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Sustainability spotlight

This study investigates the scale up of the synthesis α-pinene-derived monomers, and their subsequent application as high T_g components in copolymer coatings. The newly developed, upscaled syntheses of these terpene-derived monomers employs less hazardous and/or toxic reagents and leads to new materials and coatings that have a very high biobased content. This work aligns with UN Sustainable Development Goal 12 (Responsible Consumption and Production).

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ARTICLE

Sustainable, Upscaled Synthesis of Pinene-Derived (Meth)acrylates and their Application as High T_g Monomers in Styrene/Acrylic-Based Bioderived Copolymer Coatings†

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The improved synthesis of the pinene-derived monomers (3-pinanyl acrylate **1** and 3-pinanyl methacrylate **2**), replacing hazardous and/or expensive reagents from established methods with cheaper, more innocuous and sustainable reagents is reported; the monomers of high purity are obtained at up to 160 g scale, without need for chromatographic separation. Subsequently, these monomers (**1** and **2**) were successfully copolymerized with *n*-butyl acrylate/methacrylic acid or styrene/methacrylic acid using a radical semi-batch emulsion copolymerization process. For comparison, materials incorporating the more established terpene-derived monomer *iso*-bornyl methacrylate **3** were also prepared in analogous fashion. The obtained polymer latexes had particle sizes between 65 and 90 nm, very low polydispersities (< 0.08) and were stable for several years without any coagulum formation. Gradient liquid chromatography indicated all copolymers had relatively uniform chemical composition distributions. The *n*-butyl acrylate containing copolymers (**P1**-**P3**) were obtained with high molar masses ($M_n > 40\,000$, $M_w > 400\,000$), very high dispersities ($Đ > 9.5$), and low glass transition temperatures ($T_g < -5$ °C). The styrene-based copolymers (**P4**-**P6**) had slightly lower molar masses ($M_n > 40\,000$, $M_w > 150\,000$), lower dispersities ($Đ > 3$) and high glass transition temperatures (95 °C < T_g < 120 °C). Preliminary testing of the *n*-butyl acrylate-based materials demonstrated the potential of these copolymers for use in coatings applications. The poly(*n*-butyl acrylate)/pinanyl methacrylate copolymer **P2** was found to be harder (König hardness) and had better stain resistance properties towards water-based substances than the analogous *n*-butyl acrylate-based copolymers containing 3-pinanyl acrylate (**P1**) or *iso*-bornyl methacrylate (**P3**). Through further refinement of the copolymerization process we expect the properties of these polymers may be further tailored towards a range of coatings applications.

Sustainability spotlight

This study investigates the scale up of the synthesis α-pinene-derived monomers, and their subsequent application as high T_g components in copolymer coatings. The newly developed, upscaled syntheses of these terpene-derived monomers employs less hazardous and/or toxic reagents and leads to new materials and coatings that have a very high biobased content. This work aligns with UN Sustainable Development Goal 12 (Responsible Consumption and Production).

Introduction

Water-based polymer coatings formulations are routinely prepared as acrylic- based copolymer resins, typically via emulsion polymerization. Incorporation of different monomers, at specifically defined feed ratios, is well known to influence polymer properties; i.e. aspects such as hardness and flexibility can be easily tailored.[1]

Currently, most acrylic-based commercial resins are prepared from petrochemical sources.[2] There is growing global concern about carbon emissions linked to fossil fuel consumption.[3] Alarmingly, it has been predicted that polymer production will account for 20 % of global fossil fuel consumption by 2050.[4] In response, the chemical industry is intensifying its efforts to find more sustainable, biobased chemicals to produce high quality synthetic materials.[5] Clearly, this motivation needs to be balanced against the often-competing pressures of cost and performance. However, it has been shown that market penetration of bioderived products is possible where the product brings specific advantages, such as avoiding toxicity and facilitating degradability (e.g. epoxidized soybean oil (ESO), isosorbide and poly(lactic acid) (PLA)).[4, 6-8]

One strategy used to enhance the green credentials of polymers for coatings technology focusses on the use of plant-based building blocks containing a reactive double bond that can be exploited *via* radical polymerization.[9-12] There are numerous examples of the application of bio-based monomers in radical polymerization[13-16] and of these, terpenes appear as a versatile pool of molecules whose production and extraction does not compete with food production.[17] In this regard, we have recently focused on developing biobased radically polymerizable monomers derived from terpenes.[18-22]

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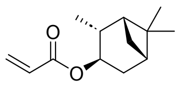
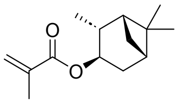
Terpenes and terpenoids are found abundantly in plant oils and many of these molecules are considered to be industrial by-products from processes including citrus processing as well as the pulp and paper industry.[23, 24] Turpentine, a by-product of the paper and pulp industry is produced on a scale of 330,000 tons per year and is comprised of mostly α- and β-pinene.[25]

From a coatings standpoint, monomers derived from α-pinene, namely 3-pinanyl acrylate (PA, **1**) and 3-pinanyl methacrylate (PMA, **2**), appear particularly promising; due to the bicyclic ring present as a pendant moiety. (Meth)acrylic polymers derived from these compounds have relatively high glass transition temperatures (T_g),[19] suggesting a potential role as 'hard' components in copolymer formulations.[26] Previous work has demonstrated their compatibility with 'soft' monomers such as limonene acrylate in the synthesis of ABA block copolymers.[19, 26]

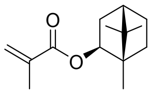
Herein, we investigate the utility of the α-pinene derived monomers PA **1** and PMA **2** in this context. We describe both their improved, scaled-up synthesis, and their use as a component in binder formulations prepared by semi-batch aqueous emulsion copolymerization. Importantly, we directly examine the effect of incorporation of the pinene-based monomers (PA **1** and PMA **2**) into the final materials, comparing them to analogous polymers derived from the more established high T_g monomer, isobornyl methacrylate (iBoMA, **3**).



