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Robust Amidation Transformation of Plant Oils into Fatty Derivatives for Sustainable Monomers and Polymers

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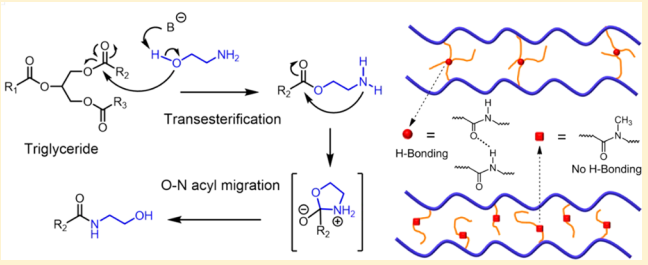
Supporting Information

ABSTRACT: Sustainable fuels, chemicals, and materials from renewable resources have recently gained tremendous momentum in a global scale, although there are numerous nontrivial hurdles for making them more competitive with petroleum counterparts. We demonstrate a robust strategy for the transformation of plant oils into polymerizable monomers and thermoplastic polymer materials. Specifically, triglycerides were converted into *N*-hydroxyalkyl fatty amides with the aid of amino alcohols via a mild base-catalyzed amidation process with nearly quantitative yields without the use of column chromatography and organic solvents. These fatty amides were further converted into a variety of methacrylate monomers, cyclic norbornene monomers and imino ether monomers. Representative polymers from selected monomers exhibit drastic different physical properties with subtle structural variations, highlighting the potential of this particular amidation reaction in the field of biomass transformation.



INTRODUCTION

With the depletion of fossil oil reserves, the utilization of plant-based materials is becoming increasingly important for sustainable development.[1−17] As feedstock for the chemical industry, plant oils stand out as one of the most important renewable resources among rich raw materials and have been widely used for the preparation of surfactants, intermediates, paints and resins, and polymers and for the production of biofuels.[5,18−25] Thus, efficient and economical transformation of their major components, triglycerides, into simple fatty derivatives is highly sought for further preparation of sustainable monomers, polymers, and materials.

Functional groups in triglycerides offer versatile organic reactions for derivatization, such as hydrolysis,[26] transesterification[27] and amidation[28] for ester groups, hydrogenation,[29] oxidation,[30,31] polymerization,[32,33] epoxidation,[34] addition,[9,35,36] and metathesis[37] for double bonds. Among these reactions, the most successful reaction in commercialization of triglycerides is their transesterification into fatty esters, mostly in the presence of methanol.[38] On the other hand, polymeric materials based on these derivatives are mostly thermosets, like alkyd resins, epoxy resins and polyurethane resins, resulting from their inherent multifunctional properties. Non-cross-linked linear polymers from plant oils have been much less reported. Plant oil based 2-oxazoline monomer has been prepared and polymerized via microwave promoted cationic ring-opening polymerization.[39] Recently, a soy-derived vinyl ether monomer was prepared through the transesterification reaction with 2-vinyloxy ethanol and polymerized by cationic polymerization to afford linear polymers.[40] Such monomers are desirable as they can eventually transform triglycerides into fatty-derived thermoplastic polymers with high atom efficiency.[41]

In synthetic organic chemistry, amidation of unactivated esters with amino alcohols assisted by a catalyst (e.g., lipases,[42,43] inorganic base,[44] organic base[45,46]) has been widely explored to form *N*-hydroxyalkyl amides, partially because of the importance of amide group in many areas, like drug development,[47] polymers,[48,49] and asymmetric catalysis.[50] It is generally believed that the reaction between esters and amino alcohols follows consecutive transesterification and rearrangement via O−N intramolecular acyl migration to form amides.[51−53] The choice of an appropriate base is critical for obtaining high yield for this reaction. Both inorganic and organic bases were used to promote the catalytic amidation with over 80% yields. Naturally derived surfactants and lubrication additives have been prepared through the amidation of triglycerides with amino alcohols using both homogeneous and solid base catalysts.[54,55]

Inspired by the above-mentioned pioneer work, herein we report strategies for the preparation of oil based monofunctional monomers and thermoplastic polymers using derivatives from the base-catalyzed amidation of plant oils. Specifically, various amino alcohols were utilized in converting triglycerides into *N*-hydroxyalkyl fatty amides with the aid of sodium methoxide to provide precursors for further derivatization (Scheme 1). The amidation process was achieved with nearly quantitative yields in the absence of column chromatography,

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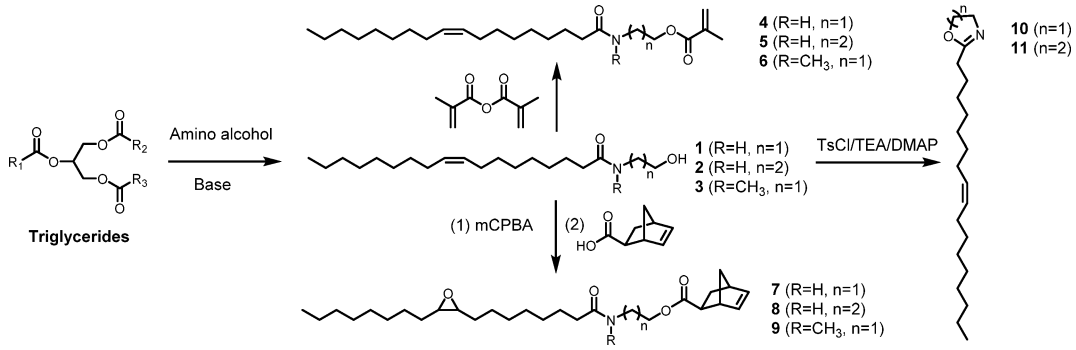
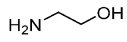
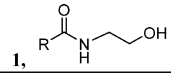
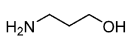
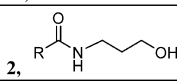
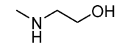
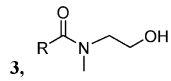
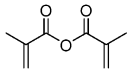
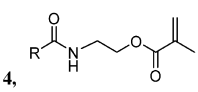
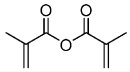
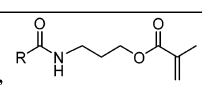
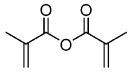
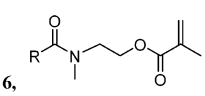
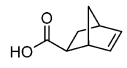
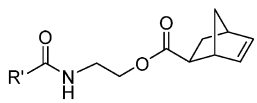
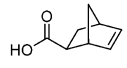
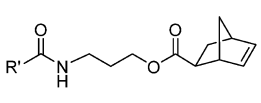
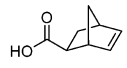
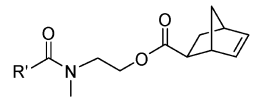
Scheme 1. Derivatization of Triglycerides into *N*-Hydroxyalkyl Fatty Amides and Corresponding Monomers[a]



