Synthesis of Bio-based Poly(Methacrylates) Using SG1-containing Amphiphilic Macroinitiators by Nitroxide Mediated Miniemulsion Polymerization

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ABSTRACT

SG1-based amphiphilic macroinitiators were synthesized from oligoethylene glycol methyl ether methacrylate (OEGMA) and 10 mol% acrylonitrile or styrene (as the controlling comonomer) to conduct the nitroxide mediated polymerization (NMP) of bio-based methacrylic monomers (isobornyl methacrylate (IBOMA) and C13 alkyl methacrylate (C13MA)) in mini-emulsion. The effect of the addition of surfactant (DOWFAX 8390), co-stabilizer (n-hexadecane) and different reaction temperatures (80, 90 and 100 °C) on polymerization kinetics was studied. We found that the NMP of IBOMA/C13MA using amphiphilic macroalkoxyamines were most effective during miniemulsion polymerization (linear trend of M_n versus conversion and high latex stability) in presence of 2 wt% surfactant and 0.8 wt% co-stabilizer (relative to monomer) at 90 °C. The effect of surfactant, co-stabilizer and temperature on particle size during the polymerization was studied and suggested a decrease in initial particle size with the addition of surfactant and co-stabilizer. Finally, the thermal properties of IBOMA/C13MA polymers, prepared by amphiphilic macroinitiators, were examined thoroughly, indicating a T_g in the range of -44 °C < T_g < 109 °C.

KEYWORDS: Miniemulsion polymerization, Methacrylates, Nitroxide mediated polymerization, Macroalkoxyamine, Bio-Based.

1 INTRODUCTION

Reversible deactivation radical polymerization (RDRP) of monomers from sustainable sources has attracted considerable attention during the last decade.¹⁻⁵ The preparation of polymers with a well-designed microstructure, the possibility of making block copolymers and narrow molecular weight distribution are some of the conventional advantages of RDRP techniques for many current technologies.⁶⁻⁸ Using bio-based monomers adds potential benefits towards decreasing the carbon footprint of the process but also may provide additional benefits to the performance not necessarily originally

expected.^{9,10} Nitroxide mediated polymerization (NMP) is among the simplest of the RDRP techniques, only requiring a low concentration of thermally labile alkoxyamine to start the polymerization.^{7,11,12} Upon heating, alkoxyamines decompose to form the persistent radical and initiating species to trigger the polymerization, which is governed by the reversible termination between the macroradicals and dormant, de-activated polymer. Initially, NMP was limited essentially to the polymerization of styrenic monomers and required high reaction temperatures exceeding 120 °C.¹³ However, the advent of alkoxyamines based on 2,2,5-tri-methyl-4-phenyl-3-azahexane-3-nitroxide (TIPNO) and N-tert-butyl-N-[1-diethylphosphono-(2,2-dimethyl- propyl)] (SG1) nitroxides improved the applicability of NMP for a wider range of monomers together with comparatively lower reaction temperatures.^{14,15} One of the most studied of the SG1-based alkoxyamines is N-(2-methylpropyl)-N-(1-(diethylphosphono-2,2-dimethylpropyl)-O-(2-carboxylprop-2yl)hydroxylamine) (BlocBuilder-MA or BB alkoxyamine, Arkema), which has been applied for the polymerization not only of styrene derivatives, but also acrylates and methacrylates, with some modification.^{16,17} With respect to the case of methacrylates, the homopolymerization of methacrylates using NMP has traditionally been difficult due to the high activation/deactivation equilibrium constant (K) of methacrylates and the cross-disproportionation effect.^{18,19} This problem can be solved by copolymerization of methacrylates with a low concentration of monomers with low K (e.g. acrylonitrile (AN) and styrene (S)) to decrease the average K.^{18,20}

In addition, the high water-solubility of BB alkoxyamine (when neutralized with base) presents interesting issues towards applications in dispersed aqueous polymerizations (e.g. emulsion, miniemulsion and suspension polymerization).²¹ To use BB for NMP in dispersed aqueous systems, one common method is to prepare macroinitiators from the desired monomers and high chain-end fidelity prior to the polymerization.²²⁻²⁵ Depending on the monomers, the SG1-terminated macroinitiator can be either water soluble or insoluble. If hydrophobic macroinitiators are used, they can act as a co-stabilizer and also initiate the polymerization within monomer/polymer particles.^{26,27} On the contrary, water-soluble macro-alkoxyamines can be used as a macromolecular surfactant and initiator simultaneously.^{21,28}

Isobornyl methacrylate (IBOMA, 71% bio carbon content, derived from pine sap) and C13-alkyl methacrylates (C13MA, 76% bio carbon content, from natural oils) can be used to synthesize copolymers with high bio-content with readily adjustable glass transition temperatures (T_gs), as IBOMA provides stiffness while C13MA provides low temperature flexibility.²⁹⁻³² The IBOMA/C13MA copolymers can be used for coating and adhesive applications. We previously synthesized IBOMA/C13MA polymers by NMP using different initiation methods (pure BB and Dispolreg 007 alkoxyamine) in organic solvents and miniemulsions.^{2,33} Herein, we polymerized IBOMA/C13MA monomers using a water-soluble macroinitiator, attempting to avoid charged species as the macroinitiator, which could degrade the alkoyxamine. The addition of an amphiphilic macroinitiator could also limit or eliminate the use of surfactants in emulsions or miniemulsions.^{23,34} This prevents the common disadvantages associated with the presence of high concentrations of surfactants in polymer structures (such as the modification of mechano-thermal properties) after drying.^{35,36} The block copolymers of oligoethylene glycol methyl ether methacrylate (OEGMA) and S were previously used as the surfactants for emulsion polymerization of S, indicating the applicability of OEGMA monomers for preparation of polymeric surfactants.³⁷ The incorporation of OEGMA can also introduce self-assembly properties³⁸⁻⁴⁰ and decrease cell adhesion and protein adsorption to the polymer structure in bio-applications^{41,42}. Qiao et al⁴³ developed SG1-based macroinitiators using OEGMA ($M_{n,Average}$ = 950 and 300 g mol⁻¹) for NMP of n-butyl methacrylate. In this

