Friedel–Craft *N*-Alkylation and *N*-Acylation of Acrylamide: A Novel Approach for Synthesis of Alkylacrylamides

B. S. LELE, M. A. GORE, M. G. KULKARNI

Polymer Science and Engineering Unit, Chemical Enginering Division, National Chemical Laboratory, Pune 411008, India

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ABSTRACT: *N*-Alkylacrylamides and *N*-acylacrylamides were synthesized by a novel synthetic approach, namely, the Friedel–Craft reaction of acrylamide with alkyl chloride and acyl chloride, respectively. The reactions took place smoothly at room temperature and the time required for the reactions was very short. The monomers so synthesized were characterized by elemental analyses, IR, and ^{1}H-NMR spectroscopy. Characterization data are in agreement with the proposed structures of the products. Thus, a convenient method for the synthesis of *N*-alkylacrylamides was developed.
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Key words: Friedel—Craft reaction; acrylamide; *N*-alkylacrylamide; *N*-acylacrylamide

INTRODUCTION

Copolymers of *N*-alkylacrylamides with various other monomers are finding diverse applications, for example, poly(napthyl-6-acrylamidocaproate–*co*–acrylic acid) as a plant growth regulator,[1] poly(*N*-dodecylacrylamide–*co*–*N*-methyl-4-vinyl pyridinium sodium) as a salt-resistant viscosity builder,[2,3] poly(*N*-stearoyl acrylamide–*co*–2(3-acrylamidopropyl)dimethyl aminoethyl isopropyl phosphate) as a phosphatidylcholine analogous material,[4] poly(*N-tert*–octylacrylamide–*co*–*N*-alkylacrylamide) as a thickner in cosmetics,[5] and poly(*N*-octylacrylamide–*co*–3-acrylamido-3-methyl butanoate sodium) for oil recovery.[6,7] Crosslinked hydrogels based on *N*-alkylacrylamides also find various applications such as in thermosensitive polymeric drug carriers,[8,9] as materials for hard contact lenses,[10] in concentrations of aqueous protein solutions,[11] and as stationary phases for HPLC.[12]

To meet these growing demands of *N*-alkylacrylamides, various methods for their synthesis have been developed. These methods can broadly be classified into three types, namely: (1) reaction of acryloyl chloride with alkylamine,[13–16] (2) pyrolysis or thermal decomposition of carboxylic acid amides,[17–21] and (3) reaction of olefins with nitriles.[22,23] Of these, methods of type (1) cannot be used to synthesize *N*-acylacrylamides (monomers) that are gaining increasing importance.[4] Methods of types (2) and (3) involve multistep harsh reaction conditions such as high temperature and pressure, and in most of the cases, small-chain-length alkylacrylamides have been synthesized. Details are as follows:

Reaction of Acryloyl Chloride with Alkylamine

Overberger et al.[13] synthesized a series of *N*-alkylacrylamides of varying alkyl chain length by reacting acryloyl chloride with alkyl amines in the presence of an acid quencher, that is, triethylamine at 0°C. This method is convenient and has been widely used by researchers to synthesize alkylacrylamides.[13–16] But it is not feasible for large-scale production because it uses acryloyl chloride which is an expensive and hazardous reagent. Besides, this method cannot be used to synthesize *N*-acylacrylamides.

Correspondence to: B. S. Lele.

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Thermal Decomposition of Carboxylic Acid Amides

A number of patents which are based on this technique have been filed. Motomasu et al.[17] reported the synthesis of *N,N*-diethylacrylamide. In this, methyl acrylate was reacted with diethylamine to give the Michael addition product methyl β *N,N*-diethylaminopropionate. This was treated with sodium methoxide for 46 h and then with phosphoric acid for 1 h at 50°C to give *N,N*-diethyl β diethylaminopropionic acid amide, which was then thermally decomposed at 180°C and 100 Torr pressure for 4 h to give *N,N*-diethylacrylamide. Similar processes for the synthesis of *N,N*-dialkylacryl and methacrylamides were reported by Maruyama et al.,[18] wherein thermal decomposition of carboxylic acid amide was carried out in the presence of H_2SO_4 at 195°C.

