

## Supporting information

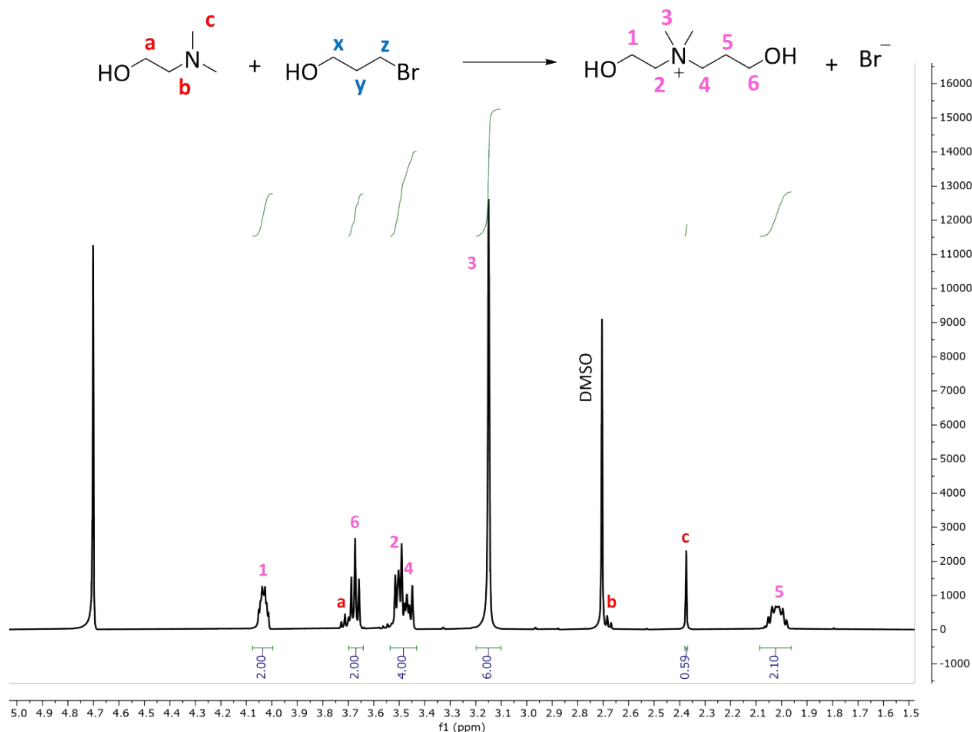
### Crosslinking CO<sub>2</sub>-Switchable Polymers for Paints and Coatings Applications

