Nitroxide Mediated Radical Polymerization of Methacryloisobutyl POSS and its Block Copolymers with Poly(*N*-acryloylmorpholine)

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Abstract

Nitroxide mediated radical polymerization (NMP) of the bulky methacryloisobutyl POSS (MA-POSS) monomer is successfully achieved after optimizing reaction conditions such as selection of controlling co-monomer, co-monomer feed molar ratio and temperature (10 mol% styrene co-monomer at 110 ºC using the commercially available BlocBuilder as the NMP initiator). The P(MA-POSS-*co*-St) with a molar mass of ~ 8000 g/mol and dispersity *Đ* ~ 1.2 is afforded under the optimized reaction conditions. The chain end fidelity is verified by chain extension experiments with *N*-acryloyl morpholine (ACM) via NMP that produces well-defined amphiphilic hybrid P(MA-POSS-*co*-St)-*b*-P(ACM)$_x$ block copolymers, where the subscript 'x' represents the degree of polymerization of (ACM) block ($182 < x < 695$). The SEC of the as-synthesized block copolymers reveals the presence of some dead P(MA-POSS-*co*-St) macroinitiator chains that could be conveniently removed by a simple purification step. Kinetic investigations reveal a first order kinetics for the polymerization of ACM using P(MA-POSS-*co*-St) as the macroinitiator under NMP conditions. The kinetic and SEC data confirms the controlled nature of the NMP of ACM with P(MA-POSS-*co*-St) as the macroinitiator. Being amphiphilic, the formed P(MA-POSS-*co*-St)-*b*-P(ACM)$_x$ hybrid block copolymers self-assembled in aqueous solution as revealed by the fluorescence spectroscopy experiments with pyrene as the probe for determination of the critical micelle concentration. However, the dynamic light scattering studies reveal the formation of significantly larger aggregates that could not be classified as true core-shell micelles. Probably, the hydrophilic/hydrophobic balance in the block copolymers under investigations does not favor the formation of true micelles in aqueous medium.

Introduction

Polyhedral oligomeric silsesquioxane (POSS) is considered as the smallest possible particle form of molecular silica because of its size in the range of 1-3 nm, of a general formula $(RSiO_{1.5})_n$, with $n \geq 6$, and R represents an organic group or hydrogen atom[1-7]. POSS derivatives reflect the true form of nanoscale hybrids, which consists of an inner core of cubic nanocage of silicon and oxygen atoms surrounded by an organic shell of reactive or unreactive groups or a mixture of both. The peripheral organic groups play an important role in enhancing the interactions of inner inorganic POSS core with organic systems, either *via* a true chemical integration or by a secondary bonding via physical blending.

Due to its stable and rigid nanocage-like well-defined structure, and its convenient assimilation into various types of hybrid nanostructures, POSS has received significant attention from a diverse spectrum of researchers, ranging from the material science and engineering to biomedical fields. Integration of the POSS cage into organic polymers either via chemical bonding or physical blending significantly improves mechanical strength, thermal stability, and reduces flammability [7-24]. The hydrophobic and biocompatible nature of POSS make it a suitable candidate for biomaterials in potential biomedical and pharmaceutical applications [25-29].

The so-called reversible deactivation radical polymerization (RDRP) and living anionic polymerization are the powerful synthetic tools that have been successfully employed to achieve well-defined POSS based hybrid (co)polymers of different composition and topologies. As an example, Hirai and his co-workers successfully polymerized MA-POSS up to a degree of polymerization (DP) = 29 with a dispersity $Đ \sim 1.04$ by living anionic polymerization[30-35] that was successfully chain extended with styrene (S) and methyl methacrylate (MMA), subsequently affording well-defined block copolymers, which could self-assemble into hierarchical nanostructures [30, 32]. In comparison to anionic polymerization, the RDRP techniques such as ATRP, NMP, and RAFT are experimentally less challenging and more versatile. Initially, ATRP and RAFT were investigated as an alternative facile route for the controlled radical polymerization of POSS monomers to synthesize well-defined polymers of desired molecular weight, architecture, and chain end functionality. Mya and co-workers reported the synthesis of high molecular weight ($M_{n(SEC)}$ = 32,000 g/mol) POSS homopolymer by RAFT using a high monomers/RAFT agent ratio. [36]. However, at high conversion the polymerization process exhibited a decrease in efficiency with a corresponding broadening of the molecular weight distribution. Similarly, Deng *et al.* [37] employed 30:1 and 60:1 monomer/RAFT agent ratio for high MW polymers, but they also faced the same problem of high dispersity in molecular weight at higher monomer conversion. The same research group later reported homopolymers of POSS-MA with lower *Đ* that were chain extended with different monomers for the synthesis of well-defined block copolymers [38-40]. POSS-MA was also copolymerized by RAFT using a macroinitiator of poly(ε-caprolactone)[41] and poly(poly(ethylene glycol) methyl ether methacrylate) [42] with a maximum DP of up to 60.

ATRP, which is a catalyst supported RDRP process, has also been employed for homopolymerization of POSS-MA. The first ATRP polymerization of POSS-MA was reported by Matyjaszewski's group [43]. They used CuCl/PMDETA as the catalyst system and obtained polymers with relatively low DP of 14 and *Đ* ~ 1.14. They also synthesized triblock and star-shaped hybrid polymers by the same method with short segments of POSS-MA (DP < 14) using methyl acrylate and butyl acrylate as comonomers. Further, the same group subsequently reported ABA triblock copolymers having POSS-MA blocks on the terminal segments with a middle block of poly(butyl acrylate) [44]. Many other reports [45-52] are also available in the literature on ATRP for the polymerization of POSS-MA to high MW POSS based hybrid polymers. Very recently

Vladimir and his co-workers succeeded in homopolymerization of POSS-MA via ATRP to achieve number average molecular weight M_n = 460,000 g/mol at 60^o C[53], thus confirming the robustness of ATRP for POSS-MA polymerization. They further synthesized P(POSS-MA)-*b*-PMMA and P(POSS-MA)-*b*-PS either by chain extension of P(POSS-MA) macroinitiator with S or MMA or by polymerization of POSS-MA using PMMA or PS as the macroinitiator. The low dispersity ($Đ$ <1.35) confirmed the controlled nature of the ATRP of POSSMA in all the reported cases.

