Incorporation of Methacryloisobutyl POSS in Bio-Based Copolymers by Nitroxide Mediated Polymerization in Organic Solution and Miniemulsion

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((Additional Supporting Information may be found in the online version of this article.))

KEYWORDS

polyhedral oligomeric silsesquioxane, miniemulsion polymerization, bio-sourced monomers, methacrylates, controlled radical polymerization.

ABSTRACT

In this study, nitroxide mediated polymerization of methacryloisobutyl POSS (POSSMA) and bio-sourced monomers: isobornyl methacrylate (IBOMA) and C13 methacrylate (C13MA, an alkyl methacrylate with an average chain length of 13 units) was conducted in solution (toluene) and miniemulsion. BlocBuilder-MA (with 10 mol% acrylonitrile (AN) controlling co-monomer, for the solvent-based system) and Dispolreg 007 (for the miniemulsion) were used as the alkoxyamine for initiation and controlling the polymerization. POSSMA/IBOMA/C13MA effective terpolymerization (having 10 mol% AN controlling co-monomer) with monomer conversion (X) <72% in toluene resulted in resins with M_n up to 21.3 kg mol^{-1} and $Đ < 1.67$. Next, terpolymerizations were conducted in water to completely remove the organic solvent resulting in polymers with M_n up to 46.7 kg mol^{-1} and $Đ < 1.65$. The successful chain extension of poly(IBOMA/AN) with a mixture of POSSMA/C13MA/AN (M_n = 74.1 kg mol^{-1} and $Đ = 1.55$) showed high chain-end fidelity, exemplified by a clear, monomodal shift in the GPC chromatogram from the macroinitiator. Finally, it was shown that the addition of 20 mol% POSSMA improved the decomposition temperature of bio-based polymers of IBOMA/C13MA by 15%.

INTRODUCTION

The incorporation of silicon-containing compounds into polymer structures has been of great interest for the past several decades[1-3]. One example of such compounds are polyhedral oligomeric silsesquioxanes (referred as POSS), with general formula of $(RSiO_{1.5})_n$, $n \geq 6$, that usually possess one or more organic substituents[4]. This organic/inorganic hybrid can have various functional groups enabling the incorporation of the POSS into different materials[5,6]. POSS-containing molecules are often cited as environmentally friendly, non-volatile and odorless and are frequently used as a nano-filler or modifier of material properties[7]. For example, POSS cages can improve anti-flammability, mechanical properties, thermal stability and biocompatibility and rheological properties[4,6,8]. Methacryloisobutyl POSS (termed herein as POSSMA) is a POSS containing molecules (n=8) with one methacrylic ligand, which can be incorporated into polymer resins to improve the hardness (T_g of poly(POSSMA)≈ 85 °C)[9] and thermal stability. The reversible-deactivation radical polymerization (RDRP) of POSSMA with different monomers was previously studied in organic solvents[10-17] and reported in dispersed aqueous media recently[18]. Nitroxide mediated polymerization (NMP), as one of the simplest RDRP techniques, can be used to prepare POSSMA-containing polymers with active chain ends, well-defined microstructures and narrow molecular weight distributions[19-21]. These features allow lower viscosities (useful for coatings applications) and better chain—to-chain compositional homogeneity (tailoring of properties), for example.

Previously, POSSMA was incorporated into bio-based polymers and composites to enhance their mechanical and thermal properties[22,23]. However, it was shown that only the addition of high POSSMA concentration (or similar POSS containing monomers) can efficiently increase the thermal stability of the product[15,24,25]. We earlier homopolymerized POSSMA and copolymerized POSSMA with C13MA, a vegetable oil-derived alkyl methacrylate with an average side chain length of 13 alkyl units. For copolymerization of POSSMA/C13MA, we observed that a 10 mol% increase in feed molar ratio of POSSMA improved the onset decomposition temperature ($T_{dec,1}$, for 10% weight loss) moderately by 4.9 to 5.8 °C[18,23]. Here, isobornyl methacrylate (IBOMA) was incorporated into statistical terpolymers of POSSMA/IBOMA/C13MA for further improvement of thermal stability without compromising the bio-content of polymer resins. IBOMA is a bio-based monomer derived from terpenes[26]. IBOMA homopolymers have a high T_g (T_g = 110 to 200 °C, depending on the molecular weight)[27-30] due to the bicyclic carbon-based group which contributes to improving hardness and thermal stability[31,32]. As C13MA has a long alkyl group, it can effectively serve as a polymerizable plasticizer, providing flexibility to the polymer chain (T_g of poly(C13MA) homopolymer = -46 °C)[27,33]. To understand the incorporation of these three monomers, via terpolymerization by NMP of POSSMA/IBOMA/C13MA monomers in toluene was first studied. BlocBuilder-MA alkoxyamine[34] (BB, from Arkema) was used to initiate the polymerization and 10 mol% acrylonitrile (AN) was added to the feed as the controlling co-monomer to improve the control over the polymerization[35]. Control is defined here as linear increase of number average molecular weight M_n with monomer conversion, relatively narrow molecular weight distribution and predetermined final number-average molecular weight for polymers[19,36,37]. We thus target bio-based poly(methacrylate) resins by NMP with tunable T_g and excellent thermal stability due to the inclusion of POSSMA[38].

To investigate further the effect of the POSS cage on the thermal stability of polymers derived from bio-based monomers, polymerization of a low concentration of POSSMA (5, 10, 20 mol% in initial feed), with IBOMA and C13MA was performed in miniemulsion. Bypassing the use of organic solvents permitted a final product essentially free of volatile organic compounds (VOCs). To initiate the nitroxide mediated miniemulsion polymerization of POSSMA/IBOMA/C13MA, Dispolreg 007 alkoxyamine[39,40] was used.

Dispolreg 007 has been used for NMP of methacrylates in organic solvents[39-41], miniemulsions[38,42] and suspensions[43].This alkoxyamine enables the NMP of methacrylic monomers at moderate temperatures (T < 100 °C) without using any controlling co-monomers[41-44]. In the last step, the influence of POSSMA and IBOMA on glass transition and decomposition temperatures of statistical and block copolymers was studied via thermal methods.

EXPERIMENTAL

Materials

Isobornyl methacrylate (IBOMA, >99%) and C13 methacrylate (Visiomer Terra C13,0-MA termed herein as C13MA, alkyl methacrylate with an average chain length of 13 units, >99%) were obtained from Evonik. To remove inhibitors before use, IBOMA and C13MA monomers were passed through a column of activated basic alumina (approximately 1 g per 50 ml monomer, Brockmann, Type 1, 150 mesh, Sigma Aldrich) and calcium hydride (5 wt% of basic alumina, 90-95% reagent, Sigma Aldrich). Methacryloisobutyl polyhedral oligomeric silsesquioxane (methacryloisobutyl POSS-MA0702 or POSSMA, from Hybrid Plastics) was used as received. Tetrahydrofuran (THF, 99.9%, HPLC grade, Fisher Scientific), n-hexadecane (~99%, Sigma Aldrich), DOWFAX™ 8390 (alkyldiphenyloxide disulfonate, Dow Chemical), Methanol (MeOH, >99%, Fisher Scientific) and toluene (>99%, Fisher Scientific) were used as received. Deuterated chloroform ($CDCl_3$, ≥99%) from Cambridge Isotopes Laboratory was used to dissolve samples for ^1H NMR. 3-(((2-Cyanopropan-2-yl) oxy) - (cyclohexyl) amino)-2, 2-dimethyl-3-phenylpropanenitrile (Dispolreg 007) alkoxyamine was synthesized according to Ballard et al's procedure[39]. N-(2-methylpropyl)-N-(1-diethylphosphono-2,2-dimethylpropyl)-O-(2-carboxyl prop-2-yl) hydroxylamine (BlocBuilder-MA™, termed herein as BB, 99%) was provided from Arkema. Reverse osmosis water (type 2 with the resistivity of ~ 1.1 MOhm·cm at 23 °C) was used for the miniemulsion polymerizations and DLS measurements. All the polymerizations and characterization tests (were necessary) were conducted under high purity nitrogen (99.998%, Praxair Canada).

