

Supporting information

Title: Amine functional reactive coalescing agents (RCA) for emission-free waterborne paints and coatings

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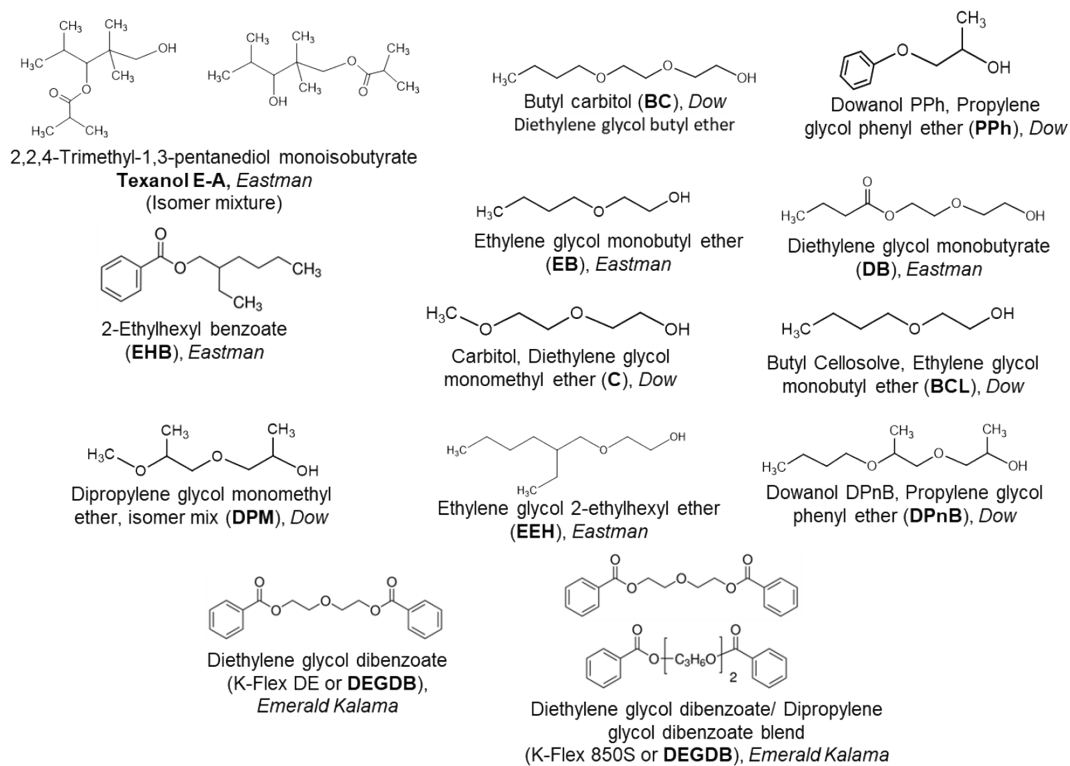


Figure S1. Example of some of the popular commercial coalescing agents.

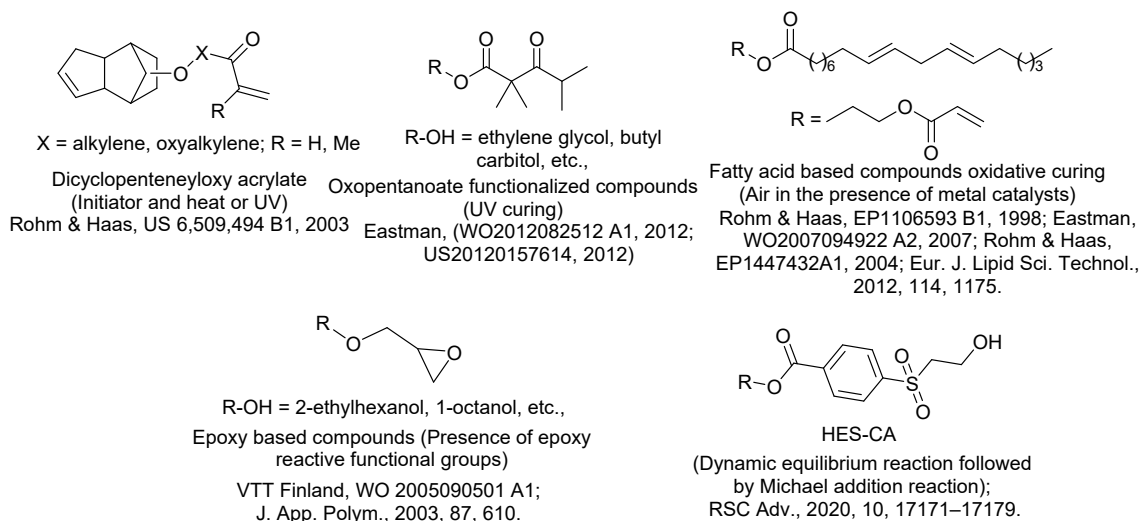


Figure S2. Some of the reactive coalescing agents (RCAs) reported in the literature.

