Novel Insights into Pressure-Sensitive Adhesives Based on Plant Oils

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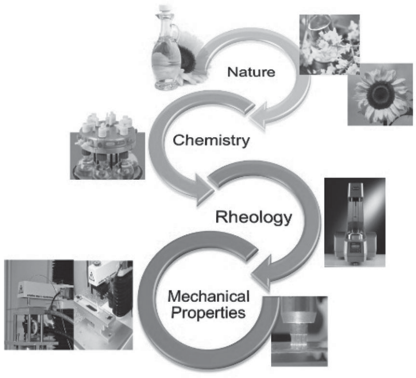
This work investigates the synthesis of bio-based pressure-sensitive adhesives and their characterization in terms of mechanical properties relevant to processing and application. The synthesis of monomers based on various fatty acids derived from vegetable oils as renewable feedstock via a one-step, a two-step, and a three-step route is described. The resulting monomers are polymerized via free radical polymerization resulting in high molecular weight polymers with adhesive properties. Adhesives are also obtained as aqueous dispersions by means of miniemulsion polymerization. In particular, the monomer acrylated methyl oleate (**4ac**) and the thereof derived polymer are intensively studied. The synthesized homopolymers show characteristic mechanical and adhesive properties similar to conventional pressure sensitive adhesives.



1. Introduction

Sustainability is an important criterion in product design and development, not only in the chemical industry. A change from fossil feedstock to renewable resources offers a great opportunity for industrial applications, as renewables are believed to be capable of fulfilling highly challenging tasks.[1–3] The use of oils and fats as renewable raw materials is well established and a subject of continued investigation.[4] The structural diversity of fatty acids depends on the oil source. It enables the design of a multitude of monomers, fine chemicals, and polymers, which can be derived in a straightforward fashion. Especially oils with high content of only one fatty acid, such as high oleic oils with a content of oleic acid exceeding 90%, have large potential for the substitution of petrochemicals currently in use.[5,6]

Besides that, the demand for adhesives has increased >25% over the last ten years.[7] Pressure-sensitive adhesives (in short PSAs) cover a production volume of about 200 tons a year in Europe (one-third as water-based dispersions), which are used in ≈25 000 different industrial products. PSAs represent a polymeric system that remains permanently tacky at room temperature and is able to adhere under slight pressure to any given substrate in very short time without any phase transition or chemical reaction.[8] Depending on the application, it can be designed to be completely removable from the surface. The global market shows a wide range of different products like sticky tapes, stamps, or different kinds of labels.[9] Typical PSAs are specifically formulated to give

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optimum flexibility and at the same time a tack and peel strength adjusted to the desired application. A sufficiently low viscosity is needed to wet the surface of the substrate and generate initial adhesion, whereas a high elasticity is needed to sustain loads (cohesion) and to enable a clean removal. Major commercial PSAs are made from petroleum-based acrylate monomers (i.e., *n*-butyl acrylate or 2-ethylhexyl acrylate), which are optionally copolymerized with some vinyl compounds.[10] One can tune the adhesive behavior in a wide range by selecting suitable comonomers affecting T_g or the surface energy and most importantly by adjusting the molecular weight as well as the degree of cross-linking and branching. When compounded with compatible resins, it is possible to tailor tack and peel, as well as creep and shear properties.

Efforts to utilize renewable materials in PSA products already discussed in the literature focused primarily on triglycerides and polyols (derived from vegetable and/or animal fats and oils) along with lactides and lactones (derived from carbohydrates).[11,12] For instance, acrylated macromonomers were synthesized through the ring-opening copolymerization of L-lactide and ε-caprolactone with 2-hydroxyethyl methacrylate and were used for copolymerization reactions with acrylic comonomers to produce polymers of high biomass content for PSA applications.[13,14] Furthermore, an approach to incorporate significant amounts of lactic acid macromonomers in the backbones of typical acrylic PSA polymers by miniemulsion polymerization was described.[15]

Different synthesis procedures for the functionalization of triglycerides have been studied, including epoxidation (for instance, enzymatically), hydroxymethylation, esterification, or acrylation.[16–20] The range of properties enables many different applications, which make fatty acids superior candidates for use as composite, engineering thermoplastic materials, or pressure-sensitive adhesives.[21–23] For example, the synthesis of renewable PSAs via photocatalyzed cationic polymerization of epoxidized soybean oil (ESO) has been reported in a patent application.[24] Sun and co-workers explored a concept for novel bio-based PSAs derived from soybean oil with the aim to raise thermal stability and transparency as well as peel strength, for use in the optical electronic applications.[25] A solvent-free PSA based on acrylated ESO was prepared via UV initiated free-radical polymerization, resulting in a high-shear performing product.[26] Moreover, copolymer networks of ESO with lactic acid oligomers for pressure-sensitive adhesive have been discussed recently.[27] It is known that ESO can be acrylated on industrial scale using acrylic acid. Hydroquinone is used as inhibitor to reduce polymerization side reactions. Different catalysts based on amines or metal organic chromium catalysts are of great interest in the direct acrylation process.[17,28] In addition, hydroxyl-containing polyesters were obtained via step-growth polymerization of epoxidized oleic acid and showed adequate adhesion but low molecular weights.[29] Wool and co-workers endeavored the design of PSA copolymers based on the fatty acid methyl ester. In their work, acrylated methyl oleate (AMO) was polymerized using emulsion and miniemulsion polymerization techniques.[23,30] They copolymerized AMO with both methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EGDMA) to improve PSA performance and described the product as a new class of bio-based adhesive materials with potential for applications in tissue engineering, wound healing, and transdermal drug delivery.[31]

For the monomer synthesis, a chromium catalyst was used to open the epoxide with acrylic acid to obtain the acrylated derivatives.[23] In contrast, a three-step synthesis route eliminating the dependency on chromium catalyst systems and leading to a slightly different monomer structure is described here. Moreover, a simpler two-step and also a one-step one-pot synthesis route are described and compared to each other. Free radical polymerization was used to achieve high molecular weight polymers. The adhesives were also formulated as aqueous dispersions by means of miniemulsion polymerization. The different polymers were compared to each other with respect to mechanical and adhesive properties and showed typical characteristics of known pressure sensitive adhesives.