[a]The fatty structure was represented by the oleic group only for the purpose of simplification.

Table 1. Amidation of HOSO with Amino Alcohols and Further Preparation of Fatty Monomers

Entry	Reactant 1	Reactant 2	Product	Solvent	Yield
1	HOSO		 **1,**	None	95%
2	HOSO		 **2,**	None	95%
3	HOSO		 **3,**	None	97%
4	**1**		 **4,**	None	96%
5	**2**		 **5,**	None	96%
6	**3**		 **6,**	None	98%
7	Epoxidized **1**		 **7,**	THF	96%
8	Epoxidized **2**		 **8,**	THF	96%
9	Epoxidized **3**		 **9,**	THF	98%
10	**1**	TsCl	 **10,**	DCM	97%
11	**2**	TsCl	 **11,**	DCM	97%

thus much appealing for sustainability. *N*-hydroxyalkyl fatty amides were further converted into noncyclic methacrylate monomers, and cyclic norbornene monomers and imino ether monomers (oxazoline and oxazine). Selected monomers were polymerized to validate the feasibility toward versatile polymers. The subtle structural variation in *N*-hydroxyalkyl amides led to polymers with drastically different properties, highlighting the opportunities for the amidation process in the preparation of biorenewable polymers and materials from plant oils.

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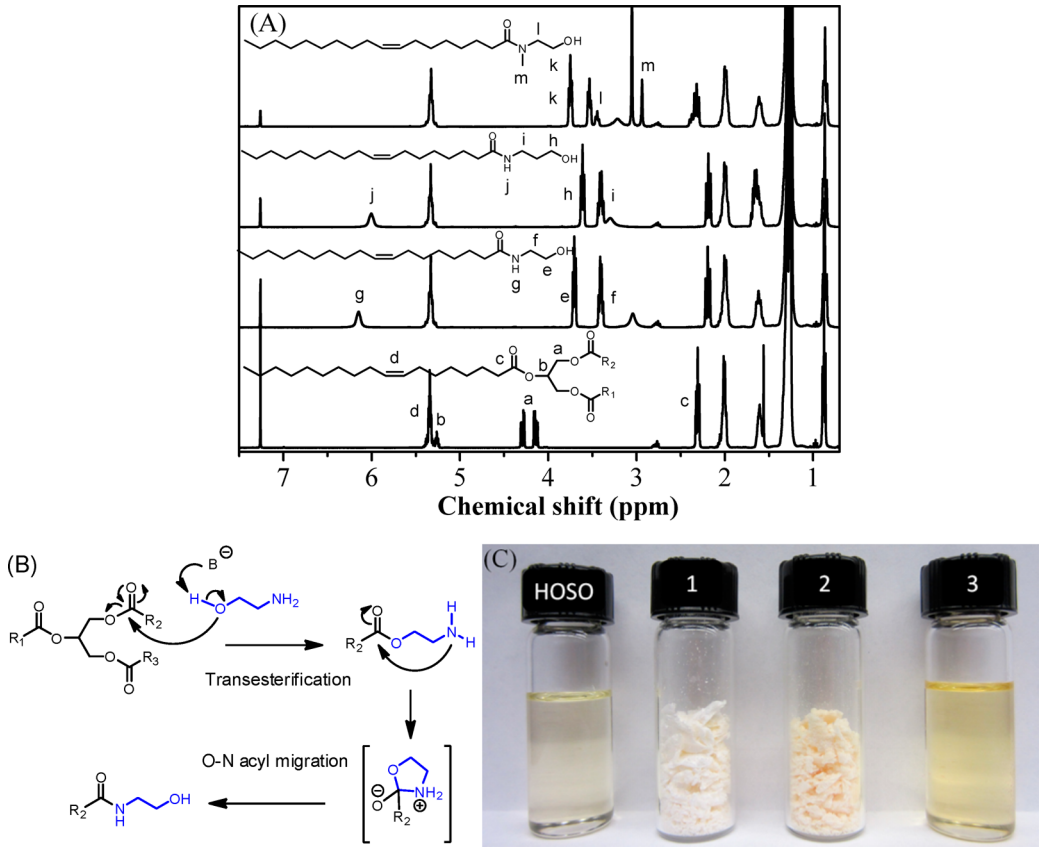

Figure 1. (A) ^{1}H NMR spectra of HOSO and *N*-hydroxyalkyl fatty amides **1**, **2**, and **3**. (B) Proposed mechanism for the amidation of triglycerides with amino alcohols, ethanol amine used as an example. (C) Photos of HOSO, **1**, **2**, and **3** at room temperature.