The literature review indicates that RAFT and especially ATRP has overcome almost all the synthesis-related issues in the homopolymerization of POSS-MA, but researchers still face some serious problems in the synthesis of POSS-based block copolymers with nitrogen containing monomers. For example, the chain extension *via* ATRP from a P(POSS-MA) macroinitiator with nitrogen-based monomers for a second or third block requires very special and expensive ligands for Cu catalyst, which makes the reaction industrially less viable. Similarly, it was noticed that the controlled polymerization of POSS-MA occurs at relatively lower rates and requires longer times for higher conversion. Similarly, the RAFT agents commonly employed are unstable after a long period and begin to emit a pungent odor due to the slow and continued degradation of the dithio group from the chain transfer agent.

Despite the several inherent limitations, such as slow polymerization kinetics, high polymerization temperature, inability to easily control the polymerization of methacrylate monomers, and problems associated with the synthesis of nitroxide and alkoxyamine, nitroxide mediated radical polymerization (NMP) still has some advantages over other RDRP methods, such as monomer compatibility, simplicity, and polymer purity (little post-polymerization purification required). NMP, even though it is the oldest among all the available RDRP techniques, there is still no reports available regarding the synthesis of POSS-based hybrid polymers *via* NMP, let alone their block copolymers. To exercise these advantages of NMP and overcome the problems associated with other RDRP methods in synthesis of POSS-based hybrid polymers, and to provide an alternate option for the synthesis of well-defined POSS-based hybrid (co)polymers of different compositions and architectures, here, we report for the first time the NMP of bulky isobutyl substituted POSS methacrylate using a low molar fraction of styrene ~ 0.10 as comonomer. The livingness of the achieved P(POSS-MA) polymers was tested by chain extension with nitrogen containing acryloylmorpholine (ACM) by NMP at 110 °C that afforded well-defined amphiphilic hybrid P(POSSMA-*co*-S)-*b*-P(ACM) block copolymers. ACM is a cyclic acrylamide with good solubility in water and organic solvents, good biocompatibility, and superabsorbent material in many specialized application areas. For example, for many years *N*-acryloylmorpholine was used in the synthesis of cross-linked networks for gel phase synthesis of peptides, [54, 55] as a polymeric support for gel chromatography, [56] semipermeable membrane for plasma separation, and capillary electrophoresis [57]. Thus, the purpose was not only to ascertain the chain end-fidelity but also to afford well-defined amphiphilic hybrid diblock copolymers, P(POSS-MA-*co*-styrene)-*b*-(poly acryloyl morpholine). Finally, the achieved hybrid block copolymers, being amphiphilic in nature, were tested for their self-assembly behaviour in nanoaggregates when dispersed in an aqueous medium.

Experimental

Materials

Basic alumina (Brockmann, type 1, 150 mesh, Sigma-Aldrich), sodium sulfate (≥99%, Sigma-Aldrich), potassium bisulfate (≥99%, Sigma-Aldrich), calcium hydride (90–95%, reagent grade, Sigma-Aldrich), sodium bicarbonate (≥99.7%, ACP Chemicals), toluene (≥98.5% certified ACS, Fisher Scientific), hexane (≥98.5% certified ACS, Fisher Scientific), methanol (≥98.5% certified ACS, Fisher Scientific), acetone (≥98.5% certified ACS, Fisher Scientific) and tetrahydrofuran (>99.9%, HPLC grade, Fisher Scientific), 2-([tert-butyl[1-(diethoxyphosphoryl)-2,2 dimethyl propyl]amino]oxy)-2-methylpropanoicacid (BlocBuilder) (99%, Arkema) were used as received. 4-acryloyl morpholine (ACM, 97%, inhibited with 1000 ppm MEHQ, was obtained from Sigma-Aldrich and was purified by passing through a column packed with basic alumina along with 5% wt. calcium hydride before use.

