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SYNTHESIS AND COPOLYMERIZATION OF *N*-TERT-BUTYLDIMETHYLSILYLACRYLAMIDE: A NEW ACRYLAMIDE PRECURSOR

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Abstract—*N*-tert-Butyldimethylsilylacrylamide, a new acrylamide precursor has been synthesized and characterized. The monomer has been copolymerized with styrene in an organic phase. The copolymers are hydrolyzed to give compositionally homogeneous styrene–acrylamide copolymers. Characterizations of the copolymers have been performed by a combination of FTIR and ^{1}H NMR spectroscopy, elemental analysis and DSC. The reactivity ratios have been determined by the Kelen Tudos method.

INTRODUCTION

Transforming a hydrophilic functionality into a hydrophobic one by silylation and incorporating it into a hydrophobic matrix followed by regeneration of the hydrophilic groups has been recognized as a useful methodology for the synthesis of polymers containing hydrophilic and hydrophobic moieties [1]. Depending on the nature of the hydrophilic and hydrophobic parts, the polymers may have a variety of applications [1,2]. Earlier we have reported solution homo- and co-polymerization of *N*-trimethylsilylacrylamide (TMSAm) and N,O-Bis(trimethylsilyl)acrylamide (BTSAm). These monomers exhibit a different reactivity pattern in copolymerization with styrene as compared to acrylamide and offer a means to synthesize compositionally homogeneous copolymers containing hydrophobic and hydrophilic moieties [3,4]. It is believed that the properties of copolymers, in particular, those containing polar and nonpolar monomers can be improved by decreasing their compositional inhomogeneity [5]. This is important for poly(acrylamide) based materials, since mechanical instability of these materials is a major hurdle which restricts their use in some important applications, for example, as support materials for affinity chromatography [6].

A variation in the silyl substituent should result in a difference in reactivity of the monomer. This will allow one to choose a precursor depending on the required properties to be tailored in the acrylamide based materials. In this paper, we report the synthesis, characterization and solution copolymerization of another new precursor of acrylamide viz. *N*-tert-butyldimethylsilyl acrylamide (TBDMSAm). It was expected that the larger size of the tert-butyldimethylsilyl group could make TBDMSAm more lipophilic (steric hindrance in hydrogen bonding) and hydrolytically stable [7]. The objective was to study the differences in copolymerization behaviour between TBDMSAm and TMSAm and to examine the effect of the silyl substituents.

EXPERIMENTAL

Materials

Benzoyl peroxide (BPO; from BDH, England) was recrystallized from methanol-chloroform. Benzene, hexane and styrene were purified as usual. Acrylamide (BDH, India) was recrystallized from chloroform. DMSO (SD Fine Chemicals, Bombay) was distilled over calcium hydride at 60°C under reduced pressure. Triethylamine (SD Fine Chemicals, Bombay) was refluxed over KOH for 6 hr, distilled under argon and collected over KOH pellets. Tert-butyldimethylsilyl-chloride (Aldrich), was used as supplied.

Instruments

The ^{13}C and ^{1}H NMR spectra were recorded using a Bruker AC-200 MHz spectrometer at 50.3 MHz and 200 MHz, respectively. Gas chromatographic analyses were performed using a Blue Star gas chromatograph model 421 and a 10% SE-30 column on chromosorb W (6′ × 1/8″) and nitrogen as a carrier gas (30 mL/min) at a column temperature of 175°C using flame ionization detector. The column was conditioned by repeated injection of hexamethyldisilazane prior to use. Elemental analyses were performed on a Carlo–Erba model CHNS-O EA 1008 elemental analyzer. Analysis for C, H and N were done using helium as the carrier gas. Intrinsic viscosities were determined using an Ubbelohde viscometer in a Schott–Geräte 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. DSCs were scanned in a Perkin-Elmer DSC 7 instrument.

