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Synthesis of *N*-Poly(alkenyl)acrylamides: A Novel Class of Acrylamido Functional Macromonomers

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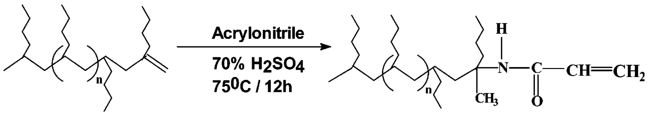
Introduction. *N*-Alkylacrylamides, such as *N*-isopropyl, *N*-*tert*-butylacrylamide, and *N*-*n*-octylacrylamide, etc., are an important class of monomers useful for the synthesis of polymers with controlled hydrophilicity and are useful as sizing agents, rheology modifiers, and water-soluble polymers.[1] Among these, *N*-isopropylacrylamide is the most important owing to the practical utility of its polymer. Poly(*N*-isopropylacrylamide) (PNIPAAM) has been widely studied for its novel thermal behavior in aqueous media.[2] *N*-Alkylacrylamides (alkyl = C_6 to C_{18}) are also widely used in the synthesis of hydrophobically modified polyelectrolytes and hydrogels.[3−6] In general, *N*-isopropyl and *N*-octylacrylamide are prepared by three methods, namely, reaction of acryloyl chloride with alkylamine,[7] pyrolysis or thermal decomposition of the corresponding carboxylic acid amides,[8] and the reaction of olefins with nitriles (Ritter reaction).[9] The nonavailability of either higher alkylamines (>18 carbon atoms) or carboxylic acid amides restricts the first two methods for the synthesis of *N*-alkylacrylamides with >18 carbon atoms. The reaction of olefins with nitriles is the most suitable method for the synthesis of *N*-alkylacrylamides and has been widely used. *N*-(*n*-Octylacrylamide) is produced by the Ritter reaction of acrylonitrile with 2,4,4-trimethyl-1-pentene.[10]

Poly(olefin) oligomers with high vinylidene unsaturation at the terminal end is a potential precursor to *N*-alkylacrylamides via Ritter reaction. Such a reaction may provide access to a wide range of hydrophobically modified acrylamides with varying chain lengths of the alkyl chain as well as branching characteristics. In this communication we wish to report the feasibility and generality of the Ritter reaction with vinylidene-terminated poly(hexene-1) oligomers. Hexene-1 was used as a representative α-olefin in view of the ease of handling a liquid monomer in the laboratory.

Experimental Section. a. Materials. Vinylidene-terminated poly(hexene-1) with M_n varying from 400 to 1000 was prepared by polymerization of hexene-1 using Cp_2ZrCl_2/MAO catalyst in the absence of a solvent. Acrylonitrile, *n*-pentane, and *n*-hexane were obtained from s.d. fine chemicals, Boisar, India, and distilled before use.

b. Preparation of Vinylidene-Terminated Poly(hexene-1). A single-necked 250 mL round-bottom flask along with a magnetic stirring bar was fitted with a septum adapter and flame-dried and cooled under argon. The flask was charged with 12.5 mL (0.1 mol) of freshly distilled hexene-1 through a hypodermic syringe. To this 3 mL of a 2 M solution of MAO (6×10^{-3} mol) was added. The reaction was initiated by addition of 0.22 mL of a 3.4×10^{-3} M solution (7.5×10^{-7} mol, stock solution prepared by dissolving 10 mg of Cp_2ZrCl_2 in 10 mL of toluene) of Cp_2ZrCl_2 at 50 °C. The reaction was terminated by adding acidified methanol. After termination the oligomer was found to separate from the unreacted monomer and methanol mixture. The supernatant liquid, which consists of unreacted monomer and methanol, was separated from the viscous oligomer. The viscous oligomer was diluted with *n*-hexane and transferred into a separating funnel, and the organic layer was washed several times with distilled water followed by sodium bicarbonate and water to remove any traces of alkali. After the work-up, the solution was dried with anhydrous sodium sulfate, and the solvent was removed in a vacuum.

