-co-MMA) (middle) and 50:50 p(DMAEMA-co-BMA) (bottom) were each tested by brushing the dried coating with a finger in a fresh nitrile glove and noting the presence of any friable powder. p(DEAEMA-co-MMA) (middle) showed no chalking but the commercial latex (top) and pDMAEMA-co-MMA showed chalking. Both switchable coatings visually exhibited much greater gloss that the commercial coating.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b

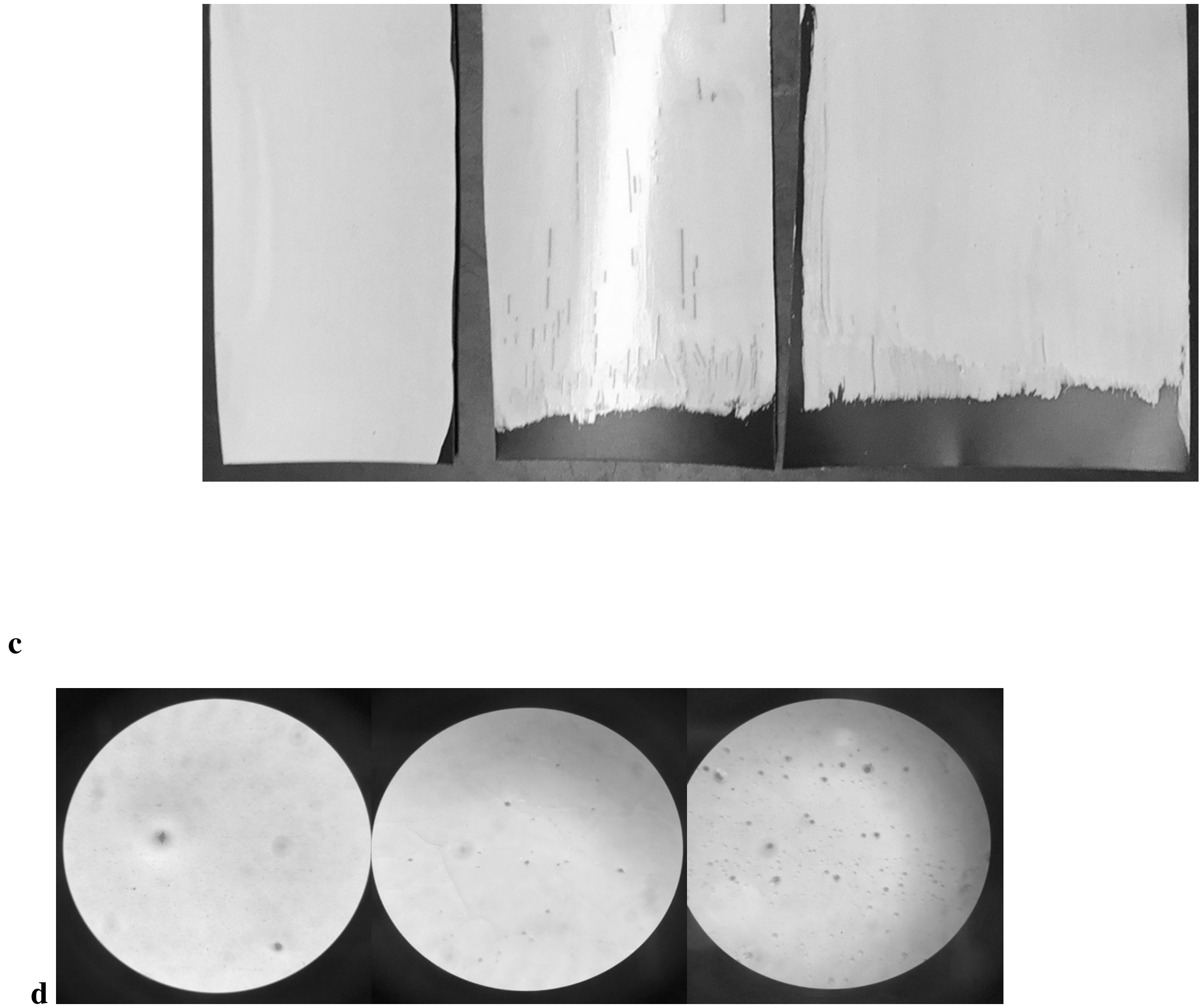

Figure S8. Room (23 ˚C) and low temperature (5 ˚C) tests for commercial latex, 80:20 p(DEAEMA-co-MMA) and 50:50 p(DMAEMA-co-BMA). a, 23 ˚C dried coatings of commercial latex (top left), 80:20 p(DEAEMA-co-MMA) (top centre) and 50:50 p(DMAEMA-co-BMA) (top right). The formulations (15 mL) for the switchable polymers were water (55 wt%), polymer (25 wt%) and TiO_2 (20 wt%). Each coating was prepared by brushing a 3 mL solution. **b,** Expanded images of the same coatings show that the copolymers have rougher finishes including pinholes that are likely caused by CO_2 bubbles that formed as the formulation was drying. **c,** Coatings made from the same formulations after application and drying at 5 ˚C. **d,** microscope images (4x magnification) of the copolymers reveal their rougher finishes including pinholes.

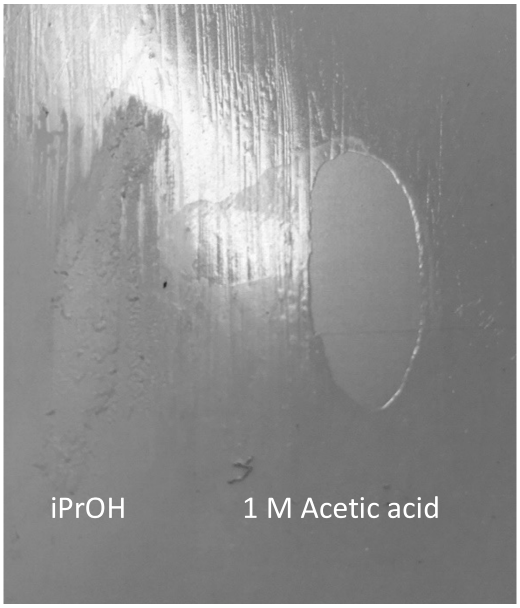

Figure S9. **Solvent testing on 60:40 pDEAEMA-co-MMA on a pre-primed aluminium plate.** Isopropanol (IPA) and 1 M acetic acid were dropped onto the dried coating then left for one minute. A lint-less wipe was then used to remove the solvent and the film was inspected for any damage caused to the film by the solvent.