Synthesis of N-*tert-butyldimethylsilylacrylamide*

Acrylamide (4 g, 0.06 mol), triethylamine (12 mL, 0.09 mol) and 100 mL of dry benzene were placed into a 500 mL three neck flask under a positive argon flow. The flask, equipped with a mechanical stirrer, was cooled in an ice bath. Tert-butyldimethylsilylchloride (10 g, 0.07 mol), was introduced under a positive flow of argon. The mixture was mechanically stirred for 8 hr at room temperature and filtered under argon. The filtrate and solvent were distilled

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Table 1. Copolymerization of *N*-tert-butyldimethylsilylacrylamide (M_1) with styrene (M_2)[a]

Sample No.	Conversion (%)	Mol% of Acrylamide in monomer	Mol% of Acrylamide in copolymer	$[\eta]^d$ (dL/g)	T_g (°C)
1	5.0[b]	11.5	12.5	0.18	108.04
2	4.5[b]	15.4	20.1	0.15	113.42
3	6.0[b]	31.1	32.1	0.19	119.06
4	5.5[b]	52.1	33.3	0.16	121.18
5	9.0[c]	67.8	44.8	0.30	134.67
6	9.0[c]	88.6	61.2	0.30	160.74

[a] Conditions: in benzene using 1 mol-% BPO at 80°C.
[b] Soluble in $CHCl_3$ (and also in DMSO) after hydrolysis.
[c] Soluble in dimethyl sulfoxide after hydrolysis.
[d] In dimethyl sulfoxide at 30 ± 0.1°C.

off, leaving a white mass which was stirred with a minimum volume of hexane (40°C) and filtered through a Grade-3 sintered disc under Ar. On cooling the filtrate in an ice bath, flakes of the *N*-tert-butyldimethylsilyl acrylamide (TBDMSAm) separated out; yield 90%, m.p. 76°C. ^1H NMR ($CDCl_3$): $\delta = 0.30$ (s, $-Si(CH_3)_2-$), 0.95 (s, $-C(CH_3)_3$), 5.0 (hump; D_2O exchangeable, —NH—), 5.65 (dd, 1H, =CH—), 6.2 (m, 2H, $CH_2=$) ^{13}C NMR ($CDCl_3$): $\delta = -5.05$ ($-Si(CH_3)_2-$), 17.41 (tertiary carbon of $-C(CH_3)_3$), 26.26 (primary carbons of $-C(CH_3)_3$), 126.4 ($CH_2=$), 132.7 (=CH—), 170.9 (>C=O).

$C_9H_{19}NOSi$ (185.3) Calc. C 58.32 H 10.33 N 7.56
Found C 58.39 H 10.28 N 7.62

Gas chromatography of a solution of TBDMSAm in dry benzene showed that the compound was 99% pure.

Copolymerization of TBDMSAm and styrene

An accurately weighed quantity of TBDMSAm was dissolved in a weighed volume of benzene. The required volume of TBDMSAm solution, styrene and the initiator solution were transferred into an ampoule through a cannula under a positive pressure of argon. Weights before and after transfer were taken to calculate the exact amount of monomers introduced. The ampoule was repeatedly evacuated after freezing the reaction mixture in liquid nitrogen and sealed under a vacuum of 10^{-3} mbar. The contents of the ampoule was polymerized at 80°C with benzoyl peroxide for a short period of time to ensure a conversion less than 10% (Table 1). The reaction was terminated by freezing the ampoule in liquid nitrogen. The solvent was then evacuated and the residue dissolved in acidulated (1.0 N HCl) DMSO. The solution was stirred for about 30 min and the hydrolyzed polymer precipitated in acetone or water. The process was repeated two times to ensure complete desilylation. The polymers which were precipitated in water (obtained from less than 60 mol% of TBDMSAm in the feed) were redissolved in neutral THF and precipitated in hexane. All copolymers were white to faint yellow powders.

^1H NMR of copolymer ($CDCl_3$ or dimethyl sulphoxide-d_6): $\delta = 0.75–2.5$ (two humps; 3H, $-CH_2-CH-$, backbone protons contributed by both monomers), 6.25–7.5 (two humps; 5H, C_6H_5-, phenyl ring protons of styrene).

I.R. of copolymers (KBr): A: Overlap C=O stretch from acrylamide 1666 cm^{-1}. B: Ring C—C stretch 1600, 1492,