1 PA



2 PMA



3 iBoMA

Experimental

Materials

All reagents and solvents were purchased from commercial suppliers (i.e. Sigma Aldrich, Fisher Scientific etc.) unless otherwise stated.

Characterisation

Gas chromatography (GC) was performed on a Shimadzu GC-2010 Pro, using a Shimadzu HS-20 headspace sampler, a SGE SilFlow GC 3 ports splitter, a retention gap (30 cm × 0.32 mm i.d. polar; CP nr 4083 or similar), a combination of SGE BP-5 30m × 0.25 mm i.d. df 1µm (SGE 054203 or similar) and SGE BP-20 30m × 0.25 mm i.d. df 1µm (SGE 054439 or similar) columns, operating with flame ionization detection (with H_2, air and N_2 as make up gas). The carrier gas was helium. Conditions involved a 120 °C sample incubation temperature, 150 °C sample and transfer line temperatures, a 150 kPa gas pressure, and a temperature ramp from 40 °C (2 min hold time) to 130 °C (at 15 °C/min), and then to 240 °C (at 25 °C/min). Gradient-liquid chromatography (GLC) was performed on a Waters uPLC H-Class system using a Waters HSS T3, 2.1 × 100 mm, 1.8 µm column and a solvent flowrate of 0.5 mL/min. Analysis was achieved with using a three solvent system: water (with 0.1 % aq. trifluoroacetic acid (TFA)), acetonitrile (MeCN), and tetrahydrofuran (THF). The gradient program was as follows: t = 0 to 0.2 min (95 % H_2O/5 % MeCN); t = 0.2 to 8 min (ramp from 95 % H_2O/5 % MeCN to 100 % MeCN); t = 8 to 8.2 min (ramp from 100 % MeCN to 100 % THF); t = 8.2 to 8.4 min (100 % THF); t = 8.4 to 8.6 min (ramp from 100 % THF to 50 % H_2O/50 % MeCN); t = 8.6 to 8.8 min (ramp from 50 % H_2O/50 % MeCN to 95 % H_2O/5 % MeCN); t = 8.8 to 12 min (95 % H_2O/5 % MeCN) Samples were injected as filtered methanol (with 0.5 % TFA) solutions. Size exclusion chromatography (SEC) was conducted on a Waters Alliance e2695 LC system with a Waters 2414 DRI detector and a Waters 2996 PDA detector, using three PLgel 10 µm Mixed-B columns. *N*-Methylpyrrolidone (NMP) containing 10 mM lithium bromide (LiBr) was used as eluent with a flow of 1 mL/min THF at 70 °C and polystyrene standards were used for the calibration. DSC was performed on a TA Instruments DSC250 using Tzero aluminium pans. Indium was used for the enthalpy and temperature calibration of the instrument and an empty pan was used as the reference. Prior to analysis all samples were dried overnight at 120 °C, under air. DSC samples (~ 5 mg) were subjected to a cool-heat-cool-heat protocol; all cooling temperature increments were 20 °C min^{-1}, while all heating temperature increments were 10 °C min^{-1}. The samples were first cooled to -85 °C then heated to 160 °C then re-cooled to -85 °C before being reheated to 160 °C. Glass transition temperature (T_g) measurements were obtained from analysis of the second heating scan. Particle size analysis was performed of a Malvern Zetasizer. ^1H and ^{13}C NMR obtained using a Bruker DPX 400 MHz spectrometer. COSY, HSQC and HMBC were used to facilitate spectral assignments. Deuterated chloroform ($CDCl_3$) was used as solvent, chemical shifts were assigned in parts per million (ppm) and referenced to the (residual) solvent.[27] All spectra were obtained at ambient temperature (22 ± 1 °C).

Scaled-up Pinene-derived Monomer Synthesis

The synthesis of the pinene-derived monomers, 3-pinanyl acrylate (PA **1**) and 3-pinanyl methacrylate (PMA **2**), and their precursor 3-pinanol were adapted from previously reported procedures.[18, 28, 29] Reaction products of high purity were obtained and characterized by comparison of gas chromatography elution times to previously reported authentic samples.[18]

Synthesis of (1*R*,2*R*,3*R*,5*S*)-2,6,6-trimethylbicyclo[3.1.1]heptan-3-ol (3-pinanol)

This synthesis was adapted from previously reported methods.[18, 29] To a solution of α-pinene (50 g, 367 mmol) in THF (250 mL) was added $NaBH_4$ (11.1 g, 294 mmol, 0.8 equiv.). To the resulting suspension acetic acid (17 mL, 294 mmol, 0.8 equiv.) was added dropwise. The mixture was left to stir for 1 h at room temperature and then heated at 50 °C for 3 h. The reaction was cooled to room temperature and was basified with 3 M aq. NaOH solution (50 mL, 150 mmol, 0.4 equiv.) was added dropwise, followed by dropwise addition of 30 % aq. H_2O_2 (45 mL, 440 mmol, 1.2 equiv.) whilst maintaining the temperature below 25 °C. The reaction was subsequently quenched with brine and extracted with petroleum ether. The combined organics were dried ($MgSO_4$), and solvent removed under reduced

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pressure. The crude product was purified by vacuum distillation (bp 68-70 °C, 1.5 mbar) to give 3-pinanol as a colourless oil that solidifies upon standing (33.1 g, 214 mmol, 58 %). The sample was of > 99 % purity, with GC retention time matching that of previously reported authentic samples.[18]