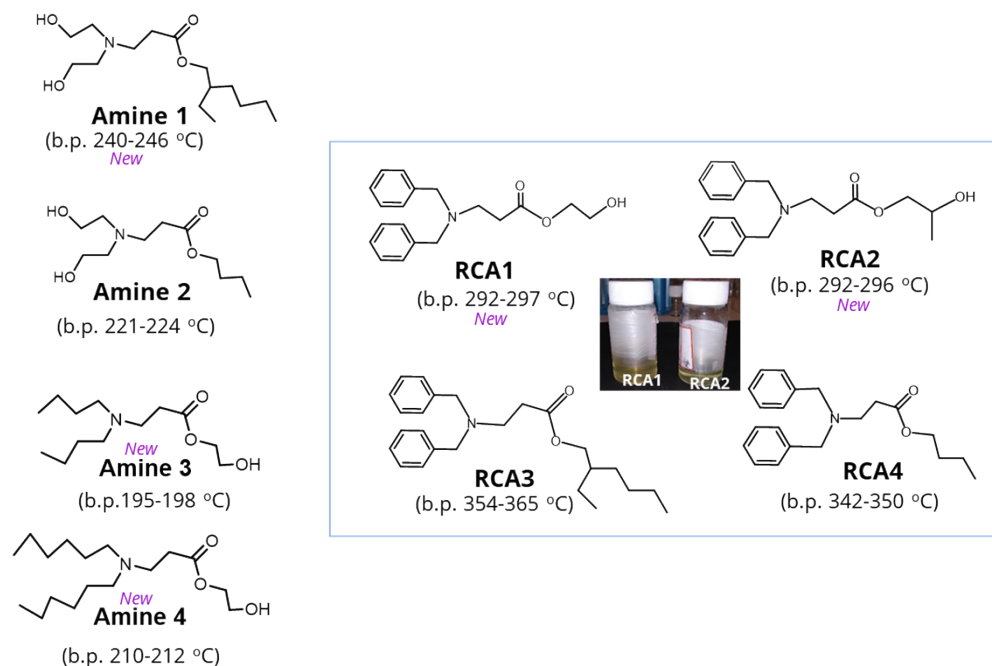


Figure S3. Amine functional reactive coalescing agents (RCAs) reported in this work.

Characterization methods

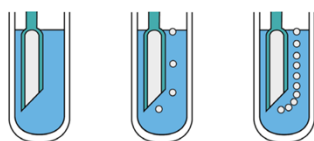
^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on an Ultrashield Bruker Avance AV400 (400 MHz) spectrometer using deuterated chloroform (CDCl_3) as the solvent. Chemical shifts for ^1H NMR were recorded in parts per million (ppm) downfield from proton signal of residual non-deuterated solvent (δ 7.26 ppm for CDCl_3 and 4.79 ppm for D_2O) as the internal signal. Coupling constants are indicated in Hertz (Hz). For ^{13}C NMR spectra, chemical shifts are reported relative to the central line of the triplet at δ 77.2 ppm for non-deuterated residuals originated from CDCl_3 . The following abbreviations are used for spin multiplicity: s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, and br=broad.

Size Exclusion chromatography (SEC) using THF flow rate 1.0 mL/min and at 40°C detector temperature was conducted on a Viscotek TDAmx which consists of three components – the GPCmax integrated solvent and sample delivery module, the TDA 302 Triple Detector Array, and the OmniSEC software. The TDA 302 incorporates RI and, Light Scattering detectors and viscometer. Only RI detector was used. 2 columns: 2 x PLgel 10um Mixed-B (500 to 10,000,000) and 1 guard column (10um) were applied in sequence for separation. THF was used as the eluent at 1.0 mL/min with column. The apparent molecular weight and dispersity (M_w/M_n) were determined with the conventional linear calibration based on polystyrene standards with calibration range of 580 to 3,000,000.

Elemental microanalysis of polymers was carried out using a Thermo Fisher Scientific FLASH 2000 CHNS/O Analyzer.

Mass spectrometry was run by the electrospray ionization time-of-flight (ESI-TOF) mode on an Agilent 6210 mass spectrometer.

Boiling point of liquids were determined using BUCHI M-565 as per Siwoloboff method (<https://www.buchi.com/en/knowledge/applications/melting-and-boiling-point-laboratory-guide>). In preparation, sample tube with an inside diameter is filled 5 to 10 mm deep with the sample liquid. A syringe was used to fill the tube. Then the boiling capillary (see figure below) is inserted into the sample tube with its open/thick end down, and the sample is put into the holding block. The start temperature is set 5 to 10 °C lower than the expected boiling point. Starting from the start temperature, the sample is heated at a temperature gradient of 1 °C/min. As the temperature rises, bubbles of gas rise slowly and regularly from the immersed end of the boiling point capillary. The boiling point of the liquid has been reached when the flow of steam bubbles reaches a frequency of 0.6 Hz (approximately 36 bubbles/ min).



The **particle size** and **MFFT** of the latex were measured respectively using Malvern DLS instrument and Rhopoint instrument (operating range, -10°C to 90°C). For MFFT measurements, the desired temperature range has been set and waited until the instrument is ready for coating. Polymer latex samples were independently applied using 75 micron cube applicator. Film formation typically takes place in 10-15 mins and MFFT of the free latices were measured in triplicate. Commercial coalescing agents Texanol, BC or RCA1-4 were independently dispersed (2 w%) with latices. The resultant dispersion was applied using the same film applicator. When films were formed, the temperature cursor was moved on the track of the film and noted down the temperature where the film coalesced over 90% of the track width. The average values from three different measurements were taken for reporting.

Volatility of liquids was determined by “EPA method 24”. Liquid of 3±1 ml was taken to an aluminum foil weighing dish using a syringe and the weight of the liquid is recorded up to three decimal. The sample was then heated at 110±3 °C for 1h inside a convection oven. Weight loss in g and wt% were accurately recorded after the experiment. The average values from three different measurements were taken for reporting.

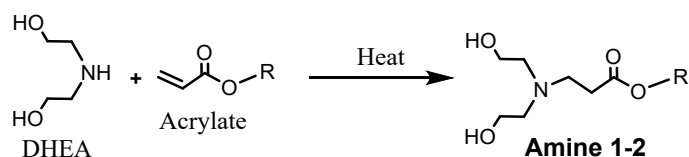
Emission of RCAs from formulations were determined using **head-space gas chromatography (HS-GC)**. A Turbomatrix (PerkinElmer) headspace sampler was used to heat samples (~2mg of RCA or ~100mg for polymer and polymer mixed with RCA) at 205 °C for 5 min before the gas sample was collected and injected to GC. Agilent 6890 GC W JASCO 2370 with atomic emission detector (AED), GC column- HP5 Agilent 19091J-41 were used for the analysis. Oven temperature 300 °C, carrier gas (He) 45 ml/min, fuel gas (H₂) for FID flow rate was 40ml/min, make-up gases for FID (compressed air and N₂) flow rate was 450 ml/min.