N-Alkylacrylamides have also been synthesized by amidation of bicyclic carboxylic acids followed by the thermal decomposition of the carboxamide. Thus, Oshima et al.[19,20] synthesized *N,N*-dimethylacrylamide by reacting dimethylamine with bicyclo[2.2.1]hept-2-ene-2-carboxylic acid in autoclave to give *N,N*-dimethylbicyclo[2.2.1]hept-2-ene-2-carboxamide, followed by its thermal decomposition at 200°C *in vacuo*. Hoke et al.[21] reported the use of pyrolysis for the preparation of *N*-alkylacrylamides. In this, *N*-(1,1-dimethyl-1-3-oxybutyl)-3-methoxy propionamide was hydrogenated in the presence of dimethylamine, *p*-toluenesulfonic acid, and a Pt catalyst to give *N*-(1,1-dimethyl–3-dimethyl aminobutyl)-3-methoxy propionamide. This was heated with NaOH at 80–90°C for 3 h to give *N*-(1,1-dimethyl–3-dimethylaminobutyl)acrylamide.

Reaction of Olefins with Nitriles

N-Alkylacrylamides have also been synthesized by reacting acrylonitrile with various olefins. Takada et al.[22] reported the synthesis of *N-tert*-octylacrylamide by reacting acrylonitrile with 2,4,4-trimethyl-1-pentene at 40°C for 3 h using 65% H_2SO_4 as a solvent. Similarly, acrylonitrile was also reacted with dimethylamine at 200°C in the presence of the Lewis acid $ZnCl_2$ to give *N,N*-dimethylacrylamide.[23] Biale[24] reported the synthesis of *N*-propylacrylamide by oxidative carbonylation. In this, $PdCl_2$, $CuCl_2$, CuCl, and propylamine in a 1 : 10 : 10 : 120 ratio were treated with methane, carbon monoxide, and oxygen to give *N*-propylacrylamide.

Thus, there is a need to develop a simpler method for the synthesis of *N*-alkyl as well as *N*-acylacrylamides which will obviate harsh reaction conditions and tedious workups. It is especially desirable that such a method be applicable for the synthesis of long-chain alkyl/acylacrylamides. In this communication, we report a novel method for the synthesis of *N*-alky- and *N*-acylacrylamides. The method is essentially a single-step reaction wherein Friedel–Craft alkylation and the acylation of acrylamide at room temperature was demonstrated.[25]

EXPERIMENTAL

Materials

Acrylamide (CH_2═CH—CO—NH_2), anhydrous aluminum chloride ($AlCl_3$), 1-hexadecanol [CH_3—$(CH_2)_{14}$—CH_2—OH], 1-docosanol [CH_3—$(CH_2)_{20}$—CH_2—OH], 1-octadecanoic acid [CH_3—$(CH_2)_{16}$—COOH], 1-dodecanoic acid [CH_3—$(CH_2)_{10}$—COOH], and thionyl chloride ($SOCl_2$) were from local suppliers. 1-Chlorohexadecane [CH_3—$(CH_2)_{14}$—CH_2—Cl], 1-chlorodocosane [CH_3—$(CH_2)_{20}$—CH_2—Cl], 1-octadecanoyl chloride [CH_3—$(CH_2)_{16}$—COCl], and 1-dodecanoyl chloride [CH_3—$(CH_2)_{10}$—COCl] were synthesized by the reaction of thionyl chloride on the respective alcohols and acids. Distilled acetone was used as a solvent for the reactions.

Instrumentation

Melting points were determined on a Mettler melting point apparatus. IR spectra were recorded on a Perkin–Elmer FTIR 1600 spectrophotometer, and ^{1}H-NMR spectra, on a Bruker 300 MHz spectrometer. Elemental analyses were done on a Perkin–Elmer elemental analyzer.

