

# Effects of Catalyst Type and Reaction Parameters on One-Step Acrylation of Soybean Oil

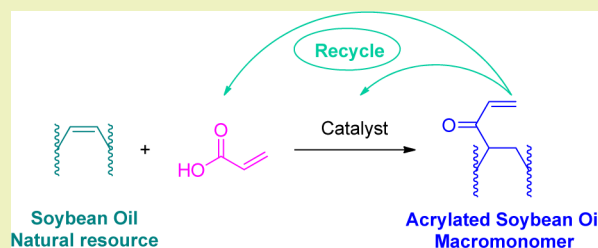
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## Supporting Information

**ABSTRACT:** Unlike the conventional synthesis of acrylated soybean oil (ASO) that usually involved several steps, a novel one-step reaction synthesis of ASO was introduced in this study. ASO was prepared directly from the addition reaction of soybean oil (SO) and acrylic acid (AA). Effects of catalyst type, reaction stoichiometry, and conditions of the one-step synthesis of ASO were investigated in detail. The products were characterized using  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, and FTIR.  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  was found to be the most effective catalyst for this addition reaction. The results indicated that high catalyst and AA concentrations greatly increased the conversion to ASO and accelerated the reaction. Side reactions, such as polymerization of AA and transesterification between triglycerides and AA, were also noted during the reaction and were examined using  $^1\text{H}$  NMR. The feasibility of recovering and reusing the catalyst and excess AA was evaluated.

**KEYWORDS:** Soybean oil, Acrylated soybean oil, Acrylation, Biobased polymers



## INTRODUCTION

Abundantly available vegetable oils are important feedstocks for many industrial chemicals and materials. Utilization of various oils for polymer materials,<sup>1–6</sup> especially the unsaturated polyesters, has received extensive investigation in recent years. Soybean oil (SO) is the most inexpensive vegetable oil and also the most produced, making it a very attractive alternative to fossil resources in certain applications. Because SO has multiple carbon–carbon doubles in its triglyceride structure, SO can be used as a macromonomer to build polymer directly by cationic polymerization.<sup>7</sup> However, these internal *cis*-double bonds of SO exhibit fairly low reactivity for free radical polymerization, which presents a major limitation for the wide application of SO-based polymer materials.<sup>8,9</sup> Introduction of easily polymerizable groups into the triglyceride structure of oil is the main approach to overcoming this obstacle. Acrylation or similar functionalizations are the most common means to introduce polymerizable groups to the structures of vegetable oils.<sup>10–14</sup> Acrylated vegetable oils have been reported as thermal and photocurable coating materials in many applications.<sup>15–18</sup> Such polymerizable groups are most conveniently introduced through reacting epoxidized oil with acrylic acid. Some hydroxyl-containing natural oils such as castor oil can form maleate half-esters through reactions with maleic anhydride, which were subsequently used as alternative prepolymers in unsaturated polyester applications.<sup>19</sup>

Because the carbon–carbon double bond is prone to capture electrophiles including protons, it would be desirable to synthesize acrylated vegetable oils via direct electrophilic addition of acrylic acids in terms of atom economy, energy savings, and cost effectiveness. In fact, addition of carboxylic acid and carbon–carbon double bond is one of the typical

methods for ester synthesis.<sup>20</sup> The addition reactions of carboxylic acids and carbon–carbon double bonds have received significant investigation in the literature, but most knowledge on this type of addition is learned from the addition reactions of small alkene molecules. Table 1 gives some examples of such addition reactions and the catalysts used.

The reactivity of enes was determined by substituents and steric hindrance of double bonds. Generally, the reactivity of the enes follows the order of bicycloalkene > small ring cycloalkane > large ring cycloalkane >  $\text{RCH}=\text{CH}_2$  >  $\text{RCH}=\text{CHR}$ . The reactivity of a carboxylic acid is determined by its acidity and molecular size, and higher acidity and smaller molecular size favors higher reactivity. For unsaturated fatty acids, both the intermolecular<sup>31,32</sup> and intramolecular<sup>27</sup> additions of double bonds and carboxylic acid need more extreme reaction conditions. The reason is the high steric hindrance of double bonds and low acidity of carboxylic acid in the molecules. However, the reaction for preparing such intermolecular addition products (so-called estolides) generally requires a large quantity of inorganic protic acid, long reaction time (up to 168 h), high temperature (up to 150 °C), and/or vacuum.<sup>33–35</sup>