RESULTS AND DISCUSSION

From Triglycerides to Fatty Amide Derivatives. High oleic soybean oil (HOSO), which contains an average of three double bonds per triglyceride, was used as the representative plant oil in this study. Amidation of unactivated esters into *N*-hydroxyalkyl amides is typically carried out via a base-catalyzed reaction, which involves transesterification and subsequent rearrangement via O−N intramolecular acyl migration. A variety of bases have been explored, including inorganic hydroxides and organic bases such as *N*-heterocyclic carbenes.[44,46] Sodium methoxide was chosen as the base in consideration of a homogeneous reaction media and facile purification process.

In a typical procedure, an amino alcohol was mixed with HOSO, followed by the addition of sodium methoxide to promote the amidation process (Scheme 1). After the reaction, *N*-hydroxyalkyl fatty amides were obtained by simply washing the reaction mixture with brine water to remove catalysts and glycerol, a side product from amidation. Using different amino alcohols, three fatty derivatives, labeled as **1**, **2**, and **3**, were prepared with yields nearly 100% (Table 1). A typical structure of *N*-hydroxyalkyl fatty amide based on the oleic group is shown in Scheme 1, as 75% of the fatty acid chains in HOSO were composed of oleic acid. The fatty amide structures were confirmed by ^{1}H NMR, as presented in Figure 1A. The spectra show the complete disappearance of protons at 5.2 ppm (−CH−) and 4.1−4.3 ppm ($-CH_2-$), associated with the glycerol core of HOSO. New peaks appeared at 3.4 ppm ($-NH-CH_2-$) and 3.7 ppm ($-O-CH_2-$) in compound **1**, 3.4 and 3.6 ppm in compound **2**, and 3.5 and 3.8 ppm in compound **3**, corresponding to methylene protons in the *N*-hydroxyalkyl groups. Peaks for the proton on nitrogen (−NH−) were found at 5.8 ppm in **1** and 5.9 ppm in **2**. A peak for the methyl group on nitrogen ($-N-CH_3-$) was shown at 3.0 ppm in **3**. The amidation process was also monitored by FTIR, which observed the diminishing ester carbonyl peak at ∼1763 cm^{-1} and the increasing amide carbonyl group at ∼1640 cm^{-1} (Figure S1). The complete disappearance of the ester group accompanied by the formation of amide bond demonstrated a quantitative conversion. As shown in many reports, a proposed mechanism of the above transformation is probably involved with cascade transesterification and acyl migration (Figure 1B). Transesterification of esters with alcohol under basic conditions is very common. The acyl migration subsequently led to more stable amides via a possible cyclic intermediate, which could be confirmed with the formation of cyclic imino ether, as described in a later section of this paper.

These fatty derivatives have quite different physical appearance. Both compounds **1** and **2** are secondary amides and are solid at room temperature, while tertiary amide compound **3** is a liquid (Figure 1C). The difference in their physical states is certainly due to the difference in their molecular structures. The presence of N−H group in **1** and **2** promotes the formation of H-bonds.

From *N*-Hydroxyalkyl Fatty Amides to Fatty Monomers. We attempted to convert these *N*-hydroxyalkyl fatty amides into a variety of noncyclic and cyclic monomers using facile reactions (Scheme 1). We first prepared methacrylate monomers.[56] Initially methacryloyl chloride was used for direct

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halide displacement to form esters. However, it was found later that such-prepared monomers often led to the formation of cross-linked polymers. One possible reason was associated with the formation of dimethacrylate between methacryloyl chloride. Thus, column chromatography must be needed to make highly pure monomers. We then employed a much more efficient transesterification reaction with the aid of methacrylic anhydride and catalytic DMAP. The reaction was very smooth and went to nearly 100% conversion with a ratio of 1:1 between *N*-hydroxyalkyl fatty amides and methacrylic anhydride without the use of any organic solvent.

Figure 2A shows ^{1}H NMR spectra of methacrylate monomers **4**, **5**, and **6**. The methylene group (−O−CH_2−)

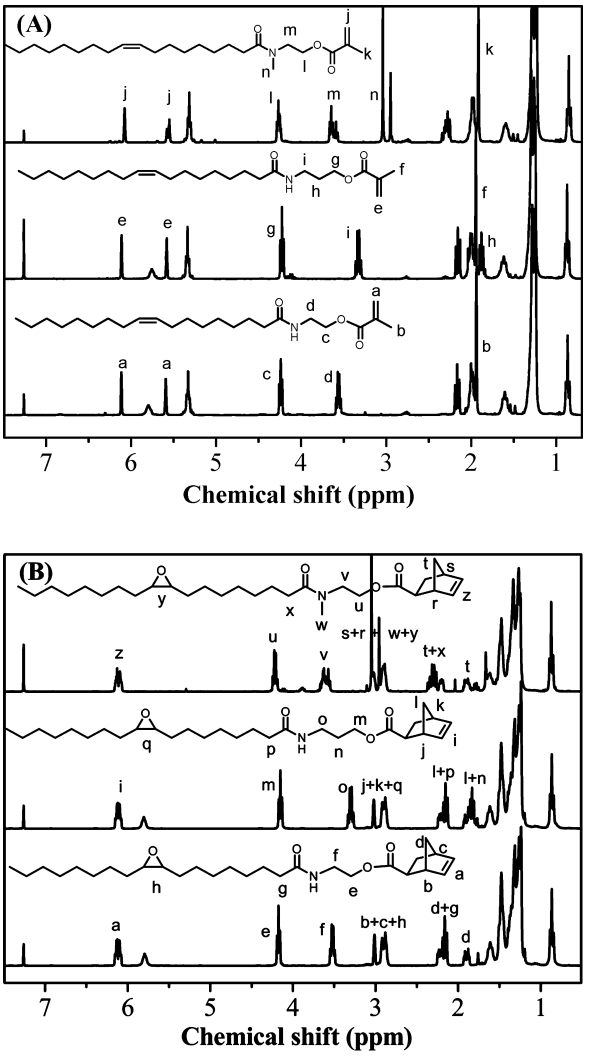

Figure 2. ^{1}H NMR spectra of (A) methacrylate monomers; (B) norbornene monomers from *N*-hydroxyalkyl fatty amides by anhydride assisted esterification.

at around 3.5 ppm shifted to 4.2 ppm after the formation of the ester group. New peaks at 6.1 ppm (−CH_2═C−), 5.6 ppm (−CH_2═C−) and 2.0 ppm (═C−CH_3) corresponded to vinyl and methyl protons next to the ester group. The successful synthesis of monomers **4**−**6** was also confirmed by ^{13}C NMR (Figure S3). This process was superior to other methacrylation methods, as it only required aqueous solution wash for the purification of monomers.