N-Alkylacrylamides

Synthesis of N*-Hexadecylacrylamide [CH_2═CH—CO—NH—CH_2—$(CH_2)_{14}$—CH_3]*

Into a 250-mL-capacity conical flask equipped with an anhydrous calcium chloride ($CaCl_2$) guard tube, 13 g 1-chlorohexadecane [CH_3—$(CH_2)_{14}$—CH_2—Cl] (0.05*M*), 3.5 g acrylamide (CH_2═CH—CO—NH_2) (0.05*M*), and 50 mL acetone were placed to obtain a clear solution. The solution was stirred with a magnetic needle at room temperature. Anhydrous aluminum chloride ($AlCl_3$), 6.5 g (0.05*M*), was added and the reaction mixture was stirred at room tempera-

ture. After 5–10 min of stirring, vigorous evolution of hydrogen chloride took place which ceased after about 5 min. (The reaction was conducted in a hood, and as the amount HCl gas so generated was less, it was allowed to exhaust. In the case of a large batch size, HCl gas can be trapped in water.) The temperature of the reaction mixture was increased to 40–50°C. It was then cooled to room temperature and poured into 500 mL cold distilled water. A white product precipitated. The product was isolated and purified by reprecipitation from acetone into cold water. The purified product was dried in a vacuum desiccator.

Yield: 65%. Melting point: 47°C. IR (nujol): 1620 cm^{-1} (—C═C—), 1660 cm^{-1} (amide carbonyl). ^{1}H-NMR ($CDCl_3$): 0.9 δ 3H triplet (—CH_3 of hexadecyl C_{16}), 1.3 δ 28H broad singlet (C_2–C_{15} methylene protons of hexadecyl), 1.7 δ 2H multiplet (—CH_2— of hexadecyl C_1), 3.5 δ 1H multiplet (—CH═CH_2), 4.0 δ 2H multiplet (—CH_2═CH—), 7.3 δ 1H triplet singlet (—NH—CH_2—).

ANAL. Calcd for ($C_{19}H_{37}NO$): C, 77.28%, H, 12.54%, N, 4.74%. Found: C, 77.25%, H, 12.53%, N, 4.72%.

Synthesis of N-*Docosanylacrylamide [CH_2═CH—CO—NH—CH_2—$(CH_2)_{20}$—CH_3]*

Into a 250-mL-capacity conical flask equipped with an anhydrous calcium chloride ($CaCl_2$) guard tube, 8.63 g 1-chlorodocosane [CH_3—$(CH_2)_{20}$—CH_2—Cl] (0.025*M*), 1.75 g acrylamide (CH_2═CH—CO—NH_2) (0.025*M*), and 50 mL acetone were placed to obtain a clear solution. The solution was stirred with a magnetic needle at room temperature. Anhydrous aluminum chloride ($AlCl_3$), 3.25 g (0.025*M*), was added and the reaction mixture was stirred at room temperature. After 5–10 min of stirring, vigorous evolution of hydrogen chloride took place which ceased after about 5 min. The product was isolated following the procedure described for the synthesis of *N*-hexadecylacrylamide.

Yield: 83%. Melting point: 65°C. IR (nujol): 1615 cm^{-1} (—C═C—), 1650 cm^{-1} (amide carbonyl). ^{1}H-NMR ($CDCl_3$): 0.8 δ 3H triplet (—CH_3 of docosanyl C_{22}), 1.2 δ 40 H broad singlet (C_2–C_{21} methylene protons of docosanyl), 1.6 δ 2H multiplet (—CH_2— of docosanyl C_1), 3.5 δ 1H multiplet (—CH═CH_2), 4.0 δ 2H multiplet (—CH_2═CH—), 7.3 δ 1H triplet (—NH—CH_2—).

