J Am Oil Chem Soc (2014) 91:337–348
DOI 10.1007/s11746-013-2375-0

ORIGINAL PAPER

Photopolymerizable Synthons from Glycerol Derivatives

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Received: 28 May 2013 / Revised: 23 September 2013 / Accepted: 17 October 2013 / Published online: 6 November 2013

Abstract Photopolymerizable monomers based on monoglycerides were prepared by a convenient two-step procedure. The first one consists of the synthesis of highly pure monoglycerides by an organocatalyzed solvent-free route. This process was carried out by condensation of bio-sourced carboxylic acids (i.e. butyric, decanoic, undecylenic or stearic acids) with glycerol carbonate or glycidol in the presence of a quaternary ammonium salt as a catalyst. The obtained bio-based monoglycerides were modified in the second step by reaction with acryloyl and methacryloyl chloride leading to a series of new diacrylated and dimethacrylated monomers. The structures of the monoglycerides, diacrylated and dimethacrylated monomers were fully characterized by spectroscopic methods. Photopolymerization investigations monitored by infrared spectroscopy were achieved under ultraviolet radiation in the presence of a photoinitiator. The resulting cross-linked materials were analyzed by thermal gravimetric analysis, gel content determination and tests of swelling in water, ethanol and methylene chloride. Data relative to the pendulum hardness of these materials are also included.

Keywords Bio-based polymers · Glycerol · Carbonate · Glycidol · Fatty acids · Monoglyceride · Photopolymerization

Introduction

Photoinitiated polymerization is a very attractive method for the synthesis of useful polymeric materials having tailor-made properties. This approach to save energy is carried out under solvent-free formulations preventing any emission of volatile organic compound, at room temperature and with very short reaction times. This ecologically friendly process finds widespread applications in fields such as coatings, adhesives or sealants, encapsulation of microcircuits, photographic printing plates, inks and composites [1]. If the range of synthetic photocurable resins available on the market is nowadays very developed, the number of photopolymerizable reactants made from renewable feedstock remains low. Hence, this area of investigation is an emerging field of research and the development of innovative photosensitive monomers from renewable resources is a topic of interest. In a recent review [2], Fertier et al. reported the existence of several photopolymerizable glycerol derivatives bearing one acrylate or methacrylate groups as well as the use of 1,3-glycerol dimethacrylate and glycerol trimethacrylate in restorative dental materials. In this context, monoglycerides bearing acrylate or methacrylate groups are good candidates for photopolymerization studies. Monoglycerides are valuable glycerol derivatives synthesized traditionally using two routes: direct esterification of glycerol with fatty acids [3] or transesterification of glycerol with oils or fatty acid methyl esters (biodiesel) [4]. The main

Electronic supplementary material The online version of this article (doi:10.1007/s11746-013-2375-0) contains supplementary material, which is available to authorized users.

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drawback of such processes is the low reaction selectivity leading to a mixture of mono-, di- and triglycerides [5]. Alternative and more selective routes have been developed. As an example, the synthesis of monoglycerides from glycidol or glycerol carbonate with fatty acids gives a well defined chemical structure [5–9]. Glycerol carbonate is a green synthon which may be synthesized following different routes [10, 11]. It is synthesized from glycerol upon conversion with carbon monoxide [12, 13] or carbon dioxide [14, 15], or transesterification between glycerol and carbonates sources [16–24]. Glycerol carbonate is a bifunctional reagent with low toxicity, good biodegradability and high boiling point, favoring its use in various branches of industry [10, 11]. It is also an intermediate in chemical synthesis and in the production of useful polymeric materials such as polycarbonates, polyglycerol esters, hyperbranched polyols, and isocyanate-free polyurethanes [25]. Moreover, glycerol carbonate is the most valuable intermediate for the production of glycidol [26–29]. Glycidol is used in a wide variety of industrial fields such as the textile, plastics, pharmaceutical, cosmetic and photochemical industries [29, 30].

The use of renewable resources for the synthesis of bio-based polymers is a current challenge [31, 32]. In this context, we report here the step-by-step synthesis of photopolymerizable synthons derived from monoglycerides and leading, after UV-irradiation, to bio-based crosslinked materials. Monoglycerides of high purity were obtained, by condensation of fatty acids with either glycerol carbonate or glycidol, in a solvent-free medium and in the presence of tetrabutylammonium iodide (TBAI) as an organocatalyst. The acrylated and methacrylated monoglycerides were efficiently synthetized by esterification with acryloyl and methacryloyl chloride. The monoglycerides and acrylated and methacrylated monoglycerides were fully characterized by NMR, FTIR, HRMS and elemental analysis. Photopolymerization experiments of acrylated and methacrylated monomers were carried out monitored by infrared spectroscopy. The role played by the concentration of photoinitiator, the intensity of irradiation, and the nature of monomers were discussed. Thermal gravimetric analysis, gel content determination, tests of swelling and analysis of the pendulum hardness were performed on the resulting bio-based polymers.

Experimental Procedures

Chemicals and Measurements

Carboxylic acids (butyric, 99 %, decanoic, 96 %, undecylenic, 98 %, stearic, 95 %), glycidol (96 %), acryloyl chloride (97 %), methacryloyl chloride (97 %), triethylamine (99 %), tetrabutylammonium iodide (97 %), petroleum ether and xylene (99 %) were purchased from Sigma-Aldrich and used without further purification. Glycerol carbonate was synthesized according to a published procedure [22]. Dichloromethane (99.9 %, Sigma-Aldrich) was used after distillation under inert atmosphere of argon over P_2O_5, and diethyl ether (99.5 %, Sigma-Aldrich) was dried and distilled under argon over Na/benzophenone complex prior to use. Water was distilled prior to be used. The photoinitiator, 2-hydroxy-2-methyl-1-phenyl-propan-1-one (Darocur 1173®) was kindly supplied by Ciba Specialty Chemicals.

The infrared spectra were recorded on a Bruker Vector 22 equipped with a Specac Golden Gate™ ATR device. ^{1}H and ^{13}C{^{1}H} NMR analyses were performed on a Bruker Avance 300 MHz spectrometer using DMSO-d6 as solvent. Elemental analyses were performed on a CHNS/O Thermo Electron Flash EA 1112 Series apparatus at the Plateforme d'Analyses Chimiques et de Synthèse Moléculaire de l'Université de Bourgogne (PACSMUB). High-resolution mass spectra (HRMS) were acquired using an LTQ Orbitrap XL mass spectrometer (Thermo-Fisher Scientific) in electrospray ionization positive (ESI+) mode. Samples were analyzed in methanol as mobile phase (25 µL injection volume) with a flow of 10 µL min^{-1} and at 275 °C (source temperature). Melting points (mp) were measured by differential scanning calorimetry (DSC Q1000 TA Instruments). Experiments were performed under nitrogen with a sample mass of 10 ± 3 mg. The instrument was calibrated using indium standard. Samples were heated from −80 to 100 °C at a heating rate of 10 °C min^{-1}. Photochemical reactions were followed by real time infrared spectroscopy using a Bruker Vertex 70 spectrometer equipped with a Specac MKII Golden Gate™ Single Reflection Diamond ATR System. Thermogravimetric analyses (TGA) were performed on a TA Instruments TGA Q500 thermoanalyzer using aluminum pans. Samples (5–10 mg) were heated from 30 to 500 °C at a rate of 20 °C min^{-1} under flowing nitrogen gas. Weight loss percentages and onset temperatures were determined using the TA Universal Analysis 2000 software accompanying the instrument. The degree of curing of each synthesized polymer was determined by applying the gel content (X_g) determination method (two tests were performed for each sample) [33]. The polymer samples (length = 6 mm, thickness = 1 mm) were rigorously weighed and heated under reflux in 20 mL of xylene for 16 h. The polymer was removed from the xylene solution and dried under vacuum (10 mbar) at 150 °C until a constant weight was achieved. The percentage of gel contents was determined according to the following equation, $X_g(\%) = (w_f/w_i) \times 100$, where, w_i and w_f represent the

weight before and after extraction respectively. The extent of swelling after irradiation was assessed in water, ethanol and methylene chloride respectively, at room temperature and for 24 h, by measuring the difference in the weight between the dried and the swollen film [34]. The swelling ratio S was determined using the following equation (where W_s and W_d are the weight of the swollen and dried films, respectively):

$$\text{Swelling } (\%) = \frac{W_s - W_d}{W_d} * 100$$

The pendulum hardness of the cured film was monitored after UV-curing using a König Pendulum hardness tester (TQC SP0500). The König test for hard coatings measures the time taken for the amplitude to decrease from 6° to 3° [35]. The König pendulum is triangular with an adjustable counterpoise and swings on two ball bearings of 5 mm diameter which rest on the test surface. The counterpoise is used to adjust the period of oscillation to the specified 1.4 s. Pendulum hardness values are expressed in seconds and are related directly to the softness of the sample [36, 37].