Methods

M_n, X and $Đ$ Measurements

Dispersity of polymers ($Đ$) and number average molecular weight (M_n) were determined by gel permeation chromatography (GPC, Waters) relative to poly(methyl methacrylate) (PMMA) standards (from Varian Polymer Standards; M_n range of 875 to 1677000 g mol^{-1}) at an operating temperature of 40 °C. Three GPC Waters Styragel columns HR1, HR2 and HR4 (with the total molecular weight range of 10^2 to 6×10^5 g mol^{-1}) and a guard column were used for measurements with a flow rate of 0.3 mL min^{-1}. For GPC, the samples were prepared by diluting in HPLC grade THF with a concentration of approximately 5 mg ml^{-1}. For samples from miniemulsion polymerizations, the monomer conversions were calculated from the areas under the normalized GPC peaks measured according to the method described in our recent study and the accuracy of the results was confirmed by comparing with the gravimetric method[18]. The polymer compositions and the monomer conversions for polymerization in toluene were measured by ^1H NMR (Bruker Avance III HD 500 MHz, 32 scans, using $CDCl_3$ deuterated solvent).

Particle Size

The Z-average particle size of miniemulsions was measured by dynamic light scattering (DLS) with a Malvern Zetasizer Nano-ZS, equipped with a 4 mW He–Ne laser at 633 nm and an avalanche photodiode detector with measurement angle of 173° at 25 °C. Latex samples were diluted with R.O. water to reach the concentration of 0.01-1000 mg ml^{-1} (10^{-3} – 1 % mass) before the DLS. 5 measurements per samples were performed to minimize the error.

Thermoanalytical Analyses

Differential scanning calorimetry (DSC, Q2000 from TA Instruments) was used to measure the T_gs of samples. Three scans per cycle (heat/cool/heat) with the heating rate of 15 °C min^{-1} and cooling rate of 50 °C min^{-1} were employed to determine T_gs during the re-heating cycle under nitrogen. The T_gs were predicted using TA universal analysis software with the inflection method. The calibration of temperature (by indium) and heat flow (by benzoic acid) was done for DSC before the tests. Thermogravimetric analysis (TGA) was performed by TGA Q500 (TA Instruments) with a ramp rate of 15 °C min^{-1} from 25 to 550 °C. The measurement of decomposition temperatures (T_{dec}s) was done in an aluminium pan under nitrogen. To provide polymer samples for DSC and TGA, latex samples were dried inside a fume hood at 23 °C for 3 days. The samples were dissolved in a minimal volume of toluene and were precipitated in excess methanol. The resulting polymer samples were then dried inside a fume hood for 6 hours and were placed under vacuum at room temperature for 12 hours. The samples from NMP in toluene were precipitated in methanol and were dried inside a fume hood and under vacuum at ambient condition for 6 and 12 hours, respectively.

Polymerization of POSSMA/IBOMA/C13MA/AN using BB alkoxyamine in Toluene

A mixture of monomers (IBOMA, C13MA, POSSMA and AN as the controlling co-monomer) and BB alkoxyamine were dissolved in 50 wt% toluene and were added into a 15 ml three-neck round-bottom glass reactor. The reactor was placed on a stirrer and a magnetic stir bar was added to the solution to mix the components before and during the polymerization. One of the necks was connected to a reflux condenser which was connected to a chiller (Neslab 740) that circulated a mixture of ethylene glycol/distilled water (20/80 vol%) to provide a coolant to the condenser at a temperature of 3 °C. A temperature controller was used to maintain the reaction temperature and was connected to a heating mantle and a temperature sensor. The heating mantle was placed on the stir plate and the reactor was placed inside the mantle. A thermocouple was placed inside a temperature well in a second neck of the reactor, and the well was sufficiently deep to permit accurate estimation of the reaction temperature. The third neck was sealed with a rubber septa and a nitrogen syringe needle was inserted to provide the purge entrance (exit was via a rubber septa at the top of the condenser) and to take samples via syringe. The solution was purged with pure nitrogen flow for 30 minutes before increasing the temperature. While still maintaining the nitrogen purge, the reactor was heated at a rate of 10 °C·min^{-1} and the starting point of the polymerization was taken when the reactor contents reached 75 ℃ ($T_{t=0}$). All the polymerizations were conducted under nitrogen atmosphere in toluene at 90 ℃. Samples for kinetic analysis were taken periodically during the polymerization. As summarized in Table 2, polymerizations were performed using BB with 10 mol% AN and different molar fractions of POSSMA, IBOMA and C13MA. An example is given to illustrate the quadripolymerization procedure. For the experiment P10/IB44/C36/AN10, to the reactor were added BB (0.08 g, 0.21 mmol), POSSMA (1.65 g, 1.75 mmol), purified C13MA (1.71 g, 6.37 mmol), IBOMA (1.70 g, 7.65 mmol), AN (0.09 g, 1.75 mmol), and toluene (5.22 g, 56.65 mmol). The polymerization was run for 210 minutes. After precipitation into methanol and recovery, the wet product was dried under vacuum at room temperature overnight. ^{1}H NMR and GPC were used to determine the composition and molecular weight, respectively (M_n= 21.3 kg mol^{-1}, $Đ$ =1.61, F_{IBOMA} = 0.06, a sample calculation of monomer conversion and polymer composition using ^{1}H NMR peaks is available in Supplementary Information). The NMP scheme of POSSMA with C13MA and IBOMA is presented in Figure 1.

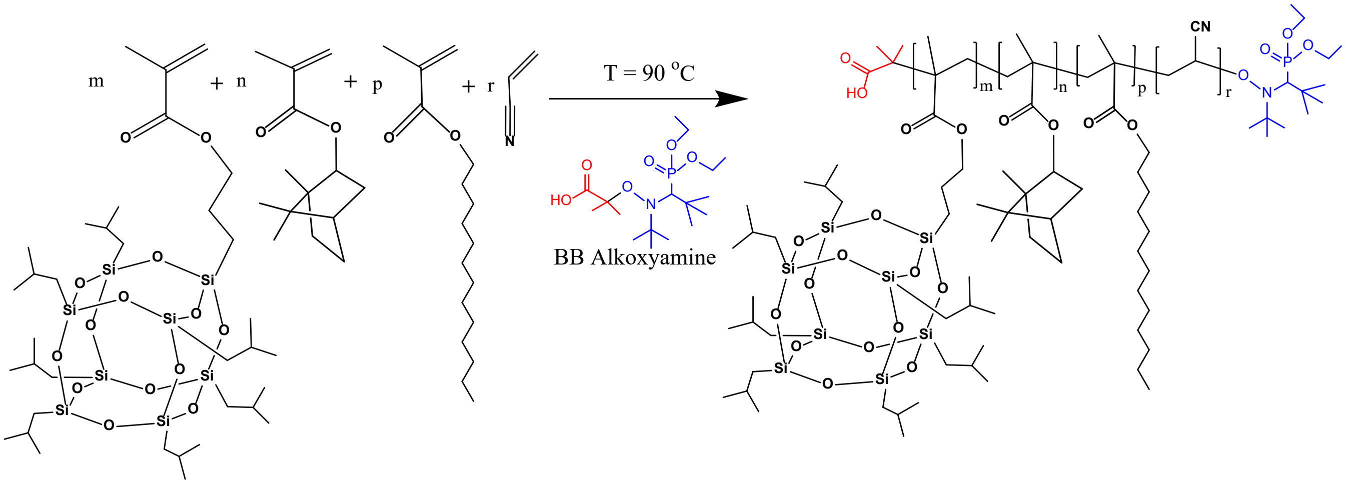

FIGURE 1. NMP scheme of p(POSSMA-*co*-C13MA-*co*-IBOMA-*co*-AN) statistical polymers using BB alkoxyamine, and AN co-monomer (10 mol% in initial feed) in 50 wt% toluene.