Experimental

Materials

Dibenzylamine, 2-hydroxyethyl acrylate, hydroxypropyl acrylate (mix of isomer), 2-ethylhexyl acrylate, ⁿbutyl acrylate, ⁿbutyl methacrylate, methyl methacrylate, methacrylic acid were purchased from Sigma Aldrich. Chloroform D (D, 99.8%) + silver foil, was obtained from Cambridge Isotope Laboratories Inc. Toluene, methanol, dichloromethane, tetrahydrofuran, and dimethylformamide were purchased from WWR chemicals. Hexane was obtained from Avantor performance materials. Activated basic alumina was obtained from Alfa Aesar. Commercial latices Joncryl 538A (**L1**) and YS800AP (**L3**) were obtained from BASF, Singapore and N-2398 (**L2**) was obtained from NIPSEA (Nippon Paint), Singapore as gift samples. Dispersing agent BYK154 was received from BYK, Singapore and white pigment rutile TiO₂, Tronox CR826 was received from Tronox, Singapore.

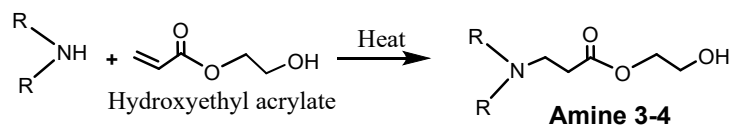
i) Synthesis of Amine 1-4:



Diethanolamine was mixed with 0.9 equivalent of 2-ethylhexyl acrylate and ⁿbutyl acrylate separately and heated at 50 °C overnight to yield 85 to 99 % conversion. The product was purified by water extraction to remove excess diethanolamine. The products were characterized with ¹H & ¹³C-NMR spectroscopy, elemental microanalysis, electrospray ionization time-of-flight mass spectroscopy (ESI-TOF MS), boiling point and volatility as per EPA method 24 (i.e. % weight loss when heated at 100 °C for 1h).

Amine 1: ¹H NMR (400 MHz, Chloroform-*d*) δ4.00-3.98 (dd), 3.55-3.52 (t), 2.89- 2.86 (t), 2.65-2.63 (t), 2.51-2.47 (t), 1.61-1.55 (m), 1.42-1.30 (m), 0.92-0.88 (t), ¹³C (101 MHz, CDCl₃) δ173.94, 67.63, 65.40, 61.11, 58.01, 51.76, 43.69, 40.35, 34.13, 31.82, 31.72, 25.13, 24.25, 14.92, 11.92. C₁₅H₃₁NO₄ Cal mass: 289.23; ESI-TOF 290.23 [M+H]⁺, Found C, 60.25; H, 10.54; N, 4.44; (Calcd C, 62.25; H, 10.80; N, 4.84). **B.p. 240-246.** Volatility (wt loss @100 °C, 1h) 14.1%.

Amine 2: ¹H NMR (400 MHz, Chloroform-*d*) δ4.07-4.03 (t), 3.54-3.51 (t), 2.87-2.84 (t), 2.64-2.61 (t), 2.49-2.45 (t), 1.63-1.56 (m), 1.43-1.33 (m), 0.94-0.90 (t). ¹³C (101 MHz, CDCl₃) δ173.62, 101.35, 65.03, 60.90, 57.80, 51.54, 33.90, 31.92, 20.24, 14.42. C₁₁H₂₃NO₄ Cal mass: 233.16; ESI-TOF 234.17 [M+H]⁺. Found C, 52.89; H, 9.34; N, 5.92; (Calcd: C, 56.63; H, 9.94; N, 6.00). **B.p. 221-224.** Volatility (wt loss @100 oC, 1h) 14.7%.



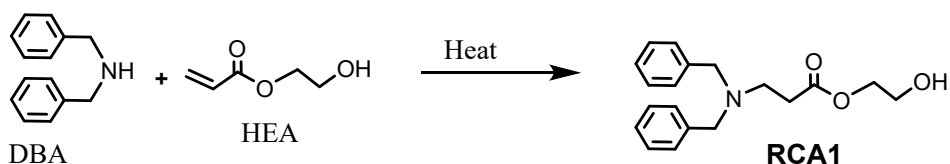
R= ⁿButyl or Hexyl

Dibutylamine or dihexylamine (1 eqv) was separately reacted with 2-hydroxyethyl acrylate (1.1 eqv) at 60 °C overnight to yield 80 to 90 % conversion. The product was purified by water extraction to remove excess 2-hydroxyethyl acrylate. The products were characterized with ¹H & ¹³C-NMR spectroscopy, elemental microanalysis, electrospray ionization time-of-flight mass spectroscopy (ESI-TOF MS), boiling point.

Amine 3: ^1H NMR (400 MHz, Chloroform-*d*) δ 4.35-4.04 (m), 3.77-3.59 (m), 2.73 (t), 2.56-2.24 (m), 1.45-1.30 (m), 1.22 (dtd), 0.96-0.69 (m). ^{13}C (101 MHz, CDCl_3) δ 172.73, 65.76, 60.74, 53.41, 49.82, 49.22, 32.84, 32.11, 29.08, 28.08, 20.71, 14.02. $\text{C}_{13}\text{H}_{27}\text{NO}_3$ Cal mass: 245.2; ESI-TOF 246.26 $[\text{M}+\text{H}]^+$. Found C, 62.82; H, 10.64; N, 5.68; Calcd. C, 63.64; H, 11.09; N, 5.71). b.p. 195-198 °C.

