

Synthesis of Model Terpene-Derived Copolymers in Supercritical Carbon Dioxide for Cosmetic Applications

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Abstract

There is currently a strong drive within the cosmetics industry to replace petroleum based solvents and polymers with renewable alternatives. Copolymers of 2-ethylhexyl acrylate (2EHA) and maleic anhydride (MA) are interesting model candidates to be used in make-up and skincare applications as cross-linkable film forming materials, but are currently synthesised in organic solvents and are derived from petroleum. Herein, we have studied and optimised the copolymerisation of these two monomers in supercritical carbon dioxide (scCO₂). The kinetics of the reaction and resulting products were compared with analogues synthesised in a 30/70 solvent mixture of ethyl acetate/isododecane (EtOAc/IDD), which mimics current industry practices. Initially, the incompatibility of these two monomers with each other in the absence of a solvent lead to mixed homo- and copolymer products during reactor pressurisation. This was overcome by devising a new synthesis approach, in which MA is first dissolved in scCO₂ at high temperature, followed by the addition of 2EHA and a radical initiator *in situ* via a HPLC pump. Copolymers synthesised using this new methodology were added to simple cosmetic formulations and evaluated for their resistance to olive oil, where they performed comparably with those synthesised in EtOAc/IDD. The renewable content of the reaction was then increased further, by substituting the monomer 2EHA with the terpene-derived alternatives isobornyl acrylate and α -pinene acrylate. This study is an important step towards materials that can achieve outstanding levels of performance in a variety of cosmetic applications, and are also more in phase with green chemistry criteria.

Keywords

2-ethylhexyl acrylate; maleic anhydride; supercritical carbon dioxide; terpene monomer, isobornyl acrylate; α -pinene acrylate

Introduction

The continued growth of populations and economies globally has created a scenario in which Earth's resources are being consumed at a rate that is unsustainable. As a result, consumer and government pressure on industries to adopt more sustainable methods of production and consumption continues to mount. The cosmetics industry is an enormous and growing economic sector worldwide, with the European cosmetic market alone valued at €78.6 billion in 2018 [1]. As the largest cosmetics company in the world, L'Oréal has a strong interest in improving the safety and sustainability profile of its products through identifying greener alternatives to the chemical feed stocks used in their manufacture [2]. This has been highlighted over the past several years in their implementation of action plans for sustainable innovation, and reporting progress annually in the form of a sustainable

development reports [3]. Recently, the program L'Oréal for the Future was launched with the ambition to transform its activities to respect the planet's limits [4]. In particular, that by 2030, 95% of ingredients in L'Oréal's formulas will be bio-based, derived from abundant minerals, or from circular processes.

Cosmetic products are complex mixtures of various additives, including one or more emollients, exfoliators, surfactants, polymers, solvents, dyes, fragrances, UV absorbers, preservatives, pH regulators, chelating agents and antioxidants, many of which are derived from petrochemical feed stocks and are manufactured in ways that can be made more sustainable [5]. A cosmetic is defined by the current European regulation for cosmetics as: "any substance or mixture intended to be placed in contact with the external parts of the human body (epidermis, hair system, nails, lips and external genital organs) or with the teeth and the mucous membranes of the oral cavity with a view exclusively or mainly to cleaning them, perfuming them, changing their appearance, protecting them, keeping them in good condition or correcting body odors [6]."

One of the main clinical signs of aging is a loss of skin "tightness" and the appearance of fine lines and deep wrinkles on the skin, which increase with age. These are the result of a modification of the structure and cutaneous functions of the skin and are often seen as being undesirable. It is known that these signs of aging can be treated using cosmetics or dermatological formulas that contain active agents, such as retinoids [7]. These active ingredients mask the effects of wrinkles by accelerating the cell renewal process and removing dead skin cells. However, a disadvantage of these active ingredients is that their effects are not immediate and can only begin to be noticed a long time after application. Consequently, a number of cosmetic manufacturers, including L'Oréal, have studied a variety of polymer-based active ingredients for their ability to rapidly alleviate the effects of skin aging, leading to a smoothing of fine lines and wrinkles, and masking the signs of fatigue [8-18].

To achieve these benefits, cosmetic products require the use of film-forming polymers that can be safely deposited on the skin and keep the product in place. Such polymers are particularly used in make-up products such as mascaras, eyeliners, eye shadows and lipsticks. To perform adequately, these film forming materials must be visually appealing and impart the formulation with a good resistance to mechanical contact, so that the deposit is not transferred during contact with the fingers or clothing. They must also provide a good resistance to contact with sources of water, such as rain, during showering or perspiration, as well as resistance to contact with the fats of foods, in particular edible oils (e.g. olive oil). Dispersions of such polymers in organic media such as hydrocarbon oils (e.g. isododecane (IDD)) have been widely investigated for this purpose [13-18]. For example, Mougin and Mondet described dispersions of acrylic polymers stabilised with poly(styrene-*block*-ethylene-co-propylene) diblock copolymers in hydrocarbon oils (e.g. paraffin oil, IDD) [16]. However, when the dry matter content (polymer + stabiliser) exceeds 25wt%, the dispersion then becomes too viscous, which causes formulation problems in cosmetic products. In addition, films obtained after application of the dispersion were not very visually appealing. In another example, Farcet et al. details dispersions in IDD and other natural oils of poly(2-ethylhexyl acrylate-*block*-methyl acrylate-*block*-2-ethylhexyl acrylate) triblock copolymers synthesised in IDD via RAFT polymerisation [13-15]. However, this method of polymerisation is difficult to achieve at industrial scale because it requires a large number of intermediate purification steps to obtain the final polymer dispersion. To overcome the difficulty linked to the industrialisation of controlled radical polymerisation processes, Portal et al. proposed an easy two-step/one-batch synthesis approach to develop poly(acrylate) copolymer dispersions in IDD [18, 19]. These dispersions showed promising long-lasting wear performance for make-up applications.

Recently, it has been discovered that model polyacrylate based copolymers of hydrophobic monomers, such as 2-ethylhexyl acrylate (2EHA) and isobornyl acrylate (IBA), with maleic anhydride (MA) have good film forming properties and a high resistance to water [8-12]. Furthermore, these acrylic polymers are easily transportable in hydrocarbon oils such as IDD and are effective tensioactive agents that help to reduce wrinkles on the skin immediately after application. Copolymers of MA with acrylic and methacrylic esters have received substantial attention in the academic and patent literature, primarily as coating and adhesive materials [20]. A particular advantage is that crosslinked films with high mechanical and water resistance may be obtained on the surface of the skin if they are formulated appropriately with a polyamine. This occurs through ring-opening reactions that readily occur between the MA and amine moieties (Figure 1) [11]. Amine terminated polydimethylsiloxanes are particularly preferred for this role due to their hydrophobicity, non-toxicity and smooth texture. A current limiting factor in the use of poly(2EHA-co-MA) and poly(IBA-co-MA) copolymers in cosmetic formulations is that they are prone to containing unacceptably high levels of monomer residue after the polymerisation, the removal of which can be costly and time consuming. Furthermore, the monomers 2EHA, IBA and MA are derived from petrochemical sources, as is the IDD that forms a major component of the solvent system typically used to synthesise such copolymers. These hydrocarbon based copolymers are not in line with the ambition of the L'Oréal group, and thus are only used as models to achieve state of the art make-up physico-chemical properties, in order to eventually replace petroleum based polymers classically used for these applications [21-23].

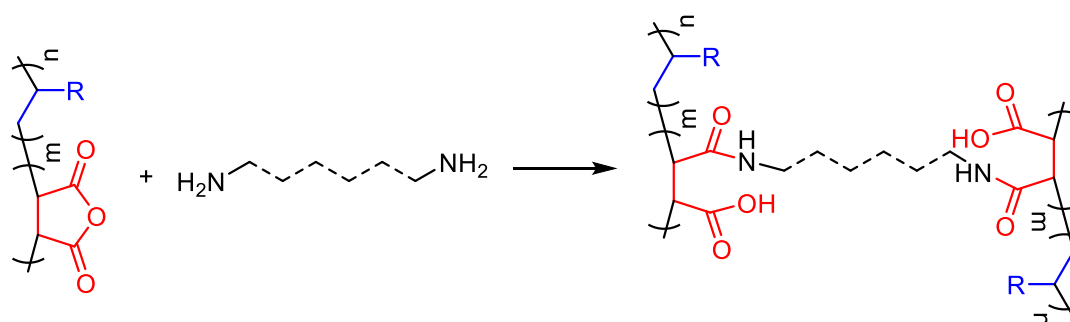


Figure 1. Crosslinking reactions between poly(MA) units and polyamines that enable copolymers containing MA to act as film-forming agents ingredients in cosmetic products. Adapted from Ref. 11.