We also prepared norbornene monomers from these *N*-hydroxyalkyl fatty amides for ring-opening metathesis polymerization (ROMP) to make poly(norbornene)s. In order to eliminate the influence of double bonds from the fatty chains that could interfere in ring-opening metathesis polymerization, epoxidation of **1**, **2**, and **3** was done with the aid of mCPBA to transform the double bonds into oxirane rings (Figure S4). Hydrogen peroxide could also be used to perform epoxidation in a more environment-benign process.[57,58] Esterification between epoxidized *N*-hydroxyalkyl fatty amides and exo-5-norbornenecarboxylic acid resulted in norbornene monomers containing oxirane groups, labeled as **7**, **8**, and **9**. The coupling reaction, catalyzed by DMAP with the assistance of trimethyl acetic anhydride that would form mixed anhydride with exo-5-norbornenecarboxylic acid,[56] was more efficient than an EDC/DMAP-assisted reaction. Almost 100% conversion was obtained after 12 h at 60 °C, when the acid and anhydride were both used in 1.1 equiv to the hydroxyl group. As shown in Figure 2B, the peak for the methylene protons (−O−CH_2−) shifted completely to 4.1−4.3 ppm with the formation of ester bonds. Also, new peaks from the carbonyl group and double bond were observed in ^{13}C NMR spectra of norbornene monomers (Figure S5).

Next, we explored the possibility to prepare cyclic monomers from *N*-hydroxyalkyl fatty amides. Cyclic imino ethers of five or six-membered systems are reactive monomers for making poly(*N*-acylalkylenimine),[59−61] which has numerous applications such as thermoresponsive hydrogels and polymer surfactants.[62,63] Such cyclic monomers are generally prepared through a condensation process between alkyl acids or nitriles with amino alcohols, which involves a high temperature catalytic system.[41] Specifically, cyclic imino ethers derived from fatty acids need high vacuum distillation for purification. One example of plant oil-derived cyclic imino ethers was a soybean oil based 2-oxazoline monomer,[39] which was prepared under a harsh condition with the use of a titanium catalyst under 200 °C. We carried out a direct dehydration of *N*-hydroxyalkyl fatty amides **1** and **2** to make cyclic imino ethers **10** and **11** in a milder condition (Scheme 1). The dehydration was assisted with *p*-toluenesulfonyl chloride, triethylamine and DMAP in a solution of DCM at room temperature.[50] Complete conversion was observed within 12 h. Both ^{1}H NMR (Figure 3A) and ^{13}C NMR (Figure S6) confirmed the structures of **10** and **11**. The peak from the N−H proton at around 6.2 ppm disappeared with the formation of the cyclic structure. The reaction followed a possible mechanism of in situ tosylation and subsequent base-catalyzed cyclization (Figure 3B). The current process provides a facile and milder strategy to obtain plant oil based cyclic imino ethers when compared with the traditional condensation method.

Representative Polymers from Fatty Monomers. To validate the impact of versatile *N*-hydroxyalkyl fatty amides on the properties of soy oil-derived polymers, we first selected methacrylate monomers for free radical polymerization (Scheme 2).

As shown in Table 2, all methacrylate monomers were polymerized to achieve conversions >90%. The N−H containing monomers **4** and **5** were found to be polymerized much faster than **6**. Over 90% conversion was obtained at 70 °C after 6 h for **4** and **5**, while it took 20 h for **6** to reach similar conversion at 80 °C. These polymers are very soluble in many organic solvents (e.g., DCM, THF, toluene), without noticeable formation of any cross-linked materials. Figure 4 shows the ^{1}H

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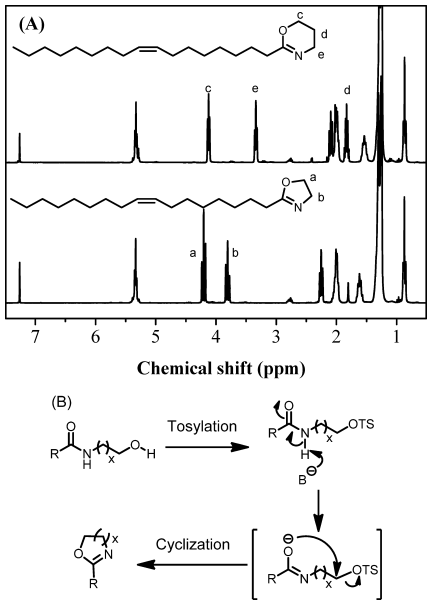


Figure 3. (A) ^{1}H NMR spectra of cyclic imino ethers derived from *N*-hydroxyalkyl fatty amides; (B) proposed mechanism for the formation of cyclic imino ethers.

NMR spectra of polymers **P1**−**P3**. The double bond in the fatty side chain was found to be stable during the polymerization process as the internal double bonds were not very active in radical polymerization.

The influence of monomer structure on the polymer properties was first observed from the physical appearance of polymers **P1**, **P2**, and **P3**. Both **P1** and **P2** can form free-standing films like thermoplastics, while **P3** is very tacky and could not form free films. DSC curves showed that the glass transition temperatures (T_g) are 45 and 30 °C, respectively, for **P1** and **P2** (Figure 4), while **P3** displayed a much lower T_g around −6 °C.