Synthesis of (1*R*,2*R*,3*R*,5*S*)-2,6,6-trimethylbicyclo[3.1.1]heptan-3-yl acrylate (3-pinanyl acrylate, 1)

This synthesis was adapted from previously reported methods.[18] 3-Pinanol (140 g, 907.6 mmol) was dissolved in dichloromethane (DCM) (320 mL) and the solution cooled to 0 °C. Triethylamine (139 mL, 998.4 mmol, 1.1 equiv.) was added in one portion. Subsequently, acryloyl chloride (81.1 mL, 998.4 mmol, 1.1 equiv.) dissolved in DCM (160 mL) was added dropwise keeping the temperature < 10 °C. The reaction mixture was stirred at < 10 °C 7 h, and left stirring at room temperature for 16 h. Afterwards, 4-methoxyphenol (MEHQ) (132 mg, 1.06 mmol, 0.12 mol%) and water (200 mL) were added and resulting layers separated. The aqueous phase was extracted once with DCM and the combined organics were washed (aq. $NaHCO_3$, then brine) and dried ($MgSO_4$) and the solvent removed under reduced pressure. The crude product was purified by vacuum distillation (bp ~65 °C, 0.6 mbar) to give 3-pinanyl acrylate **1** as a colourless liquid (164.0 g, 787.9 mmol, 87 %). The sample was of > 95 % purity, with GC retention time matching that of previously reported authentic samples.[18]

Synthesis of (1*R*,2*R*,3*R*,5*S*)-2,6,6-trimethylbicyclo[3.1.1]heptan-3-yl methacrylate (3-pinanyl methacrylate, 2)

This synthesis was adapted from previously reported methods.[18, 28] 3-Pinanol (50 g, 324.1 mmol) was melted (~60 °C) after which copper (II) tetrafluoroborate ($Cu(BF_4)_2$) (1.12 g, 3.24 mmol, 1 mol%), methacrylic anhydride (77 mL, 486 mmol, 1.5 equiv.) and phenothiazine (183 mg, 0.82 mmol, 0.25 mol%) were added and the resultant mixture was heated at 80 °C for 5 h. The reaction mixture was stirred at room temperature for 18 h after which water was added (100 mL) and the layers separated. The organic phase was extracted three times with petroleum ether. The combined organics were washed with 2 % aq. NaOH, dried ($MgSO_4$) and the solvent removed under reduced pressure. The crude product was purified by fractional vacuum distillation (Vigreux) (bp 70-74 °C, 0.9 mbar) to give 3-pinanyl methacrylate **2** as a colourless liquid (64.9 g, 291.9 mmol, 90 %). The sample was of > 95 % purity, with GC retention time matching that of previously reported authentic samples.[18]

Polymer Synthesis

All emulsion copolymerization experiments were done at 80 °C, using ammonium persulfate (9.5 mM) as initiator and sodium lauryl sulfate (18.8 mM) as surfactant. At the end of the feed process, a 'burn-up' reaction was performed to further reduce residual monomer levels, using *t*-butyl hydroperoxide in combination with isoascorbic acid. This synthesis of the poly[(*n*-butyl acrylate)-*co*-(3-pinanyl acrylate)-*co*-(methacrylic acid)] (**P1**) is shown as an example, below. Modifications from this procedure for the preparation of the other butyl acrylate-based polymers (**P2** and **P3**) and styrene-based copolymers (**P4**-**P6**) were achieved by substitution of the monomers used as per the details given in Table 1 (and Table S1, supporting information).

Residual monomer concentrations were determined using head-space GC for butyl acrylate (BA), styrene (St) and isobornyl methacrylate (iBoMA, **3**). High-performance liquid chromatography (HPLC) was used to determine residual monomer concentrations for methacrylic acid, PA **1** and PMA **2.**

Synthesis of poly[(*n*-butyl acrylate)-*co*-(3-pinanyl acrylate)-*co*-(methacrylic acid)]

To a round-bottomed flask equipped with a condenser, thermometer and mechanical stirrer demineralized water (351.4 mL) and 30 % aq. sodium lauryl sulfate solution (13.8 mL) were added. The contents of the reactor were heated to 80 °C. At 80 °C a monomer feed consisting of demineralized water (222.0 mL), 30% aq. sodium lauryl sulfate solution (6.9 mL), *n*-butyl acrylate (326.3 g; 63 wt% of total monomers), 3-pinanyl acrylate (181.2 g; 35 wt% of total monomers) and methacrylic acid (10.4 g; 2 wt% of total monomers) was added over a period of 180 minutes. An initiator feed, comprising of ammonium persulfate (2.6 g) in demineralized water (49.2 mL) was fed to the reactor in parallel over a period of 180 minutes. At the end of the addition of the monomer feed, demineralized water (7.4 mL) wase used to rinse the feed tank and the washings were added to the reactor. A temperature of 80 °C was maintained for a further 60 minutes. Subsequently, a slurry comprising of demineralized water (0.7 mL), 30 % aq. sodium lauryl sulfate solution (0.14 mL), and *t*-butylhydroperoxide (0.46 g) was added, followed by a solution of isoascorbic acid (0.32 g) in demineralized water (5.8 mL) and the temperature was maintained at 80 °C for another 30 minutes. At 80 °C a neutralizing solution consisting of demineralized water (3 mL) and 25 % aq. ammonium (3 mL) was fed in for 15 minutes. The reactor content was cooled to 30 °C and the preservative proxel ultra 10 (6.1 mL) was added. The solids content of the emulsion was corrected to 44 % using demineralized water, resulting in a stable latex of poly[(*n*-butyl acrylate)-*co*-(3-pinanyl acrylate)-*co*-(methacrylic acid)] (**P1**).