Scheme 1. Ritter Reaction of Vinylidene-Terminated Poly(hexene-1) with Acrylonitrile



c. Ritter Reaction of Vinylidene-Terminated Poly(hexene-1) with Nitriles. A two-necked round-bottom flask, fitted with a dropping funnel and reflux condenser, was charged with 5.2 g (0.1 mol) of acrylonitrile and 70% H_2SO_4 (2 mL) was transferred into the round-bottom flask at room temperature. The contents of the flask was flushed with N_2 and heated to 75 °C. Neat poly(hexene-1), M_n = 380, 3.8 g (0.01 mol), was added to the flask using a dropping funnel over a period of 1 h. After the addition, the reaction was continued for a period of an additional 12 h. The reaction was performed under an inert atmosphere of nitrogen. The reaction was worked up by addition of 10−15 mL of distilled water and extraction of the organic phase into diethyl ether. Evaporation of the ether resulted in a viscous liquid. The viscous liquid was redissolved in methanol, and a small amount of methanol insoluble fraction was separated from the solution. The clear methanol solution was evaporated and the product redissolved in *n*-pentane. The *n*-pentane solution was slowly evaporated yields a solid product, 4.2 g (yield > 95%).

d. Analysis. The number-average molecular weight (M_n) of *N*-poly(alkenyl)acrylamides was determined by VPO as well as ^{1}H NMR. Structural analysis was carried out by both ^{1}H and ^{13}C NMR. The peaks due to acrylamide group were observed at 6.2, 5.5, and 5.2 ppm for the corresponding protons of CH_2, CH, and NH, respectively, in ^{1}H NMR. M_n of *N*-poly(alkenyl)acrylamide was calculated on the basis of protons of a vinyl group. The number-average degree of functionality (F_n) was calculated as $F_n = M_n$ by VPO/M_n by ^{1}H NMR. FT-IR spectra were obtained on a Perkin-Elmer 16 PC spectrophotometer. A spectrum was recorded in KBr pellet as well as in chloroform solution. Spectra were corrected for both KBr and $CHCl_3$ absorption. DSC analysis was carried out using Perkin-Elmer DSC-7 by scanning in the temperature range of −60 to 85 °C at a rate of 5 °C/min under a N_2 atmosphere. The functionalized oligomer sample was crystallized on a copper plate, and the WAXS pattern was obtained in reflection

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Table 1. Ritter Reaction of Vinylidene-Terminated Poly(hexene-1) with Acrylonitrile[a]

	poly(hexene-1)									
			end groups[b] (mol %)					M_n after functionalization		
run no.	M_n	mol	vinylidene	internal	acrylonitrile (mol)	yield (g)	conv (%)	VPO (a)	^{1}H NMR (b)	F_n (mol %) a/b
1	380	0.01	98.0	2.0	0.1	4.2	95.0	440	490	89
2	550	0.01	97.0	3.0	0.1	5.8	95.0	610	720	85
3	1080	0.005	94.0	6.0	0.05	5.6	94.0	1140	1440	80

[a] Reaction conditions: reaction temperature = 75 °C, reaction time = 12 h, 2 mL of 70% H_2SO_4 catalyst. [b] Determined by ^{1}H NMR.

