

Synthesis and Polymerization of the Acrylamide Derivatives of Fatty Compounds

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ABSTRACT: The Ritter reaction of plant oil triglycerides (such as soybean and sunflower oil) with acrylonitrile was used to introduce acrylamide functionality on the triglyceride. Acrylonitrile and triglycerides were reacted in the presence of H_2SO_4 , and acrylamide derivatives were obtained in yields of 45 and 50% for sunflower oil and soybean oil, respectively. Radical initiated copolymerization of the acrylamide derivatives of the triglycerides with styrene produced semirigid polymers. Characterization of new monomers and polymers was done by 1H -NMR, ^{13}C -NMR, IR, and MS. The swelling behavior of the crosslinked network polymers was determined in different solvents. Glass transition temperature (T_g) of the cured resin was also determined by differential scanning calorimeter to be 40°C for soybean based polymer and 30°C for sunflower-based polymer. Homo- and

copolymerization behavior of acrylamide derivatives of methyl oleate (MOA) and methyl 10-undecenoate (MUA) were also investigated. The reactivity ratios of these monomers with respect to styrene were determined by the Fineman-Ross method using 1H -NMR spectroscopic data. The reactivity ratios were $r_{sty} = 1.776$; $r_{moa} = 0.512$ for MOA, and $r_{sty} = 1.142$; $r_{mua} = 0.507$ for MUA, respectively. Photopolymerization behaviors of MOA and MUA were also investigated using the photoDSC technique and the rate of polymerization of MUA is higher than that of MOA under the same conditions. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 2264–2272, 2005

Key words: renewable resources; Ritter reaction; photopolymerization; biodegradable

INTRODUCTION

The production of biodegradable materials from renewable resources, especially from plant oil triglycerides, has been especially attractive since the 1970s. Encouragement of the use of environmentally sound and sustainable renewable natural resources is one of aim of Agenda 21.¹ Unlike petroleum reserves, plant oil triglycerides are biodegradable, renewable, and more socially acceptable as raw materials and are likely to be a major raw material for the chemical industry in the future. Vegetable oils are currently the most important renewable feedstock of the chemical industry.² The internal *cis* double bonds of triglycerides are too unreactive for free radical polymerization. Therefore, to be useful as a monomer for radical polymerization, the triglyceride molecule must be suitably functionalized. Continuing with our efforts to functionalize triglycerides,^{3–7} we report here the synthesis of the acrylamide derivative of triglycerides by

the Ritter reaction, followed by free radical initiated polymerization through the acrylamide unsaturation.

Ritter⁸ found that the reaction of alkenes with nitriles in the presence of concentrated sulfuric acid and hydrolysis of the product yields an amide. The alkene is protonated by the mineral acid to form a carbocation, which then reacts with the nucleophilic nitrogen atom of the nitrile. Hydrolysis of the product results in an amide as shown in Figure 1.

The first applications of Ritter reaction to fatty compounds were done by Swern and Roe.⁹ Acetonitrile, propionitrile, acrylonitrile, benzonitrile, cyanoacetic acid, malononitrile, and succinonitrile were added to the double bond of oleic acid in the presence of sulfuric acid to give good yields of the amidostearic acids. Sarel et al.¹⁰ isolated the products of acrylonitrile and fatty compounds such as linoleic and methyl oleate. Application of Ritter reaction to the fatty acids and their methyl esters was reported in the literature but application to the triglycerides was not reported. In this work we report the addition of acrylonitrile to sunflower and soybean oil triglycerides by the Ritter reaction. The chemistry is shown in Figure 2.

EXPERIMENTAL

Reagents and instruments

The soybean oil (Marsa, Adana, Turkey) used was food grade and was used without further purification.

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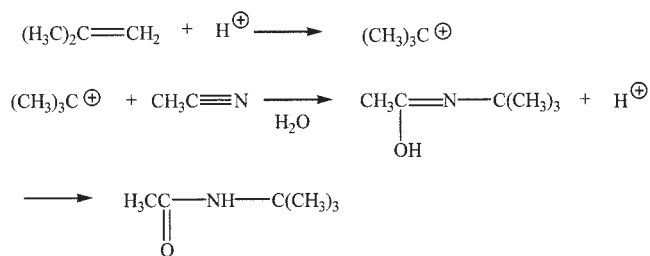


Figure 1 Amide formation by the Ritter reaction with acetonitrile.⁸

High oleic sunflower oil, methyl oleate (83% methyl oleate, 7% methyl linoleate), and methyl linoleate (64% methyl linoleate, 24% methyl oleate) were obtained from Henkel KGaA (Dusseldorf, Germany). Acrylamide derivative of methyl 10-undecenoate (MUA) was synthesized by and received from Prof. Jürgen O. Metzger, University of Oldenburg, Germany. CDCl_3 (Aldrich, Milwaukee, WI) was used for $^1\text{H-NMR}$ analysis. The 2,2'-azobis(isobutyronitrile) (AIBN) was obtained from Fluka (Buchs, Switzerland) and was purified by recrystallization from methanol. Benzoyl peroxide (BPO) was obtained from Fisher (Fisher Scientific Co., NJ). The photoinitiator 2,2-dimethoxy-2-phenylacetophenone (Irgacure 651, Ciba-Geigy) was used as received. Acrylonitrile was obtained from Merck (Whitehouse Station, NJ).

$^1\text{H-}$ and $^{13}\text{C-NMR}$ spectra were recorded on Varian 400-MHz NMR (Varian Associates, Palo Alto, CA) using TMS as internal standard operating at 399.986 MHz for proton and 100.587 MHz for carbon. TMS was used as an internal reference and CDCl_3 as an internal lock. Mass spectrum was obtained using a Finnigan MAT 212-mass spectrometer (MasCom GmbH, Bremen, Germany). The IR analysis was performed on a Genesis FTIR spectrometer (New Castle, DE) using NaCl windows. The glass transition temperature (T_g) for homo- and copolymers was evaluated using differential scanning calorimetry (DSC). DSC measurements were carried out for the polymers at temperatures from -100 to 150°C using modulated differential scanning calorimetry with a TA Instrument Universal V2-5H system (Giancarlo Scientific, Pittsburgh, PA) at a heating rate of $10^\circ\text{C}/\text{min}$ under a nitrogen atmosphere. Photopolymerizations were done with a TA Instrument Universal (Q 100) with a differential photocalorimeter accessory containing a high-pressure mercury lamp.