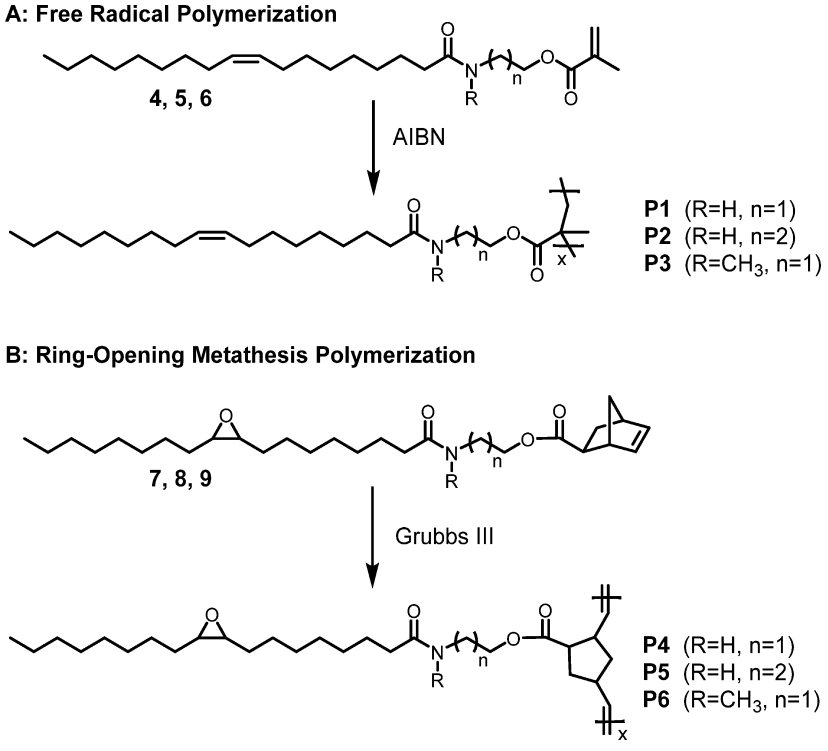
Table 2. Properties of Polymers P1−P6 Prepared by Free Radical Polymerization of Methacrylate Monomers (4−6) and ROMP of Norbornene Monomers (7−9)

polymer	monomer	$Đ$	M_n (g/mol)	T_g (°C)
P1	**4**	1.5	15 300	45.5
P2	**5**	2.2	49 100	30.0
P3	**6**	1.8	63 000	−6.2
P4	**7**	1.2	22 300	−27.0
P5	**8**	1.1	22 900	−30.7
P6	**9**	1.2	89 100	−32.7

Compared with **P3**, the higher T_g of **P1** and **P2** could be explained by the presence of hydrogen bonding from the secondary amide group. As shown in Figure 2 and Figure 4, the signal for the amide proton underwent a low-field shift from a narrow peak at 5.8 ppm to a broadened peak around 7.0 ppm after the polymerization, indicating the formation of hydrogen bonding between pendant amide groups.[64] Thermogravimetric analysis (TGA) indicated that polymer **P1** shows two degradation stages. According to the derivative TGA curves of **P1**−**P3**, the two maximum degradation temperature of **P1** was calculated to be 320.7 and 465.2 °C, while **P2** and **P3** show better thermal stability with maximum degradation temperatures of 378.2 °C, 412.5 °C, 465.2 °C, and 388.5 °C, 432.2 °C respectively (Figure S8). These results demonstrated that methacrylate polymers **P1**−**P3** have high thermal stability.

Due to the intermolecular hydrogen bonding and thus high T_g, **P1** and **P2** may exhibit mechanical properties like thermoplastics. Moreover, due to the facile preparation, we carried out the synthesis of polymer **P2** at a one pound scale.

Scheme 2. (A) Free Radical Polymerization of Methacrylate Fatty Monomers and (B) ROMP of Norbornene Monomers



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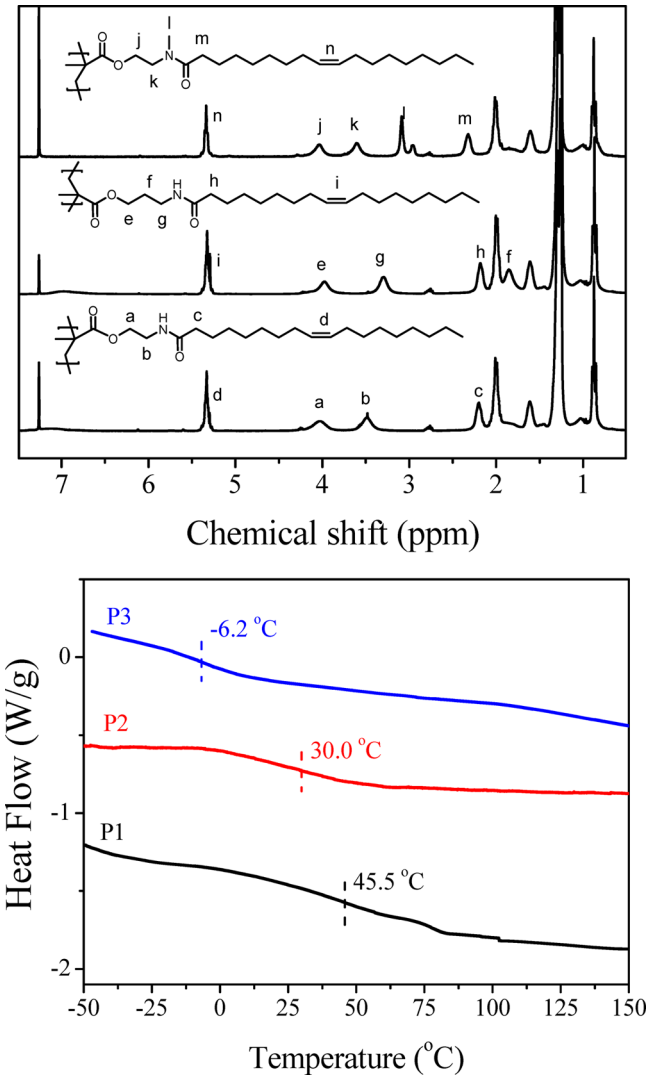

Figure 4. ^{1}H NMR spectra and DSC curves of polymers **P1**−**P3** prepared by free radical polymerization.