Carbon dioxide (CO₂) has received much attention and is considered by many as an undesirable substance, which is a real problem for the world. However, it should be possible to create value from CO₂ by reducing and preventing emissions, as well as allowing companies to be the main actors in a responsible and sustainable new scenario [24, 25]. Centi et al. reported several aspects and opportunities for companies connected to the use of CO₂ as a starting material [24]. These included the improvement of the public image of the companies, the reduction of costs for the carbon emissions, the development of new products or processes using a low value compound, and so on, contributing to a circular economy. Tcvetkov et al. reviewed different carbon dioxide sequestration projects and showed that CO₂ can be a valuable resource for many industries [26]. The direct use of captured CO₂, as a supercritical solvent (scCO₂), has gained significant attention in recent years. This solvent aligns with the 12 Principles of Green Chemistry developed by Paul Anastas and John Warner [27].

Supercritical fluids are highly compressed gases which combine the properties of gases and liquids: the solvating power of a liquid but the mass transport properties of a gas [28, 29]. scCO₂ is a renewable solvent that is derived from many industrial waste streams and is relatively cheap, nontoxic, non-flammable and is an effective polymerisation medium [30]. In addition, scCO₂ also has an easily

accessible critical point ($T_c = 31.1\text{ }^\circ\text{C}$, $P_c = 73.8\text{ bar}$), and in many respects exhibits solvent properties similar to those of hydrocarbon oils [31]. On depressurisation, the CO_2 reverts to its gaseous state and can be removed easily, leaving a solvent free product. This leads to a large number of possibilities to formulate with different type of solvents, and not only IDD as per the classical procedure. The solubility properties of scCO_2 can also be exploited to selectively extract small molecule impurities from polymers and improve their safety profile [31].

To address the need for monomer sources that are derived from naturally occurring compounds, our research group has recently described the radical polymerisation of a variety of terpene-based (meth)acrylates [32, 33]. Terpenes are a diverse family of naturally occurring compounds that are abundant in nature and do not compete directly with food sources, thus making them attractive feedstocks for renewable polymers. Turpentine, the volatile fraction isolated from pine resin, is the primary source of a variety of terpenes and is produced on a scale of about 330,000 metric tonnes per year [34, 35]. Among other factors, the composition of turpentine depends on the tree species and age, but its major components are α -pinene and β -pinene [36]. In the context of cosmetic applications, a feature of monomers derived from terpenes are that their structures are predominantly composed of hydrocarbons, making them highly soluble in the oily solvents used for their formulation. This is highlighted by the copolymers described above containing IBA, which can be derived from terpenes and is an isomer of the terpene-derived monomer α -pinene acrylate (α PA).

Herein, we describe a methodology for reproducibly synthesising copolymers of MA and 2EHA in scCO_2 . The ambition of the L'Oréal group is to develop performing, sustainable and eco-responsible hydrocarbon polymers, like polyesters or functionalised polysaccharides, for various cosmetic applications. These acrylate based copolymers will be considered as models to reach this target for make-up and skincare products. Such reactive model copolymers are promising materials to reach a high enough level of performance to substitute silicone based polymers for make-up applications. The impact of a greener process will be observed on the final physico-chemical properties of a make-up deposit. In particular, the kinetics of the reaction and resulting products were compared with analogues synthesised using L'Oréal's current process in the solvent mixture (Ethyl acetate (EtOAc)/IDD) (30/70). The IDD solubility of the copolymers synthesised in scCO_2 was investigated, and the materials were then cast from this solvent into dyed films onto substrates and tested for resistance to olive oil. We then used this greener process to synthesise terpene-derived copolymers of poly(2EHA-co-IBA) and poly(2EHA-co- α PA) in scCO_2 , which exhibit similar properties to those synthesised in the EtOAc/IDD (30/70) solvent mixture.

Experimental Section

Reagents

The following reagents were purchased from commercial suppliers and used without further purification: 2,2'-Azobis(isobutyronitrile) (AIBN, Sigma Aldrich, 98%), maleic anhydride (MA, Sigma Aldrich, 99%), isododecane (IDD, L'Oréal), ethyl acetate (EtAOc, Sigma Aldrich, $\geq 99.5\%$), bis(3-aminopropyl) terminated polydimethylsiloxane (average $M_n \sim 50\,000\text{ g/mol}$, CAS Number 106214-84-0, Sigma Aldrich), α -pinene (Sigma Aldrich, 98%), borane dimethylsulfide ($\text{BH}_3\cdot(\text{CH}_3)_2\text{S}$, Sigma Aldrich), titanium(IV) butoxide (Alfa Aesar $\geq 99\%$), CO_2 ($\geq 99.99\%$, BOC special gases). 2-ethylhexyl acrylate (2EHA, Sigma Aldrich, 98%), isobornyl acrylate (IBA, Sigma Aldrich, technical grade), and α -pinene acrylate (α PA) were filtered through a plug of basic alumina to remove inhibitor prior to use.

Instrumentation and Characterisation

All reactions in sCO_2 were performed in a 60 mL high-pressure autoclave built in-house, previously used for dispersion polymerisations. All reactions were completed at least in duplicate to confirm their experimental reproducibility prior to obtaining the data reported here.

Gel permeation chromatography (GPC) was performed in THF (HPLC grade, Fisher Scientific) as eluent at room temperature using two Agilent PL-gel mixed-D columns in series with a flow rate of 1 mL min^{-1} . A multi-angle light scattering (MALS, Wyatt Optilab Dawn 8+) detector, along with a differential refractometer (DRI, Agilent 1260), were used for sample detection. The system was calibrated using PMMA standards (molecular weight range: $1,400 - 540,000 \text{ g mol}^{-1}$).

^1H nuclear magnetic resonance (^1H NMR) spectra were obtained using a Bruker DPX 400 MHz spectrometer. Samples were dissolved in CDCl_3 and the solvent peak was used as a reference, set to 7.24 ppm. 2EHA conversion was calculated by comparing the integral values of the alkene peak at 6.10 ppm with the peak at 3.97 ppm corresponding to the CH_2 group adjacent to the ester in polymerised 2EHA. The polymer peak was integrated from 3.65 – 4.30 ppm and the overlapping intensity of the monomer peak was subtracted from the combined integral value. In the case of poly(2EHA-*co*-MA) copolymers, copolymer composition was calculated by comparing the integral values over the range of 2.75 – 3.60 ppm for MA with integral values over the range of 3.60 – 4.40 ppm, accounting for the number of protons. For poly(2EHA-*co*-IBA), integral values between 2.70 – 3.80 ppm and 4.25 – 5.10 ppm were compared. For poly(2EHA-*co*- α PA), integral values between 2.75 – 3.80 ppm and 4.50 – 5.50 ppm were compared.

Differential scanning calorimetry (DSC) was performed using a TA Instruments differential scanning calorimeter (TA-Q2000). All samples were subjected to a heating, cooling and heating cycle from $-90 \text{ }^\circ\text{C}$ to $200 \text{ }^\circ\text{C}$ using heating and cooling rates of $10 \text{ }^\circ\text{C/min}$ and a nitrogen flow rate of 60 mL/min . All samples were sealed in hermetic aluminium pans (TA Instruments T-zero sample pan) with lids. T_g values of copolymers were recorded from the second heating cycle.

Poly(2EHA-*co*-MA) synthesis in EtOAc/IDD.

MA (1 g, 0.0102 mol), 2EHA (4 g, 0.0217 mol), AIBN (0.05 g, 3.045×10^{-4} mol) and a 2.25 g/5.25 g EtOAc/IDD mixture (7.5 g total) were combined in a vial containing a magnetic stirrer and sealed with a septum. The solution was stirred at room temperature to create a homogeneous solution and then purged with argon for 30 min while in an ice bath. The vial was then placed into an oil bath and stirred at $65 \text{ }^\circ\text{C}$ for 24 hr. During this time the viscosity of the solution was observed to increase and the solution turned pale yellow in colour. The product was analysed via ^1H NMR spectroscopy and GPC before being dried under high vacuum at $50 \text{ }^\circ\text{C}$ for several days to afford the polymer product as a tacky yellow liquid.