Film Properties

König Hardness

Films were prepared on glass, by application of an 80 μm thick wet layer of polymer emulsion, containing 5% BYK 346 surfactant (used to improve substrate wetting). After drying for one day at room temperature, samples with dry film thickness (DFT) 40 μm were obtained. These were measured using a König pendulum hardness tester. The König hardness of the films is given as the time (in seconds) taken for the pendulum to decrease in amplitude from 6° to 3°.

Stain resistance

Films were prepared on Leneta card, by application of a 100 μm thick wet layer of polymer emulsion, containing 5 % BYK 346 surfactant. After drying for one day at room temperature the stain resistance of the films to water, 50 % aqueous ethanol, and coffee (i.e. including water, milk and sugar) was tested and ranked by visual inspection on a scale from 0 to 5 (0 = no stain resistance; 5 total stain resistance).

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Results and Discussion

Monomer Synthesis

The monomers PA **1** and PMA **2** have previously be reported by our group.[18] On standard laboratory scale (up to 10 g) PA **1** or PMA **2** are easily accessible by a facile two-step synthesis from α-pinene via hydroboration/oxidation and subsequent esterification; borane dimethyl sulfide ($BH_3{\cdot}SMe_2$) was the hydroboration reagent, and (meth)acrylation was achieved using the relevant acyl chloride.[18]

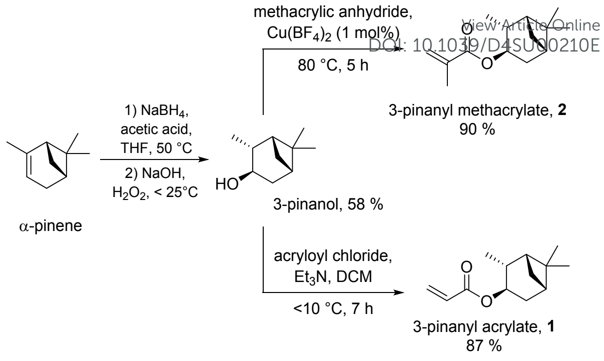
For scale up for potential commercial use, neither of the above protocols are ideal either from economic or sustainability standpoints.‡ As such, we sought to improve our syntheses in terms of cost and scale to improve industrial feasibility, whilst exploiting sustainable reactions and methods of product isolation and purification, where possible. We discovered the combination of sodium borohydride/acetic acid mediated hydroboration[29] and hydrogen peroxide induced oxidation delivered 3-pinanol in reasonable yield (58 %) at increased lab scale following purification by distillation (> 50 g) (see Scheme 1, left), directly from α-pinene. We expect that these yields could be improved with further optimisation. Notably, this method provides a more sustainable pathway to the alcohol, at a fraction of the cost of the initial synthesis.

Next, we developed a new approach for the preparation of the methacrylate-based monomer PMA **2** from 3-pinanol, using methacrylic anhydride and catalytic copper (II) tetrafluoroborate,[28] to install the ester functionality . This delivered the product **2** (> 60 g) in excellent yield (90 %) and high purity after distillation (see Scheme 1, right upper).

For the scaled-up synthesis of the acrylate monomer PA **1** from 3-pinanol we used a standard acryloyl chloride method adapted from that reported in our previous investigation,[18] due to the lack of commercial availability of acrylic anhydride. This gave the desired monomer PA **1** (> 160 g) in high purity (distillation) and high yield (87%) (see Scheme 1, right lower).‖

Polymer synthesis

Acrylic and styrene/acrylic dispersions are well established as alternatives to solvent borne resins.[30] As such, we selected *n*-butyl acylate (BA) or styrene (St) as the major components (63 wt%) in the prepared copolymer formulations, due to their wide industrial applicability (see Scheme 2). This allowed us to investigate the effects of PA **1,** PMA **2**, and iBoMA **3** (incorporated at 35 wt%) on copolymerization performance and the final physical properties. Methacrylic acid (MAA), a latex stabilising monomer, was used in small amounts (2 wt%) in all formulations.



Scheme 1: Synthesis of PA **1** and PMA **2** from α-pinene in two-steps via hydroboration/oxidation and (meth)acrylation.

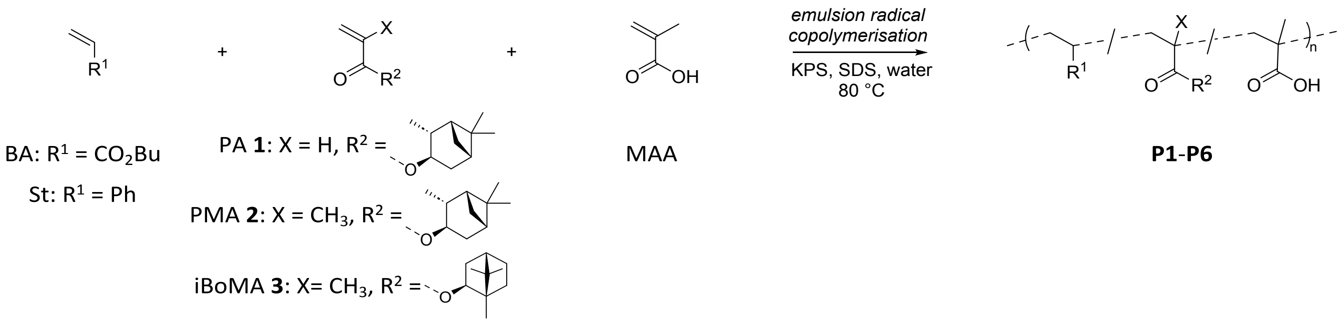
With reasonable quantities of the monomers PA 1 and PMA 2 in hand, we were able to utilise them in copolymerization of industrial relevance as outlined below.

