**Supporting information**

# Biosourced terpenoids for the development of sustainable acrylic pressure-sensitive adhesives *via* emulsion polymerisation

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**Keywords**: Pressure-sensitive adhesives, terpenoids, emulsion polymerisation, renewable monomers, sustainability

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## 1. Materials

Citronellol (95 %), tetrahydrogeraniol (>98 %), L-menthol (>99 %) were purchased from Sigma-Aldrich and their (meth)acrylate counterparts were synthesised following a previously reported protocol starting from the respective alcohols and using (meth)acrylic acid.[1] Isobornyl methacrylate (tech.) and potassium persulfate (KPS) (>99 %) and were purchased from Merck and used as received. Acrylic acid (99.5 %), methyl methacrylate (99 %) and 2-ethylhexyl acrylate (>99 %) were used as received from Acros Organics. Sodium bicarbonate (>99 %) was purchased from Carl Roth and used as such. Acetone was used as purchased from VWR and Dowfax 2A1 (45 wt.%) was kindly provided by The Dow Chemical Company.

## 2. Seeded semi-batch emulsion polymerisation

In order to obtain latexes for pressure-sensitive adhesives with a 40-45 % solid weight content (SWC), seeded semi-batch emulsion polymerisation was performed. In a first step, a batch emulsion polymerisation was performed in a 1 L single-jacked glass reactor, to synthesise the seed (particle size ~80 nm) with a 20 % SWC, on a 500 g scale. The formulation of the batch emulsion polymerisation is given in Table S1. The monomer ratio depends on the envisioned properties and can be found in Table S3. The batch emulsion that was continuously degassed *via* $N_2$ bubbling, also during polymerisation, was started by adding a KPS shot and was performed at 70 °C. The conversion was followed *via* gravimetry and the particle size was monitored *via* Dynamic Light Scattering (DLS). In gravimetry, the samples were put in a vacuum oven at 40 °C overnight, ensuring a complete removal of residual monomer. A conversion higher than 95 % was obtained in all cases within 4 hours but the polymerisation was left stirring overnight at the same conditions to decrease the amount of residual KPS in the system. In the second step, 100 g of the seed latex synthesised in the first step, was loaded into a 250 mL glass single-jacked reactor. The emulsion was again continuously degassed by $N_2$ bubbling at 70 °C and the polymerisation was initiated with a KPS shot. 41,9 g of neat monomer mixture (same monomer ratio as in the batch emulsion polymerisation, Table S2) was fed to the seed over 4 hours (240 min) *via* syringe pumps at a feeding rate of 0.167 g/min. The conversion was again followed *via* gravimetry and the particle size *via* DLS. After the feeding, the synthesis was continued for an additional hour before taking a sample for DLS and gravimetry of the final latex at 300 min. >95 % conversion was obtained at the end of the process in all cases. The emulsion was again left to react overnight at the same condition to decrease the amount of residual KPS.

In the case of PSA6, the synthesis was stopped after the batch polymerisation (87 % conversion), as the seeded semi-batch emulsion polymerisation (40 % overall conversion) resulted in coagulation and destabilised the final PSA latex. To increase the SWC of the batch emulsion polymerisation latex to the desired 40 %, the latex was carefully concentrated in vacuo at avoid excessive foaming.

**Table S1**: Formulation of the batch emulsion polymerisation on 500 g scale.

| Materials | | wbm % [a] | Amount (g) |
|---|---|---|---|
| **Low $T_g$ monomers** | **2EHA** | 0-84 | 0-84 |
| | **THGA** | 0-84 | 0-84 |
| | **CA** | 0-4 | 0-4 |
| | **CMA** | 0-4 | 0-4 |
| **High $T_g$ monomers** | **MMA** | 0-14 | 0-14 |
| | **MnMA** | 0-14 | 0-14 |
| | **iBnMA** | 0-7 | 0-7 |
| **Functional monomer** | **AA** | 2 | 2 |
| **Surfactant** | **Dowfax 2A1** | 3 | 6.67[b] |
| **Initiator** | **KPS** | 0.5 | 0.5 |
| **Buffer** | **$NaHCO_3$** | 0.2 | 0.2 |
| **Continuous phase** | **Deionised water** | | 400 |
| | **Acetone[c]** | 10 | 10 |

[a] weight based on total monomer content.

[b] Dowfax 2A1 was received as a 45 wt.% sample.

[c] 10 wt.% of acetone was added in the batch emulsion polymerisation during the synthesis of PSA6.

**Table S2**: Formulation of the feed during the seeded semi-batch emulsion polymerisation (total = 42 g) based on 100 g of seed and an aimed SWC of 45 %.

| Materials | | wbm % [a] | Amount (g) |
|---|---|---|---|
| **Seed** | | | 100 |
| **Low $T_g$ monomers** | **2EHA** | 0-84 | 0-34.5 |
| | **THGA** | 0-84 | 0-34.5 |
| | **CA** | 0-4 | 0-1.68 |
| | **CMA** | 0-4 | 0-1.68 |
| **High $T_g$ monomers** | **MMA** | 0-14 | 0-5.76 |
| | **MnMA** | 0-14 | 0-14 |
| | **iBnMA** | 0-7 | 0-2.93 |
| **Functional monomer** | **AA** | 2 | 0.84 |
| **Initiator** | **KPS** | 0.5 | 0.2095 |
| **Water KPS shot** | **Deionised water** | | 3 |

[a] weight based on total monomer content of the feed (42 g in total).