2. Experimental Section

2.1. Materials

Methyl oleate (**1a**) as well as methyl erucate (**1b**) were synthesized according to a standard laboratory procedure[32] (>90%, respectively), hydrogen peroxide solution (35%, Aldrich), Novozyme 435 (lipase acrylic resin from *Candida antarctica*, Aldrich), methanol (99.9%, Aldrich), ethanol (≥99.8%, Aldrich), sulfuric acid (96%, Acros Organics), acryloyl chloride (>97%, Aldrich), triethylamine (99%, Aldrich), sodium chloride (>99.5%, Aldrich), sodium sulfate (99%, Acros Organics), sodium bicarbonate (>99%, Fisher Scientific), acrylic acid (99%, Aldrich), *N*-bromosuccinimide (NBS, 99%, Aldrich), potassium iodide (99%, Aldrich), sodium thiosulfate (>99%, Aldrich), sodium hydroxide (99%, Aldrich), 2,2′-azobis(2-methylpropionitrile) (AIBN, >98%, Aldrich), sodium dodecyl sulfate (SDS, 99%, Aldrich), chloroform-d (99.8 at% D, Armar Chemicals). Solvents (technical grade) were used without further purification. Moreover, unless otherwise noted, all reactions were carried out under argon atmosphere.

2.2. Methods

Thin layer chromatography (TLC) experiments were performed on silica gel coated aluminum foil (silica gel 60 F_{254}, Merck). Compounds were visualized by staining with Seebach solution (mixture of phosphomolybdic acid hydrate, cerium-(IV)-sulfate, sulfuric acid, and water).

NMR (nuclear magnetic resonance) spectra were recorded on a Bruker AVANCE DPX system at 300 MHz for ^{1}H NMR and 75 MHz for ^{13}C NMR. Chemical shifts (δ) are reported in parts per million relative to tetramethylsilane (TMS, $\delta = 0$ ppm) as internal standard. $CDCl_3$ was used as solvent and the resonance signal at 7.26 (^{1}H) and 77.16 ppm (^{13}C) served as reference for δ.

GC-MS (EI) (gas chromatography-mass spectrometry by electron ionization) chromatograms were recorded using a Varian 431 GC instrument with a capillary column FactorFour VF-5ms (30 m × 0.25 mm × 0.25 μm) and a Varian 210 ion trap mass detector. Scans were performed from 40 to 650 m/z at rate of 1.0 scans s^{-1}. The oven temperature program was: initial temperature 95 °C, hold for 1 min, ramp at 15 °C min^{-1} to 220 °C, hold for 4 min, ramp at 15 °C min^{-1} to 300 °C, hold for 2 min. The injector transfer line temperature was set to 250 °C. Measurements were performed in the split–split mode (split ratio 50:1) using helium as carrier gas (flow rate 1.0 mL min^{-1}).

Polymers were characterized via gel permeation chromatography (GPC), using a LC-20AD (Shimadzu) system equipped with a SIL-20A autosampler and a RID-10A refractive index detector in tetrahydrofuran (THF) (flow rate 1 mL min^{-1}) at 50 °C and with the following column system: main-column PSS SDV analytical (5 μm, 300 × 8 mm, 10 000 Å) with a PSS SDV analytical precolumn (5 μm, 50 × 8.0 mm). Determination was carried out relative to PMMA standards (Polymer Standards Service) ranging from 1.1 to 981 kDa.

Glass transition temperatures (T_g) were determined via differential scanning calorimetry (DSC) using a Mettler Toledo DSC821e calorimeter in the range of −75 to 250 °C under a nitrogen atmosphere and a heating rate of 10 K min^{-1}. Sample mass was in the range of 6–10 mg.

Particle size (d_{DLS}) was obtained using a dynamic light scattering (DLS) instrument (Malvern Instruments, Zeta Sizer Nano S) with a scattering angle of 176.1°. The reported diameter is an intensity-weighted average particle size (z-average), comprised of five measurements analyzed in ten runs. The reported polydispersity index values (PD_{DLS}) are those given by the instrument and are not conventional PDI values. These PD_{DLS} values are referred to as Malvern polydispersity. A value close to 0.01 indicates a narrow distribution. The latex samples were diluted ≈1:15 with distilled water prior to DLS analysis.

The experimental setup used for the tack measurements was based on a commercial device Texture Analyzer TA.XTplus (Stable Micro Systems, UK) modified with a quartz force sensor (Kistler Instrumente GmbH, Germany) covering a force range of ±500 N with a threshold of 1 mN. Probe tack tests were performed at 21 °C. Probe velocity for bonding was set to 0.1 mm s^{-1}, a contact force of 10 N and a contact time of 1.0 s were chosen. Detachment followed at a release rate of 1.0 mm s^{-1} using a 5 mm flat cylindrical probes made of steel with a surface roughness (R_a) of 2.9 nm. The work of adhesion (tack) was calculated as the integral of the nominal stress versus strain curve.[33]

For peel tests a 90° peel device (FINAT No. 2) was used in combination with the TA.XTplus Analyzer. In each test, a 15 mm wide carrier foil (coated with the given polymer) was peeled at a constant speed of 4.0 mm s^{-1} from a fixed glass plate at an angle of 90°. The peel force was determined as the average force detected during a peel distance of 80 mm.

Storage and loss modulus (G', G'') were determined from small amplitude oscillatory shear experiments using a Physica MCR-501 (Anton Paar, Austria, Graz) rotational rheometer equipped with a plate/plate fixture of 8.0 mm diameter and a selected gap width of 1 mm. Temperature sweeps were recorded at a given frequency of 1.0 Hz and 0.01 deformation in the range from −30 to 150 °C with a heating rate of 5 K min^{-1}.

2.3. Synthesis Procedure

2.3.1. Monomer Synthesis in a Three-Step Procedure (**A**, **B**, **C**)

The synthesis route is described based on methyl oleate as representative (see also Figure 1).