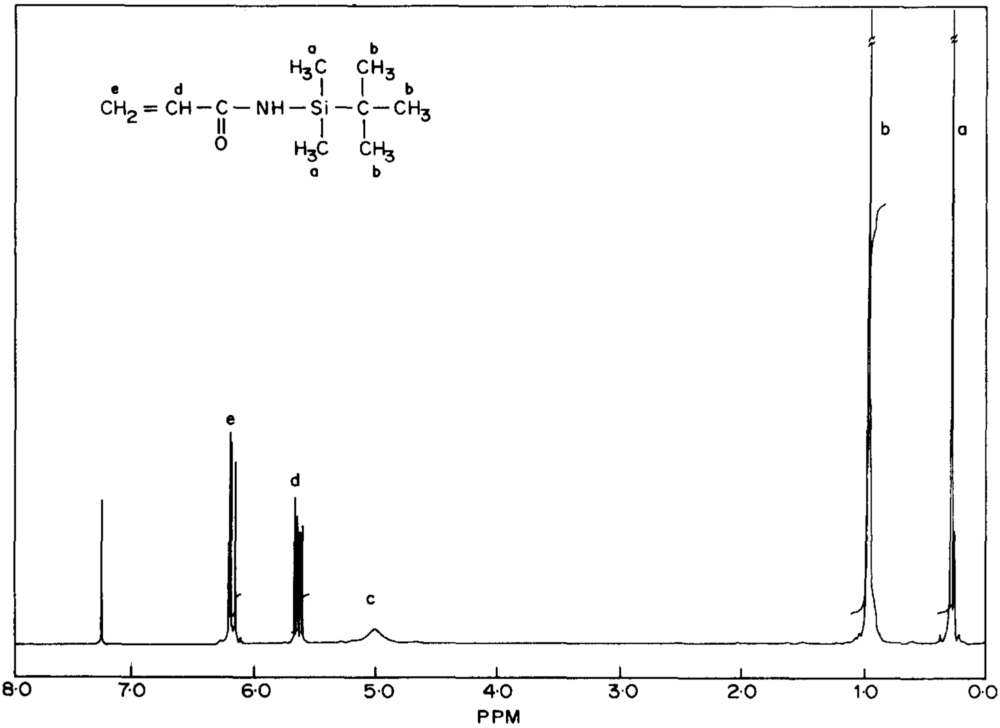


Fig. 1. ^1H NMR spectrum of *N*-tert-butyldimethylsilylacrylamide.

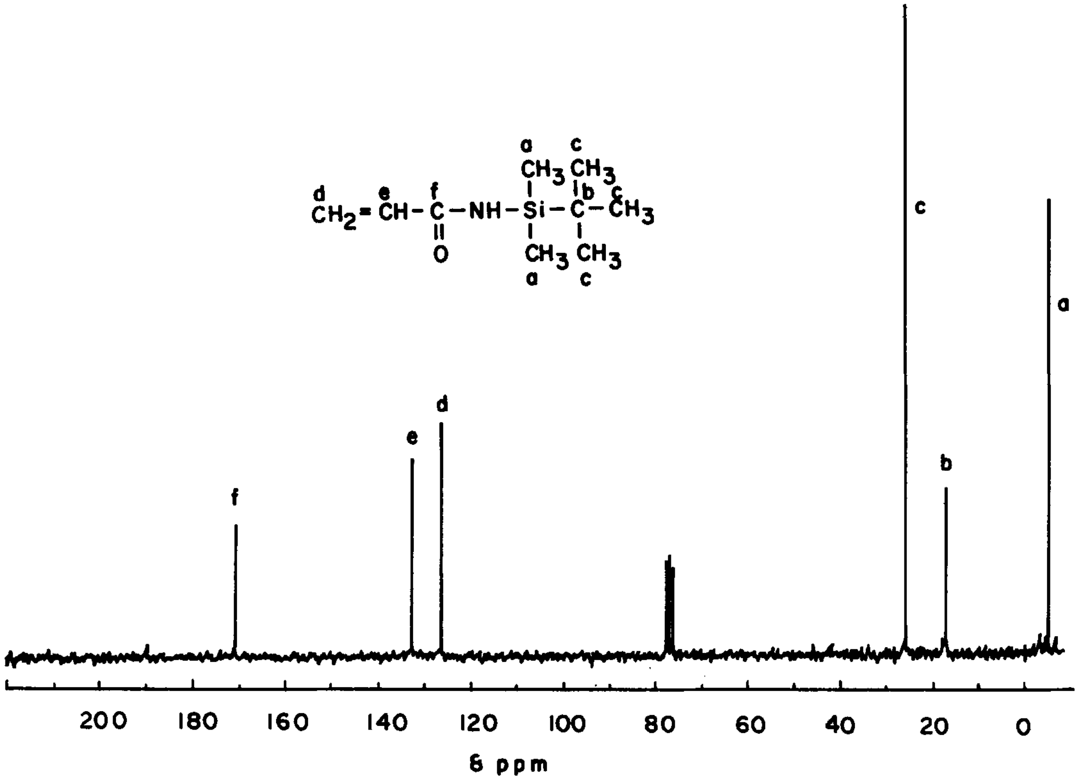


Fig. 2. ^{13}C NMR spectrum of *N*-tert-butyldimethylsilylacrylamide.

