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Controlled Polymerization of N-trimethylsilyl Methacrylamide: A New Polymethacrylamide Precursor

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Summary

N-trimethylsilyl methacrylamide (TMS-MAm), a new methacrylamide precursor, has been synthesized and characterized. 2,2'-Azoisobutyronitrile (AIBN) initiated radical polymerization of TMS-MAm was carried out in N,N-dimethylformamide (DMF) and toluene using the triazolinyl radical (T•) as additive. The mechanism of "self regulation" that triazolinyl offers is found to work well in the solution polymerization process over a reasonably wide range of temperature up to 79% conversion. Molecular weight distributions below or close to the theoretical limit of 1.5 and high degree of end functionalization could be achieved. The polymers obtained could be easily converted to polymethacrylamide under mild conditions.

Introduction

In the area of functional polymer synthesis, production of narrow molecular weight distributions (MWDs) of homopolymers and the ability to make block copolymers by reinitiation through living or functionalized chain ends of the first block continue to be two important goals[1,2]. For monomers containing unsubstituted amide functionality, synthesizing narrow molecular weight distribution polymers or block copolymers have not been possible in the past by anionic or group transfer polymerization techniques, possibly because of the instability of silylated amide functionality towards anionic initiators [3]. There are two reports so far on controlled radical polymerization of unsubstituted acrylamide. In one, the monomer has been solution polymerized in DMF using surface tethered initiator systems to obtain surface tethered polyacrylamide having Mn in the range of 13 kD to 15 kD and polydispersity between 1.15 and 1.30 [4]. In the other, the monomer has been polymerized by the RAFT polymerization technique. For RAFT of acrylamide, the solvent required is an aqueous buffer or DMSO, both not quite compatible with a non-polar monomer if used as a second monomer for block copolymerization [5]. There are several reports of controlled radical polymerization of substituted (meth)acrylamides such as N-isopropyl acrylamide [6, 7], N-tert-butylacrylamide [8], N,N-dimethylacrylamide [7,8], and N-(2-hydroxypropyl)-methacrylamide [8,9], where success have been achieved in making homopolymers with narrow molecular weight distribution and in synthesis of block copolymers in some cases. However, to the best of our knowledge, there is no published report on synthesis of unsubstituted polymethacrylamide having

relatively narrow molecular weight distribution. It is not certain that the initiator systems offering control for acrylamide will also work for methacrylamide; just as initiator systems good for acrylates are not necessarily good for methacrylates [10]. In this paper we describe a convenient methodology for synthesis of unsubstituted polymethacrylamide via controlled radical polymerization of N-trimethylsilyl methacrylamide - a new methacrylamide precursor. For functional monomers possessing active hydrogen(s), silylation of the functionality improves the lipophilicity of the monomer thereby altering its solubility and reactivity [2]. What needs investigation is if such a change in the reactivity is positive in responding to initiator systems designed for controlled radical polymerization. Suitability of this approach for controlled radical polymerization of methacrylamide has been investigated in this work using triazolinyl as the stable free radical additive.

Experimental

Materials

Methacrylamide (Aldrich) and chlorotrimethylsilane (Aldrich) were used as received. N,N-dimethylformamide (DMF) (Fischer Chemicals) was purified by keeping overnight with activated molecular sieves followed by filtration and distillation over phosphorous pentoxide under reduced pressure. Tetrahydrofuran (THF), toluene and hexane were dried and distilled under argon over blue sodium benzophenone. Triethylamine was refluxed for 6h. over KOH beads, distilled under argon and collected over KOH. The triazolinyl radical (T•, scheme-1) was synthesized according to Neugebauer et. al. by ring closure of N-phenylbenzohydrazonyl chloride with α-phenylbenzylamine, followed by oxidation of the triazolin by $K_3Fe(CN)_6$ (mass spectrum signal at m/z 374.5) [11]. For synthesis of triazolinyl, phenyl hydrazine and α-phenyl benzyl amine were obtained from Aldrich and used as received. 2,2´ azobisisobutyronitrile (AIBN) (Fluka) was recrystallized from methanol.