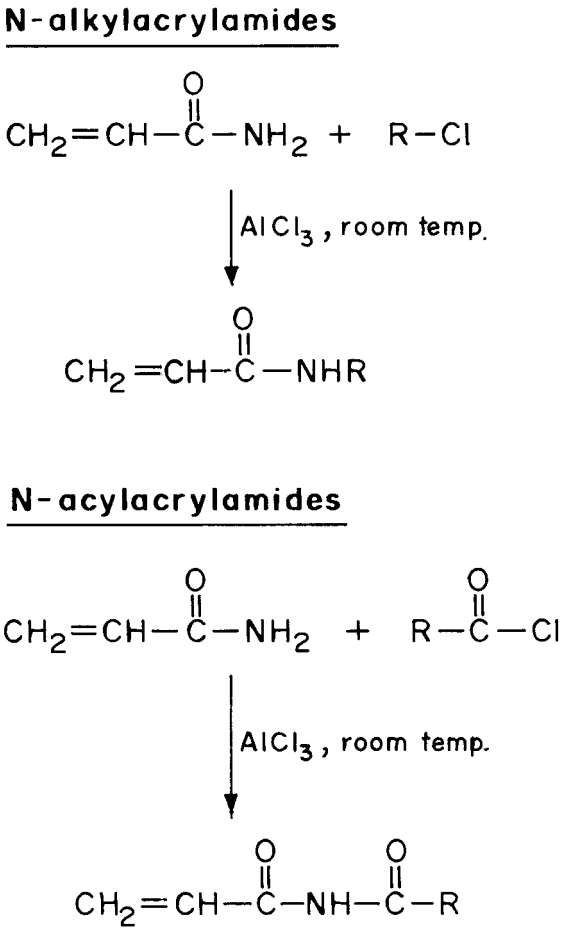

Figure 1 Reaction scheme.

ANAL. Calcd for ($C_{25}H_{49}NO$): C, 75.94%; H, 12.40%; N, 3.54%. Found: C, 75.96%; H, 12.38%; N, 3.55%.

N-Acylacrylamides

Synthesis of N-*Dodecanoylacrylamide [CH_2═CH—CO—NH—CO—CH_2—$(CH_2)_9$—CH_3]*

Into a 250-mL-capacity conical flask equipped with a calcium chloride ($CaCl_2$) guard tube, 10.9 g 1-dodecanoyl chloride [CH_3—$(CH_2)_{10}$—COCl] (0.05*M*), 3.5 g acrylamide (CH_2═CH—CO—NH_2) (0.05*M*), and 50 mL acetone were placed to obtain a clear solution. The solution was stirred with a magnetic needle at room temperature. Anhydrous aluminum chloride ($AlCl_3$), 6.5 g (0.05*M*), was added and the reaction mixture was stirred at room temperature. After 5–10 min of stirring, vigorous evolution of hydrogen chloride took place which ceased after about 5 min. The product was