A: *Methyl 9, 10-epoxy Oleate*: 40 g of fatty acid methyl ester **1a** (1 eq., 135 mmol) was dissolved in 120 mL toluene, and subsequently 0.80 g Novozyme 435 was added. Then, 40 mL hydrogen peroxide solution (35%) was added dropwise to the stirred mixture. After 2 h reaction time at 40 °C, again 20 mL hydrogen peroxide solution (35%) was added. The reaction process was monitored by TLC until complete formation of the epoxidized fatty acid methyl ester was indicated. After filtration, the organic layer was separated, washed several times with water and brine, dried over Na_2SO_4 and evaporated to dryness, to obtain the methyl 9, 10-epoxy oleate **2a** as a colorless wax in quantitative yield (41.8 g). TLC (n-hexane/ethyl acetate 5:1) $R_f = 0.54$. ^{1}H NMR ($CDCl_3$, 300 MHz) $\delta = 0.88$ (t, $J = 6.7$ Hz, 3 H, CH_3), 1.22–1.50 (m, 24 H, 12 CH_2), 1.50–1.62 (m, 2 H, CH_2), 2.21–2.31 (m, 2 H, CH_2CO), 2.81–2.93 (m, 2 H, 2 CH), 3.62 (s, 3 H, $COOCH_3$) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) $\delta = 14.02$ (CH_3), 22.60 (CH_2), 24.84 (CH_2), 26.50 (CH_2), 26.54 (CH_2), 27.72 (CH_2), 27.76 (CH_2), 28.98 (CH_2), 29.11 (CH_2), 29.16 (CH_2), 29.27 (CH_2), 29.47 (CH_2), 29.49 (CH_2), 31.80 (CH_2), 34.01 (CH_2), 51.37 (OCH_3), 57.17 (CH), 57.22 (CH), 174.22 (CO) ppm. FAB of $C_{19}H_{36}O_3$ ($M + H^+ = 313.27$). HRMS (FAB) of $C_{19}H_{36}O_3$ $[M + H]^+$ calc. 313.2743 found 313.2722.

B: *9(or 10)-Hydroxy-10(or 9)-methoxyoctadecanoate*: 40 g of **2a** (1 eq., 128 mmol) was dissolved in methanol (≈30 eq., 125 mL) and concentrated sulfuric acid was added dropwise (≈150 drops, 3.75 mL). The reaction mixture was refluxed for 5 h and then cooled to room temperature. After neutralization with $NaHCO_3$ and filtration, the solution was evaporated to dryness. The residue was diluted with 150 mL ethyl acetate and 100 mL distilled water. The organic layer was separated, washed several times with water and saturated sodium chloride solution, dried over Na_2SO_4 and evaporated to dryness, to receive the crude product as a yellowish mixture. After purification by column chromatography (n-hexane/ethyl acetate 9:1 to 5:1), methyl 9(or 10)-hydroxy-10(or 9)-methoxyoctadecanoate **3ac** was obtained as a colorless oil (30.9 g, 70%). TLC (n-hexane/ethyl acetate 5:1) $R_f = 0.43$. ^{1}H NMR ($CDCl_3$, 300 MHz, mixture of regioisomers) $\delta = 0.87$ (t, $J = 6.5$ Hz, 3 H, CH_3), 1.19–1.71 (m, 27 H, OH, 13 CH_2), 2.30 (t, $J = 7.5$ Hz, 2 H, CH_2CO), 2.98 (q, $J = 5.5$ Hz, 1 H, CH), 3.37–3.53 (m, 1 H, CH), 3.40 (s, 3 H, OCH_3), 3.66 (s, 3 H, $COOCH_3$) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, mixture of regioisomers) $\delta = 14.17$ (CH_3), 22.74 (CH_2), 24.79 (CH_2), 24.94 (CH_2), 24.95 (CH_2), 25.84 (CH_2), 28.99 (CH_2), 29.15 (CH_2), 29.18 (CH_2), 29.27 (CH_2), 29.43 (CH_2), 29.45 (CH_2), 29.49 (CH_2), 29.65 (CH_2), 29.68 (CH_2), 29.79 (CH_2), 29.80 (CH_2), 29.90 (CH_2),

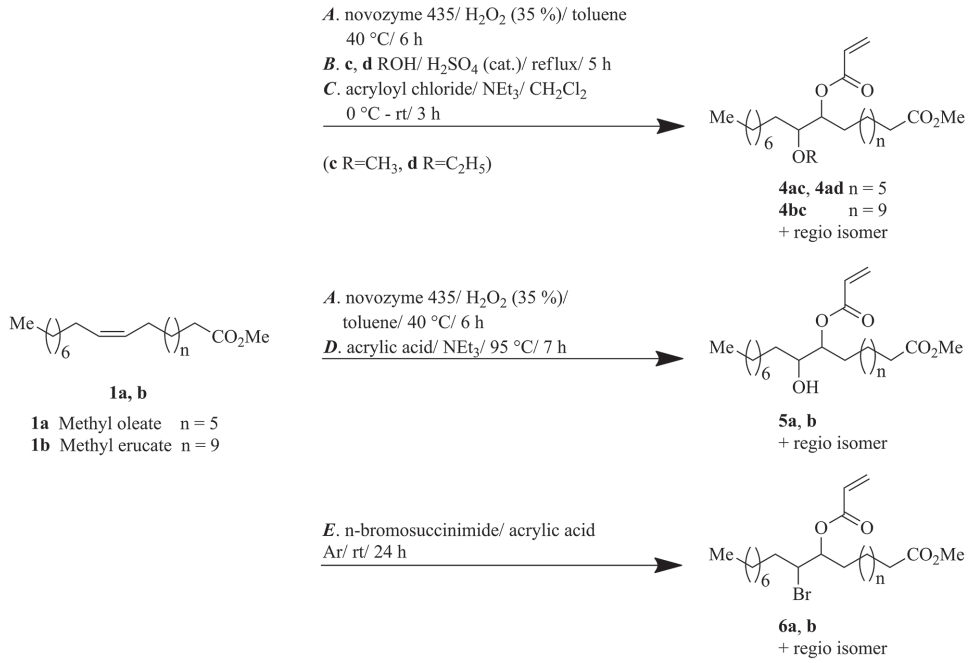

Figure 1. Synthesis pathways to oleate and erucate derivatives **4ac** (AMO), **4ad**, **4bc**, **5a**,**b**, and **6a**,**b**.

31.79 (CH_2), 31.80 (CH_2), 33.24 (CH_2), 33.39 (CH_2), 34.14 (CH_2), 51.50 (CH_3OO), 58.19 (OCH_3), 72.66 (CHOH), 84.40 ($CHOCH_3$), 174.36, 174.33 ($COOCH_3$) ppm. FAB of $C_{20}H_{40}O_4$ ($M + H^+$ = 345.3, $M + Na^+$ = 367.3, $M—OH^+$ = 327.4). HRMS (FAB) of $C_{20}H_{40}O_4$ $[M + H]^+$ calc. 345.3005 found 345.3003.