Synthesis of Monoglycerides **1–4**

General Procedure

A mixture of glycerol carbonate (80 mmol), carboxylic acid (40 mmol) and the catalyst tetrabutylammonium iodide (TBAI) (0.5 mol% compared to carboxylic acid) was placed in a 250-mL two-necked round-bottom flask fitted with a magnetic stir bar and a reflux condenser. The mixture was heated at 140–142 °C. After 24 h, diethyl ether (50 mL) was added to the reaction mixture and the resulting solution was washed with water (3 × 10 mL) to eliminate the quaternary ammonium salt. The organic layer was dried over magnesium sulfate ($MgSO_4$) and evaporated under vacuum. The residue was dissolved in 20 mL of petroleum ether, and the pure monoglyceride was obtained by precipitation upon cooling.

The synthesis of monoglycerides from glycidol was carried out using the same procedure at lower temperature (120 °C) and shorter reaction times (30–60 min, depending on the fatty acid chain length).

2,3-Dihydroxypropyl butyrate (**1**): Colorless liquid (1.3 g, 82 %). IR (ATR, neat): ν_{max}/cm^{-1} 3374 (OH), 2963 and 2876 (CH), 1728 (C=O), 1173 and 1048 (C–O). ^{1}H NMR (300 MHz, DMSO-d6, Me_4Si) δ 0.89 (3 H, t, $J = 7.6$ Hz, CH_3), 1.56 (2 H, m, CH_2CH$_2$CO), 2.28 (2 H, t, $J = 7.2$ Hz, CH_2CO), 3.35 (2 H, m, CH_2OH), 3.64 (1 H, m, C*H*OH) 3.91 (1 H, dd, $J = 6.4$ Hz, $J = 11.2$ Hz, COOC*H*H), 4.03 (1 H, dd, $J = 4.5$ Hz, $J = 11.1$ Hz, COOCH*H*), 4.61 (1 H, t, $J = 6$ Hz, CH$_2$O*H*), 4.85 (1 H, d, $J = 5$ Hz, CHO*H*). ^{13}C{^{1}H} NMR (75 MHz, DMSO-d6, Me_4Si) δ 13.39 (*C*H$_3$), 17.89, 35.33 (CH$_3$(*C*H$_2$)$_2$), 62.61 (*C*H$_2$OH), 65.44 (COO*C*H$_2$), 69.27 (*C*HOH), 172.77 (*C*O). HRMS (ESI) *m/z* calculated for $C_7H_{14}NaO_4$ $[M+Na]^+ = 185.07843$; found: 185.07772. Elemental analysis (found: C, 52.13; H, 9.14. $C_7H_{14}O_4$ requires C, 51.84; H, 8.70 %).

2,3-Dihydroxypropyl decanoate (**2**): White solid (2.1 g, 83 %), mp 51 °C. IR (ATR, neat): ν_{max}/cm^{-1} 3230 and 3200 (OH), 2920 and 2850 (CH), 1728 (C=O), 1173 and 1048 (C–O). ^{1}H NMR (300 MHz, DMSO-d6, Me_4Si) δ 0.86 (3 H, t, $J = 6.5$ Hz, CH_3), 1.24 (12 H, m, CH$_3$(CH_2)$_6$), 1.51 (2 H, q, $J = 5$ Hz, CH_2CH$_2$CO), 2.28 (2 H, t, $J = 7.5$ Hz, CH_2CO), 3.35 (2 H, m, CH_2OH), 3.62 (1 H, m, C*H*OH), 3.91 (1 H, dd, $J = 6.4$ Hz, $J = 11.2$ Hz, COOC*H*H), 4.02 (1 H, dd, $J = 4.5$ Hz, $J = 11.1$ Hz, COOCH*H*), 4.62 (1 H, t, $J = 6$ Hz, CH$_2$O*H*), 4.86 (1 H, d, $J = 5$ Hz, CHO*H*). ^{13}C{^{1}H} NMR (75 MHz, DMSO-d6, Me_4Si) δ 13.89 (*C*H$_3$), 22.04, 24.41, 28.41, 28.59, 28.66, 28.80, 31.22, 33.45 (CH$_3$(*C*H$_2$)$_8$), 62.61 (*C*H$_2$OH), 65.44 (COO*C*H$_2$), 69.26 (*C*HOH), 172.9 (*C*O). HRMS (ESI) *m/z* calculated for $C_{13}H_{26}NaO_4$ $[M+Na]^+ = 269.17233$; found: 269.17139. Elemental analysis (found: C, 63.03; H, 10.99. $C_{13}H_{26}O_4$ requires C, 63.38; H, 10.64 %).

2,3-Dihydroxypropyl undec-10-enoate (**3**): White solid (2.2 g, 84 %), mp 44 °C. IR (ATR, neat): ν_{max}/cm^{-1} 3230 and 3200 (OH), 2919 and 2850 (CH), 1728 (C=O), 1641 (C=C), 1173 and 1048 (C–O). ^{1}H NMR (300 MHz, DMSO-d6, Me_4Si) δ 1.26 (10 H, m, CH$_2$=CHCH$_2$(CH_2)$_5$), 1.52 (2 H, q, $J = 6$ Hz, CH_2CH$_2$CO), 2.02 (2 H, m, CH$_2$=CHCH_2), 2.26 (2 H, t, $J = 7.4$ Hz, CH_2CO), 3.41 (2 H, m, CH_2OH), 3.62 (1 H, m, C*H*OH), 3.90 (1 H, dd, $J = 6.4$ Hz, $J = 11.2$ Hz, COOC*H*H), 4.05 (1 H, dd, $J = 4.5$ Hz, $J = 11.1$ Hz, COOCH*H*), 4.61 (1 H, t, $J = 6$ Hz, CH$_2$O*H*), 4.90 (1 H, d, $J = 5$ Hz, CHO*H*), 4.92–5.03 (2 H, m, CH_2=CH), 5.8 (1 H, m, *C*H$_2$=C*H*). ^{13}C{^{1}H} NMR (75 MHz, DMSO-d6, Me_4Si) δ 24.39, 28.21–28.65, 33.12, 33.45 (CH$_2$=CH(CH_2)$_8$), 62.61 (*C*H$_2$OH), 65.44 (COO*C*H$_2$), 69.27 (*C*HOH), 114.56 (*C*H$_2$=CH), 138.77 (CH$_2$=*C*H), 172.89 (*C*O). HRMS (ESI) *m/z* calculated for $C_{14}H_{26}NaO_4$ $[M+Na]^+ = 281.17233$; found: 281.17134. Elemental analysis (found: C, 64.96; H, 10.76. $C_{14}H_{26}O_4$ requires C, 65.09; H, 10.14 %).

2,3-Dihydroxypropyl stearate (**4**): White solid (3.1 g, 86 %), mp 72 °C. IR (ATR, neat): ν_{max}/cm^{-1} 3230 and 3200 (OH), 2915 and 2849 (CH), 1729 (C=O), 1176 and 1048 (C–O). ^{1}H NMR (300 MHz, DMSO-d6, Me_4Si) δ 0.86 (3 H, t, $J = 6.6$ Hz, CH_3), 1.24 (28 H, m, CH$_3$(CH_2)$_{14}$), 1.51 (2 H, q, $J = 7$ Hz, CH_2CH$_2$CO), 2.28 (2 H, t, $J = 7.3$ Hz, CH_2CO), 3.35 (2 H, m, CH_2OH), 3.62 (1 H, m, C*H*OH), 3.91 (1 H, dd, $J = 6.4$ Hz, $J = 11.2$ Hz, COOC*H*H), 4.02 (1 H, dd, $J = 4.5$, $J = 11.1$ Hz, COOCH*H*), 4.61 (1 H, t, $J = 6$ Hz, CH$_2$O*H*), 4.82 (1 H, d,

$J = 5$ Hz, CHO*H*). $^{13}C\{^1H\}$ NMR (75 MHz, DMSO-d6, Me_4Si) δ 13.90 (*C*H_3), 22.04, 24.41, 28.42–28.97, 31.24, 33.45 ($CH_3(CH_2)_{16}$), 62.61 (*C*H_2OH), 65.45 (COO*C*H_2), 69.26 (*C*HOH), 172.9 (*C*O). HRMS (ESI) *m/z* calculated for $C_{21}H_{42}NaO_4$ $[M+Na]^+ = 381.29753$; found: 381.29625. Elemental analysis (found: C, 70.14; H 12.69. $C_{21}H_{42}O_4$ requires C, 70.34; H, 11.81 %).