Synthesis

Selection of co-monomer and optimization of molar ratio of the co-monomer

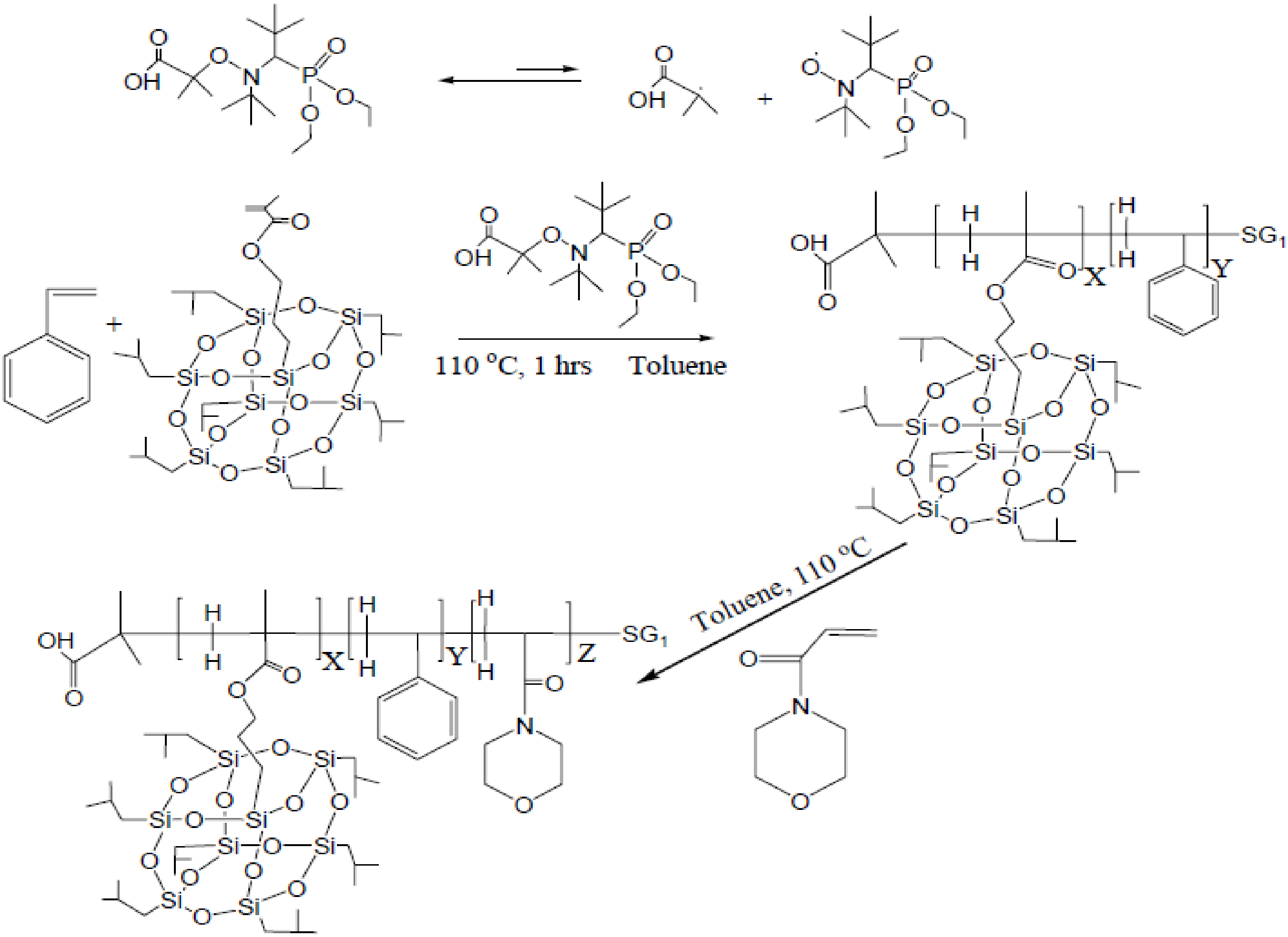
A suitable comonomer is required for the successful polymerization of POSS-MA by NMP. For this purpose, three monomers, namely ACM, S, and acrylonitrile were tested as comonomers under the same experimental conditions for the polymerization of POSS-MA. Using toluene as solvent and BlocBuilder as the initiator, the NMP of POSS-MA was proceeded separately for 1 h in the presence of 10 mole% of the three different comonomers at 110 ºC. In each case, the target molecular weight of the copolymer was set to 40 kg mol^{-1}. After 1 h of the reaction, the final product was characterized by SEC. The % monomer conversion and SEC data, as discussed in the *Results and Discussion* section, suggested that S as the comonomer could be more efficient to successfully polymerize POSS-MA by NMP. After selecting S as the comonomer for NMP polymerization of POSS-MA, the effect of the molar ratio of the co-monomer was also studied by changing the molar ratio of S in the initial monomer feed (5 mole %, 10 mole % 15 mole %, and 20 mole %) under the same polymerization conditions.

NMP of POSS-MA with styrene as the comonomer

After selecting styrene as the comonomer and its appropriate molar ratio (10 mole %), the NMP of POSS-MA was studied in detail. The NMP of POSS-MA along with 10 mole % S and BlocBuilder as the initiator was carried out at 110 ºC in 50 wt. % toluene solution. In a typical reaction, 0.3 g (0.78 mmol) BlocBuilder was added to a three neck 25 mL round bottom flask along with 10 g (7.8 mmol) POSS-MA and 0.12 g (1.15 mmol) styrene. The same flask was also provided with 10.5 g of toluene. The reactor was sealed with a rubber septum having the thermocouple placed in the solution and connected to a temperature controller. The reaction mixture was purged with ultra-pure nitrogen for 20 min before raising the temperature to 110 ºC at a heating rate of 6-7 ºC/min. The reaction starting time was considered when the target temperature reached. For kinetic analysis, about 0.1 mL aliquot was taken every 10 min. for 1 h. and was analyzed with SEC and ^{1}H-NMR spectroscopy. The reaction was stopped by placing the reactor in ice cold water. The unreacted POSS-MA was removed by precipitating the reaction mixture in an excess of acetone. The precipitation process was repeated three times to ensure the complete removal of unreacted POSS-MA. The product was isolated as a white powder which was recovered after drying in vacuum oven overnight at room temperature.

Synthesis of P(POSSMA-co-styrene)-b-P(acyloylmorpholine) diblock copolymers

To check the chain end fidelity of the synthesized P(POSSMA-*co*-S) copolymer chains and to achieve diblock copolymers, chain extension was carried out with water-soluble ACM under similar NMP conditions as discussed above for the MA-POSS polymerization. In one of the experiments, 0.6 g (0.086 m mol) macroinitiator (P(POSSMA-*co*-S)), 2.4 g (0.017 mmol) ACM, and 3 g toluene were added to a three neck 10 mL round bottom flask. The mixture was purged with nitrogen for 30 min and then the temperature was raised to 100 ºC. A slow flow of nitrogen gas over the reaction mixture was kept for the whole span of the experiment. About 0.1 mL sample was taken periodically and was analyzed with SEC and ^{1}H-NMR spectroscopy for the reaction progress. The reaction was stopped when the reaction mixture became very viscous and unable to stir any further. The crude diblock copolymer was first precipitated two times in methanol to remove the unreacted ACM and then precipitated two times in a 40 % hexane/methanol mixture to remove the dead macroinitiator. The final product was obtained as a white powder after drying in vacuum oven overnight at 40 ºC. The whole reaction scheme is outlined in Scheme 1.



Scheme. 1: Different steps involved in the synthesis of p(POSS-*co*-St)-*b*-p(NAM) diblock copolymers by NMP.

Characterization

Number average molecular weight, M_n and dispersity, *Đ* of the synthesized polymers were determined by SEC (Waters Breeze HPLC system). The SEC was equipped with RI (2414) detector, a guard column, and three Waters Styragel HR columns, having molecular weight measurement ranges of 0-5, 0.5-20, and 5-500 kg mol^{-1}. PMMA standards in THF at 40 °C were used for the column calibration. HPLC grade THF was used as mobile phase with a flow rate of 0.3 mL min^{-1} at 40 °C.

^{1}H-NMR spectra were recorded in $CDCl_3$ on Varian mercury spectrometer, operating at 300 MHz.