C: *Methyl 9(or 10)-acryloyloxy-10(or 9)-methoxyoctadecanoate*: 30 g of 9(or 10)-hydroxy-10(or 9)-methoxyoctadecanoate **3ac** (1 eq., 87.0 mmol) was dissolved in 100 mL dichloromethane and cooled down with an ice bath to 0 °C. Acryloyl chloride (2 eq., 174 mmol, 17.5 mL) was added to the stirred solution. Then, triethylamine (6 eq., 522 mmol, 72.8 mL) was added slowly and dropwise during 1 h. The reaction progress was monitored by TLC. After 3–4 h the volatiles were removed under reduced pressure and the residue was dissolved in ethyl acetate and water. The organic layer was separated, washed with water and brine, dried over Na_2SO_4 and evaporated to dryness, which led to a dark orange colored oil. The crude product was purified by silica column chromatography (*n*-hexane/ethyl acetate 10:1 to 5:1) to obtain methyl 9(or 10)-acryloyloxy-10(or 9)-methoxy-octadecanoate **4ac** as a colorless oil (25 g, 72%). TLC (*n*-hexane/ethyl acetate 5:1) R_f = 0.68. ^{1}H NMR ($CDCl_3$, 300 MHz, mixture of regioisomers) δ = 0.87 (t, J = 6.7 Hz, 3 H, CH_3), 1.18–1.52 (m, 22 H, 11 CH_2), 1.54–1.69 (m, 4 H, 2 CH_2), 2.29 (t, J = 7.5 Hz, 2 H, $COCH_2$), 3.13–3.24 (m, 1 H, CH), 3.42 (s, 3 H, OCH_3), 3.66 (s, 3 H, $COOCH_3$), 5.01–5.09 (m, 1 H, CH), 5.82 (dd, J = 10.4, 1.5 Hz, 1 H, = CH_2^a), 6.15 (dd, J = 17.4, 10.2 Hz, 1 H, COCH), 6.41 (dd, J = 17.4, 1.5 Hz, 1 H, = CH_2^b) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, mixture of regioisomers) δ = 14.01 (CH_3), 24.81 (CH_2), 24.83 (CH_2), 25.53 (CH_2), 25.55 (CH_2), 25.58 (CH_2), 25.60 (CH_2), 28.95 (CH_2), 28.97 (CH_2), 29 (CH_2), 29.05 (CH_2), 29.14 (CH_2), 29.16 (CH_2), 29.23 (CH_2), 29.35 (CH_2), 29.41(CH_2), 29.43 (CH_2), 29.45 (CH_2), 29.53 (CH_2), 29.55 (CH_2), 29.66 (CH_2), 29.79 (CH_2), 29.82 (CH_2), 31.76 (CH_2), 31.78 (CH_2), 33.98 (CH_2), 51.34 ($OOCH_3$), 58.49 (OCH_3), 74.34 ($CH_{acrylate}$), 81.50, 81.52 ($CHOCH_3$), 128.56 (CH ═ CH_2), 130.62 (CH_2═ CH), 165.91 ($CO_{acrylate}$), 174.16, 174.18 ($COOCH_3$) ppm. FAB of $C_{23}H_{42}O_5$ ($M + H^+$ = 399.3, $M–OMe^+$ = 367.3, $M–AcrylCO_2^+$ = 327.3). HRMS (FAB) of $C_{23}H_{42}O_5$ $[M + H]^+$ calc. 399.3105 found 399.3107.

2.3.2. Monomer Synthesis in a Two-Step Procedure (**A**, **D**)

The synthesis route is described based on methyl oleate as representative (see also Figure 1).

D: *Methyl 9(or 10)-acryloyloxy-10(or 9)-hydroxyoctadecanoate*: In the first step, the epoxide **2a** was obtained following procedure ***A***. 10 g of epoxide **2a** (1 eq., 32.0 mmol) was mixed with 2 eq. acrylic acid (64.0 mmol, 4.39 mL) and 1 eq. triethylamine (32.0 mmol, 4.43 mL). Subsequently, the reaction mixture was purged with argon for 10 min. The reaction mixture was heated to 90 °C for 7 h. After cooling to room temperature, the solution was quenched with an excess of a water/ethyl acetate mixture. The organic layer was separated and washed several times with water, $NaHCO_3$ solution, and brine. After drying over Na_2SO_4, the organic layer was evaporated to dryness. The crude mixture was purified by column chromatography (*n*-hexane/ethyl acetate 30:1 to 4:1) to obtain the pure product methyl 9(or 10)-acryloyloxy-10(or 9)-hydroxyoctadecanoate **5a** as colorless oil (7.80 g, 64%). TLC (*n*-hexane/ethyl acetate 5:1) R_f = 0.55; ^{1}H NMR ($CDCl_3$, 300 MHz, mixture of regioisomers) δ = 0.86 (t, J = 6.1 Hz, 3 H, CH_3), 1.17–1.52 (m, 22 H, 11 CH_2), 1.53–1.75 (m, 5 H, OH, 2 CH_2), 2.27 (t, J = 7.5 Hz, 2 H, CH_2CO), 3.57–3.64 (m, 1 H, CH), 3.65 (s, 3 H, $COOCH_3$), 4.85–4.95 (m, 1 H, CH), 5.85 (dd, J = 10.3, 1.4 Hz, 1 H, = CH_2^a), 6.12 (dd, J = 17.3, 10.4 Hz, 1 H, COCH), 6.40 (dd, J = 17.3, 1.4 Hz, 1 H, = CH_2^b) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz, mixture of regioisomers) δ = 14.05 (CH_3), 22.61 (CH_2), 22.63 (CH_2), 24.84 (CH_2), 24.90 (CH_2), 25.49 (CH_2), 25.57 (CH_2), 27.11 (CH_2), 27.17 (CH_2), 29.21 (CH_2), 29.28 (CH_2), 29.39 (CH_2), 29.48 (CH_2), 29.64 (CH_2), 29.72 (CH_2), 30.60 (CH_2), 31.82 (CH_2), 31.86 (CH_2), 34.01 (CH_2), 34.05 (CH_2), 51.39 ($OOCH_3$), 72.58 (COH), 76.80 ($CH_{acrylate}$), 128.40 (CH═CH_2),

130.97 (CH_2═ CH), 166.13 ($CO_{acrylate}$), 174.27 ($COOCH_3$) ppm; FAB of $C_{22}H_{40}O_5$ (M + H^+ = 385.3, M + Na^+ = 407.3, M–AcrylCO_2^+ = 313.3); HRMS (FAB) of $C_{22}H_{40}O_5$ $[M + H]^+$ calc. 385.2876 found 385.2874.