study, the SG1-based amphiphilic macroinitiators were synthesized from OEGMA ($M_{n,Average} = 500 \text{ g mol}^{-1}$) and 10 mol% controlling comonomers (AN or S) to use for the emulsion polymerization of bio-based methacrylates. We adopted a similar approach to use a non-ionic poly(OEGMA)-rich macroinitiator for the polymerization of IBOMA and C13MA, hopefully leading to water-based coating/adhesive materials, where we characterized the macroinitiator, studied the kinetics of miniemulsion polymerization and assessed the colloidal and thermal stability of polymers derived from the NMP process using BlocBuilder type initiators. With this study, we hope to develop convenient VOC-free emulsions derived from largely bio-based monomers for coatings and adhesives (with possibility of sophisticated architectures) with minimal environment impact.

2 EXPERIMENTAL

2.1 Materials

Isobornyl methacrylate (IBOMA, >99%, Evonik), C13.0 alkyl methacrylate (C13MA, methacrylic esters with an average alkyl chain length of 13 monomer units, >99%, Evonik), oligoethylene glycol methyl ether methacrylate (OEGMA, *M_{n,Average}* = 500 g mol⁻¹, >99%, Aldrich) and acrylonitrile (AN, >99%, Aldrich) were used to prepare the polymers. The monomers were passed through a column filled of a mixture of basic alumina (Brockmann, Sigma Aldrich) and calcium hydride (5 wt% relative to basic alumina, 90-95% reagent, Sigma Aldrich) to remove inhibitors. N-(2-methylpropyl)-N-(1-diethylphosphono-2,2dimethylpropyl)-O-(2-carboxylprop-2-yl) hydroxylamine (BlocBuilder-MA™, BB,99%, Arkema) alkoxyamine was used to initiate the polymerizations. DOWFAX[™] 8390 surfactant (35 wt% active content) and n-hexadecane (99%) were received from Dow Chemical and Sigma Aldrich, respectively. Methanol (MeOH, >99%), tetrahydrofuran (THF, 99.9%, HPLC grade) and toluene (>99%) solvents were obtained from Fisher Scientific. To prepare samples for ¹H NMR test, samples were dissolved in deuterated chloroform (CDCl₃, \geq 99%, Cambridge Isotopes Laboratory). Reverse osmosis water (type 2 with the resistivity of ~ 1.10 MOhm cm at 25 °C) was used to prepare the latexes. All the polymerizations were conducted under nitrogen (99.99%, Praxair).

2.2 Methods

2.2.1 M_n, X and Đ Measurements

Monomer conversions (X) were measured gravimetrically using the procedure mentioned in our previous study². Number average molecular weight (M_n) and molecular weight distribution (D) were measured by gel permeation chromatography (GPC, Waters) relative to PMMA standards (Varian Polymer Standards; M_n range of 875 to 1677000 g mol⁻¹) at 40 °C in THF (HPLC grade). The GPC samples were dried to remove the water. Next, the THF (HPLC grade) solvent was added to dilute the samples to the concentration of ~5 mg.ml⁻¹. Three GPC columns of HR1, HR2 and HR4 Styragel® (for THF solvent) with molecular weight measurement ranges of $10^2 - 5 \times 10^3$ g mol⁻¹, $5 \times 10^2 - 2 \times 10^4$ g mol⁻¹ and $5 \times 10^3 - 6 \times 10^5$ g mol⁻¹, respectively, were used to measure M_n s and Ds. A guard column was connected to the inlet to protect the GPC columns. Polymer compositions were determined by ¹H NMR (Bruker Avance III HD 500 MHz, 16 scans) using deuterated CDCl₃.

2.2.2 Thermoanalytical Analyses

Latex samples were dried inside a fume hood for 48 h and then under vacuum for 24 h. Dried samples were fully dissolved in toluene to prepare them for precipitation. Then, samples were precipitated in methanol to remove solvents and unreacted monomers completely before thermoanalytical analyses. The samples were dried again inside a fume hood for 24 h and then under vacuum overnight at room temperature prior to measurement. Differential scanning calorimetry (DSC, Q2000, TA Instruments) was used to measure T_ms and T_gs of polymers. T_ms and T_gs were calculated by inflection method. For each sample, three scans per cycle (heat/cool/heat) with heating rate of 15 °C min⁻¹ and cooling rate of 50 °C min⁻¹ was performed under nitrogen. The calibration of DSC was carried out using indium and benzoic acid standards before the test. The thermal stability of samples were placed in aluminium pans and were heated up to 600 °C with the heating rate of 15 °C min⁻¹ to measure the decomposition temperatures ($T_{dec}s$).

2.2.3 Particle Size and Zeta Potential

Particle size and zeta potential of samples were measured by a Malvern Zetasizer Nano-ZS (with a 4 mW He–Ne laser at 633 nm and an avalanche photodiode detector) at 25 °C. For the dynamic light scattering (DLS), samples were diluted with RO water to an approximate concentration of 0.01-1000 mg ml⁻¹ ($10^{-3} - 1\%$ mass). The reported particle size for each sample is the average of 5 measurements. To determine zeta potential, samples were diluted by adding 0.1 ml of final latex samples in 111 ml of RO water and the pH \approx 7 was set for all the samples.