BA-based copolymers

Initially, we prepared the BA-based materials by semi-batch emulsion copolymerization of BA with PA **1**, PMA **2** or iBoMA **3** (and MAA) at 80 °C (see Table 1, Entries 1-3). To determine the copolymerization efficiency, samples were taken during the polymerization process after 15, 30, 60, 90, and 120 minutes during the monomer feed, at the *t*-butylhydroperoxide/isoascorbic acid promoted ‘burn-up’ reaction (at 150 minutes) and at the end of the process (at 180 minutes).

In general, the level of residual BA and terpene monomer (**1**, **2** or **3**) slowly increases across the 120 mins feed time, with the ratio between the monomers remaining fairly constant (see Figure 1 (a)). Following the ‘burn-up’ reaction, quantitative (> 99.9 %) monomer consumption was achieved for all samples.

The size of the BA-based copolymer particles increased with cumulative monomer feed (and therefore total monomer conversion), while the particle size polydispersity index (PDI) remained low (see Figure 1 (b)). The final obtained latexes (**P1**-**P3**) showed particles sizes of 65 to 90 nm and very low PDI (< 0.06) (see Table 1). All samples were highly stable with no sign of coagulum over several years.



Scheme 2: Emulsion radical copolymerization of terpene derived monomers PA **1**, PMA **2** or iBoMA **3** with BA or St (and MAA).

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Table 1: Analytical details of final polymers BA-based (**P1** - **P3**) or St-based (**P4**-**P6**) acrylic copolymer formulations prepared via semi-batch aqueous emulsion radical copolymerization with the terpene derived comonomers PA **1**, PMA **2** and iBoMA **3**.

Entry	Sample label	Copolymer[a]	M_n (g/mol)[b]	M_w (g/mol)[b]	$Đ$[b]	Biobased content (wt. %)[c]	Particle size (nm)[d]	PDI[d]	Solids content (%)[e]	T_g (°C)[f]	$T_{g,\text{predicted}}$ (°C)[g]	MFFT (°C)[h]
1	**P1**	P(BA$_{63\%}$-*co*-PA$_{35\%}$-*co*-MAA$_{2\%}$)	43 100	417 700	9.69	27	67	0.06	44.6	-13.5	-19	< 0
2	**P2**	P(BA$_{63\%}$-*co*-PMA$_{35\%}$-*co*-MAA$_{2\%}$)	52 400	1 077 000	20.55	26	87	0.03	43.4	-2.0	-7	< 0
3	**P3**	P(BA$_{63\%}$-*co*-iBoMA$_{35\%}$-*co*-MAA$_{2\%}$)	45 900	494 300	10.77	25	88	0.01	44.1	4.0	-9	< 0
4	**P4**	P(St$_{63\%}$-*co*-PA$_{35\%}$-*co*-MAA$_{2\%}$)	47200	186 000	3.94	27	87	0.03	44.1	97.5	96	> 60
5	**P5**	P(St$_{63\%}$-*co*-PMA$_{35\%}$-*co*-MAA$_{2\%}$)	50 300	210 900	4.19	26	87	0.03	44.3	114.0	121	> 60
6	**P6**	P(St$_{63\%}$-*co*-iBoMA$_{35\%}$-*co*-MAA$_{2\%}$)	47 600	158 000	3.31	25	94	0.08	44.4	113.5	116	> 60

[a]Monomer feed ratios (wt %) are given as subscripts in the name abbreviations; [b]from SEC data (NMP eluent); [c]for total solids content from radiocarbon analysis[31]; [d]from DLS analysis; [e]calculated from gravimetry; [f]from DSC analysis, the T_g is reported as the onset temperature; [g]calculated from the Fox equation[32] (using the following homopolymer T_g: PBA = -54 °C,[33] PSt = 100 °C,[33] PMAA = 228 °C,[33] PiBoMA =150 °C,[34] PPA = 84 °C,[19] PPMA = 168 °C[19]); [h] the minimum film forming temperatures (MFFTs) are outside the temperature range of our tester (0-60 °C) and are hence presented as estimates only.