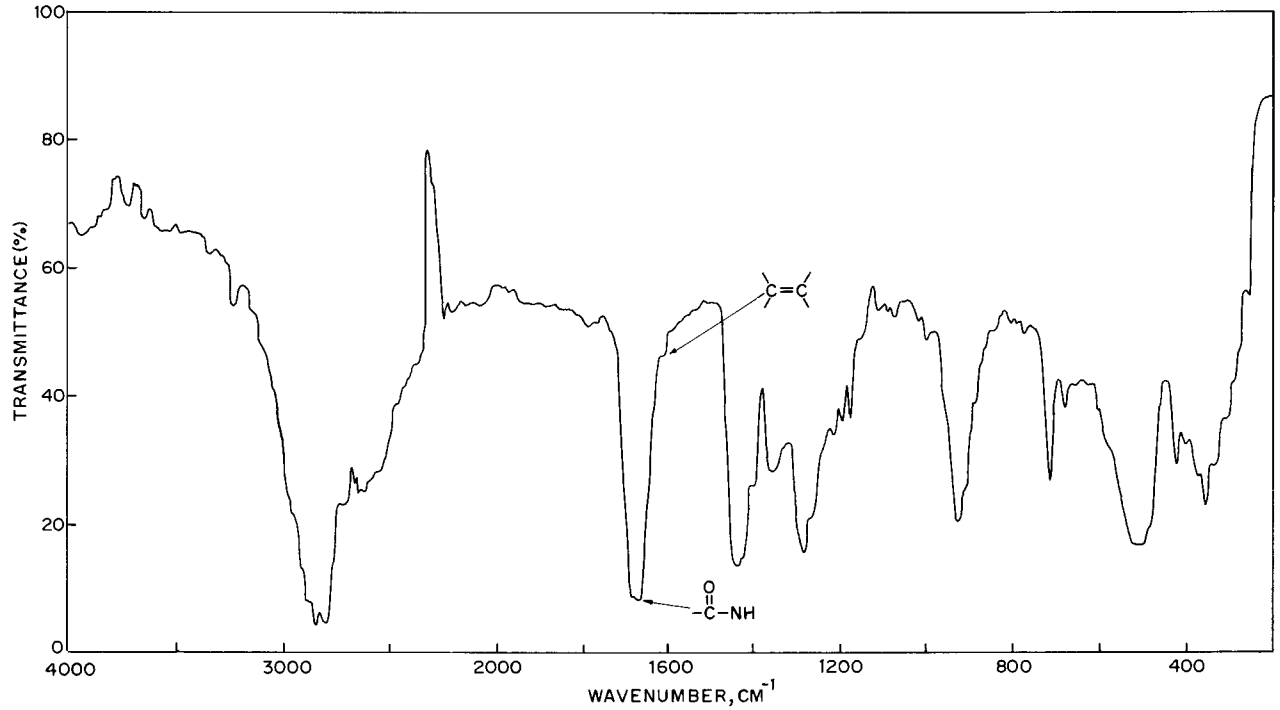

Figure 2 IR spectrum of *N*-octadecanoylacrylamide.

isolated following the procedure described for the synthesis of *N*-haxadecylacrylamide.

Yield: 50%. Melting point: (waxy solid; the product is a soft waxy solid at room temperature which exhibits a melting range when heated above room temperature). IR (nujol): 1630 cm^{-1} (—C═C—), 1680 cm^{-1} (amide carbonyl). ^{1}H-NMR ($CDCl_3$): 0.9 δ 3H triplet (—CH_3 of dodecanoyl C_{12}), 1.3 δ 16H broad singlet (methylene protons of dodecanoyl C_3–C_{10}), 1.6 δ 2H triplet (—CH_2— of dodecanoyl C_{11}), 2.4 δ 2H triplet (—CH_2— of dodecanoyl C_2), 2.7 δ 1H multiplet (—CH═CH_2), 3.7 δ 2H multiplet (CH_2═CH—), 7.2 δ singlet 1H (—CO—NH—CO—).

ANAL. Calcd for ($C_{15}H_{27}NO_2$): C, 71.14%; H, 10.67%; N, 5.53%. Found: C, 71.10%; H, 10.68%; N, 5.55%.

Synthesis of N-*Octadecanoylacrylamide* [CH_2═CH—CO—NH—CO—CH_2—$(CH_2)_{15}$—CH_3]

Into a 250-mL-capacity conical flask equipped with an anhydrous calcium chloride ($CaCl_2$) guard tube, 15.1 g 1-octadecanoyl chloride [CH_3—$(CH_2)_{16}$—COCl] (0.05*M*), 3.5 g acrylamide (CH_2═CH—CO—NH_2) (0.05*M*), and 50 mL acetone were placed to obtain a clear solution. The solution was stirred with a magnetic needle at room temperature. Anhydrous aluminum chloride ($AlCl_3$), 6.5 g (0.05*M*), was added and the reaction mixture was stirred at room temperature. After 5–10 min of stirring, vigorous evolution of hydrogen chloride took place which ceased after about 5 min. The product was isolated following the procedure described for the synthesis of *N*-hexadecylacrylamide.

Yield: 80 %. Melting point: 56°C. IR (nujol): 1610 cm^{-1} (—C═C—), 1650 cm^{-1} (amide carbonyl). ^{1}H-NMR (DMSO-d_6): 0.8 δ 3H triplet (—CH_3 of octadecanoyl C_{18}), 1.3 δ 28H broad singlet (C_4–C_{17} methylene protons of octadecanoyl), 1.5 δ 2H triplet (—CH_2— of octadecanoyl C_3), 2.2 δ 2H triplet (—CH_2— of octadecanoyl C_2), 2.5 δ 1H multiplet (—CH═CH_2), 3.3 δ 2H multiplet (CH_2═CH—), 7.1 δ 1H singlet (—CO—NH—CO—).