## 3. Instrumentation and methods

### *Instrumentation*

**Particle size** was analysed by Dynamic Light Scattering using a Zetasizer Nano-ZS Malvern apparatus (Malvern Instruments Ltd.) using disposable cuvettes. A He-Ne laser was used at 633 nm as excitation light source and scattered light was measured at an angle of 173°. Gas **Chromatography analysis** was performed on an Agilent 7890A system equipped with a VWR Carrier-160 hydrogen generator and an Agilent HP-5 column of 30 m length and 0.320 mm diameter. An FID detector was used and the inlet was set to 240 °C with a split injection of ratio 25 : 1. Hydrogen was used as carrier gas at a flow rate of 2 mL min−1. The oven temperature was increased with 20 °C min−1 from 50 °C to 120 °C, followed by a ramp of 50 °C min−1 to 240 °C. The complete molar mass distribution of each latex was determined using **AF4/MALS/RI**. The separation was carried out using AF4 fractionation equipment on a 27.5 cm trapezoidal channel mounted on PEEK (polyether ether ketone) upper and lower blocks with a stainless-steel frit. The channel thickness spacer was 490 μm. A DAWN Heleos II detector (Wyatt Technology) acquires data from 18 angles and at 658 nm. The accumulation wall was a Nadir regenerated cellulose membrane with a cut-off molar mass of 10,000 Da. The AF4 flow was controlled with a Wyatt Eclipse 3 AF4 Separation System controller (Wyatt Technology, USA). The preparation of the samples was done by directly dissolving the latex in THF in a concentration of 3-5 mgPol.mLTHF-1. The samples were left stirring overnight before injection (100 μL) without filtering. The AF4/MALS/RI data was analysed using the ASTRA software version 6.1 (Wyatt Technology, USA). The absolute molar mass was calculated from the MALS/RI data using the Debye plot (with second-order Berry formalism) and dn/dc = 0.068. The dn/dc is determined experimentally using a linear poly(THGA) synthesized by free radical polymerization (Mn = 278000 g/mol). An exponential cross-flow from 3 ml.min-1 to 0.05 mL.min-1 was used, plus an additional constant flow at 0.05 mL.min-1. The **gel content** was determined via Soxhlet extraction. The molecular weight and dispersity of the soluble fraction was checked via **Size Exclusion Chromatography (SEC)**. The analysis was performed using a Varian PL GPC50plus instrument with a refractive index detector, equipped with two 300 x 7,5 mm PIgel 5 μm MIXED-D columns at 40 °C. Polystyrene standards were used for calibration and THF as eluent at a flow rate of 1 mL/min. Samples were injected using a PL AS RT autosampler. **Thermogravimetric analyses (TGA)** were performed on a Mettler Toledo TGA/SDTA851e in a temperature window of 25−800 °C at a heating rate of 10 °C/min under a nitrogen atmosphere. The glass transition temperature was determined *via* **differential scanning calorimetry (DSC)**, performed on a Mettler Toledo DSC 1 equipped with a liquid nitrogen cooling system in a temperature window of −100 °C to 150 °C at a rate of 10 °C/min. Aluminum crucibles (40 µL) and lids were used to analyse a ± 5 mg sample.

### *Film Preparation*

The adhesive films were prepared by casting the latex over a flame-treated polyethylene terephthalate (PET) sheet (29 µm thick) using a gap applicator of 60 µm with reservoir. A film of approximately 24 µm was obtained after drying. Films for probe tack testing were casted a glass plate using a gap applicator with a gap of 250 µm in order to obtain a film of 100 µm. All films were dried at 23 °C and 50 % humidity overnight and protected from dust.

### *Characterisation of the adhesive performance*

The **peel, loop and probe tack tests** were performed with a TA.HD Plus Texture Analyzer (Texture Technologies, Hamilton, MA). All tests were performed at 23 °C and 50 % humidity. Four samples were tested for each formulation on stainless steel, glass and polyethylene (PE) substrates. The average values with standard deviation were reported in **Table 2**. The **shear resistance failure time and holding temperature** was determined using SAFT equipment (Sneep Industries). Static shear measurements were done using SAFT equipment at room temperature (30 °C). These tests were also run four times and average times and temperatures with their standard deviation were reported in **Table 2**. **Rheology experiments** were performed using an Anton Paar MCR 302 in parallel plate PP08 geometry. All experiments were performed using a normal force of 5 N. Dynamic frequency sweeps were performed at room temperature from $10^{-2}$ rad/s to $10^{2}$ rad/s. The temperature sweep measurement was performed at 1 Hz and a deformation of 0.05 % in a temperature range between -25 °C and 150 °C. To obtain the master curve *via* the Time-Temperature superposition, shift factors ($a_T$) were applied for each PSA formulation with 100 °C as the reference temperature. In all cases a Williams-Landel-Ferry model (pMEHA model, $c_1$ = -11,58; $c_2$ = 208,9; $T_{ref}$ = 373K) was used to fit the plot of $\omega a_{T,100°C}$ versus temperature.

## 4. Thermal analysis data

**Table S3:** The glass transition temperatures ($T_g$) of the polymers derived from the acrylic monomers considered in this study.

| | Monomer | Glass Transition Temperature ($T_g$) (°C) |
|---|---|---|
| Soft | **Tetrahydrogeranyl acrylate (THGA)** | -62 |
| | **Citronellyl acrylate (CA)** | -59 |
| | **Citronellyl methacrylate (CMA)** | -43 |
| Hard | **Menthyl acrylate (MnMA)** | 76 |
| | **Isobornyl methacrylate (iBnMA)** | $155^{a}$ |
| | **Methyl methacrylate (MMA)** | $105^{b}$ |
| | **Acrylic Acid (AA)** | $101^{b}$ |

$^{a}T_g$ of poly(isobornyl methacrylate) was found in the literature.[64]
$^{b}T_g$'s of poly(methyl methacrylate) and poly(acrylic acid) were adopted from Sigma-Aldrich.