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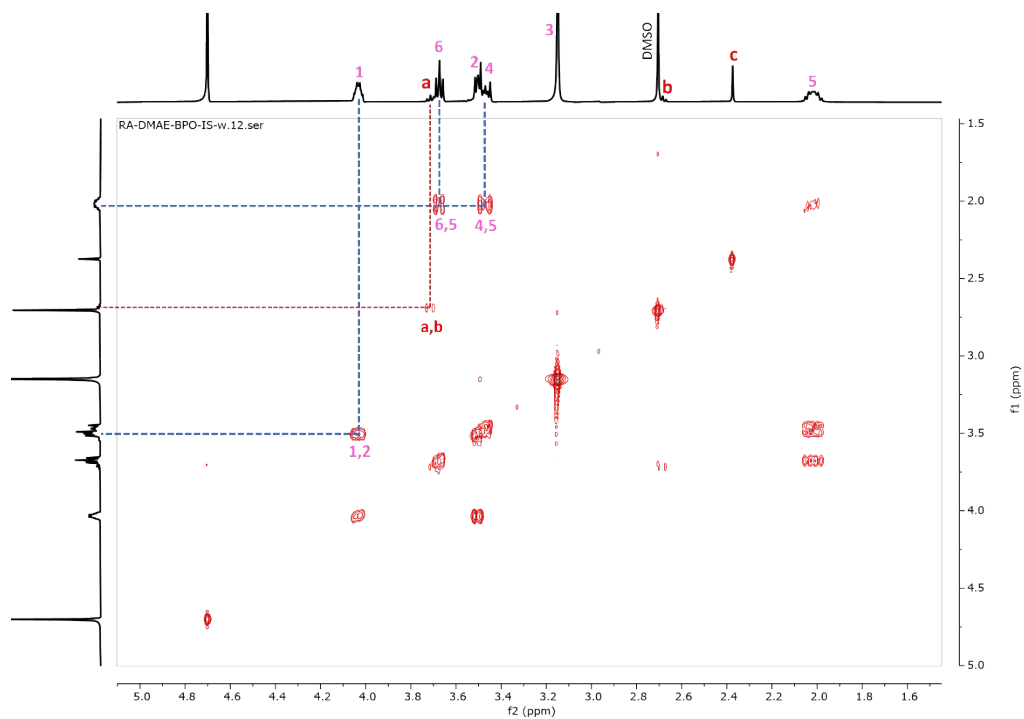
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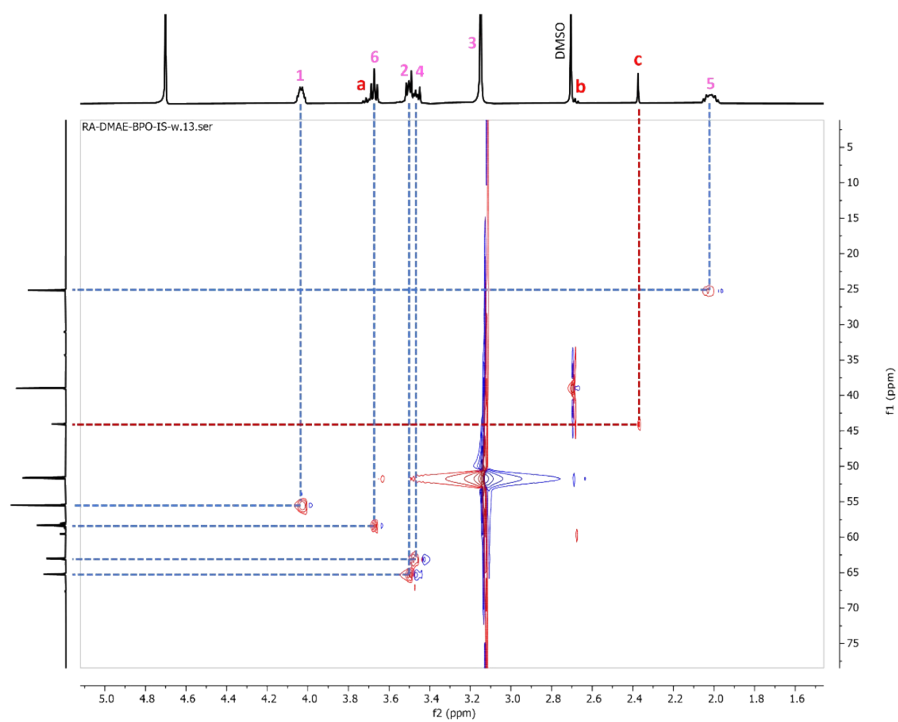
The following NMR spectra including 1D-<sup>1</sup>H NMR, 2D-COSY, and 2D-HSQC are associated with the DMAE-BPO mixture after 1 week.