Analyses

TMS-methacrylamide was characterized by ^1H and ^{13}C NMR, FTIR, elemental analysis and mass spectroscopy. NMR spectra were obtained using a 250 MHz Bruker NMR spectrometer, FTIR spectra were obtained using a Thermo Nicolet Nexus 670 FTIR spectrometer, microanalysis of the monomer was done by Micro-Analysis Inc., Wilmington, DE and mass spectra were recorded in a Micromass AutoSpec mass spectrometer by chemical ionization in the positive ion mode. Triazolinyl radical purity was checked by mass spectrum. Polymerization conversions were measured from ^1H NMR spectra. Molar mass and molar mass distributions were measured by gel permeation chromatography (GPC) of the silylated polymer using SDV-gel columns in toluene and DMF with polystyrene standards. Both RI and UV detectors were used for GPC characterizations. The UV detector of the GPC was set at 280 nm to follow the absorption due to triazolinyl end functionality of the polymers.

Synthesis of N-trimethylsilyl methacrylamide

Methacrylamide (MAm, 8.2g, 96 mmol), triethylamine (14 mL, 100 mmol) and 220 mL of dry THF were placed in a 500 mL three neck flask containing a magnetic stir bar under a positive argon flow. The flask was cooled in an ice bath kept over

a magnetic stirrer. While stirring in the cold (0-5°C), chlorotrimethylsilane (12.5 mL, 98 mmol) was slowly transferred into the reaction mixture using a double end needle. The mixture was stirred for 8h. at room temperature and filtered under argon. The solvent and volatiles were distilled off, leaving a yellowish solid residue. The residue was stirred with a minimum volume of dry hexane at room temperature and filtered under argon. On cooling the filtrate in an ice bath, shiny white flakes of N-trimethylsilyl methacrylamide (TMS-MAm) separated out; yield 85%, melting point 66°C. IR (KBr, ν, cm^{-1}) [12,13]: 3392, 3201, 3101, 2962 (s, CH_3 of C-CH_3, asymmetric stretch), 2931 (m, CH_2, asymmetric stretch), 2906, 1667 (vs, C=O stretch, amide I band), 1607 (vs, N-H bend, amide II band), 1457, 1436, 1409, 1390, 1374, 1295 and 1251 (s, CH_3 of Si-CH_3, symmetric stretch), 1185, 1109, 1013, 933, 869 (s, $SiCH_3$ rock plus probably some Si-C stretch interaction), 846, 755, 741, 701, 650, 644, 628. Anal. calcd. for $C_7H_{15}NOSi$ (157.29) C, 53.45; H, 9.61; N, 8.91. Found C, 53.15; H, 9.50; N 9.05; MS: m/z (%) = 158.1 (24) [$M+H^+$], 142.1 (100) [M^+-CH_3]; ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.25 (singlet, -$NSi(CH_3)_3$), 1.8 (singlet, -CH_3), 5.0, 5.4 (doublet, =CH_2), 5.0 (broad singlet, -NH-); ^{13}C NMR (250 MHz, C_6D_6): δ 0.0 (-$NSi(CH_3)_3$), 19.0 (-CH_3), 119.5 (=CH_2), 142.5 (=C<), 173.5 (>C=O).

Polymerization

Polymerizations were done in toluene or DMF solutions. In a typical procedure, a clean and dry 25 ml. Schlenk flask fitted with a magnetic bar was flashed with high purity argon. Under argon atmosphere inside a glove bag, the monomer TMS-MAm, AIBN (0.1, 0.5, 1.0 or 5.0 mol% of monomer) and 1.5 molar equivalents of triazolinyl with respect to AIBN were carefully transferred into the Schlenk flask and the flask was sealed with a septum. To it was added required volume of solvent (to make [M]=1.0 mol/L) using a cannula under a positive pressure of argon. The solution was stirred at room temperature for few minutes and later degassed by the 'freeze thaw' technique for three times. The contents of the flask were allowed to come to room temperature and the flask was placed in an oil bath at 100°C for ten minutes. The flask was then taken out and put into another oil bath heated to the polymerization temperature. Freezing the Schlenk flasks in liquid nitrogen terminated the reactions. The product mixture, immediately after it melted, was directly submitted for GPC and was scanned by ^{1}H NMR for conversion. After taking samples for NMR and GPC, the reaction mixture was again degassed and put back into the oil bath for continuation of polymerization. Thus samples were taken out at different time intervals to determine the reaction progress in terms of conversion and polymer molecular weight.