Synthesis of methyl oleate acrylamide adduct (MOA)

An acrylamide derivative of methyl oleate was synthesized and characterized according to the procedure described by Metzger and Biermann.¹¹ No $^{13}\text{C-NMR}$ is

available for this product; therefore, a detailed NMR analysis was made.

$^{13}\text{C-NMR}$ (CDCl_3) δ : 14.93 ($-\text{CH}_3$), 22.34–35.37 ($-\text{CH}_2-$), 51.63 ($-\text{OCH}_3$), 49.4 ($-\text{CHNH-}$), 125.9, 131.2 [$-\text{CHNH}(\text{C}=\text{O})\text{CH}=\text{CH}_2$], 165.0 [$-\text{NH}(\text{C}=\text{O})\text{CH}=\text{CH}_2$], 174.12 [$-(\text{C}=\text{O})\text{OCH}_3$].

Synthesis of methyl linoleate acrylamide adduct (MLA)

MLA was synthesized by the procedure described by Sarel¹⁰ with the following modifications. A well-stirred mixture of methyl linoleate (mixture containing 64% methyl linoleate, 24% methyl oleate), 1.5 g (1.6 mmol equivalent double bond), and acrylonitrile, 5.3 g (100 mmol), was cooled in an ethanol bath to -20°C while 4.2 mL (30 mmol) of 98% H_2SO_4 was added dropwise during 1 h. The cooling bath was then removed and the mixture was stirred at room temperature for 1 h. The reaction temperature was maintained at room temperature by external cooling. After 1 h, the mixture was poured, with stirring, onto approximately 300 mL of crushed ice and stirred for 1 h. A total of 100 mL of CH_2Cl_2 was added, stirred for 30 min, and separated from the aqueous phase. The dichloromethane layer was then extracted with NaHCO_3 (aq), dried with Na_2SO_4 , and filtered and the solvent was evaporated. A total of 2.2 g of crude reaction product was obtained as a viscous oil. The intensity of the ($-\text{OCH}_3$) protons and acrylamide vinyl protons was compared by $^1\text{H-NMR}$ and the yield of

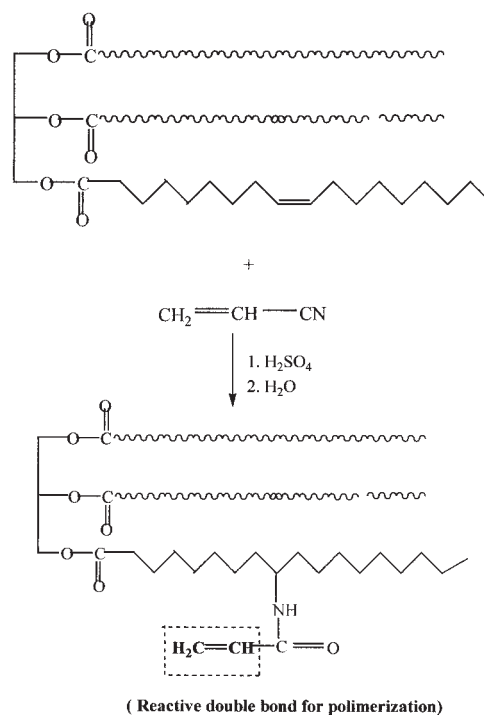


Figure 2 The Ritter reaction of triglycerides.

the desired acrylamide derivative was 60%. ^1H and IR data were in agreement with Ref. [10] and ^{13}C -NMR data was as follows:

^{13}C -NMR (CDCl_3) δ : 13.97 ($-\text{CH}_3$), 22.53–35.37 ($-\text{CH}_2-$), 51.63 ($-\text{OCH}_3$), 49.2, 49.0 and 48.8 ($-\text{CHNH}-$), 125.6, 131.2, [$-\text{CHNH}(\text{C}=\text{O})\text{CH}=\text{CH}_2$], 165.6, 165.2 and 165.0 [$-\text{NH}(\text{C}=\text{O})\text{CH}=\text{CH}_2$], 174.12 [$(-\text{C}=\text{O})\text{OCH}_3$].

Synthesis of sunflower oil acrylamide adduct (SUA)

A total of 6.3 g (7 mmol) sunflower oil and 4.1 g (76 mmol) acrylonitrile were mixed and stirred at 0°C . Then 2.5 mL (46 mmol) of H_2SO_4 was added dropwise at such a rate as to maintain the temperature around 0°C (addition took 30 min). The mixture was then stirred for 1 h at room temperature by external cooling. Then the mixture was poured into 300 mL crushed ice and stirred for 1 h to complete hydrolysis. The mixture was then adjusted to pH 10 with NaHCO_3 (aq) and extracted with CH_2Cl_2 . The CH_2Cl_2 layer was separated, dried with Na_2SO_4 and then evaporated to give 7.1 g viscous oily product. By comparing the intensities of the proton in the α -position to the ester carbonyl and acrylamide vinyl protons' NMR signal intensities, the yield of acrylamide derivative of sunflower oil (SUA) was determined to be 50% based on the triglyceride.

^1H -NMR (CDCl_3) δ : 0.95 ($-\text{CH}_3$), 1.2 ($-\text{CH}_2-$), 1.4 [$-\text{CH}_2-\text{CH}_2-\text{C}(=\text{O})-$], 4.11 [$-\text{O}-\text{CH}_2-\text{CH}(\text{O}-)-\text{CH}_2-\text{O}-$], 5.6 ($-\text{NH}-\text{CO}-\text{CH}=\text{CH}_2$), 6.2 ($-\text{NH}-\text{CO}-\text{CH}=\text{CH}_2$), 6.1 ($-\text{NH}-\text{CO}-\text{CH}=\text{CH}_2$), 3.95 [$-\text{CH}(\text{CH}_2)-\text{NH}-$].