Fluorescence spectroscopy

The fluorescence probe method was used to investigate critical micelle concentration (CMC) of the synthesized block copolymers in aqueous medium, using pyrene as the fluorescent probe. Fluorescence spectra were recorded on a Varian Cary Eclipse fluorescence spectrofluorometer, where the excitation and emission bandwidths were fixed at 3 nm. The polymer solution of known concentration was first prepared in a 0.5 μM solution of pyrene. The same solution was further diluted for the next measurement by adding a known amount of 0.5 μM pyrene solution. Thus, the polymer concentration decreased continuously, and pyrene concentration remained constant in all the samples. However, all these solutions were shaken and equilibrated at ambient temperature for sufficient time before measurements. Excitation wavelength was fixed at 340 nm and emission spectra were recorded in the range of 350 to 500 nm. The ratio of peak intensities at 384 nm and 373 nm of the emission spectra were plotted as a function of block copolymer concentration for the estimation of the CMC.

Dynamic laser light scattering

Hydrodynamic particle size of the aggregates formed by the synthesized hybrids was determined by dynamic laser light scattering in aqueous medium, using Malvern Zetasizer Nano ZS. All the measurements were carried out at fixed scattering angle of 90^o at room temperature. For each reading, the solution of known concentration was first stabilized overnight and then filtered through Millipore filter having 0.45μm pore size.

Result and discussion

Though NMP is the oldest among all the controlled radical polymerization techniques, it is still challenging to polymerize methacrylic monomers. This is further exacerbated if the monomer is particularly sterically hindered. The challenge in polymerizing methacrylates by NMP arises due to the slow recombination of alkoxyamine radical with the growing radical that leads to lower control and poorly defined polymers[58-60]. Changes to alkoxyamine structure have been attempted to minimize side reactions like β-H abstraction with some moderate success although efficient cross-over to different monomer blocks (i.e. methacrylate to styrenic) has only recently been demonstrated. With the commercially available alkoxyamine BlocBuilder, two alternate strategies could be adopted. The first is the addition of a small excess of alkoxyamine radical that reduces the probability of irreversible termination by capping the growing radicals [61]. Second, the use of a low mole fraction of a comonomer that is readily controllable by NMP (eg. S, acrylonitrile) will result in the probability of the chain terminated by the controlling comonomer – thereby staying longer in the dormant state [62-64]. POSS-MA is a bulky methacrylate type monomer and its homopolymerization by NMP seems not feasible and to the best of our knowledge, therefore, there is no report on the NMP of POSS-MA. Herein, we applied NMP for the first time to successfully polymerize POSS-MA using a small fraction of S as co-monomer at 110 ºC using BlocBuilder as the initiator. Initially, trial experiments were carried out for the selection of the comonomer for the NMP of POSS-MA. Under similar experimental conditions, 10 mole % S, ACM, and acrylonitrile in the initial monomer mixture were separately employed as the comonomer with POSS-MA using BlocBuilder as the NMP initiator. For acrylonitrile, the reaction seems to be relative slower with < 30% monomer conversion after 1 h and with no further change in conversion even after 5 hrs of the reaction, suggesting that most if not all the comonomer was consumed and that no more is available for controlling MA-POSS. For S and ACM, under similar conditions, the monomer conversion was recorded ~ 40 % with narrower molecular weight distribution ($Đ = 1.32$) for S controlling comonomer compared to the case with ACM controlling comonomer ($Đ$ = 1.44) as depicted in Figure 1 (SEC traces recorded after 1 h reaction time). Thus, styrene was selected as the comonomer for the NMP of POSS-MA for further study.

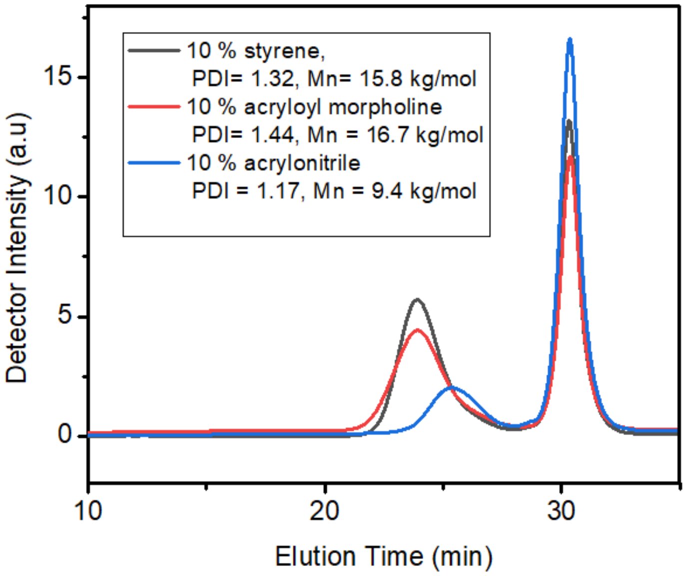


Figure. 1: SEC chromatograms of P(POSS-MA) copolymers with the respective comonomer after 1 h reaction time. All the reactions were conducted in 50 wt % toluene solution at 110 ºC.

In addition, the higher polymerization temperature that can be used when styrene was employed as the co-monomer for the NMP of POSS-MA allowed for more rapid polymerization without an effect on the molecular weight distribution. The lower polymerization temperature used for the other two monomers, especially acrylonitrile, is necessary as its high volatility may result in its loss from the reaction media (although we attempted to minimize this with the cooling condenser. The loss of acrylonitrile would provide a mixture richer in POSS-MA increasing the probability of irreversible termination reactions. Further, the effect of the molar ratio of S in the reaction mixture was also evaluated. With 5 mole % S, higher Đ and lower polymer yield was found. An increase in yield was observed by using 15 and 20 mole % controlling S comonomer with comparable Đ to that when 10 mole % S was used. Thus, for optimum polymerization conditions, the molar ratio of POSS-MA and styrene was kept 90:10. Figure 2 depicts SEC traces of P(POSS-MA-*co*-S) as function of polymerization time achieved under the optimized NMP conditions (10 mole% S as the comonomer, BlocBuilder as the initiator, toluene as solvent,110 ºC).