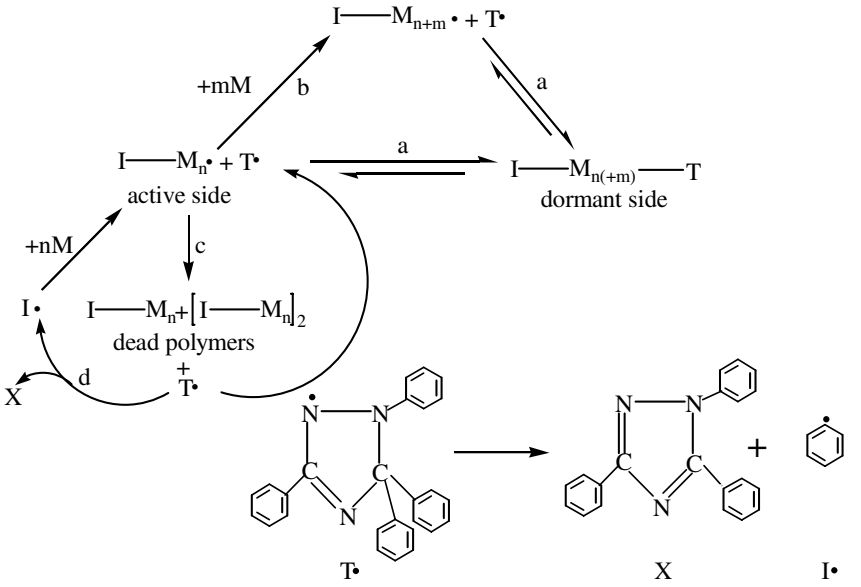
Deprotection of the silyl group

In order to deprotect the silyl groups, the polymer solution was stirred with a mixture of 4N HCl and THF (1:1, v/v) at room temperature for about 30 min. The mixture was poured into large excess of methanol when the polymethacrylamide precipitated. The polymer was reprecipitated from aqueous solution in methanol [2].

Results and Discussion

Functional monomer silylation has been well explored for polymerization of monomers for two different reasons. There are many examples where silylation

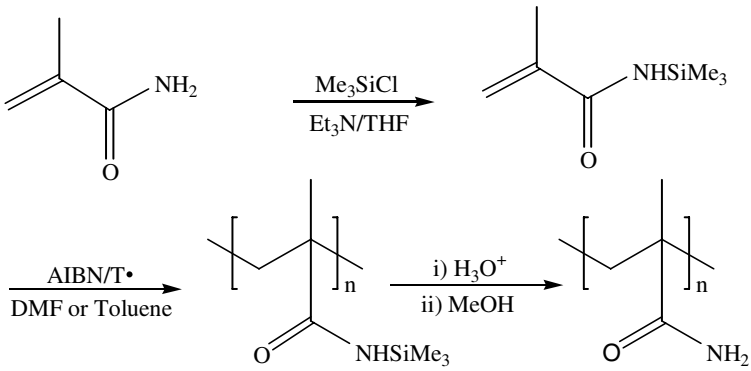
protected the functionality thus preventing any interference by the reactive protons during polymerization. In few other cases, silylation simply improved solubility or reactivity in the polymerization medium. For acrylamide, a water soluble monomer containing amide functionality, silylation offers improved reactivity in solution copolymerizaion with styrene – an organic soluble monomer [2]. Our present study describes a new and hitherto unexplored advantage of amide silylation namely to bring about control in free radical polymerization of methacrylamide in presence of triazolinyl as a stable free radical additive. Control could be achieved in terms of attaining relatively narrow molecular weight distribution and in reinitiating homopolymerization upon temporary freezing; latter being an essential requirement for initiation of second block in block copolymer synthesis. Thus, our work deals with standardizing the conditions for synthesizing homopolymers of TMS-MAm having molecular weight distributions below the theoretical limit of 1.5 for controlled radical polymerization and bearing triazolinyl end functionality.



Scheme 1. Triazolinyl SFR controlled polymerization and mechanism of self regulation

The triazolinyl radical was used as an additive along with AIBN initiator for solution polymerization of TMS-MAm in toluene and DMF. In controlled radical polymerization processes assisted by an added SFR, the amount of side reactions of the growing free macroradical is minimized by reducing its concentration by virtue of an equilibrium with the SFR (Scheme 1, path 'a'). Since unwanted side reactions of the free macroradical (Scheme 1, path 'c') cannot be suppressed quantitatively, the concentration of the SFR increases with time. In consequence the controlling equilibrium shifts further to the dormant side and the polymerization gets slower and finally may stop. This problem restricted the suitability of TEMPO, the first SFR used in controlled polymerization, to monomers like styrene that are able to compensate the loss of growing centers by thermal initiation [14]. Unlike most nitroxide-type radicals [15], the free triazolinyl (T•) slowly decomposes over the period of polymerization as