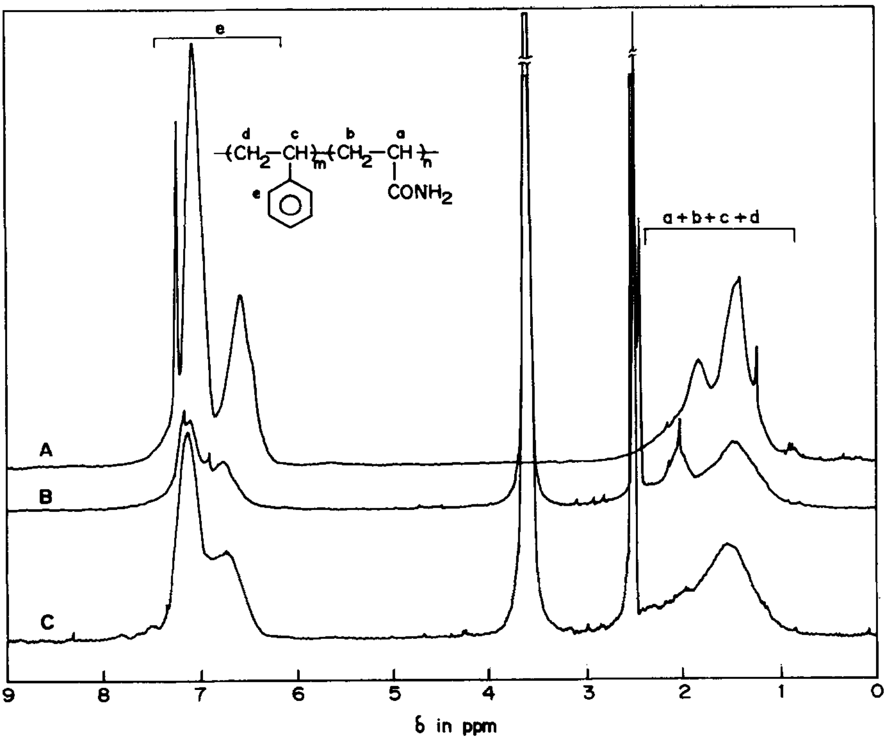
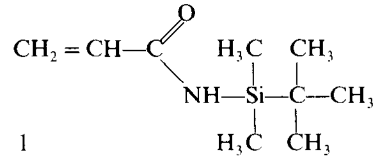


Fig. 3. ^{1}H NMR spectra of styrene-acrylamide copolymers. A: Feed mole ratio TBDMSAm:styrene = 15.4:84.6 ($CDCl_3$), B: Feed mole ratio TBDMSAm:styrene = 88.6:11.4 (DMSO-d_6), C: Feed mole ratio: TBDMSAm:styrene = 52.1:47.9 (DMSO-d_6).

1452 cm^{-1}, styrene. C: Out-of-plane C—H bend, 758 cm^{-1}, styrene. E: out of plane C—C bend 700 cm^{-1}, styrene.

RESULTS AND DISCUSSION

N-tert-Butyldimethylsilylacrylamide (TBDMSAm) was characterized by ^{1}H and ^{13}C NMR spectra. In the ^{1}H NMR spectrum, one peak was observed in the silyl region ($\delta = 0.30$) corresponding to six protons (Fig. 1). Another peak appeared at $\delta = 0.95$ corresponding to the nine protons of the tert-butyl group. The ^{13}C NMR spectrum of TBDMSAm confirms the structure (Fig. 2). Elemental analysis and gas chromatographic analysis were employed for ascertaining the purity of TBDMSAm.



TBDMSAm (1) was copolymerized with styrene using BPO as the initiator. The copolymer compositions were determined by elemental analysis and from ^{1}H NMR spectra. Comparison of the peak area in the region $\delta = 0.75$–2.5 with that due to vinylic protons contributed by both monomers with the area of the protons due to the aromatic group appearing in the region $\delta = 6.25$–7.5 enables the estimation of the copolymer composition. Samples obtained from