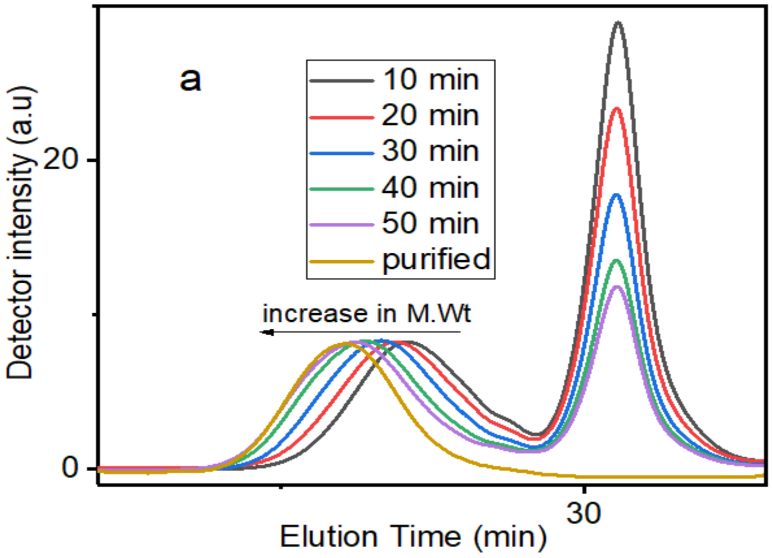


Figure 2: SEC chromatograms of P(POSS-*co*-S) copolymer (initial %mole fraction of styrene in the feed = $f_{S,0}$ = 10%) recorded in THF from samples taken at at different time intervals. The polymerization conditions were 110 ºC in 50 wt% toluene.

A systematic shift in SEC chromatograms toward lower elution time (higher molecular weight) with time could be seen in Figure 2 that indicates the progress of the reaction. The SEC traces of the polymer samples are monomodal and the *Đ* remained low (< 1.28) throughout the reaction that strongly suggests the controlled nature of the polymerization. Figure 3 shows the ^{1}H-NMR spectrum of the purified P(POSS-MA-*co*-S), where signals ***a*** and ***b***, respectively, appearing at δ ~ 0.6 ppm and δ ~ 0.95 ppm correspond to methylene (-CH_2-) protons directly attached to the Si atom of the POSS cage and methyl protons of the *i*-butyl groups attached to the POSS cage, while the signal ***c*** at δ ~ 1.7 ppm corresponds to the methine protons of the *i*-butyl groups.

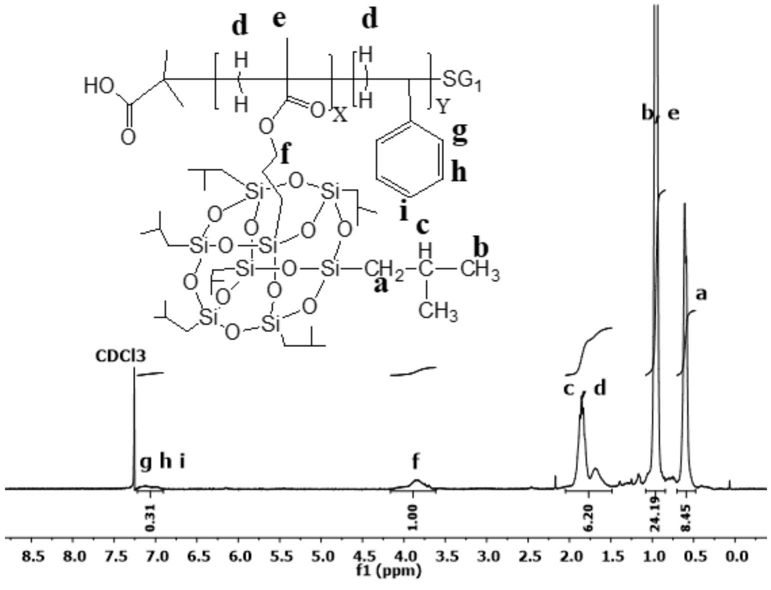


Figure 3: ^{1}H-NMR spectrum of the purified P(POSS-*co*-St) copolymer recorded in chloroform-*d*.

The incorporation of styrene into the copolymer structure could be confirmed by the detection of the aromatic proton signal at δ ~ 7.1 ppm. The molar composition of the prepared copolymer, P(POSS-MA-*co*-S) was estimated by comparing the integrated areas of the aromatic proton signals and signal ***a*** from the POSS segments and it was found to be almost the same as that of the feed molar composition. In conclusion, the monomodal molecular weight distribution and relatively lower Đ and the presence of POSS and aromatic signals in the ^{1}H-NMR spectrum suggests the successful polymerization of the POSS-MA by NMP using S controlling comonomer. Further, in the ^{1}H-NMR spectrum, shown in Figure 3, no vinyl proton signals attributed to the monomer could be detected, which suggests that the product is free from the unreacted POSS-MA and that the adopted purification procedure resulted in complete removal of the unreacted monomer from the sample.

To confirm the chain-end fidelity of the achieved P(POSS-MA-*co*-S) copolymer, chain extension experiments were carried out with acryloyl morpholine (ACM) that not only confirmed the living nature of the achieved p(POSS-MA-*co*-S) copolymer chains but also afforded amphiphilic hybrid P(POSS-MA-*co*-S)-*b*-P(ACM) diblock copolymers.

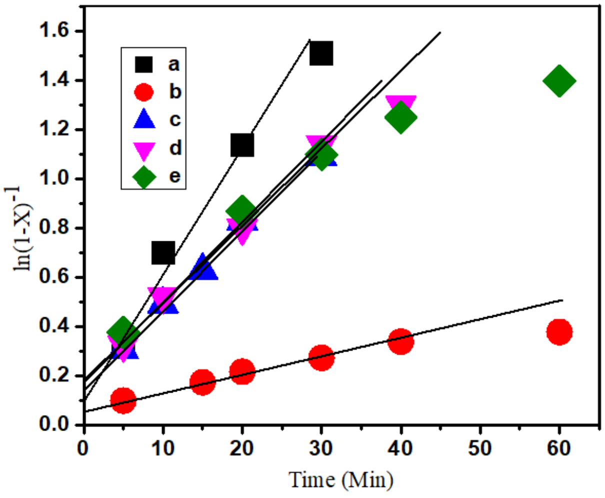


Figure. 4: Semi logarithmic kinetic plots of the NMP of acryloyl morpholine at 110 ºC, using the synthesized p(POSS-MS-*co*-S) as the macroinitiator. Series ***b*** (red circles) shows the kinetic data of the same reaction carried out at 100 ºC. See Table 1 for the experimental parameters indicating the conditions for the other series (a, c, d and e).