Except in our recent report, direct synthesis of acrylated soybean oil via addition of acrylic acid<sup>36</sup> and SO has not been reported. There are only two similar reactions reported that could form free radical polymerizable derivatives from the common vegetable oil in one step. One reaction was the bromoacrylation of castor oil that involved acrylic acid and a

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Table 1. Catalysts of Reactions between Carboxyl Groups and C=C

acids	enes	catalysts	references
(methyl)acrylic acids	(cyclo)alkenes	polyphosphoric acid	21
F-carboxylic esters	1-octene	N/A	22
aliphatic acids	(cyclo)alkenes	SO <sub>3</sub> H-functionalized ionic liquids	23
aliphatic acids	cycloalkenes	sulfamic acid	24
phenols and carboxylic Acids	(cyclo)alkenes	Ph <sub>3</sub> PAuCl	25
phenols, carboxylic acids and tosylamides	(cyclo)alkenes	trifluoromethanesulfonic acid	26
olefinic acids	olefinic acids	Amberlyst 15, Nafion SAC-13, and Nafion NR-50	27
carboxylic acids	(cyclo)alkenes	iron triflate	28
2-phenylbenzoic acid	(cyclo)alkenes	Ru(II)–xantphos	29
acrylic acid	cycloalkenes	BF <sub>3</sub> ·Et <sub>2</sub> O	30
oleic acid	oleic acid	silica-supported HClO <sub>4</sub>	31
oleic acid	oleic acid	HClO <sub>4</sub> , H <sub>2</sub> SO <sub>4</sub> , PTSA, and BF <sub>3</sub> ·Et <sub>2</sub> O montmorillonite K-10 clay	32

large excess of *N*-bromosuccinimide (5.3 equiv of castor oil),<sup>37,38</sup> and the other was acrylamido derivatization of sunflower oil and soybean oil via the Ritter reaction at  $-20$  °C using 98% H<sub>2</sub>SO<sub>4</sub> as cosolvent.<sup>9</sup> For the acrylation of the double bonds in vegetable oils, polymerization of acrylic acid and vaporization of acrylic acid (AA) under the reaction conditions are potential concerns. Therefore, the selection of catalyst is very important for achieving the acrylation of the low active double bonds at moderate reaction conditions. Among the reported catalysts, boron trifluoride etherate (BF<sub>3</sub>·Et<sub>2</sub>O) was found to be a highly efficient catalyst for addition of AA to double bonds. Using only 0.33 mol % BF<sub>3</sub>·Et<sub>2</sub>O on the basis of norbornene, the yield of acrylated norbornene reached 80% at 80 °C for 3 h.<sup>30</sup> BF<sub>3</sub>·Et<sub>2</sub>O was also used as a catalyst for the preparation of oleic estolides, and the reaction at 50 °C for 7 days yielded a conversion of 71%.<sup>32</sup> In a recent study, we demonstrated that direct acrylation of SO could be effectively achieved under the catalysis of BF<sub>3</sub>·Et<sub>2</sub>O at 80 °C.<sup>36</sup> High catalyst concentration and large excess AA both greatly increased the conversion to ASO.

In this work, direct acrylation of SO under the catalysis of several different Lewis acids and protic acids were studied in detail and compared. In addition, influences of reaction temperature and stoichiometry on conversion of the double bonds to acrylate and on the possible side reactions were studied in detail. The major objective of this study is to identify the proper catalyst and reaction conditions for direct acrylation of SO. Furthermore, recovery and reuse of the excess reagents were also explored. The results from this study could provide important information for the potential scale-up of the laboratory synthesis in the industrial process.

## EXPERIMENTAL SECTION

**Materials.** Soybean oil (SO) was purchased from MP Biomedicals (Solon, OH). The iodine value of SO was determined by the ASTM D5554-95 (2011) standard method and was found to be 123.4 g/100 g SO, which was equivalent to 205.7g/mol double bonds. Thionyl chloride (SOCl<sub>2</sub>), acrylic acid (AA), and Amberlyst 15 were purchased from ACROS Organics, and the latter was a macro reticular polystyrene-based ion-exchange resin with sulfonic acid groups. Boron trifluoride etherate (BF<sub>3</sub>·Et<sub>2</sub>O), ferric chloride (FeCl<sub>3</sub>), and stannic chloride (SnCl<sub>4</sub>) were purchased from Alfa Aesar. Titanium tetrachloride (TiCl<sub>4</sub>), methanesulfonic acid (MsOH), and 4-methylbenzenesulfonic acid (PTSA) were purchased from Sigma-Aldrich. Hydroquinone (HQ), sodium bicarbonate (NaHCO<sub>3</sub>), diethyl ether (Et<sub>2</sub>O), dichloromethane (DCM), and hexane were