RESULTS AND DISCUSSION

As described in the introduction, most of the previously cited processes' harsh reaction conditions, for example, high temperature and pressure, were used. Also, in most of the cases, *N*-alkylacrylamides having small alkyl chain lengths were synthesized.

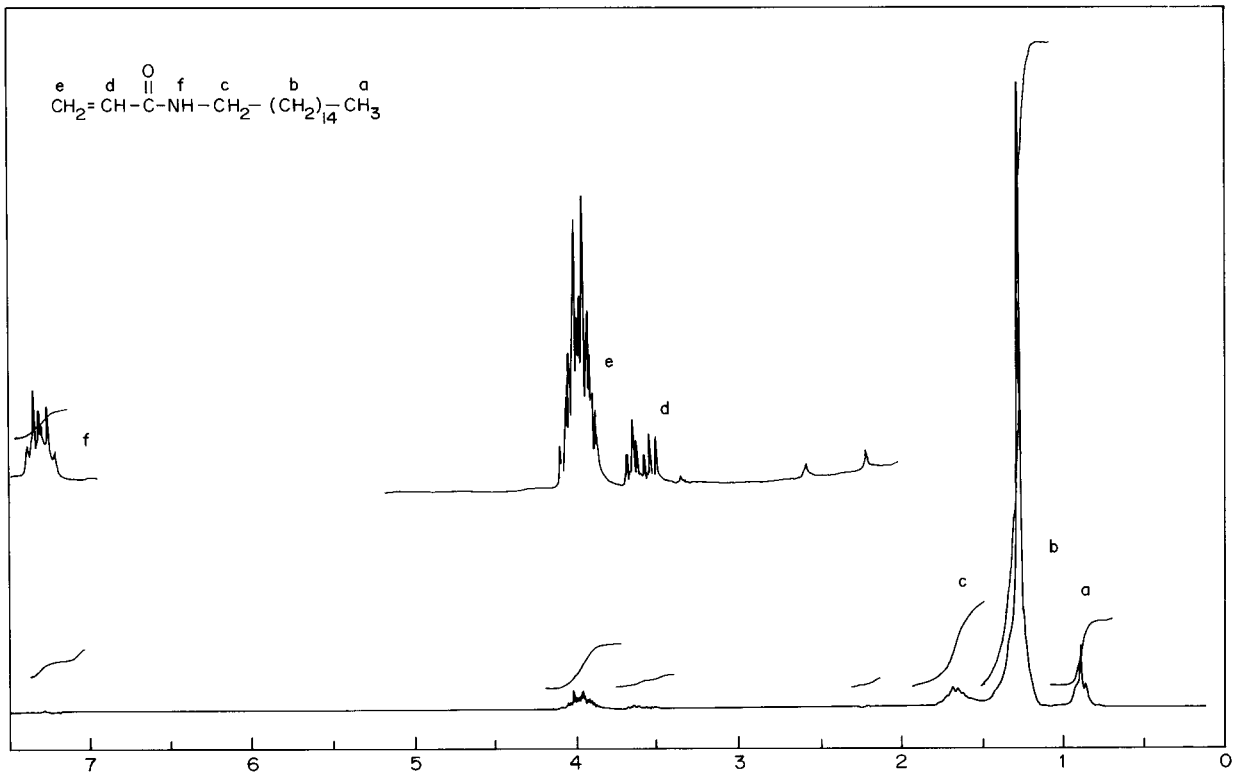

Figure 3 ^{1}H-NMR spectrum of *N*-hexadecylacrylamide.

Friedel–Craft *N*-Alkylation and *N*-Acylation of Acrylamide

Friedel–Craft alkylation is an effective and convenient method which is widely used to synthesize linear alkyl benzenes (LABs). Despite this, its use in the synthesis of *N*-alkylacrylamides has not been reported yet. In this work, we used the Friedel–Craft reaction wherein acrylamide is reacted with alkyl chloride and acyl chloride in the presence of anhydrous aluminum chloride ($AlCl_3$) to give *N*-alkyl and *N*-acylacrylamide, respectively. The reaction scheme is shown in Figure 1.