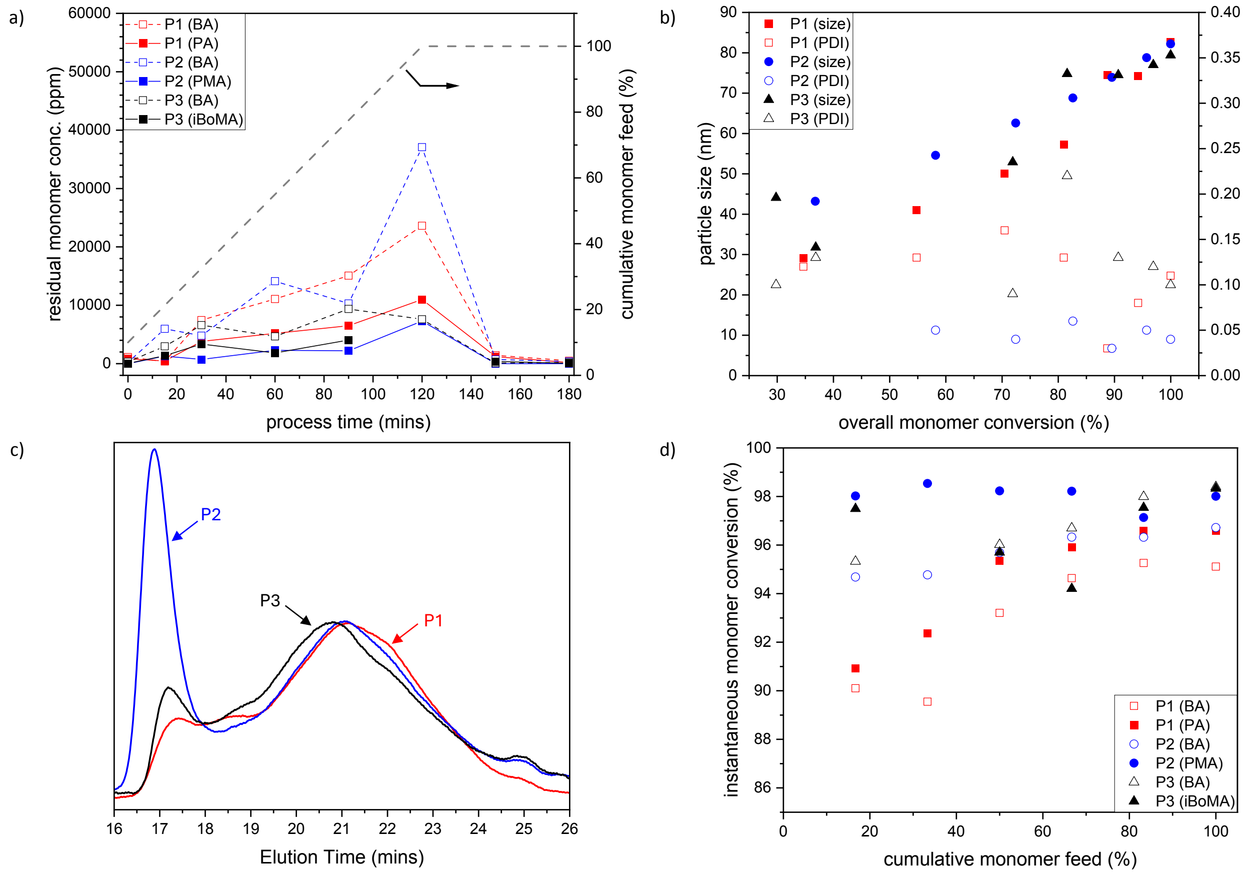

Figure 1: (a) Plot of residual BA (open symbols) and PA **1**, PMA **2** or iBoMA **3** (closed symbols) concentrations versus time (the grey dashed line indicates the semi-batch feed profile in cumulative % of the monomers with time); (b) evolution of PBA-based polymer particle size (closed symbols) and polydispersity index (open symbols) with total monomer conversion; (c) SEC traces of BA-based copolymers; and (d) instantaneous monomer conversion for BA (open symbols) and PA, PMA or iBoMA (closed symbols) versus cumulative monomer feed, for BA/PA/MAA (**P1**, red), BA/PMA/MAA (**P2**, blue) and BA/iBoMA/MAA (**P3**, black) semi-batch emulsion radical copolymerizations. Note, data relating to MAA are omitted for clarity. **P1**-**P3** refer to the sample labels given in Table 1.

In each case, the final polymers (**P1**-**P3**) have high molar mass (M_n > 40 000, M_w > 400 000) and very high dispersity ($Đ$ > 9.5) (see Table 1, Entries 1-3). Additionally, bimodality is observed in each of the SEC traces (see Figure 1 (c)), with the high molar mass fraction being most prominent for the polymer (**P2**) made with the methacrylate co-monomer, PMA **1**. The ‘burn up’ of the residual monomers present after the 120 min feed profile gives rise to the high molar mass peak in the molar mass distributions; the build-up of a higher concentration of residual BA in formation of **P2** (see Figure 1 (a), blue dashed line) than that observed for the **P1** or **P3** reactions, results in a more prominent high molar mass fraction in the **P2** sample.

Early in the reaction (i.e. feed < 40 %), lower overall monomer conversion for the PA **1** system (**P1**) is observed than that for either of the reactions incorporating the other co-monomers (see Figure 1 (d)). This is likely caused by differences

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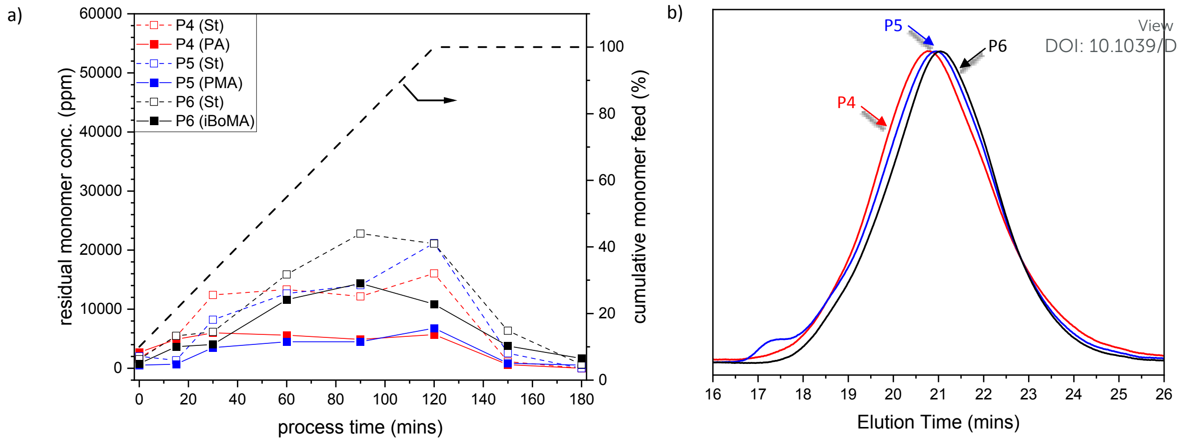

Figure 2: (a) Plot of residual St (open symbols) and PA **1**, PMA **2** or iBoMA **3** (closed symbols) concentrations versus time (the grey dashed line indicates the semi-batch feed profile in cumulative % of the monomers with time, and (b) SEC traces of St-based copolymers, for St/PA/MAA (**P4**, red), BSt/PMA/MAA (**P5**, blue) and St/iBoMA/MAA (**P6**, black) semi-batch emulsion radical copolymerizations. Note, data relating to MAA are omitted for clarity. **P4-P6** refer to the sample labels given in Table 1.

