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Synthesis and Polymerization of *N,O*-Bis(trimethylsilyl)acrylamide: A Protected Acrylamide[†]

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Introduction. Protecting groups in functional monomers make it possible to use polymerization techniques which would be incompatible with the unprotected monomer. This approach has attracted considerable attention in recent years, and monomers such as *p*-aminostyrene and maleimide have been polymerized using anionic initiators.[1,2] There is, however, no example of a protected acrylamide monomer in the literature. Unprotected acrylamide is known to undergo free-radical polymerization, and hydrogen-transfer polymerization is promoted by anionic initiators to give poly(β-alanine).[3] We undertook the synthesis, characterization, and polymerization of the simplest of the protected acrylamides, namely, *N,O*-bis(trimethylsilyl)acrylamide (BTSAm). Before this work, we found only two reports on the synthesis of BTSAm,[4,5] but without evidence for the isolation or unequivocal characterization of this monomer.

A patent issued to Ciba-Geigy described a thermal polymerization of BTSAm.[6] However, here too, the monomer as well as the polymer was neither isolated nor characterized.

In this paper, we report the synthesis, isolation, and characterization of the BTSAm monomer, its homopolymerization, and its copolymerization using free-radical initiators.

Experimental Section. Materials. Benzoyl peroxide (BPO) and 2,2′-azobis(isobutyronitrile) (AIBN) were recrystallized from methanol–chloroform and methanol, respectively. All solvents and monomers were purified using standard procedures. Acrylamide was recrystallized from chloroform. Triethylamine (SD fine chemicals, Bombay, India) was refluxed over KOH, distilled, and collected over KOH pellets. Chlorotrimethylsilane (Spectrochem India Ltd.) was distilled over calcium hydride. Oligo(α-methylstyryl)lithium was freshly prepared from α-methylstyrene and commercially available *n*-BuLi (1.6 M solution in hexanes; Aldrich) in the mole ratio of 4:1 at −40 °C, by stirring for 2 min.

Instruments. The ^{13}C and ^{1}H NMR spectra were recorded using a Bruker AC 200-MHz NMR spectrometer at 50.3 and 200 MHz, respectively. ^{29}Si NMR was recorded in the solid state using a Bruker MSL-300 NMR spectrometer at 59.6 MHz. Gas chromatographic analyses were performed using a Blue Star gas chromatograph Model 421 and a 10% SE-30 column on Chromosorb W (6 ft × $^{1}/_{8}$ in.) and nitrogen as a carrier gas (30 mL/min) at a column temperature of 175 °C using an FID detector. The column was conditioned by repeated injection of hexamethyldisilazane prior to use. Elemental analyses were performed on a Carlo-Erba Model CHNS-O EA1108 elemental analyzer. Intrinsic viscosities were determined using an Ubbelohde viscometer in a Schott-Gerate Model CK-100/CT-1450/AVS-440 automatic viscometer. Copolymer analyses were carried out by a combination of FTIR spectroscopy using a Perkin-Elmer PC-16 FTIR spectrometer, ^{1}H NMR spectra, and elemental analysis.

Preparation of *N,O*-Bis(trimethylsilyl)acrylamide (BTSAm). Acrylamide (4.2 g, 0.059 mol) and about 50 mg of copper wire pieces were placed in a 500-mL, four-neck flask under a positive argon flow. Triethylamine (180 mL) was transferred into the same flask, and the flask was cooled in an ice bath. Chlorotrimethylsilane (18.5 g, 0.17 mol) was added to the flask by means of a hypodermic syringe. The reaction mixture was allowed to gently reflux for 10 h. The contents of the flask was filtered under argon and filtrate distilled to remove unreacted triethylamine and chlorotrimethylsilane followed by vacuum distillation at 54 °C (5.5 mbar) to give BTSAm in 65% yield. Trace impurities of the monosilylated derivative could be separated from BTSAm by cooling the product to 0–10 °C when the monosilylated derivative crystallized out.

^{1}H NMR ($CDCl_3$): δ 0.20 and 0.35 (two singlets, $=NSi(CH_3)_3$ and $O\text{-}Si(CH_3)_3$, respectively), 5.55 (t, 1H, $=CH-$), 6.02 (d, 2H, $=CH_2$).

^{13}C NMR ($CDCl_3$): δ 0.58 and 1.36 ($=NSi(CH_3)_3$ and $-OSi(CH_3)_3$); 124.48 ($=CH_2$), 131.58 ($=CH-$), 156.29 ($OC=N$).