As discussed earlier, ACM is a cyclic acrylamide with good solubility in water and organic solvents, good biocompatibility, and can be used as a superabsorbent material in special application areas. Thus, its combination with the POSS segments could lead to novel materials for potential biomedical applications. The progress of the NMP of ACM with P(POSS-MA-*co*-S) as the macroinitiator was monitored by ^{1}H-NMR spectroscopy. The monomer conversion of ACM was calculated by comparing the integration areas of vinylic protons of unreacted ACM (δ~ 5.5-6.3 ppm) with methylene protons of POSS (δ ~ 0.65 ppm) of the macroinitiator (^{1}H-NMR data not shown here). The semi-logarithmic kinetic plots given in Figure 4 suggest that the NMP of ACM using the synthesized P(POSS-MA-*co*-S) as the macroinitiator follows the first order kinetics. The same reaction seems to be very slow when carried out at 100 °C as indicated by the series ***b*** denoted in Figure 4 and with relatively higher Đ (Table 1, Sample B).

Table 1: Experimental Parameters and ^{1}H-NMR and SEC data.

Sample ID	[M]/[I]	Temp. (°C)	Time (min.)	Conversion (%)	M_n 1x 10^3 kg/mol (^{1}H-NMR)	M_n 1x 10^3 kg/mol (SEC)	*Đ*
p(POSS-MA-*co*-S)	15 :1	110	60	62	------	7900	1.23
A	180:1	110	30	78	33.6	25	1.34
B	350:1	100	60	32	37.7	35	1.54
C	350:1	110	30	66	79.1	46	1.50
D	450:1	110	40	73	102.4	49	1.62
E	500:1	110	60	75	106.1	53.5	1.55

Figure 5 depicts SEC traces of the unpurified and the respective purified block copolymer sample along with the SEC profile of the macroinitiator. The SEC trace of the unpurified block copolymer clearly shows a shoulder at higher elution time that could be attributed to the presence of dead macroinitiator chains in the sample. However, after a facile purification step, as discussed in the

Experimental Section, the unreacted P(POSS-MA-*co*-S) was conveniently removed from the final product as evident from the monomodal SEC trace after purification. Figure 6 depicts the SEC traces of all the block copolymers after purification, where the monomodal molecular weight distribution and the absence of any shoulder due to the unreacted macroinitiator chains could be observed. The SEC traces shift to lower elution time with increase in molar mass of the sample. The characteristic data of all the synthesized and purified block copolymers of various compositions are given in Table 1. Figure 7 is the representative ^{1}H-NMR spectrum of the synthesized amphiphilic hybrid P(POSS-MA-*co*-S)-*b*-P(ACM) diblock copolymer. In addition to the signals of the P(POSS-MA) segments as discussed above, the characteristic signals of the P(ACM) block could be seen in the

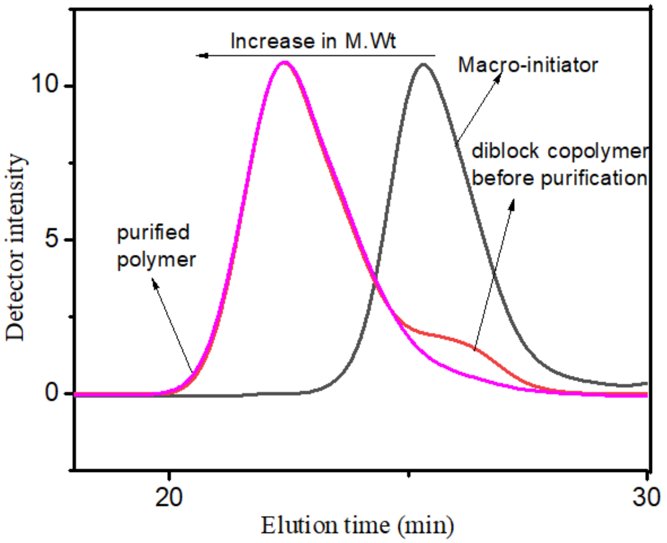


Figure. 5: SEC chromatograms of P(POSS-MA-*co*-St) macroinitiator, and the respective as synthesized and purified P(POSS-MA-*co*-St)-*b*-P(AMC) diblock copolymers.

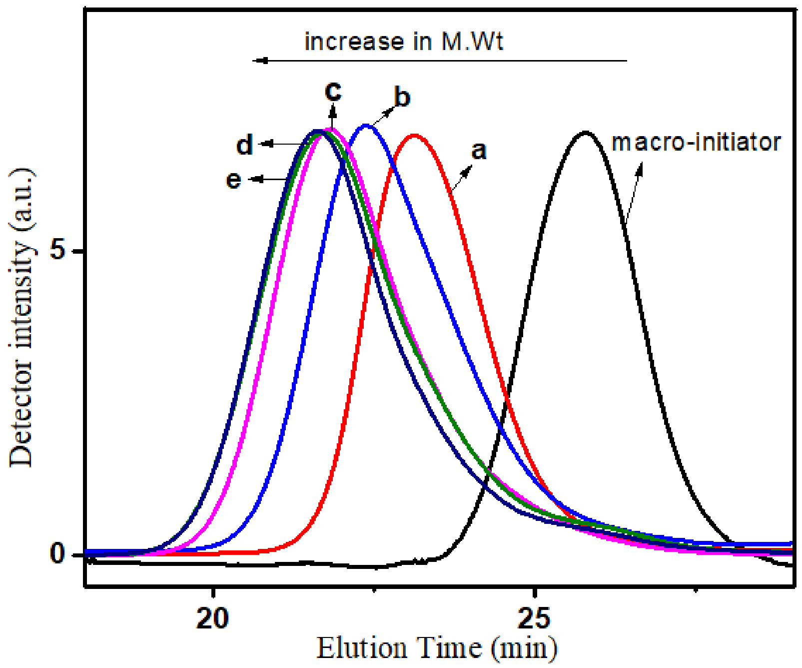


Figure.6: SEC chromatograms of all the synthesized P(POSS-MA-*co*-S)-*b*-P(ACM) diblock copolymers after purification. The code from ***a*** to ***e*** represents the respective samples listed in Table 1.