Figure 5A presents a picture of ∼1 lb **P2** in a 2 L beaker with a free-standing film of **P2**. Dog-bone specimens were cut from the film for tensile testing (Figure 5B). A photo of **P3** was also given in Figure 5C, and the polymer was too soft to form a film. A typical nominal stress-nominal strain curve of **P2** obtained at room temperature is shown in Figure 5D. The elongation at break was found to be 140% with stress at break about 2.0 MPa. The drastic difference between **P2** and **P3** probably results from the chemical structure of the side chains as illustrated in Figure 5E. Polymer chains of **P2** can form strong interaction with each other through hydrogen bonding with N−H bond on the secondary amide group as the donor and carbonyl oxygen as the acceptor, while no such significant interaction presents between polymer chains of **P3**, which has tertiary amide group.

Ring-opening metathesis polymerization (ROMP) of norbornene monomers **7**, **8**, and **9** were then carried out in the presence of Grubbs III catalyst.[65] The properties of norbornene polymers **P4**−**P6** were summarized in Table 2. The polymerization went to nearly complete conversion in less than 20 min, as confirmed by the disappearance of the double bond from norbornene ring at 6.1−6.2 ppm and the appearance of double bond in the polymer backbone at 5.1−5.5 ppm (Figure 6). Peaks associated with the pendant chains were retained after the polymerization, which indicated no cross-linking occurred in the absence of double bond in the side chain.

The T_g of **P4**−**P6** was determined from the DSC thermograms, as shown in Figure 6. The T_g of all polymers prepared by ROMP was around −30 °C. The presence of secondary amide groups in the side chains of **P4** and **P5** did not lead to appreciable difference from polymer **P6** with tertiary amide group. It suggested that hydrogen bonds from the pendant amide groups in **P4** and **P5** could be weaker than those in polymers **P1** and **P2**. Additional evidence can be found by comparing ^{1}H NMR spectra of these polymers (Figure 4 and Figure 6), the chemical shifts of amide proton in **P4** and **P5** were less than those in **P1** and **P2** after the polymerization. The T_gs of **P4**−**P6** are comparable with those of poly(norbornene)s from saturated C_{18} fatty ester of norbornene methanol (T_g = −32 °C and T_m = 5.9 °C), as reported by the Meier group.[66] However, no melting point was observed for **P4**−**P6**, possibly due to the presence of oxirane ring within the side chain. **P4**−**P6** showed good thermal stability with similar two stage degradation behaviors to **P1**−**P3** (Figure S10).

CONCLUSIONS

In conclusion, highly efficient catalytic amidation reactions between plant oils with amino alcohols were utilized for the preparation of fatty amide derivatives, which were then used as a powerful chemical platform for further derivatization into a variety of monomers and thermoplastic polymers. Most plant oil derived intermediates and monomers (methacrylates, norbornenes and cyclic imino ethers) were obtained with nearly quantitative yields without laborious column separation. Selected monomers were further polymerized to yield polymers that exhibit appreciable structure-dependent properties. The strategy developed in the current work might pave a path for the facile preparation of renewable monomers and thermoplastic polymers with targeted properties from plant oils.

EXPERIMENTAL SECTION

Materials. Plenish high oleic soybean oil (HOSO) was provided by Dupont. Ethanolamine (99%, Aldrich), 3-amino-1-propanol (99%, Aldrich), *N*-methyl ethanolamine (98%, Aldrich), methacrylic anhydride (94%, Aldrich), trimethylacetic anhydride (99%, Aldrich), exo-5-norbornenecarboxylic acid (97%, Aldrich), 4-dimethylaminopyridine (DMAP, 99%, Aldrich), Grubbs catalyst (2nd Generation, Aldrich), sodium methoxide (5.4 M solution in methanol, 30 wt %, Acros Organics), triethylamine (TEA, 99%, Alfa Aesar), *p*-toluenesulfonyl chloride (TsCl, 98%, Alfa Aesar), 3-chloroperbenzoic acid (mCPBA, 70−75%, Alfa Aesar), and 5-norbornene-2-methylamine (mixture of isomers, 98%, TCI) were used as received. Grubbs Catalyst (3rd generation) was prepared according to a previous report.[67] Azobis(isobutyronitrile) (AIBN, 98%, Aldrich) was recrystallized from methanol. All other reagents were from commercial resources and used as received unless otherwise mentioned.