Synthesis of the Diacrylated and Dimethacrylated Monoglycerides **5–12**

General Procedure

To a solution of monoglyceride (6.5 mmol) in dichloromethane (80 mL) was added triethylamine (15 mmol). The solution was cooled at 0 °C under an argon atmosphere and acryloyl or methacryloyl chloride (15 mmol) was added dropwise. The reaction mixture was stirred 30 min at 0 °C, then 3 h at room temperature. The solution was washed with NaOH aqueous solution (1 mol L^{-1}), and the organic layer was dried over $MgSO_4$. The solvent was evaporated under vacuum leading to the photopolymerizable monomer.

3-(Butyryloxy) propan-1,2-diyl diacrylate (**5**): Yellow liquid (2.5 g, 91 %). IR (ATR, neat): ν_{max}/cm^{-1} 2920 and 2850 (CH), 1728 (C=O), 1617 and 1636 (C=C), 1167 and 1048 (C–O). ^1H NMR (300 MHz, DMSO-d6, Me_4Si) δ 0.89 (3 H, t, $J = 7$ Hz, C*H*$_3$), 1.56 (2 H, m, C*H*$_2$CH$_2$CO), 2.33 (2 H, t, $J = 7.2$ Hz, C*H*$_2$CO), 4.36 (4 H, m, COOC*H*$_2$ and COOC*H*$_2$), 5.38 (1 H, m, COOC*H*), 6.03–6.37 (6 H, m, C*H*=C*H*$_2$ and C*H*=C*H*$_2$). $^{13}C\{^1H\}$ NMR (75 MHz, DMSO-d6, Me_4Si) δ 13.24 (*C*H_3), 17.79 (*C*H_2CH$_2$CO), 35.12 (*C*H_2CO), 61.66, 62.14 (COO*C*H_2 and COO*C*H_2), 69.20 (COO*C*H), 127.71, 127.75 (*C*H=CH$_2$ and *C*H=CH$_2$), 132.09, 132.28 (CH=*C*H$_2$ and CH=*C*H$_2$), 164.68, 164.97 (*C*O–CH=CH$_2$ and *C*O–CH=CH$_2$), 172.34 (*C*O). HRMS (ESI) *m/z* calculated for $C_{13}H_{18}NaO_6$ $[M+Na]^+ = 293.09956$; found: 293.09871. Elemental analysis (found: C, 57.63; H, 6.46. $C_{13}H_{18}O_6$ requires C, 57.77; H, 6.71 %).

3-(Decanoyloxy) propan-1,2-diyl diacrylate (**6**): Yellow liquid (2.3 g, 95 %). IR (ATR, neat): ν_{max}/cm^{-1} 2924 and 2854 (CH), 1729 (C=O), 1617 and 1636 (C=C), 1171 and 1048 (C–O). ^1H NMR (300 MHz, DMSO-d6, Me_4Si) δ 0.86 (3 H, t, $J = 7$ Hz, C*H*$_3$), 1.23 (12 H, m, $CH_3(CH_2)_6$), 1.49 (2 H, q, $J = 6.8$ Hz, C*H*$_2$CH$_2$CO), 2.29 (2 H, t, $J = 7.2$ Hz, C*H*$_2$CO), 4,26 (4 H, m, COOC*H*$_2$ and COOC*H*$_2$), 5.32 (1 H, m, COOC*H*), 5.96–6.37 (6 H, m, C*H*=C*H*$_2$ and C*H*=C*H*$_2$). $^{13}C\{^1H\}$ NMR (75 MHz, DMSO-d6, Me_4Si) δ 13.86 (*C*H_3), 22.02, 24.32, 28.29, 28.58, 28.61, 28.75, 31.21, 33.45 ($CH_3(CH_2)_8$), 61.67, 62.14 (COO*C*H_2 and COO*C*H_2), 69.20 (COO*C*H), 127.71, 127.75 (*C*H=CH$_2$ and *C*H=CH$_2$), 132.10, 132.26 (CH=*C*H$_2$ and CH=*C*H$_2$), 164.65, 164.96 (*C*O–CH=CH$_2$ and *C*O–CH=CH$_2$), 172.47 (*C*O). HRMS (ESI) *m/z* calculated for $C_{19}H_{30}NaO_6$ $[M+Na]^+ = 377.19346$; found: 377.19223. Elemental analysis (found: C, 64.54; H, 8.13. $C_{19}H_{30}O_6$ requires C, 64.38; H, 8.53 %).

3-(Undec-10-enoyloxy) propan-1,2-diyl diacrylate (**7**): Yellow liquid (1.8 g, 94 %). IR (ATR, neat): ν_{max}/cm^{-1} 2925 and 2854 (CH), 1728 (C=O), 1617 and 1636 (C=C), 1041 and 1170 (C–O). ^1H NMR (300 MHz, DMSO-d6, Me_4Si) δ 1.29 (10 H, m, CH$_2$=CHCH$_2$(C*H*$_2$)$_5$), 1.55 (2 H, q, $J = 5$ Hz, C*H*$_2$CH$_2$CO), 2.07 (2 H, m, CH$_2$=CHC*H*$_2$), 2.34 (2 H, t, $J = 7.2$ Hz, C*H*$_2$CO), 4.37 (4 H, m, COOC*H*$_2$ and COOC*H*$_2$), 5.01 (2 H, m, C*H*$_2$=CHCH$_2$), 5.38 (1 H, m, COOC*H*), 5.83 (1 H, m, CH$_2$=C*H*CH$_2$), 6.01–6.41 (6 H, m, CO–C*H*=C*H*$_2$ and CO–C*H*=C*H*$_2$). $^{13}C\{^1H\}$ NMR (75 MHz, DMSO-d6, Me_4Si) δ 24.80, 28.71–29.12, 33.61, 33.75 (CH$_2$=CH(*C*H$_2$)$_8$), 62.16, 62.63 (COO*C*H_2 and COO*C*H_2), 69.69 (COO*C*H), 114.97 (*C*H$_2$=CHCH$_2$), 128.19, 128.24 (CO–*C*H=CH$_2$ and CO–*C*H=CH$_2$), 132.53, 132.69 (CO–CH=*C*H$_2$ and CO–CH=*C*H$_2$), 139.22 (CH$_2$=*C*HCH$_2$), 165.13, 165.43 (*C*O–CH=CH$_2$ and *C*O–CH=CH$_2$), 172.93 (*C*O). HRMS (ESI) *m/z* calculated for $C_{20}H_{30}NaO_6$ $[M+Na]^+ = 389.19346$; found: 389.19216. Elemental analysis (found: C, 65.27; H, 8.14. $C_{20}H_{30}O_6$ requires C, 65.55; H, 8.25 %).

3-(Stearoyloxy) propan-1,2-diyl diacrylate (**8**): Yellow solid (3.5 g, 93 %), mp 32.5 °C. IR (ATR, neat): ν_{max}/cm^{-1} 2955, 2916 and 2849 (CH), 1728 (C=O), 1617 and 1634 (C=C), 1166, 1042 (C–O). ^1H NMR (300 MHz, DMSO-d6, Me_4Si) δ 0.85 (3 H, t, $J = 7.2$ Hz, C*H*$_3$), 1.24 (28 H, m, $CH_3(CH_2)_{14}$), 1.49 (2 H, q, $J = 6.9$ Hz, C*H*$_2$CH$_2$CO), 2.29 (2 H, t, $J = 7.2$ Hz, C*H*$_2$CO), 4.30 (4 H, m, COOC*H*$_2$ and COOC*H*$_2$), 5.32 (1 H, m, COOC*H*), 5.99–6.31 (6 H, m, C*H*=C*H*$_2$ and C*H*=C*H*$_2$). $^{13}C\{^1H\}$ NMR (75 MHz, DMSO-d6, Me_4Si) δ 13.88 (*C*H_3), 22.03, 24.31, 28.28–28.95, 31.24, 33.27 ($CH_3(CH_2)_{16}$), 61.67, 62.14 (COO*C*H_2 and COO*C*H_2), 69.20 (COO*C*H), 127.72, 127.76 (*C*H=CH$_2$ and *C*H=CH$_2$), 132.11, 132.26 (CH=*C*H$_2$ and CH=*C*H$_2$), 164.66, 164.96 (*C*O–CH=CH$_2$ and *C*O–CH=CH$_2$), 172.48 (*C*O). HRMS (ESI) *m/z* calculated for $C_{27}H_{46}NaO_6$ $[M+Na]^+ = 489.31866$; found: 489.31720. Elemental analysis (found: C, 69.97; H, 10.60. $C_{27}H_{46}O_6$ requires C, 69.49; H, 9.94 %).