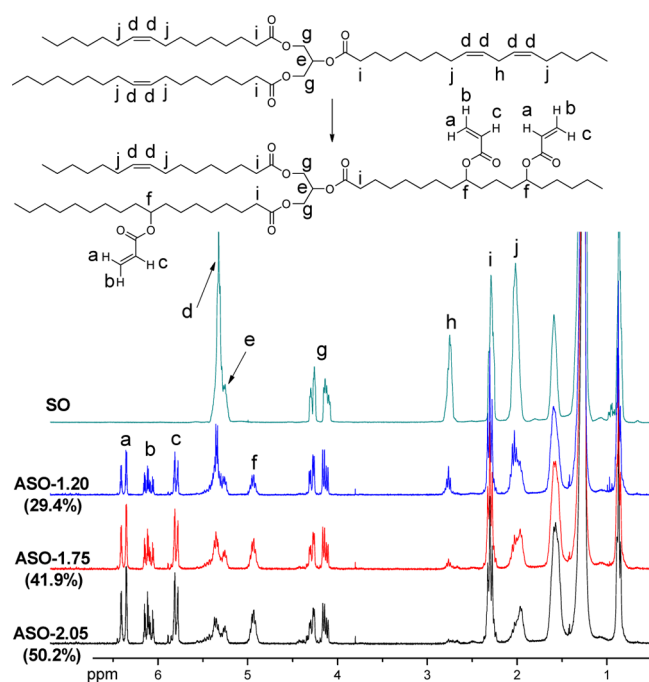
purchased from Fisher Scientific. FeCl<sub>3</sub> and SnCl<sub>4</sub> were dehydrated by refluxing with SOCl<sub>2</sub> prior to use. Other reagents were used as received.

**Synthesis.** SO, AA, and catalyst were charged to a flask with a condenser and reacted under magnetic stirring. Effects of stoichiometry, temperature, and reaction time on the acrylation conversion were studied. On the basis of the size of the reactions, two different workup procedures were employed. For the small size reactions utilized in the investigation of reaction conditions, the reaction mixture was poured into hexane and washed by NaHCO<sub>3</sub> aq and brine to remove AA and catalyst. After the organic layer was dried with MgSO<sub>4</sub>, the solvent was removed to obtain the product. For the large size reactions used to demonstrate the recovery of the catalyst and unreacted AA, the excess AA and catalyst were removed by distillation at 35–45 °C under reduced pressure, and the recovered reagents were collected to be reused. The remaining reaction mixture was poured into hexane and treated similarly following the above procedure for the small size reaction.

**Characterizations.** Proton and carbon-13 nuclear magnetic resonance (<sup>1</sup>H and <sup>13</sup>C NMR) spectra of the samples in deuterated chloroform (CDCl<sub>3</sub>) were recorded using a Varian Mercury Vx 300 at 25 °C and at frequencies of 300 and 75 MHz, respectively. Fourier transform infrared spectrometry (FTIR) analysis was conducted on a Nicolet NEXUS 670 FT-IR spectrometer. The FTIR samples were prepared by casting the DCM solution of the sample onto KBr plates.

## RESULTS AND DISCUSSIONS

**Structural Characterizations and Determination of Degree of Acrylation.** Figure 1 shows the <sup>1</sup>H NMR spectra for SO and ASO and gives their proton attributions. Because the methylene group (H<sub>i</sub>) linked to the carbonyl group in the fatty acid was stable in the reaction and exhibited a distinct chemical shift from that of other protons, its peak was chosen as the internal standard. The triglyceride structure of SO was confirmed by comparing the peak area ratio of H<sub>i</sub> (2.20–2.40 ppm) to H<sub>g</sub> (4.05–4.35 ppm) in SO, which was found to be exactly 6:4. Comparing the peak areas of related protons in the <sup>1</sup>H NMR spectrum of ASO can determine the acrylation degree of the double bonds. The content of the double bonds in the starting SO was determined by comparing the peak areas of H<sub>d</sub> and H<sub>i</sub>. Because the peaks of the double bond protons (H<sub>d</sub>) overlapped with those of the methine protons (H<sub>e</sub>) of the glycerol residue, the peak area associated with H<sub>d</sub> was calculated by subtracting the portion of H<sub>e</sub> from the total peak area, which was around 5.17–5.44 ppm. According to the triglyceride structure of SO, the peak area of H<sub>e</sub> should be one-fourth of that of H<sub>g</sub> whose chemical shifts (4.05–4.35 ppm)