Miniemulsion Polymerization of POSSMA/IBOMA/C13MA

Terpolymerizations of POSSMA/IBOMA/C13MA was conducted in miniemulsion at 90 °C. Avoidance of organic solvent to dissolve the solid POSSMA was possible since the POSSMA monomer was completely soluble in the other liquid monomers. Unlike the polymerizations in toluene, which were initiated by BB, oil-soluble Dispolreg 007 alkoxyamine was used to initiate the NMP in miniemulsion. A favourable feature of Dispolreg 007 was the lack of necessity of a controlling co-monomer and its possible deleterious effect on the final polymer's properties. A schematic representation of the miniemulsion polymerization of POSSMA/IBOMA/C13MA is depicted in Figure 2. The experimental set-up for solution and miniemulsion polymerization was essentially the same. To prepare the miniemulsions, the hydrophobe and aqueous phases were made separately based on the recipe described in Table 1. Dispolreg 007 (alkoxyamine) and 0.8 wt% n-hexadecane (co-stabilizer) based on monomers' weight were added to a mixture of POSSMA, IBOMA and C13MA. DOWFAX 8390 surfactant (2 wt% based on monomers) was dissolved in water for the preparation of the aqueous phase. The two phases were mixed together for 30 minutes with stirring and were sonicated for 10 minutes (Hielscher sonicator UP200S, 50% duty cycle and amplitude 70%) in a cold water bath. The prepared latex was poured into the reactor and was purged with nitrogen for 30 minutes. The polymerization was conducted under ultra-pure nitrogen atmosphere at 90 °C ($T_{t=0}$ = 75 °C and heating rate of 10 °C min^{-1}). For the purpose of illustration, P5/IB47.5/C47.5 experiment ($M_{n,target}$ = 45 kg mol^{-1}) was conducted in miniemulsion under N_2 atmosphere at 90 °C. POSSMA (1.34 g, 1.419 mmol), IBOMA (3.62 g, 13.479 mmol) and C13MA (3.00 g, 13.479 mmol) were mixed with Dispolreg 007 (0.06 g, 0.177 mmol) and n-hexadecane (0.06 g, 0.281 mmol) to make the hydrophobic phase. The aqueous phase (Dowfax 8390 (0.16 g, 0.247 mmol) and water (24.71 g, 1371.569 mmol)) was stirred with monomer solution for 30 minutes and the final emulsion was sonicated for 10 minutes before polymerization.

TABLE 1. Polymerization Recipe for the nitroxide-mediated miniemulsion terpolymerization of POSSMA/IBOMA/C13MA.

Component	Amount
Monomer (1) – POSSMA	Varies based on the experiment (0.044-0.141 M)
Monomer (2) – IBOMA	Varies based on the experiment (0.282-0.420 M)
Monomer (3) – C13MA	Varies based on the experiment (0.282-0.420 M)
Alkoxyamine (Dispolreg 007)	0.006 M
DOWFAX™ 8390	2 wbm%[a]
n-hexadecane	0.8 wbm%
Water	3 times the total weight of all components

[a] wt% based on the monomers

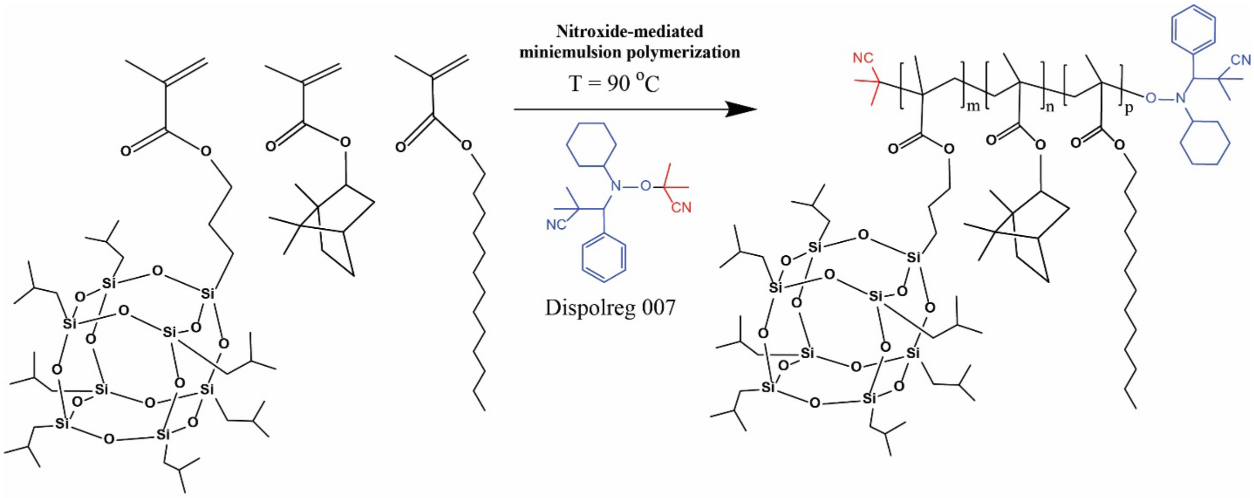

FIGURE 2. Schematic representation of nitroxide mediated emulsion polymerization of POSSMA/IBOMA/C13MA using Dispolreg 007 at 90 °C. 2 wt% DOWFAX 8390 (surfactant) and 0.8 wt% n-hexadecane (co-stabilizer) based on the weight of the monomers were added to stabilize the particles in miniemulsion.

RESULTS AND DISCUSSION

Polymerization of POSSMA with IBOMA/C13MA/AN in Toluene

Incorporation of POSSMA into IBOMA/C13MA co-monomers (with BB and 10 mol% AN as the controlling co-monomer) was done to obtain copolymers with improved thermal stability and hardness as IBOMA and POSSMA are known to produce polymers with relatively high T_g. First, a series of quadripolymerizations was undertaken in toluene, varying only one experimental parameter, namely the molar ratio of POSSMA in feed, ranging from 10 to 50 mol% (see Table 2 for experimental conditions). The weight ratio of 1:1 for IBOMA/C13MA was used for all syntheses in 50 w% toluene at 90 °C using BB with 10 mol% AN for 210 min. All kinetic plots were linear with respect to the reaction time but does not necessarily infer chain fidelity (Figure 3 (a)). Increasing POSSMA fraction from 0.1 to 0.5 decreased the apparent rate constant k_p [P$^\bullet$] ([P$^\bullet$] is the concentration of active polymer radicals and k_p is the rate constant of chain propagation) significantly from (14.0 ± 0.1) × 10^5 s^{-1} to (1.8 ± 0.1) × 10^5 s^{-1} (Table 3). Such a decrease with increasing POSSMA fraction was expected as seen earlier in POSSMA/C13MA copolymerizations[23]. The polymer composition was listed in Table 3 and shows the successful incorporation of POSSMA in polymers (Figure S1 in Supplementary Information shows an example ^{1}H NMR spectrum for finding the polymer composition).

M_n versus conversion plots show a relatively linear rise for all samples with subsequent plateauing at higher conversions > 60% (Figure 3 (b)). Such a deviation from theoretical prediction line could be due to the irreversible termination reactions as seen in our previous studies[38,45]. Further, in Figure 3 (b), Đ increases with conversion for all the experiments initiated with BB in toluene. This is probably caused by disproportionation between propagating radicals and the nitroxide at high conversions as reported elsewhere for polymerizations SG1 alkoxyamines[46]. Both Đ and M_n were also decreased from 1.61 to 1.45 and from 21.3 to 14.6 kg mol^{-1}, respectively, as POSSMA increased from $f_{POSSMA,0}$ = 0.10 to 0.50 in the initial monomer composition. The apparent decrease in final M_n values upon increasing POSSMA composition in the initial monomer mixture can be ascribed primarily due to its higher molecular weight compared to the other monomers, as the theoretical degree of polymerization was nearly halved on going from $f_{POSSMA,0}$ = 0.10 to 0.50.