**Figure S1.** 1-week <sup>1</sup>H NMR spectrum of DMAE-BPO mixture without added acid including integration values of the product and residual starting materials peaks.

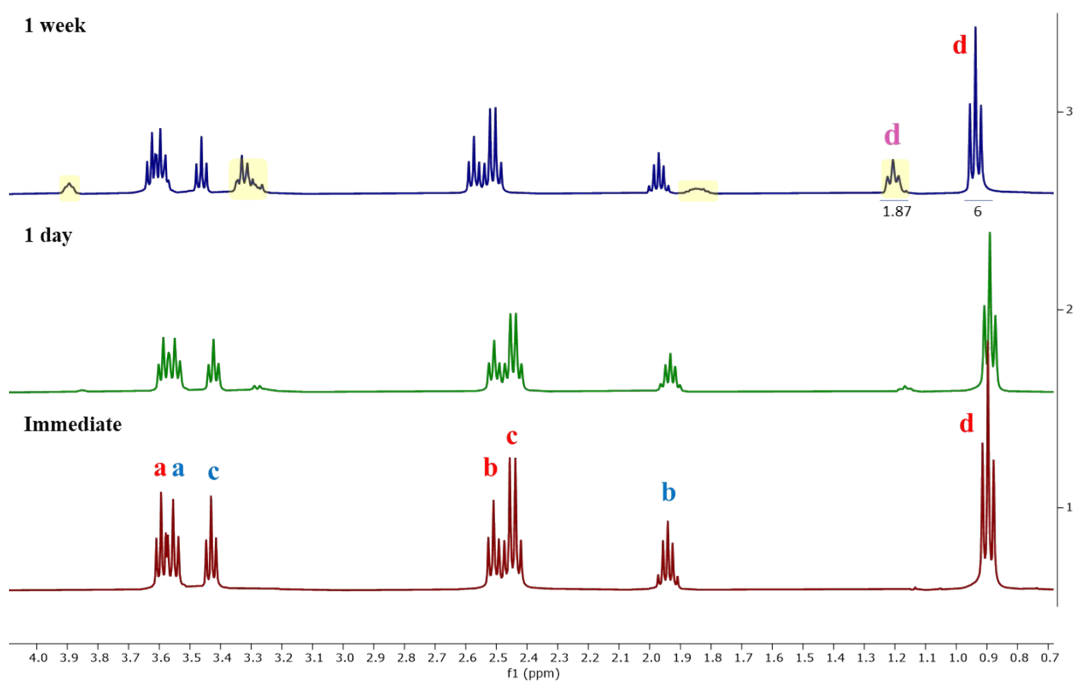
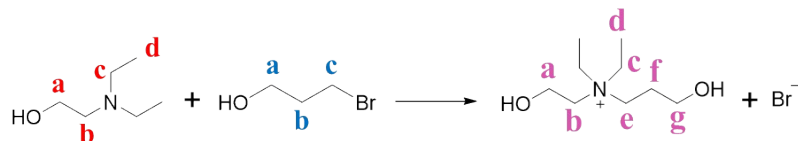