2.3.3. Monomer Synthesis in a One-Step Procedure (E)

The synthesis route is described based on methyl oleate as representative (see also Figure 1).

E: *Methyl 9(or 10)-acryloyloxy-10(or 9)-bromooctadecanoate*: In an argon purged flask, 10 g of the fatty acid methyl ester **1a** (1 eq., 34.0 mmol) was mixed with 10.0 eq. acrylic acid (340 mmol, 23.3 mL) and 1.80 eq. *n*-bromosuccinimide (61.2 mmol, 10.9 g).[20] The reaction mixture was stirred for 2 d protected from light at room temperature. The reaction mixture was quenched by an excess amount of diethyl ether and H_2O (1:1). The ether layer was separated, washed several times with KI solution, sodium thiosulfate solution, aqueous NaOH (10%) solution, and with water and brine, before it was dried over Na_2SO_4 and evaporated to dryness. Purification by silica column chromatography provided **6a** as yellowish oil (9.98 g, 66%). TLC (*n*-hexane/ethyl acetate 5:1) R_f = 0.62; ^{1}H NMR ($CDCl_3$, 300 MHz, mixture of regioisomers) δ = 0.82 (t, J = 6.6 Hz, 3 H, CH_3), 1.17–1.52 (m, 22 H, 11 CH_2), 1.53–1.72 (m, 4 H, 2 CH_2), 2.25 (t, J = 7.5 Hz, 2 H, CH_2CO), 3.66 (s, 3 H, $COOCH_3$), 3.98–4.05 (m, 1 H, CH), 4.95–5.04 (m, 1 H, CH), 5.85 (dd, J = 10.3, 2.4 Hz, 1 H, = CH_2^a), 6.09 (dd, J = 17.3, 10.3 Hz, 1 H, COCH), 6.37 (dd, J = 17.3, 1.6 Hz, 1 H, ═ CH_2^b) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, mixture of regioisomers) δ = 14.08 (CH_3), 22.62 (CH_2), 24.84 (CH_2), 25.22 (CH_2), 25.29 (CH_2), 27.60 (CH_2), 27.66 (CH_2), 28.68 (CH_2), 28.96 (CH_2), 29.16 (CH_2), 29.30 (CH_2), 31.79 (CH_2), 32.20 (CH_2), 34 (CH_2), 35.01 (CH_2), 51.41 ($COOCH_3$), 57.54 (CBr), 75.14 ($CH_{acrylate}$), 128.18 (CH ═ CH_2), 131.36 (CH_2═ CH), 165.51 ($CO_{acrylate}$), 174.18 ($COOCH_3$) ppm. FAB of $C_{22}H_{39}BrO_4$ (M + H^+ = 446.3, M–AcrylCO_2^+ = 375.3). HRMS (FAB) of $C_{22}H_{39}BrO_4$ $[M+H]^+$ calc. 446.2730 found 446.2729.

2.3.4. Solvent-/Bulk Polymerization

All monomers were reacted as described in the representative procedure for **4ac**: 2 g of monomer **4ac** (1 eq., 5 mmol) was mixed with 0.60 mol% AIBN (4.92 mg). The mixture was purged with argon for several minutes. The polymerization was performed at 75 °C for up to 6 h. After the reaction, the polymer was dissolved in toluene and precipitated by slowly dropping into ice-cold methanol as colorless and highly viscous material (1.60 g, yield >78%). ^{1}H NMR for **P4ac** ($CDCl_3$, 300 MHz) δ = 0.88 (t, J = 6.7 Hz, 3 H, CH_3), 1.14–1.51 (m, 24 H, 12 CH_2), 1.52–1.70 (m, 4 H, 2 CH_2), 2.17–2.29 (m, 3 H, CH_2CO, CHCO), 3.03–3.20 (m, 1 H, CH), 3.28 (s, 3 H, OCH_3), 3.65 (s, 3 H, $COOCH_3$), 4.71–4.90 (m, 1 H, CH) ppm; DSC T_g = –59 °C.

2.3.5. Miniemulsion Polymerization

AIBN (0.60 mol%, 2.46 mg) was added to 1 g of monomer **4ac** (1 eq., 2.50 mmol). Then, water (3 mL) and SDS (0.01 eq., 0.025 mmol, 7.21 mg) as emulsifier were mixed and added to form a pre-emulsion by continuous stirring for 10 min. Then, an ultrasonic tip (ultrasonic sonifier horn 3/8 in., Branson) was used to break up the monomer droplets and to obtain a homogeneous and stable miniemulsion. Cooling with an ice bath prevented prepolymerization. Each polymerization was performed directly after ultrasonic treatment at 75 °C within a reaction time of 1.5–3 h.

3. Results and Discussion

3.1. Monomer Synthesis

The investigation of a three-step synthesis pathway, as an alternative route to previously reported procedures, to generate acrylate functionalized fatty acids was conducted without the previously used chromium catalyst system.[23,28] The involved reactions (epoxidation, ring opening, and acrylation) make this procedure favorable from both an economic and ecological viewpoint, regardless of the additional reaction step. The investigated routes, subdivided in three procedures are shown in Figure 1.

Procedure ***A*** comprises the enzymatic epoxidation of methyl oleate as well as methyl erucate.[18,34,35] The epoxide was received as a colorless wax in quantitative yields in both cases. Without further purification, the ring opening was then performed either with methanol or ethanol.[36,37] A hydroxy in combination with a methoxy or ethoxy group was thus obtained (mixture of regioisomers). Yields of ≈70% were obtained in this step. After purification, further esterification/acrylation by adding acryloyl chloride and trimethylamine led to the formation of methoxyacrylate (or ethoxyacrylate) fatty acid derivatives in yields of 72%.[38] Noteworthy, purification by column was absolutely necessary, because it is well known that free radical polymerization is very sensitive toward impurities. Most importantly, a formed diacrylate byproduct was reduced to a minor content (<2%). Adversely, preconditioning toward high purity causes a lack of yield. Nevertheless, an overall yield of 49% could be achieved via reactions ***A***, ***B***, and ***C*** (compare Figure 1).