Characterizations. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Mercury 300 spectrometer with tetramethylsilane (TMS) as an internal reference. Molecular weights and distribution of polymers were determined using a gel permeation chromatography (GPC) equipped with a 2414 RI detector, a 1525 Binary Pump and three Styragel columns. The columns consisted of HR 1, HR 3 and HR 5E in the effective molecular weight ranges of 100−5K, 500−30K, and 2K−4M respectively. THF was used as eluent at 35 °C with a flow rate of 1.0 mL/min. The system was calibrated with polystyrene standards obtained from Polymer Laboratories. GPC samples were prepared by dissolving the sample in THF with a concentration of 3.0 mg/mL and passing through microfilters with average pore size of 0.2 μm. Fourier transform infrared spectrometry (FTIR) spectra were taken on a

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Macromolecules XXXX, XXX, XXX−XXX

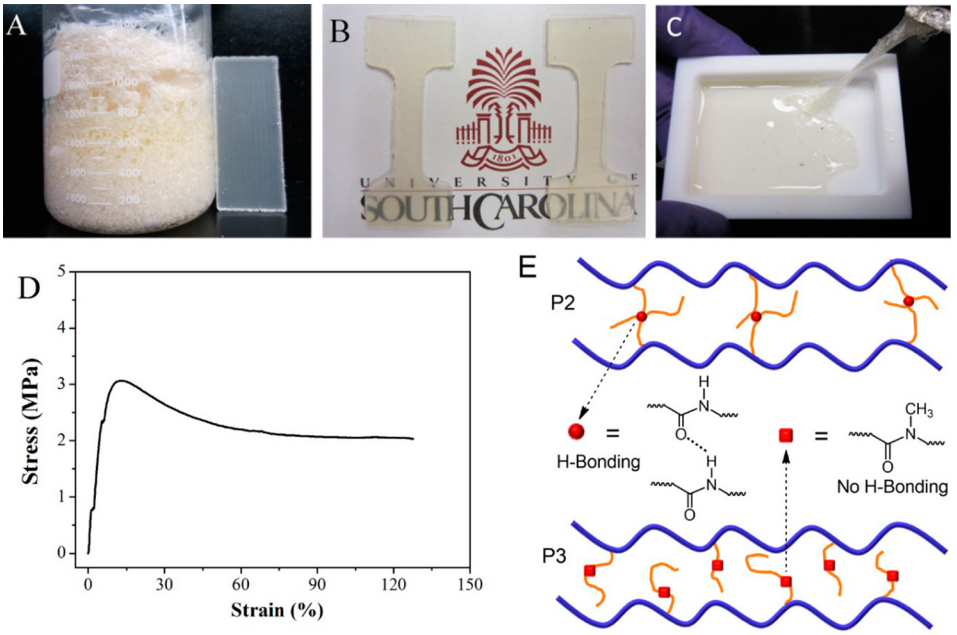

Figure 5. (A)Polymer **P2** (1 lb) with a solvent-cast film; (B) specimens for tensile-stress test; (C) **P3** in a mold; (D) stress−strain curve of **P2**; (E) illustration of H-bonding in **P2**, in comparison with **P3**.

PerkinElmer spectrum 100 FTIR spectrometer. The glass transition temperature (T_g) of polymers was tested through differential scanning calorimetry (DSC) conducted on a DSC 2000 instrument (TA Instruments). Samples were first heated from −70 to +200 °C at a rate of 10 °C/min. After cooling down to −70 °C at the same rate, the data were collected from the second heating scan. A 10 mg amount of each sample was used for the DSC test with nitrogen gas at a flow rate of 50 mL/min. Thermogravimetric analysis (TGA) was conducted on a Q5000 TGA system (TA Instruments), ramping from 25 to 600 °C with a rate of 10 °C/min. Each test cost around 10 mg of the sample. Tensile stress−strain testing was carried out with an Instron 5543A testing instrument. The films were prepared by casting a DCM solution of the polymer in a PTFE mold. After the evaporation of solvent, the film was put under vacuum for 4 h at room temperature and 4 h at 60 °C. Dog-bone shaped specimens were cut from the film with a length of 20 mm and width of 5.0 mm before tested at room temperature with the crosshead speed of 20 mm/min.

*Synthesis of N-hydroxyalkyl Fatty Amides (**1**−**3**).* HOSO (100 g, around 0.344 mol ester group) was charged into a 500 mL round-bottom flask and purged with nitrogen in an 100 °C oil bath for 1 h before cooling down to 60 °C. For the preparation of compound **1**, ethanolamine (27 g, 0.443 mol) was added to the cooled HOSO. Then, sodium methoxide dissolved in methanol (1.5 mL, 0.008 mol) was added to the mixture. The solution was kept stirring at 60 °C until the complete conversion of the ester bond as confirmed by FTIR. Normally, it took around 4 h to obtain complete conversion for all the amidation process. The crude product was poured into dichloromethane and washed twice with brine before being dried over anhydrous magnesium sulfate. After filtration and removing the solvent under reduced pressure, the product was obtained in yield between 95%−97%. Compound **2** and **3** were prepared in the same method using amino propanol and *N*-methyl ethanolamine as the amidation agent.

*Synthesis of Methacrylate Monomers (**4**−**6**).* Compound **3** (102 g, 0.300 mol), methacrylic anhydride (49 g, 0.300 mol) and DMAP (0.366g, 0.003 mol) were charged together into a 500 mL round-bottom flask and put into an oil bate set at 60 °C. After stirring overnight, 10 mL of deionized water was added into the reactor and stirred for 1 h. The solution was then poured into DCM, washed with brine for twice and dried with anhydrous magnesium sulfate. After filtration and evaporation of DCM, compound **6** was obtained in a state of liquid at room temperature. Compound **4** and **5** were prepared in the same method.

Epoxidation of N-Hydroxyalkyl Fatty Amides. Compound **1** (10.2 g, 30 mmol) was dissolved together with mCPBA (9.0 g, 36 mmol) in 100 mL DCM and put into an ice−water bath. Na_2CO_3 (4.5 g, 42 mmol) was added into the solution. The solution was kept in ice−water bath for 30 min and stirred at room temperature for 3 h. The product was subsequently washed with $Na_2S_2O_3$, $NaHCO_3$, NaCl before dried over anhydrous $MgSO_4$. The dried solution was filtered through a short column with basic Al_2O_3. With the evaporation of DCM, the epoxidized product was obtained. The epoxidized compound **1** and **2** were solid, while epoxidized compound **3** is a liquid.