^{13}C -NMR (CDCl_3) δ : 13.87 ($-\text{CH}_3$), 22.42–34.81 ($-\text{CH}_2-$), 49.4 ppm ($-\text{CHNH}-$), 61.85 [$(-\text{C}=\text{O})\text{OCH}_2-$], 68.74 [$(-\text{C}=\text{O})\text{OCH}-$], 129.44, 129.74, ($-\text{CH}=\text{CH}-$), 172.38, 172.77, 172.81 [$(-\text{C}=\text{O})\text{OCH}_2-$], 165 ($\text{CH}_2=\text{CH}-\text{CO}-\text{NH}-$), 131 ($\text{CH}_2=\text{CH}-\text{CO}-\text{NH}-$), 125 ($\text{CH}_2=\text{CH}-\text{CO}-\text{NH}-$).

IR (Film) ν (cm^{-1}): 3278, 1548 (s, NH), 2957 (s, CH), 2860 (s, CH), 1743 (s, C = O), 1465 (m, CH_2 , Def.), 1404 (m, = CH_2 , Def.), 1264 (m, C-O-C, Def.), 1186 (m, CO, Def.; C-O-C, Def.), 1624 (C = O amide), 984, 1656, 951 (m, = CH, Def., characteristic for vinyl group conjugated with carbonyl).

MS (EI) m/z : 955 [M^+]; 884 [$\text{M}^+-\text{NH}-\text{C}(=\text{O})-\text{CH}=\text{CH}_2$].

Synthesis of soybean oil acrylamide adduct (SOA)

The procedure for the Ritter reaction of sunflower oil was repeated using 6.0 g (7.0 mmol) soybean oil and 8.2 g (150 mmol) acrylonitrile and 2.5 mL (46 mmol) H_2SO_4 . The reaction was followed and quenched as discussed above. A total of 7.0 g of a brown viscous oily product was obtained. By comparing the intensities of the proton in the α -position to the ester car-

bonyl and acrylamide vinyl protons' NMR signal intensities, the yield of acrylamide derivatives of SOA was determined to be 45% based on the triglyceride.

^1H -NMR (CDCl_3) δ : 0.95 (CH_3-), 1.2 ($-\text{CH}_2-$), 1.4 [$-\text{CH}_2-\text{CH}_2-\text{C}(=\text{O})-$], 4.11 [$-\text{O}-\text{CH}_2-\text{CH}(\text{O}-)-\text{CH}_2-\text{O}-$], 5.6 ($-\text{NH}-\text{CO}-\text{CH}=\text{CH}_2$), 6.2 ($-\text{NH}-\text{CO}-\text{CH}=\text{CH}_2$), 6.1 ($-\text{NH}-\text{CO}-\text{CH}=\text{CH}_2$), 3.90 [$-\text{CH}(\text{CH}_2)-\text{NH}-$].

^{13}C -NMR (CDCl_3) δ : 13.99 ($-\text{CH}_3$), 22.57–37.70 ($-\text{CH}_2-$), 49.3, 49.1 and 48.9 ($-\text{CHNH}-$), 61.85 [$(-\text{C}=\text{O})\text{OCH}_2-$], 68.74 [$(-\text{C}=\text{O})\text{OCH}-$], 129.44, 129.74, ($-\text{CH}=\text{CH}-$), 172.38, 172.77, 172.81 [$(-\text{C}=\text{O})\text{OCH}_2-$], 165.6 ($\text{CH}_2=\text{CH}-\text{CO}-\text{NH}-$), 131–125 ($\text{CH}_2=\text{CH}-\text{CO}-\text{NH}-$).

IR (Film) ν (cm^{-1}): 3278, 1548 (s, NH), 2957 (s, CH), 2860 (s, CH), 1744 (s, C = O), 1453 (m, CH_2 , Def.), 1407 (m, = CH_2 , Def.), 1243 (m, C-O-C, Def.), 1186 (m, CO, Def.; C-O-C, Def.), 1624 (C = O amide), 984, 1656, 952 (m, = CH, Def., characteristic for vinyl group conjugated with carbonyl).

Polymerization of the MOA and MUA

Radical homopolymerization.

The radical initiated homopolymerization of the MOA and MUA was carried out neat or in dioxane solvent in the presence of AIBN or BPO as radical initiator. In a typical run, 0.3 g of MOA was mixed with 0.004 g AIBN in CH_2Cl_2 . After evaporation of the solvent, the vial was purged with N_2 , sealed, and heated to 85°C for 5 h. At the end of 5 h a soft crosslinked polymer was obtained. When the polymerized sample was triturated with CHCl_3 , 25% of the unreacted MOA was recovered, while UMA gave 15% unreacted monomer under the same conditions. Homopolymerizations of MOA and UMA in dioxane were carried out similarly and the products were precipitated by an excess amount of methanol. In solution polymerization highly viscous products with a conversion of 35% for MUA and 25% for MOA were obtained.

Copolymerization with styrene.

In a typical run, MOA was mixed with 50% of its own weight of styrene and 1.5% AIBN was added. The mixtures were purged with N_2 for 10 min, sealed, and heated in an oil bath at 80°C for 24 h. The polymer thus obtained was purified dissolving in CH_2Cl_2 and precipitating in an excess amount of methanol and finally dried under a vacuum before characterization. A semirigid solid was obtained with a conversion of 75%. Copolymerization of MUA with styrene gave 74% conversion under the same conditions.

Photopolymerization procedure.

Typically 3.5 mg of a sample was placed in an aluminum DSC pan. The initiator solution (Irgacure 651, in

CH₂Cl₂) was added with a microsyringe to give a final concentration of 2% in the monomer. After evaporation of the solvent, the samples were photocured for 10 min at room temperature under nitrogen. Monochromatic 365-nm ultraviolet light was used and the light intensity was 1.0 mW/cm². Conversion-time plots and the rates of polymerizations were calculated.¹²

Polymerization of acrylamide adduct of triglycerides (SUA and SOA)

Homopolymerization.

In a simple procedure, 1.01 g of SUA was mixed with 0.012 g benzoyl peroxide, purged with N₂, sealed, and heated to 85°C for 5 h. The homopolymerizations of SUA and SOA were accompanied by a slow viscosity increase.