2.3 Preparation of SG1-based Amphiphilic Macroinitiators

SG1-based macroinitiators were synthesized before the polymerizations. The polymerization setup consisted of a 50 ml three neck round bottom flask with a magnetic stir bar, connected to a reflux condenser at 3°C. The condenser was filled with a mixture of ethylene glycol and distilled water (20/80 vol%). The setup was placed inside a heating mantle on a magnetic stirrer to apply a constant stirring while heating and controlling the reaction temperature. The heating mantle was connected to a temperature controller with a temperature sensor. The temperature sensor was placed inside the reactor from one of the side necks to measure the reaction temperature and control the heating rate. To the reactor was added a mixture of 90 mol % OEGMA and (10 mol% AN or S), BB alkoxyamine and 50 wt% toluene. To achieve high chain end fidelity for macroinitiators, the reaction stopped at low conversions to prevent termination events. As an example, for preparation of p(OEGMA-stat-AN) macroinitiator (M_n = 7200 g mol⁻¹ and D = 1.24), theoretical molecular weight at 100% monomer conversion (target M_n) of $M_{n,target} =$ 15000 g mol⁻¹ was considered for the polymerization and the reaction was stopped after 45 min (X= 33.3 %). OEGMA (91.55 g, 143.72 mmol), AN (0.85 g, 15.97 mmol), BB (2.35 g, 6.16 mmol) were dissolved in 50 wt% toluene and the solution was added to the reactor. The solution was purged with nitrogen for 30 min before heating. The solution was heated to 90 °C at a heating rate of 10 °C min⁻¹, while the nitrogen bubbling continued during the polymerization. The t=0 was considered when the temperature reached 75 °C. The samples were taken periodically for ¹H NMR and GPC. The final solution was dialyzed using a dialysis membrane (Spectra/Por 6; MWCO = 1 kD) in deionized water to purify the macroalkoxyamines

from the unreacted monomers and toluene. Then, the final solution was dried completely to obtain the pure macroinitiator.

2.4 Nitroxide Mediated Miniemulsion Polymerization of IBOMA/C13MA Using SG1-based Amphiphilic Macroinitiators

Nitroxide mediated miniemulsion polymerization of IBOMA, C13MA or a mixture of both monomers in the presence of 10 mol% AN or S controlling comonomers was conducted at 90 °C. The polymerization setup was similar to the one used for the preparation of macroinitiators with some adjustment for the miniemulsion polymerization conditions. To prepare the miniemulsion, the amphiphilic macroinitiator was added to water (with or without DOWFAXTM 8390 surfactant) and mixed for 15 minutes to prepare the aqueous phase. IBOMA, C13MA and AN (with or without addition of n-hexadecane) were mixed for 15 minutes to prepare the organic phase. Next, the two solutions were mixed together in a beaker with a magnetic stirrer for another 30 minutes to make a homogeneous miniemulsion. Finally, the miniemulsion was sonicated for 10 minutes in a cold-water bath using a Hielscher sonicator UP200S (50% duty cycle and amplitude of 70%) and transferred to the reactor. The latex solid content of 21 wt% and $M_{n,target}$ of 45 kg mol⁻¹ were set for all the polymerizations. The initial latex was purged with nitrogen for 30 min before the polymerization for deoxygenation of the system. The nitrogen flow was kept inside the reactor during the polymerization.

3 RESULTS AND DISCUSSION

3.1 Synthesis of Macroinitiators

The first step of miniemulsion polymerization was the preparation of SG1-based macroinitiators. The macroinitiators were synthesized from OEGMA along with 10 mol% of the controlling co-monomer, either S or AN. OEGMA is a non-ionic water-soluble monomer that was used to make amphiphilic macroinitiators and polymeric surfactants ^{37,44} while BlocBuilder (BB) alkoxyamine was used as the unimolecular initiator. Consequently, OEGMA polymerized with BB served as the dual surfactant/initiator. Figure S1 (Supplementary Information) displays more details about the NMP of OEGMA and preparation of macroinitiator. Figure 1 presents a schematic for the preparation of macroinitiators (with 10 mol% AN as the controlling comonomer).



Figure 1. Schematic reaction for synthesis of p(OEGMA-*stat*-AN) macroinitiator. Nitroxide mediated polymerization of OEGMA monomers ($M_n \approx 500 \text{ g mol}^{-1}$) with 10 mol% AN (controlling comonomer) was conducted in toluene at 90 °C using BB.

Two different macroinitiators were synthesized, employing two different controlling co-monomers; i.e. AN and S; to investigate the effect of the controlling co-monomer on the efficiency of the macroinitiator. Table 1 presents the characterization of macroinitiators used in this study.

Macroinitiator	$f_{\rm OEGMA,0}$ ^a	F _{OEGMA,0} ^b	Reaction time (min)	M _{n,target} ^c (g mol ⁻¹)	<i>M_{n,final} ^d</i> (g mol⁻¹)	Đ ^d
p(OEGMA-stat-AN) macroinitiator ^e	0.90	0.91	45	15000	7200	1.24
p(OEGMA- <i>stat</i> -S) macroinitiator	0.90	0.95	10	15000	5500	1.19

Table 1 Molecular characteristics of the macroinitiators

 $^{\it a}$ The molar ratio of OEGMA monomer in the initial feed for preparation of macroinitiator.

^c Target number average molecular weight (theoretical number average molecular weight at 100% monomer conversion)

^{*d*} final number average molecular weight ($M_{n,final}$) and dispersity of polymer chains (D) measured by GPC with PMMA standards in THF at 40 °C.

 e SG1-based macroinitiator prepared by the NMP of OEGMA and 10 mol% controlling comonomer (AN or S) in presence of BB alkoxyamine.