Table 2: Film properties of PBA-based copolymers (**P1**-**P3**)

Entry	Sample label	Copolymer	König hardness (s)[a]	Stain resistance[b]			
				water (24 h)	50 % aq. ethanol (1 h)	coffee (1 h)	(16 h)
1	**P1**	P(BA$_{63\%}$-*co*-PA$_{35\%}$-*co*-MAA$_{2\%}$)	7.0 ± 0.3	3	3	4	2
2	**P2**	P(BA$_{63\%}$-*co*-PMA$_{35\%}$-*co*-MAA$_{2\%}$)	22.0 ± 0.9	4	2	4	3
3	**P3**	P(BA$_{63\%}$-*co*-iBoMA$_{35\%}$-*co*-MAA$_{2\%}$)	14.0 ± 0.6	3	3	4	3

[a]König hardness of copolymer films prepared on glass, values are average of duplicate analyses, DFT = 40 µm; [b]stain resistance of films prepared on card, ranked by visual inspection on a scale from 0 to 5 (0 = no stain resistance; 5 total stain resistance), values in parentheses indicate exposure time.

in the copolymerization kinetics between the acrylate/methacrylate systems (**P2** and **P3**) and the acrylate/acrylate system (**P1**).§ The broad molar mass distributions observed in each case are attributed to changes in polymerization reaction kinetics over the course of the reaction due to the starved feed nature of the process, rather than any drastic composition drift caused by differences in comonomer reactivity. The relative chemical uniformity of the obtained materials is confirmed by GLC data, where each polymer (**P1**-**P3**) is observed as a single narrow peak (see Figure S1, supporting information). Notably, both 3-pinanyl-containing polymers (**P1** and **P2**) remained completely soluble, as indicated by the GLC (see Figure S1, supporting information), and solution NMR analysis following freeze drying of the latexes (see Figures S2-S5, supporting information). This confirmed no significant crosslinking of the copolymers occurs under the current reaction conditions. This contrasts with our prior observations from solution polymerization, where polymers of PMA **2** were found to crosslink via H-abstraction from the tertiary carbon of pinanyl moiety.[35]

All PBA-based emulsion polymers (**P1**-**P3**) had low T_gs (i.e. ~-5 to -20 °C), which were very close to that predicted by the Fox equation[32] (see Table 1, entries 1-3). This demonstrates materials with predictable thermal properties can be readily prepared through this copolymerization process. As expected, based on the monomer feed compositions all BA-based polymer emulsions had ~25 % bioderived content based upon radiocarbon analysis of total solids (see Table 1).

St-based copolymers

To further investigate the copolymerization performance of the terpene-derived monomers (**1**-**3**) in industrially relevant systems, we prepared St-based copolymers via analogous methods to that discussed above. Again, samples were taken across the experiment; during the monomer feed regime (at 15, 30, 60, 90, and 120 minutes), during the 'burn-up' reaction (at 150 minutes) and at the end of the process (at 180 minutes). The amount of residual monomer St and either **1**, **2** or **3** remains relatively low across the reaction (see Figure 2, (a)), indicating acceptable rates of copolymerization throughout the process. The final St-based polymers were obtained with high molar mass (M_n > 40 000, M_w > 150 000) and reasonably high dispersity ($Đ$ > 3) (see Table 1, Entries 4-6). All molar mass distributions for the St samples were unimodal (see Figure 2 (b)), in contrast to the BA-based samples.# Particles sizes were all close to 90 nm, with very low PDI (< 0.08).

The T_gs of the St-based polymers (**P4**-**P6**) were relatively high (i.e. between 95 and 120 °C) (see Table 1, entries 4-6) Again, the T_gs were in agreement to those predicted by the Fox equation.[32]

As with the BA-copolymers, the St-based polymer emulsions had ~25 % bioderived content based upon total solids (see Table 1), in line with the monomer feed compositions.

Preliminary coatings applications testing for poly(*n*-butyl acrylate)-based formulations

To investigate the potential of the copolymers incorporating the pinene-based high T_g monomers (PA **1** and PMA **2**) towards coatings applications we conducted preliminary, industry standard hardness (on glass) and stain resistance (on Leneta card) tests for the low T_g PBA-based formulations. For comparison, data for the iBoMA **3**

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containing PBA-copolymer **P3** was also undertaken (see Table 1). The minimum film forming temperatures (MFFTs) for the St-containing copolymers were too high to allow good film formation and, hence, relevant testing.

Due to the presence of the acrylate co-monomer PA **1**, the PBA-based polymer **P1** had by far the lowest hardness on the König scale of the samples tested (7 s, see Table 2, entry 1); in view of their higher T_gs the PBA polymers (**P2** and **P3**) containing methacrylate-based comonomers had much higher König hardness values as expected. Interestingly, polymer **P2** which contains the pinene-based monomer (**2**) has the highest König value (22 s, see Table 1, entry 2), with the iBoMA (**3**) containing polymer **P3** being slightly softer (17 s, see Table 1, entry 3). Hardness values can be further improved via the T_g by optimising the BA/P(M)A ratio in the copolymer.

All three coating formulations had good to very good water stain resistance over a 24 h period, with the PMA **2** containing polymer **P2**, visually outperforming the other two formulations (**P1** and **P3**) (see Table 2). In contrast, when exposed to 50% aqueous ethanol solution, **P2** performed marginally poorer than **P1** and **P3** (see Table 2). All three of the polymer coatings (**P1**-**P3**) had excellent coffee stain resistance at 1 h, with performance decreasing as expected when exposed for 24 h (see Table 1**).** Notably, the polymers **P2** and **P3** which each contain a methacrylate-based comonomer behaved similarly, outperforming the acrylate-comonomer containing polymer **P1**.