The molecular weight distributions for experiments in toluene were presented in Figure S2 (Supplementary Information).

TABLE 2. Experimental condition for NMP of POSSMA/IBOMA/C13MA/AN in toluene using BB at 90 °C.

Experiment ID	$f_{POSSMA,0}^{a}$	$f_{IBOMA,0}$	$f_{C13MA,0}$	[BB]$_0^b$ (M)	[POSSMA]$_0$ (M)	[C13MA]$_0$ (M)	[IBOMA]$_0$ (M)	[AN]$_0$ (M)	[Toluene]$_0$ (M)
P10/ IB44/C36/AN10[c]	0.10	0.44	0.36	0.02	0.18	0.65	0.78	0.18	5.77
P20/ IB38/C32/AN10	0.20	0.38	0.32	0.02	0.32	0.51	0.62	0.16	6.50
P30/ IB33/C27/AN10	0.30	0.33	0.27	0.03	0.45	0.40	0.49	0.15	7.11
P40/ IB27/C23/AN10	0.40	0.27	0.23	0.03	0.55	0.31	0.38	0.14	7.62
P50/ IB22/C18/AN10	0.50	0.22	0.18	0.03	0.64	0.23	0.28	0.13	8.07

[a] Initial molar fraction of POSSMA in the initial feed (considering all constituent monomers). All syntheses done at 90 °C in toluene initiated by BB and targeting $M_{n,target}$ =25 kg mol^{-1}.

[b] Concentration of BB in the initial feed [mol L^{-1}].

[c] Polymerization of POSSMA, IBOMA, C13MA and AN with the initial concentrations of 10, 44, 36 and 10 mol%, respectively. AN with the initial concentration of 10 mol% was used as the controlling co-monomer for all the experiments using BB in toluene.

TABLE 3. Molecular characterization and kinetic data of poly (POSSMA/IBOMA/C13MA/AN prepared in 50 wt% toluene using BB at 90 °C.

Experiment ID	F_{POSSMA}^{a}	F_{IBOMA}^{a}	F_{C13MA}^{a}	X^b (%)	Đ^c	M_n^c (kg mol^{-1})^c	k_p^d [P$^\bullet$] (10^5 s^{-1})^d
P10/IB44/C36/AN10[e]	0.06	0.67	0.21	72.2	1.61	21.3	14.0 ± 0.1

P20/IB38/C32/AN10	0.15	0.46	0.29	59.5	1.67	19.5	12.1 ± 0.2
P30/IB33/C27/AN10	0.24	0.40	0.24	69.4	1.55	17.9	7.9 ± 0.1
P40/IB27/C23/AN10	0.30	0.38	0.20	52.4	1.45	12.8	4.0 ± 0.1
P50/IB22/C18/AN10	0.44	0.29	0.16	42.3	1.45	14.6	1.8± 0.1

[a] F_{POSSMA} , F_{IBOMA} and F_{C13MA} indicate the molar fraction of POSSMA, IBOMA and C13MA (considering AN co-monomer) as determined by ^{1}H NMR in CDCl$_3$. A sample calculation to determine the composition is available in Supplementray Information,

[b] Overall monomer conversion measured by ^{1}H NMR in CDCl$_3$.

[c] The final product's number average molecular weight (M_n) and dispersity (Đ) were determined using GPC relative to PMMA standards at 40 °C.

[d] Apparent rate constant derived from the semi-logarithmic slopes of ln[(1-X)$^{-1}$] (where X = conversion) versus time in the first 60 minutes of polymerization. Error bars were determined by finding the standard error on each slope (linear fit of semi-logarithmic plot).

[e] Polymerization of POSSMA, IBOMA, C13MA and AN with the initial concentrations of 10, 44, 36 and 10 mol%, respectively. AN with the initial concentration of 10 mol% was used as the controlling co-monomer for all the experiments using BB in toluene.

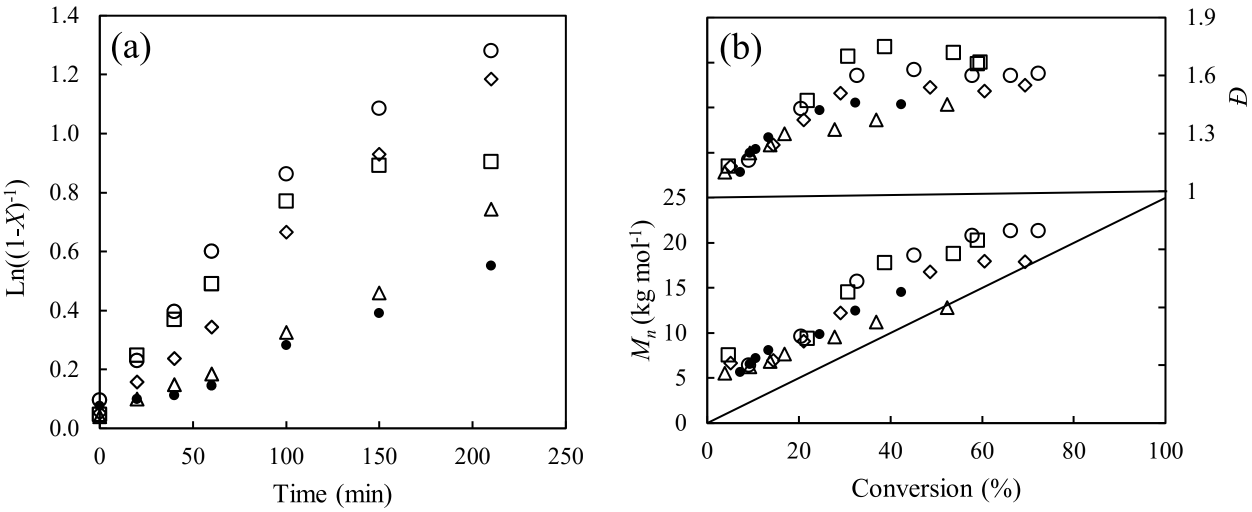

FIGURE 3. (a) Semi-logarithmic kinetic plots of ln[(1-X)$^{-1}$] (X = monomer conversion) versus polymerization time and (b) number average molecular weight M_n, and dispersity Đ versus conversion (X) for NMP of IBOMA/C13MA/POSSMA using BB and $f_{AN,0}$= 0.1 at 90 °C: P10/IB44/C36/AN10 (open circles, ○), P20/IB38/C32/AN10 (open squares, □), P30/IB33/C27/AN10 (open diamonds, ◊), P40/IB27/C23/AN10 (open triangles, Δ), P50/IB22/C18/AN10 (filled circles, ●).