described in Scheme 1, path 'd' [16,17]. Thus superfluous SFR is removed from the controlling equilibrium and its excess never rises to an extent that could stop the polymerization. Furthermore, an initiating phenyl radical I• is formed upon every decomposition of triazolinyl T• and the loss of active centers is partially compensated. In consequence thermal initiation is no longer necessary to hold up the concentration of active centers. Though recent publications report success in the controlled radical polymerization of acrylic monomers using TEMPO and certain new nitroxides [10,14,18-21], these SFRs still fail in the case of methacrylic monomers. The results on employing triazolinyl for the controlled polymerization of methylmethacrylate (MMA) were very encouraging [16,17], and tempted us to examine the suitability of triazolinyl for controlled radical polymerization of other (meth)acrylic monomers. Methacrylamide (MAm) was an obvious choice. However, methacrylamide and its polymer are water soluble while for polymerization of any monomer using triazolinyl SFR, a less polar polymerization medium is neccesary where triazolinyl, the monomer and the growing polymer chains are soluble. Unlike the parent methacrylamide monomer and its polymer, the silylated monomer (TMS-MAm) and polymer thereof are highly soluble in both DMF and toluene; and the pendant silylated amide functionalities of a polymer are readily hydrolyzable to amide functionalities [2]. Therefore solution polymerization of TMS-MAm was carried out in DMF and toluene in presence of triazolinyl (Scheme 2).



Scheme 2. Silylation of methacrylamide, polymerization and desilylation

Kinetics of polymerization was followed in two ways. After distributing the reaction mixture in several schlenck flasks, polymerization in one of the flasks was monitored by freezing at different time intervals and taking out aliquots to charcterize by ^{1}H NMR and GPC. Polymerization in the remaining flasks were individually terminated exactly at the same time intervals. Consistency was observed in the results obtained by following the kinetics in both ways. This indicated that termination of the polymerization by freezing in liquid nitrogen during the course does not result in any loss of end functionality.

The monomer concentration was kept constant at 1.0 mol/L. Concentration of AIBN was 0.1, 0.5, 1.0 or 5.0 mol% of monomer. Triazolinyl concentration was always kept 1.5 molar equivalents with respect to AIBN. Experimental data and typical results are shown in Table 1. Controlling influence of triazolinyl on the polymerization could be

Table 1. Molecular weight data for poly TMS-Methacrylamide; concentration of monomer for all experiments: 1 mol/l

Expt.	Solvent, temp.	[AIBN]/[M]	Time (h.)	Conversion (%)	M_n[a] g.mol^{-1}	M_w/M_n
1	Toluene, 94°C	0.001	3.9	3.7	n.d.	--
			4.3	10.5	36400	1.31
			4.75	22.5	44500	1.5
			6	23.5	50500	1.37
			11.2	28	53200	1.47
			23	32	55100	1.54
			35	37.1	63300	1.45
2	Toluene, 66°C	0.005	76.4	34.6	42800	1.42
3	Toluene, 66°C	0.01	76	35.7	38800	1.32
4	Toluene, 74°C	0.05	24	100	16200	1.83
5	DMF, 66°C	0.005	6.8	10.7	23900	1.52
			13.3	27.6	25600	1.54
			18	35.7	27700	1.56
			22.5	44.2	27900	1.54
			38	59.3	28800	1.5
			58.5	74.6	31300	1.52
6	DMF, 66°C	0.01	7.5	15.6	18100	1.54
			18.3	42.4	19100	1.47
			24	51.9	19600	1.47
			40	64.2	20600	1.46
			58.6	79.4	21400	1.46

[a] values measured by GPC, calibrated with polystyrene standards, n.d.: not detected

recognized by molecular weight distribution values below or close to the theoretical limit of 1.5 [22], and/or the developing molecular weights with conversion, depending on the experimental conditions. To affect a fast initiator decomposition the reaction mixtures have initially been heated to 100°C for 10 minutes. Nevertheless, polymers were not detectable by GPC during the initial 3 - 4 hours of the reactions indicating a considerable inhibition period. Such an inhibition period is also observed with triazolinyl controlled polymerization of TMS-HEMA, a 2-hydroxyethylmethacrylate (HEMA) precursor. Reason for such observation has been generalized as follows [23]: In this phase the triazolinyl SFR present in a large excess is able to scavenge all other generated radicals and the polymerization equilibrium (Scheme 1, path 'a') is on the dormant side. Due to the aforementioned self regulation process (Scheme 1, path 'd') the excess of free triazolinyl is lowered with increasing reaction time. The controlled polymerization process begins when the excess of triazolinyl SFR to all other radical species falls below a certain level. At this point the equilibrium shifts to the active side and steady chain propagation begins. The excess triazolinyl SFR also keeps compensating the termination processes (Scheme 1, path 'c') by generating initiating phenyl radicals (Scheme 1, path 'd'). Consequently, a plot of ln[Mo]/[M] versus time based on the data taken from Table-1 show a linear behavior in case of