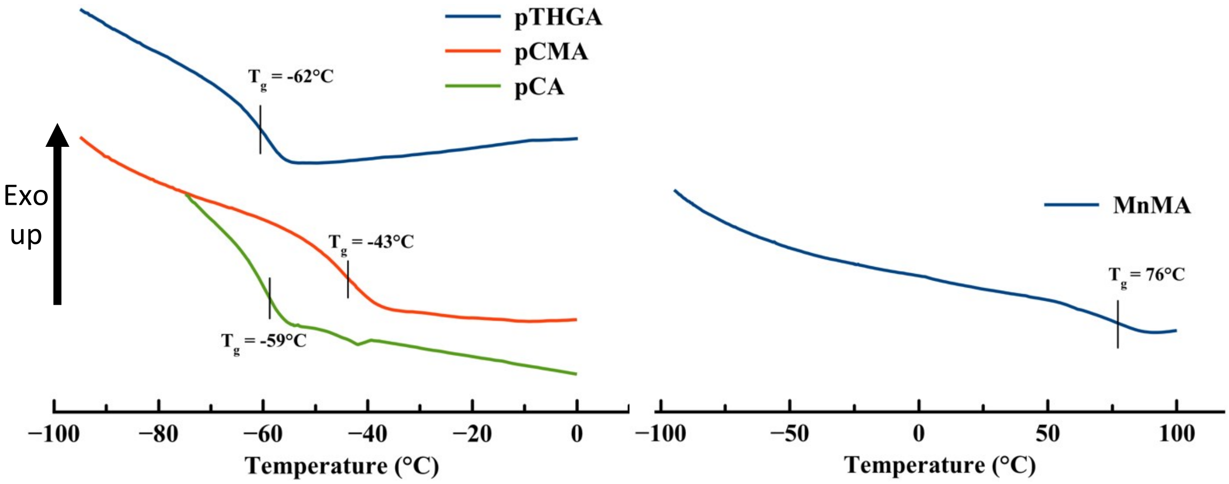

***Figure S1.*** *DSC thermograms for the homopolymers of the terpenoid-based monomers used in this study (second heating step).*

**Table S4**: Monomeric formulation and thermal properties of the synthesised PSAs.

| | **Monomer ratio (wt.% monomer)** | **$T_g$ (°C)** | **$T_{d,5\%}$ (°C)** |
|---|---|---|---|
| **1** | **2EHA:MMA:AA (84:14:2)** | -43 | 344 |
| **2** | **THGA:MMA:AA (84:14:2)** | -42 | 333 |
| **3** | **THGA:CA:MMA:AA (82:2:14:2)** | -40 | 323 |
| **4** | **THGA:CA:MMA:AA (80:4:14:2)** | -40 | 336 |
| **5** | **THGA:CMA:iBnMA:MMA:AA (80:4:7:7:2)** | -34 | 302 |
| **6** | **THGA:MnMA:AA (84:14:2)** | -43 | 320 |