3.2 Nitroxide Mediated Miniemulsion Polymerization of IBOMA/C13MA Using Amphiphilic Macroalkoxyamines

The macroinitiators were subsequently used for the nitroxide mediated miniemulsion polymerization of IBOMA, C13MA or IBOMA/C13MA with the mixture of 50:50 $\frac{[IBOMA]_0}{[C13MA]_0}$. We investigated the effect of different reaction conditions, reaction temperatures and monomer compositions on polymerization

^b Molar fraction of OEGMA in polymer composition.

kinetics and latex stability. Table 2 lists the experimental conditions and kinetic results of polymerizations. For all the experiments, we set the same target molecular weight ($M_{n,target} = 45000 \text{ g mol}^{-1}$) and initial macroinitiator concentration ([MI]₀ = 0.005 mol L⁻¹). Apparent rate constant of polymerization ($k_P[P^*]$), was measured from the slope of kinetic plots (ln((1-X)⁻¹) versus reaction time) in the first 60 minutes of polymerization. The results are discussed in detail in the following sections.

Table 2 Experimental conditions and kinetic results for nitroxide- mediated miniemulsion polymerization

 of IBOMA/C13MA using SG1-based amphiphilic macroinitiators.

		DOWFAX	N-hexadecane	Mn.final ^b		[MI]₀ ^d	[IBOMA]	[C13MA]0	[AN]₀	6		$\mathbf{k}_{\mathbf{P}}[\mathbf{P}^{\bullet}]^{f}$
Experiment ID	Experiment ID	8390 (wt%) ^a	(wt%) ^a	(kg mol ⁻¹)	X° (%)	(M)	(M)	(M)	(M)	Đ	Т ^е (°С)	(10 ⁵ s ⁻¹)
	IBOMA90/AN10-1 ^g	0	0	37.2	31.7	0.005	0.972	0	0.108	1.83	90	9 ± 0.8
	IBOMA90/AN10-2	0	0.8	35.6	49.3	0.005	0.965	0	0.107	1.84	90	23 ± 6.3
	IBOMA90/AN10-3	2	0	44.2	88.9	0.005	0.956	0	0.106	1.66	90	38 ± 0.9
	IBOMA90/AN10-4	2	0.8	40.8	97.7	0.005	0.948	0	0.105	1.71	90	52 ± 3.2
	IBOMA90/AN10-5	2	0.8	41.7	92.8	0.005	0.948	0	0.105	2.19	80	48 ± 4.0
	IBOMA90/AN10-6	2	0.8	41.4	94.3	0.005	0.948	0	0.105	1.89	100	148 ± 10.7
	IBOMA90/AN10-7 ^h	2	0.8	27.9	61.7	0.005	0.972	0	0.108	1.81	90	132 ± 0.1
	C13MA90/AN10	2	0.8	39.5	88.3	0.005	0	0.770	0.086	2.19	90	21 ± 0.1
	BOMA45/C13MA45 /AN10	2	0.8	43.9	91.4	0.005	0.425	0.425	0.094	2.16	90	33 ± 0.8

^{*a*} wt% based on the weight of all monomers.

^b final number average molecular weight (*M_{n,final}*) and dispersity of polymer chains (*D*) measured by GPC with PMMA standards in THF at 40 °C.

^c monomer conversion (X) were measured gravimetrically.

^{*d*} Initial concentration of macroinitiator (mol L⁻¹).

^e Reaction temperature (°C).

 f Apparent rate constant of polymerization, measured from the slope of $\ln((1-X)^{-1})$ versus reaction time in the first 60 minutes of polymerization. Error bars were calculated based on the standard error for each slope (linear fit of semi-logarithmic plot).

^{*g*} Nitroxide mediated miniemulsion polymerization of IBOMA/AN with the initial molar ratio of 90:10 [mol/mol]. 10 mol% AN was added as the controlling comonomer. The polymerization was initiated by p(OEGMA-*stat*-AN) macroinitiator (M_n = 7200 g mol⁻¹ and \mathcal{D} = 1.24). ^{*h*} The polymerization initiated by p(OEGMA-*stat*-S) macroinitiator (M_n = 5500 g mol⁻¹ and \mathcal{D} = 1.19).

3.2.1 The Effect of Controlling Comonomers on the Efficiency of Macroinitiators

To study the effect of the comonomers (AN or S) on the ability of the macroinitiator to chain extend to form a second block, NMP was carried out in miniemulsion for IBOMA (90 mol%) /AN (10 mol%) monomer mixtures (experiment IBOMA90/AN10-4 (use of a p(OEGMA-*stat*-AN) macroinitiator) versus IBOMA90/AN10-7 (use of a p(OEGMA-*stat*-S) macroinitiator). Figure 2 shows a) the semi-logarithmic kinetic plots versus polymerization time and b) M_n versus conversion. Using p(OEGMA-*stat*-S) macroinitiator, the miniemulsion polymerization of IBOMA/AN stopped after 12 minutes as the latex lost its stability and the coagulation and precipitation of particles occurred in the early time. It seems that S increased the hydrophobicity of macroinitiator and reduced the efficiency of surfactant macroinitiator to stabilize the system. The lack of stability for the latex containing p(OEGMA-*stat*-S) macroinitiator is

reflected in the D of the starting point of polymerization (t=0, D = 2.9). Therefore, p(OEGMA-*stat*-AN) macroinitiator was used for the next series of studies in miniemulsion.



Figure 2. The effect of changing comonomers (AN or S) of macroinitiator on copolymerization of IBOMA/AN ($f_{AN,0} = 0.1$) (a) Kinetic plots of $ln((1-X)^{-1})$ (X= monomer conversion) versus reaction time (b) Number average molecular weight M_n and D versus conversion (X). IBOMA90/AN10-4 (filled circles, \bullet); IBOMA90/AN10-7 (open triangles, Δ).