polymerizations done in DMF indicating controlled chain growth (Figure 1). However, for the polymerizations done in toluene, the variation was not linear. Differences in the kinetics of the polymerization depending on the solvents used were quite observable.
In the initial set of experiements, homopolymerization reactions were done in toluene at 94°C (expt.1, table 1) and the reactions were found to reinitiate after temporary freezing (Figure 2). This was an indication for good degree of end functionality in the polymers.

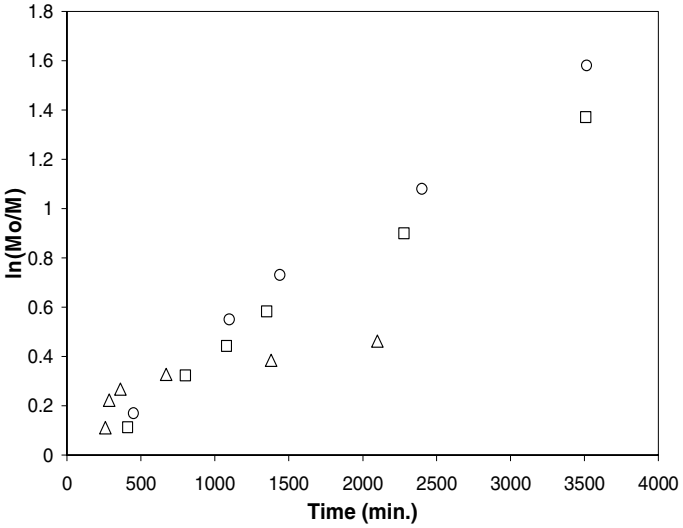


Figure 1. Semilogarithmic time-conversion plot for solution polymerization of TMS-MAm in: toluene at 94°C, [I]/[M] = 0.001 [Δ]; DMF at 66°C, [I]/[M] = 0.005 [□]; and DMF at 66°C, [I]/[M] = 0.01 [o]; data from experiments 1, 5 and 6 respectively in Table 1

An experimental advantage with the triazolinyl controlled polymerizations is that end functionalization of the polymer chains can be analyzed by UV spectroscopy, provided the polymer itself does not absorb at the λ_{max} for triazolinyl that is at 280 nm. A high degree of end functionalization should result in an overlapping UV-RI signal in the GPC when the UV detector is set at 280 nm [17]. The end functionality of the samples obtained in toluene, however, were not adequately high to result an overlapping UV-RI GPC signal. A reason for this observation could be fast decomposition of triazolinyl under the condition of this reaction [16,24]. Therefore the polymerization was studied at much lower temperature of 66°C to see if a good degree of end functionalization could be achieved. The initiator concentration of 0.1 mole% of monomer was found to be too low to result any polymerization at 66°C and was raised to 0.5 and then to 1.0 mole% of the monomer (Table 1, exp. 2 and 3). Even with such high initiator concentration the polymerizations were quite slow at 66°C and triazolinyl end functionality was not strongly detectable either, though reinitiation was possible in all cases. Increasing the initiator concentration to 5.0 mole% of monomer and doing the polymerizations at 74°C resulted in much faster polymerization rate and quantitative yield in polymer formation but the molecular weight distribution obtained was much broader than the theoretical limit of 1.5 (Table 1, exp.4). Further

optimization of the conditions was possible using toluene. However, it seemed to be a better option to find an alternative solvent that might offer more flexible reaction conditions without losing control over the process. The polymerization solvent was therefore changed from toluene to DMF. A comparison of the results of experiments 2 and 3 with those of 5 and 6 respectively shows that the polymerization rate in DMF is about four times faster than the same in toluene under otherwise similar conditions though the resulting molecular weights and their distributions are in the same range for similar degrees of conversion. The reason for this observation was not investigated here but the influence of aromatic solvents on the polymerization rate constant in free radical polymerization of MMA may be mentioned in this regard [25]. The lower polymerization rate in toluene could be a result of possible charge-transfer interactions between the aromatic solvent and the growing centers.