3-(Butyryloxy) propan-1,2-diyl bis(2-methylacrylate) (**9**): Yellow liquid (2.3 g, 94 %). IR (ATR, neat): ν_{max}/cm^{-1} 2963 (CH), 1719 (C=O), 1637 (C=C), 1145 and 1048 (C–O). ^1H NMR (300 MHz, DMSO-d6, Me_4Si) δ 0.87 (3 H't, $J = 7$ Hz, C*H*$_3$), 1.54 (2 H, m, C*H*$_2$CH$_2$CO), 1.86 (6 H, S, C*H*$_3$C=CH$_2$ and C*H*$_3$C=CH$_2$), 2.28 (2 H, t, $J = 7.2$ Hz, C*H*$_2$CO), 4.33 (4 H, m, COOC*H*$_2$ and COOC*H*$_2$), 5.31 (1 H, m, COOC*H*), 5.71–6.02 (4 H, m, CH$_3$C=C*H*$_2$ and CH$_3$C=C*H*$_2$). $^{13}C\{^1H\}$ NMR (75 MHz, DMSO-d6, Me_4Si) δ 13.70 (*C*H_3), 18.21, 18.23, 18.31 (CH$_3$*C*H$_2$, C*H*$_3$C=CH$_2$ and C*H*$_3$C=CH$_2$), 35.62 (*C*H$_2$CO),

62.09, 62.73 (COO*C*H_2 and COO*C*H_2), 69.85(COO*C*H), 126.62, 126.69 (CH_3C=CH_2 and CH_3C=*C*H_2), 135.90, 135.92 (CH_3C=*C*H_2 and CH_3C=*C*H_2), 166.2, 166.49 (*C*O–C=CH_2), 172.81 (1 C, *C*O). HRMS (ESI) *m/z* calculated for $C_{15}H_{22}NaO_6$ $[M+Na]^+ = 321.13086$; found: 321.13016. Elemental analysis (found: C, 59.78; H, 7.72. $C_{15}H_{22}O_6$ requires C, 60.39; H, 7.43 %).

3-(Decanoyloxy) propan-1,2-diyl bis(2-methylacrylate) (**10**): Yellow liquid (2.7 g, 92 %). IR (ATR, neat): ν_{max}/cm^{-1} 2924 and 2854 (CH), 1721 (C=O), 1636 (C=C), 1173 and 1048 (C–O). ^{1}H NMR (300 MHz, DMSO-d6, Me_4Si) δ 0.89 (3 H, t, $J = 7.1$ Hz, C*H*$_3$), 1.28 (12 H, m, $CH_3(CH_2)_6$), 1.55 (2 H, q, $J = 7.2$ Hz, C*H*$_2$CH$_2$CO), 1.91 (6 H, s, C*H*$_3$C=CH$_2$ and C*H*$_3$C=CH$_2$), 2.34 (2 H, t, $J = 6$ Hz, C*H*$_2$CO), 4,42 (4 H, m, COOC*H*$_2$ and COOC*H*$_2$), 5.36 (1 H, m, COOC*H*), 5.75–6.07 (4 H, m, CH_3C=C*H*$_2$ and CH_3C=C*H*$_2$). ^{13}C{^{1}H} NMR (75 MHz, DMSO-d6, Me_4Si) δ 14.27 (*C*H$_3$), 18.19, 18.32 (*C*H$_3$C=CH$_2$ and *C*H$_3$C=CH$_2$), 22.53, 24.84, 28.84–29.28, 31.74, 33.78 (CH_3(*C*H$_2$)$_8$), 62.09, 62.72 (COO*C*H$_2$ and COO*C*H$_2$), 69.83 (COO*C*H), 126.36, 126.54 (CH_3C=CH_2 and CH_3C=*C*H$_2$), 135.90, 135.92 (CH_3C=*C*H$_2$ and CH_3C=*C*H$_2$), 166.12, 166.42 (*C*O–C=CH_2), 172.85 (*C*O). HRMS (ESI) *m/z* calculated for $C_{21}H_{34}NaO_6$ $[M+Na]^+ = 405.22476$; found: 405.22376. Elemental analysis (found: C, 65.88; H, 9.35. $C_{21}H_{34}O_6$ requires C, 65.94; H, 8.96 %).

3-(Undec-10-enoyloxy) propan-1,2-diyl bis(2-methylacrylate) (**11**): Yellow liquid (1.7 g, 97 %). IR (ATR, neat): ν_{max}/cm^{-1} 2924 and 2854 (CH), 1721 (C=O), 1637 (C=C) 1173 and 1048 (C–O). ^{1}H NMR (300 MHz, DMSO-d6, Me_4Si) δ 1.29 (10 H, m, CH_2=CHCH$_2$(C*H*$_2$)$_5$), 1.55 (2 H, q, $J = 7$ Hz, C*H*$_2$CH$_2$CO), 1.91 (6 H, s, C*H*$_3$C=CH$_2$ and C*H*$_3$C=CH$_2$), 2.07 (2 H, m, CH_2=CHC*H*$_2$), 2,37 (2 H, t, $J = 7$ Hz, C*H*$_2$CO), 4,41 (4 H, m, COOC*H*$_2$ and COOC*H*$_2$), 5.04 (2 H, m, C*H*$_2$=CHCH$_2$), 5.42 (1 H, m, COOC*H*), 5.76–6.07 (5 H, m, CH_3C=C*H*$_2$, CH_3C=C*H*$_2$ and CH_2=C*H*CH$_2$). ^{13}C{^{1}H} NMR (75 MHz, DMSO-d6, Me_4Si) δ 18.21, 18.22 (*C*H$_3$C=CH$_2$ and *C*H$_3$C=CH$_2$), 24.83, 28.72–29.12, 33.62, 33.78 (CH_2=CH(*C*H$_2$)$_8$), 62.10, 65.84 (COO*C*H$_2$ and COO*C*H$_2$), 69.84 (COO*C*H), 114.92 (*C*H$_2$=CHCH$_2$), 126.58, 126.62 (CH_3C=CH_2 and CH_3C=*C*H$_2$), 135.89, 135.91 (CH_3C=*C*H$_2$ and CH_3C=*C*H$_2$), 139.19 (CH_2=*C*HCH$_2$), 166.15, 166.45 (*C*O–C=CH_2), 172.89 (*C*O). HRMS (ESI) *m/z* calculated for $C_{22}H_{34}NaO_6$ $[M+Na]^+ = 417.22476$; found: 417.22344. Elemental analysis (found: C, 66.93; H, 8.95. $C_{22}H_{34}O_6$ requires C, 66.98; H, 8.68 %).

3-(Stearoyloxy) propan-1,2-diyl bis(2-methylacrylate) (**12**): Yellow solid (2.3 g, 91 %), mp 25 °C. IR (ATR, neat): ν_{max}/cm^{-1} 2922 and 2852 (CH), 1724 (C=O), 1637 (C=C), 1173 and 1048 (C–O). ^{1}H NMR (300 MHz, DMSO-d6, Me_4Si) δ 0.85 (3 H, t, $J = 7.1$ Hz, C*H*$_3$), 1.24 (28 H, m, $CH_3(CH_2)_{14}$), 1.49 (2 H, q, $J = 7.2$ Hz, C*H*$_2$CH$_2$CO), 1.86 (6 H, s, C*H*$_3$C=CH$_2$ and C*H*$_3$C=CH$_2$), 2.28 (2 H, t, $J = 7.2$ Hz, C*H*$_2$CO), 4.35 (4 H, m, COOC*H*$_2$ and COOC*H*$_2$), 5.31 (1 H, m, COOC*H*), 5.75–6.07 (4 H, m, CH_3C=C*H*$_2$ and CH_3C=C*H*$_2$). ^{13}C{^{1}H} NMR (75 MHz, DMSO-d6, Me_4Si) δ 13.86 (*C*H$_3$), 17.78, 18.07 (*C*H$_3$C=CH$_2$ and *C*H$_3$C=CH$_2$), 22.04, 24.35, 28.29–28.95, 31.24, 33.31 (CH_3(*C*H$_2$)$_{16}$), 61.61, 62.24 (COO*C*H$_2$ and COO*C*H$_2$), 69.37 (COO*C*H), 126.18, 127.23 (CH_3C=CH_2 and CH_3C=*C*H$_2$), 135.90, 135.92 (CH_3C=*C*H$_2$ and CH_3C=*C*H$_2$), 165.69, 166.01 (*C*O–C=CH_2), 172.45 (*C*O). HRMS (ESI) *m/z* calculated for $C_{29}H_{50}NaO_6$ $[M+Na]^+ = 517.34996$; found: 517.34822. Elemental analysis (found: C, 70.25; H, 10.55. $C_{29}H_{50}O_6$ requires C, 70.41; H, 10.19 %).