Conclusions

We have described the improved synthesis and scale up of the pinene-derived monomers 3-pinanyl acrylate (PA, **1**) and 3-pinanyl methacrylate (PMA, **2**). Additionally, we have reported their copolymerization performance in the preparation of copolymer emulsions based on BA or St and examined the preliminary performance of the BA-based copolymer formulations through hardness and stain resistance testing, following industry norms.

Key developments in monomer syntheses include the replacement of hazardous and expensive reagents for established transformations. The one-pot hydroboration/oxidation of α-pinene was readily achieved using $NaBH_4$ and AcOH in THF, followed by H_2O_2 and NaOH, to give 3-pinanol in moderate yield (58 %), while reaction of 3-pinanol with methacrylic anhydride and catalytic $Cu(BF_4)_2$) provided PMA **2** in high yield (90 %). Importantly, both of these syntheses are sustainable, cost efficient and scalable. Additionally, PA **1** was readily prepared at > 100 g sale through reaction of 3-pinanol with acryloyl chloride in high yield (87 %), demonstrating the ease of access to larger volumes of these materials.

Copolymerization performance of PA **1** and PMA **2** was assessed by preparing copolymers with BA or St (and MAA) by semi-batch emulsion copolymerization. Analogous materials prepared from the more established monomer iBoMA **3** were prepared as a reference. Successful copolymerization of the monomers **1**-**3** with BA (and MAA) gave latexes (**P1**-**P3**) with particles sizes between 65 to 90 nm and with very low PDI (< 0.06). The BA-based copolymers (**P1**-**P3**) had high molar mass (M_n > 40 000, M_w > 400 000) and very high dispersity ($Đ > 3.5$). The BA-based materials showed bimodal molar mass distributions and low T_gs (~-5 to -20 °C). Throughout the reactions the monomer feed ratios remained relatively constant, particle size was found to increase with monomer conversion, and particle size dispersity PDI remained low (< 0.2). Copolymerization of the monomers **1**-**3** with St (and MAA) behaved similarly, giving latexes (**P4**-**P6**) with particle sizes close to 90 nm and with very low PDI (< 0.08). The St-based copolymers (**P4**-**P6**) had high molar mass (M_n > 40 000, M_w > 150 000), reasonably high molar mass dispersity ($Đ > 3$). In contrast to the BA-cases, the St-based copolymers had monomodal molar mass distributions and relatively high T_gs (~95 to 120 °C). Importantly, GLC indicated all the copolymers (**P1**-**P6**) had relatively uniform chemical composition distributions.

Preliminary coatings application testing was performed on the low T_g BA-based materials (**P1**-**P3**). Overall, the PMA-containing polymer (**P2**) appeared to the best performing coating material; in comparison to the iBoMA-containing polymer (**P3**), **P2** was harder and had slightly better stain resistance. The PA-containing polymer (**P1**) was the softest coating, which is in line with it having the lowest T_g, and displayed similar in stain resistance to the iBOMA-containing material (**P3**).

In summary, we have demonstrated the industrially relevant scale up of the monomers PA **1** and PMA **2** using sustainable and cost-efficient processes, successfully incorporated them into copolymers via emulsion polymerization, and finally demonstrated the potential of these new polymers as coating materials. We expect through refinement of the copolymerization process the properties of the polymers derived from these renewable monomers may be improved further. Companies that are interested in steps to bring pinene (meth)acrylates to the market are invited to contact the authors.

Author Contributions

Maria Pin-No - investigation, methodology, formal analysis, writing-original draft; Philippa L. Jacob - writing-original draft, writing-review & editing; Vincenzo Taresco - writing-review & editing; Maud Kastelijn - investigation, methodology, formal analysis, writing-original draft, writing-review & editing; Tijs Nabuurs – conceptualisation, methodology, writing-original draft; writing-review & editing; Chandres Surti -supervision, project administration; John Bilney - supervision, project administration; John Daly - supervision, project administration; Daniel J. Keddie - formal analysis, visualization, writing-original draft, writing-review & editing; Steven M. Howdle - conceptualisation, funding acquisition, resources, supervision, project administration, writing-review & editing; Robert A. Stockman - conceptualisation, funding acquisition, resources, supervision, project administration, writing-review & editing.

Conflicts of interest

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There are no conflicts to declare.

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Notes and references

‡$BH_3 \cdot SMe_2$ is toxic, flammable, and preventatively expensive. It also has limited commercial availability for use on larger scales. Both methacryloyl chloride and acryloyl chloride are also toxic highly reactive reagents, and thus would be best avoided from a sustainability standpoint.

‖Previously, we have also reported this synthesis using the reagent propanephosphonic acid anhydride (T3P) and acrylic acid (see reference 18). While this approach is more sustainable than the route reported here, it is currently not economically (and industrially) viable at the reported scale because of the current cost of T3P.

§Clearly the MAA presence in each of these systems will also play a role in the copolymerization kinetics. Due to its low feed ratio MAA is omitted from the discussion here to aid in the direct comparison across the copolymerizations using the acrylate (PA) and methacrylate (PMA & iBoMA) terpene-derived comonomers.

This is attributed to the differences in polymerization rates for the 'burn up' reactions of the two different copolymerization systems, (i.e. the BA-based high k_p systems, and the St-based low k_p systems). Note, as fresh initiator is added in the 'burn-up' step of the reactions, the kinetics differ to that of the main polymerization reactions.

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Further data is available upon request to the authors.