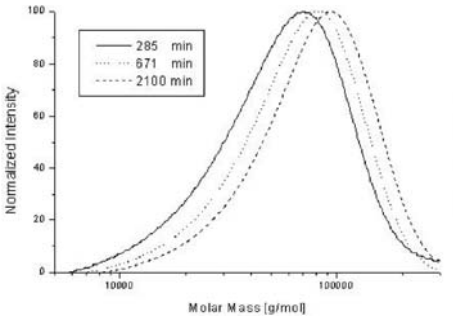


Figure 2. GPC, Expt 1, Table 1 showing reinitiation in toluene

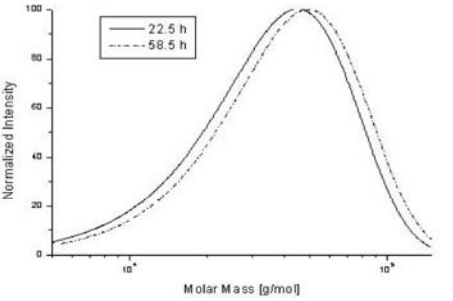


Figure 3. GPC, Expt 5, Table 1 showing reinitiation in DMF

In DMF molecular weight distributions below or very close to the theoretical limit of 1.5 could be obtained for more than 79% conversion and quite reproducible results were obtained regarding ability of chain ends to reinitiate polymerization (Figure 3).

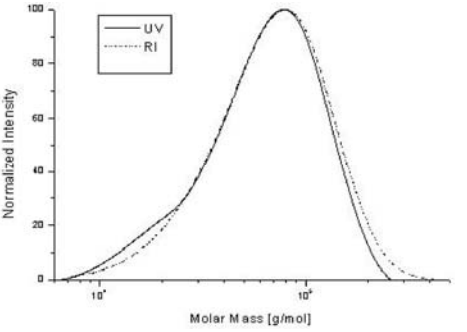


Figure 4. Overlapping UV and RI signals showing high degree of Triazolinyl functionalization of TMS-MAm homopolymer

Furthermore, poly(TMS-MAm) obtained in DMF in presence of triazolinyl shows a strong signal under UV detection at 280 nm that overlaps with the RI signal (Figure 4). Poly(TMS-MAm) itself exhibits no UV activity at this wavelength. This strongly supports incorporation of triazolinyl in the polymer chains. Poly TMS-MAm is found

to be soluble in methanol. Hexane and water are found to be two good non-solvents suitable for precipitation of poly TMS-MAm. Precipitation in water, however, resulted in considerable hydrolysis of the polymer. Therefore, isolation of the polymers free of unreacted monomer could be done only by precipitating and washing in warm and dry hexane. The polymers so obtained could be easily redissolved in dry DMF and further reacted to a second monomer [26].
Another criterion for a controlled polymerization is shown to be fulfilled in Figure 5. Here, growth of polymer chains is established by the steady (linear) increase of molar mass with conversion. However, development of the experimentally determined molecular weights does not begin in the origin of the graph. This is often observed for triazolinyl controlled polymerizations and is believed to be due to an "uncontrolled" growth of a small amount of long chain polymers during the initial heating phase at 100°C [23].

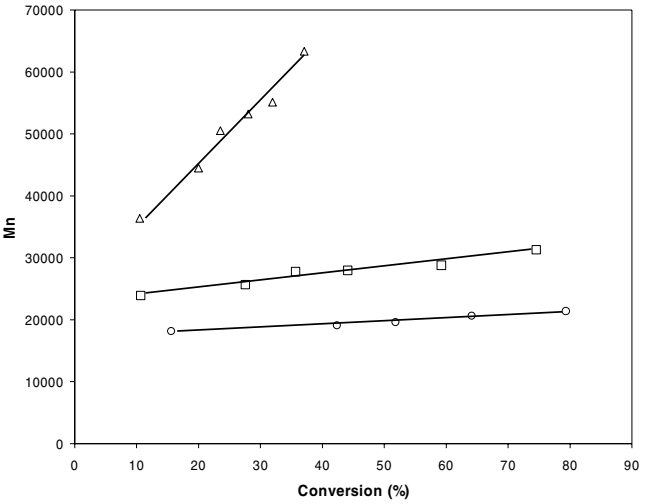


Figure 5. Development of molar mass versus conversion for the solution polymerization of TMS-MAm in: toluene at 94°C [Δ], [I]/[M] = 0.001; DMF at 66°C, [I]/[M] = 0.005 [□]; and DMF at 66°C, [I]/[M] = 0.01 [o]; data from experiments 1, 5 and 6 in Table 1