Synthesis of Photopolymers **Poly5-12**

General Procedure

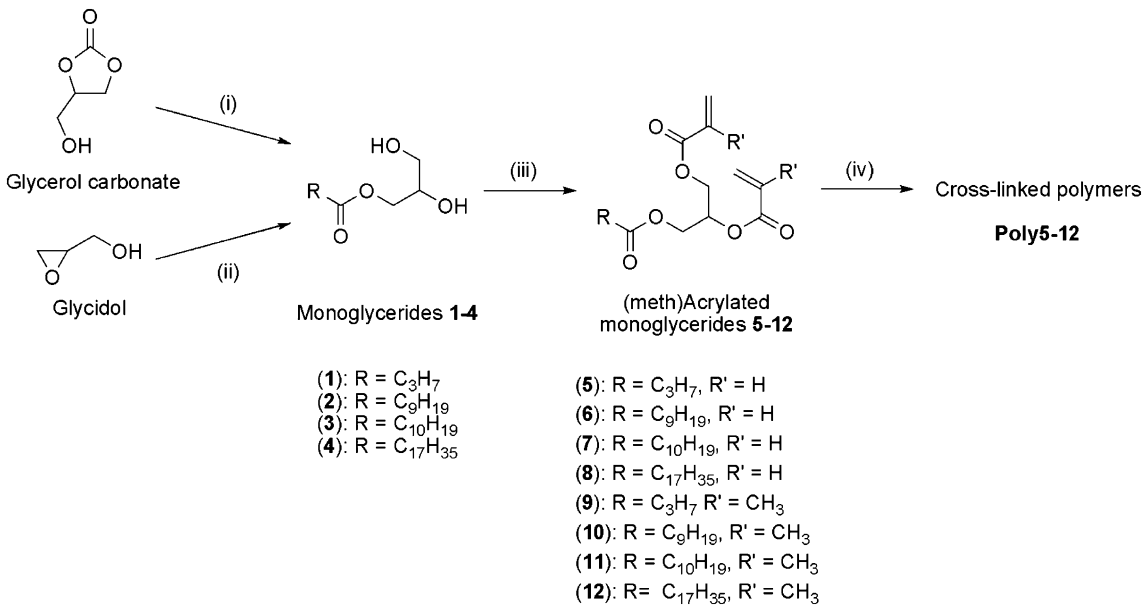
A drop of the diacrylated or dimethacrylated monoglyceride containing 3 % wt of Darocur 1173® was deposited and spread out over the ATR diamond crystal with a polyethylene film and a quartz filter to ensure a uniformity of the surface analysis. The ATR crystal can be set at a chosen temperature by thermal regulation. UV radiation from a 365-nm LED (Hamamatsu Lightningcure™ LC-L1) was introduced into the FTIR spectrometer sample chamber by a flexible light guide so that it did not interfere with the IR beam. The light intensity of the monochromatic radiation was controlled by a UV radiometer (VLX-3W Vilber-Lourmat) at the sample surface. The intensity of the absorption band at 810 cm^{-1}, attributed to C=C of acrylic and methacrylic moieties, was measured. A reference band at 1065 cm^{-1} was used to calculate the conversion of the reactive groups as follows:

$$\chi_{C=C} = \frac{\frac{A_0^{810}}{A_0^{1065}} - \frac{A_t^{810}}{A_t^{1065}}}{\frac{A_0^{810}}{A_0^{1065}}} \times 100$$

where $(A_{810}/A_{1065})_0$ and $(A_{810}/A_{1065})_t$ are relative absorbance of C=C bonds before curing and at a given curing time *t*, respectively. In addition, during these experiments, the films were protected against the oxygen inhibition using a polyethylene film. Therefore experiments were carried out under laminated conditions, i.e. in the absence of atmospheric oxygen. The TGA and values of gel content determination for each photopolymers are given in discussion section.

Results and Discussion

The synthetic pathways and the structures of monoglycerides, diacrylated and dimethacrylated monoglycerides synthesized in this study are summarized in Scheme 1.



Scheme 1 Synthetic and polymerization pathways. (*i*) RCO_2H (R=C_3H_7, C_9H_{19}, $C_{10}H_{19}$, $C_{17}H_{35}$), $(C_4H_9)_4NI$, 140–142 °C, 24 h; (*ii*) RCO_2H, $(C_4H_9)_4NI$, 120 °C, 30–60 min; (*iii*) H_2C=CR'COCl (R′=H or CH_3), RT, CH_2Cl_2, 3 h; (*iv*) Darocur 1173® (3 % wt), UV-irradiation (365 nm, I_0 = 130 mW cm^{-2}), room temperature

Synthesis of Monoglycerides

The condensation of decanoic acid as the representative carboxylic acid with glycerol carbonate or glycidol was first examined in the presence of TBAI ($(C_4H_9)_4NI$) as a catalyst. The progress of the reaction was monitored by IR spectroscopy. The formation of the product was revealed by the appearance of the ester carbonyl absorption at 1737 cm^{-1}, accompanying the disappearance of the carboxylic acid carbonyl band at 1695 cm^{-1}. The pendant hydroxyl groups of monoglyceride are characterized by strong absorptions at 3230 and 3200 cm^{-1}.

The yield of monoglyceride was low (14 %) and the reaction is poorly selective when glycerol carbonate was used (24 h reaction time). The formation of numerous by-products, such as esters and cyclic carbonates is observed. Indeed, the $^{13}C\{^1H\}$ NMR spectrum shows the presence of unreacted decanoic acid (174.4 ppm), and also in evidence were several carbonyl peaks in the 150–180 ppm range (Fig. 1a). The hydroxyl groups probably undergo a competitive esterification. However, upon reaction with glycidol (same molecular ratio as above, carboxylic acid/glycidol = 1:2), good yields (>80 %) were obtained in shorter reaction times (50 min). The $^{13}C\{^1H\}$NMR spectrum exhibits only one major peak at 172.9 ppm (Fig. 1b) corresponding to the 2,3-dihydroxypropyl decanoate. The 2,3-dihydroxypropyl decanoate structure was established on the basis of the ^{1}H-NMR spectrum (DMSO-d6), which revealed a triplet at 4.62 ppm and a doublet at 4.86 ppm for the hydroxyl groups (CH_2OH and CHO*H*, respectively). Hence, the reaction is totally selective leading to the unique formation of the α-isomer monoglyceride.

^{1}H-NMR studies were used to calculate the conversion rate of carboxylic acid. Figure 2 shows the ^{1}H-NMR spectra of the reaction medium as a function of time. The appearance of new signals at 2.28 ppm (identified by * in Fig. 2) corresponding to the -C*H*$_2$C(O)O- of the new ester function is observed concomitantly to the decrease of the signal at 2.17 ppm (identified by § in Fig. 2) corresponding to -C*H*$_2$COOH of the acid function. The conversion of carboxylic acid was calculated as follows:

$$\text{Conversion} = \left(1 - \frac{I_2}{I_1 + I_2}\right) \times 100$$

where I_1 and I_2 correspond to the signals integrations at 2.28 ppm and 2.17 ppm respectively.

In order to optimize the conversion of the carboxylic acid, various parameters were studied. Figure 3 shows the carboxylic acid conversion curves versus time with reaction temperatures in the range 90–130 °C. According to this study, the temperature of 120 °C was chosen as the best reaction temperature leading to a complete conversion in a short reaction time.