**Figure S2.** The 2D-COSY spectrum of DMAE-BPO mixture without added acid after 1 week.

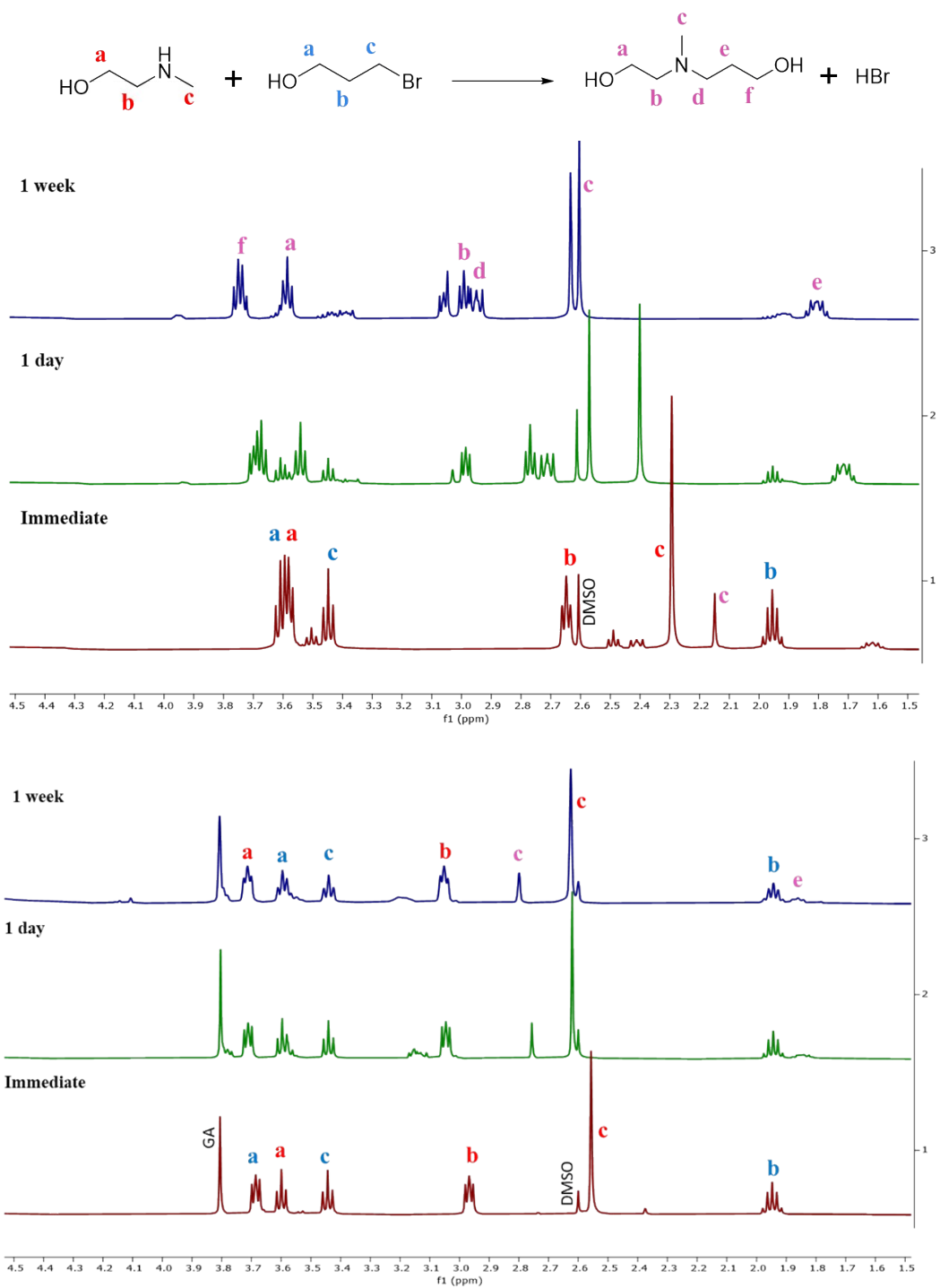


**Figure S3.** The 2D-HSQC spectrum of DMAE-BPO mixture without added acid after 1 week.

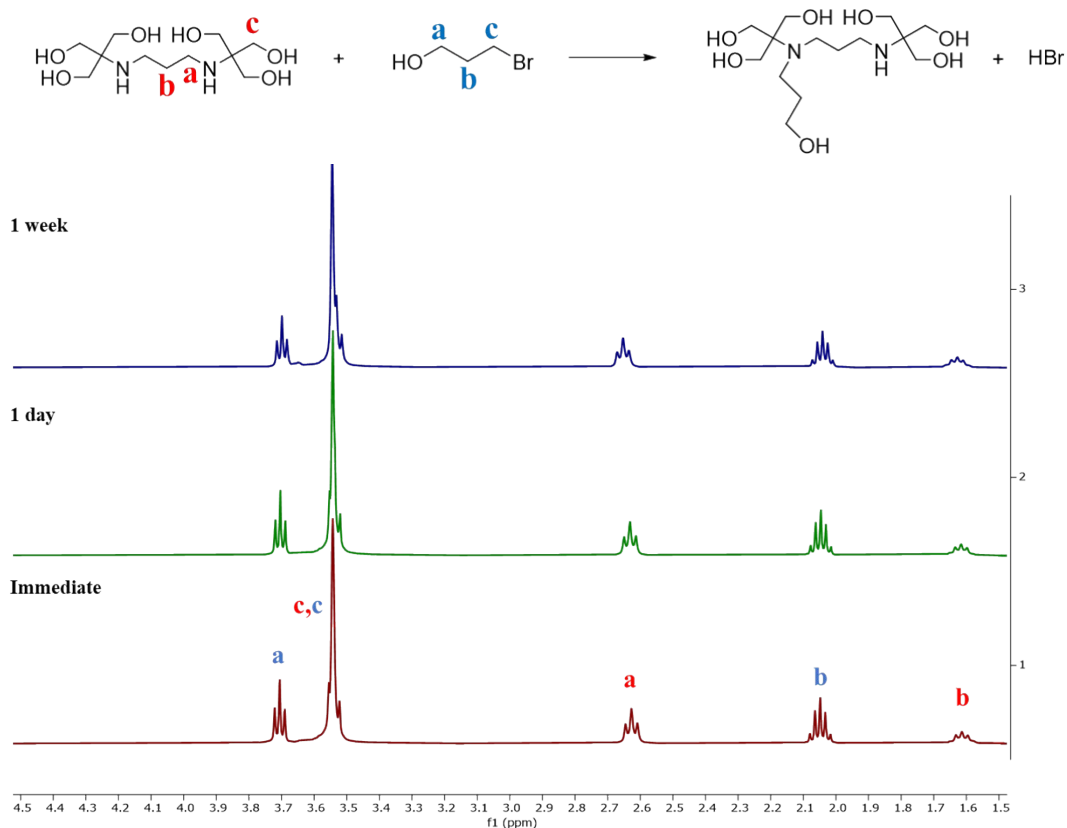
The following  $^1\text{H}$  NMR spectra correspond to the reactions that are provided in Table 1 in two conditions: a) when the amine is protonated and; b) when the amine is neutral.



**Figure S4.** Overlaid  $^1\text{H}$  NMR spectra of DEAE and BPO without added acid. All peaks that appeared in the immediate spectrum are associated with the starting materials with new highlighted ones associated with the product in the 1-week spectrum.