3.2.2 The Effect of Surfactant and Co-stabilizer On the Stability and Kinetics of Polymerization

Having identified the p(OEGMA-stat-AN) as the macroinitiator that cleanly chain extended a mixture of IBOMA/AN in miniemulsion, optimization around this point ensued. This involved conducting the miniemulsion polymerizations with and without the addition of surfactant (DOWFAX 8390) and costabilizer (n-hexadecane). IBOMA90/AN10-1 was prepared without using any additional surfactant or costabilizer. IBOMA90/AN10-2 (no surfactant), IBOMA90/AN10-3 (no co-stabilizer) and IBOMA90/AN10-4 (with surfactant and co-stabilizer) were also prepared with the same experimental conditions (same initial monomer composition, $M_{n,target}$ = 45 kg mol⁻¹, T = 90 °C and same preparation steps), but with different the surfactant and co-stabilizer content. Hereinto, the amount of DOWFAX 8390 surfactant and nhexadecane co-stabilizer were considered to be 2 and 0.8 %wt based on the monomer charged. The results indicate that addition of both 2 %wbm (wt% based on monomers) of DOWFAX 8390 and 0.8 %wbm of n-hexadecane, increased the apparent rate constant ($k_{\rm P}[P^{\bullet}]$) from 9×10⁻⁵ s⁻¹ to 52×10⁻⁵ s⁻¹ (Table2), while maintaining the control over the polymerization. According to Figure 3 (a) and (b), we conclude that the addition of 2 %wbm of surfactant is necessary to stabilize the miniemulsion and enhance the control over the polymerization. Addition of small amount of n-hexadecane (0.8 %wbm) as the stabilizer increases the polymerization rate, decreases the D and the M_n increases linearly with conversion. Therefore, 2 %wbm of DOWFAX and 0.8 %wbm of n-hexadecane were used for the next series of syntheses.



Figure 3. The effects of adding surfactant and stabilizer on copolymerization of IBOMA/AN ($f_{AN,0} = 0.1$) (a) Kinetic plots of $ln((1-X)^{-1})$ (X= monomer conversion) versus reaction time (b) Number average molecular weight M_n and D versus conversion (X). IBOMA90/AN10-1 (filled circles, •); IBOMA90/AN10-2 (filled triangles, \blacktriangle); IBOMA90/AN10-3 (open circles, o); IBOMA90/AN10-4 (open triangles, \varDelta).

3.2.3 The Effect of Reaction Temperature on the Kinetics of Polymerization

Next, the effect of temperature on the polymerization of IBOMA and AN was investigated for three different temperatures of 80, 90 and 100 °C (Figure 4). For all reaction temperatures, a linear kinetic trend was observed in semi-logarithmic kinetic plots versus reaction time in the beginning of the reaction (t < 50 min). However, the irreversible terminations occurred at higher rates for polymerizations at 80 or 100 °C. The un-controlled increase of M_{n} s with X was also observed for polymerizations at 80 and 100 °C. At 100 °C, the polymerization rate was high ($k_P[P^*] = 148 \pm 11 \times 10^5 \text{ s}^{-1}$) and the reaction stopped after 67 min resulted in an uncontrolled polymerization. The uncontrolled polymerization at 100 °C could also be due to the reaction temperature higher than the lower critical solution temperature (LCST) of macroinitiators, resulting in ineffective surfactancy. For comparison, LCST of 84-90 °C was reported for <mark>OEGMA-based homopolymers.^{45,46} The polymerization rate at 80 °C was lower than 90 °C ($k_{
m P}[{
m P}^{ullet}]$ = 48 \pm </mark> 4×10^5 s⁻¹ and $52 \pm 3 \times 10^5$ s⁻¹ at 80 and 90 °C, respectively) and the reaction time was the longest (210 min). The low reaction temperature (80 °C) resulted in a low dissociation rate of nitroxide and the higher probability of termination events would increase due to lower dissociation and propagation rates.⁷ However, the polymerization at 80 °C was uncontrolled with a sigmoidal trend of M_n versus X and resulted in polymers with high dispersities (θ up to 2.25). The lowest θ s were at 90 °C ($\theta \approx 1.71 \sim 1.82$) and the M_n versus X showed a good resemblance to the theoretical line with dominance of termination events at high conversions (X > 92%). Hence, the reaction temperature of 90 °C was chosen for the NMP of IBOMA/C13MA using p(OEGMA-*stat*-AN) macroinitiator.



Figure 4. The effect of temperature on nitroxide mediated miniemulsion polymerization of IBOMA/AN $(f_{AN,0} = 0.1)$ (a) Kinetic plots of $\ln((1-X)^{-1})$ (X= monomer conversion) versus reaction time (b) Number average molecular weight M_n and D versus conversion (X). IBOMA90/AN10-5 (T= 80 °C, filled circles, \bullet); IBOMA90/AN10-4 (T= 90 °C, gray triangles, \blacktriangle); IBOMA90/AN10-6 (T= 100 °C, open diamonds, \diamond).