The monosilylated acrylamide was synthesized by reacting acrylamide with 1.2 equiv of both chlorotrimethylsilane and triethylamine in dry benzene for 6 h. Filtrate from the product mixture was distilled to yield crystals of *N*-(trimethylsilyl)acrylamide (TMSAm) which was recrystallized from dry hexane. Yield: 84%. Mp: 58 °C.

^{1}H NMR ($CDCl_3$): δ 0.28 (s, $-NHSi(CH_3)_3$), 5.3 [hump (D_2O exchangeable), $-NH-$], 5.65 (dd, 1H, $=CH-$), 6.2 (m, 2H, $CH_2=$).

Gas chromatography of a solution of TMSAm in dry benzene showed that the compound was more than 98% pure.

Free-Radical Polymerization and Copolymerization of BTSAm. The monomer, benzene, and the required quantity of initiator solution were transferred into ampules through a cannula under a positive pressure of argon. The ampules were sealed in vacuo, and the contents were polymerized at 80 and 70 °C with BPO and AIBN, respectively, for 6 h. The contents of the ampules were transferred under argon to a round-bottomed flask, solvent was removed under vacuum, and the residue was washed with dry hexane to remove any unreacted monomer. The polymer was dried. Yield: 70–75%. Elem anal. [poly(BTSAm)] N: found 6.38; theory, 6.50.

^{1}H NMR ($CDCl_3$): δ 0.0–0.5 (m, 18H, $-OSi(CH_3)_3$ and $=NSi(CH_3)_3$), 1.5–2.5 (two humps, 3H, $-CH_2CH<$). ^{29}Si NMR (solid state, MAS at 3.0 kHz, Me_4Si standard, taken without proton decoupling): δ −9.55 ($dbdNSi(CH_3)_3$), 16.41 ($-OSi(CH_3)_3$). The same procedure was used for the copolymerization of BTSAm.

Deprotection of Poly(BTSAm). The polymer (1 g) could be quantitatively deprotected by treatment with a 0.5 N HCl/THF mixture (1:1, v/v, 5–10 mL) and was precipitated in excess methanol.

^{1}H NMR ($CDCl_3$, or DMSO-d_6, or CD_3CN/D_2O): δ 0.75–2.5 (3H, two humps, $-CH_2CH-$, backbone protons contributed by both monomers, 6.25–7.5 (two humps, 5H, C_6H_5- phenyl ring protons of styrene).

IR (KBr, cm^{-1}): A, overtone or combination bands indicative of monosubstituted aromatic 1984–1760, styrene; B, overlap $C=O$ stretch from acrylamide, 1668; C, ring C$\overset{\cdots}{-}$C stretch 1598, 1492, 1450, styrene; D, out-of-plane C–H bend 760, styrene; E, out-of-plane C–C bend 702, styrene.

Results and Discussion. *N,O*-Bis(trimethylsilyl)acrylamide (BTSAm) was characterized by ^{1}H and ^{13}C

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Table 1. Polymerization of *N,O*-Bis(trimethylsilyl)acrylamide in Benzene

exp no.	[M] (mol/L)	[I] (mol/L)	conv to poly(BTSAm) (%)	$[\eta]^a$ of poly(BTSAm) (dL/g)	conv to polyacrylamide (%)	$[\eta]^b$ of polyacrylamide (dL/g)	silyl content[c] after wash (%)
				Initiator AIBN			
1	0.40	0.02	75	0.11	75	0.12	99
2	0.40	0.01	74	0.12	74	0.13	95
3	2.00	0.02	100		100	0.46	
				Initiator BPO			
4	0.40	0.02	74	0.14	74	0.21	96
5	0.40	0.01	70	0.14	73	0.24	96
6	2.00	0.02	100		100	0.52	

[a] In benzene at 30 ± 0.1 °C. [b] In water at 30 ± 0.1 °C. [c] Estimated from the ratio of relative integration of silyl protons of the polymer; 100% indicates that the observed ratio is identical to that expected, i.e., 1:6.