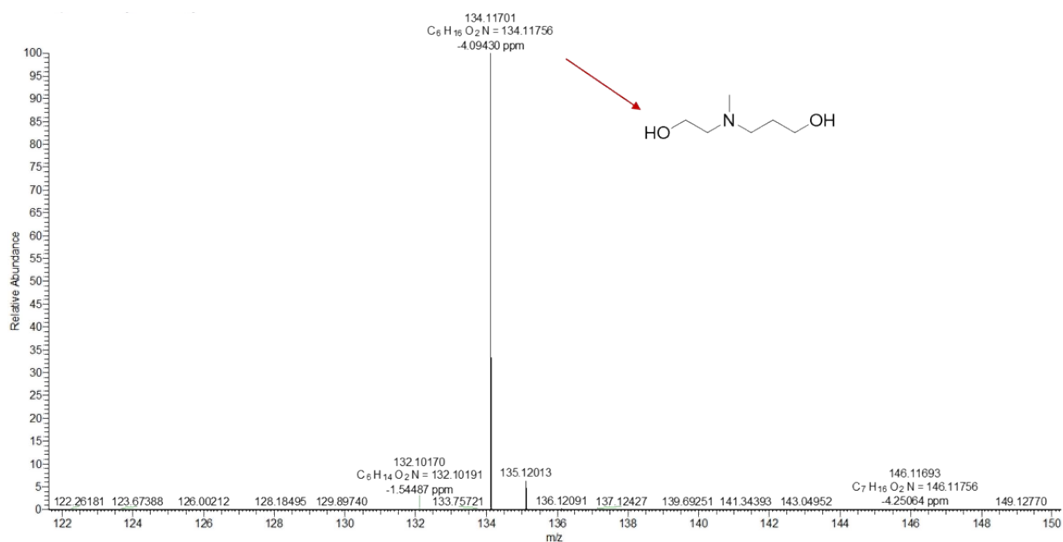


**Figure S5.** Overlaid  $^1\text{H}$  NMR spectra of MAE and BPO, in the absence of acid (above) and the same mixture with the addition of glycolic acid (below).

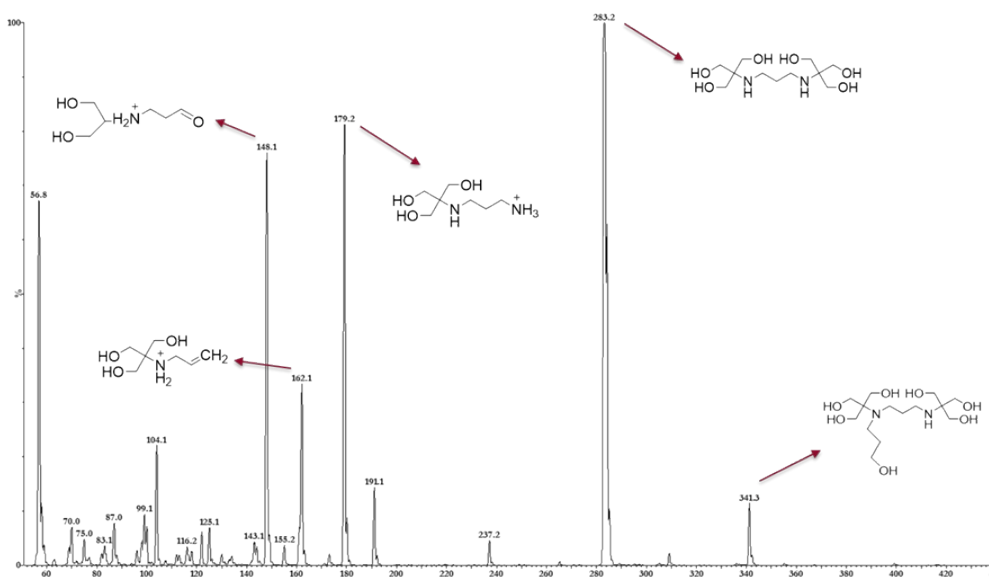


**Figure S6.** Overlaid <sup>1</sup>H NMR spectra of BTP and BPO, when the amine is in the neutral state. All peaks displayed in the spectra belong to the starting materials and there is no evidence of forming the possible product over 1 week.

The following figures display the mass spectra of each mixture of model compounds studied by  $^1\text{H}$  NMR. All samples were made in Milli-Q water and stored for 1 week prior to the test.