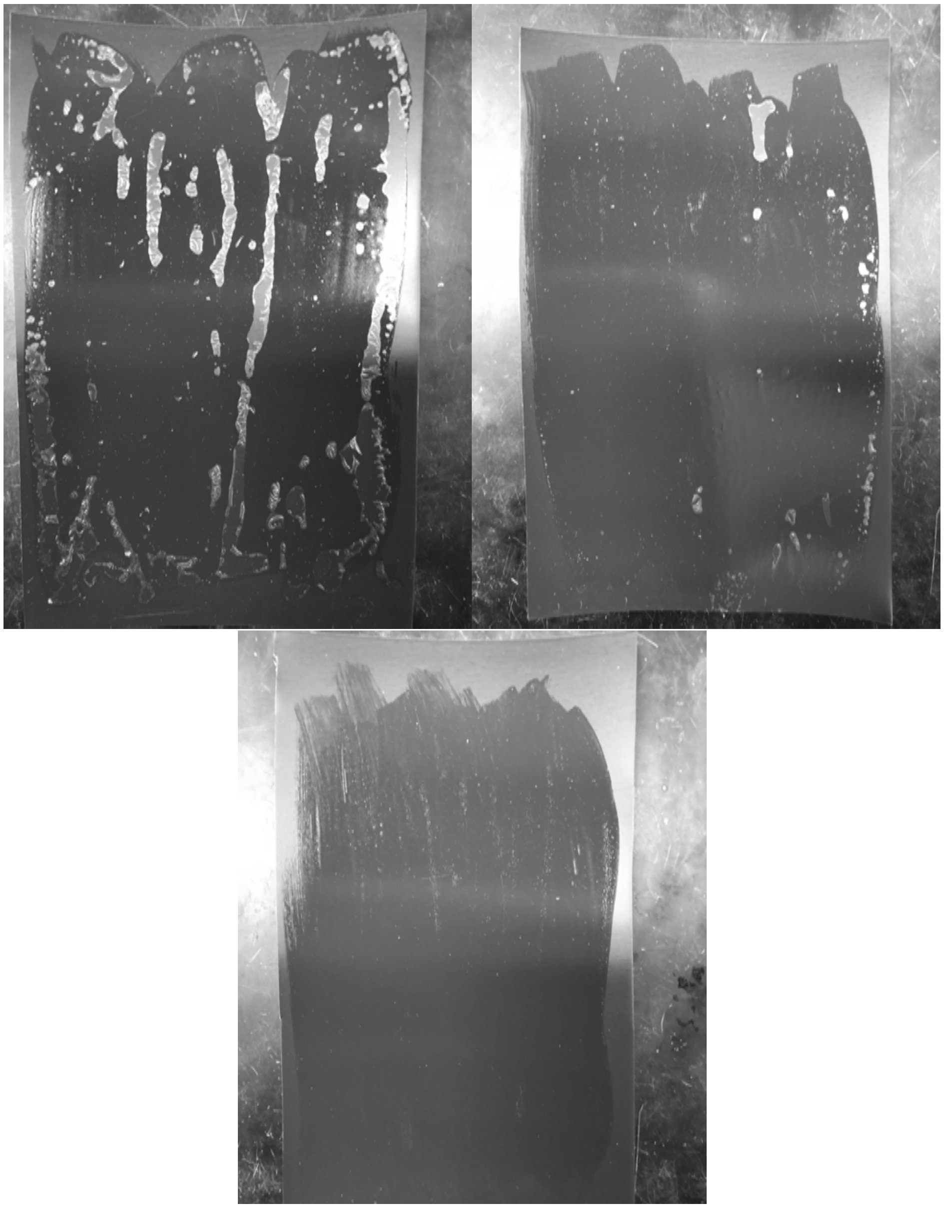

Figure S10. **Crosslinking the CO$_2$-responsive responsive polymer.** Three solutions of 20 wt% ptBAEMA in carbonated water were made. To those solutions, varying ratios of crosslinking agent (1,4-butanediol diglycidyl ether) to amine groups were added. Once brushed onto a pre-primed aluminium plate and dried, the coating with no crosslinker (top left) was rough and uneven. The coating was smoother but still had some rough domains when using a ratio of 3 crosslinking agents for every 100 amine groups (top right). When 3 crosslinking agents for every 10 amine groups was used, a smoother coating without rough domains was obtained (bottom).

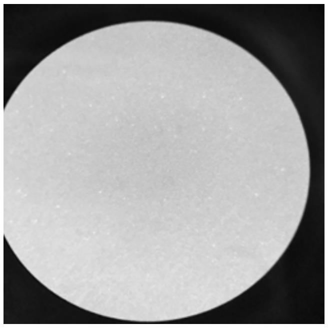

Figure S11. Microscope image of crosslinked ptBAEMA on a pre-primed aluminium plate. A dried coating (23 ˚C for 24 h) cast from ptBAEMA (20 wt%) in carbonated water with 1,4-butanediol diglycidyl ether in a ratio of 3 crosslinking agents for every 100 amine groups.

References

1 S. J. Miraglia and K. G. Mayhan, *J. Appl. Polym. Sci.*, 1989, **38**, 2303–2307.

2 D. J. Heldebrant, P. G. Jessop, C. A. Thomas, C. A. Eckert and C. L. Liotta, *J. Org. Chem.*, 2005, **70**, 5335–5338.