Batch synthesis of poly(2EHA-*co*-MA) in sCO_2 .

MA (2 g, 0.0204 mol) and AIBN (0.1 g, 6.09×10^{-4} mol) were added directly to a 60 mL autoclave base, before it was sealed and purged with a positive flow of CO_2 for 30 min. During this time, 2EHA (8 g, 0.0434 mol) was degassed in a separate vial by bubbling with argon for 30 min at $0 \text{ }^\circ\text{C}$, before being charged into the autoclave under a positive flow of CO_2 . The autoclave was then pressurised to 50 bar at room temperature and then heated to $65 \text{ }^\circ\text{C}$, during which time the pressure increased to ~ 75 bar. The autoclave was then increased to a pressure of 275 bar and stirred at 300 rpm for 24 hr. The heating jacket was then removed and the autoclave was cooled to $0 \text{ }^\circ\text{C}$ in an ice bath before being vented over a period of 10 min. The product was collected as a viscous and very tacky clear liquid, and analysed via ^1H NMR spectroscopy and GPC.

Two-stage synthesis of poly(2EHA-co-MA) in scCO₂.

MA (2 g, 0.0204 mol) was added directly to a 60 mL autoclave which was then sealed and purged with a positive flow of CO₂ through the keyhole for 30 min. The keyhole was then sealed and the autoclave pressurised to 50 bar at room temperature, before being steadily increased to 200 bar and 65 °C, and allowed to stir at 300 rpm for 60 min. During this time, AIBN (0.1 g, 6.09 × 10⁻⁴ mol) was dissolved in 2EHA (9 mL, ~8 g, 0.0434 mol) and degassed by bubbling with argon for 30 min at 0 °C. This solution was then injected into the autoclave using a HPLC pump (Jasco) at a rate of 1 ml min⁻¹, causing an increase of pressure inside the autoclave to ~275 bar. The autoclave was stirred at 300 rpm for 24 hr, after which the heating jacket was removed and the autoclave was cooled to 0 °C in an ice bath. At this point the autoclave was either vented over a period of 10 min, or flushed with a steady flow of CO₂ for 15 min to remove residual monomer and then vented over a period of 10 min. The product was collected as viscous and very tacky clear liquid.

Synthesis of 2,6,6-Trimethylbicyclo[3.1.1]heptan-3-ol (isopinocampheol).

α-Pinene (50 g, 0.3670 mol) was placed in a 500 mL 3-neck round bottom flask and a thermometer as well as a dropping funnel with a rubber septum were connected. The vessel was placed under vacuum (ca. 1 mBar) for 5 minutes before back-filling with nitrogen. 40 mL tetrahydrofuran (THF) was added to the reaction mixture and BH₃·(CH₃)₂S (14.418 g, 0.1784 mol) was placed into the dropping funnel. The flask was lowered into an ambient temperature water bath and a silicone oil gas bubbler was connected to the vessel. The BH₃·(CH₃)₂S in the dropping funnel was added slowly to the reaction mixture, maintaining the reaction temperature between 30 – 35 °C. After 30 minutes the water bath was removed. The reaction was heated to 50 °C and left to react for another 2 hours at that temperature. The reaction mixture was cooled to 0 °C with an ice bath and 200 mL of 3M NaOH was added dropwise. 12 mL of 30% H₂O₂ and 1 mL of 3M NaOH were mixed in the dropping funnel before adding this mixture slowly to the reaction. This was repeated 4 times so that a total volume of 60 mL of 30% H₂O₂ was added to the reaction mixture. The reaction was then left to react for 30 minutes at ambient temperature before heating it to 90 °C and leaving it to react for another 30 minutes. The reaction was cooled to ambient temperature with a water bath and NaHCO₃ (22 g, 0.2619 mol) was added. Any residual THF was removed with a rotavap. The reaction mixture was placed in a separating funnel and the organic phase was extracted with 4 portions of 30 mL petroleum ether. The petroleum ether fractions were combined and washed with 3 portions of 15 mL MgSO₄ brine (0.15 g/mL) the organic phase was further dried over anhydrous MgSO₄ before filtering and placing in a 250 mL round bottom flask. The petroleum ether was removed with a rotavap and the product was purified by vacuum fractional distillation. No condenser was connected to the distillation setup and the collecting flask was immersed in liquid nitrogen. The product was a white, semi-crystalline waxy solid. Yield: 42 g (76%). ¹H NMR spectroscopy was used to confirm the product structure.

Synthesis of 2,6,6-Trimethylbicyclo[3.1.1]heptan-3-yl acrylate (α-pinene acrylate, αPA).

Isopinocampheol (20 g, 0.1297 mol) was placed in a 250 mL round bottom flask along with ethyl acrylate (47 g, 0.4694 mol) and a magnetic stirrer. Titanium(IV) butoxide (0.1 g, 0.2938 mmol) and BHT (0.05 g, 0.2269 mmol) were added. A still head with a thermometer, a Vigreux section, a condenser, a vacuum take-off adapter and a receiving flask were attached to complete the fractional distillation setup. Vacuum was applied until the internal pressure was at 200 mBar before back-filling with Ar. This process was repeated 4 times to ensure all the oxygen had been removed from the system. The reaction mixture was heated to 120 °C using a pre-heated oil bath. The setup was sealed, by closing the valve of the Schlenk line that was connected to the take-off adapter, to prevent ethyl acrylate from distilling out of the reaction mixture too quickly. Every 15 minutes, the pressure would be reduced to allow 2 to 3 mL of liquid to distil off. For the final few distillation steps, the pressure had to be reduced below ambient so that the distillate could reach the condenser. Once the desired

volume was collected, the pressure was returned to ambient by back-filling with Ar and the setup was sealed once more. After 2 hours, the reaction was cooled to room temperature before replacing the receiving flask and applying high vacuum to remove all the residual ethyl acrylate, butyl acrylate, ethanol and n-butanol. The product was isolated from the reaction mixture by vacuum distillation and obtained as a clear, colourless liquid. Yield: 23.9 g (88%). ¹H NMR spectroscopy was used to confirm the product structure.

Poly(IBA-co-MA) synthesis in EtOAc/IDD.

MA (0.25 g, 0.0026 mol), isobornyl acrylate (IBA) (1.125 g, 0.0054 mol), AIBN (0.01375 g, 8.373 × 10⁻⁵ mol) and a 0.6 g/1.4 g EtOAc/IDD mixture (2 g total) were combined in a vial containing a magnetic stirrer and sealed with a septum. The solution was stirred at room temperature to create a homogeneous solution and then purged with argon for 30 min while in an ice bath. The vial was then placed into an oil bath and stirred at 65 °C for 24 hr. During this time the viscosity of the solution was observed to increase and the solution turned pale yellow in colour. The product was analysed via ¹H NMR spectroscopy and GPC before being dried under high vacuum at 90 °C for several days to afford the polymer product as a pale orange, hard solid.

Poly(αPA-co-MA) synthesis in EtOAc/IDD.

The reaction was performed as described for the synthesis of poly(IBA-co-MA), with the exception that α-PA was substituted for IBA. The product was collected as a hard, orange coloured solid.

Two-stage synthesis of poly(IBA-co-MA) in scCO₂.

The reaction was performed as described for the two-stage synthesis of poly(2EHA-co-MA) in scCO₂, with the exception that IBA (9.05 g, 0.0434 mol) was substituted for 2EHA. The product was collected as a hard, off-white, craggy solid.

Two-stage synthesis of poly(αPA-co-MA) in scCO₂.

The reaction was performed as described for the two-stage synthesis of poly(2EHA-co-MA) in scCO₂, with the exception that αPA (9.05 g, 0.0434 mol) was substituted for 2EHA. The product was collected as a hard, yellow, craggy solid.

Olive oil resistance test.

To compare the performance *in vitro*, simple lipstick formulations consisting of poly(2EHA-co-MA) copolymers, IDD, gellant, and pigments were evaluated (Table 1).

Table 1: Simple formulations for *in vitro* evaluation of poly(2EHA-co-MA) copolymers.