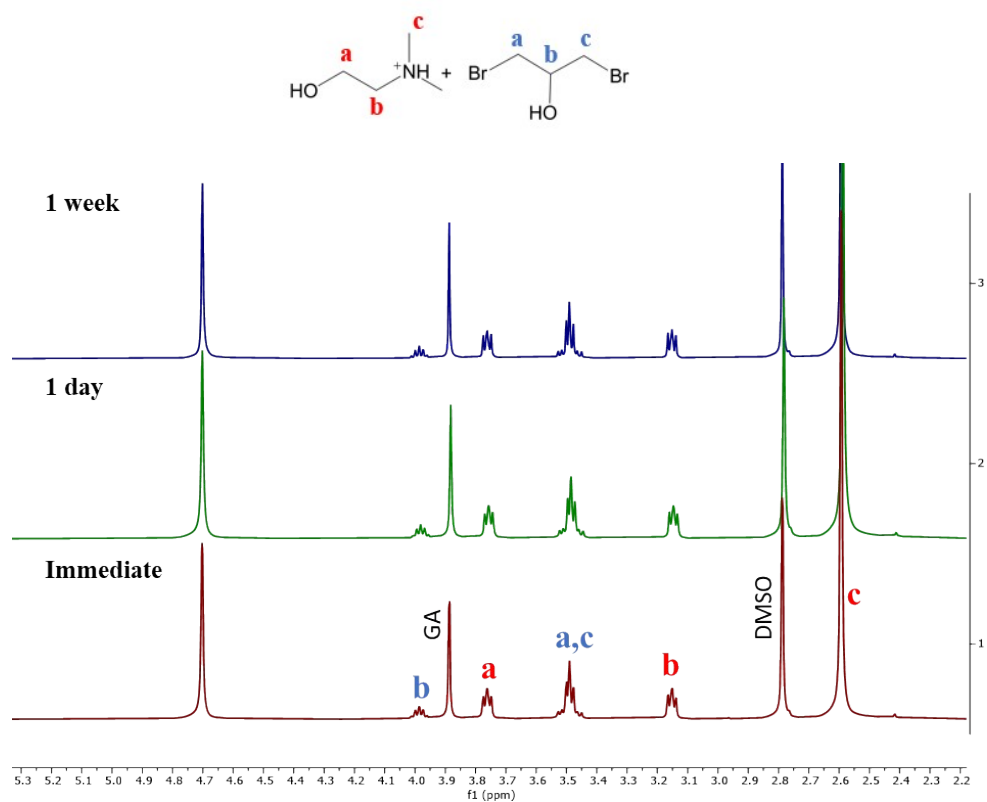


**Figure S7.** Mass spectrum of the mixture of MAE and BPO in water after 1 week.

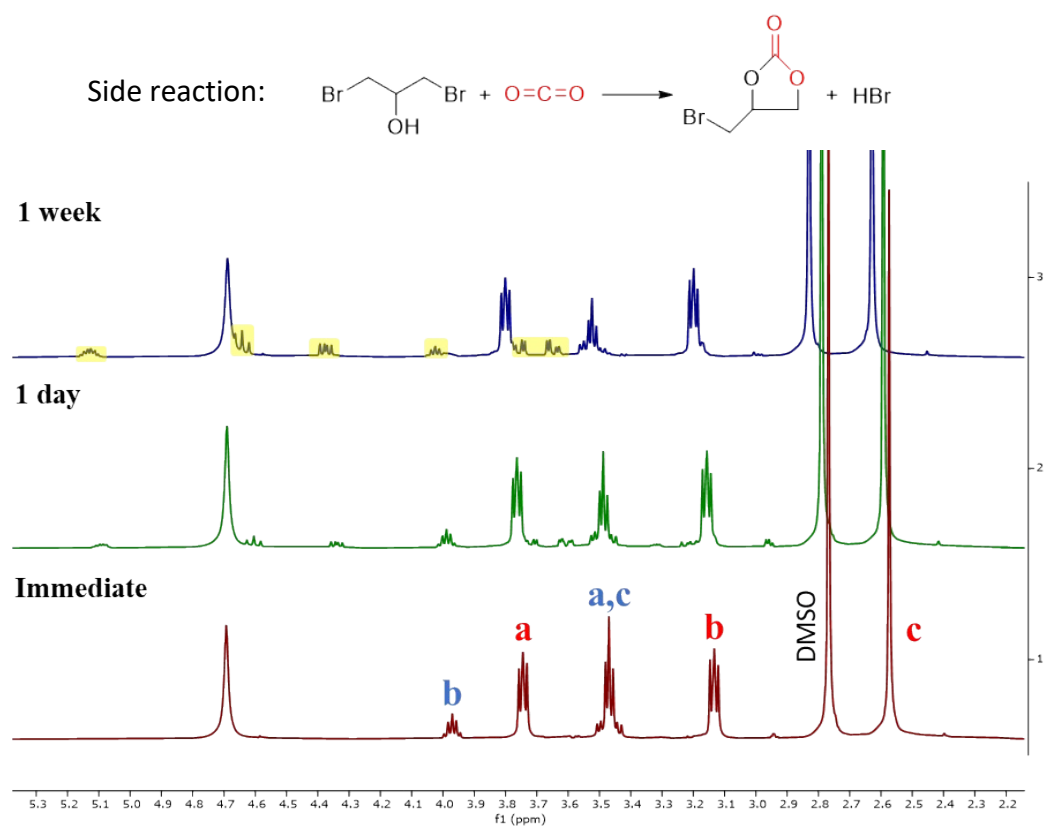


**Figure S8.** Mass spectrum of the mixture of BTP and BPO in water after 1 week.

The following  $^1\text{H}$  NMR spectra were conducted to analyze the reactivity of the coating solution using the DBPO crosslinking agent in the presence of  $\text{CO}_2$ .



**Figure S9.** Overlaid  $^1\text{H}$  NMR spectra of DMAE and DBPO, when the amine (DMAE) is protonated using GA. All peaks presented in the spectrum are associated with the protonated amine and the crosslinking agent.