range of δ ~ 3 - 4 ppm (signal ***2***, and ***3*** that correspond to methylene protons of morpholine ring) and at δ ~ 2.5 ppm (signal ***1*** that corresponds to methine backbone proton). The degree of polymerization of P(ACM) block was calculated by comparing integral areas of signals ***1*** at δ ~ 2.2-2.7 ppm with signal ***a*** at δ ~ 0.6 ppm of the P(POSS-MA) segments and molecular weights of the block copolymers were calculated as:

$$M_n = \text{M.Wt of p(POSS-MA-}co\text{-S)} + \text{D.P x M.Wt of acryloyl morpholine}$$

The data are tabulated in Table 1. The M_n values calculated from ^{1}H-NMR spectrum was found to be

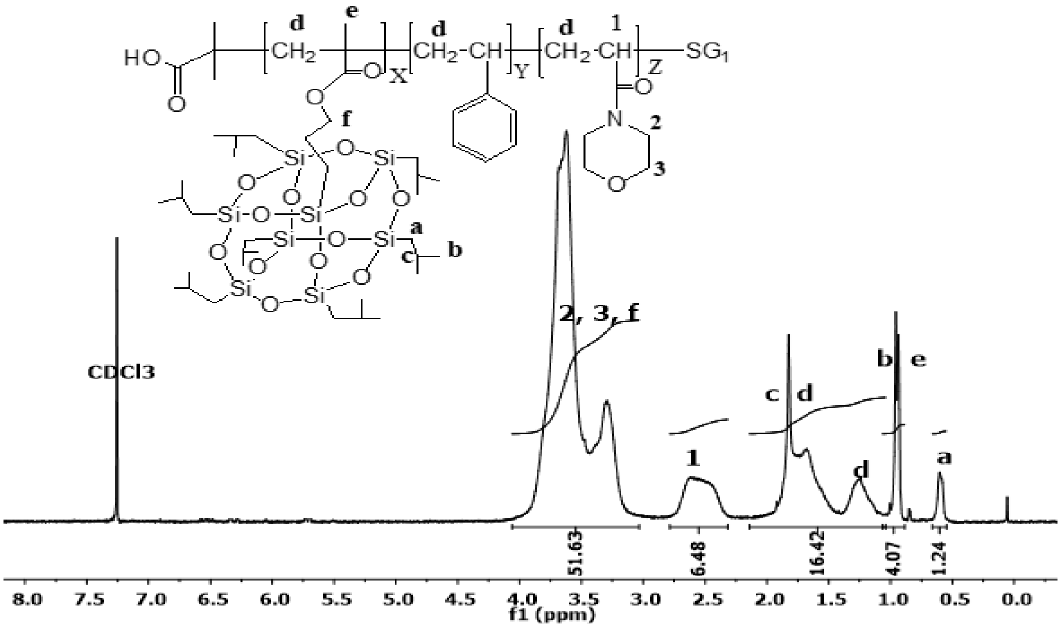


Figure 7: ^{1}H-NMR spectrum of P(POSS-MA-*co*-St)-*b*-P(ACM) diblock copolymer, recorded in chloroform-*d*.

higher than those obtained from SEC data (Table 1). This difference could partially due to the use of PMMA as standards for SEC column calibration (eg. polymers of the same degree of polymerization may possess different hydrodynamic volumes in THF). Significant discrepancies in polymer molecular weight obtained from ^{1}H NMR spectroscopy and SEC measurements under similar situations have also been reported by other groups[65-67]. Still, by employing NMP of ACM by using the synthesized P(POSS-MA-*co*-S) as the macroinitiator, well-defined amphiphilic hybrid P(POSS-MA-*co*-S)-*b*-P(ACM) diblock copolymers were achieved (Table 1).

Finally, because of the amphiphilic nature of the synthesized P(POSS-MA-*co*-S)-*b*-P(ACM) diblock copolymers; the P(ACM) segment being water soluble at ambient temperature and

P(POSS-MA-*co*-S) being the hydrophobic segment, their preliminary self-assembly behavior in aqueous medium was also studied. The critical micelle concentration (CMC) was first estimated by fluorescence spectroscopy with pyrene as the fluorescence probe. Figure (8a) depicts a set of emission spectra of [0.5 µM] pyrene in aqueous solution with varying block copolymer (P(POSS-MA-*co*-S)-*b*-P(ACM)$_{504}$) concentration. The CMC of the corrresponding block copolymer was determined from the plot of the ratio of I_3/I_1 versus the logarithm of block copolymer concentration. The intersection of the two tangents was defined as the CMC as shown in Figure 8(b), where CMC was calculated to be 0.06 mg/mL. The CMC of the synthesized block copolymers with fixed hydrophobic block length and varying length of the hydrophilic P(ACM)$_x$ block were determined and the data are given in Table 2. The CMC of the block copolymers could be tuned by changing the hydrophilic/hydrophobic balance, thus, the lowest CMC (0.002 mg/mL) was observed for block copolymer with the shortest P(NAM)$_{182}$ segment among the synthesized block copolymers, while the highest CMC ~ 0.6 mg/mL was found for the