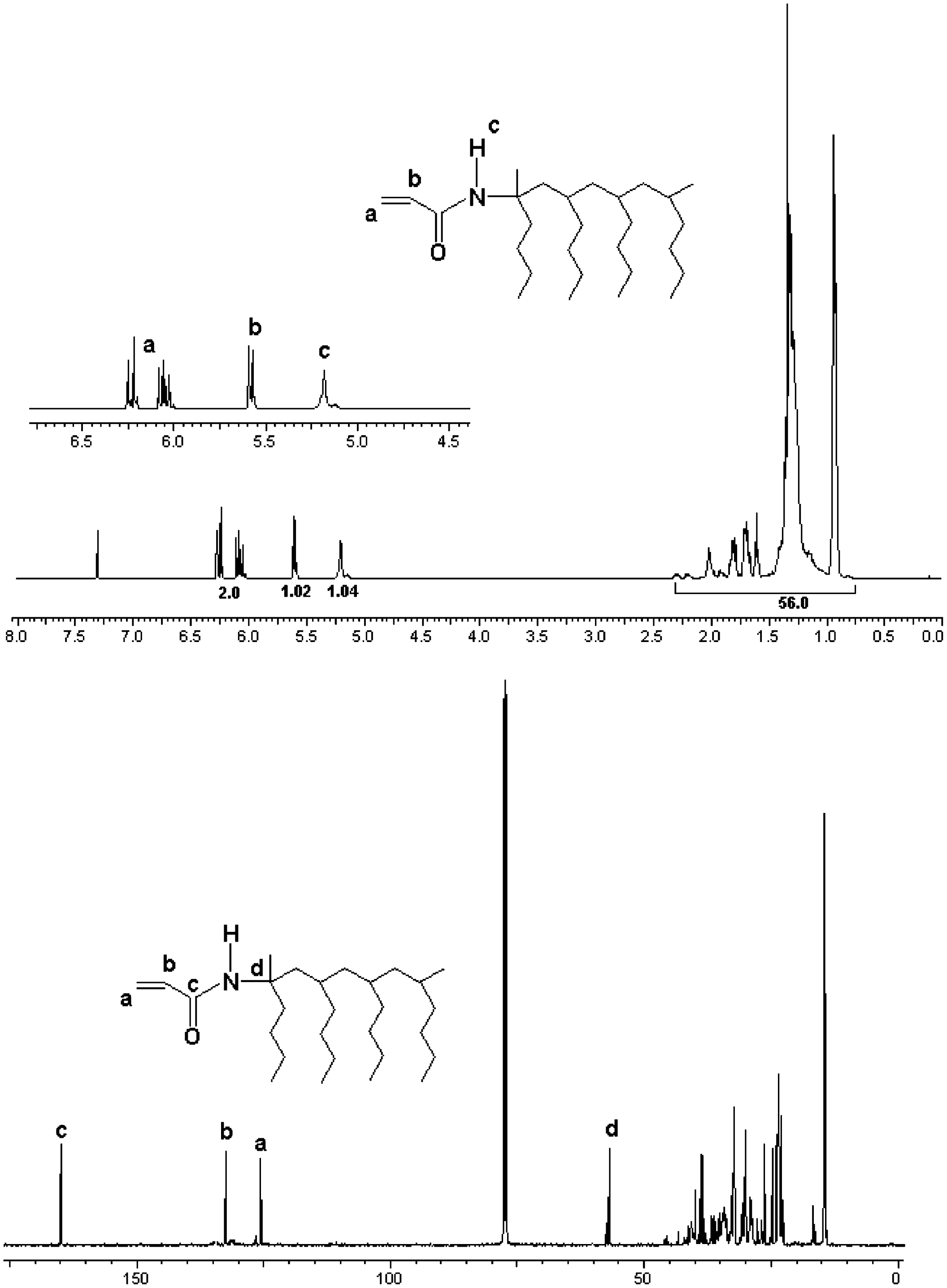
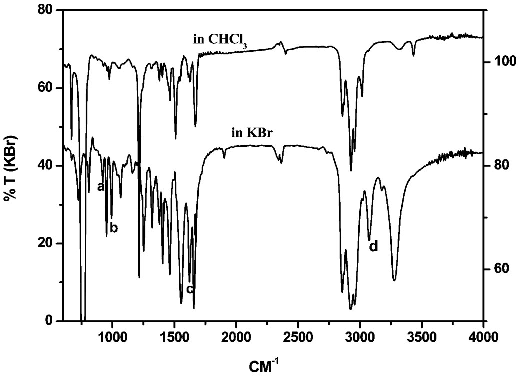


Figure 1. (a, top) ^{1}H NMR (500 MHz) of *N*-poly(alkenyl)acrylamide (from run 1, Table 1). (b, bottom) ^{13}C NMR (125.77 MHz) of *N*-poly(alkenyl)acrylamide (from run 1, Table 1).

mode using a Rigaku Dmax 2500 diffractometer fitted with a diffracted beam graphite monochromator. The radiation was Cu Kα and scanned between $2\theta = 2°$ and 30°. The generator was operated at 40 kV and 150 mA. SEM was performed using a Leica Cambridge (Stereoscan 440) scanning electron microscope. The crystals



Peaks: **a** (920 cm^{-1}) and **b** (990 cm^{-1}) = C-H alkene bending, **c** (1622 cm-1) = C=C stretching, **d** (3070 cm-1) = C-H alkene stretching.

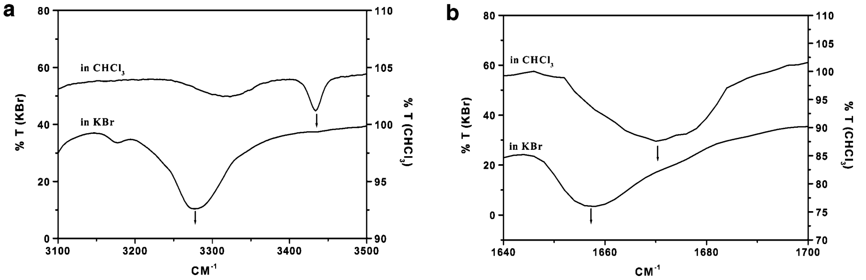


Figure 2. Full FT-IR spectra of *N*-poly(alkenyl)acrylamide in KBr and CHCl$_3$. (a) FT-IR spectra of *N*-poly(alkenyl)acrylamide in KBr and CHCl$_3$ (expanded region). (b) FT-IR spectra of *N*-poly(alkenyl)acrylamide in KBr and CHCl$_3$ (expanded region).

of *N*-poly(alkenyl)acrylamide were grown on gold in an automatic sputter coater by slow evaporation of solvent from *n*-pentane solution (Polaron equipment Ltd., scanning electron microscope coating unit E 5000, UK).