Ingredients	Formulation
Acrylate-co-Maleic Anhydride copolymer	25% of active material
Thickener	5wt%
Pigment Paste (40wt% pigment in isododecane)	5wt%
Isododecane	To complete the formulation to 100wt%

A thin film from the formulation was drawn down on a Byko-chart Black Scrub Panel from Byk. Byko-chart substrate is a classical neutral substrate, and the copolymers in IDD have good wettability on this substrate. The lipstick film was dried on the *in vitro* substrate for at least 24 hr at 20 °C. To crosslink

this first deposit, a second thin film of a top coat layer was applied to half of the first layer. It consisted of bis(3-aminopropyl) terminated polydimethylsiloxane at 50wt% in IDD. This second layer was dried again for at least 24 hr at 20 °C. Then, 5 mL of olive oil was dropped onto the film and left for 5 min. A cotton pad was pressed onto the film 15 times to see how much colour was transferred to the pad, and the damage to the film on the substrate was observed and evaluated.

Results and Discussion

Synthesis of poly(2EHA-co-MA) in EtOAc/IDD.

L'Oréal regularly synthesise large scale (>kg) batches of a particular poly(2EHA-co-MA) copolymer. This copolymer is comprised of the monomers 2EHA and MA, and is currently produced by mixing the two monomers in a 2:1 molar ratio and using 1wt% (relative to monomer) of a radical generating molecule (e.g. AIBN) to initiate the polymerisation. The polymerisation is performed by first using a solvent mixture of EtOAc/IDD (30/70) to dissolve the reactants in a 40wt% solution, and then heating the solution in a sealed vessel between 60 – 100 °C for several (up to 24) hours (Figure 2).

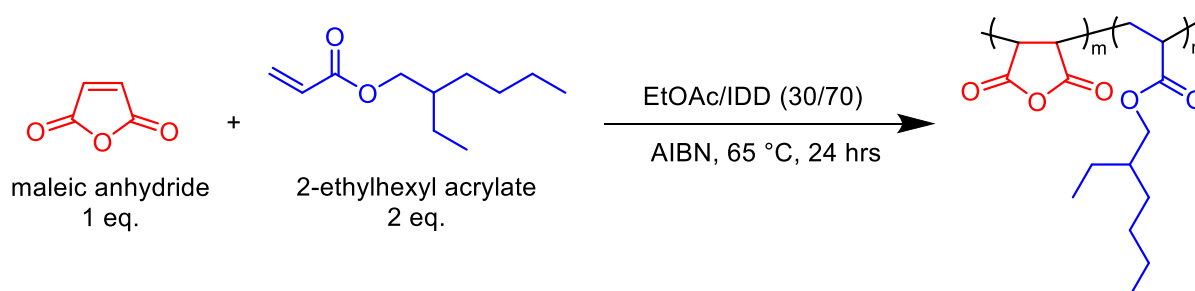


Figure 2. Monomer structures and general polymerisation conditions used for synthesising the copolymer poly(2EHA-co-MA).

The reaction depicted in Figure 2 was initially performed on a moderate scale, using 4 g of 2EHA and 1 g of MA in 7.5 g of an EtOAc/IDD (30/70) mixture. After reacting for 24 hours, during which time the viscosity of the solution increased and a pale yellow colour appeared, the crude solution was analysed by ¹H NMR spectroscopy (SI Figure S1). This spectrum indicated that the polymerisation had achieved a high monomer conversion (>95%). Furthermore, the appearance of two broad peaks at ~3.0 ppm and ~4.0 ppm, assigned to the pendant and backbone protons of the 2EHA and MA repeat units, respectively, were evidence that both monomer species had been incorporated into the final polymer product. A comparison of the integral values of these peaks indicated that the ratio of the two monomer species incorporated into the copolymer product was similar to that expected based on the reagent quantities used. There was however a slight bias toward 2EHA and approximately 6mol% of the MA added at the beginning of the reaction did not polymerise (see Table 2). GPC data taken from the solution corroborated that polymerisation had occurred, returning a number average molecular weight (M_n) value of 17.5 kDa and a broad dispersity (\mathcal{D}) of 3.45 (SI Figure S2a). A portion of the remaining volatiles in reaction mixture could be removed by placing the sample under high vacuum for several days. After this time the colour was observed to have darkened slightly and the viscosity had increased, giving the product with a consistency similar to honey (SI Figure S2b).

Combined Monomer Synthesis of poly(2EHA-co-MA) in scCO₂.

The solubility of 2EHA and MA in scCO₂ was qualitatively evaluated at 65 °C and 275 bar using a viewing cell autoclave prior to undertaking any polymerisation reactions. 2EHA was found to be readily miscible with scCO₂, but MA could only be dissolved up to a concentration of ~4wt% under these conditions. This imposed a combined monomer concentration limit of ~17.5wt% on the polymerisation reactions in scCO₂. Therefore, the 2EHA and MA quantities were scaled to 8 g and 2 g,

respectively, for compatibility with the autoclave volume (60 mL), giving a much more dilute system than for the solvent based synthesis (0.21 g monomer/g CO₂ versus 0.67 g monomer/g EtOAc/IDD). Due to the lack of solubility of MA in the monomer 2EHA, polymerisations in scCO₂ were initially performed by dissolving AIBN in the liquid monomer 2EHA, and then charging this solution with a syringe into an autoclave containing the crystalline MA. The mechanical stirrer was engaged and the autoclave was pressurised to the CO₂ liquid point (~50 bar), heated to 65 °C, which induced a pressure increase to 75 bar, followed by the addition of CO₂ to reach a pressure of 275 bar. This entire process takes between 15 – 30 min, after which the reaction was left to proceed for 24 hours. Initially, venting the autoclave after cooling it to room temperature proved extremely difficult due to solubility of the resulting copolymer in scCO₂ and its tackiness. This caused it to continually be expelled from the autoclave and restricted flow out of the exit tap. To circumvent this issue the autoclave had to first be cooled to 0 °C in an ice bath for subsequent reactions, which causes the copolymer to precipitate.

Rather than a yellow liquid, the resulting product was almost colourless in appearance. A ¹H NMR spectrum indicated that both monomer species had successfully achieved a high degree of conversion (>90 %), although it is noted here that some minor losses of monomer may have occurred during the venting process. However, the GPC trace of the crude product was strongly bimodal and clearly indicated the presence of two distinct polymeric species with drastically different M_n values. The polymerisation was repeated twice more and again bimodal distributions were obtained, with different relative areas between the two species (SI Figure S3).

Synthesis of poly(2EHA-co-MA) in scCO₂ via *In Situ* Staggered Monomer Addition.

An observation made in performing the combined monomer syntheses described above was that unlike AIBN, the MA monomer is almost completely insoluble in the monomer 2EHA in the absence of a co-solvent. Thus, we speculated that prior to transition of the CO₂ from a gas to a liquid, it would be possible for the 2EHA monomer to homopolymerise due to the absence of oxygen in the system, presence of AIBN, and the increased temperature. Furthermore, MA would likely take some time to dissolve in the scCO₂ due to it being a crystalline solid, rather than a liquid as for the 2EHA. This could lead to a heterogeneous two-part polymerisation reaction, in which 2EHA would initially homopolymerise in a bulk-like or expanded phase process. The high reactivity of acrylate monomers such as 2EHA would enable this process to occur rapidly, well within the 15 – 30 min required to bring the autoclave up to reaction conditions. Once the MA was then solubilised, this monomer would begin to participate in the polymerisation, changing the rate of reaction and causing the formation of the desired polymeric species. This potentially explains the bimodal molecular weight distribution profiles observed in the prior reactions (Figure 3a-e).