To further simplify the monomer synthesis and to obtain higher yields, a direct ring opening of the epoxide with acrylic acid was investigated using triethylamine as catalyst to obtain the hydroxyacrylate derivative (procedure ***D***), inspired by literature focusing on triglyceride modification.[39,40] The procedure was adopted and transferred to methyl oleate (and methyl erucate) based epoxides. The synthesis of the methyl oleate based monomer was optimized toward an equal molar ratio of the epoxide to AA. Table 1 summarizes the results and confirms that two equivalents of AA lead to high conversions of up to 88%.

Increasing the amount of AA caused polymerization to polyacrylic acid (PAA, or copolymer) at a temperature of 95 °C. Polymerization was also observed at longer reaction times as well as in up-scaled reactions

Table 1. Conversion in the ring opening of the oleate based epoxide, EMO (procedure ***D***).

EMO:AA:cat.[a)] eq.	Conversion[b)] [%]
1:4:1	77
1:3:1	80
1:2:1	88
1:1:1	78

[a)]Epoxide:acrylic acid:trimethylamine; reaction 7 h/95 °C; [b)]^{1}H-NMR results.

(probably due to a less efficient heat transfer). Similar results were obtained by varying the amount of catalyst, concomitantly lowering the conversion for both higher and lower concentrations. Hydroquinone was thus added as inhibitor according to a literature report (0.3 wt%).[41] However, by using a ratio of reactants of 1:2:1 (compare Table 1), additional hydroquinone became redundant since no polymerization product was observed after 7 h reaction time. Purification of the crude mixture by silica column chromatography with a mixture of hexane/ethyl acetate was again mandatory to obtain the pure monomer. Better overall yields of about 64% were achieved after purification.

In view of a technical upscale, an alternative one-pot procedure (procedure ***E***) was then considered. The acrylate group was directly introduced to the double bond of the fatty acid methyl ester. In this case, bromoacrylated monomers were obtained by the use of *N*-bromosuccinimide. The reaction pathway is shown in Figure 1. Reaction conditions were adopted from procedures described elsewhere.[20,38] A significant excess of AA used in previous reports was proven to be unnecessary. The amount of AA could be reduced to ten equivalents, leading to conversions of 81%. The synthesis was performed for 24 h at room temperature without observing polymerization side reactions. Increasing the reaction time to 48 h showed only a slight influence on the conversion (89%), as Table 2 illustrates. Yields of 66% were obtained after purification by silica column chromatography in this one-step procedure.

The reduction of the synthesis steps from three to only one came along with a reduction in time consumption and with an increase in yield, as expected. The yields increased from 48% to 66%. Side reactions like polymerization only occurred for the ring-opening reaction using AA. Polymerization was not observed in any other reaction procedure. Of course, side reactions as well as incomplete conversions were obtained in the three-step synthesis reducing the yields. Considering the amount of waste produced (*E*-factor),[42] the one-step procedure showed the lowest *E*-factor, indicating its improved sustainability. The *E*-factor was calculated without considering the purification step leading to *E*-factors of 25.0, 6, and 1.60 for the three-, two-, and one-step procedure, respectively.

Finally, each acrylate was able to participate in a free radical polymerization because of the high reactivity of the introduced acrylic double bond.[43] Most importantly for this study, all polymers derived from the described monomers showed similar adhesive properties, despite their small structural variations.

3.2. Polymer Synthesis in Bulk

With all monomers in hand, polymerization was performed batchwise using 2 g of monomer for each trial. AIBN (2,2′-azobis(2-methylpropionitrile)) served as thermal initiator (0.60 mol%, Figure 2).

The reactions were carried out in bulk to obtain highly viscous polymeric material. Precipitation yielded about 78% of highly viscous, colorless to yellowish (mainly **P6** derivatives) and most importantly tacky polymers. Molecular weights of up to 700 kDa (M_w) were obtained by this bulk polymerization procedure. All samples were characterized by GPC. Therefore, polymers were dissolved in tetrahydrofuran and solutions were purified through a filter syringe. A gel content lower than 2% was determined gravimetrically for all cases.

Table 2. Conversion of the one-pot bromoacrylation (procedure ***E***).

FAME:AA:cat.[a)] eq.	Conversion[b)] [%]	FAME:AA:cat.[a)] eq.	Conversion[b)] [%]
1:250 : 2	91	–	–
1:125:2	79	1:125 : 1	62
1:75 : 2	60	1:75:1	65
1:10:2	74	1:10:1	81
1:10:2[c)]	89	1:10:1[c)]	89

[a)]Fatty acid methyl ester:acrylic acid:*N*-bromosuccinimde per eq. double bond. Reaction 24 h/rt; [b)]^{1}H-NMR; [c)]per eq. double bond. Reaction 48 h/rt.