In the present example, methacrylamide – an aqueous soluble monomer – becomes soluble in non-aqueous polymerization media upon silylation and becomes amenable to controlled radical polymerization. Thus amide group silylation significantly improves the monomer reactivity towards controlled polymerization. However, such a polarity and solubility change might not always improve monomer reactivity since other factors such as steric crowding of the propagating chain head may also play a role. For example alkyl α-trimethylsilyloxyacrylate, a captodative monomer, has some polymerizability when the alkyl group is methyl, ethyl, n-propyl, i-propyl or i-butyl. However, if the substitution is trimethylsilyl, that is, if the monomer is trimethylsilyl α-trimethylsilyloxyacrylate, polymerizability is very poor [27]. Thus inspite of introduction of a silyl group in the ester functionality, monomer response towards free radical polymerization is negative. So far, amide functionality, upon silylation, is observed to respond very positively towards free radical polymerization – both in statistical copolymerization [2] as well as in controlled polymerization.

Furthermore, solubility of a monomer, its polymer, initiator and the SFR additive is a necessary condition for controlled radical polymerization, but may not be sufficient. For example, inspite of good solubility of 2-Hydroxyethylmethacrylate (HEMA) and its polymer in DMF, silylation of the hydroxyl functionality was essential for controlled radical polymerization of HEMA using Triazolinyl [23]. This indicates silylation does more to the monomer than just making it soluble – functional group silylation alters the polarity of the monomer molecule and that, in turn, alters the stability of the propagating macroradical and the dormant species it forms with the SFR additive. Therefore, if a monomer does not undergo controlled radical polymerization as such and bears an active hydrogen that can be silylated, there is a possibility that the silylated monomer would undergo controlled radical polymerization. N-vinyl formamide, N-vinyl acetamide etc. are such monomers that are yet to be tested for controlled radical polymerization by employing this methodology.

Conclusion

It was previously observed that silylation makes hydroxyethyl methacrylate amenable to controlled radical polymerization using Triazolinyl SFR. Present paper concludes that silylation makes methacrylamide amenable to controlled radical polymerization as well. It is possible to improve the lipophilicity or reactivity of such monomers by substituting the reactive hydrogen(s) with alkyl or aryl groups. However, silyl substitution adds the advantage of regenerating the original functionality. The methodology of triazolinyl controlled polymerization of TMS-MAm is useful for synthesizing poly(methacrylamide) having narrow MWD and is also likely to be useful for making amphiphilic block copolymers having unsubstituted methacrylamide as the first block. Furthermore, the silylated amide functionality of poly(TMS-MAm) can be manipulated following reported transformations [28-30].

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References

[1] Hirao A, Nakahama S (1990) Prog. Polym. Sci., 15: 299-335

[2] Dasgupta A, Sivaram S (1997) J. Macromol. Sci. (Rev. Macromol. Chem. Phys.), C37(1): 1-59. For polymerization of monomers bearing amide functionalities, see: Dasgupta A, Sivaram S (1994) Macromolecules 27: 1665; Dasgupta A, Sivaram S (1994) Macromolecular Chemistry and Physics 195:3361

[3] Anionic polymerization of protected N-isopropylacrylamide using trialkylaluminum offered highly isotactic poly (N-isopropylacrylamide), a substituted polyacrylamide; see: Kitayama T, Shibuya W, Katsukawa K (2002) Polym. J., 34: 405. However, synthesizing unsubstituted polyacrylamide requires polymerizing a monomer such as N,O-Bis(trimethylsilyl)acrylamide. This monomer was not possible to polymerize using n-butyl lithium or 1,1-diphenyl ethyl lithium initiators. Dasgupta A, Chakrapani S, Sivaram S unpublished results. Instability of silyl protection towards anionic initiators is also observed for silyl enol ethers; see: Hirao A, Kato K, Nakahama S (1992) Macromolecules, 25: 535-540