3.2.4 Nitroxide Mediated Miniemulsion Polymerization of IBOMA/C13MA Mixtures Using P(OEGMAstat-AN) Macroinitiator

Nitroxide mediated miniemulsion polymerization of IBOMA/C13MA/AN mixtures (10 mol% AN as the controlling comonomer) was conducted using p(OEGMA-stat-AN) macroinitiator (M_n = 7200 g mol⁻¹, D = 1.24), 2 %wbm of DOWFAX 8390 and 0.8 %wbm n-hexadecane at 90 °C. Figure 5 shows a schematic representation of the miniemulsion polymerization of IBOMA/C13MA/AN. The kinetic plots were linear in all cases up to \sim 100 min and slightly deviated at t > 100 min (Figure 6 (a)). The polymerization rate increased by increasing the ratio of [IBOMA]₀/[C13MA]₀ and these kinetic results are summarized in terms of the slopes of $\ln((1-X)^{-1})$ versus time $(k_{P}[P^{\bullet}])$. Figure 6 (b) indicates that M_{n} increased linearly with conversion and remained relatively close to the theoretical prediction line for all polymerizations studied. However, the final Ds of samples were high (1.71 < D < 2.19) and the D increased by decreasing the ratio of [IBOMA]₀/[C13MA]₀ in the miniemulsion. This might be due to the long aliphatic chains of C13MA, which caused the formation of particles early in the nucleation stage. The high \mathcal{D} for polymers prepared by chain extension of amphiphilic macroinitiators was expected, probably due to chain transfer reaction and higher termination rate compare to the polymerizations with alkoxyamines such as BB. The high Dwas also observed in similar studies on NMP using amphiphilic macroinitiators.⁴⁷ As an example, Delaittre et al²² synthesized poly(S) (D = 2, $M_n = 100$ kg mol⁻¹) by nitroxide mediated emulsion polymerization using SG1-terminated poly(acrylic acid) macroinitiator (D = 1.17, $M_p = 1900$ g mol⁻¹) at 120 °C and 3 bar pressure, though the particle size was considerably smaller (particle size = 65 nm). Dire et al²³ also observed D > 2for the NMP of methyl methacrylate using SG1-based methacrylic acid macroinitiator in emulsion. Another reason could be the use of AN, which is a partially water-soluble controlling comonomer for the NMP of methacrylates using BB.⁴⁸ Consequently, some of the AN monomers may not be available inside the monomer droplets to control the polymerization rate, resulting a relatively high \mathcal{D} (\mathcal{D} >1.7).



Figure 5. Miniemulsion polymerization of IBOMA/C13MA using p(OEGMA-*stat*-AN) macroinitiator in presence of DOWFAX 8390 and n-Hexadecane at 90 °C. Amphiphilic macroinitiators were synthesized and dissolved in the aqueous phase prior to miniemulsion polymerization.



Figure 6. The miniemulsion polymerization of different ratios of IBOMA/C13MA/AN using p(OEGMA-*stat*-AN) macroinitiator (a) Kinetic plots of $ln((1-X)^{-1})$ (X= monomer conversion) versus reaction time (b)

Number average molecular weight M_n and D versus conversion (X). IBOMA90/AN10-4 (filled circles, •); C13MA90/AN10 (gray triangles, \blacktriangle); C13MA/IBOMA45/AN10 (open diamonds, \diamond).

Figure 7 demonstrates the GPC peaks shift for the chain extension of p(OEGMA-*stat*-AN) macroinitiator with IBOMA/AN ($f_{IBOMA,0} = 0.9$) and C13MA/AN ($f_{C13MA,0} = 0.9$) at 90 °C. The ability of the chains to reinitiate a second batch of monomer was observed by seeing the GPC peaks shift toward higher molecular weights with monomer conversion, with very little dead macrointiator observed.



Figure 7. Molecular weight distribution of polymers for chain extension of p(OEGMA-*stat*-AN) macroinitiator with (a) IBOMA90/AN10-4 ($f_{IBOMA,0} = 0.9$) and (b) C13MA90/AN10 ($f_{C13MA,0} = 0.9$).

3.3 Particle Size and Colloidal Stability of IBOMA/C13MA Polymer Latexes

Figure 8 illustrates the Z-average particle size of the latex samples as measured with DLS. Initially, we studied the effect of addition of co-stabilizer (n-hexadecane) and surfactant on particle size. For the IBOMA90/AN10-1 experiment (without surfactant or co-stabilizer), the particle size varied from 0.5-2 μ m. The p(OEGMA-*stat*-AN) macroinitiator acted as a dual surfactant/initiator and stabilized the miniemulsion. The particle size decreased during the polymerization, indicating the transition from monomer droplets to polymer particles, however we cannot rule out the temperature sensitivity of the p(OEGMA-stat-AN) macroinitiator which could alter viscosity and surfactant ability. As the polymerization progressed, the nonionic macroinitiator was not able to provide as effective stabilization and the particles started to coagulate and precipitate. This resulted in an uncontrolled polymerization for the IBOMA90/AN10-1 experiment. In the IBOMA90/AN10-2 experiment, 0.8 wt% hexadecane (relative to the monomers), was added to the organic phase to aid the stability of the colloid. Consequently, the monomer droplet size decreased significantly (from 2050 nm for IBOMA90/AN10-1 to 656 nm for IBOMA90/AN10-2). However, the macroalkoxyamines were unable to stabilize the colloids and coagulation still occurred at higher conversions. Addition of 2 wbm% DOWFAX for IBOMA90/AN10-3 experiment (without n-