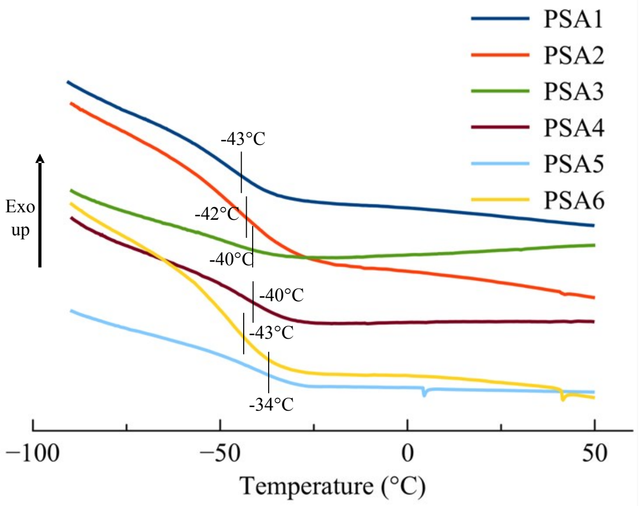

**Figure S2**: DSC thermograms of all six PSA formulations (second heating step).

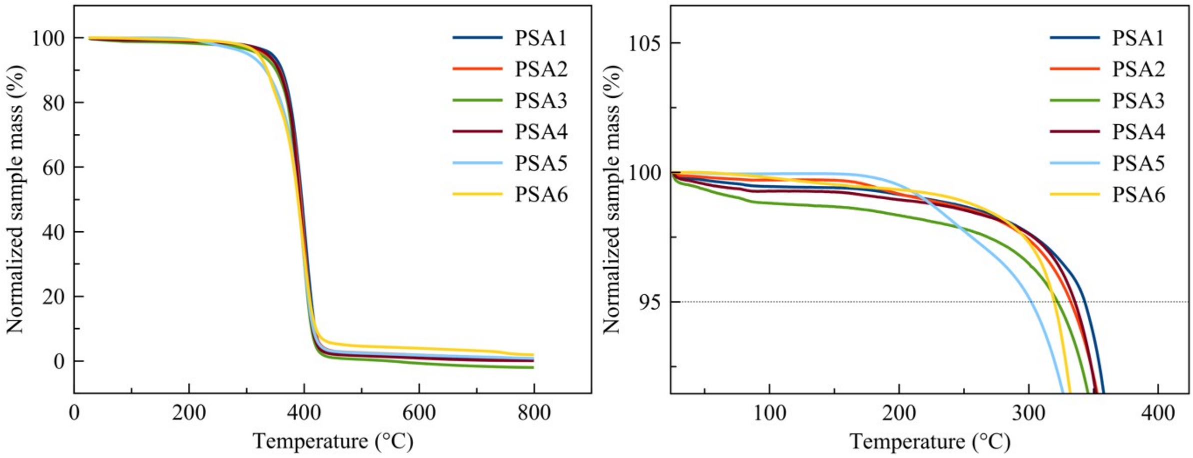

**Figure S3**: TGA thermograms of the six PSA formulations (left) with a zoom on the 5% loss mass region (right).

## 5. Size Exclusion Chromatography data for the soluble fraction after Soxhlet extraction

**Table S5:** Data from SEC analysis after soxhlet extraction of the different PSA formulations.

| PSA | Monomer ratio (wt.% monomer) | $M_n$ (kDa)[a] | Đ[a] |
|---|---|---|---|
| **1** | 2EHA:MMA:AA (84:14:2) | 34.4 ± 2.3 | 2.92 ± 0.32 |
| **2** | THGA:MMA:AA (84:14:2) | 38.5 ± 0.9 | 2.72 ± 0.17 |
| **3** | THGA:CA:MMA:AA (82:2:14:2) | 16.4 ± 0.8 | 1.87 ± 0.07 |
| **4** | THGA:CA:MMA:AA (80:4:14:2) | 13.8 ± 1.4 | 1.76 ± 0.15 |
| **5** | THGA:CMA:iBnMA:MMA:AA (80:4:7:7:2) | 10.7 ± 2.4 | 1.63 ± 0.13 |
| **6** | THGA:MnMA:AA (84:14:2) | 74.7 ± 11.5 | 3.84 ± 1.15 |

## 6. Conversion data of the seeded semi-batch emulsion polymerisations

### 6.1. PSA1

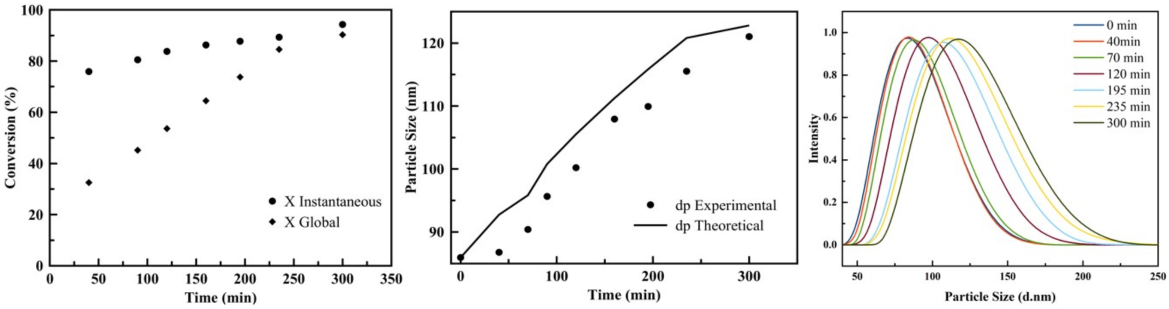

**Figure S4:** From left to right: the instantaneous and global conversion as a function of time, the evolution of the particle size as a function of time and the corresponding DLS results obtained for **PSA1** during feeding in the seeded semi-batch emulsion polymerisation (rate = 0.167 g/min).

### 6.2. PSA3

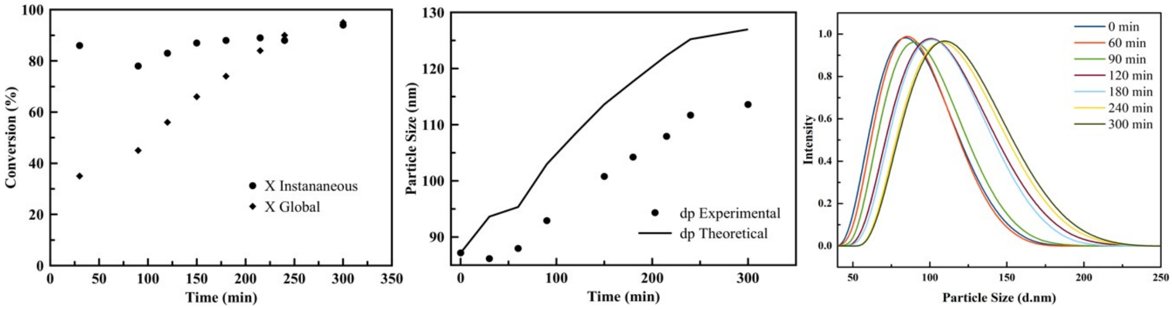

**Figure S5:** From left to right: the instantaneous and global conversion as a function of time, the evolution of the particle size as a function of time and the corresponding DLS results obtained for **PSA3** during feeding in the seeded semi-batch emulsion polymerisation (rate = 0.167 g/min).