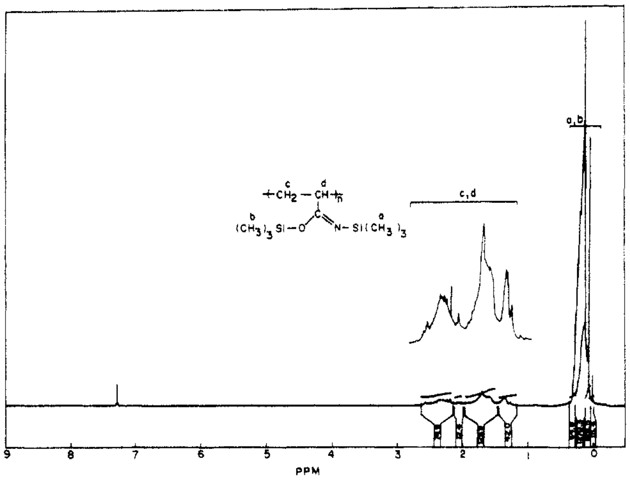
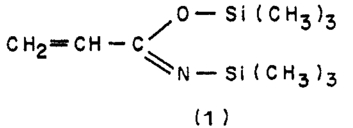


Figure 1. ${}^1H$ NMR of the poly[*N,O*-bis(trimethylsilyl)acrylamide].

NMR spectra. In the ${}^1H$ NMR spectrum, two peaks were observed in the silyl region (0.20 and 0.35 ppm) corresponding to nine protons each. This indicates that BTSAm is present exclusively in the imidate form (1), similar to



$$CH_2{=}CH{-}C\overset{O-Si(CH_3)_3}{\underset{N-Si(CH_3)_3}{\Big\langle}}$$

(1)

the bis(trimethylsilyl) derivative of acetamide.[7] The ${}^{13}C$ NMR spectrum of BTSAm confirms the structure. Attempts to obtain reproducible elemental analysis of BTSAm failed due to handling problems due to its extreme sensitivity to atmospheric moisture. Gas chromatographic analysis was therefore employed for ascertaining the purity. A freshly distilled sample of BTSAm was found to be more than 95% pure by GC (retention time 1.06 min). The major impurity was the monosilylated acrylamide which was established by comparison of the GC retention time of an authentic sample (retention time 0.81 min).

BTSAm (1) was polymerized using AIBN and BPO as initiators (Table 1). The poly(BTSAm) samples were isolated under careful exclusion of moisture and characterized by ${}^1H$ and ${}^{29}Si$ NMR as well as intrinsic viscosity in benzene. The ${}^1H$ NMR spectrum of the polymer washed with hexane to remove unreacted monomer is shown in Figure 1. The fact that the silyl groups were intact in the polymer after polymerization and workup was confirmed by estimation of the silyl content from NMR (Table 1). The ${}^{29}Si$ NMR spectrum of the polymer in the solid state shows two distinct silicon peaks of almost equal intensity (Figure 2) which indicates that the polymer also exists in the imidate form like the monomer.

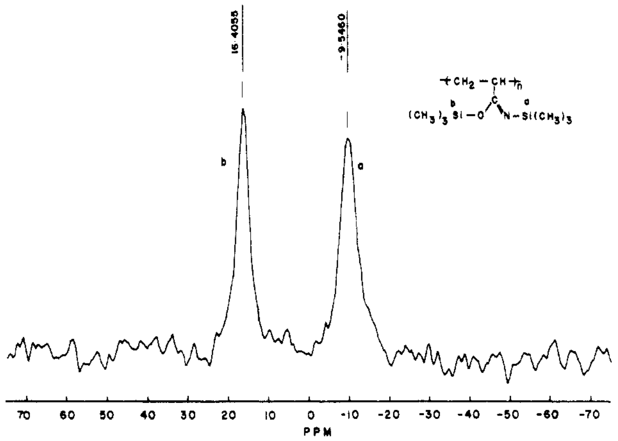


Figure 2. CP-MAS ${}^{29}Si$ NMR of poly[*N,O*-bis(trimethylsilyl)acrylamide].

The polymer is stable indefinitely as long as it is protected from moisture. Poly(BTSAm) could be quantitatively deprotected under mild conditions to polyacrylamide.