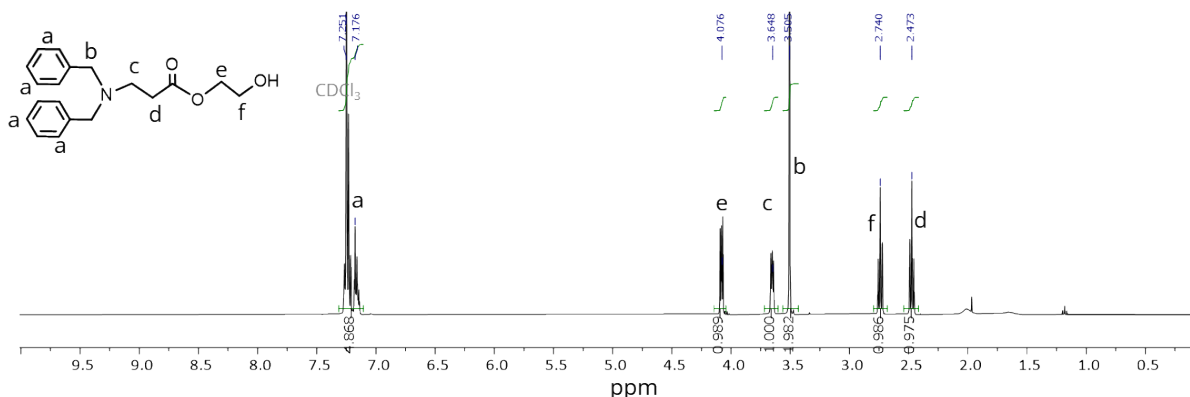
Amine 3: ^1H NMR (400 MHz, Chloroform-*d*) δ 3.76-3.64 (m), 2.71 (t), 2.45 (t), 2.41-2.32 (m), 1.43 -1.29 (m), 1.21 (td), 0.88- 0.72 (m). ^{13}C (101 MHz, CDCl_3) δ 172.79, 65.74, 60.75, 53.75, 49.86, 32.91, 31.73, 27.26, 25.97, 22.64, 14.01. $\text{C}_{17}\text{H}_{35}\text{NO}_3$ Cal mass: 301.26; ESI-TOF 302.23 $[\text{M}+\text{H}]^+$. Found C, 66.21; H, 11.32; N, 4.46; Calcd. C, 67.73; H, 11.70; N, 4.65). b.p. 210-212 °C.

ii) Synthesis and characterization of RCAs

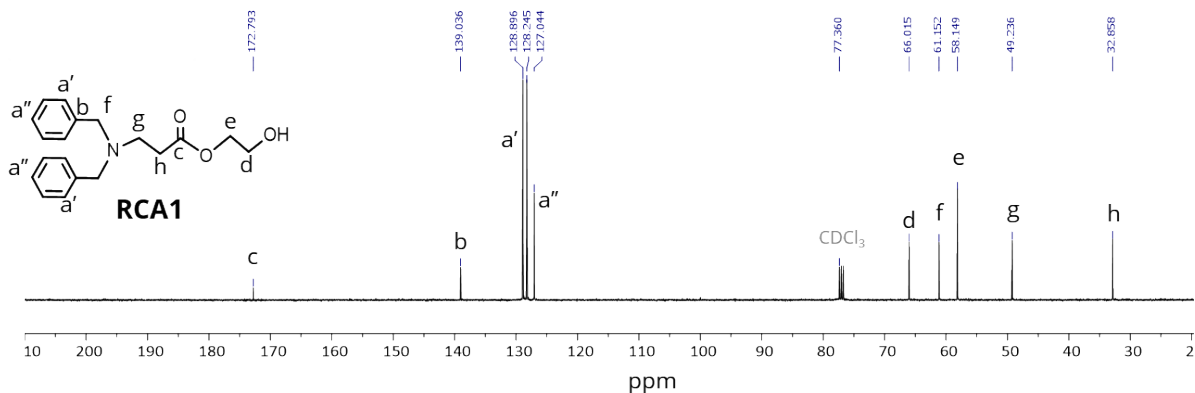


RCA1: Dibenzylamine (2 mL, 10.4 mmol) was added to 50 mL single neck RB flask at atmospheric conditions followed by slow addition of 2-hydroxyethyl acrylate (1.31 mL, 11.4 mmol) compound at RT. The reaction continued for 30h at 50 °C and ^1H -NMR shows monomer conversion of 88.2%. The reaction mixture stirred in water for 30 min to remove any excess 2-hydroxy ethyl acrylate monomer and extracted with CHCl_3 solvent followed by rotary evaporator and vacuum dry at RT yielding 78% of compound and further purified by column chromatography to ensure purity yields light pale yellowish color viscous liquid. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.13-7.27 (m), 4.07 (t), 3.76-3.73 (t), 3.65 (t), 3.50 (s), 2.74 (t), 2.47 (t); ^{13}C NMR (101 MHz, CDCl_3) δ 172.79, 139.04, 128.89, 128.25, 127.04, 66.01, 61.15, 58.15, 49.24 and 32.86; b.p. 292-297 °C. $\text{C}_{19}\text{H}_{23}\text{NO}_3$ Cal mass: 313.17; ESI-TOF 314.17 $[\text{M}+\text{H}]^+$.

^1H NMR spectrum of **RCA1**



^{13}C NMR spectrum of **RCA1**



RCA2, **RCA3** and **RCA4** were synthesized in a similar way as **RCA1**, by reacting dibenzylamine with hydroxypropyl acrylate (mix of isomer), 2-ethylhexyl acrylate, ⁿbutyl acrylate respectively. Characterization details of these compounds are given below.

RCA2: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.40-7.38 (d), 7.33-7.29 (t), 7.24-7.21 (t), 3.94-3.88 (m), 3.77 (b), 3.60 (s), 2.82-2.77 (dd), 2.57-2.50 (m), 1.17-1.16 (d), 1.11-1.10 (d); ^{13}C NMR (101 MHz, CDCl₃) δ 173.27, 173.08, 141.12, 130.27, 129.65, 128.36, 72.90, 70.69, 66.38, 66.06, 59.28, 50.69, 50.60, 33.96, 33.76, 20.71, 17.33; Calcd: C, 73.37; H, 7.70; N, 4.28, Found: C, 73.18; H, 7.81; N, 4.34; b.p. 292-296 °C. C₂₀H₂₅NO₃ Cal mass : 327.18; ESI-TOF 328.19 [M+H]⁺.

RCA3: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.40-7.38 (d), 7.30-7.33 (t), 7.21-7.25 (t), 3.96-3.94 (m), 3.60 (s), 2.87 (s), 2.84 (s), 2.81-2.77 (t), 2.55-2.51 (t), 1.52 (m), 1.28 (m), 0.89-0.85 (m); ^{13}C NMR (101 MHz, CDCl₃) δ 173.23, 140.92, 130.09, 129.50, 128.22, 67.37, 59.08, 50.45, 40.12, 33.66, 31.63, 24.94, 24.11, 14.82, 11.80; Calcd: C, 78.7; H, 9.25; N, 3.67, Found: C, 78.23; H, 9.20; N, 3.64; b.p. 354-364 °C. C₂₅H₃₅NO₂ Cal mass: 381.27; ESI-TOF 382.27 [M+H]⁺.