### 6.3. PSA4

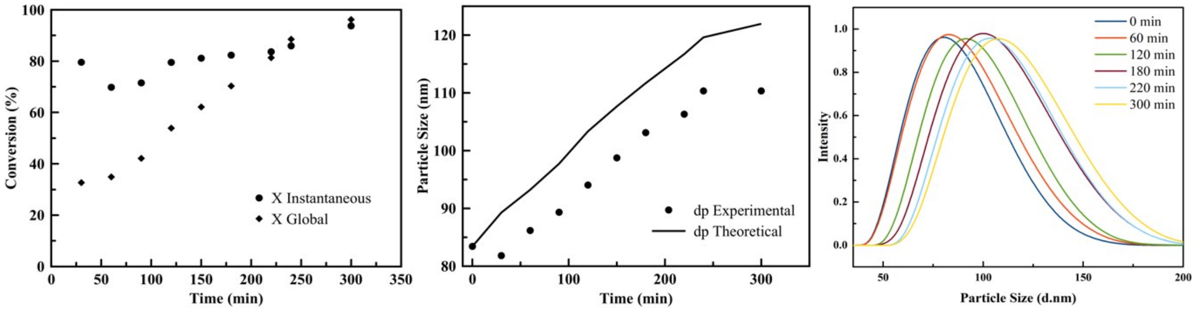

**Figure S6:** From left to right: the instantaneous and global conversion as a function of time, the evolution of the particle size as a function of time and the corresponding DLS results obtained for **PSA4** during feeding in the seeded semi-batch emulsion polymerisation (rate = 0.167 g/min).

### 6.4. PSA5

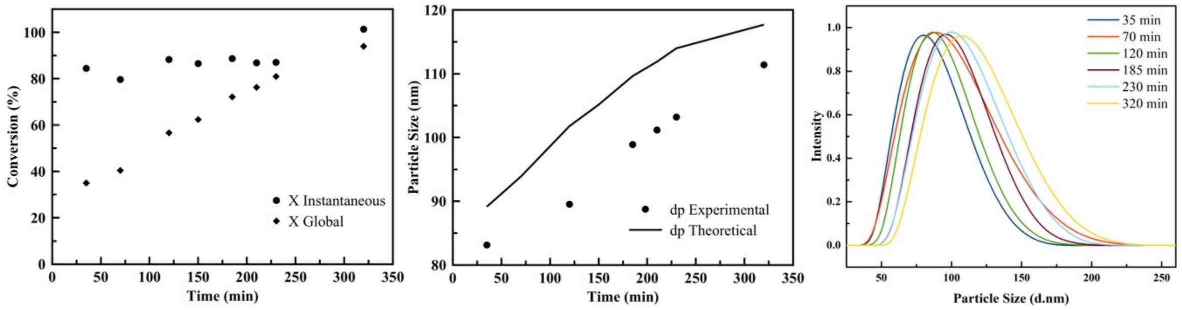

**Figure S7:** From left to right: the instantaneous and global conversion as a function of time, the evolution of the particle size as a function of time and the corresponding DLS results obtained for **PSA5** during feeding in the seeded semi-batch emulsion polymerisation (rate = 0.167 g/min).

### 6.5. PSA6

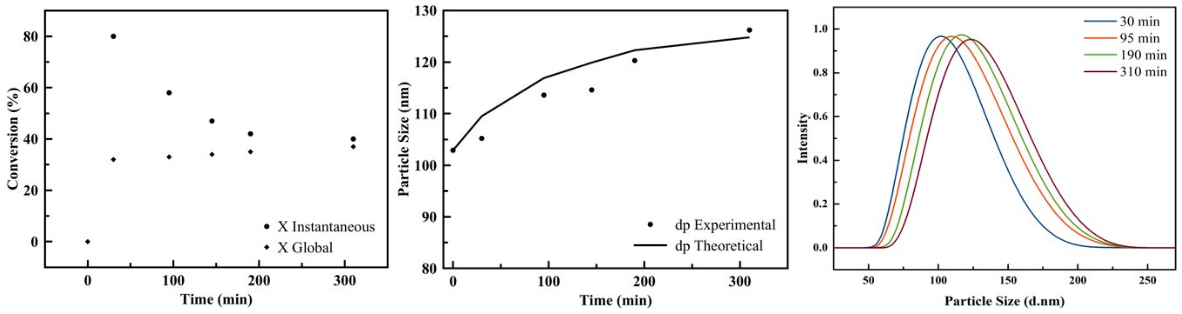

**Figure S8:** From left to right: the instantaneous and global conversion as a function of time, the evolution of the particle size as a function of time and the corresponding DLS results obtained for **PSA6** during feeding in the seeded semi-batch emulsion polymerisation (rate = 0.167 g/min).

Figure S8 shows that a low conversion was obtained for the seeded semi-batch emulsion polymerisation of PSA6. The monomer mixture in this process is quite hydrophobic, which in seeded semi-batch emulsion polymerization results in low polymerization rates due to two effects. The first one is the reduction in the radical entry rate. As the concentration of monomer in the aqueous phase, where the radicals are produced, is low, the sulfate radicals do not find monomer to react with as they are too hydrophilic. Therefore, they will stay in the aqueous phase until they undergo bimolecular termination. The second effect is the slow mass transfer of the monomer from the entering droplets to the polymerization loci (polymer particles).

Both the radical entry rate and the mass transfer can be increased by making the aqueous phase more organic-like, for example by adding acetone. The results in batch polymerization showed the positive effect of the acetone. However, the low conversion obtained in semi-batch, showed that addition of acetone was not enough. As the rate determining step for this mass transfer is the mass transfer from droplets to the aqueous phase, a possible way to overcome this problem is to use an emulsion feed[2] but this was not explored in the present article.