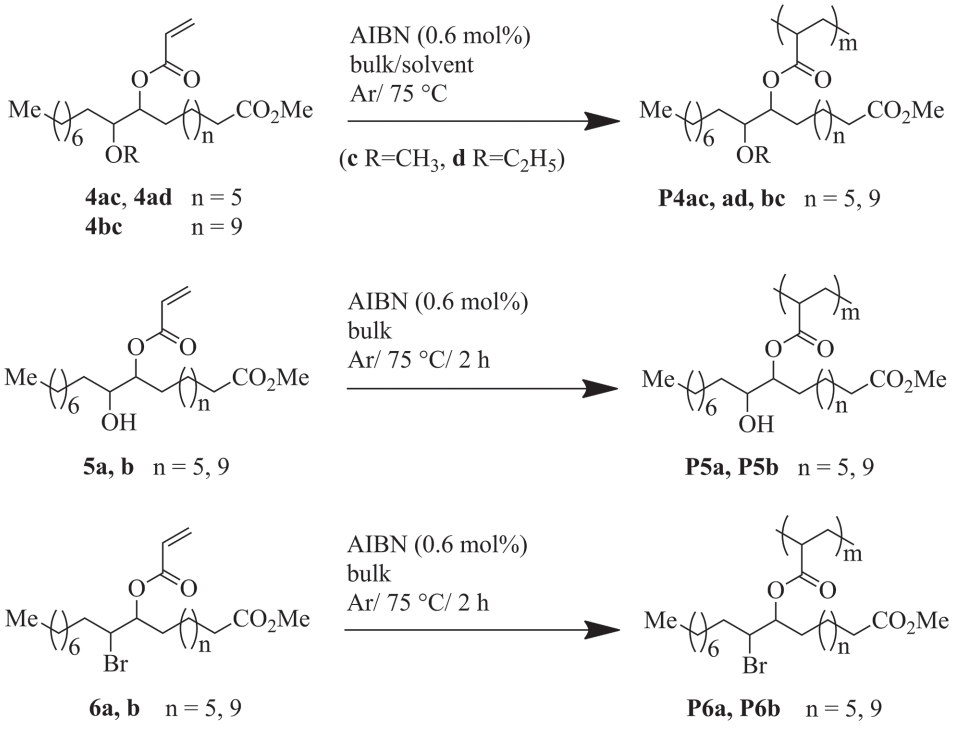

Figure 2. Homopolymerization to obtain polymers **P4ac**, **P4ad**, **P4bc**, **P5a**, **P5b**, **P6a**, and **P6b**.

Higher M_w was obtained for **P4** derivatives compared to **P5** and **P6** derivatives (compare Table 3), which is desirable according to further PSA application. The latter reached molecular weights of about 300 kDa (M_w), which is at the lower end of typical PSA formulations.[44] Additionally, **P4** polymers showed a high dispersity ($Đ$), probably due to the formation of short- and long-chain branches through intra- and intermolecular chain transfer to polymer. Such side reactions are well known in free radical polymerization of acrylic monomers.[45–47] For the **P5** and **P6** derivatives, a lower dispersity of 2 was obtained. Increasing the reaction time forced gel formation in almost all cases. A better reproducibility in the case of **P4** was achieved using a solvent mixture of acetone/petrol ether in a 24 h synthesis. A lower molecular weight of 300 kDa was obtained with good reproducibility. However, all obtained polymers showed typical characteristics of PSAs.

Table 3. Number (M_n) and weight (M_w) average molecular weight as well as dispersity ($Đ$) of synthesized polymers according to GPC.

Polymer	M_n [kDa]	M_w [kDa]	$Đ$
P4ac-miniemulsion	80	300	4
P4ac/high	120	650	5
P4ac/low	90	270	3
P5a	130	280	2
P6a	110	270	2

3.3. Polymer Synthesis in Miniemulsion

The methyl oleate based monomer **4ac** (AMO) was used to study the miniemulsion polymerization of acrylated fatty acid derivatives. The miniemulsion was prepared as described in the Section 2.3.4. Different surfactant concentrations were used to vary the particle diameter, and the initiator concentration was varied to change molecular weight. Table 4 lists the variation of molecular weight with initiator concentration as well as the particle size variation with surfactant concentration. The molecular weight increases with decreasing initiator concentration and the particle size decreases with increasing surfactant concentration, as expected.[48,49]

An oil-soluble initiator (AIBN) was used for the miniemulsion polymerization instead of common water soluble alternatives, since this leads to increased polymerization rates. In this respect, Thomas and co-workers have shown that it is possible to achieve high molecular weights if low initiator concentrations are used.[50] Using the miniemulsion technique, it was possible to create polymer molecular weights up to about 800 kDa. The dispersions showed long-term stability (>2 years) and were synthesized without costabilizer. The reaction time determined whether a soluble polymer (1.5 h) or a nonsoluble

Table 4. Results of miniemulsion polymerization. Left: Variation of molecular weight with initiator concentration. Right: Variation of particle size with surfactant concentration.

Entry[a)]	AIBN [mol%]	M_n [kDa]	M_w [kDa]	$Đ$	d_{DLS}[b)] [nm]	Entry[c)]	SDS eq.	d_{DLS}[b)] [nm]	PD_{DLS}[d)]
A	1.50	43	230	5	370	D	0.01	374	0.03
B	1	66	190	3	374	E	0.10	276	0.03
C	0.50	91	760	8	392	F	1	70	0.04
						G	2	46	0.03

[a)]Variation of initiator concentration using 0.01 eq. SDS/75 °C/1.5 h; [b)]Particle diameter; [c)]Variation of SDS concentration using 1 mol% AIBN/75 °C/1.5 h; [d)]Polydispersity index values (PD_{DLS}) are those referred to as Malvern polydispersity. A value closer to 0.01 indicates a narrower distribution.

cross-linked latex (3 h) was obtained. Soluble polymers obtained within 1.5 h were chosen for comparison with solution polymerization products.

3.4. Adhesive Performance

3.4.1. Viscoelastic Properties

Characterization of linear viscoelastic properties was performed by means of temperature sweeps in oscillatory shear mode at fixed frequency. Figure 3 illustrates the performance of different polymers prepared in this study.

The storage modulus (G') is plotted versus temperature.[23,30] The data for all products synthesized here lie in a similar range, but the storage modulus characterizing the elastic material response especially at high temperatures is significantly lower than that of the commercial petroleum-based copolymer Acronal V212 (BASF SE) used here as a reference for typical PSA polymers (see Figure 3).

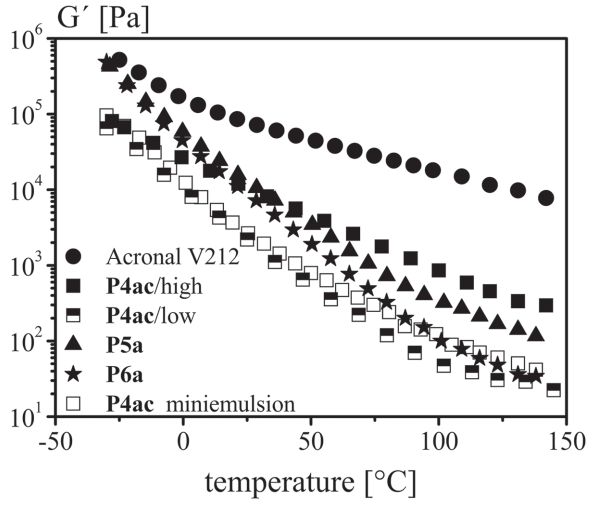

Figure 3. Storage modulus versus temperature of bulk and miniemulsion homopolymers (for molecular weights see Table 3) compared to a commercial acrylate copolymer Acronal V212 provided as aqueous dispersion.