RCA4: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.38-7.36 (d), 7.32-7.29 (t), 7.24-7.20 (t), 3.99 (t), 3.58 (s), 2.86 (s), 2.83 (s), 2.77 (t), 2.51 (t), 1.56-1.49 (m), 1.38-1.28 (m), 0.91-0.87 ((t); ^{13}C NMR (101 MHz, CDCl₃) δ 173.16, 140.97, 130.09, 129.48, 128.20, 64.94, 59.09, 50.46, 33.68, 31.93, 20.27, 14.48; Calcd: C, 77.50; H, 8.36; N, 4.30; Found: C, 77.80; H, 8.32; N, 4.31; b.p. 342-350 °C. C₂₁H₂₇NO₂ Cal mass: 325.20; ESI-TOF 326.21 [M+H]⁺.

iii) Interaction study of **RCA1** with methacrylic acid (**MAA**)

MAA (7 mg, 81 micromol) and RCA1 (26 mg, 83 micromol) were weighed into a glass vial mixed and dissolved in CDCl₃ (0.8 ml) before analysing with NMR spectroscopy. Separately NMR spectra of MAA (7 mg, 81 micromol) and RCA1 (26 mg, 83 micromol) mixture in CDCl₃ (0.8 ml) were also recorded for comparison purpose.

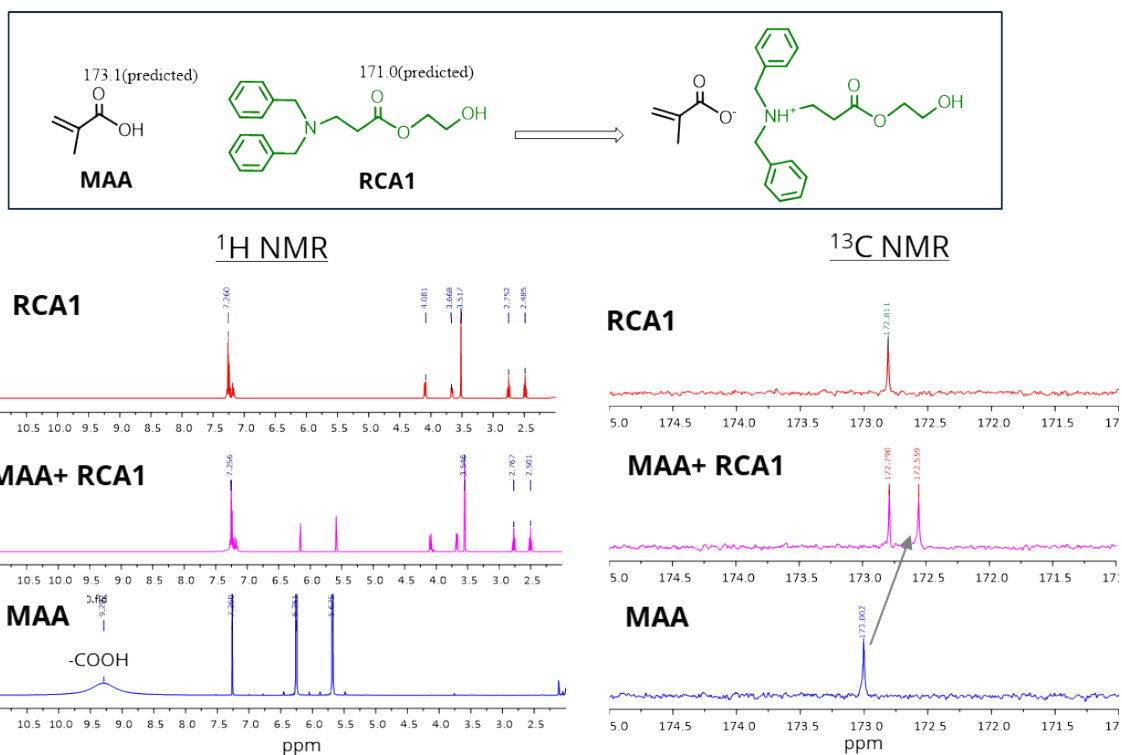
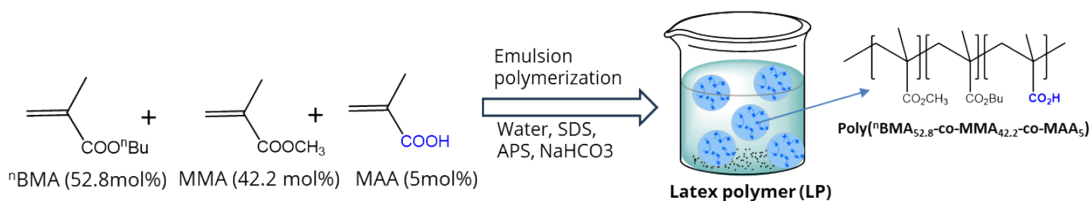
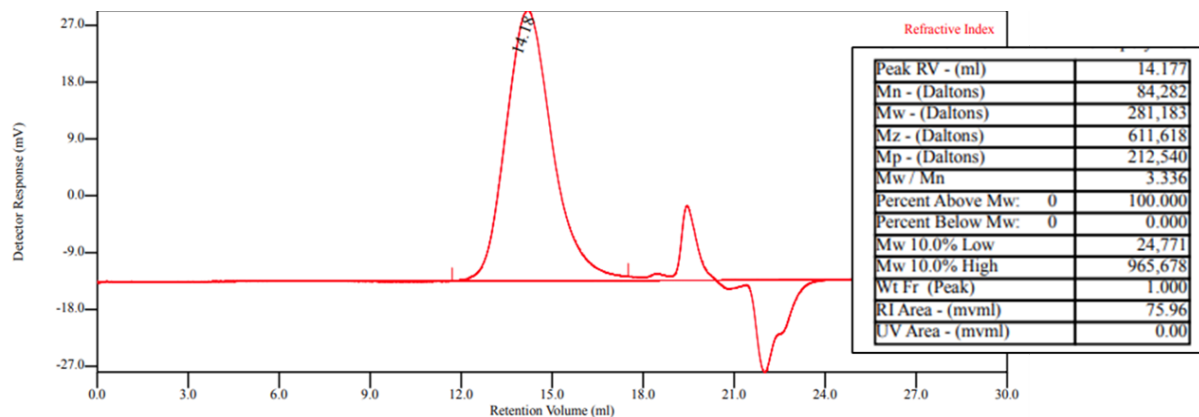