**Figure S10.** Overlaid  $^1\text{H}$  NMR spectra of DMAE and DBPO when the amine is protonated by exposure to  $\text{CO}_2$  (compared with **Figure S9**). The highlighted peaks correspond to the by-product as a result of the reaction of the DBPO (crosslinking agent) with  $\text{CO}_2$ .

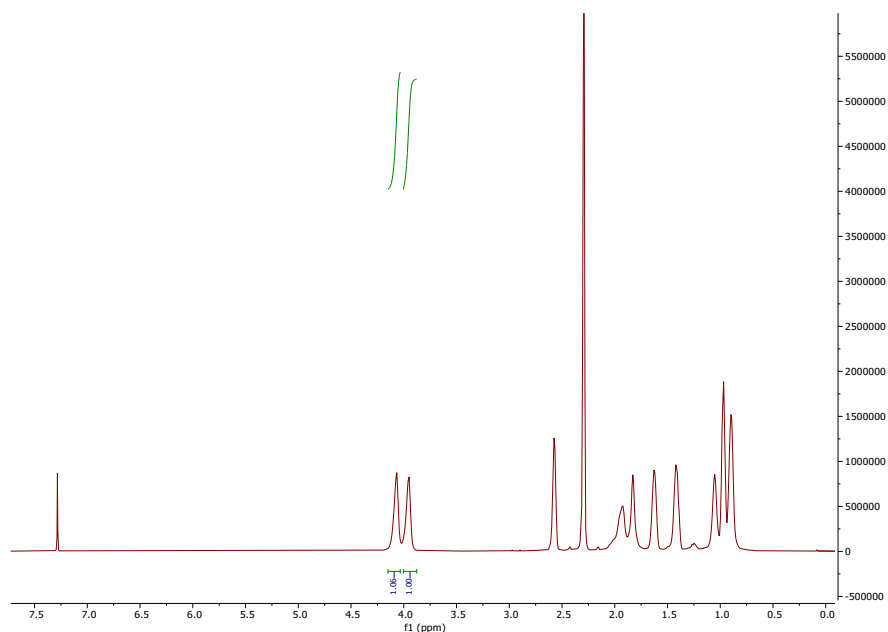


The properties of the synthesized CO<sub>2</sub>-switchable copolymers are shown in the following table followed by their <sup>1</sup>H NMR spectra.

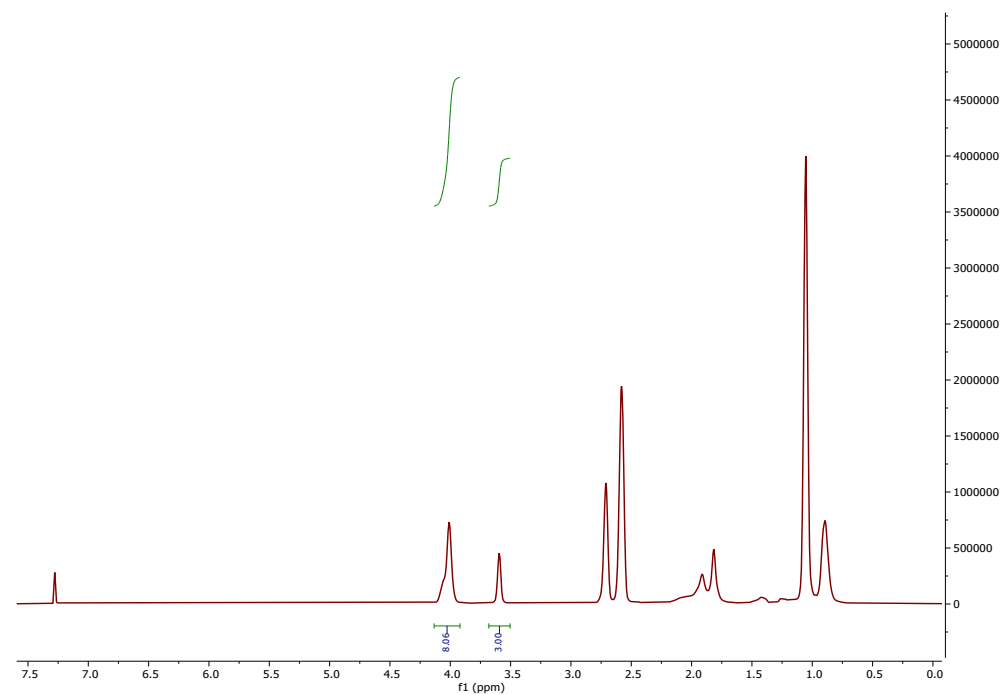
**Table S1.** CO<sub>2</sub>-switchable copolymer composition and properties.