The first important fact to be highlighted is the criterion of Dahlquist for PSAs, stating that the upper limit of the elastic modulus at room temperature has to be lower than 3.3×10^5 Pa, which is fulfilled for polymers **P4ac**, **P5a**, and **P6a** including the derivatives and miniemulsion product.[51] Second, the low elasticity at high temperatures indicates a weak cohesion and shear strength especially in comparison to the commercial copolymer. But this can be further improved by, e.g, introducing appropriate comonomers resulting in a lower molecular weight between entanglements. Especially a broad molecular weight distribution including a fraction of ultrahigh molecular weight, long-chain branched or cross-linked molecules will lead to the required increase of elasticity at high temperatures. This is confirmed by sample **P4ac**/high. Its higher M_w and polydispersity compared to **P4ac**/low obviously results in the expected increase in elasticity required for good cohesive properties.

3.4.2. Tack and Peel Performance

Tack tests were performed at room temperature using a cylindrical flat steel probe. Detachment of polymer due to cohesive failure was observed for all polymers synthesized here but not for the Acronal V212. The corresponding tack data are shown in Figure 4. As expected, Acronal V212 exhibits the highest tack value whereas the values for the synthesized homopolymers seem to be very similar and are in a reasonable range for PSA applications. This can be attributed to the viscoelastic influence, which is dominant in cohesive failure detachment. Noteworthy, the commercial petroleum-based copolymer Acronal V212 is a well-performed dispersion with defined polymer microstructure including a special composition of comonomer as well as specific additives, resulting in an improved T_g and improved adhesive performance. In contrast, the here synthesized polymers are pure bulk homopolymer with very low T_g's in the range of –60 °C. As outlined above, an appropriate degree of cross-linking or long-chain branching thus has to be introduced to achieve adhesive

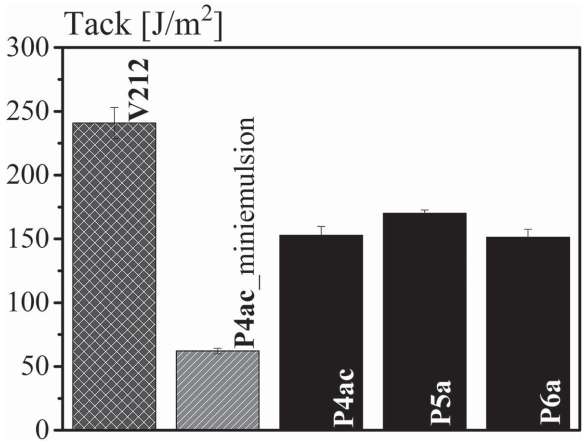

Figure 4. Tack of AMO-homopolymers compared to that of the commercial acrylate copolymer Acronal V212. Debonding rate: 1 mm s^{-1}; probe diameter: 5 mm.

failure and higher tack. The polymer from miniemulsion polymerization shows the lowest tack reaching only one-third of the value found for the other materials. Since its storage modulus and molecular weight are similar to those of the other products, we attribute this to a contamination of the sample with residual monomer disturbing the wetting of the substrate as well as the bulk performance as it can act as a plasticizer.

Peel strength is a key parameter for the performance of a PSA. Figure 5 shows the results of the 90° peel tests performed as described in Section 2.2.

The carrier foils coated with biohomopolymer were peeled off by cohesive failure, leaving residue on the glass substrate. Adhesive break was observed for Acronal V212. The peel value obtained for the Acronal V212 is 4.3 N/15 mm. The synthesized biohomopolymers exhibit lower values around 2.0–3.0 N/15 mm, which are still in a reasonable range for typical PSA applications. Peel measurements seemed to be more sensitive toward molecular

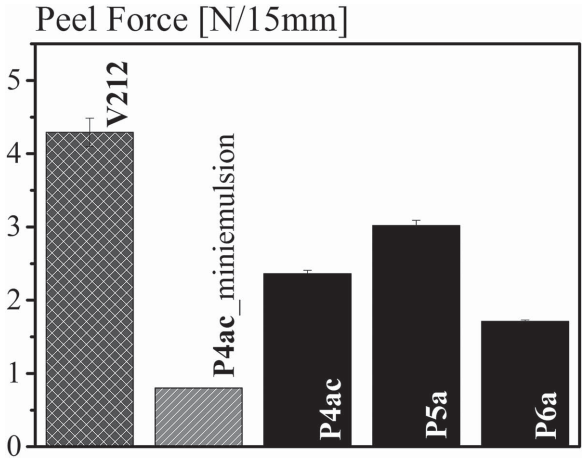

Figure 5. Peel force in 90° at 4 mm s^{-1} per 15 mm width.

weight (M_n), since the values vary in the order: **P5a** >**P4ac**/high >**P6a** >**P4ac**-mini. Hydrogen bonding may explain the exceeding value of **P5a**. The overall lower values compared to the Acronal V212 are again attributed to the low viscoelastic performance of bulk homopolymers as mentioned within the results for tack tests. The low value found for the polymers obtained from miniemulsion polymerization can again be attributed to the presence of nonreacted monomer. For applications requiring a clean removal of polymer foils/stripes (adhesive failure) the molecular weight has to be further increased, also long-chain branching or chemical cross-links may be introduced as already mentioned above.

Comparable results to the above mentioned overall adhesive performance was also obtained with the polymer of the erucate derivatives. In general, now significant difference was observed comparing oleate and erucate based polymers.

4. Conclusions

Different procedures including a one-, two-, and three-step synthesis of acrylate monomers based on methyl oleate as well as methyl erucate were explored. Polymerization was performed in bulk, solution, and miniemulsion polymerization in order to create high molecular weight bio-based polymers for use in pressure-sensitive adhesives. The dispersions were synthesized with small amounts of emulsifier, but without costabilizer and exhibited long-term stability (>1 year). All polymers were characterized with respect to their linear viscoelastic properties. Furthermore, standard tack and peel tests were performed to judge the applicability of the synthesized polymers as PSAs. The resulting modulus, tack, and peel values are well in the range of typical, conventional PSA polymers. Further improvement of PSA performance may be achieved by introducing an appropriate degree of weak cross-linking, long-chain branching, or suitable comonomers. Nevertheless, pressure-sensitive adhesives based on renewable resources provide an attractive alternative to the market controlling fossil resource based products for certain applications.

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