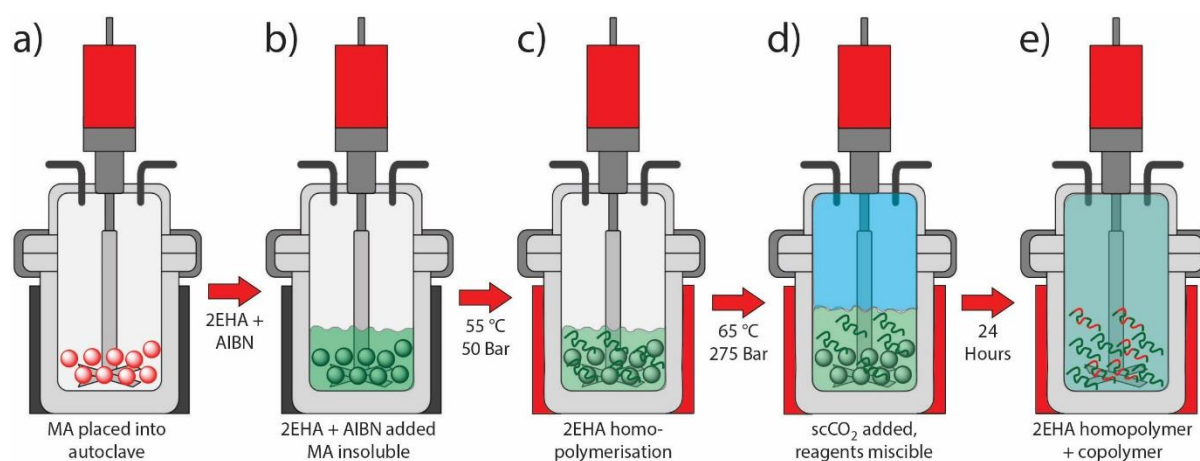


Figure 3. Graphical representation of the expanded phase copolymer synthesis in $scCO_2$. The figures depict the hypothesised mechanism for the formation of two separate polymeric species. **a)** MA is not soluble in 2EHA so must be placed into the autoclave separately. **b)** 2EHA solubilises AIBN, allowing it to polymerise initially in bulk-like conditions **(c)** when the autoclave is heated initially as part of the pressurisation process. **d)** Upon increasing the pressure to reaction conditions an expanded phase reaction is formed and the monomer species, including MA, dissolve. **e)** The newly dissolved MA is then able to participate in the polymerisation process, leading to the formation of copolymers alongside the homopolymer 2EHA.

To verify this hypothesis, a timed solubility test of the MA was performed in $scCO_2$ using a static viewing autoclave. ~ 2 g of MA was loaded into a small vial and left to stir at a pressure and temperature of 275 bar and 65 °C, respectively (SI Figure S4). Under these conditions it was noted that the monomer took close to 30 min to fully dissolve, adding further validity to the hypothesis that the higher molecular weight polymeric contamination present in the batch-like reaction products is poly(2EHA) homopolymer.

To overcome this problem, an alternative reaction protocol was devised based on our group's previous use of HPLC pumps to add secondary monomers *in situ* to polymerisation reactions at high pressure (Figure 4) [37]. In this method, the MA monomer was initially added to an autoclave that was then taken to 200 bar and 65 °C and left stirring for one hour; this would provide sufficient time to create a homogeneous solution of MA dissolved in the $scCO_2$. Following this, the 2EHA monomer containing the appropriate quantity of dissolved AIBN was injected into the autoclave using a HPLC pump. This signalled the beginning of the reaction, after which it was left for 24 hours. We note here that this injection causes an increase in the pressure of the reaction up to the desired value of ~ 275 bar, so in general, no further adjustment of the pressure was required.

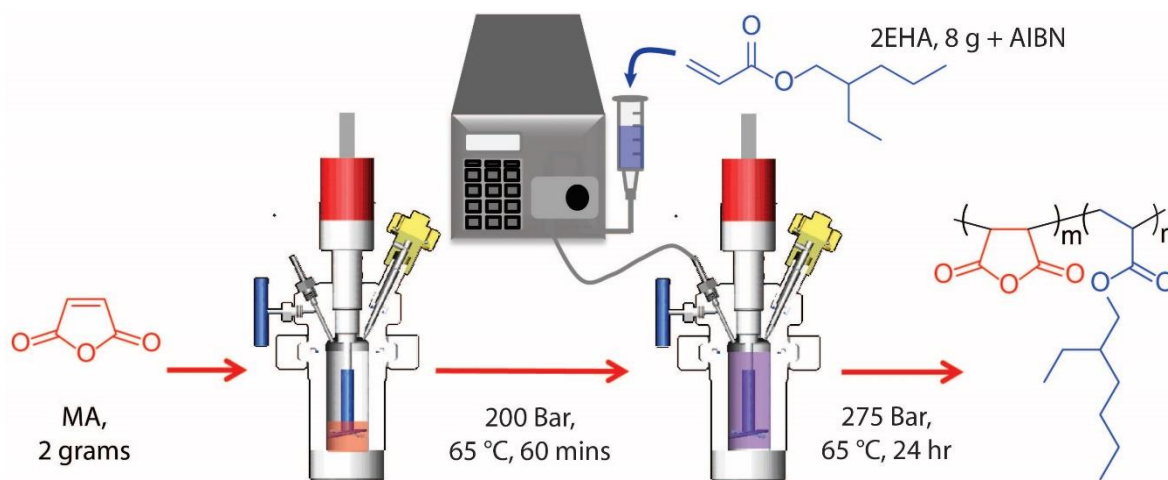


Figure 4. Improved polymerisation method developed to ensure a homogeneous polymerisation in $scCO_2$. A HPLC pump is used to add the AIBN containing 2EHA monomer *in situ*, after first dissolving the MA monomer in the $scCO_2$.

The 1H NMR spectrum of the final product obtained using this alternative approach revealed that the ratio of the two monomer species matched that added to the autoclave (Table 2 and Figure 5). Critically however, the GPC data of the product now only returned a single molecular weight distribution, further corroborating that the secondary polymeric species observed previously was 2EHA homopolymer (Figure 6). The product was also quite similar in physical appearance to those obtained previously, but the yellow colouration was considerably reduced (SI Figure S5). The tackiness of the product at room temperature is expected given its low T_g value and molecular weight, which was determined via DSC to be -6.5 °C (Table 2 and SI Figure S6).

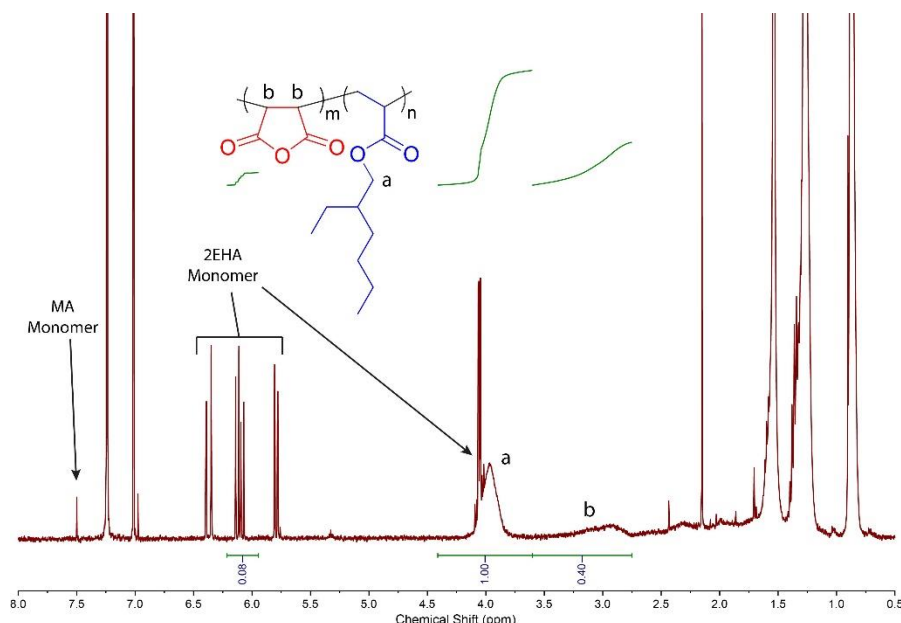


Figure 5. ^1H NMR spectrum of poly(2EHA-co-MA) synthesised in scCO_2 via staggered monomer addition.

To check the reproducibility of this new synthetic approach, the reaction was completed twice more. Once using the exact same conditions, and a second time in the presence of only 50% of the original AIBN quantity, because this is well known to influence the molecular weight of free radical polymerisation reactions. In both cases a single molecular weight distribution was again obtained, and the M_n values of all three copolymer products behaved predictably (Table 2 and Figure 6). In contrast to the reactions in EtOAc/IDD, ^1H NMR spectroscopy revealed that the composition values for the reactions in scCO_2 matched very closely with the initial feed ratio (Table 2). ^1H NMR data also showed that the conversion values for polymerisations in scCO_2 had been reduced somewhat to $\sim 80\%$ (Table 2). Furthermore, it was observed that the molecular weight values of the copolymers synthesised via this route in scCO_2 were between 12.4 – 13.6 kDa, 2.55 – 2.80 fold lower than for the sample produced in EtOAc/IDD. The \mathcal{D} values of these samples were also significantly narrower, with average value of 2.51, versus 3.57 for the polymerisation in EtOAc/IDD.