Copolymerization with styrene.

Copolymerization of the SUA and SOA with styrene were carried out by using free radical initiator BPO. SOA and SUA were mixed with styrene to give a yellow-colored transparent solution containing 50% (w/w) styrene. Benzoyl peroxide (1%, w/w) was added and the mixtures were purged with N₂ for 10 min. The samples were sealed and heated at 85°C for 24 h. Samples were extracted with chloroform to remove unreacted monomer. SUA–styrene copolymer showed 9% unreacted monomers (both styrene and SUA); SOA–styrene copolymer gave 4% unreacted monomers under the same reaction conditions.

Determination of reactivity ratios of styrene with MOA and MUA

Copolymerization of styrene with MOA and MUA was carried out with 10 different feed ratios. The recipe for the synthesis of the copolymer 50 : 50 (w/w) of styrene and MUA was as follows: 0.33 g of styrene, 0.33 g of MUA, and 0.008 g AIBN were mixed in dioxane in a closed vessel, degassed, and heated at 80°C in an oil bath. The copolymerization was stopped at a low conversion by cooling the samples to 0°C. Then the resulting copolymers were precipitated by adding a large quantity of methanol and the conversions were determined gravimetrically to be about 10%. The homopolymer, polystyrene (PS), was insoluble in acetone although the copolymer was soluble. The precipitate was then extracted with acetone to separate polystyrene homopolymer. Indeed, homopolymer of styrene was not observed in any of the experiments. The copolymers were washed well with methanol and dried in a vacuum before characterization.

RESULTS AND DISCUSSIONS

Synthesis of the acrylamide adducts

Soybean oil contains 50–55% linoleic and 30% oleic acids and high oleic sunflower oil contains 84% oleic acid in their structures. Therefore, as a model compound we decided to examine the reactivity of the methyl oleate and methyl linoleate for the Ritter reaction. The resulting products would also provide acrylamide adducts that would be useful as NMR models to identify the structure of acrylamide adducts of triglycerides. Methyl oleate was reacted with acrylonitrile in the presence of SnCl₄ by the procedure described by Metzger and Biermann.¹¹ FTIR, MS, and ¹H-NMR spectra were similar to those found in the literature.^{9–11}

It was observed by Swern⁹ and Sarel et al.¹⁰ that during the synthesis of acrylamide derivative some polymerization of the methyl linoleate also took place. We used excess amounts of acrylonitrile (25 mol excess) to prevent dimerization or polymerization of ML. The ML that was used in this work consisted of 25% methyl oleate and 65% methyl linoleate. ¹H-NMR signal intensities of the methoxy group (–OCH₃) and double bonds (–CH = CH–) of this mixture have a ratio of 0.96 : 1. This corresponds with an average of 1.6 double bonds per molecule. When this mixture was converted to the acrylamide derivative (MLA), the NMR signal intensities of the methoxy and the fatty double bond protons were in the ratio of 5 : 1, indicating that 80% of the double bonds had been consumed. When the NMR signal intensities of the methoxy group and the acrylamide vinyl protons were compared, it was found that only 60% of the fatty double bonds had been converted to the acrylamide adduct. We conclude that dimerization or oligomerization consumed the remaining 20% of the fatty double bonds. The ¹H-NMR spectrum of MLA is in agreement with the data reported in the literature.¹⁰ Figure 3 shows the structure of the acrylamide adducts of methyl oleate, methyl linoleate, and methyl 10-undecanoate.

Different conditions were used to achieve higher yields for the acrylamide derivative of triglycerides. For 1 equivalent of sunflower oil molecule, 10 equivalents of acrylonitrile and 7.5 equivalents of H₂SO₄ were used to achieve high yields. For 1 equivalent of soybean oil, 100 equivalents of ACN and 18 equivalents of H₂SO₄ were used to increase the acrylamide yield and prevent oligomerization or dimerization.

Soybean oil and high oleic sunflower oil have an average number of 4.2 and 2.7 double bonds per molecule as determined by their iodine numbers. So soybean oil has more positions per triglyceride to react with acrylonitrile compared to high oleic sunflower oil. Soybean oil has 50–55% linoleic acid in its structure, so dimerization or oligomerization could not be

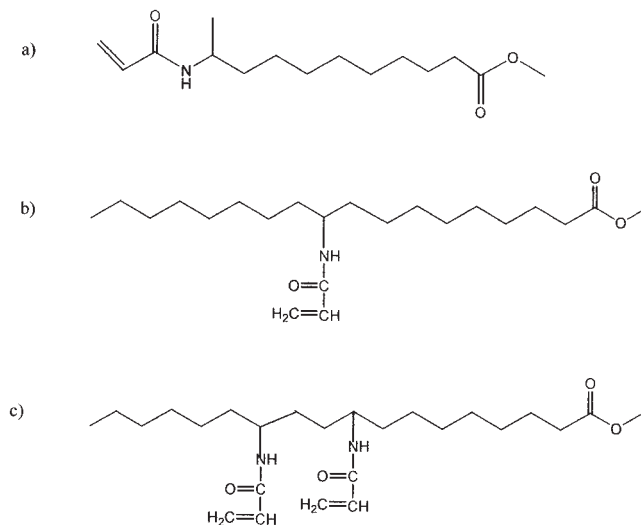


Figure 3 Acrylamide derivative of (a) methyl 10-undecenoate (MUA); (b) methyl oleate (MOA); (c) methyl linoleate (MLA).

prevented as discussed above. By comparing the intensities of the proton in the α -position to the ester carbonyl and acrylamide vinyl protons' NMR signal intensities, acrylamide yield of SUA was 50% and that of SOA was 45%. These correspond to 1.5 and 1.3 acrylamide groups per triglyceride for sunflower and soybean oils, respectively.