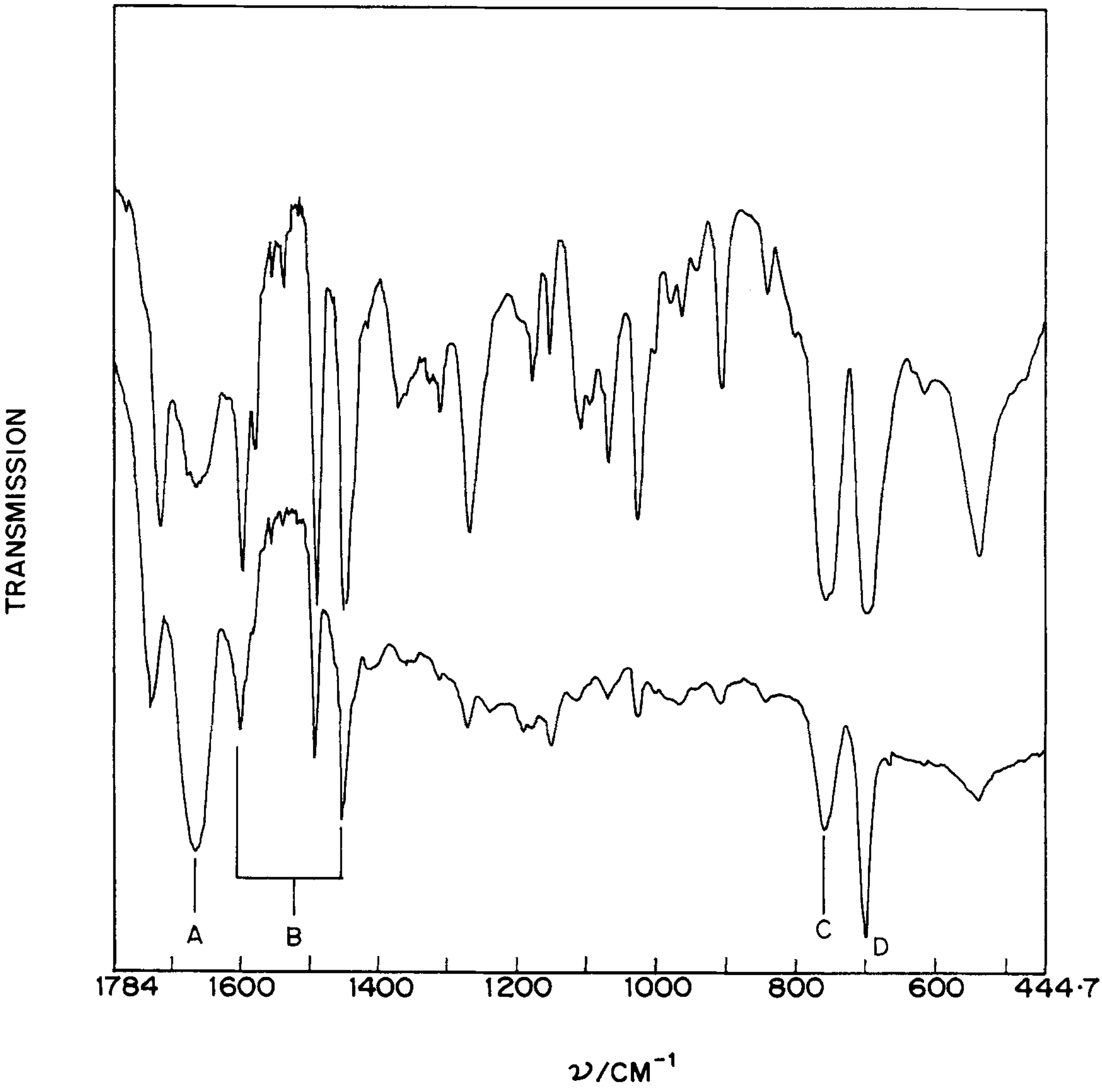


Fig. 4. FTIR spectra of a hydrolyzed copolymer of TBDMSAm : styrene = 52.1 : 47.9 mole ratio (lower curve) and of a mixture of polyacrylamide and polystyrene homopolymers of 30 : 70 mole ratio (upper curve).

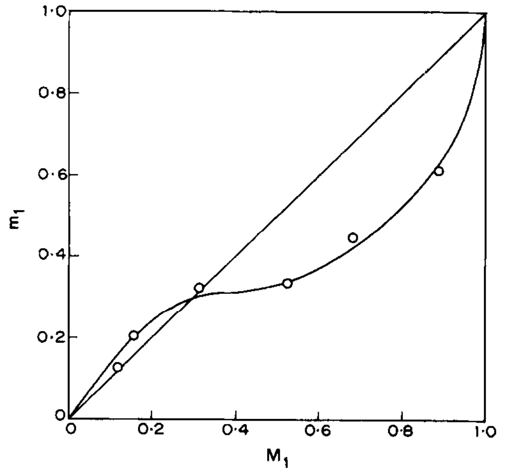


Fig. 5. Plot of the mole fraction of acrylamide in the instantaneously formed copolymer (m_1) vs the mole fraction of TBDMSAm in the feed (M_1). Conditions:solvent, benzene; initiator, BPO; [M] = 0.50 mol/L; [I] = 0.005 mol/L; temp. 80°C.