hexadecane) and IBOMA90/AN10-4 (with 0.8 wbm% n-hexadecane) along with the amphiphilic macroinitiator, provided much better colloidal stability for the miniemulsion polymerization, especially at higher conversions. For these two experiments, the particle size steadily decreased during the polymerization, and limiting to about 200-300 nm after 30 minutes. The particle size dispersity was high for most of the samples, which indicates the presence of particles with multiple size distributions.⁴⁹ This phenomenon can be ascribed to using two different surfactants (DOWFAX 8390 and amphiphilic macroinitiator) to stabilize the system. Further, the macroinitiator's solubility in the aqueous phase may not have been sufficiently high to avoid droplet nucleation. It was possible that macroinitiator molecules were engulfed into the bulk of the monomer droplets to initiate the polymerization and were not acting as surfactants at the interface. Similarly, Nicolas et al⁵⁰ observed broad particle size distribution for nitroxide mediated miniemulsion polymerization of n-butyl acrylate and S using an SG1-based watersoluble alkoxyamine (synthesized from BB and tri(ethylene glycol) diacrylate) and DOWFAX 8390 surfactant. The particle size versus reaction time is shown at different temperatures of 80, 90 and 100 °C (Figure 8 (b)) and the particle size for polymerization of IBOMA, C13MA and 10 mol% AN (controlling monomer) is depicted in Figure 8 (c). Using the macroinitiator, the particle size in all experiments except for IBOMA90/AN10-6, decreased drastically in the first 45 minutes of the reaction and stayed quite constant until the end of polymerization. This occurred due to the disappearance of monomer droplets and the formation of polymer particles in the latex.





Figure 8. (a) Average particle size versus reaction time. IBOMA90/AN10-1 (filled circles, •); IBOMA90/AN10-2 (filled triangles, \blacktriangle); IBOMA90/AN10-3 (open circles, o); IBOMA90/AN10-4 (open triangles, \triangle). (b) The effect of reaction temperature on particle size during the copolymerization of IBOMA/AN monomers using p(OEGMA-*stat*-AN) macroinitiator, 2 %wbm DOWFAX 8390 and 0.8 %wbm n-hexadecane. IBOMA90/AN10-5 (filled circles, •); IBOMA90/AN10-4 (gray triangles); IBOMA90/AN10-6 (open diamonds, \diamond). (c) Z-average particle size for IBOMA/C13MA/AN polymerization with time using p(OEGMA-*stat*-AN) macroinitiator, 2 %wbm DOWFAX 8390 and 0.8 %wbm n-hexadecane. IBOMA90/AN10-5 (filled circles, •); IBOMA90/AN10-4 (gray triangles); IBOMA90/AN10-6 (open diamonds, \diamond). (c) Z-average particle size for IBOMA/C13MA/AN polymerization with time using p(OEGMA-*stat*-AN) macroinitiator, 2 %wbm DOWFAX 8390 and 0.8 %wbm n-hexadecane. IBOMA90/AN10-4 (filled circles, •); C13MA90/AN10 (gray triangles, \blacktriangle); IBOMA45/C13MA45/AN10 (open diamonds, \diamond).

The adsorption of surfactant on the surface of polymer particles directly affects the colloidal stability.⁵¹ As the anionic surfactant (DOWFAX 8390) was used to stabilize the latex, the surface charge of polymer particles was negative. To quantify the surface charge of the particles, zeta-potentials were measured for the IBOMA/C13MA experiments (Table 3). The zeta-potential values were between -38 to -43 mV, suggesting a high degree of stability for the particles.⁵²

Table 3 Zeta-potential and final particle size for the polymer particles in miniemulsion.

Experiment ID	Final particle size (nm) ^a	PDI ^a	Zeta potential (mV) ^b
IBOMA90/AN10-4	157	0.345	-43.0
C13MA90/AN10	221	0.160	-39.8
IBOMA45/C13MA45/AN10	185	0.122	-38.3

^{*a*} Z-average particle size and dispersity of the polymer particles in latex measured by DLS at room temperature. The reported results are the average of 5 measurements.

^b Zeta potential results for polymer latexes (pH = 7).

3.4 Thermal properties of IBOMA/C13MA Polymers Prepared in Miniemulsion

To investigate the effect of OEGMA-based macroinitiator on thermal properties of IBOMA/C13MA/AN copolymers, TGA and DSC were performed on IBOMA90/AN10-4, C13MA90/AN10 and IBOMA45/C13MA45/AN10 samples and the results were presented in Table 4. Polymer compositions were listed in Table 4 (Figure S2 in Supplementary Information, shows the polymer composition of IBOMA45/C13MA45/AN10). Theoretical glass transition temperature ($T_{g,theo}$) for the samples were estimated by Fox equation, neglecting the effect of p(OEGMA-*stat*-AN) macroinitiator⁵³:

$$\sum_{i} w_{i} \left(1 - \frac{T_{g,theo}}{T_{g,i}} \right) = 0$$
⁽¹⁾

where w_i corresponds to the mass fraction of monomers and $T_{g,i}$ is the T_g of the individual homopolymers prepared from the monomers. Herein, $T_{g,IBOMA} = 110 \text{ °C}^{2,54}$, $T_{g,C13MA} = -46 \text{ °C}^{54,55}$ and $T_{g,AN} = 95 \text{ °C}^{54,56}$ were taken as the literature values to calculate the $T_{g,theo}$ s of polymer samples. The measured T_g s were slightly lower than $T_{g,theo}$ s, suggesting a decrease in T_g s due to the existence of residual n-hexadecane in polymer samples.^{57,58} Furthermore, initiation with p(OEGMA-*stat*-AN) macroinitiators can also lower the T_g s due to the presence of OEGMA (T_g OEGMA homopolymer ($T_{g,p(OEGMA)}$) = -60 to -53 °C⁵⁹⁻⁶²) as part of the copolymer. The T_g s increased with increasing the IBOMA content in polymers. A T_m at -19 °C was detected for the C13MA-rich polymer. It should be noted that a T_m for co/terpolymers with high C13MA content was observed in previous studies.^{2,63} Table 4 shows the decomposition temperature for 10% weight loss ($T_{dec,1}$), decomposition temperature for maximum weight loss ($T_{dec,max}$) and decomposition temperature at the end of measurement ($T_{dec,2}$) for IBOMA90/AN10-4, C13MA90/AN10 and IBOMA45/C13MA45/AN10. Figure 9 presents the TGA traces for the polymers. From these results, degradation of polymers containing IBOMA occurred in two stages, due to the formation and elimination of camphene at temperatures above ~ 300 °C.^{2,64,65}