$^1\text{H-NMR}$ data of SUA are given in Figure 4(a). The carbon bearing amine ($-\text{CH-NH-C}(=\text{O})\text{CH}=\text{CH}_2$) appears as a multiplet at 3.9 ppm. Acrylamide vinyl protons were seen at 5.6, 6.1, and 6.2 ppm. Vinyl protons at 5.2 ppm and allylic hydrogens at 2.00 ppm almost disappeared as expected. Figure 4b shows the $^{13}\text{C-NMR}$ spectrum of the SUA. A carbon bearing amine appears at 49.4 ppm and also a new amide appears at 165 ppm. Acrylamide double bonds appear at 131 and 125 ppm. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra of the SOA were more complex than that of SUA because acrylonitrile has a higher number of sites to attack. Spectral analyses were similar to that of SUA.

Triglycerides have a complex mixture of fatty acids in their structure. We used high oleic sunflower oil. Its

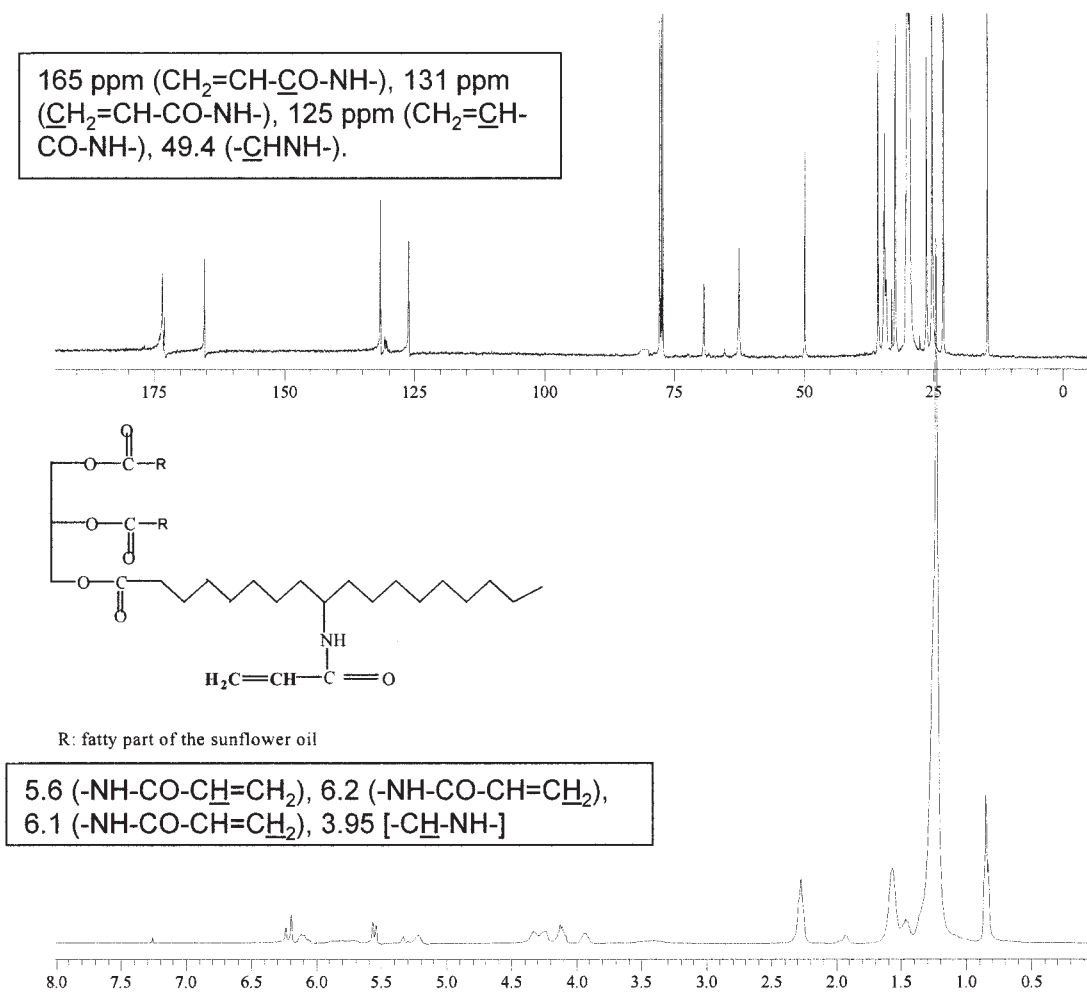


Figure 4 (a) $^1\text{H-NMR}$ spectrum and (b) $^{13}\text{C-NMR}$ spectrum of sunflower oil acrylamide (SUA).