feed mole ratios TBDMSAm:Styrene = 15:85 to 50:50 after hydrolysis were soluble in $CDCl_3$, NMR spectra of copolymers containing more than 40 mol% acrylamide were recorded in dimethyl sulfoxide (DMSO-d_6) (Fig. 3). The results are shown in Table 1.

In Fig. 4, the FTIR spectrum of a mixture of two homopolymers is compared with that of a copolymer. Changes in the relative absorbances at different wavelengths, particularly in the region 1300–900 cm^{-1}, are most likely due to the vibrational coupling occurring because of frequent alternation of the comonomer moieties in the polymeric chain [8].

On the basis of the copolymer compositions (Fig. 5) the reactivity ratios for TBDMSAm (M_1) and styrene (M_2) determined by the Kelen Tudos methods were $r_1 = 0.04$ and $r_2 = 0.68$ ($r_1 r_2 = 0.03$). A reduced value of r_1 as compared to the same for TMSAm (for copolymerization of TMSAm (M_1) and styrene (M_2), $r_1 = 0.18$ and $r_2 = 0.89$ at 80°C, $r_1 r_2 = 0.16$) indicates a reduced reactivity of TBDMSAm towards its own monomer, presumably on account of the bulkier silyl substitution.

DSC was used to characterize the thermal properties of the copolymers. A steady increase in the values of T_g due to incorporation of more and more polar acrylamide moieties in the copolymer has been observed. The presence of only one glass transition is taken as evidence for the absence of macroscopic phase separation and therefore implies that the copolymer samples are fairly homogeneous. This is often taken as an indication of randomness as opposed to blockiness of the copolymer [9].

Thus, TBDMSAm is a new lipophilic acrylamide precursor which can be used for the synthesis of a variety of random copolymers of acrylamide with homogeneous distribution of hydrophilic and hydrophobic groups. In two ways TBDMSAm is better than TMSAm. Firstly, because it is less sensitive towards moisture, tert-butyldimethylsilyl substituted amide functionalities are likely to be more stable pendant sites in the polymer for further derivatization [10]. Secondly, the larger size of the silyl group in TBDMSAm compared to TMSAm, results in an improved randomness of the copolymer.

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REFERENCES

1. J. Liu and G. E. Wnek, *Macromolecules*, **27**, 4080 (1994).
2. R. Kroger, H. Menzel and M. L. Hallensleben, *Macromol. Chem. Phys.* **195**, 2291 (1994) and the references therein.
3. A. Dasgupta and S. Sivaram, *Macromolecules*, **27**, 1665 (1994).
4. A. Dasgupta and S. Sivaram, *Macromol. Chem. Phys.* **195**, 3361 (1994).
5. S. I. Kuchanov, *Adv. Polym. Sci.* **103**, 1 (1992) and the references 321, 322 and 323 therein.
6. Poor mechanical stability of acrylamide based supports have prevented it from becoming very popular for use in affinity separations, in spite of having some major advantages like resistance to microbial attack, relatively good pH stability (pH = 2–10), excellent chemical stability, and low nonspecific binding characteristics (due to the lack of a biopolymer matrix based on sugar residues). G. T. Hermanson, A. Krishna Mallia and Paul K. Smith in *Immobilized Affinity Ligand Techniques*, p. 16. Academic Press, 1993.
7. H. Mori, O. Wakisaka, A. Hirao and S. Nakahama, *Macromol. Chem. Phys.* **195**, 3213 (1994).
8. J. L. Koenig, *Spectroscopy of Polymers*, p. 80. Amer. Chem. Soc., Washington D. C., 1991.
9. J. F. Rabek, *Experimental Methods in Polymer Chemistry*, p. 565. Wiley Interscience: New York, 1980.
10. (a) I. Fleming, Organic silicon chemistry, in *Comprehensive Organic Chemistry*, (edited by Sir Derek Barton and W. David Ollis), p. 603. Pergamon Press, Vol. 3, and reference 309 therein.
    (b) H. R. Kricheldorf and O. Stober, *Euro. Polym. J.* **22**, 1377 (1992).