Table 4 Thermal ch	naracterization of	IBOMA/C13MA/AN	polymers	starting	from p	o(OEGMA-st	at-AN)
macroinitiator prepa	ared by NMP in m	iniemulsion					

Experiment ID	T _m ″ (°C)	Т _g ^{<i>a</i>} (°С)	T _{g,theo} ^b (°C)	T _{dec,1} c (°C)	T _{dec,max} ^c (°C)	T _{dec,2} ^c (°C)	F IBOMA ^d	F _{C13MA}	F OEGMA	<i>M_{n,final}^e</i> (kg mol ⁻¹)
IBOMA90/AN10-4	-	109	110	227	281	463	0.86	0	0.07	40.8
C13MA90/AN10	-19	-44	-42	225	371	470	0	0.84	0.08	39.5
IBOMA45/C13MA45/AN10	-	-3	9	229	293	479	0.41	0.45	0.10	43.9

^{*a*} T_m (melting point) and T_g (glass transition temperature) measured by DSC under nitrogen atmosphere using (heat/cool/heat) method in the temperature range of -80 to 140 °C. The heating rate of 15 °C min⁻¹ and cooling rate of 50 °C min⁻¹ was considered for the measurement.

^b T_{g,theo} (theoretical glass transition temperature) estimated by Fox equation.⁵³

^c Decomposition temperatures (T_{dec} s) measured by TGA under nitrogen atmosphere at a heating rate of 15 °C min⁻¹. $T_{dec,1}$ (T_{dec} for 10% weight loss or onset of decomposition), $T_{dec,max}$ (T_{dec} at which highest weight loss occurs) and $T_{dec,2}$ (T_{dec} at the end of decomposition).

^d Molar fraction of IBOMA in polymer composition, determined by ¹H NMR in CDCl₃. ¹H NMR spectra for IBOMA45/C13MA45/AN10 is available in Figure S2 (Supplementary Information).

^{*e*} Final number average molecular weight ($M_{n,final}$) and dispersity of polymer chains (D) measured by GPC with PMMA standards in THF at 40 °C.



Figure 9. TGA thermograms for IBOMA90/AN10-4 (—, black line), IBOMA45/C13MA45/AN10 (—, blue line) and C13MA90/AN10 (—, red line) samples under nitrogen with heating rate of 15 °C min⁻¹.

4 CONCLUSIONS

In this study, nitroxide mediated miniemulsion polymerization of two bio-based methacrylic monomers (in presence of 10 mol% AN controlling comonomer), using SG1-terminated amphiphilic macroinitiators, was investigated. Isobornyl methacrylate (IBOMA) and C13 alkyl methacrylate (C13MA) were the hydrobphobic monomers studied. Two different macroinitiators were synthesized from poly (ethylene glycol) methyl ether methacrylate (OEGMA, $M_{n,Average} = 500$ g mol⁻¹) by changing the controlling comonomer (AN or S, 10 mol%) with the former being more effective in providing the control of the miniemulsion polymerization of IBOMA/C13MA in terms of linear growth of M_n with conversion and low D. The p(OEGMA-*stat*-AN) macroinitiator was used as the sole surfactant/initiator for the miniemulsion polymerization of the IBOMA or C13MA; but the best colloidal stability and control over the polymerization was accomplished in the presence of 2 wt% DOWFAX 8390 surfactant and 0.8 wt% nhexadecane co-stabilizer (based on the weight of monomers). IBOMA/AN polymers with $\mathcal{D} = 1.71$ were successfully synthesized (X = 97.7%, $M_n = 40.8$ Kg mol⁻¹). Subsequent temperature optimization studies revealed best polymerization control in terms of lower dispersity, occurred at 90 °C. After finding the optimal experimental conditions, the NMP of C13MA or IBOMA/C13MA with the mixture of $50:50 \frac{[IBOMA]_0}{[C13MA]_0}$ was also conducted in presence of p(OEGMA-*stat*-AN) macroinitiator, 2 wbm% DOWFAX and 0.8 wbm% n-hexadecane in miniemulsion at 90 °C. As a result, polymers with M_n s up to 43.9 kg mol⁻¹, $\mathcal{D} < 2.19$ and $88.3\% \le X \le 91.4\%$ were produced, with good colloidal stability (-38 mV $\le \zeta$ potential ≤ -43 mV). Finally, the thermal properties were investigated revealing that increasing the IBOMA content increased the T_g of the polymers and was characterized by a two-stage decomposition by TGA analysis.

ACKNOWLEDGMENTS

McGill Engineering Doctoral Award (MEDA) scholarship from the Faculty of Engineering, McGill University, Natural Sciences and Engineering Research Council (NSERC CRDPJ 518396-17 with Safran Cabin) and PRIMA Quebec with Safran Cabin (Project # R15-46-004) are gratefully acknowledged for their financial support. We also thank the Centre Québécois sur les Matériaux Fonctionnels (CQMF) for the use of the DSC and TGA.

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Conflict of Interest

There are no conflicts to declare.

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Graphical Abstract



This paper investigates the nitroxide mediated miniemulsion polymerization of bio-based isobornyl methacrylate and C13 alkyl methacrylate using a SG1-based non-ionic amphiphilic macroinitiator. Adding surfactant and co-stabilizer improved polymerization control (lower dispersity and higher colloidal stability). We studied the effect of the initiator on the polymerization kinetics, its associated colloidal stability and resulting thermal properties of homo/copolymers.