**Figure 1.**  $^1\text{H}$  NMR spectra of soybean oil (SO) and acrylated soybean oil (ASO) with different degrees of acrylation.

were also clearly distinguished from that of other protons. Therefore, the average number of double bonds per SO molecule can be determined using eq 1.

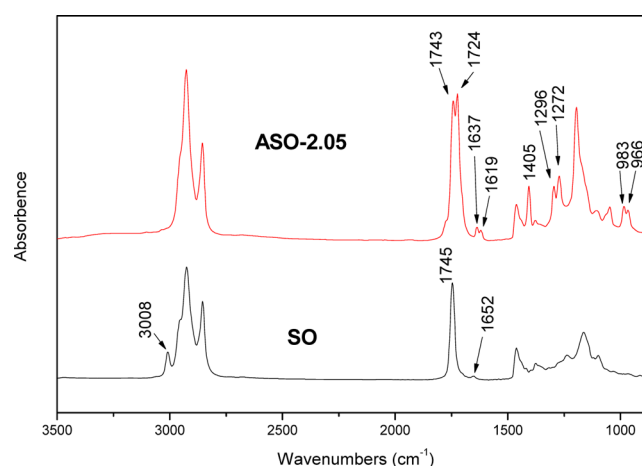
$$\text{Double bonds per SO molecule} = \frac{(A_{d,e} - A_g/4)/2}{A_i/6} \quad (1)$$

In this study, the average number of double bonds per SO molecule was found to be 4.08. On the other hand, the average number of acrylate per ASO molecule can be determined by comparing the peak areas of  $\text{H}_a$  (6.30–6.50 ppm) and  $\text{H}_i$  (2.20–2.40 ppm) in the spectra of ASO using eq 2.

$$\text{Acrylate groups per ASO} = \frac{A_a}{A_i/6} \quad (2)$$

The average numbers of acrylate groups per triglyceride of the samples shown in Figure 1 were found to be 1.20, 1.71, and 2.05, respectively. On the basis of the average double bond number of 4.08 in the original SO, the calculated conversions of double bonds to acrylates were 29.4% (ASO-1.20), 42.9% (ASO-1.75), and 50.2% (ASO-2.05), respectively. The peak areas of the protons associated with acrylate ( $\text{H}_a$ ,  $\text{H}_b$ ,  $\text{H}_c$ , and  $\text{H}_f$ ) increased with the rise in acrylation degree, while the peak areas of the protons associated with double bonds ( $\text{H}_d$ ,  $\text{H}_h$ , and  $\text{H}_j$ ) decreased accordingly. As shown in Figure 1, there were two types of allyl protons ( $\text{H}_h$  and  $\text{H}_j$ ) in the linoleate residues. After one of the two unconjugated double bonds was acrylated, the content of methylene protons ( $\text{H}_h$ ) between two double bonds decreased. The peak of  $\text{H}_h$  almost completely disappeared in the spectrum of ASO-2.05, while the peak of  $\text{H}_d$  partially remained. Similarly, the peaks of allyl  $\text{H}_j$  would not completely disappear unless all the double bonds were reacted. The structure of ASO was also examined using  $^{13}\text{C}$  NMR (Figure S1, Supporting Information).

Figure 2 shows the FTIR spectra of SO and ASO-2.05. The characteristic C–H stretching of C=C–H in SO at  $\sim 3008$



**Figure 2.** FTIR spectra of soybean oil (SO) and acrylated soybean oil (ASO-2.05).

$\text{cm}^{-1}$  disappeared after the addition reaction. A new peak at  $1724 \text{ cm}^{-1}$  that was attributed to the vibration of C=O of the acrylate groups was noted. The peaks at  $1637$  and  $1619 \text{ cm}^{-1}$  attributed to the vibration of C=C in acrylate groups were much more obvious than the peak at  $1652 \text{ cm}^{-1}$  attributed to the C=C vibration in SO. The peak at  $1405 \text{ cm}^{-1}$  was attributed to the scissoring vibration of  $\text{CH}_2$  in  $\text{CH}_2=\text{C}$  of the acrylate. The vibration of CH in acrylate  $\text{CH}=\text{C}$  was seen in the peaks at  $1296$  and  $1272 \text{ cm}^{-1}$ . The peaks at  $966 \text{ cm}^{-1}$  were attributed to the rocking vibration of  $\text{CH}_2$  in  $\text{CH}_2=\text{C}$  in the acrylate groups.