[4] Huang X, Wirth MJ (1999) Macromolecules, 32: 1694-1696
[5] Thomas DB, Convertine AJ, Myrick LJ, Scales CW, Smith AE, Lowe AB, Vasilieva YA, Ayres N, McCormick CL (2004) Macromolecules, 37: 8941-8950
[6] Ganachaud F, Monteiro MJ, Gilbert RG, Dourges M-A, Thang SH, Rizzardo E (2000) Macromolecules, 33: 6738-6745
[7] Senoo M, Kotani Y, Kamigaito M, Swamoto M (1999) Macromolecules 32: 8005-8009
[8] Teodorescu M, Matyjaszewski K (2000) Macromolecular Rapid Communications, 21: 190-194 and reference 10 therein
[9] Godwin A, Hartenstein M, Mueller AHE, Brocchini S (2000) Polymer Preprints, 41(1): 1002-1003
[10] There are reports on controlled radical polymerization of n-butyl acrylate and t-butyl acrylate using 4-oxo-TEMPO by the Xerox research group: see: Listigovers NA, Georges MK, Odell PG, Keoshkerian B (1996) Macromolecules, 29: 8992-8993. The same group later used certain reducing additives along with 4-hydroxy TEMPO for controlling the concentration of free nitroxides in acrylate polymerization [14]. Certain new types of nitroxides have been found to be even more promising in controlling the polymerization of acrylates [19, 20, 21]. However, such initiator systems are not reported to be useful for methacrylic monomers
[11] Neugebauer FA, Fischer H (1995) Tetrahedron, 51: 12883-12898
[12] Lin-Vien D, Colthup NB, Fateley WG, Grasselli JG The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules, Academic Press, 1991
[13] Silverstein RM, Webster FX Spectrometric Identification of Organic Compounds, 6th Ed., John Wiley & Sons, 1998
[14] Keoshkerian B, Georges MK, Quinlan M, Veregin R, Goodbrand R (1998) Macromolecules, 31: 7559-7561
[15] Lacroix-Desmazes P, Lutz J-F, Chauvin F, Severac R, Boutevin B, (2001) Macromolecules, 34: 8866-8871; the nitroxide used in this reference namely, N-tert-butyl-N-(1-diethylphosphono-2,2-dimethylpropyl)-N-oxyl (DEPN), is reported to undergo slow decomposition forming t-butyl radicals. This nitroxide was first introduced by Benoit et.al. [20,21]. Certain similar alkoxyamine additives have also been reported to undergo decomposition that apparently results in loss of control over the polymerization process [19]
[16] Steenbock M, Klapper M, Müllen K, Bauer C, Hubrich M (1998) Macromolecules, 31: 5223-5228
[17] Steenbock M, Klapper M, Müllen K (1998) Macromolecular Chemistry and Physics, 199: 763-769
[18] Li D, Brittain WJ (1998) Macromolecules, 31: 3852-3855
[19] Benoit D, Chaplinski V, Braslau R, Hawker CJ (1999) J.Am.Chem.Soc., 121: 3904-3920
[20] Benoit D, Grimaldi S, Finet JP, Tordo P, Fontanille M, Gnanou Y, (1997) Polymer Preprints, 38(1): 729-730
[21] Benoit D, Grimaldi S, Robin S, Finet JP, Tordo P, Gnanou Y (2000) J. Am. Chem. Soc., 122: 5929-5939
[22] Rudin A The Elements of Polymer Science and Engineering, 2nd Ed., Academic Press, 227-230, 1999
[23] Dasgupta A, Brand T, Klapper M, Müllen K (2001) Polymer Bulletin, 46: 131-138. Also see reference [24], section 5
[24] Klapper M, Brand T, Steenbock M, Müllen K in Controlled/living radical polymerization: progress in ATRP, NMP, and RAFT, Matyjaszewski, K., (ed) ACS Symposium Series No. 768, pp 152-167 (2000)
[25] Bamford CH, Brumby S (1967) Makromol. Chem., 105: 122-131
[26] Methacrylamide-b-Styrene copolymers could be characterized indicating styrene incorporation: FTIR (KBr, cm^{-1}): 1659, C=O stretch, methacrylamide; 1599, 1484, ring C=C stretch, styrene; 700, out-of-plane C-C bend, styrene. Wide difference in polarity of the two segments make the block copolymers insoluble in most of the common solvents making it impossible to characterize them by GPC.

[27] Penelle J, Verraver P, Raucq P, Marchand-Brynaert J (1995) Macromol. Chem. Phys., 196: 857-867
[28] Condensation of silylated amide with acid chloride forms an imide linkage: See: Kricheldorf, H.R., Stober, O. (1992) Euro. Polym. J., 28: 1377-1382
[29] For conversion of –CONHSiMe$_3$ to –CN, see: Silicon in Polymer Synthesis, Kricheldorf, H.R Ed. Springer Verlag: Berlin-Heidelberg-New York, Appendix B, section 1, 469-473, 1996
[30] Hofmann degradation converts the amide functionality into amine. For application of the reaction in polymer modifications, see: Yamamoto, Y., Sefton, M.V., (1996) J. Appl. Polym. Sci., 61: 351-358