Copolymer properties	DMAEMA:BMA	DEAEMA:MMA
Monomer molar ratio	50:50	80:20
Copolymer molar ratio from <sup>1</sup> H NMR	48:52	81:19
Mn (kDa)	28.5	41.6
Dispersity ( <i>D</i> )	2.0	1.9
Predicted T <sub>g</sub> (°C) <sup>a</sup>	19.5	26.2
Experimental T <sub>g</sub> (°C)	19	27

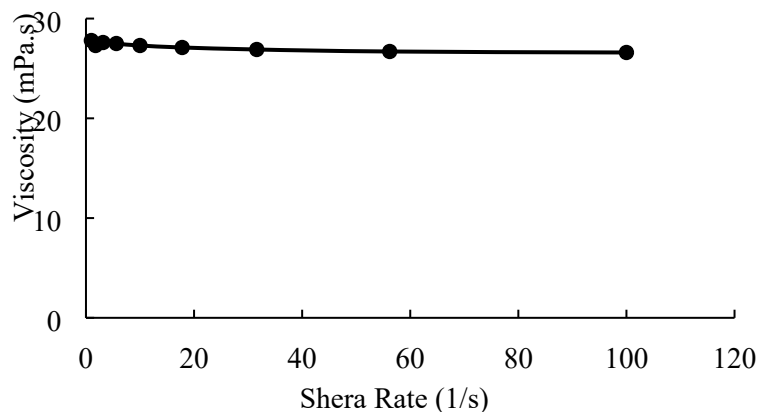
a) T<sub>g</sub> predicted from the Flory-Fox equation.



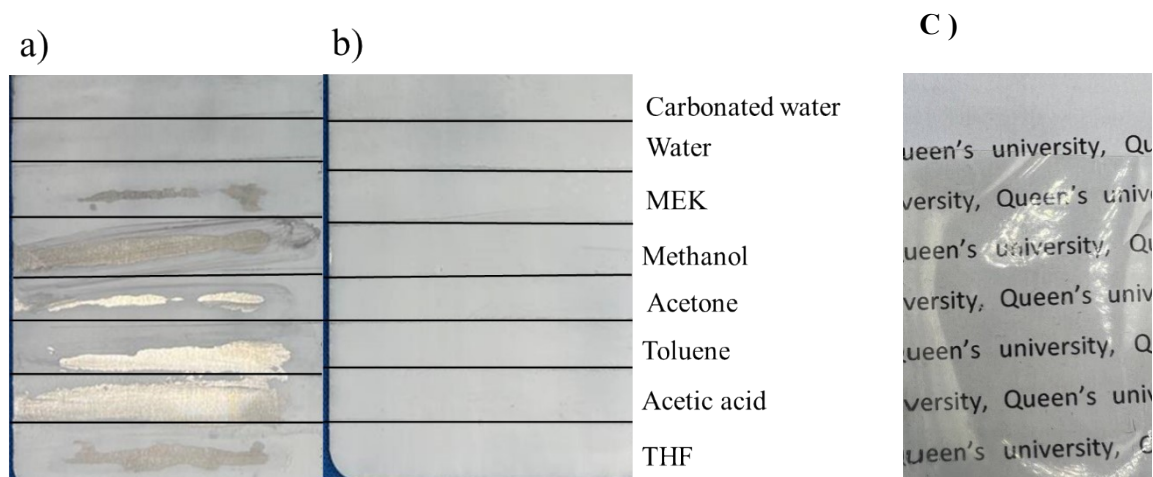
**Figure S11.** <sup>1</sup>H NMR spectrum (500 MHz) of purified 50:50, poly (DMAEMA-co-BMA) in CDCl<sub>3</sub>. Integrations of DMAEMA methylene protons attached to oxygen (4.07 ppm) and BMA methylene protons attached to oxygen (3.95 ppm) were used to determine the final composition of the copolymer.



**Figure S12.**  $^1\text{H}$  NMR spectrum (500 MHz) of purified 80:20, poly (DEAEMA-co-MMA) in  $\text{CDCl}_3$ . Integrations of DEAEMA methylene protons attached to oxygen (4 ppm) and MMA terminal methyl protons (3.5-3.6 ppm), were used to determine the final composition of the copolymer.



**Figure S13.** Viscosity versus the shear rate of the solution containing 20 wt% of CO<sub>2</sub>-switchable poly (DMAEMA-co-BMA) in carbonated water at 20 °C.



**Figure S14.** The result of the double rubbing test with various solvents on uncrosslinked (a), and crosslinked (1:10, BBEE:DMAEMA repeating unit) (b) coated films. Titanium oxide was added to the solution for the coatings made for the double rub tests. This figure is after a 50-times double-rub with each solvent. Figure S14 (C), shows the coating without adding pigments and additives, resulting in a clear and transparent film.