#### Effects of Catalyst Types on Acrylation Conversion.

Table 2 shows the effects of various catalysts on the conversion of SO acrylation. The selected catalysts can be classified into two types, Lewis acids and protic acids. On the basis of the acid-catalyzed hydration of alkene,<sup>39</sup> the mechanism of protic acid-catalyzed soybean oil acrylation is proposed in Scheme 1. First, the carbon–carbon double bond captured the proton to form a carbocation. Subsequently, acrylic acid acted as a nucleophile attacked the carbocation, followed by deprotonation of the oxonium ion to obtain the acrylate ester. By comparing the results of entries 1–7 and 1–8, it is noted that the reaction catalyzed by PTSA resulted in a higher degree of acrylation than the reaction catalyzed by MsOH in the first 6 h. This result suggests that the reaction conversion increased with the acidity of the selected acid. Because the PTSA has a  $\text{p}K_a$  of  $-5.4$ <sup>40</sup> but MsOH has a  $\text{p}K_a$  of  $-1.9$ ,<sup>41</sup> PTSA was a stronger protic acid than MsOH. However, the conversion of entry 1–7 was lower than that of entry 1–8 at 24 h, and the conversion of entry 1–2 at 24 h was even lower than that at 6 h. These results might be due to the polymerization of ASO that will be discussed below. The polymerization side reaction was probably more likely to occur on the ASO with higher degree of acrylation. Amberlyst 15 is an ion-exchange resin based on a macro-reticular polystyrene with sulfonic acid groups and has a similar acidity like that of PTSA. Compared to PTSA, however, Amberlyst 15 exhibited much lower catalytic activity because it was suspended in the reaction medium, and the catalysis was a heterogeneous reaction. In contrast, PTSA was soluble in the reaction medium and could accelerate the reaction effectively.

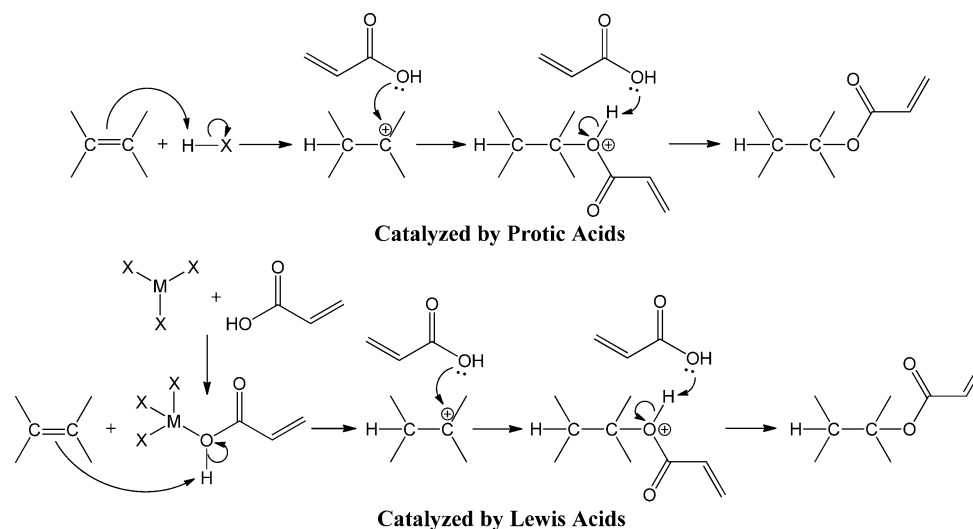
The mechanism of Lewis acid-catalyzed soybean oil acrylation is also proposed in Scheme 1. Lewis acid and acrylic acid formed a complex in a similar way like Lewis acid initiated cationic polymerization in the presence of a proton donor,<sup>42</sup>