Terpolymerization of POSSMA/C13MA/IBOMA Monomers in Miniemulsion

The copolymerization of IBOMA/C13MA was previously done in organic solvent (toluene) and in aqueous miniemulsion[38,45]. To study the effect of POSSMA on the miniemulsion polymerization of IBOMA/C13MA mixtures, terpolymerization of IBOMA/C13MA/POSSMA was conducted using similar reaction conditions at 90 ^{o}C. For miniemulsion polymerization, the feed molar ratio of 1:1 was set for IBOMA/C13MA, while the [POSSMA] varied for in each experiment. Table 4 illustrates the experimental conditions for terpolymerization of IBOMA/C13MA/POSSMA. The molecular weight distributions were monomodal with Đ < 1.65 for all samples taken during the polymerizations. The GPC peaks for NMP in miniemulsion were depicted in Figure S3 (Supplementary Information). The high M_n in the beginning of the polymerization (Figure 4 (b)) was probably due to the strong penultimate effect associated with Dispolreg 007, which results in slow initiation[38,39,41,42]. It should be noted that this curvature was not observed in the solution polymerizations as strongly, since BB was used as the alkoxyamine in the solution polymerizations. At $X >$ 50%, the slope of M_n versus X plots slightly decreases and approaches the theoretical prediction. This can be ascribed to not all chains initiating at the same rate during the early part of the polymerization but eventually at higher conversions, all chains are growing at nearly the same rate, with M_n approaching closer to the theoretical value. The k_p $[P^\bullet]$ trend for polymerizations in miniemulsion was different from the kinetic results of polymerization in toluene (Table 5). For P5/IB47.5/C47.5 experiment, the amount of POSSMA in polymer was negligible (< 1%). Therefore, its k_p $[P^\bullet]$ does not follow the trend of other terpolymers prepared in miniemulsion. The k_p $[P^\bullet]$ for P10/IB45/C45 and P20/IB40/C40 does not increase with increasing composition of POSSMA in the terpolymers. Similarly, the k_p $[P^\bullet]$ for POSSMA/IBOMA/C13MA/AN in toluene decreased by increasing the POSSMA content in initial feed. It should be noted that the difference between alkoxyamines used in miniemulsion and organic solvent-based (Dispolreg 007 versus BB) resulted in different polymerization rates. Compartmentalization effects in miniemulsion could be also responsible for the higher polymerization rates[47,48]. The monomer conversion for miniemulsion polymerizations were generally higher than the polymerizations in toluene at a given time ($74.4\% < X_{miniemulsion} < 96.1\%$ compared to $42.3\% < X_{toluene} < 72.2\%$; for the reaction time of 210 minutes except P5/I47.5/C47.5 experiment with reaction time of 150 minutes and X of 74.4% in miniemulsion), although the $M_{n,target}$ for polymerization in miniemulsion and toluene were 45 and 25 kg mol^{-1}, respectively. The semi-logarithmic kinetic plots with time in Figure 4 (a) were linear for all the experiments up to 150 minutes. Afterwards, the polymerization rate decreased, and the logarithmic kinetic plots tended to plateau, which suggested irreversible termination reactions were becoming more prevalent.

TABLE 4. Experimental formulation for nitroxide mediated miniemulsion polymerization of POSSMA/IBOMA/C13MA using Dispolreg 007 at 90 °C.

Experiment ID	$f_{POSSMA,0}{}^{a}$	$f_{IBOMA,0}$	$[POSSMA]_0{}^{b}$ (M)	$[C13MA]_0$ (M)	$[IBOMA]_0$ (M)	[Dispolreg 007] (M)
P5/IB47.5/C47.5	0.050	0.475	0.044	0.420	0.420	0.006
P10/IB45/C45	0.100	0.450	0.081	0.366	0.366	0.006
P20/IB40/C40	0.200	0.400	0.141	0.282	0.282	0.006

[a] Initial molar fraction of POSSMA in the initial feed (considering all constituent monomers). All miniemulsion polymerizations were performed at 90 °C initiated by Dispolreg 007 with $M_{n,target}$ =45 kg mol^{-1}.
[b] Concentration of POSSMA in the initial feed [mol L^{-1}].

TABLE 5. Molecular characterization and kinetic data for miniemulsion polymerization of POSSMA/IBOMA/C13MA ($M_{n,target}$ = 45 kg mol^{-1}) using Dispolreg 007 at 90 °C.

Experiment ID	$F_{POSSMA}{}^{a}$	$F_{IBOMA}{}^{a}$	X^{b} (%)	$Đ^{c}$	$M_n{}^{c}$ (kg mol^{-1})	$k_p{}^{d}$ $[P^\bullet]$ (10^5 s^{-1})^{d}
P5/IB47.5/C47.5	0.006	0.46	74.4	1.51	46.7	14.0 ± 0.3
P10/IB45/C45	0.10	0.43	96.1	1.65	47.6	37.7 ± 0.4
P20/IB40/C40	0.21	0.39	90.3	1.58	45.0	32.7 ± 0.9

[a] F_{POSSMA} and F_{IBOMA} indicate the molar fraction of POSSMA and IBOMA in polymers determined by ^{1}H NMR in CDCl$_3$.
[b] Overall monomer conversion (%) based on the areas under the normalized GPC peaks.

[c] The final number average molecular weight (M_n) and dispersity ($Đ$) were measured by GPC relative to PMMA standards in THF at 40 °C. The target number average molecular weight ($M_{n,target}$) for all the miniemulsion polymerizations was 45 kg mol^{-1}.

[d] Apparent rate constant derived from the semi-logarithmic slopes of ln[(1-X)$^{-1}$] (where X = conversion) versus time in the first 60 minutes of polymerization. Error bars were determined by finding the standard error on each slope (linear fit of semi-logarithmic plot).

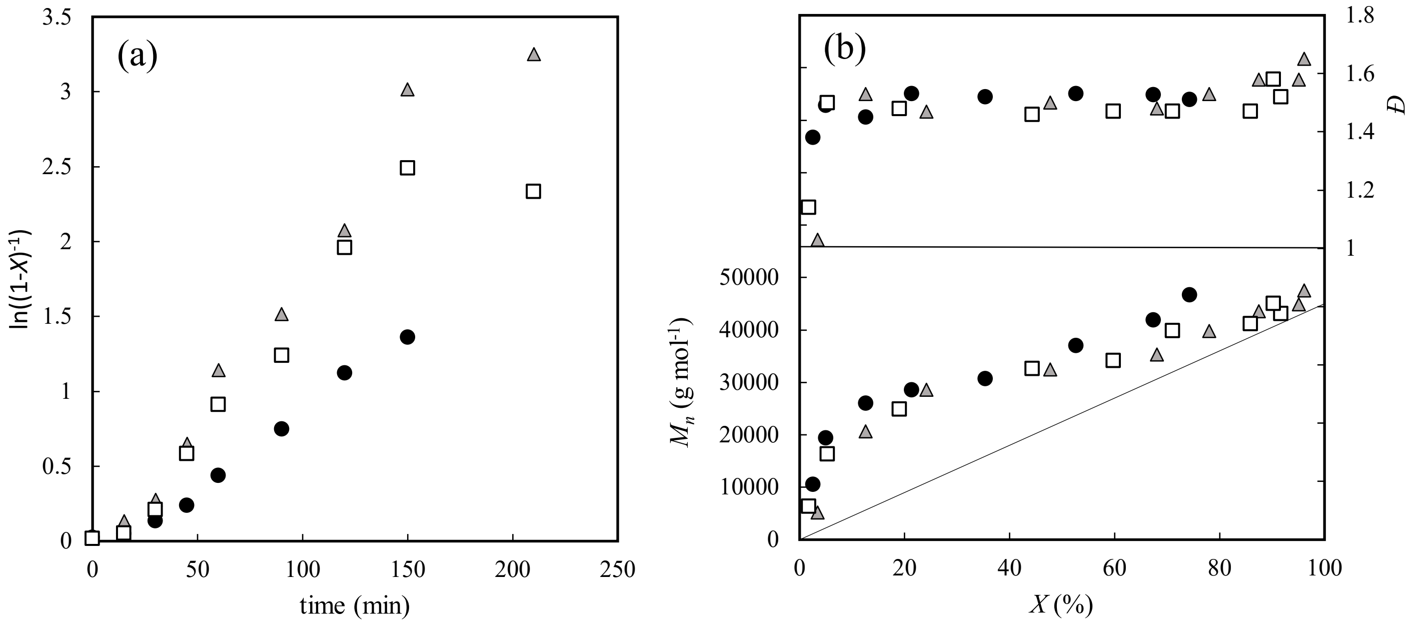

FIGURE 4. The miniemulsion terpolymerization of different ratios of POSSMA/IBOMA/C13MA using Dispolreg 007 initiator at 90 °C: (a) Semi-logarithmic kinetic plots of ln[(1-X)$^{-1}$] (X = monomer conversion) versus reaction time; (b) Number average molecular weight M_n and dispersity $Đ$ versus conversion (X). P5/IB47.5/C47.5 (filled circles, ●); P10/IB45/C45 (gray triangles, ▲); P20/IB40/C40 (open squares, □). Composition of terpolymers is provided in table 5.