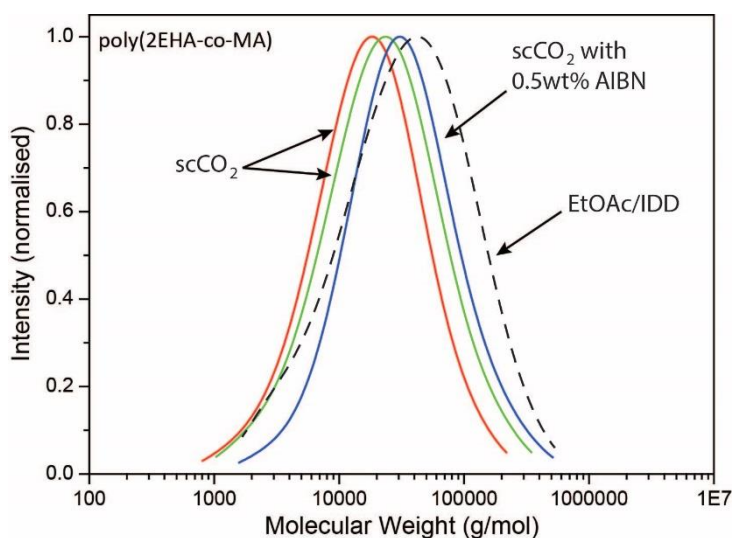


Figure 6. Molecular weight distribution data for poly(2EHA-co-MA) copolymers synthesised using staggered monomer addition in scCO_2 . The distribution shown using dashed lines is the data for the same copolymers synthesised in EtOAc/IDD.

An added benefit of performing polymerisation reactions in scCO₂ is the high solubility of low molecular weight species, such as acrylate monomers, and an often low solubility of the resulting polymer products [31]. This often opens up the possibility of using a CO₂ flushing or extraction step post polymerisation to strip unreacted monomers and other small molecules away from the polymer. Trace MA left behind in the product is of particular concern in cosmetic applications due to its toxicity [38]. To demonstrate this benefit, a poly(2EHA-co-MA) copolymer synthesised in scCO₂ was loaded back into an autoclave cooled to 0 °C and pressurised to 75 bar, under which conditions CO₂ is in a liquid state. For the crude polymer product not subjected to an extraction step, the ratio of the two MA protons in the polymer backbone to their residual monomer equivalents was 56:1. By contrast, the polymer product subjected to a 15 minutes extraction step instead returned a ratio of 1028:1, equivalent to an ~18 fold reduction in the monomer residue present (SI Figure S7a). This demonstrates that CO₂ is an effective tool for the extraction of residual monomeric species from these copolymers, with the potential to produce safer products with no unpleasant smells or colouration, without a considerable time or cost penalty (SI Figure S7b).

Table 2. Copolymerisation reactions (*t* = 24 hours, *T* = 65 °C) between 2EHA and MA.

Copolymer	Solvent	Feed Ratio, 2EHA:MA (mol)	Polymer Composition, 2EHA:MA (mol) ^a	AIBN wt%	Conversion (%) ^a	<i>M_n</i> (kDa) ^b	<i>D_w</i> ^b	<i>T_g</i> (°C) ^c
p(2EHA-co-MA)	EtOAc/IDD (30/70)	67:33	73:27	1	94.4	34.7	3.57	N/O ^d
p(2EHA-co-MA)	scCO ₂	67:33	68:32	1	83.7	13.6	2.50	-6.5
p(2EHA-co-MA)	scCO ₂	67:33	68:32	1	79.1	12.4	2.52	N/O ^d
p(2EHA-co-MA)	scCO ₂	67:33	67:33	0.5	77.9	20.2	2.53	N/O ^d

^afrom ¹H NMR, ^bfrom GPC in THF relative to PMMA standards, ^cfrom DSC, ^dnot observed.

Polymerisation kinetics of poly(2EHA-co-MA) in EtOAc/IDD and scCO₂.

In an effort to understand the origins of the differences in conversion and product characteristics between the reactions performed in EtOAc/IDD and scCO₂, the reactions were repeated and monitored periodically via ¹H NMR and GPC over a 24 hour period. We note here that sampling a single polymerisation reaction in scCO₂ proved to be too difficult on account of the tacky nature of the product. Thus, a series of reactions were performed under identical conditions and halted at different time points for comparison. The conversion versus time plots for 2EHA show that both reactions exhibit typical first order behaviour for free radical polymerisations in dilute solutions that avoid the effects of auto-acceleration (SI Figure S8a). Between the two systems, the polymerisation of poly(2EHA-co-MA) proceeds much more quickly in EtOAc/IDD, reaching a conversion of ~80% in 6 hours. By contrast, the polymerisation in scCO₂ had only achieved a conversion of ~60% in this time, and required close to 24 hours to reach 80% conversion. The discrepancy between these two systems is largely attributed to the monomer and AIBN concentration being more than twice as high for the reaction in EtOAc/IDD versus in scCO₂, due to the limitations of MA solubility. The decomposition rate of AIBN is also known to vary in scCO₂ relative to typical organic solvents and this could also be a contributing factor [39].

Intriguingly, corresponding GPC data reveals that for both polymerisation systems *M_n* decreases as a function of conversion (see SI Figure S9 and S10 for GPC traces). For the reaction in EtOAc/IDD, *M_n* of

the product at the first recorded time point (15 min) is 102.5 kDa, which then steadily decreases throughout the reaction to a final value of 34.7 kDa after 24 hours (SI Figure 8b). This corresponds to a decrease of 66% between the first and last recorded time point. During this time \bar{D} increases considerably from 1.90 to 3.57. In $scCO_2$, the same general trend in M_n and \bar{D} is followed, but the values of M_n are much smaller, decreasing from 27.9 kDa at the beginning of the reaction to 13.6 kDa at the end, an overall decrease of 49%. Based on the data available, we speculate that the difference in molecular weight between the two systems throughout the reaction could be due to the much higher viscosity of the EtOAc/IDD based reaction in comparison to the more dilute $scCO_2$ system. This may have induced a partial Trommsdorff–Norrish (TN) effect towards the latter stages of the polymerisation, in which diffusion controlled termination events are inhibited [40]. The TN effect is well known to alter the characteristics of polymerisation reactions, in particular by increasing in their molecular weight and \bar{D} values by reducing the ability of the growing chains to terminate. Aforementioned differences in radical stability and solubility between the two solvents are also possible culprits.

Considering the somewhat unusual evolution of molecular weight with time, a previous study has reported that the final molecular weight values of copolymers of methyl methacrylate with MA decreased as a function of MA feed ratio. Possible chain transfer effects between the solvent were cited in this case, but in this example no kinetic studies were performed [41]. Another explanation is that the solubility or decomposition rate of the initiator in the reaction media changes as the polymerisations proceed and the monomer concentration decreases. If these effects were to induce a gradual increase in the concentration of radicals in solution, then the molecular weight of the products would consequently be reduced. Recently, Philipps et al. have also highlighted intrinsic problems with using GPC elugrams to characterise molecular weight of (block) copolymers with distinctly different physico-chemical properties [42]. These considerations could also be relevant here given the much higher expected rigidity of MA in comparison the EHA and slight tapering through the polymerisation. In any case, it is clear that the polymerisations undertaken in $scCO_2$ are more controlled than those in EtOAc/IDD, presumably as a result of either the reduced reagent concentration and/or the much lower density of $scCO_2$ in comparison to the EtOAc/IDD mixture. We intend to investigate this phenomenon further in the future.

Next, changes in the composition of each copolymer were analysed and plotted as a function of conversion (SI Figure 11). This plot shows that there is a considerable difference in the way monomers are incorporated during the polymerisation between the two systems. In EtOAc/IDD, the polymer chains at the first time point (15 mins) appear to be composed of 2EHA exclusively. MA is then gradually incorporated during the polymerisation until a constant value of 17wt% (27mol%) is reached after 8 hours at 85% 2EHA conversion, beyond which no further MA is incorporated. By contrast, the copolymer composition during the polymerisation in $scCO_2$ is far more consistent, with the chains already containing 14wt% (24mol%) MA at the first time point (2 hours), which then continues to increase for the entire duration of the reaction to a value of 20wt% (32mol%) incorporation that closely matches the initial feed ratio.