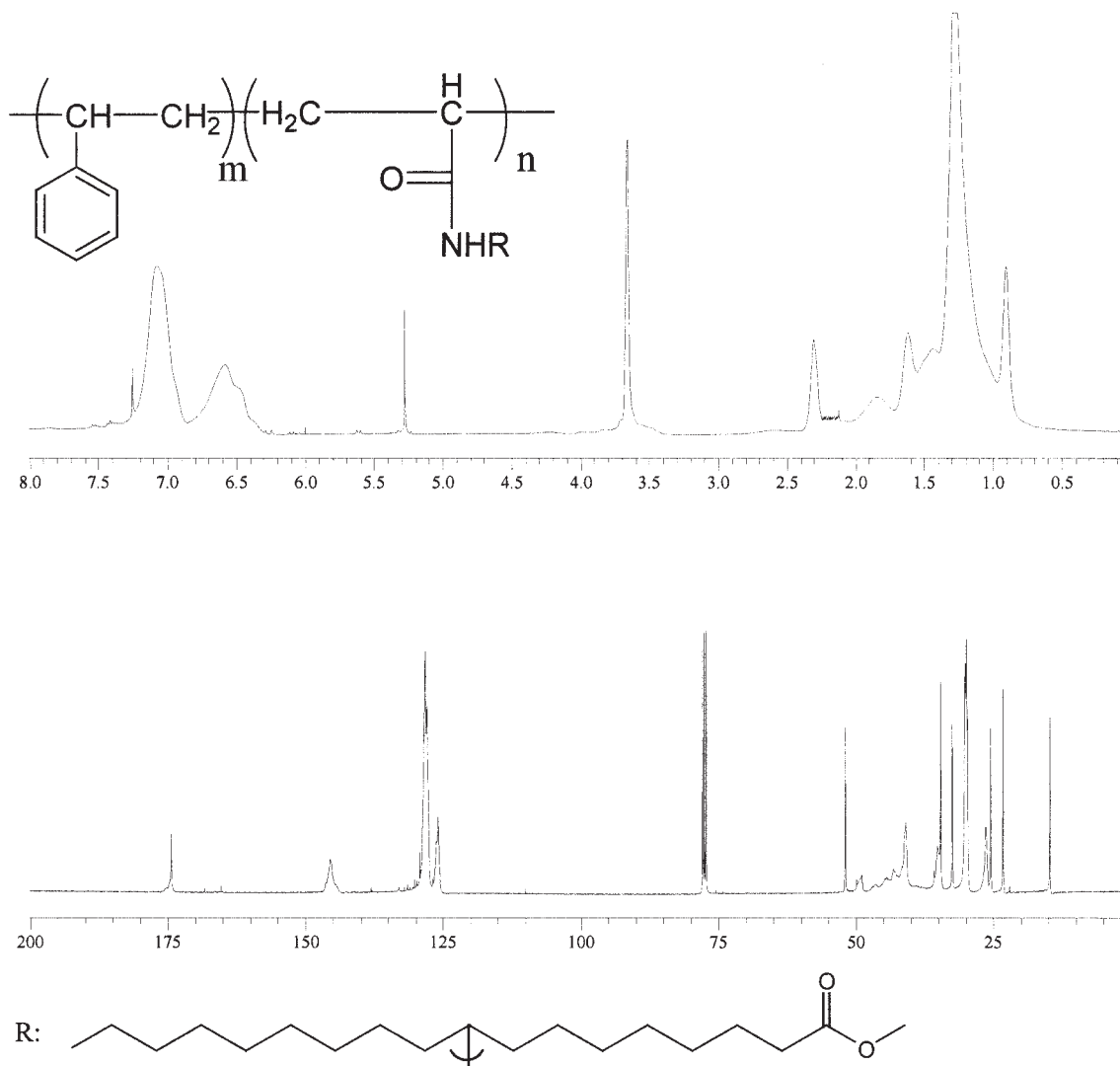


Figure 5 (a) $^1\text{H-NMR}$ spectrum and (b) $^{13}\text{C-NMR}$ spectrum of the copolymer of methyl oleate acrylamide (MOA) and styrene.

average molecular weight is about 884 and the acrylamide adduct of sunflower oil should show at least mono addition by mass spectrometry. The mass spectrum showed that the mono addition product $[\text{M}^+]$ is at 955. Acrylamide elimination $[\text{M}^+-\text{NH}-\text{C}(=\text{O})-\text{CH}=\text{CH}_2]$ was seen at 884.

Polymerization of the MOA and MUA

The radical initiated homopolymerization of MOA and MUA was carried out as neat and in dioxane solvent in the presence of AIBN or BPO. Bulk polymer products were soft solids that did not dissolve in common solvents. These polymers are lightly crosslinked, probably due to local overheating during the highly exothermic reaction. Solution polymerization resulted in soluble highly viscous polymers. Polymerization of MOA and MUA with styrene was

carried out in the presence of AIBN and after workup semirigid polymers were obtained.

The FTIR spectrum indicated characteristic absorption bands for the copolymer of MOA and styrene. Characteristic bands for acrylamide vinyl group at 984 and 951 cm^{-1} disappeared. Additional absorptions from the benzene ring of the styrene were observed at 3059, 3025, 1601, and 1493 cm^{-1} . The strong bands at 699 and 758 cm^{-1} were indicative of a monosubstituted aromatic ring. The $^1\text{H-NMR}$ spectrum of MOA-styrene copolymer is given in Figure 5(a). Vinyl protons disappeared and new peaks belonging to the $(-\text{CH}_2-\text{CH}-\text{C}(=\text{O})-\text{O}-)$ appeared at 1.6 ppm. The styrene copolymer showed characteristic benzene signals at 7.05–6.52; the other characteristic peaks at 1.85 (benzylic CH-) and 1.43 ppm ($-\text{CH}_2-$ backbone proton) were not assigned well because they overlapped with the MOA signals. Figure 5(b) shows the $^{13}\text{C-NMR}$

spectrum of the copolymer of MOA and styrene and it was observed that all acrylamide double bond were consumed and the backbone methine (-CH-) was absorbed at around 40 ppm as a shoulder. The methylene (-CH₂-) groups gave a signal at 35.2 ppm but this signal coincided with the carbons of the long alkyl side chains of the MOA. The aromatic carbons showed splitting around 125, 127, and 128 ppm. The quaternary carbon of the phenyl ring gave a signal at 145 ppm. The amide signal (-CO-NHR) was shifted to 174 ppm and coincided with ester carbonyl after polymerization. Some multiple splitting (or broadening) occurred in carbon peaks, which are not only due to the structures, but also due to random sequencing of monomer units in the copolymer. Spectral analysis of the MUA-styrene copolymer was similar and could be interpreted in a similar way.

To determine the monomer ratio in the copolymer chain, respective resonance signals were used. For styrene copolymer benzene ring signals at 6.5–7.0 ppm were compared with methyl signal (-C(=O)-O-CH₃) of the MOA and MUA at 3.6 ppm. The mole fraction of styrene in copolymer composition was found by the following equation where **I** represents the integration value of the NMR signals:

$$\text{Mole fraction} = \frac{3\mathbf{I}_{\text{phenyl}}}{3\mathbf{I}_{\text{phenyl}} + 5\mathbf{I}_{\text{methyl}}}$$

The monomer mole ratio of the MOA-styrene copolymer was 22% MOA and 78% styrene in the feed and 25 and 75% in the product as determined by NMR. The same ratio in the MUA-styrene copolymer was 27 to 73% in the feed and 43 to 57% in the product.

Determination of reactivity ratios

In liquid molding resins that require a reactive diluent such as unsaturated polyesters and vinyl esters, the amount of reactive diluent is dictated by reactivity ratio as well as the final viscosity of the product. The composition of a copolymer is usually different from the composition of the feed because the reactivity of each monomer is different.¹³ The reactivity ratios were obtained at about 10% conversion. The polymerization was stopped by cooling the samples to 0°C and the polymers were precipitated using methanol as nonsolvent. Precipitated polymers were extracted with acetone, which dissolved the copolymer but not the styrene homopolymer.