Several percentages of catalyst were used to determine the optimum catalyst to acid ratio. Figure 4 shows that the reaction is efficiently catalyzed with only 0.5 mol% of catalyst. The decanoic acid conversion reaches about 100 % after 50 min of reaction. As the catalyst is not recycled after reaction, the lowest $(C_4H_9)_4NI$ catalyst loading selected was 0.5 mol%.

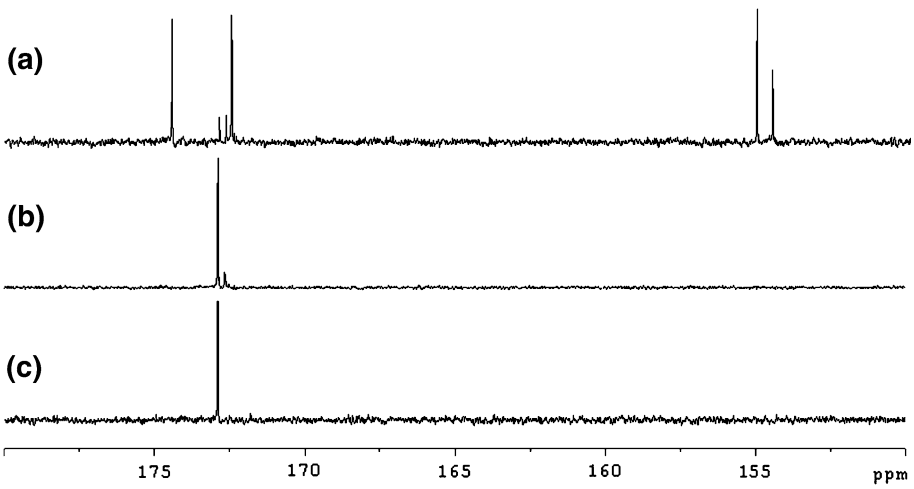


Fig. 1 $^{13}C\{^{1}H\}$ NMR spectra of the products obtained by esterification reaction with decanoic acid. **a** Decanoic acid/glycerol carbonate 1:1, 142 °C, 24 h; **b** decanoic acid/glycidol 1:1, 120 °C, 30 min; **c** monoglyceride after purification

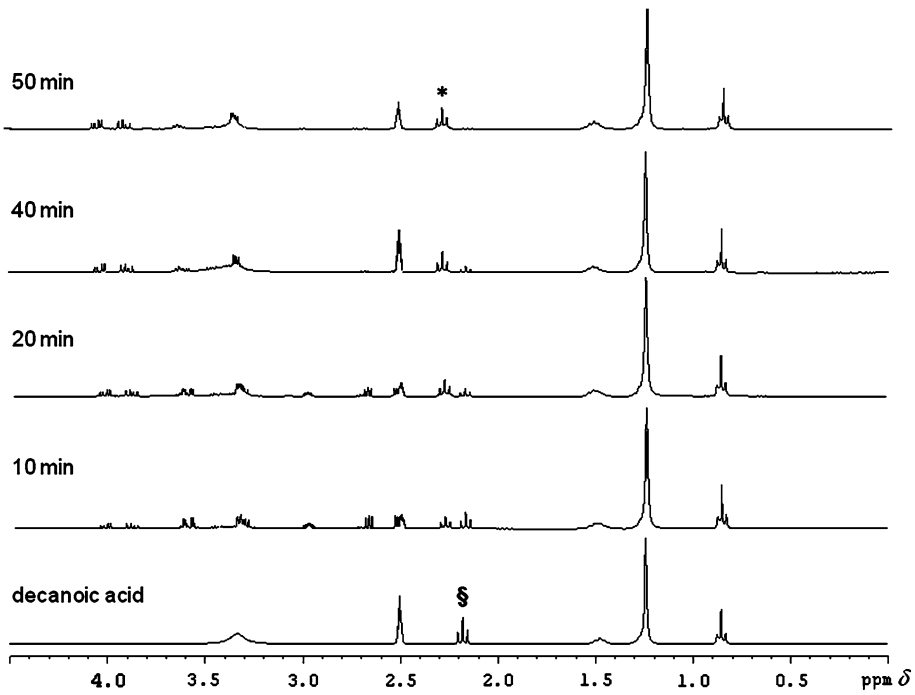


Fig. 2 ^{1}H-NMR spectra of the compound resulting from the esterification reaction of decanoic acid/glycidol 1:2, at 120 °C

Figure 5 shows the effect of glycidol/fatty acid ratio on the conversion reaction. The excess of glycidol is required to reach a quantitative conversion. A 2:1 ratio is sufficient to obtain the best conversion with the shortest reaction time.

The influence of the carboxylic acid chain length on the conversion has been also studied and is reported in Fig. 6. Four carboxylic acids (butyric, decanoic, undecylenic and stearic acids) were reacted with glycidol using the optimum reaction conditions determined above (glycidol/acid = 2:1 mol, $T = 120$ °C and 0.5 mol% of $(C_4H_9)_4NI$). The long chain (C18) carboxylic acid reacts more slowly than its shorter C4 homologue. This can be explained either by the precipitation of the final product (2,3-dihydroxypropyl stearate) leading to an increase in the heterogeneity of the reaction mixture (it is worth noting that in the case of butyric acid the final product is liquid) or by the steric hindrance due to the long alkyl chains.

Acrylation and Methacrylation of the Monoglycerides

In order to get photopolymerizable monomers, the free alcohol functions of the α-monoglycerides were esterified using acryloyl and methacryloyl chloride. The resulting diacrylated and dimethacrylated monomers (**5–12**) were fully characterized by spectroscopic methods (see the experimental section). The yields of acrylation and methacrylation are higher than 90 %. All products are yellow liquids excepted for **8** and **12** which are yellowish semi-solids. The esterification of the hydroxyl functions was

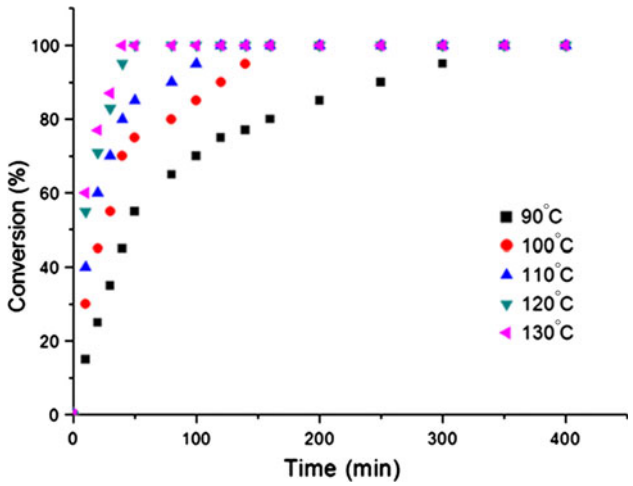


Fig. 3 Diagram showing the conversion of the carboxylic acid versus time at various temperatures in the range 90–130 °C (decanoic acid/glycidol 1:2, 0.5 mol% of TBAI). (color online)

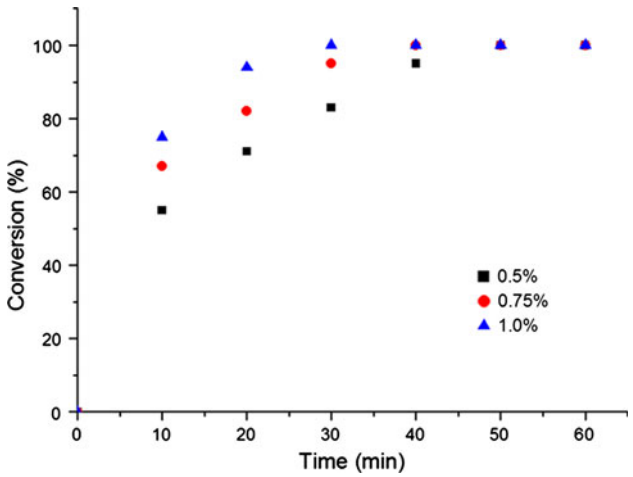


Fig. 4 Effect of the catalyst (TBAI) concentration on the acid conversion: decanoic acid/glycidol 1:2, 120 °C. (color online)

ascertained by FTIR analyses, showing the disappearance of the monoglyceride -OH vibration bands. Furthermore, the presence of acrylate and methacrylate groups was proven by the appearance of the characteristic bands corresponding to vinyl double bonds at ca. 1617 and 1636 cm^{-1}. The ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra are in accordance with the proposed structures (Scheme 1) revealing the characteristic resonances of the vinylic pendant groups.