A higher incorporation of 2EHA in the case of the polymerisation in EtOAc/IDD is unsurprising given that the reactivity ratio of 2EHA is expected to be much higher than that of MA based on data available from its copolymerisation with related monomer systems (e.g. MMA) [20]. For the case where the two monomer reactivity ratios are drastically different, $r_1 > 1$ and $r_2 < 1$, the copolymer will contain a larger amount of the more reactive monomer in random placement in the chain. Although the monomer reactivity ratios for the copolymerisation of 2EHA with MA has not been reported, as an example, the reactivity ratios between the similarly structured monomer MMA and MA are 3.10 and 0.03,

respectively [43]. Under the assumption of a similarly large difference in reactivity ratio between 2EHA and MA, less MA will be incorporated into the polymer compared to the amount available in solution. The more consistent incorporation of MA in $scCO_2$ therefore implies that the reactivity ratio difference between the two monomers is greatly reduced in this solvent. The reactivity ratios of monomer pairs with MA are known to vary considerably with the solvent used for their polymerisation. Again, taking the copolymerisation of MMA-MA as an example, the reactivity ratio (r_1) of MMA increased as a function of solvent polarity from 0.50 in cyclohexane, 0.90 in carbon tetrachloride, 3.10 in toluene, 3.40 in tetrahydrofuran and 3.85 in chloroform [20]. Given the extremely low polarity of $scCO_2$ as a solvent, a lower reactivity ratio between 2EHA and MA in this solvent may be expected. The concentration and/or viscosity of the polymerisation may also have a large influence, but further investigation into these effects are beyond the scope of this work.

Synthesis of Terpene-Derived Copolymers with MA in $scCO_2$ via *In Situ* Monomer Addition.

L'Oréal have an interest in substituting the monomers used for the synthesis of their polymer products with chemically similar alternatives derived from sustainable sources. Terpenes derived from citrus (e.g. d-limonene) and wood waste (e.g. the α - and β -pinenes) have shown to be a promising feedstock for the synthesis of such monomers, and are already available on the multi-tonne scale relatively cheaply [34]. In choosing terpene derived monomer replacements for 2EHA, several factors need to be considered, including solubility of the copolymers in IDD and $scCO_2$, monomer reactivity, monomer availability and ease of synthesis. A preliminary screening process showed α PA to be the preferred monomer for use (Figure 7). This is because it is of the same monomer class as 2EHA, is derived from a one of the most commercially available terpenes (α -pinene) and can be synthesised relatively simply and in very high yields in comparison to many other alternatives (e.g. >95%, versus 63% for α -pinene methacrylate) [32]. Furthermore, the monomer IBA, which is an isomer of α PA, is available commercially and thus would serve as a useful proxy system in our initial studies.

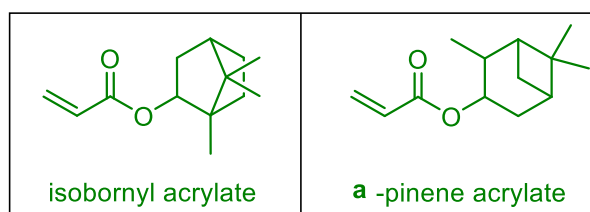


Figure 7. Chemical structures of IBA and α PA monomers.

IBA was the first monomer used for copolymerisation with MA in the same EtOAc/IDD (30/70) mixture used for the 2EHA based copolymers. The molar ratio of the two monomers was kept unchanged from that used for the reactions with 2EHA, meaning that a slightly larger mass of IBA (9.05 g) relative to MA (2 g) was required due to its higher molecular weight. After being allowed to polymerise at 65 °C for 24 hours, a 1H NMR spectrum of the crude product showed that both monomers had polymerised to high conversion, and that the resulting polymer had a composition similar to that targeted from the monomer quantities used (Table 3). Fortunately, both terpene monomers possess a proton adjacent to the acrylate group which makes identification of the final composition very simple. The GPC data for this product returned a unimodal molecular weight distribution, and an M_n value very similar to that for the 2EHA copolymer (SI Figure S12a). By contrast, the \bar{D} value was significantly higher. We again attribute this to the TN effect, which likely occurred to an even greater extent towards the end of the reaction given that the product was obtained as a glassy solid, rather than a tacky liquid (SI Figure S12b). Upon repeating the reaction comparable values of composition, M_n and \bar{D} were obtained, confirming its reproducibility.

Table 3. Copolymerisation reactions ($t = 24$ hours, $T = 65$ °C) between terpene-based acrylates and MA.

Copolymer	Solvent	Feed Ratio, Acrylate:MA (mol)	Polymer Composition, Acrylate:MA (mol) ^a	AIBN wt%	Conversion (%) ^a	M_n (kDa) ^b	\bar{D} ^b	T_g (°C) ^c
p(IBA-co-MA)	EtOAc/IDD (30/70)	67:33	66:34	1	96.9	14.0	3.86	92.9
p(IBA-co-MA)	scCO ₂	67:33	67:33	1	95.2	10.5	4.01	86.5
p(α PA-co-MA)	EtOAc/IDD (30/70)	67:33	66:34	1	97.7	13.4	5.25	64.3
p(α PA-co-MA)	scCO ₂	67:33	68:32	1	94.7	15.4	5.07	67.0

^afrom ¹H NMR, ^bfrom GPC in THF relative to PMMA standards, ^cfrom DSC, ^dnot observed.

After successfully synthesising and reproducing the copolymerisation of poly(IBA-co-MA) in EtOAc/IDD, the synthesis was then performed in scCO₂ using the same *in situ* addition method. The resulting polymer product was instead obtained as a hard and craggy white solid (SI Figure S12c). Both ¹H NMR and GPC confirmed that the characteristics of the product were similar to that for the reaction in EtOAc/IDD (Table 3, SI Figure S13). Interestingly however, although M_n was somewhat lower for the copolymer synthesised in scCO₂, the value of \bar{D} was unchanged. Due to the solid appearance of the crude copolymer products, the T_g values of the copolymers were also analysed using DSC. Unlike most acrylate monomers, many terpene-derived acrylates are characterised by unusually high T_g values as a result of their more rigid pendant groups [32]. T_g values of 92.9 °C and 86.5 °C were obtained for the poly(IBA-co-MA) copolymers synthesised in EtOAc/IDD and scCO₂, respectively (SI Figure S14). We attributed the slight difference in the T_g values for these copolymers to their different molecular weight values. Entanglement relaxation for polymers in this degree of polymerisation (N) range are still likely to be governed by Rouse dynamics ($\tau_{\text{Rouse}} \sim N^2$) rather than by reptation ($\tau_{\text{reptation}} \sim N^3$), and thus are expected to exhibit a strong dependence of T_g on molecular weight [44].

α PA was synthesised from isopinocampheol via a titanium(IV) butoxide-catalysed transesterification with ethyl acrylate and obtained in high yield. Isopinocampheol is the alcohol-derivative of α -Pinene, and first had to be synthesised from the terpene using a hydroboration/oxidation reaction with BH₃·(CH₃)₂S [32]. The structure of isopinocampheol (intermediate) and α PA were confirmed with 1D and 2D ¹H NMR spectroscopy (SI Figures S15 – S18). Monomer in hand, copolymerisation reactions of α PA with MA were then performed in both EtOAc/IDD and scCO₂, as described for the IBA copolymers. ¹H NMR spectra and GPC data recorded of the copolymers revealed that, on the whole, their characteristics and physical appearance closely matched their poly(IBA-co-MA) counterparts (Table 3, Figure 8, SI Figure S19). We note here that by contrast to the copolymerisation reactions of 2EHA in scCO₂, the conversion values of IBA and α PA were approximately 10% higher. T_g values of 64.3 °C and 67.0 °C were obtained for the copolymers of α PA synthesised in EtOAc/IDD and scCO₂, respectively. These values are within range of those obtained previously for homopolymers of poly(α PA) with similar molecular weight values [32]. The T_g value for the scCO₂ synthesised poly(α PA-co-MA) copolymer was also found to be lower than for poly(IBA-co-MA), but this was not surprising given that the T_g value of poly(α PA) is lower than that of poly(IBA).