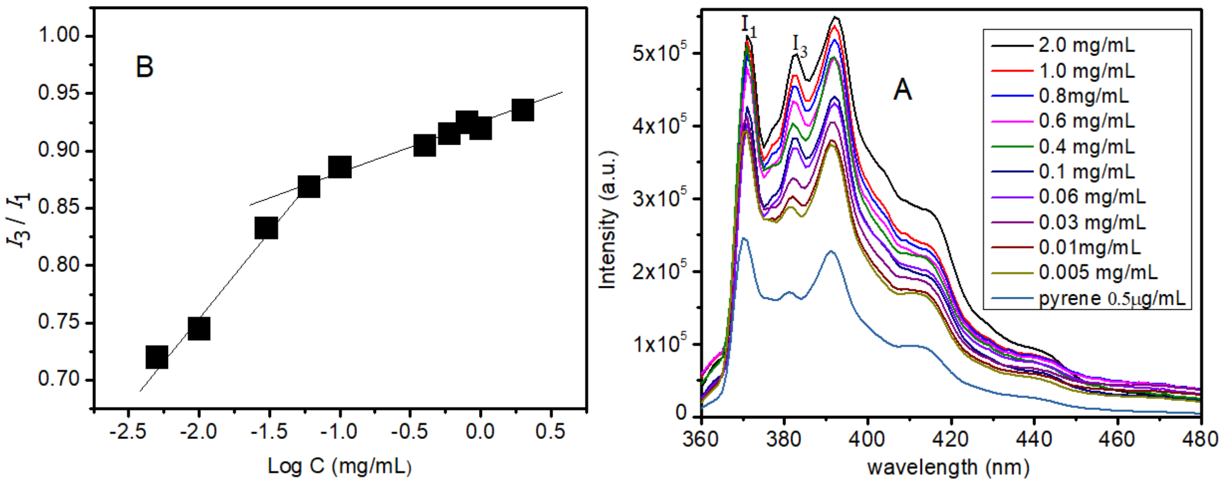


Figure 8: (a) Emission spectra of pyrene in aqueous solution having different concentration of p(POSS-MA-*co*-S)-*b*-p(ACM)$_{504}$ diblock copolymers and fixed concentration of pyrene. Plot of I_3/I_1 vs. log of concentration for the same diblock copolymers.

Table. 2: Critical micelle concentration and hydrodynamic particle size data.

Sample	**CMC (mg/mL)**	***R*$_h$ (nm)**
P(POSS-MA-*co*-S)-*b*-P(ACM)$_{182}$	0.002	144 284
P(POSS-MA-*co*-S)-*b*-P(ACM)$_{210}$	0.007	107 234
P(POSS-MA-*co*-S)-*b*-P(ACM)$_{504}$	0.06	117
P(POSS-MA-*co*-S)-*b*-P(ACM)$_{669}$	0.2	104
P(POSS-MA-*co*-S)-*b*-P(ACM)$_{695}$	0.7	94

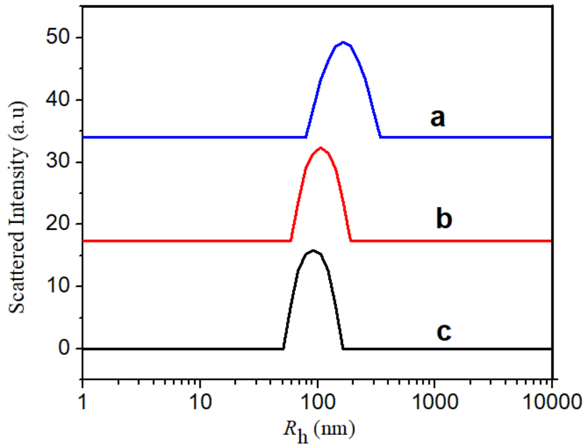


Figure 8: Hydrodynamic radius, *R*$_h$ of the aggregates formed by P(POSS-*co*-S)-*b*-P(ACM)$_x$ diblock copolymers, with x = 504 (a), 669 (b), and 695 (c), respectively (copolymer concentration = 1 mg /mL).

block copolymer with longest P(ACM)$_{695}$ block as given in Table 2. Although P(ACM) is considered a strongly hydrophilic polymer, the lower CMCs of the block copolymers suggest that POSS nanocages have sufficiently altered the solution behaviour of the block copolymers. This is supported by other observation of block copolymers in aqueous solution where the CMC decreased with increased hydrophobicity of the short hydrophobic block. Further, the hydrodynamic size of the particle formed by the synthesized hyrbrid amphiphilic P(POSS-MA-*co*-St)-*b*-P(ACM)$_x$ block copolymer in aqueous modium was also estimated by dynamic light scattering. Figure (9) shows hydrodynamic radii (R_h) of the self-assembled nanostructures formed by different diblock copolymers at abient temperature at concentration well-above their resepctive CMC. A unimodal particle size distribution with hydrodynamic radius, R_h = 117 nm, 104 nm, and 71 nm was recorded for the aggregates formed, respectively by P(POSS-MA-*co*-S)-*b*-P(ACM)$_{504}$, P(POSS-MA-*co*-S)-*b*-P(ACM)$_{675}$, P(POSS-MA-*co*-S)-*b*- P(ACM)$_{695}$. The large hydrodynamic particle size suggests that these aggregates are not true core-shell type of micelles. Li *et al.* [68] reported the micelle formation of poly(*n*-butyl methacrylate) (PBMA)-*block*-poly(*N*-acryloylmorpholine) (PNAM) diblock copolymers in aqueous medium where the length of PBMA varied from 28 to 62 units and that of the hydrophilic P(NAM)$_x$ was varied from 80 to 271 units. In all the cases they observed the formation of micelles in the range of $R_h \sim 12.5$ nm to 41.5 nm. In the current system, it appears that the hydrophobic/hydrophilic balance between short P(POSS-MA) segments and very long hydrophilic P(ACM) chains does not favor the formation of true micelles.

Conclusion

Nitroxide mediated radical polymerization (NMP) was successfully employed for the first time for the copolymerization of Methacryloisobutyl POSS (MA-POSS) at 110 ºC in the presence of 10 mol % styrene (S) as controlling comonomer with BlocBuilder as the NMP initiator. ^{1}H NMR spectroscopy confirmed > 60 % conversion of MA-POSS with ~ 10 mole% of S in the formed P(MA-POSS-*co*-S) copolymer. SEC traces suggested the controlled nature of the polymerization of MA-POSS with monomodal molar mass distribution and low dispersity (Đ = 1.23). The chain end fidelity of the formed P(MA-POSS-*co*-S) was confirmed by employing it as the macroinitiator for the NMP of *N*-acryloyl morpholine (ACM). ^{1}H NMR data revealed that NMP of ACM followed first order kinetics with relatively low dispersity of the achieved block copolymers(1.34-1.62). The SEC traces of the as-synthesized P(MA-POSS-*co*-S)-*b*-P(ACM)$_x$ block copolymers showed the presence of some unreacted macroinitiator chains that could be easily removed by a simple purification step that afforded well-defined P(MA-POSS-*co*-S)-*b*-P(ACM)$_x$ block copolymers with monomodal molar mass distribution indicated by SEC traces. Our initial self-assembly investigation revealed the formation of relatively large aggregates in aqueous medium ~ 100 nm.

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