Results and Discussion. Reaction of nitriles with "in situ" generated carbocations to give *N-tert*-alkylamides (Ritter reaction) is one of the well-known methods for the introduction of nitrogen functionality at a tertiary carbon atom. A variety of N-substituted amides have been prepared using either *iso*-olefins or *tert*-alcohols and an acid catalyst. Therefore, it was decided to extend the Ritter reaction to terminal vinylidene unsaturated poly(hexene-1) in the presence of nitriles to give *N*-poly(alkenyl)alkylamides (Scheme 1). We reasoned that the terminal vinylidene unsaturation bearing an *iso*-olefin could form a tertiary carbocation in the presence of an acid catalyst, capable of undergoing a Ritter reaction.

The Ritter reaction was carried out using vinylidene-terminated oligomers of poly(hexene-1) with acrylonitrile using 70% H_2SO_4 catalyst. The results obtained are shown in Table 1. Reaction was carried out by direct addition of oligomers of poly(hexene-1)s with number-average molecular weight (M_n) less than 1000 (runs 1−3 in Table 1). A number-average degree of functionality (F_n) = 0.9 was obtained for lower molecular weight oligomer (M_n = 400). However, F_n decreased to 0.80 when the M_n increased to 1000.

Control experiments performed in the absence of acrylonitrile did not result in oligomerization of hexene-1 as evidenced by the fact that the M_n values of the oligomer remained unchanged. The rate-determining step in a Ritter reaction is believed to be the formation of carbocation in the presence of an acid catalyst. The tertiary carbocation formed is immediately trapped by an excess of acrylonitrile (5-fold excess) present in the reaction system. This reaction is, generally, faster than a competing isomerization reaction. No evidence for isomerized oligomer was observed in the reaction product.

N-Poly(alkenyl)acrylamide obtained from runs 1 and 2 were found to be solid materials after slow evaporation of an *n*-pentane solution, unlike the corresponding oligo(hexene-1)s, which are free-flowing liquids. This behavior was attributed to the intermolecular hydrogen bonding between amide groups. The sample obtained from run 3 was found to be semisolid in nature. *N*-Poly(alkenyl)acrylamides were found to be soluble in both polar and nonpolar solvents such as methanol, acetonitrile, chloroform, and *n*-pentane. The corresponding oligo(hexene-1)s are not soluble in polar solvents like methanol and acetonitrile. This solubility behavior is indicative of the amphiphilic nature of *N*-poly(alkenyl)acrylamides.

The ^{1}H NMR and ^{13}C NMR spectra of *N*-poly(alkenyl)acrylamide obtained from run 1 (Table 1) are shown in parts a and b of Figure 1, respectively, and confirm the structure of the oligomers.

A more detailed examination of the solid sample from run 1 (Table 1) was carried out. FT-IR spectra of samples were recorded in KBr pellet and in chloroform solution (Figure 2). The N−H stretch bands in KBr and chloroform solution appeared at 3278 and 3434 cm^{-1}, respectively. Secondary amide groups engaged in amide−amide hydrogen bonds display N−H strech bands in the range 3250−3370 cm^{-1}.[11] The C=O stretch in CHCl$_3$ and in KBr appeared at 1671 and 1658 cm^{-1}, respectively. The frequency shift in the IR provides evidence of strong intermolecular hydrogen bonding. A differential scanning chromatograph was recorded by heating the sample from −60 to 85 °C (Figure 3a). A melting endotherm was observed at 54 °C (ΔH = 58.3