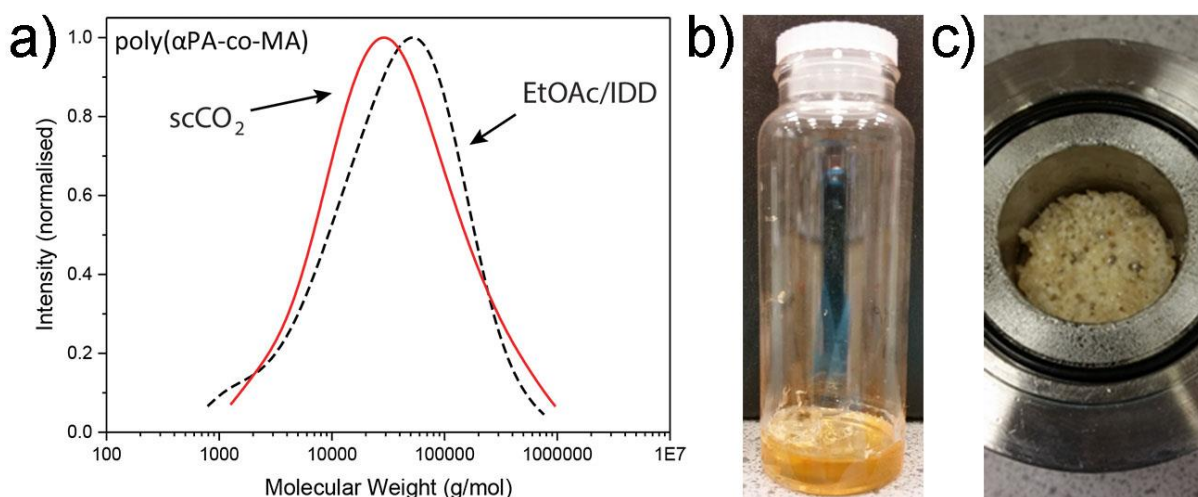


Figure 8. **a)** Molecular weight distribution data poly(α PA-co-MA) copolymers. **b)** Poly(α PA-co-MA) synthesised in EtOAc/IDD. **c)** Poly(α PA-co-MA) synthesised in $scCO_2$.

Cosmetic Performance Testing of Copolymers Synthesised in EtOAc/IDD and $scCO_2$.

The copolymers poly(2EHA-co-MA), poly(IBA-co-MA) and poly(α PA-co-MA) synthesised in EtOAc/IDD and $scCO_2$ were evaluated for use as additives to cosmetic formulations. In the first test, the solubility of the six copolymers in pure IDD was evaluated at several weight fractions. Critically, no difference between the poly(2EHA-co-MA) copolymers was observed, with both samples showing solubility in IDD as high as 50wt%. By contrast, the four terpene derived copolymers were only soluble in IDD at concentrations <33wt%, meaning that future batches will need to be tweaked to increase this value, likely by increasing the feed ratio of the terpene-derived monomer relative to MA.

Copolymers of poly(2EHA-co-MA) are added to lipstick products as film-forming agents, where they provide resistance to food residues that come into contact with the product when the wearer is eating. Oils and fats such as olive oil are known to rapidly degrade the integrity of lipstick layers and decrease their visual appeal. To compare the olive oil resistance of poly(2EHA-co-MA) synthesised in $scCO_2$ to that produced by L'Oréal in EtOAc/IDD, each copolymer was first dissolved in IDD at a concentration of 50wt% along with a small quantity of pigment, and a thickener. Films were then solvent cast onto a series of *in vitro* substrates. These films were designated as the control test samples, half of which were then subjected to an additional coating step with bis(3-aminopropyl) terminated polydimethylsiloxane (PDMS) after drying for at least 24 hours. The amine end groups of the PDMS are able to undergo crosslinking reactions with the MA units to consolidate the polymer films. The films were then allowed to soak in olive oil for several minutes and the removal of colour from the surface was tested by swabbing with a cotton pad. The first layer, consisting of poly(2EHA-co-MA) copolymer only, is extremely sensitive to olive oil. This is not very surprising due to the high solubility of this hydrocarbon based copolymer in IDD. However, after application of the top coat PDMS layer and subsequent crosslinking reaction between both layers, the deposit becomes extremely resistant to olive oil, a very interesting property for lip-based applications. Critically, the poly(2EHA-co-MA) copolymer synthesised in $scCO_2$ performed equally (or even slightly better) to the analogue synthesised in EtOAc/IDD in these tests (Figure 9).

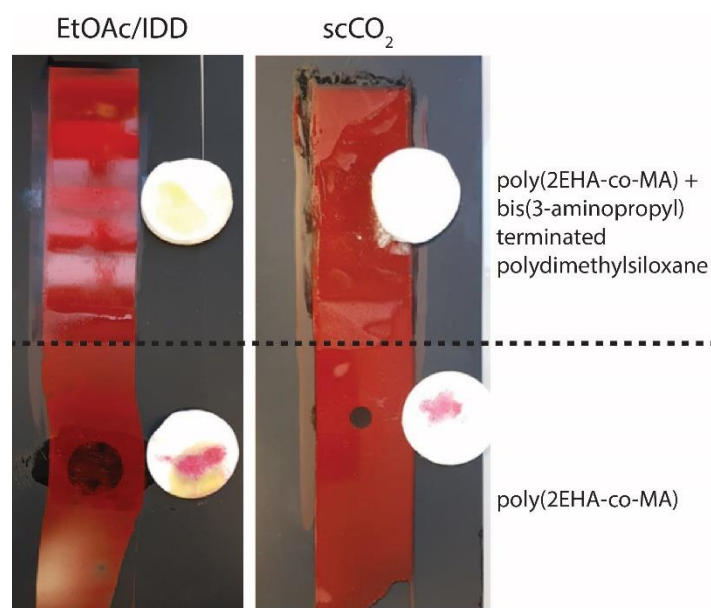


Figure 9. Olive oil resistance tests of films prepared using poly(2EHA-co-MA) copolymers, synthesised in EtOAc/IDD (left) versus in scCO₂ (right). The films at the top of the image were first crosslinked with an extra layer of bis(3-aminopropyl) terminated polydimethylsiloxane.

Conclusions

In order to replace petroleum-based solvents and polymers classically used in make-up and skincare applications, acrylate-based copolymers were synthesised in the greener solvent scCO₂ as model alternatives. These copolymers were first introduced by L'Oréal Research & Innovation teams and correspond to reactive polymers that are soluble in an oily phase. Terpene-derived variants of these copolymers were also synthesised for the first time.

Copolymers of poly(2EHA-co-MA) were synthesised in EtOAc/IDD (30/70) using a 2:1 molar feed ratio of 2EHA and MA, according to the synthetic procedure used by L'Oréal. The products had a molecular weight of ~35 kDa and showed a bias toward the incorporation of 2EHA based on feed ratio. Copolymers of poly(2EHA-co-MA) synthesised in scCO₂ via a batch-like process were unsuccessful and returned bimodal molecular weight distributions. This was attributed to the lack of solubility of the monomer MA in the monomer 2EHA, and the relatively lengthy process required to pressurise and heat CO₂ in an autoclave to a point where it is able to solubilise MA. As a result, the polymer product was likely a mixture of homopolymer 2EHA mixed with poly(2EHA-co-MA). It was found that this issue could be circumvented by first dissolving MA in scCO₂ and only then injecting the 2EHA monomer containing AIBN into the autoclave *in situ* using a HPLC pump.

Using this staggered process, polymers with the expected composition values based on feed ratio and unimodal molecular weight distributions were obtained, but their M_n values were more than 2.5 fold smaller than that obtained in EtOAc/IDD. It was also found that monomer impurities could largely be removed from the polymer product via a short (15 min) CO₂ flushing process at 0 °C.

The copolymerisation of terpene-derived monomers with MA was then studied in EtOAc/IDD, and in scCO₂ using the same *in situ* addition process. Between the two methods and two monomers used, the four polymer products were largely comparable to their poly(2EHA-co-MA) counterparts in terms of composition and M_n values, but possessed much higher T_g and D values and were less soluble in pure IDD. Finally, the suitability of poly(2EHA-co-MA) copolymers synthesised in scCO₂ for application in lipstick products was evaluated in comparison to the copolymers synthesised in EtOAc/IDD (30/70),

and no difference in their performance was observed. This demonstrates that scCO₂ may serve as an alternative, greener solvent system for the synthesis of poly(2EHA-co-MA) copolymers for cosmetic applications with low levels of monomer contamination.

In conclusion, this study is an important step forward in understanding the impact of greener processes on the physico-chemical properties of model film forming copolymers, bringing us closer to a system that can meet both L'Oréal's green chemistry criteria and achieve outstanding levels of performance in a variety of cosmetic applications. L'Oréal's future objective is to apply this green technology to other natural origin polymers.

Acknowledgements

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Data Availability

The data that support the findings of this study are available from the corresponding author, SMH, upon reasonable request.

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