Latex Particle Size

The average particle size for POSSMA/IBOMA/C13MA terpolymers was determined by DLS for the samples taken during the polymerization (Figure 5). The particle size for monomer droplets (t = 0 of polymerization) was in the size range of 286-299 nm and slightly decreased in the course of polymerization to reach final particle sizes of 243-258 nm. No precipitation or coagulation of polymer particles was observed during the miniemulsion polymerization and the particle size did not increase with reaction time, suggesting the high colloidal stability of the latexes and insignificant occurrence of Ostwald ripening events[49-51]. This is probably due to the use of highly hydrophobic monomers in the system which improves the stability of the resulting polymerization loci in dispersed aqueous media. The representative particle size distributions over time (experiment: P10/IB45/C45) were shown in Figure S4 (Supplementary Information). The particle size of POSSMA/IBOMA/C13MA terpolymers was smaller than IBOMA/C13MA (50:50 molar ratio) miniemulsions studied at the same experimental conditions (particle size for POSSMA/IBOMA/C13MA latexes = 240-299 nm and for IBOMA50/C13MA50 = 321-549 nm)[38]. This illustrates that POSSMA may also act as a polymerizable co-stabilizer in miniemulsion and may reduce the required concentration of non-polymerizable co-stabilizers. However, it cannot be the sole co-stabilizer for miniemulsions and the addition of costabilizers (typically about 0.8 wbm% n-hexadecane) is required as previously observed for the miniemulsion polymerization of POSSMA/C13MA[18].

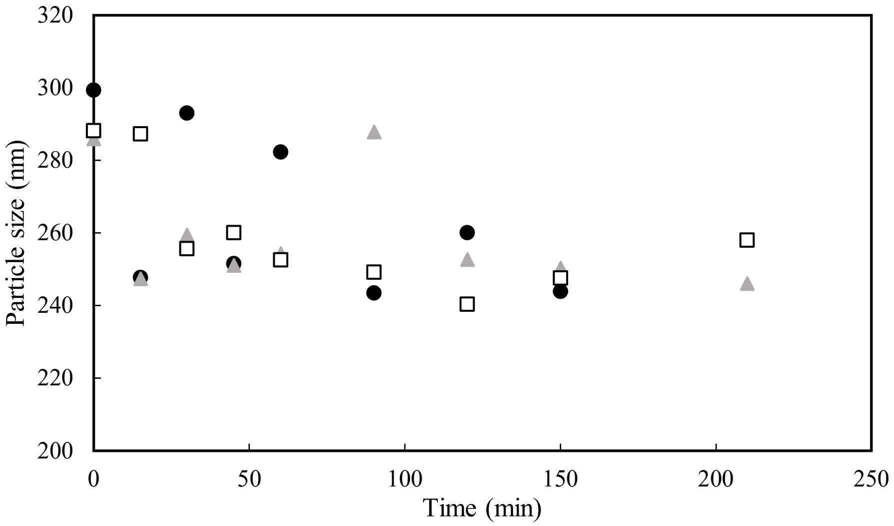

FIGURE 5. Z-average particle size for terpolymerization of POSSMA/IBOMA/C13MA versus reaction time. P5/IB47.5/C47.5 (filled circles, ●); P10/IB45/C45 (gray triangles, ▲); P20/IB40/C40 (open squares, □).

Preparation of block copolymer of p(IBOMA/AN)-*b*-p(POSSMA/C13MA/AN)

One observation during polymerization that suggests chain end fidelity is the steady shift of the molecular weight distribution over time, while remaining monomodal. Figure S2, S3 in Supplementary Information depicts the movement of the GPC peak to higher molecular weights for the experiments in toluene and miniemulsion over time. To further study the possibility of making block copolymers of POSSMA/IBOMA/C13MA and confirm the chain end fidelity, the block copolymerization of POSSMA/IBOMA/C13MA was attempted by the chain extension of IBOMA/AN copolymer (Poly(IBOMA) with 10 mol% AN in initial feed, M_n =11.0 kg mol^{-1} and $Đ$ = 1.38) with a mixture of POSSMA/C13MA/AN monomers (initial molar ratio of monomers [1:8:1], respectively). The formulation of chain extension study and properties of macroinitiator and the final product are listed in Table 6. The block copolymer product had a monomodal molecular weight distribution with relatively low $Đ$ (M_n =74.1 kg mol^{-1} and $Đ$ = 1.55), indicating high activity of the chain ends, permitting the possibility of making block and gradient polymers. Figure 6 compares the GPC chromatogram of the poly(IBOMA)-rich macroinitiator with the chain-extended product. The $Đ$ of the copolymer was slightly elevated after the chain extension ($Đ$ = 1.55 compared to 1.38) as exemplified by the minor low molecular weight tailing, which demonstrates the presence of a low concentration of dead macroinitiator chains. The ^{1}H NMR spectra for chain extension is available in Supplementary Information (Figure S5 and S6).

TABLE 6. Summary of chain extension for p(IBOMA/AN) macroinitiator with POSS/C13MA/AN in 50 wt% toluene at 90 °C after 5 hours.

A. Macroinitiator

Experiment ID	X^a (%)	$[BB]_0$ (M)	$[IBOMA]_0$ (M)	$[AN]_0$ (M)	$[Toluene]_0$ (M)	M_n^b (kg mol^{-1})	$M_{n,target}^c$ (kg mol^{-1})	$Đ^b$	Time^d (min)
p(IBOMA/AN)-macroinitiator	28	0.018	1.997	0.222	5.022	11.0	25	1.38	50

B. Formulation and Characterization of Chain-Extension

Experiment ID	X^a (%)	$[MI]_0^e$ (M)	$[POSSMA]_0$ (M)	$[C13MA]_0$ (M)	$[AN]_0$ (M)	$[Toluene]_0$ (M)	M_n (kg mol^{-1})	$M_{n,target}$ (kg mol^{-1})	$Đ$	Time^d (min)
p(IBOMA/AN)-*b*-p(POSSMA /C13MA/AN)	77	0.006	0.157	1.258	0.184	6.087	74.1	80	1.55	300
	F_{POSSMA}^e	F_{IBOMA}	F_{C13MA}	F_{AN}	f_{POSSMA}^g	f_{C13MA}	f_{AN}			
	0.11	0.21	0.64	0.07	0.10	0.80	0.10			

[a] Overall monomer conversion measured by ^1H NMR in $CDCl_3$.

[b] The final number average molecular weight (M_n) and dispersity ($Đ$) were measured by GPC relative to PMMA standards at 40 °C in THF.

[c] The target number average molecular weight to synthesize poly(IBOMA/AN)-macroinitiator.

[d] The reaction time (minutes).

[e] The concentration of macroinitiator (MI) in initial feed (mol L^{-1}).

[f] Molar fraction of POSSMA in the polymer chain measured by ^1H NMR in $CDCl_3$.

[g] Initial molar fraction of POSSMA in the initial feed for chain-extension (considering all constituent monomers).