BTSAm was copolymerized with styrene using BPO initiator. The copolymer compositions were determined by elemental analysis and from ${}^1H$ NMR spectra. Comparison of the peak area in the region δ 0.75–2.5 due to vinylic protons contributed by both monomers with the area of the protons due to aromatic group δ 6.25–7.5 enables estimation of the copolymer composition. Samples obtained from the feed ratio BTSAm:styrene = 10:90 to 40:60 were soluble in $CDCl_3$. NMR of copolymers containing greater than 40 mol% acrylamide were recorded in DMSO-d_6. The NMR of the copolymer obtained from a feed ratio of BTSAm:styrene = 92.8:7.2 was recorded in CD_3CN–D_2O (3:7, v/v) (Figure 3). In the FTIR spectra, the regions 1984–1760 and 1300–900 cm^{-1} showed substantial changes in the peak positions and absorbances when compared to the IR of the synthetic mixture of the two homopolymers (Figure 4). This is most likely due to the vibrational coupling occurring because of frequent alternation of the comonomer moieties in the polymeric chain.[9]

On the basis of the copolymer compositions (Figure 5), the reactivity ratios for BTSAm (M_1) and styrene (M_2), determined by the Kelen–Tudos method, were $r_1 = 0.28$ and $r_2 = 0.47$ (Table 2). Since styrene–acrylamide copolymers are insoluble in benzene, for acrylamide contents above 35%, copolymerization in methanol has to be used to obtain reactivity ratios estimated as $r_1 = 0.49$ and $r_2 = 1.37$.[10] The values of r_1 and r_2 are both less than unity in the case of BTSAm and styrene, indicating frequent alternation of the comonomers.

BTSAm failed to undergo anionic polymerization in THF at −40 °C (CH_3CN–dry ice) with oligo(α-methylstyryl)lithium initiator. This observation is similar to that

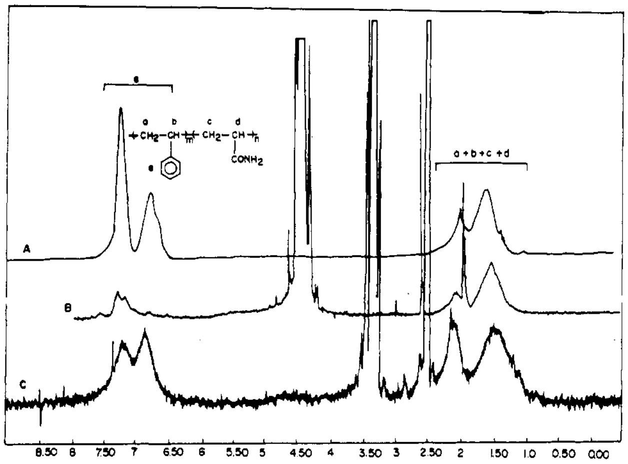


Figure 3. ^{1}H NMR spectra of acrylamide–styrene copolymers. (A) Feed ratio, BTSAm:styrene = 9.6:90.4 ($CDCl_3$). (B) Feed ratio, BTSAm:styrene = 92.8:7.2 (CD_3CN–D_2O, 3:7, v/v). (C) Feed ratio, BTSAm:styrene = 79:21 (DMSO-d_6).

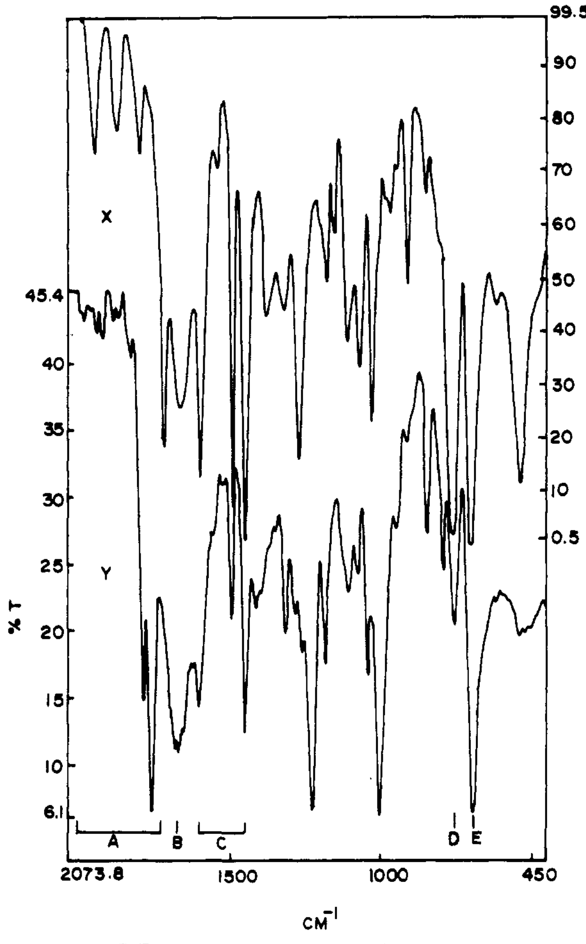


Figure 4. FTIR spectra of a synthetic mixture of poly(acrylamide)–poly(styrene) (20:80 mole ratio) (X) and of the hydrolyzed copolymer of BTSAm:styrene = 25.7:74.3 mole ratio (Y).

reported for trimethylsilyl enol ether of 4-vinylacetophenone by Nakahama and co-workers[11] and could be attributed to the rapid desilylation of the trimethylsilyl group by the organolithium reagent.