Table 2. Results of ASO Synthesis under the Catalysis of Various Catalysts

entry	catalyst	acrylate content <sup>a</sup>				other conditions
		2 h	4 h	6 h	24 h	
1-1	TiCl <sub>4</sub>	0.02	0.06	0.03	0.16	SO, 3.65 mmol; <sup>b</sup> catalyst, 5 mmol; AA, 100 mmol; HQ, 0.25 mmol; temp =80 °C
1-2	SnCl <sub>4</sub>	1.35	1.53	1.74	1.52	
1-3	FeCl <sub>3</sub>	1.80	1.91	2.25	2.42	
1-4	BF <sub>3</sub> ·Et <sub>2</sub> O	2.32	2.60	2.94	3.26	
1-5	BF <sub>3</sub> ·Et <sub>2</sub> O + HQ	2.48	2.88	3.01	3.25	
1-6	Amberlyst 15	0.17	0.26	0.38	1.04	
1-7	PTSA <sup>c</sup>	0.89	1.20	1.56	2.08	
1-8	MsOH	0.40	0.90	1.30	2.62	

<sup>a</sup>Average acrylate number per ASO molecule was tracked by <sup>1</sup>H NMR. <sup>b</sup>Content of double bonds in SO was determined by iodine value titration. <sup>c</sup>Monohydrate.

Scheme 1. Proposed Synthesis Mechanisms of ASO Catalyzed by Protic Acids and Lewis Acids

Table 3. Results of BF<sub>3</sub>·Et<sub>2</sub>O-Catalyzed Synthesis of ASO under Various Conditions

entry <sup>a</sup>	temp (°C)	BF <sub>3</sub> ·Et <sub>2</sub> O (equiv)	AA (equiv)	acrylate content <sup>c</sup>				polymerization of AA
				2 h	4 h	6 h	24 h	
2-1	60	0.14	6.86	0.20	0.36	0.48	0.77	partially after 24 h total in 5 min
2-2	80	0.14	13.71	0.19	0.25	0.31	0.62	
2-3	100	0.14	27.43	0.00	0.00	0.00	0.00	
2-4	60	0.68	13.71	1.26	1.84	2.03	2.76	totally after 24 h
2-5	80	0.68	27.43	1.85	2.35	2.50	3.00	
2-6	100	0.68	6.86	1.99	2.00	2.06	0.00	
2-7	60	1.37	27.43	1.20	1.71	2.05	2.89	
2-8	80	1.37	6.86	2.22	2.07	2.03	1.54	
2-9	100	1.37	13.71	2.36	–	2.98	2.91	

<sup>a</sup>1.5 g SO (equivalent to 7.3 mmol double bonds) was used in every entry. <sup>b</sup>Equivalents of the reagent used with respect to 1 equiv of double bonds of SO. <sup>c</sup>Average acrylate number per ASO molecule measured by <sup>1</sup>H NMR.

and then the double bond of SO was protonated by this complex. Because the double bonds in SO are internal alkenes that are linked with two electron-donating alkyl groups, they have increased electron density and can attack the protons. The rest of the process was the same as that in the protic acid catalyzed reaction. The result indicates that the catalytic activities of the Lewis acids used in this study are in the order of BF<sub>3</sub>·Et<sub>2</sub>O > FeCl<sub>3</sub> > SnCl<sub>4</sub> ≫ TiCl<sub>4</sub>, which coincides with the relationship of acidity of these Lewis acids reported in the literature.<sup>43</sup>

**Effects of Reaction Conditions on BF<sub>3</sub>·Et<sub>2</sub>O-Catalyzed ASO Synthesis.** Because of its high catalytic activity, BF<sub>3</sub>·Et<sub>2</sub>O was chosen as the catalyst to further evaluate the effects of reaction conditions on SO acrylation, including stoichiometry, reaction temperature, and time. A 3 × 3 orthogonal experiment design was employed to evaluate the effects of each parameter, and each reaction parameter was fixed at three levels. The selected temperatures were 60, 80, and 100 °C. The selected BF<sub>3</sub>·Et<sub>2</sub>O levels were 0.14, 0.68, and 1.37 equiv, and selected AA levels were 6.86, 13.71, and 27.43 equiv. The experiment results are given in Table 3. The results suggest that high



catalyst and AA concentrations both favored the SO acrylation in terms of degree of conversion and reaction rate. While high temperature promoted SO acrylation, it also accelerated the potential side reactions (entries 2-3 and 2-6). Higher temperatures promoted the acrylation reaction to reach the equilibrium of conversion sooner. With 0.68 equiv or more catalyst, the acrylate number in the resulting ASO could reach to  $\sim 3.00$  per molecule on average (entries 2-5 and 2-9). Prolonging reaction time increased acrylate content in all cases except in entries 2-6 and 2-8. In the latter two cases, the conversion to acrylate reached the limitation in the first 2 h. Further increasing the reaction time enhanced the likeliness of side reactions of AA, SO, and ASO.