As mentioned earlier in the introduction, our aim was to demonstrate the applicability of this reaction for the synthesis of long-chain *N*-alkylacrylamides. Thus, we selected two long-chain alkyl chlorides, namely, 1-chlorohexadecane [CH_3—$(CH_2)_{14}$—CH_2Cl] and 1-chlorodocosane [CH_3—$(CH_2)_{20}$—CH_2—Cl] and two long-chain acyl chlorides, namely, 1-dodecanoyl chloride [CH_3—$(CH_2)_{10}$—COCl] and 1-octadecanoyl chloride [CH_3—$(CH_2)_{16}$—COCl], for reacting with acrylamide (CH_2═CH═CO—NH_2). Stoichiometric amounts of acrylamide and alkyl/acyl chloride were dissolved in acetone and then a stoichiometric amount of a Lewis acid catalyst, anhydrous $AlCl_3$, was added to the reaction mixture. After stirring for 5–10 min at room temperature, vigorous evolution of hydrogen chloride gas took place, indicating *N*-alkylation and *N*-acylation of acrylamide. The reaction was over only in a few minutes. The reaction was exothermic, which increased the temperature of the reaction mixture from room temperature (25°C) to 40–50°C. It was cooled to room temperature and then the products were isolated as described in the Experimental section. Fifty-to-eighty percent yields were obtained.

Characterization of *N*-Alkyl- and *N*-Acylacrylamides

The products synthesized in this study were characterized for melting point, IR, ^{1}H-NMR, and elemental analyses. As an example, the IR spectrum of *N*-octadecanoylacrylamide [CH_2═CH—CO—NH—CO—CH_2—$(CH_2)_{15}$—CH_3] is shown in Figure 2. It shows a sharp peak at 1650 cm^{-1} that corresponds to an amide bond and a small shoulder at 1610 cm^{-1} that corresponds to a carbon–

carbon double bond. Satisfactory IR spectra for all the other compounds were obtained. (See data listed in the Experimental section.) Figure 3 shows the ^{1}H-NMR spectrum of *N*-hexadecylacrylamide [CH_2═CH—CO—NH—CH_2—$(CH_2)_{14}$—CH_3]. It can be seen that the signals in the spectrum are in accordance with the proposed structure of the product. Particularly, the peak at 7.3 δ that corresponds to —N<u>H</u>—CH_2— exhibits a triplet due to coupling of the —NH proton with adjacent —CH_2— protons. A similar triplet for —N<u>H</u>—CH_2— coupling is also observed in the ^{1}H-NMR spectrum of *N*-docosanylacrylamide [CH_2═CH—CO—NH—CH_2—$(CH_2)_{20}$—CH_3]. In this context, it may be noted that such —NH—CH_2— coupling is not possible in the case of *N*-acylacrylamides since —NH— is flanked at both the ends by carbonyl groups (—CO—NH—CO—). Accordingly, the ^{1}H-NMR spectra for *N*-dodecanoylacrylamide [CH_2═CH—CO—NH—CO—CH_2—$(CH_2)_9$—CH_3] and *N*-octadecanoylacrylamide [CH_2═CH—CO—NH—CO—CH_2—$(CH_2)_{15}$—CH_3] exhibited a singlet for —CO—N<u>H</u>—CO— at 7.2 δ and 7.1 δ, respectively. The compounds synthesized in this study were also characterized for elemental analyses. The data listed in the Experimental section show that the calculated and found values of the percentage of C, H, and N are in close agreement. These characterization data further support the formation of *N*-alkyl- and *N*-acylacrylamides by the Friedel–Craft reaction.

CONCLUSIONS

N-alkyl- and *N*-acylacrylamides were synthesized by the Friedel–Craft alkylation and the acylation of acrylamide using anhydrous aluminum chloride as a catalyst. The reactions proceeded smoothly at room temperature and the time required for the reaction was very short. The long-chain *N*-alkyl- and *N*-acylacrylamides synthesized in this work indicate the general applicability of this approach for the synthesis of a wide range of alkylacrylamides. Thus, a novel, single-step method synthesis of alkylacrylamides was developed which obviates harsh and multistep conventional reaction conditions.

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