Figure S4. Overlaid ¹H NMR and ¹³C NMR spectra of MAA, MAA+RCA1 and RCA1 in CDCl₃.

iv) **Synthesis of in-house latex polymer (LP) (poly (¹³BMA_{52.8}-co-MMA_{42.2}-co-MAA₅)) for reactivity study**



In a 250 mL glass jacketed reactor was charged with 125 g of distilled water, 2.0 g of sodium dodecyl sulphate, 0.885 g of ammonium persulfate and 650 mg of NaHCO₃. The solution was purged with argon for 30 min at room temperature. The monomer mixture (¹³BMA, MMA and MAA: 46.26, 26.04g and 2.662g respectively (i.e. 5mol% MAA) (total 85.66ml)) was degassed with argon for 40 min at room temperature and added via syringe for 3 hrs (≈ 27 mL/h). The glass reactor was connected to Lauda water heater and the reaction was continued for 6 h at 65 °C. Finally, the reaction mixture was heated to 80 °C for 1.0 h to complete the polymerization reaction and no fouling was observed in the reaction. The latex pH was measured as 5.63, which was adjusted to ≈ 10.0 using a few drops of NH₃ (aq) for long term stabilization. The latex particle size was measured using Malvern DLS instrument ($Z_{ave} = 63$ nm, PDI = 0.075), solid content 39 wt% and calculated T_g (Fox) 50 °C. MFFT measured was 56 °C (average of three measurements using Rhopoint instrument). Latex polymer M_n 84300, M_w 281200 and PDI 3.34.



SEC chromatogram and analysis result of LP

v) **Reactivity study of RCA1 with LP (poly(ⁿBMA_{52.8}-co-MMA_{42.2}-co-MAA₅)) by ¹H NMR and head-space GC analysis**

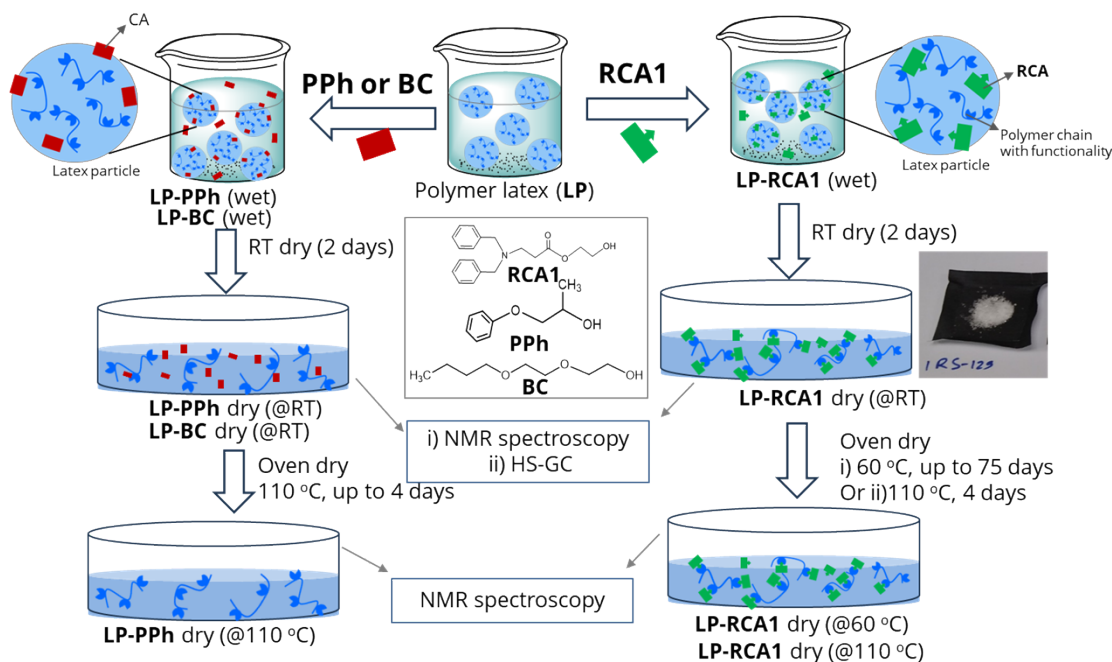


Figure S5. Scheme of preparation CA (**PPh** or **BC**) or **RCA1** blend with LP and characterization of produced materials with ¹H NMR and HS-GC. Unreactive coalescing agents, **PPh** or **BC** were used a control to compare performance with **RCA1**.

Residual sample analysis (¹H NMR) of low temperature treatment: **RCA1** (1g, 2 wt% respect to latex) was blended with -COOH containing latex, **LP** (49 g) in a glass beaker using dispermat (LC75-E, 200-500 rpm, 15 min) and the mixture was allowed to dry at room temperature for 2 days (in glass vial). Then the polymer film was ground with a spatula to make polymer powder/flakes (**LP-RCA1** dry @RT). The sample (open glass vial) was then heated at 60 °C inside a convection oven for days. Samples were collected time to time (d=0, 7, 17 and 70) for NMR spectroscopy. Typically, 25 mg of polymer sample (**LP-RCA1** dry @60

°C, xd) was dissolved in 0.8 ml of CDCl_3 , and 25 μl of separately prepared stock solution of DMF in CDCl_3 was added to it by micro-syringe as internal standard. The resultant solution was scanned for 64 times to record ^1H NMR spectra.

Head-space GC analysis: The **LP-RCA1** dry (@RT) sample (~100mg) was taken in a clean HS-GC quartz vial. The sample was heated inside a Turbomatrix headspace sampler at 205 °C and the gas phase content was injected to Agilent 6890 GC W JASCO 2370 system connected with atomic emission detector (AED) (GC column- HP5 Agilent 19091J-41). Oven temperature 300 °C, H_2 flow 40ml/min, airflow 450 ml/min, make up (He) flow 45 ml/min. Two controls were also analyzed where i) 4 mg of **RCA1** was loaded in a HS-GC quartz vial for similar analysis and ii) where 96 mg of **LP** dry sample was physically mixed with 4 mg of **RCA1** before HS-GC analysis.