**Polymerization during Acrylation.** Table 3 shows that polymerization of AA was likely to occur at higher temperatures or lower  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  concentrations (entries 2-2, 2-3, and 2-6). Because the presence of the electron-withdrawing carboxyl group, AA is not subject to cationic polymerization. However, free radical polymerizations of AA and the resulting ASO might still occur with the progress of the acrylation reaction. In some of the experiments in Table 3, white precipitates were noted at 24 h of reaction. These white products were water-soluble and were found to be poly(acrylic acid) by  $^1\text{H}$  NMR (Figure S2, Supporting Information). In addition, cationic polymerization of the double bonds of SO was also possible. Hydroquinone (HQ) was used as a free radical inhibitor during the study. There was not a significant difference in the acrylation degree between the reactions with (entry 1-4) and without (entry 1-5) the inhibitor HQ. The slightly higher acrylate content in the product of entry 1-5 was probably due to the acrylated HQ in the product. The evidence was noted in the aromatic protons of HQ diacrylate at 7.16 ppm (Figure S3, Supporting Information).<sup>44</sup> That indicates the acrylation of HQ also occurred under this reaction condition. In other words, use of HQ as a free radical inhibitor did not deter the occurrence of free radical polymerization during acrylation of SO.

**Transesterification during Acrylation.** The transesterification between triglyceride and acrylic acid was monitored in some reactions. Figure 3 shows the  $^1\text{H}$  NMR spectra of the methylene groups of the glycerol residue in glycerol triacrylates, ASO, and SO. The chemical shifts of the methylene protons of the glycerol residue in SO triglyceride shifted to low field ( $\text{H}_a$  to  $\text{H}_b$ ) after the fatty ester was replaced by an acrylate ester. Transesterification was not significant at 60 °C, while almost all the fatty esters were replaced by acrylate esters at 100 °C.

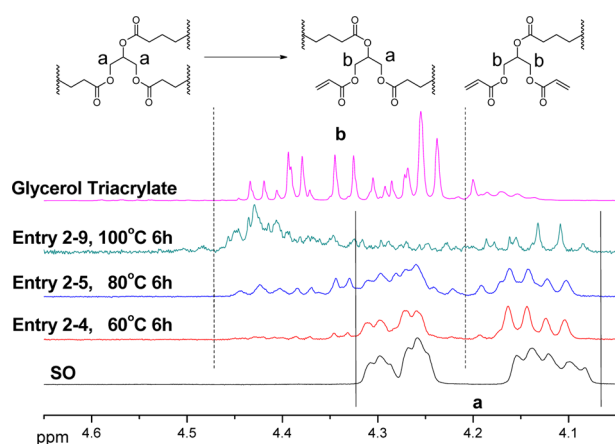


Figure 3.  $^1\text{H}$  NMR characterization of transesterification.

Therefore, high temperature is not suitable for the acrylation reaction. In summary, the reaction condition for achieving high conversion yield of acrylation and reducing side reactions should be performed at relatively low temperatures, i.e., 60–80 °C, and the suitable equivalents of  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  and AA, 0.68–1.37 and 13.71–27.43, respectively.

**Recovery and Reuse of AA and  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ .** High AA and  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  dosages were required to achieve high conversion of the double bonds to acrylates, so it was also of interest to recycle the excess reagent and catalyst. Because of their low boiling points, excess AA and  $\text{BF}_3$  could be recovered conveniently by distillation after reaction. Table 4 gives the

Table 4. Recovery of AA and  $\text{BF}_3$  and Reuse in Acrylation of SO

entry	degree of acrylation <sup>a</sup>		recovered AA and $\text{BF}_3$		recovery ratio
	3 h	6 h	theory <sup>b</sup>	experiment	
3-1	66.3%	70.0%	147g	113.4g	77.1%
3-2	61.3%	71.6%	147g	126.3g	85.9%