**General note:** A recurrent phenomenon in the online particle size measurements for most latex syntheses is the higher theoretical particle size towards the experimental one. This could be explained by the fact that secondary nucleation took place during the seeded semi-batch emulsion polymerisation step of the latex synthesis. However, this event only occurred to a small extent as stable latexes without coagulum were obtained.

### 6.6. Calculation of the theoretical particle size dp

The theoretical particle size dp (by volume) is calculated using the volume of one particle assuming the absence of secondary nucleation ($N_p$ constant),

$$V_p = \frac{4}{3}\pi\left(\frac{d_p}{2}\right)^3 = \frac{V_{pol}}{\emptyset_{pol}^{p} N_p}$$

The $V_{pol}$ is the total volume of polymer, hence the sum of the volume of polymer in the seed and in the feed. The volume of polymer in the seed depends on the solids content of the seed and the amount of seed divided by the density (fixed as $\rho$ = 1152 kg.m$^{-3}$). The volume of polymer in the feed depends on the solids content of the feed and the weight of the feed (calculated using time, instantaneous conversion, the feeding rate and the sum of the feed fraction of each monomer). $N_p$ is the number of particles of the seed and $\Phi_p$ the volume fraction of the polymer.

## 7. Asymmetric flow field flow fractionation (AF4) results

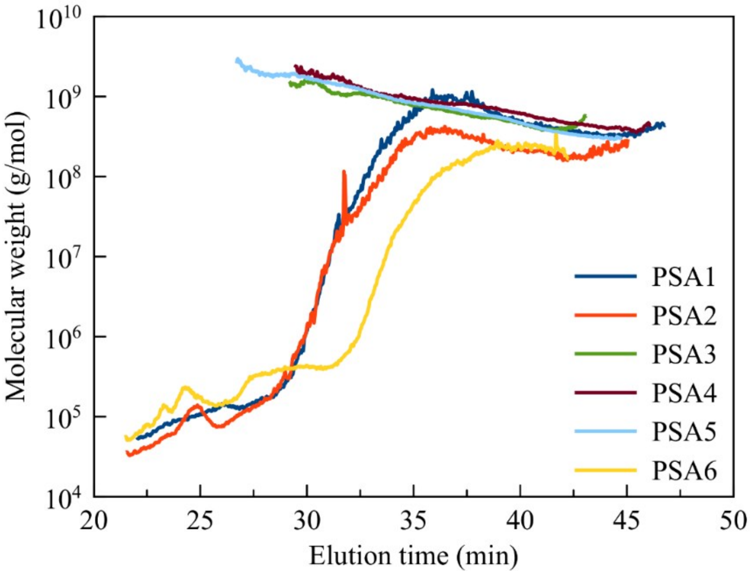

**Figure S9:** Molecular weight as a function of elution time by AF4.

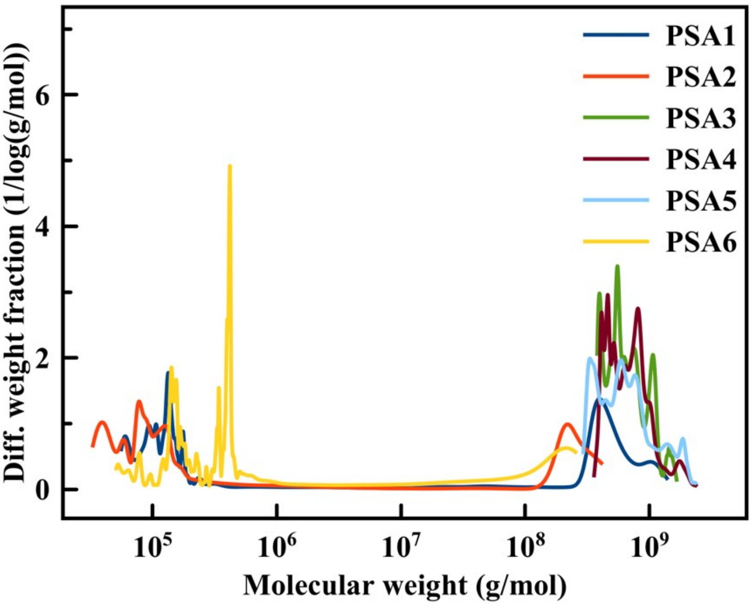

**Figure S10:** Differential molecular weight fraction as a function of the molecular weight, measured *via* AF4.

## 8. Rheology data of the six PSA formulations

### 8.1. Master curve obtained using the Time-Temperature Superposition principle

#### 8.1.1. Master curve of PSA1

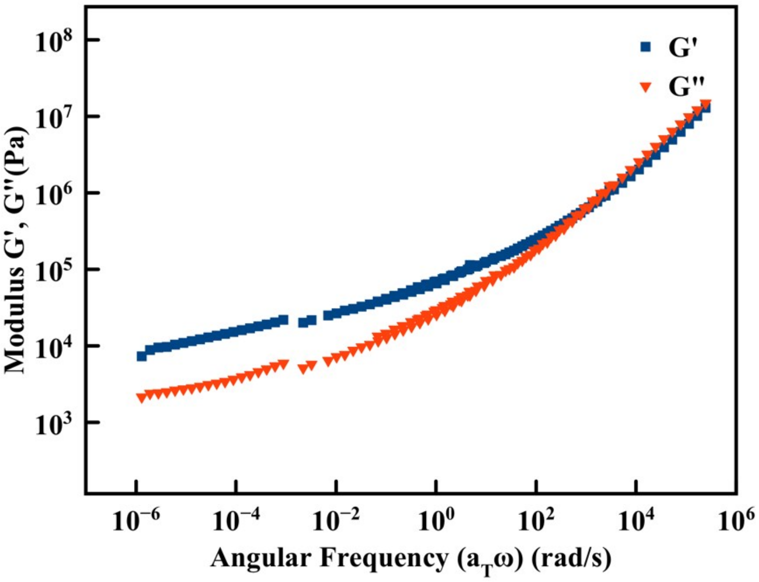

**Figure S11:** Master curve of PSA1 obtained using the Time-Temperature Superposition principle ($T_{ref}$ = 25 °C).

#### 8.1.2. Master curve of PSA2

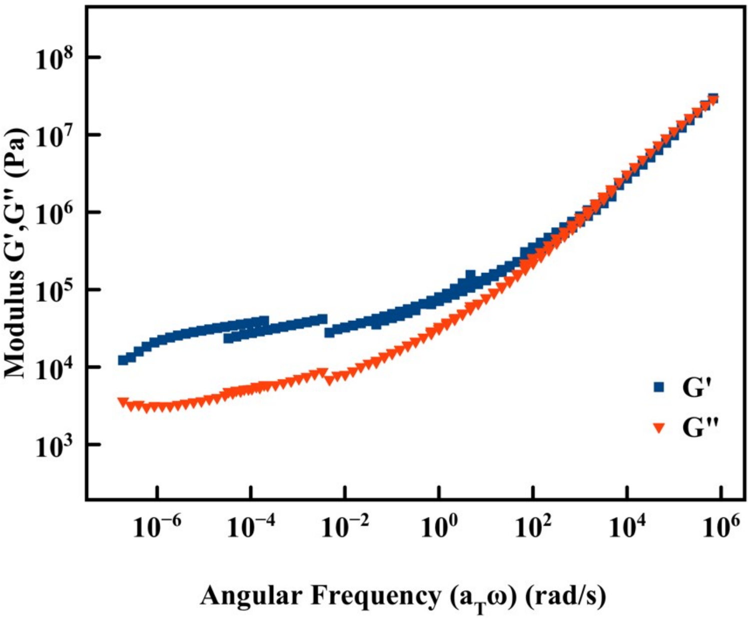

**Figure S12:** Master curve of PSA2 obtained using the Time-Temperature Superposition principle ($T_{ref}$ = 25 °C).

### 8.1.3. Master curve of PSA3

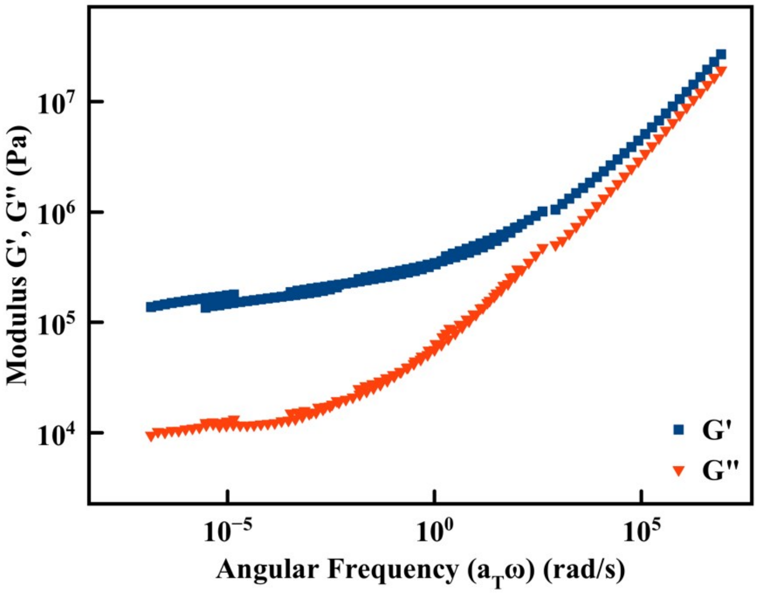