*Synthesis of Norbornene-Functionalized Monomers (**7**−**9**).* Epoxidized compound **1** (1.0 g, 2.91 mmol), pivalic anhydride (0.6 g, 3.2 mmol, exo-5-norbornenecarboxylic acid (0.441 g, 3.2 mmol) and DMAP (3.7 mg, 0.03 mmol) were dissolved in 3 mL THF and stirred in an oil bath of 60 °C. After stirring for 20 h, 1.0 mL water was added into the solution and stirred for 1 more hour. DCM was added to dissolve the product and washed with $NaHCO_3$ and NaCl aqueous solution. The product **7** was obtained after drying the organic phase and evaporation the solvent. Monomers **8** and **9** were prepared with the same method.

*Synthesis of Cyclic Imino Ethers (**10** and **11**).* Compound **1** (3.25g, 10 mmol), DMAP (0.122g, 1 mmol), and TEA (3.3 mL, 22 mmol) were dissolved within 40 mL of DCM in a 100 mL round-bottom flask. The solution was put into an ice−water bath and stirred for 30 min before TsCl (1.91g, 10 mmol) dissolved in DCM was added. The reaction was stirred at room temperature for 20 h and the solution was washed subsequently by aqueous solution of NH_4Cl (twice), $NaHCO_3$, and water. The organic phase was dried by anhydrous $MgSO_4$ and flushed through silicone gel to get a liquid product **10**. Compound **11** was prepared in a similar way from compound **2**.

*Synthesis of Polymer **P1** and **P2** by Free Radical Polymerization.* Monomer **4** (5.0 g, 12.7 mmol) and AIBN (0.02 g, 0.12 mmol) were dissolved in 10 mL toluene. The solution was purged with nitrogen for 15 min and put into a preheated oil bath set at 70 °C. After 6 h, the solution was directly poured slowly into methanol at room temperature under stirring. The polymer at the bottom was washed twice with methanol and dried under vacuum at 60 °C to get **P1**. Polymer **P2** was prepared when monomer **5** was used.

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Macromolecules XXXX, XXX, XXX−XXX

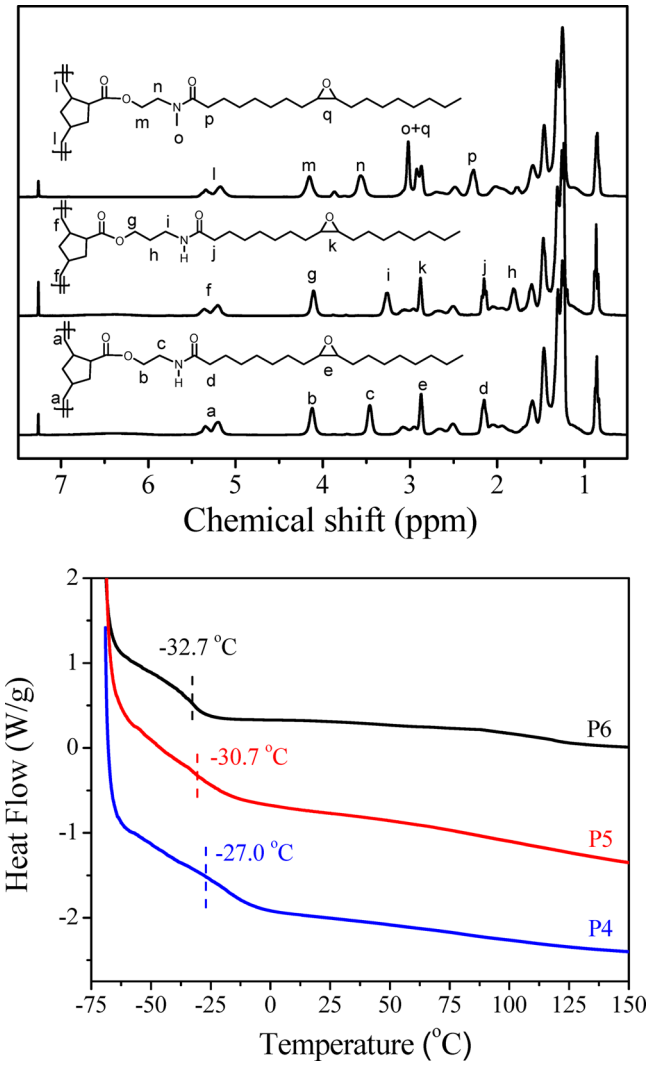

Figure 6. ^{1}H NMR spectra and DSC curves of polymers **P4**–**P6** prepared by ROMP.

Synthesis of Polymer ***P3*** *by Free Radical Polymerization.* Monomer **6** (5.0 g, 12.7 mmol) and AIBN (0.02 g, 0.12 mmol) were dissolved in 5 mL toluene. The solution was purged with nitrogen for 15 min and put into a preheated oil bath set at 80 °C. After polymerization for 20 h, the solution was directly poured into methanol at room temperature under stirring. The polymer at the bottom was washed twice with methanol and dried under vacuum at 60 °C.

Synthesis of Polymers ***P4***–***P6*** *by ROMP.* Norbornene monomer **7** (300 mg, 0.645 mmol) was dissolved in 5.0 mL DCM and nitrogen was purged through the solution for 10 min. Grubbs third catalyst (2.5 mg, 0.0034 mmol) dissolved in 1.0 mL was purged with nitrogen and transferred into the monomer solution to start the polymerization. To the reacting solution, several drops of ethyl vinyl ether were added to stop the polymerization after 20 min and stirred for another 10 min when full conversion of the monomer was confirmed by ^{1}H NMR. Methanol was added into the concentrated solution to precipitate the polymer out followed by washing with methanol for twice. The polymers were dried under vacuum overnight to get **P4**. **P5** and **P6** were prepared from monomers **8** and **9**.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional experimental data including FTIR and ^{1}H and ^{13}C NMR spectra, GPC traces, and TGA and DTG curves. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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