Residual sample analysis (^1H NMR) of high temperature treatment: The **LP-RCA1** dry (@RT) sample prepared above was heated at 110 °C inside a convection oven for 4 days. Samples were collected time to time (d= 0, 2, and 4) for NMR spectroscopy. Typically, 25 mg of polymer sample taken in an 1ml glass vial, dissolved in 0.8 ml of CDCl_3 , and 25 μl of separately prepared stock solution of DMF in CDCl_3 was added to it by micro-syringe as internal standard. The resultant solution was scanned for 64 times to record ^1H NMR spectra.

For the comparative study high boiling commercial coalescing agent, **PPH** (b.p. 243 °C) was used instead of **RCA1** as control.

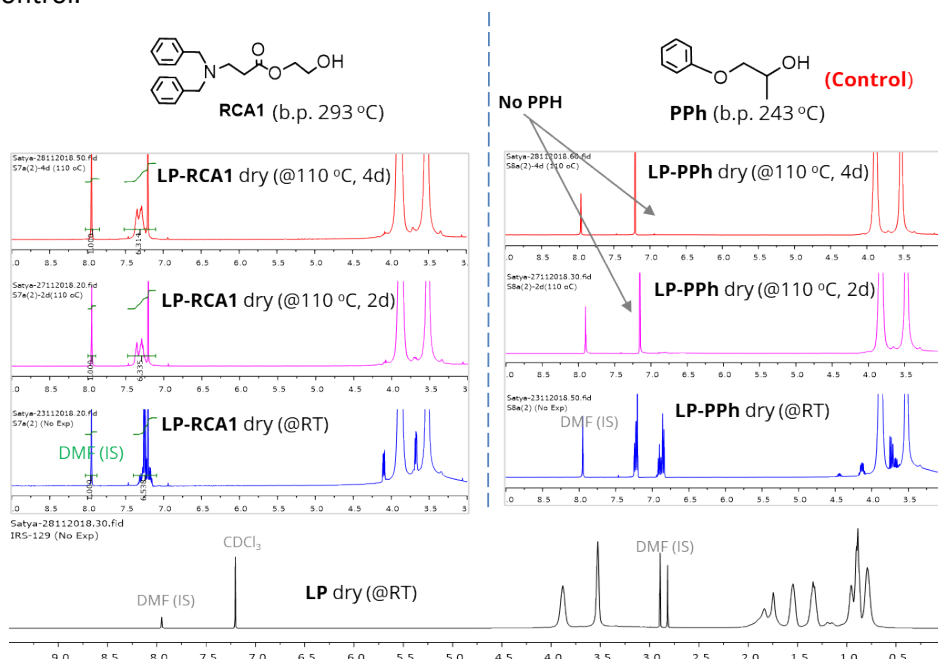


Figure S6. Residual sample analysis (^1H NMR) of high temperature treated **LP-RCA1** and **LP-PPH** dry blends (see **Figure S5**). **PPh** was used as non-reactive control.

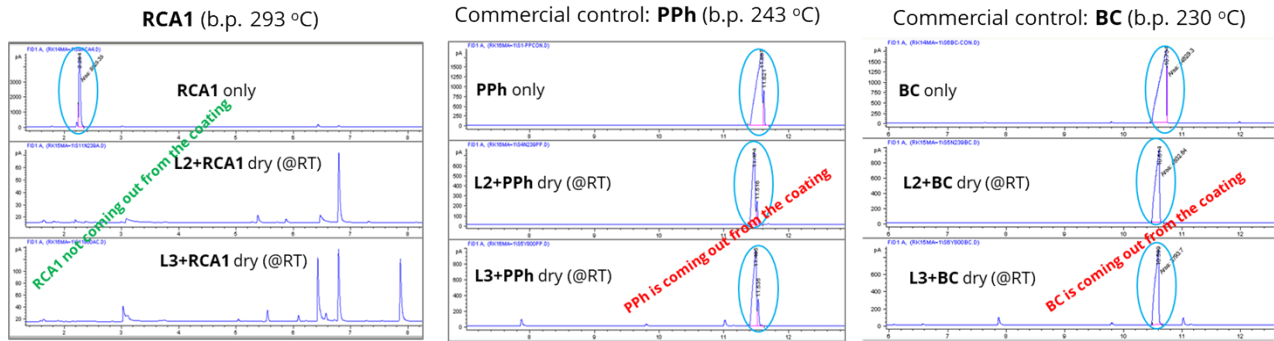


Figure S7. Overlaid head-space gas chromatography (HS-GC) analysis of **RCA1** formulation (2 wt%) with commercial latices. **PPh** and **BC** were used as commercial control as un-reactive coalescing agents.

