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

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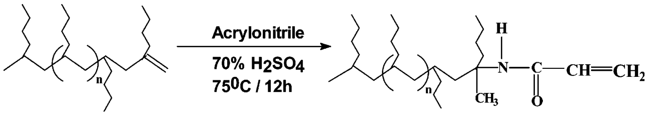
Introduction. *N*-Alkylacrylamides, such as *N*-isopropyl, *N*-*tert*-butylacrylamide, and *N*-*n*-octylacrylamide, etc., are an important class of monomers useful for the synthesis of polymers with controlled hydrophilicity and are useful as sizing agents, rheology modifiers, and water-soluble polymers.[1] 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.

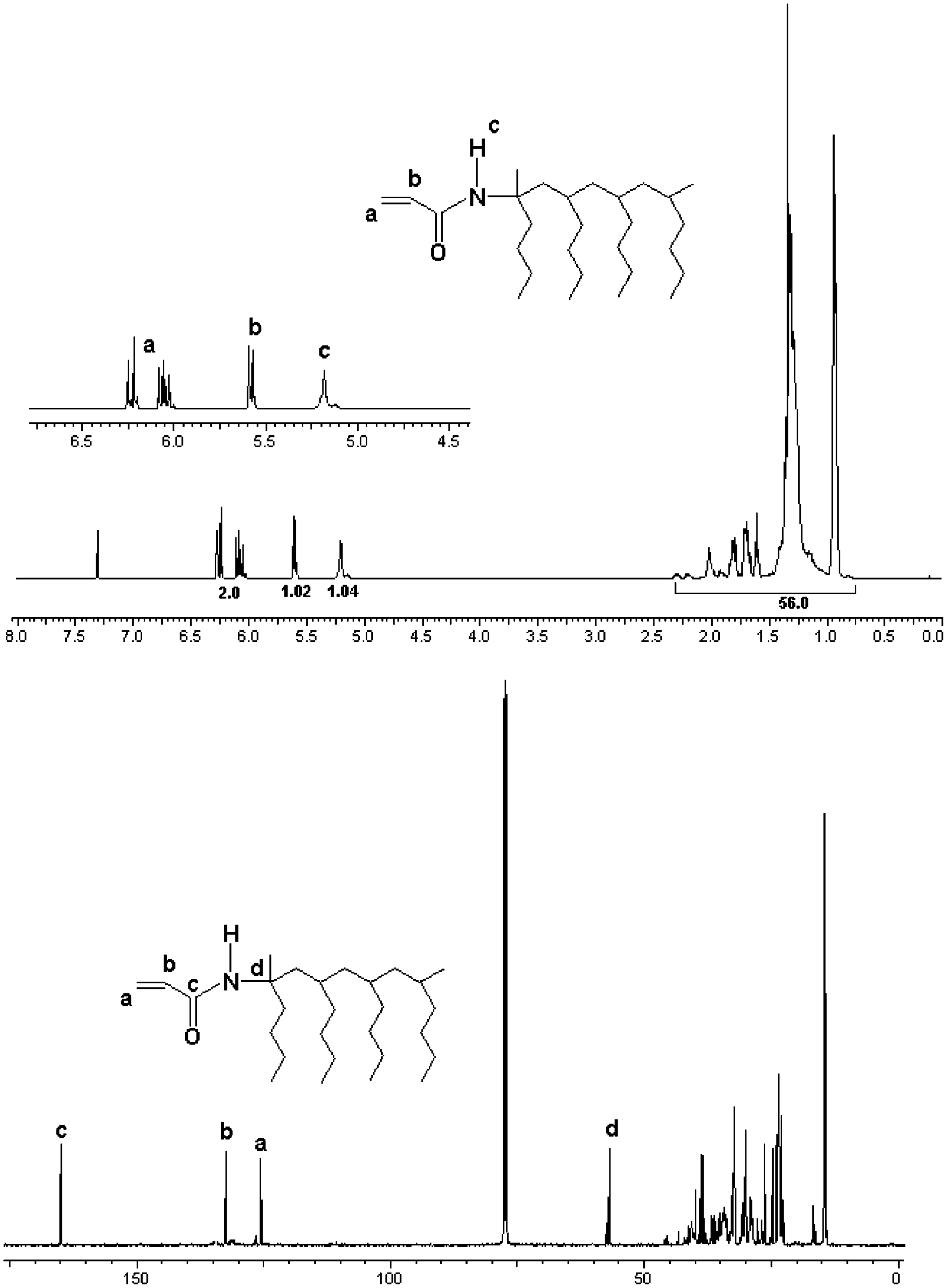

Figure 1. (a, top) ^{1}H NMR (500 MHz) of *N*-poly(alkenyl)acrylamide (from run 1, Table 1). (b, bottom) ^{13}C NMR (125.77 MHz) of *N*-poly(alkenyl)acrylamide (from run 1, Table 1).

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