Photopolymerization of (Meth)acrylated Monoglycerides

The radical photopolymerization of each monomer (**5–12**) [using 2-hydroxy-2-methyl-1-phenyl-propan-1-one (Darocur 1173®) as photoinitiator [38] (Scheme 2)] leading to

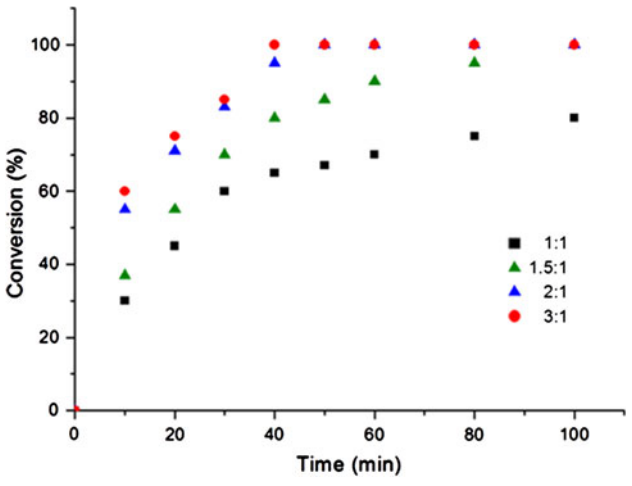


Fig. 5 Effect of the glycidol/decanoic acid ratio on the esterification reaction. TBAI 0.5 mol%, 120 °C. (color online)

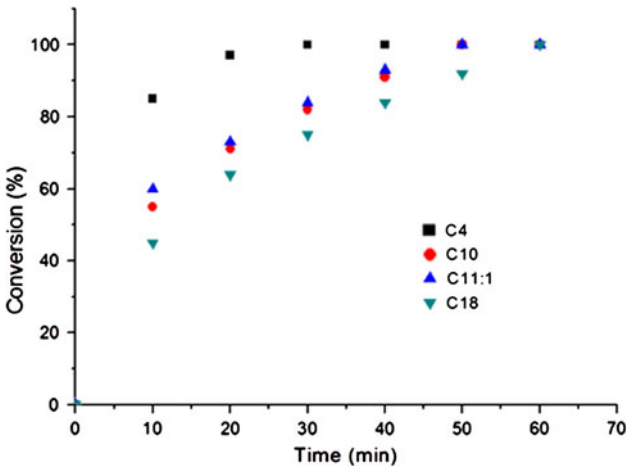
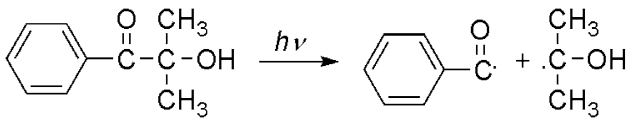


Fig. 6 Effect of the carboxylic acid chain length. Carboxylic acid/glycidol 1:2; TBAI 0.5 mol%, 120 °C. (color online)



Scheme 2 Darocur 1173® photolysis

the corresponding polymers (**Poly5–12**) has been systematically investigated (Scheme 1). Acrylated and methacrylated derivatives exhibit a similar behavior under UV-irradiation. Below, a careful description of the synthesis of the material from the decanoic acid (**Poly6**), is provided.

Figure 7 shows the FTIR spectra of **6** as a function of time under UV-irradiation (Darocur 1173® 3 % wt). The kinetics of polymerization of one of the methacrylated monomers (compound **10**), also prepared from the

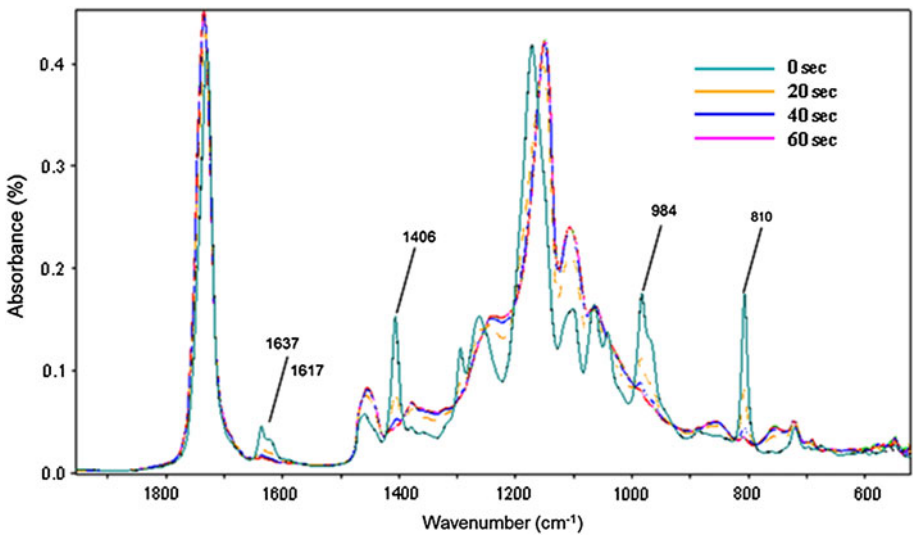


Fig. 7 FTIR spectra of 3-(decanoyloxy) propan-1,2-diyl diacrylate (**6**) as a function of time under UV-irradiation (365 nm, $I_0 = 130$ mW cm^{-2}) in the presence of 3 % Darocur 1173®. (color online)

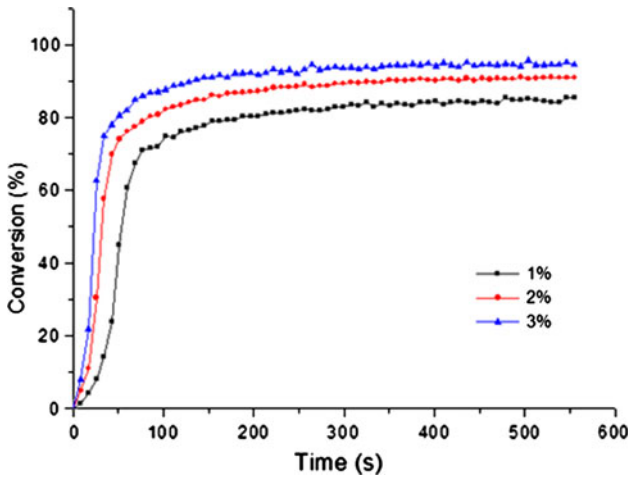


Fig. 8 Evolution of the acrylate double bond conversion of 3-(decanoyloxy) propan-1,2-diyl diacrylate (**6**) as a function of Darocur 1173® concentration (room temperature, $I_0 = 130$ mW cm^{-2}, 365 nm). (color online)

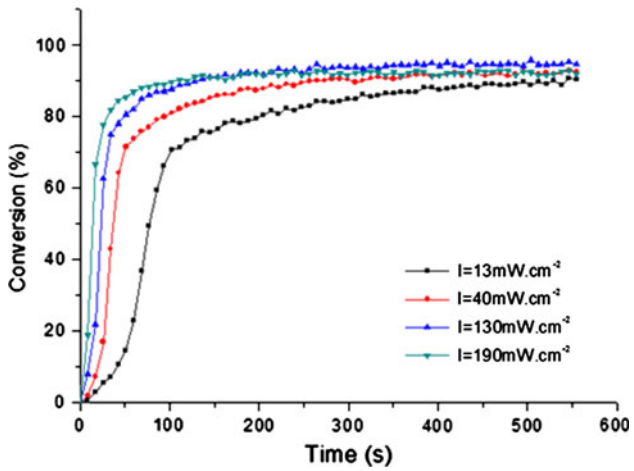


Fig. 9 Effect of UV light intensity on the kinetics of the acrylate double bond conversion of 3-(decanoyloxy) propan-1,2-diyl diacrylate (**6**) (room temperature, 3 % wt Darocur 1173®). (color online)

decanoic acid, is depicted in the supporting information (Figure S1).

The occurrence of the polymerization is clearly confirmed by the strong decrease in the intensity of the acrylate moiety peaks at 1617–1636 cm^{-1} (C=C stretching bond), 1406 cm^{-1} (in-plane CH_2 deformation), 984 and 810 cm^{-1} (out-of-plane deformation).

This effect is due to the direct implication of the C=C bonds in the cross-linking reaction, induced by photopolymerization [39]. The conversion of the (meth)acrylate group for all monomers exceeds 90 % after irradiation under UV (Darocur 1173® 3 % wt, 6 min exposure, $I_0 = 130$ mW cm^{-2} at 365 nm). The bio-based polymers are obtained as translucent pale yellow solids. The photoinitiator concentration and the irradiation intensity were then optimized.