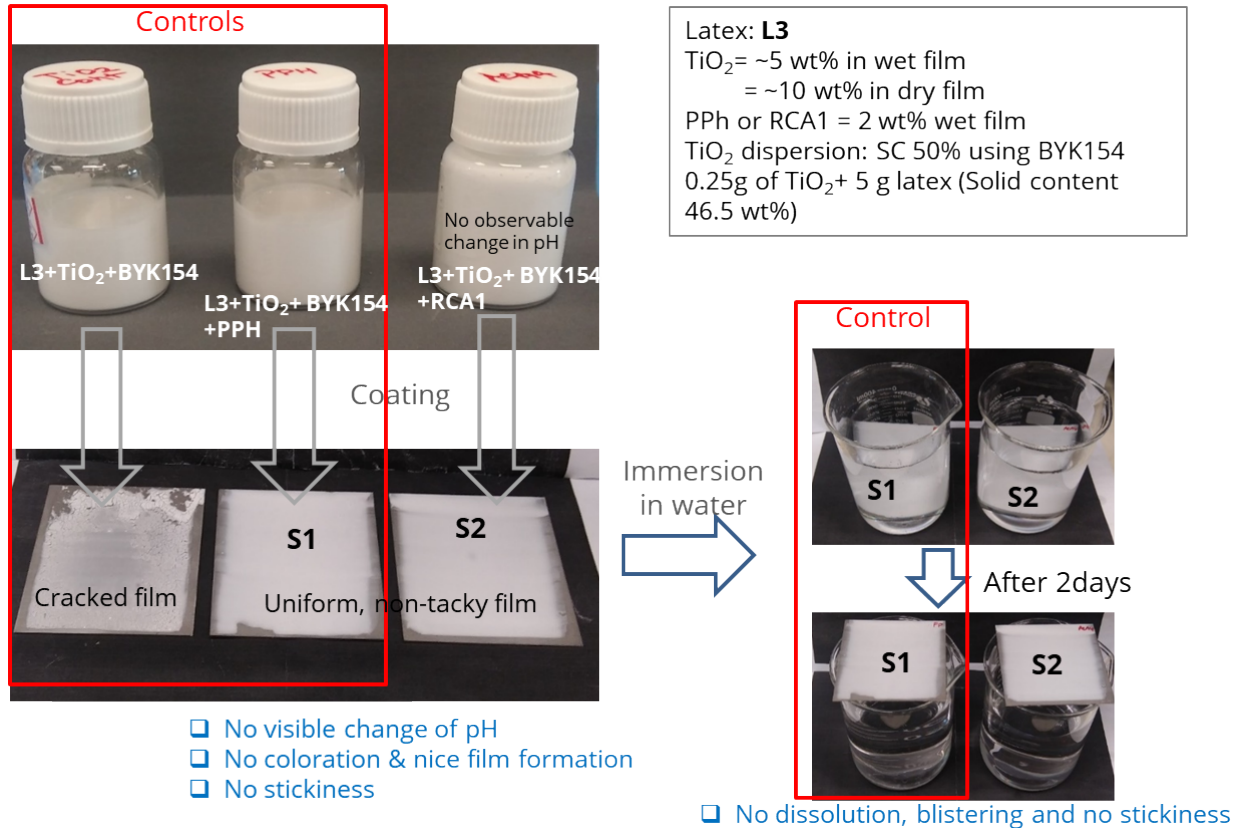
vi) Formulation of coatings using CAs and RCAs

Step I- Preparation of TiO₂ dispersion: BYK154 (50 mg) was dispersed with deionized water (10g) in a 50 ml glass beaker using Dispermat LC75-E at 300 rpm (lightweight dissolver discs, 30mm diameter) for 5min. TiO₂ (Tronox CR826) (10 g) was slowly added to it and the mixture was dispersed at 600 rpm for 15 min. Theoretical solid content of the dispersion was 50%.

Step II- Latex- TiO₂ mixture: Next, commercial latex **L3** (18g) was taken into another 50 ml glass beaker and stirred at 400 rpm. TiO₂ dispersion (2g) was then added dropwise using plastic dropper and stirred at 800 rpm for 15 min.

Step III- Formulation of final coating: Finally, 9.7g of mixture of latex and TiO₂ dispersion was transferred to another beaker and stirred at 400 rpm. **RCA1** (300 mg) was added dropwise and stirred for 30 min. CA/RCA content was 2 wt% (wet).

Two control formulations, first one, without using any coalescing agent and, second one, using a commercial coalescing agent **PPh** (2 wt%) were also produced using above procedure. All these formulations were then coated on steel plates using a blade applicator, air dried and film formation was observed.



Latex: **L3**
 TiO₂ = ~5 wt% in wet film
 = ~10 wt% in dry film
 PPH or RCA1 = 2 wt% wet film
 TiO₂ dispersion: SC 50% using BYK154
 0.25g of TiO₂+ 5 g latex (Solid content 46.5 wt%)

Figure S8. Pigmented wet coatings formulated using RCA1, coating application to produce dry coating films.

vii) UV exposure of dry coatings

A few microscopic glass slides were coated with formulation produced using **RCA1 (Figure S8)** and dried at room temperature before exposing to high energy UV light (Omniscure S2000 with light guide, 250-450 nm, irradiance 50 mW/cm²) for 100 hours (equivalent to 56 days outdoor exposure considering 10 hours of sunlight available each day). No sign of discoloration or color development was observed as seen in the photograph below.



Omniscure S2000
 Irradiance = 50 mW/m²; Exposure time = 100 hours
 This is equivalent to 563 hrs continuous sunlight exposure,
 equivalent to 56 days (10 hours/ day).

Figure S9. Photograph of dry coating (formulated with RCA1) before and after UV exposure.

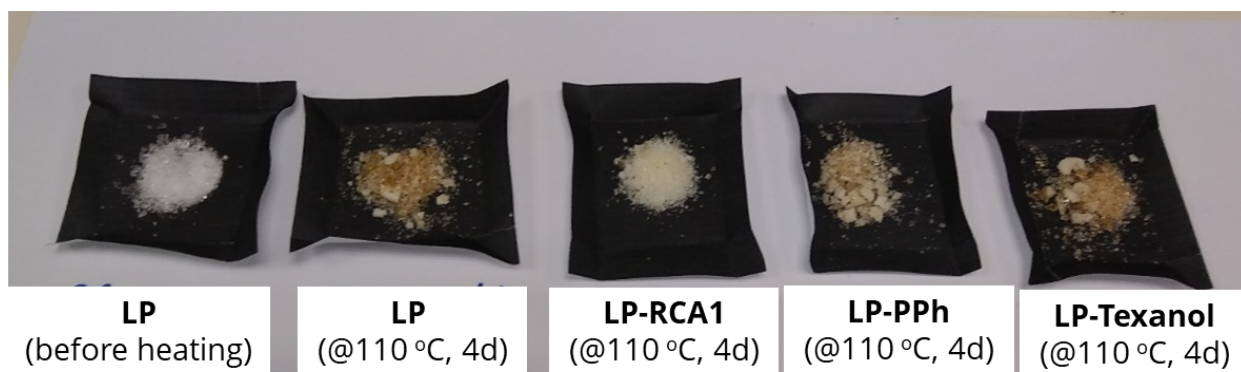


Figure S10. Photograph of dry samples before and after heating at 100 °C, 4 days.

The End