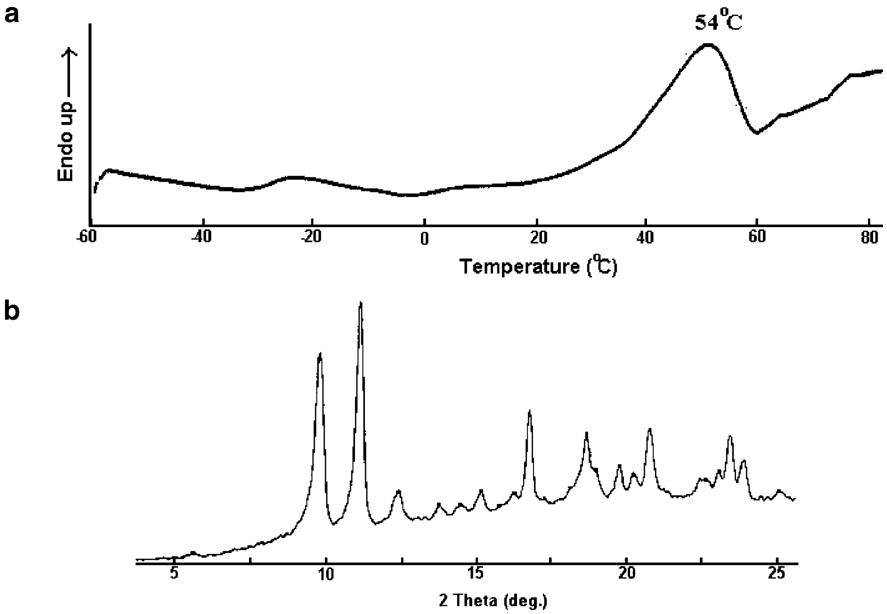


Figure 3. (a) DSC of *N*-poly(alkenyl)acrylamide (run 1). (b) WAXS pattern of *N*-poly(alkenyl)acrylamide (run 1).

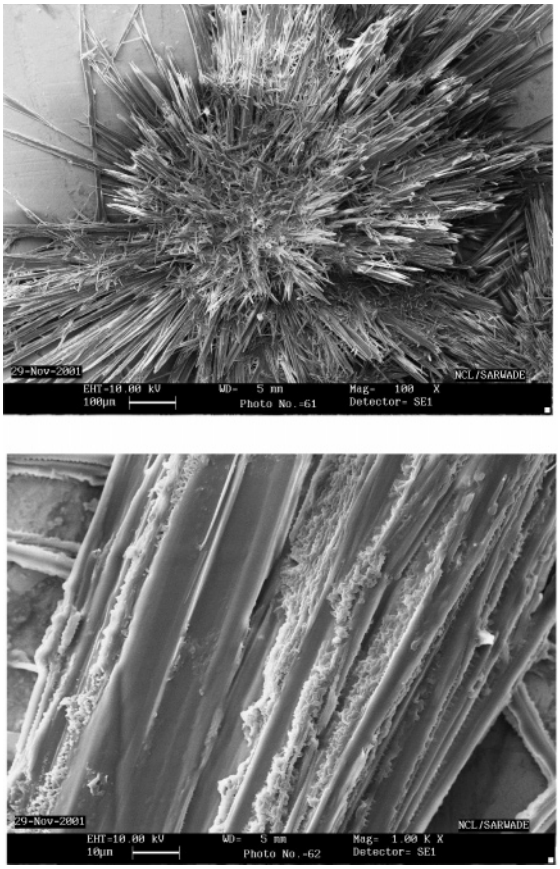


Figure 4. Scanning electron micrographs of *N*-poly(alkenyl)-acrylamides (run 1).

J/g), which can be attributed to the disruption of hydrogen bonding. The WAXS diffraction pattern (Figure 3b) exhibited sharp peaks, characteristics of a crystalline material. The scanning electron micrograph (Figure 4) exhibited a prolific growth of dendritic crystals with rodlike fibrils.

Conclusions. A polyolefin bearing terminal alkylamide functional group could be synthesized by Ritter reaction of terminal vinylidene double bonds in poly(hexene-1) with acrylonitrile using an acid catalyst. This is the first example of a postpolymerization functionalization of terminal vinylidene double bond in a polyolefin with a terminal functional acrylamide functional group.[12] The number-average degree of functionality (F_n) as high as 90 mol % was obtained. *N*-Poly(alkenyl)-acrylamide was found to be aggregated via intermolecular hydrogen bonding as evidenced by FT-IR and the appearance of an endothermic melting transition in DSC. Further analysis by WAXS and scanning electron microscopy reveals the occurrence of rodlike dendritic structure. *N*-Poly(alkenyl)acrylamide is a useful macromonomer and may find applications in the synthesis of novel hydrophobically modified polymers.

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(12) Poly(hexene-1) also undergoes a Ritter reaction with acetonitrile and benzonitrile to yield *N*-poly(alkenyl)acetamide and *N*-poly(alkenyl)benzamide (unpublished results).

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