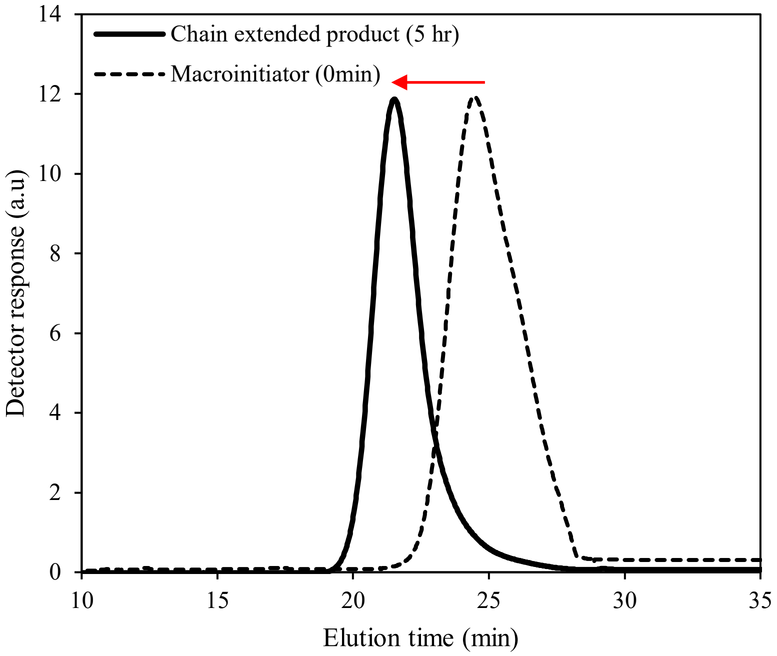

FIGURE 6. GPC peaks for the chain extension of p(IBOMA/AN) with POSSMA/C13MA/AN (the controlling co-monomer was in an initial concentration of 10 mol% AN). The dashed line depicts the GPC peak for p(IBOMA macroinitiator (M_n = 11.0 kg mol^{-1}, $Đ$ = 1.38) and the solid black line is the GPC peak of the block copolymer after 5 hours polymerization (M_n = 74.1 kg mol^{-1}, $Đ$ = 1.55). The preparation of the poly(IBOMA/AN) macroinitiator and the chain extended product were conducted under nitrogen atmosphere in 50 wt% toluene at 90 °C. The complete characterization of macroinitiator and block copolymer is available in Table 6.

The Thermal Stability of POSSMA Containing Bio-Based Polymers

The thermal properties of the polymer resins were investigated to show the effect of incorporating POSSMA into the IBOMA/C13MA chains. The decomposition temperatures (T_{dec}s) were determined by TGA and illustrated that the addition of POSSMA slightly increases the onset of decomposition ($T_{dec,1}$ or T_{dec} for 10% weight loss). However, this was not the case for $T_{dec,max}$ (T_{dec} for the maximum rate of weight loss) and $T_{dec,2}$ (end of decomposition). $T_{dec,max}$ and $T_{dec,}$2 did not show a significant change with increasing the POSSMA content in the polymers. The decomposition temperatures for all samples are summarized in Table 7. TGA traces were depicted in Figure S7 and S8 (Supplementary Information) for the POSS-containing polymers prepared in miniemulsion and the solvent-based system. For POSSMA/IBOMA/C13MA terpolymers, a two stage decomposition was observed, where the second peak was at 365-455 °C. This corresponds to the cleavage of the O-isobornyl bond in IBOMA and the formation and elimination of camphene at higher temperatures[52]. For polymers made by miniemulsion, the addition of 20 mol% POSSMA in the feed improved the $T_{dec,1}$ by 32 °C compared to the copolymer of IBOMA/C13MA ($[\mathrm{IBOMA}]_0/[\mathrm{C13MA}]_0$ = 1:1) in a similar system with a $T_{dec,1}$ of 211 °C[38]. As shown in Figure 7, this indicates that the incorporation of high concentration of inorganic POSS cages improves the thermal stability of the resin. A similar trend was previously observed for the free radical copolymerization of MMA with octavinyl-POSS[53]. Kotal et al[24] also observed a 14 to 46 °C increase in $T_{dec,1}$ by incorporating 4-17 wt% of thiol functionalized POSS compound (as initiator) in poly(MMA). However, it was not the case for using POSSMA as fillers in composites. Tanaka et al[54] showed that the addition of only 1mol% POSSMA into poly(MMA) as fillers enhanced thermal stability of composites ($T_{dec,composite}$ for 50% weight loss = 344.0 °C compared to 321.6 °C for poly(MMA)) although a slight decline in T_{dec} for 5%weight loss was observed after the addition of POSSMA filler. The presence of IBOMA also improved the $T_{dec,1}$. For instance, a study of p(POSSMA/C13MA/AN) containing 10 mol% POSSMA showed $T_{dec,1}$ = 220 ℃ while P10/IB44/C36/AN10 with 10 mol% POSSMA and 44 mol% IBOMA in feed (prepared in toluene) had the $T_{dec,1}$ = 240 ℃. Previous studies on the addition of POSSMA into the bio-based polymers also indicated that $T_{dec,1}$ slightly increases by increasing the molar ratio of POSSMA in the feed, although this change was not significant. In one of the studies of the NMP of POSSMA/C13MA/AN (10 mol% AN, using BB alkoxyamine) in toluene, it was observed that increasing the molar ratio of POSSMA in feed composition by 10% improves the $T_{dec,1}$ by 5.7 °C[23]. For the miniemulsion polymerization of POSSMA/C13MA using Dispolreg 007, this increase in $T_{dec,1}$ was about 4.9 °C for 10% increase in the initial concentration of POSSMA[18].

Interestingly, the block copolymer from p(IBOMA/AN)-*b*-p(POSSMA/C13MA/AN) experiment exhibits a compratively higher $T_{dec,max}$. Furthermore, the $T_{dec,1}$ was slightly higher for p(IBOMA/AN)-*b*-p(POSSMA/C13MA/AN) compared to P20/IB38/C32/AN10, which had an approximately similar overall composition but higher content of POSSMA and IBOMA. This is probably due to the existence of two phase separated blocks in p(IBOMA/AN)-*b*-p(POSSMA/C13MA/AN), where one block becomes flexible during heating and delays the decomposition of the second block. A similar result was observed for block copolymers of IBOMA/C13MA compared to their counterpart statistical copolymers[45].

The glass transition temperatures (T_gs) were measured by DSC and are listed in Table 7. The addition of IBOMA ($T_{g,p(IBOMA)}$= 110-200 °C[27-30] depending on the chain length) and POSSMA ($T_{g,p(POSSMA)}$= 85°C)[9] is expected to provide stiffness to the chains, while the long aliphatic chain in C13MA ($T_{g,p(C13MA)}$ = -46 °C) is expected to provide enhanced flexibility[55]. Accordingly, higher concentrations of POSSMA in the final polymer resulted in generally higher T_gs (for fixed ratios of the other co-monomers). The T_gs for polymers prepared in miniemulsion and toluene with similar compositions are approximately in the same range, suggesting similarity of the polymers prepared by the two different polymerization processes. This can also be validated by comparing the T_{dec} results for polymers with similar compositions prepared in organic solvent (toluene) and dispersed aquous media. Therefore, hybrid polymers of POSSMA and bio-based monomers like C13MA and IBOMA can be produced in dispersed aqueous media without compromising the thermal properties.

TABLE 7. Thermal characterization of POSSMA containing polymers prepared by NMP in solution (solvent: toluene) and miniemulsion

Experiment ID	T_g^{a} (°C)	$T_{dec,1}$^{b} (°C)	$T_{dec,max}$^{b}(°C)	$T_{dec,2}$^{b} (°C)	F_{POSSMA}^{c}	F_{IBOMA}	F_{C13MA}^{d}	M_n^{e} (kg mol^{-1})
Solvent-based system (prepared in 50 wt% toluene)								
P10/IB44/C36/AN10	32	240	309	467	0.06	0.21	0.67	21.3
P20/IB38/C32/AN10	41	245	307	475	0.15	0.29	0.46	19.5
P30/IB33/C27/AN10	50	250	312	473	0.24	0.24	0.40	17.9
P40/IB27/C23/AN10	73	254	315	470	0.30	0.20	0.38	12.8
P50/IB22/C18/AN10	80	257	300	480	0.44	0.16	0.29	14.6
p(IBOMA/AN)-*b*-p(POSSMA/C13MA/AN)	-33, 91	251	326	463	0.12	0.20	0.66	74.1
Water-borne system (prepared in miniemulsion)								
P5/IB47.5/C47.5	17	208	303	468	0.01	0.46	0.53	46.7
P10/IB45/C45	23	218	302	468	0.10	0.43	0.47	47.6
P20/IB40/C40	37	243	317	471	0.21	0.39	0.40	45.0

[a] T_g (glass transition temperature) measured by DSC under nitrogen atmosphere using three scans per cycle (heat/cool/heat) at a heating rate of 15 °C min^{-1} and cooling rate of 50 °C min^{-1}.