<sup>a</sup>Acrylation conversion of the double in SO which was tracked by  $^1\text{H}$  NMR. <sup>b</sup>Theoretical mass of recovered AA and  $\text{BF}_3$  is assumed to be the total weight of all the  $\text{BF}_3$  and the unreacted AA.

comparison of acrylation of SO using fresh and recycled AA and  $\text{BF}_3$ . First, the acrylation was performed at 80 °C for different times with all new reagents (entry 3-1) that were composed of 0.073 mol (15 g) SO, 2 mol (144 g) AA, and 0.1 mol (14.2 g)  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ . After the reaction mixture was cooled to room temperature, hydroquinone (36 mg) was added as inhibitor, followed by distillation of the catalyst and the unreacted AA under high vacuum at 35–45 °C.  $\text{Et}_2\text{O}$  was not noted in the  $^1\text{H}$  NMR spectrum of the recovered reagent mixture. AA could also act as a ligand for  $\text{BF}_3$ . Because AA was added 10 times that of  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ , the  $\text{Et}_2\text{O}$  ligand might be mostly substituted by AA during acrylation reaction. It was noted that the coordination compounds of one  $\text{BF}_3$  and one carboxylic acid were not stable under heating, while the coordination compounds of one  $\text{BF}_3$  and two carboxylic acids were stable. For example, the boiling points of the stable  $\text{BF}_3$  coordination compounds of  $\text{BF}_3 \cdot 2\text{CH}_3\text{COOH}$  and  $\text{BF}_3 \cdot 2\text{CH}_3\text{C}(\text{H}=\text{CHCOOH})$  were 53–54 °C/10 mmHg and 81–82 °C/12.5 mmHg, respectively.<sup>45</sup> While  $\text{BF}_3 \cdot 2\text{AA}$  was supposed to be generated at the reaction stage and distilled and collected at the recovery stage, the free  $\text{Et}_2\text{O}$  dissociated from  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  was difficult to collect because of its very low boiling point. The total weight of the recovered AA and  $\text{BF}_3$  was 113.4 g (entry 3-1). If all the added  $\text{BF}_3$ , which was added in the form of  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  and was equivalent to 6.8 g, was presumably recovered completely, the recovered AA should be 106.6 g. The recovered AA and  $\text{BF}_3$  was supplemented with 37.4 g fresh AA (entry 3-2), and the mixture was reacted under the same conditions in entry 3-1. Table 4 shows that the degrees of acrylation for the ASO prepared using the recovered AA and  $\text{BF}_3$  at 3 and 6 h were almost same as the ASO made from fresh AA and catalyst. This result suggests that the recovery of AA and  $\text{BF}_3$  is feasible and reusable for the acrylation.

## CONCLUSIONS

Direct acrylation of SO was achieved via addition reaction of soybean oil and acrylic acid. Catalyst used, stoichiometry, and reaction conditions all exhibited great influences on the acrylation of SO. Both Lewis acids and protic acids displayed

acidity-dependent catalytic activity on SO acrylation, which were in the order of  $\text{BF}_3 \cdot \text{Et}_2\text{O} > \text{FeCl}_3 > \text{SnCl}_4 > \text{TiCl}_4$  and  $\text{PTSA} > \text{MsOH} > \text{Amberlyst 15}$ , respectively. In general, Lewis acids demonstrated higher catalytic activity than protic acids except for  $\text{TiCl}_4$ . High catalyst and AA concentrations accelerated the acrylation and resulted in high conversion of the double bonds to acrylates. High temperature greatly accelerated SO acrylation, but it also tended to promote the side reactions. Side reactions including polymerization of AA, overaddition of ASO by acrylic acid, and transesterification between ASO and AA were noted, but these reactions were largely controlled with proper selection of reaction parameters. Our results demonstrate that in order to maximize conversion to ASO and maintain control of side reactions, acrylation should be performed in a temperature range of 60–80 °C with 0.68–1.37 equivalent  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  and 13.71–27.43 AA, respectively. The catalyst ( $\text{BF}_3$ ) and excess AA can be recovered by distillation and reused.

## ■ ASSOCIATED CONTENT

### 🔍 Supporting Information

$^{13}\text{C}$  NMR spectrum of ASO,  $^1\text{H}$  NMR spectra of poly(acrylic acid), and HQ diacrylate. 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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