Influence of the Photoinitiator Concentration

The photocrosslinking reaction of **6** depending of Darocur 1173® concentration (1–3 %) wt was studied (Fig. 8).

As expected [40], final conversions and polymerization rates increase with the amount of Darocur 1173®. A 3 % wt photoinitiator concentration leads to the best polymerization yield. In all experiments, the ultimate conversion is higher than 80 %. It is then noteworthy that the proximity of the two acrylate double bonds does not disturb the polymerization reaction, allowing a quite complete polymerization.

Influence of the Irradiation Intensity

A formulation composed of **6** and 3 % wt of photoinitiator was irradiated at intensities varying from 13 to 190 mW cm^{-2} (Fig. 9). An increase in the light intensity accelerates

Table 1 Characterization of the photo-cured materials by determinations of temperatures corresponding to 5 %, 50 % weight loss and maximum degradation, percentages of gel content (X_g), pendulum hardness and swelling ratio

Polymer[a]	$T_{5\ \%}$ (°C)	$T_{50\ \%}$ (°C)	T_{max} (°C)	X_g^b (%)	Hardness[c]	Swelling ratio (%)[d e | f]
Poly5	365	419	423	99	88 ± 3	1.5 | 11.4
Poly6	345	420	425	98	62 ± 1	5.4 | 19.3
Poly7	382	437	447	98	102 ± 1	1.0 | 7.0
Poly8	315	415	420	100	30 ± 3	7.0 | 23.0
Poly9	287	406	429	97	75 ± 2	1.7 | 9.0
Poly10	280	402	422	99	58 ± 1	5.4 | 18.0
Poly11	390	446	455	96	91 ± 1	1.2 | 8.0
Poly12	307	421	426	100	28 ± 3	8.0 | 11.4

[a] Poly-x represents the polymer obtained by photopolymerization of x

[b] Percentage of gel content [33]

[c] Pendulum hardness values are expressed in seconds [35]

[d] 0 % In water even after 1 month of immersion

[e] Measured in ethanol

[f] Measured in dichloromethane

the kinetics of the Darocur 1173®photolysis, leading to an increase in the polymerization rate. This behavior has been already explained by an increase in the amount of primary radicals produced [41]. The conversion increases with light intensity up to 130 mW cm^{-2} and a decrease is observed above this value. For a light intensity of 190 mW cm^{-2} the polymerization rate is faster but the conversion is lower. This effect is due to the termination of radical polymerization by initiator combination.

Preliminary Characterization of the Photo-Cured Materials

Thermal Degradation

Table 1 reports the degradation temperatures, recorded by TGA under nitrogen atmosphere for the series of synthesized polymers. The temperature corresponding to 5 %, 50 % weight loss and maximum degradation rate are labelled as $T_{5\ \%}$, $T_{50\ \%}$ and T_{max}. The cross-linked polymers are thermally stable till about 300 °C (Fig. 10). **Poly7** and **Poly11** polymers built from unsaturated fatty acid have a higher thermal stability ($T_{5\ \%} = 382$ and 390 °C respectively). Moreover, $T_{5\ \%}$ depends on the acrylate or methacrylate moiety. It is noteworthy that the degradation behavior ($T_{50\ \%}$ and T_{max}) is comparable.

Gel Content Determination

The degree of cross-linking is difficult to quantify and cannot be directly measured. The determination of gel content gives information on this parameter. This type of measurement has been carried out on the materials (**Poly5–12**) showing high gel content values (from 96 to 100 %, Table 1), and that it is in accordance with a quite complete cross-linking structure.

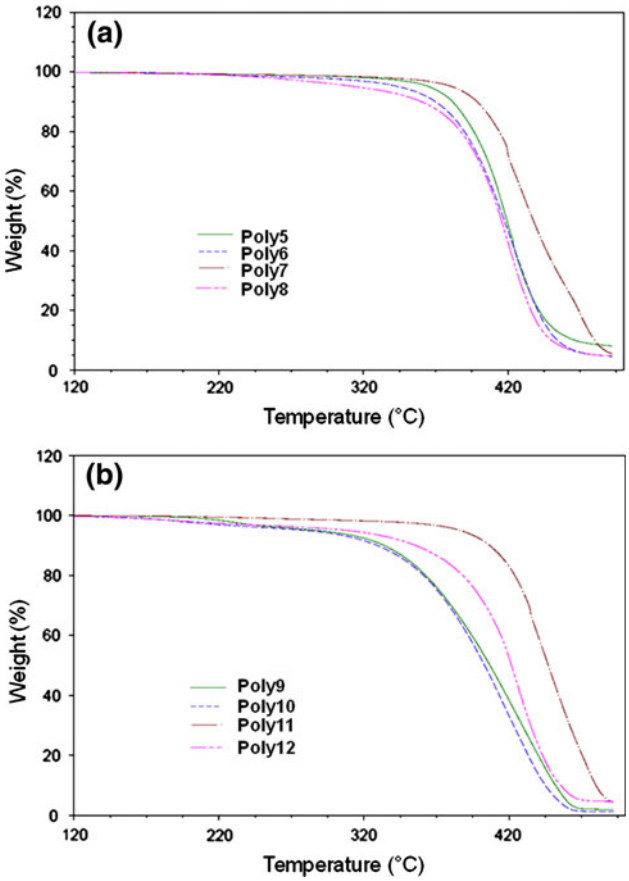


Fig. 10 Thermogravimetric analysis of **a** acrylate-based polymers and **b** methacrylate-based polymers. (color online)

Pendulum Hardness

König pendulum hardness values for acrylated (**Poly5–8**) and methacrylated (**Poly9–12**) polymers were measured and are also presented in Table 1. Both types of materials exhibit comparable results of hardness. For each series, acrylates or methacrylates, we observed that the increase of the length of alkyl chains leads to a decrease in hardness that which can be explained by a higher flexibility. However, and as for the thermal degradation study, **Poly7** and **Poly11** showed a distinctive behavior, with higher hardness values due to the participation of terminal unsaturation in the cross-linking process, increasing the degree of cohesion and rigidity. Compared to the hardness data available in the literature for UV-cured epoxy-acrylates [42], **Poly5–12** are more flexible materials and the flexibility can be modulated according to the chain lengths of the fatty acids used.

Swelling Measurements

Measurements of swelling ratios for **Poly5–12** were investigated (Table 1). Whatever the polarity and nature of the solvent used (water, ethanol and dichloromethane), the swelling ratio measured for each acrylated (**Poly5–8**) and methacrylated (**Poly9–12**) polymer remains very low (0 % in water even after 1 month of immersion), which corroborates the conclusion of the gel content determination, also underlining the formation of highly cross-linked materials. Similar results of swelling are obtained in both series of polymers, acrylates and methacrylates.

Conclusion

In summary, we described a convenient two-step procedure for the synthesis of photopolymerizable monomers. Moreover, it is based on a sustainable chemistry approach. Hence, the selective preparation of pure α-monoglycerides from fatty acids and glycidol using and organocatalyst and solvent-free conditions proceeds in higher yields. Several reaction parameters were successively and rigorously optimized including the molar excess of glycidol, the reaction temperature, the amount of catalyst and the fatty acid chain length. These monoglycerides were subsequently used for the synthesis of diacrylated and dimethacrylated photopolymerizable monomers. The photopolymerization reaction was studied using Darocur 1173® as photoinitiator and parameters such as photoinitiator amount and irradiation light intensity were discussed. The resulting materials show a high thermal stability as confirmed by TGA studies and comparable to those measured in the past for UV-cured acrylates [42], and a degree of cross-linking close to 100 % as evidenced by the gel content determination experiments. The complete characterization of the synthesized materials and photopolymerization kinetic studies are still ongoing, and potential applications for Braille printing are being examined.

Acknowledgments The authors acknowledge the Centre National de la Recherche Scientifique (CNRS, France), the National Institut of Applied Sciences (INSA of Rouen, France), the University of Burgundy (Dijon, France), the Region Bourgogne and the Tom'S 3D company (F. Jaffiol) for support of this work and for a PhD fellowship to AM. The authors are grateful to the Dr. J.-C. Chambron for his suggestions, which are particularly appreciated and were helpful in the preparation of this manuscript. The Dr. Richard Decreau is also thanked for the correction of the manuscript in English.

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