[b] $T_{dec,1}$ ($T_{10\%}$ or onset of decomposition), $T_{dec,max}$ (temperature at which highest weight loss occurs) and $T_{dec,2}$ (end of decomposition) measured by TGA under nitrogen atmosphere at a ramp rate of 15 °C min^{-1}.

[c] Molar fraction of POSSMA in polymers determined by ^{1}H NMR in $CDCl_3$.

[e] The final number average molecular weight (M_n) was estimated using GPC relative to PMMA standards at 40 °C in THF.

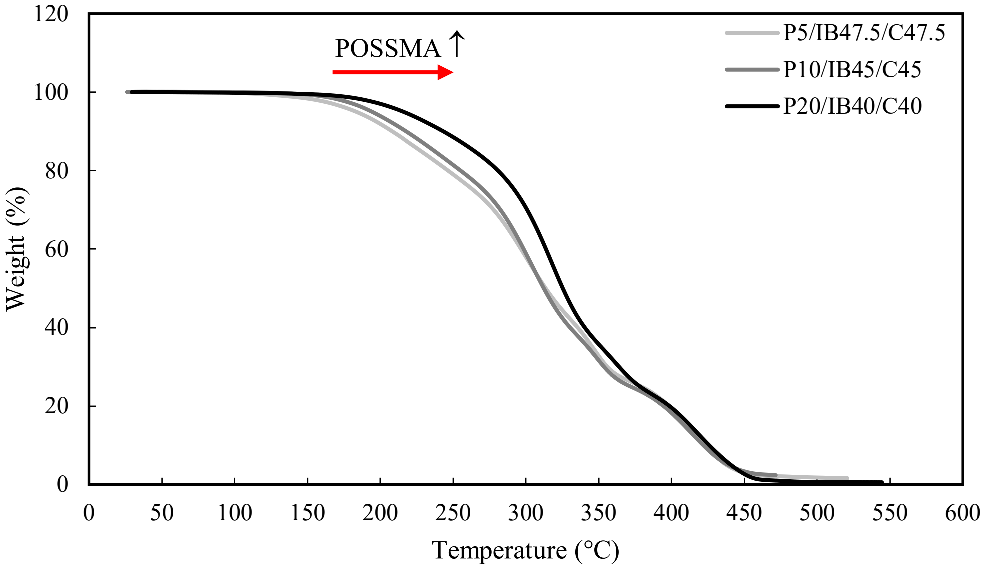

FIGURE 7. TGA thermograms for POSSMA/IBOMA/C13MA terpolymers prepared in miniemulsion. The feed molar ratio of IBOMA/C13MA remained constant for all the terpolymerizations [molar ratio 1:1]. The initial mol % of POSSMA increased from 5 to 20%.

CONCLUSIONS

Nitroxide mediated polymerization of POSSMA/IBOMA/C13MA was successfully conducted in organic solvent (toluene) and miniemulsion. The results showed the successful incorporation of POSSMA monomer into the bio-based monomer mixture of IBOMA/C13MA. Polymers with M_n up to 21.3 kg mol^{-1} ($M_{n,target}$ = 25 kg mol^{-1}, POSSMA content < 44% and 1.45 < $Đ$ < 1.67) were synthesized in toluene. However, monomer conversion (X) decreased at 210 minutes by increasing the amount of POSSMA in the monomer feed. The X decreased from 72.2% to 42.3% as POSSMA feed content increased from 10% to 50%. The possibility of making block copolymers with IBOMA, C13MA and POSSMA monomers was investigated by the chain extension of poly(IBOMA)-rich macroinitiator (M_n = 11.0 kg mol^{-1} and $Đ$ = 1.38) with a mixture of POSSMA and C13MA (Molar ratio of 1:8) for 5 hours in toluene at 90 ^{o}C (using BB as the unimolecular initiator and 10 mol% AN controlling co-monomer). The resulting block copolymer (M_n = 74.1 kg mol^{-1} and $Đ$ = 1.55) had a monomodal molecular weight distribution without significant tailing, suggesting a very low concentration of dead chains. Next, the controlled radical terpolymerization of POSSMA/IBOMA/C13MA was conducted in miniemulsion to avoid the use of organic solvents and improve the incorporation of POSSMA (i.e. higher monomer conversion in the dispersed system). The POSSMA containing polymers with IBOMA and C13MA with M_n up to 46.7 kg mol^{-1} and $Đ$ < 1.65 were prepared in dispersed aqueous media using Dispolreg 007 at 90 °C. The resulting polymer latexes were colloidally stable with final average particle size = 243-258 nm. The addition of POSSMA improved the thermal stability of the resins and inhibited the pyrolysis due to the inorganic POSS cages. The most significant improvement was in the onset of decomposition ($T_{dec,1}$), in which $T_{dec,1}$ of the solvent-based polymers improved approximately by 4 °C per 10 mol% increase in POSS content while $T_{dec,1}$ of miniemulsion-based polymers improved by 23 °C per 10 mol% increment in POSS ratio.

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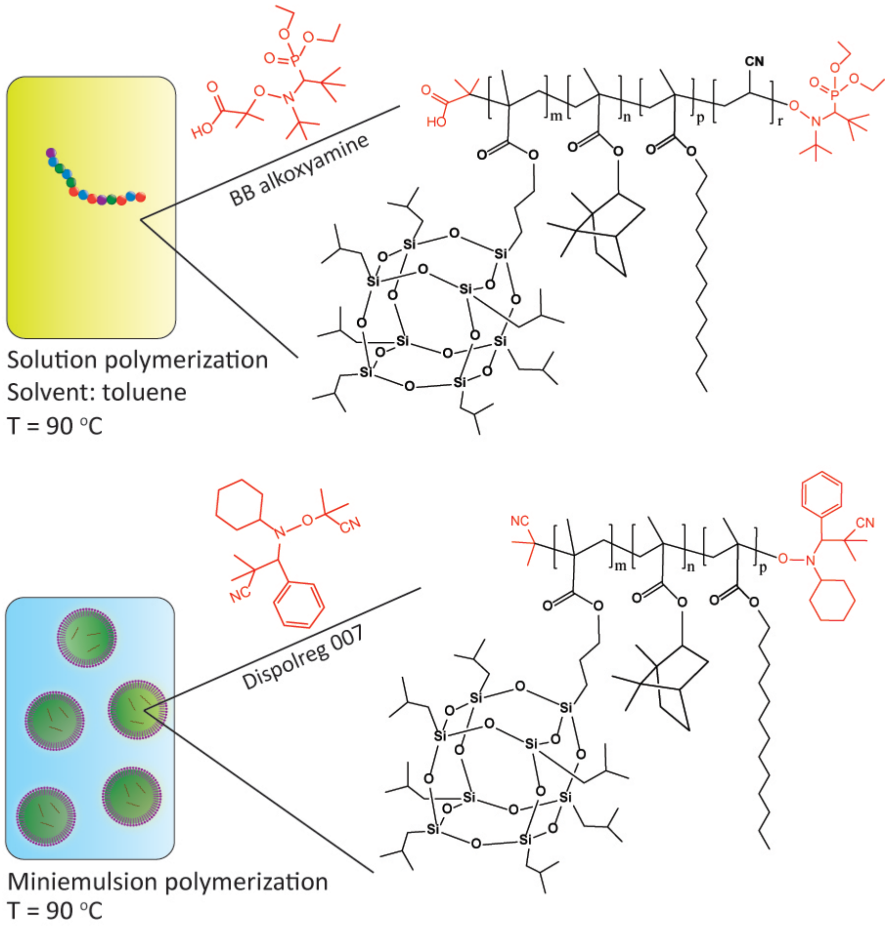
GRAPHICAL ABSTRACT



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