**Figure S13:** Master curve of PSA3 obtained using the Time-Temperature Superposition principle ($T_{ref}$ = 25 °C).

### 8.1.4. Master curve of PSA4

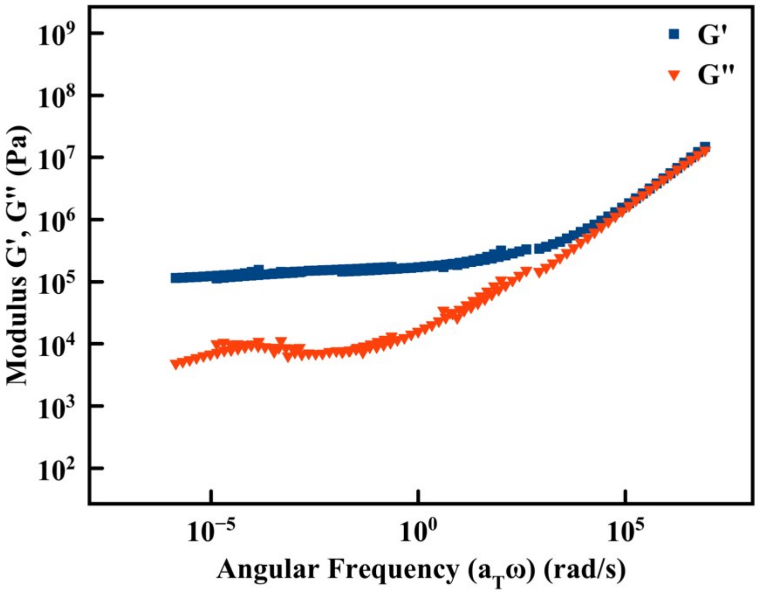

**Figure S14:** Master curve of PSA4 obtained using the Time-Temperature Superposition principle ($T_{ref}$ = 100 °C).

### 8.1.5. Master curve of PSA5

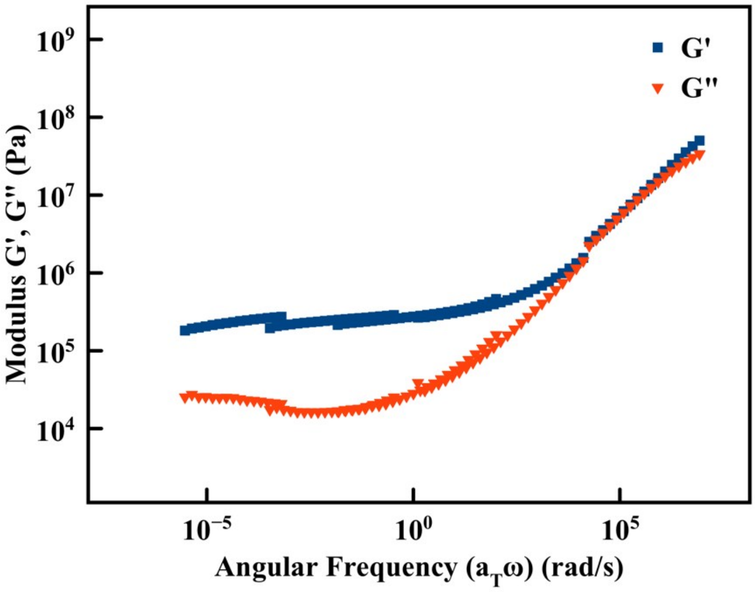

**Figure S15:** Master curve of PSA5 obtained using the Time Temperature Superposition principle ($T_{ref}$ = 25 °C).

### 8.1.6. Master curve of PSA6

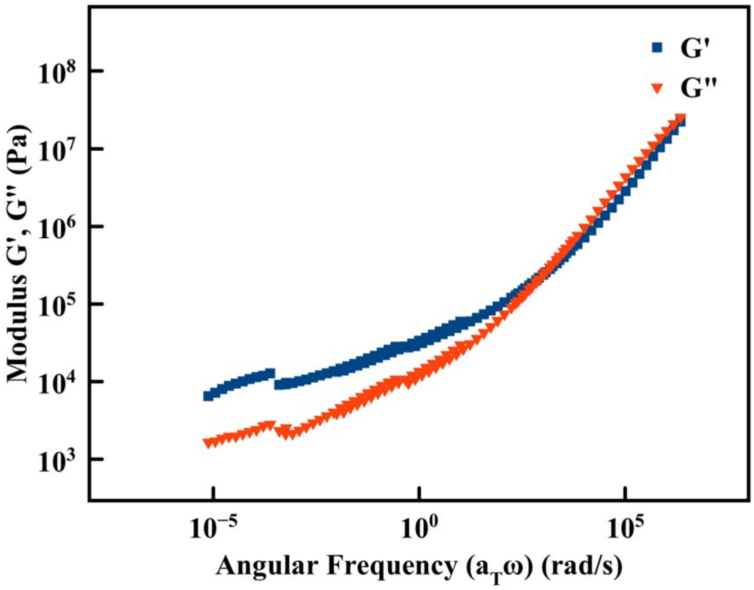

**Figure S16:** Master curve of PSA6 obtained using the Time-Temperature Superposition principle ($T_{ref}$ = 25 °C).

## 8.2. Temperature Sweep data of the six PSA formulations

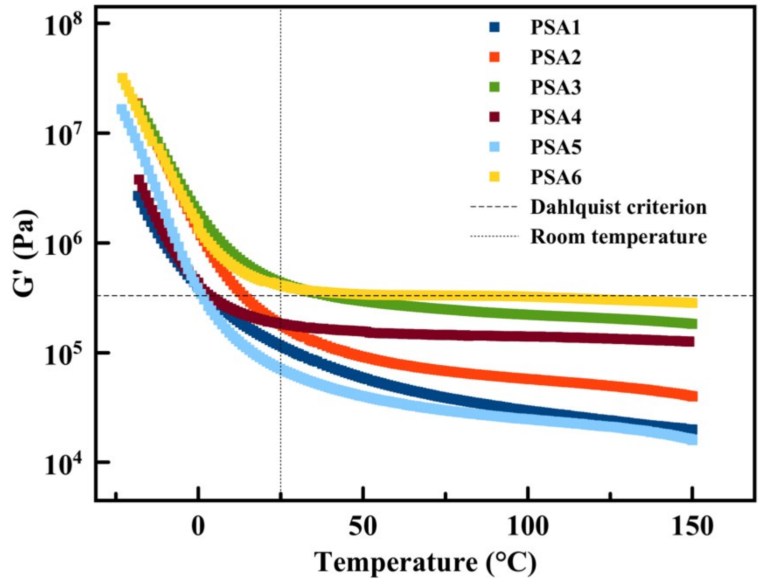

**Figure S17:** Temperature sweep measurements for the six PSA formulations performed in order to check if the G' is within the Dahlquist criterion (G'(Pa)<3,3.$10^5$ Pa) at room temperature (25 °C).

## 9. References

1 M. A. Droesbeke and F. E. Du Prez, *ACS Sustain. Chem. Eng.*, 2019, **7**, 11633–11639.

2 M. Vicente, J. R. Leiza and J. M. Asua, *AIChE J.*, 2001, **47**, 1594–1606.