The reactivity ratios of MOA (r_{moa}), MUA (r_{mua}) with styrene (r_{sty}) were determined by the Fineman-Ross¹⁴ method. The equation used for the Fineman-Ross method is

$$\frac{f_1\{F_1 - F_2\}}{f_2F_1} = \frac{F_2\left\{\frac{f_1}{f_2}\right\}}{F_1\left\{\frac{f_2}{f_1}\right\}}r_1 - r_2$$

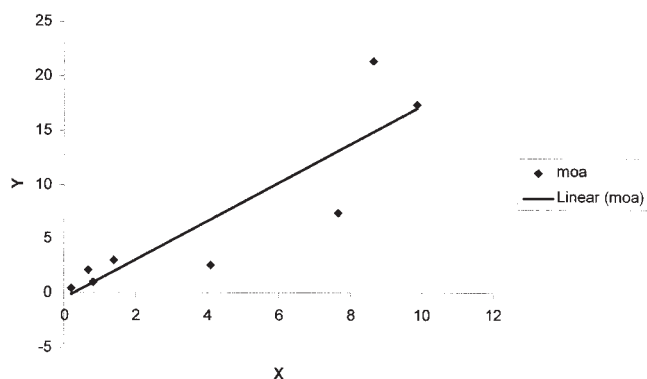


Figure 6 Fineman-Ross plot for MOA-styrene copolymer.

A plot of the $f_1/f_2\{F_1 - F_2/F_1\}$, which assigned as Y versus $F_2/F_1\{f_1^2/f_2^2\}$ (assigned as X) gives a straight line with slope equal to r_1 and intercept equal to $-r_2$. F_1 and F_2 are the instantaneous compositions (mole fractions) of the monomers in the copolymer and f_1 and f_2 are the mole fractions of the monomers. The Fineman-Ross plots of MOA are shown in Figure 6 (plots of MUA are not shown). Corresponding reactivity ratios of styrene and MOA are $r_{\text{styrene}} = 1776$ and $r_{\text{moa}} = 0512$ while UMA and styrene were $r_{\text{mua}} = 0507$ and $r_{\text{styrene}} = 1142$.

The copolymer equation was proposed by Mayo and Lewis¹⁵ with the parameters r_1 and r_2 defined by

$$r_1 = k_{11}/k_{12} \text{ and } r_2 = k_{22}/k_{21}$$

The parameters r_1 and r_2 are defined as monomer reactivity ratios and r_1 is the ratio of the rate constant for a reactive propagating species. The variable r_2 is similarly defined for the other monomer. The $r_1 \times r_2$ value of the copolymer MOA-styrene is 0909, indicating that the copolymer has tendency toward ideal copolymer structure. The r_1/r_2 ($= k_{11}/k_{22}$) value of MOA-styrene is 3.46, which indicates that styrene is about four times as reactive as MOA and that styrene will be incorporated into the copolymer faster. Hence, during the polymerization, although both monomers are being consumed, the styrene monomer is being consumed almost four times as fast as MOA, while the $r_1 \times r_2$ value of the MUA-styrene copolymer is 0.578, which indicates that tendency toward alternation copolymer structure. The r_1/r_2 value of MUA-styrene is 2.25, which indicates that styrene is approximately two times as reactive as MUA. This analysis also shows that MUA is more reactive than MOA in styrene copolymerization. Table I shows several values of r_1 and r_2 reported in the literature for the various substituted acrylamides and styrene.

The reactivities of the synthesized monomers, MOA and MUA, in photopolymerization were also investigated with photo-DSC. The observed propagation rate

TABLE I
Reactivity Ratios of Styrene (r_1) with Different Acrylamide (r_2)^a

Styrene (1)/ acrylamides (2)	<i>N</i> -octadecyl acrylamide	<i>N</i> -octyl acrylamide	<i>N</i> -tert-octyl acrylamide	MUA ^b	MOA ^c
r_1	1.41	2.7	2.8	(1.142) ^d	(1.776) ^d
r_2	0.200	0.2	0.25	(0.512) ^d	(0.512) ^d

^a Reference: Polymer Handbook, third ed.; Brandrup, J.; Immergut, E. H., Eds.; Wiley: New York, 1989.

^b Acrylamide derivative of methyl 10-undecanoate.

^c Acrylamide derivative of methyl oleate.

^d Reactivity ratios were obtained by the Fineman–Ross method.

(R_p) values are given in Figure 7. A conversion-time plot showed that a conversion of 85% was reached for MUA within 2 min, whereas 55% conversion was reached for MOA within 2 min. The polymerization rate generally increases with conversion and the same behavior was observed of the MUA and MOA. Figure 7 shows that the rate of polymerization for MUA is apparently greater than that of MOA. The reactivities of the monomers depend on the polar, resonance, and steric effects of the substituents. For example, acrylate monomers having α -alkyl substituents larger than methyl show poor or no polymerizability under free radical conditions due to steric effects.^{16,17} It was expected that long alkyl groups of MOA would decrease the polymerization rate to some extent and this is indeed found to be the case.

Polymerization of SUA and SOA

The radical initiated bulk homopolymerization of SUA and SOA was carried out in the presence of BPO. In each system, the polymerizations were observed with a viscosity increase. The allylic positions and the naturally occurring tocopherols in the oil are excellent chain transfer agents and free radical inhibitors; therefore, achieving high molecular weights is not possible by free radical pathway. The large *N*-substituted free end group (about 24 carbons) acts as a steric inhibitor and prevents propagation. The homopolymers of SUA and SOA are both soft solids.

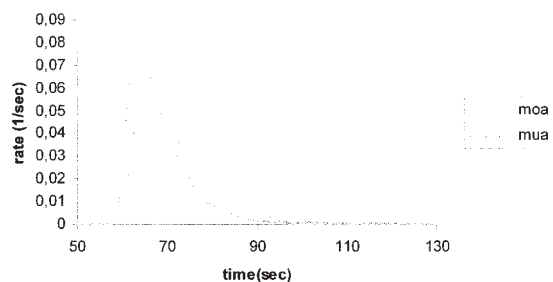


Figure 7 R_p values of MOA and MUA by photopolymerization.