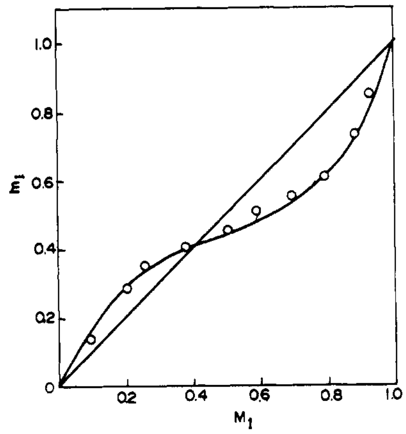


Figure 5. Plot of the variation of the mole fraction of acrylamide in the copolymer with the mole fraction of BTSAm in the feed. Conditions: solvent, benzene; initiator, BPO; [M] = 2.0 mol/L; [I] = 0.02 mol/L.

Table 2. Copolymerization of BTSAm (M_1) with Styrene (M_2)[a]

sample no.	conv (%)	mol % acrylamide in monomer (BTSAm)	mol % acrylamide in copolymer
1	4.0[b]	9.6	13.5
2	4.0[b]	20.3	28.6
3	3.5[b]	25.7	35.0
4	5.0[b]	37.8	40.8
5	2.5[c]	50.1	45.6
6	5.0[c]	59.0	51.0
7	3.5[c]	69.5	56.2
8	3.0[c]	79.0	60.4
9	5.0[c]	88.3	73.6
10	4.5[d]	92.8	85.0

[a] Conditions: in benzene using 1 mol % BPO at 50 °C. [b] Soluble in THF. [c] Soluble in DMSO. [d] Soluble in CH_3CN–D_2O (3:7, v/v).

In conclusion, BTSAm is a lipophilic protected acrylamide which can be polymerized by free-radical initiators. Unlike acrylamide it can be copolymerized in nonpolar solvents with nonpolar monomers without precipitation of the copolymers. BTSAm can thus be conveniently used, without any limitations of solubility in organic solvents, for synthesizing a wide variety of copolymers containing hydrophilic and hydrophobic groups.

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References and Notes

(1) Nakahama, S.; Hirao, A. *Prog. Polym. Sci.* **1990**, *15*, 299.
(2) Yamaguchi, K.; Hirao, A.; Suzuki, K.; Takenaka, K.; Nakahama, S.; Yamazaki, N. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 395. Matsumoto, A.; Oki, Y.; Horie, A.; Otsu, T. *Chem. Lett.* **1991**, 1141.
(3) Breslow, D. S.; Hulse, G. E.; Matlack, A. S. *J. Am. Chem. Soc.* **1957**, *79*, 3760.
(4) Birkofer, L.; Ritter, A.; Giessler, W. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 96.
(5) Koetzsch, H. J.; Vahlensieck, H. J. Ger. Offen. DE 3,443,960 (C1.C07F7/18), June 5, 1986, Appl. Dec 1, 1984; *Chem. Abstr.* **1986**, *105*, P191383w.
(6) Gruber, U.; Greber, G.; Kriemler, H. P. Ger. Offen. 2,353,356, May 9, 1974; *Chem. Abstr.* **1974**, *81*, 170460q.
(7) Yoder, C. H.; Copenhafer, W. C.; DuBeshter, B. *J. Am. Chem. Soc.* **1974**, *96*, 4283.
(8) The multiplicity of the peaks in the silyl region could arise due to tacticity differences of the polymer.
(9) Koenig, J. L. *Spectroscopy of Polymers*; American Chemical Society: Washington, DC, 1991; Chapter 4, p 80.
(10) Chuang, J. C.; Morawetz, H. *Macromolecules* **1973**, *6*, 43.
(11) Hirao, A.; Kato, K.; Nakahama, S. *Macromolecules* **1992**, *25*, 535.