Copolymerization of the SUA and SOA with styrene was carried out using the free radical initiator BPO. Sunflower oil has a higher number of acrylamide groups per triglyceride than soybean oil, so it reached a gelled state more quickly. The liquid solution of the SUA and styrene was transformed into a soft rubber and at the end of 1 h, a transparent, orange-colored semirigid solid polymer was obtained. Meanwhile, copolymerization of SOA and styrene gelled in 1 h and it became a soft solid at the end of 2 h. Unfortunately, it was impossible to analyze the polymers with ¹H-NMR, since the polymers were insoluble in common solvents. Polymers were extracted in CHCl₃ to remove unreacted monomers and styrene homopolymer. SUA–styrene copolymer gave 9% and SOA–styrene copolymer gave 4% weight loss upon extraction.

The swelling behavior and insolubility in common solvents proved the crosslinked structure. The samples were placed in a closed container containing CCl₄ and sample lengths were measured in particular time intervals with a traveling microscope. The experiment was continued until the solvent uptake ceased. The swelling ratio (q) was obtained by the equation¹⁸

$$q = V/V_0 = (L/L_0),$$

where V_0 and V are the volumes of unswollen and swollen composites, and L_0 and L are the lengths of the unswollen and swollen composites, respectively. Figure 8 shows the swelling behaviors of the copolymers.

Thermal properties of the cured resins were tested by DSC at a heating rate of 10°C/min and temperature

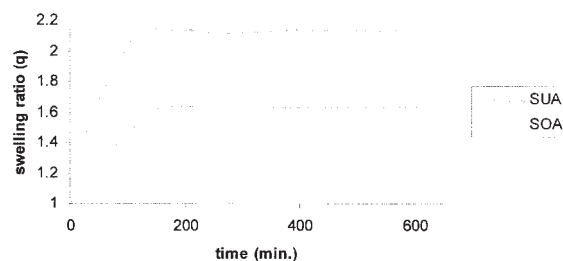


Figure 8 Swelling behaviour of sunflower–styrene and soybean–styrene based polymer.

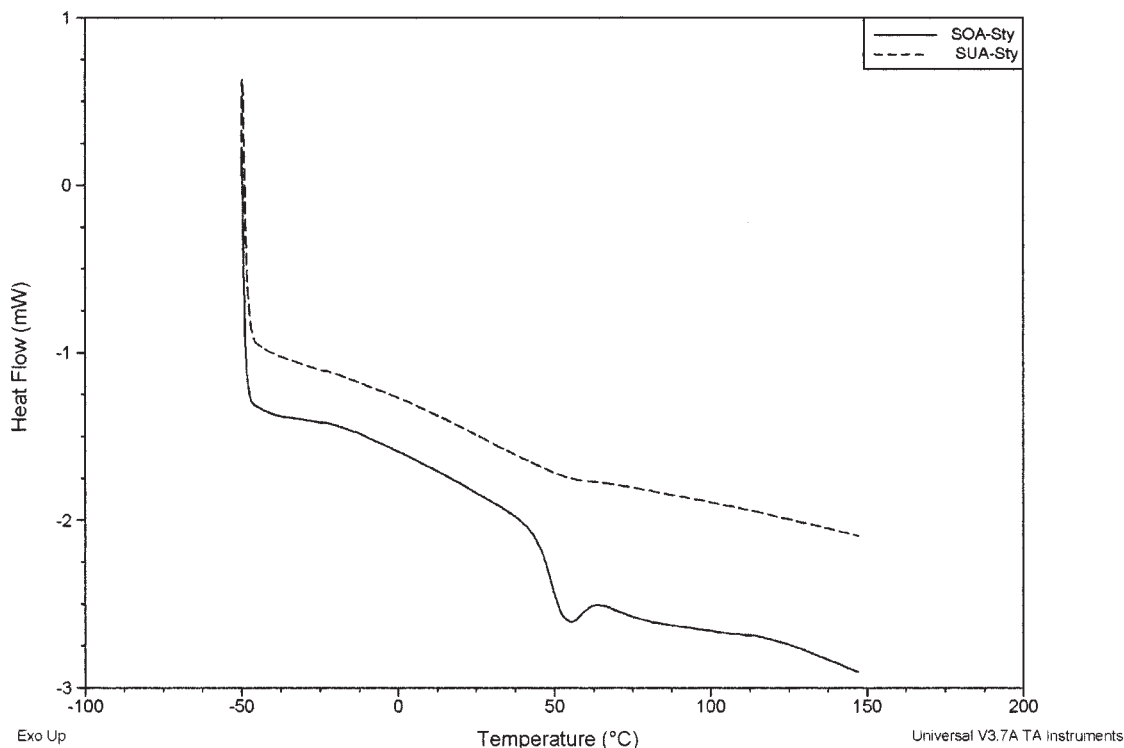


Figure 9 DSC spectra of SUA-styrene and SOA-styrene based copolymers.

ranges from -100 to 250°C . Sunflower-based copolymer showed lower T_g (30°C) than soybean-based copolymer (40°C), as shown in Figure 9. There is no practical method for determining the contribution of triglyceride dimers and oligomers formed during the Ritter reaction to the T_g of the final products. Meanwhile, MOA-styrene copolymer showed T_g at 34°C and MUA-styrene copolymer showed T_g at 50°C .

CONCLUSIONS

Soybean and sunflower oil triglycerides were reacted with acrylonitrile to produce acrylamide derivatives by the Ritter reaction. These new monomers were copolymerized with styrene and the copolymer properties were investigated. Polymerization behavior of acrylamide derivatives of methyl oleate and methyl 10-undecenoate were also investigated and their reactivity ratios were calculated with respect to the styrene monomer. Polyacrylamide is known for its hydrophilicity, while the plant oil acrylamides we synthesized are quite hydrophobic. We are now investigating copolymers of the two with the hopes of achieving unique hydrophobic-hydrophilic behavior.

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