Polymer Chemistry

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/polymers

Journal Name RSCPublishing

ARTICLE

Nitroxide-mediated surfactant-free emulsion copolymerization of methyl methacrylate and styrene using poly (2-(diethyl) aminoethyl methacrylate-*co*-styrene) as a stimuli-responsive macroalkoxyamine

Ali Darabi,[a] Abbas Rezaee Shirin-Abadi,[a] Julien Pinaud,[b] Philip G. Jessop,*[c] and Michael F. Cunningham*[ac]

The SG1-mediated copolymerization of 2-(diethyl)aminoethyl methacrylate (DEAEMA) and a small percentage of styrene (S) was performed with different initiating systems including a monocomponent initiating system using an alkoxyamine of *n*-hydroxysuccinimidyl BlocBuilder (NHS-BlocBuilder) at 80 ºC and a bicomponent initiating system using 2,2'-azobis[2-(2-imidazolin-2-yl)propane] (VA-061) as the initiator and N-tertbutyl-N-(1- diethylphosphono-2,2-dimethylpropyl) nitroxide (SG1) as the nitroxide at 100 ºC. The resultant macroalkoxyamines, poly(DEAEMA-*co*-S)-SG1, were used as pH-sensitive macroinitiators in the nitroxide-mediated surfactant-free emulsion copolymerization of methyl methacrylate (MMA) and styrene at 90 ºC, which proceeded via a polymerization-induced self-assembly (PISA) process, leading to the *in-situ* formation of pH-responsive amphiphilic block copolymers. The reaction was well-controlled with high initiation efficiency and exhibited excellent livingness as evidenced by evolution of the molar mass distribution. The final latex particles were pH-sensitive with excellent colloidal stability and monomodal size distribution.

Introduction

Preparation of stimuli-responsive materials exhibiting reversible changes in chemical or physical properties in response to external triggers by living radical polymerization (LRP) has been an active area of research during the last decade.[1,2] Tertiary amine-based polymers, an important category of stimuli-responsive polymers which are pH and/or temperature-responsive, have potential applications in emulsion polymerization,[3] block copolymers synthesis,[4] and the biomedical field[5] (gene or drug delivery).[6,7] In particular, the monomers 2-(diethylamino) ethyl methacrylate (DEAEMA) and 2-(dimethylamino)ethyl methacrylate (DMAEMA) have been polymerized employing different LRP techniques. Atom transfer radical polymerizations (ATRP) of DMAEMA and 2-(dimethylamino)ethyl acrylate (DMAEA) were reported, respectively, by Matyjaszewski and Zhu groups.[8,9] Gan et al.[10] prepared well-defined poly(DEAEMA) via ATRP and then used the synthesized poly(DEAEMA) as a macroinitiator for producing poly(DEAEMA-*b*-tBMA). Reversible addition fragmentation chain transfer (RAFT) radical polymerization has been applied successfully in the synthesis of different stimuli-responsive (co)polymers.[11] RAFT of DMAEMA in water was carried out using 4,4'-azobis(4-cyanopentanoic acid) (V501) as a water-soluble initiator and 4-cyanopentanoic acid dithiobenzoate (CPADB) as a chain transfer agent.[12] D'Agosto et al.[13] investigated the effect of several parameters such as the ratio of RAFT agent to initiator, the concentration of the monomer, and the ratio of monomer to RAFT agent on the RAFT polymerization of DMAEMA. Iodine transfer polymerization of DEAEMA has also been performed by Goto et al.[14] at 60 ºC in bulk. In this elegant study, the control of the polymerization could be achieved by employing ammonium iodide to reversibly activate the chain-end.

In contrast, there are few reports of nitroxide-mediated polymerization (NMP) of functional monomers with a tertiary amine group, likely because of the challenges in achieving a well-controlled and living polymerization. Lokaj et al.[15] first reported the NMP of DMAEMA using polystyrene (PS) macroinitiator in bulk. Bian and Cunningham[16] studied the effects of temperature, solvent

---

[a] Department of Chemical Engineering, Queen's University, 19 Division Street, Kingston, Ontario, Canada K7L 3N6. E-mail: michael.cunningham@chee.queensu.ca; Fax: +1-613-533-6637; Tel: +1-613-533-2782

[b] Institut Charles Gerhardt Montpellier UMR5253 CNRS-UM2-ENSCM-UM1 - Equipe Ingénierie et Architectures Macromoléculaires, Université Montpellier II – Bat 17 – cc1702, Place Eugène Bataillon, 34095 Montpellier Cedex 5, France

[c] Department of Chemistry, Queen's University, 90 Bader Lane, Kingston, Ontario, Canada K7L 3N6. E-mail: jessop@chem.queensu.ca; Fax: +1-613-533-6669; Tel: +1-613-533-3212

polarity, chain transfer to polymer, and excess nitroxide on the NMP of DMAEA initiated by an SG1-based alkoxyamine**.** Maric and Zhang[17] performed nitroxide-mediated copolymerization of DMAEMA and styrene using *n*-hydroxysuccinimidyl BlocBuilder (NHS-BlocBuilder) in bulk at 80 ºC. The livingness of the PDMAEMA was tested by chain extension with a DMAEMA/styrene mixture.

DMAEMA and DEAEMA can be used in their protonated form to stabilize latex particles during emulsion polymerization. When CO_2 is employed as a protonating agent, this allows the development of easily coagulable/redispersable latexes. Zhao et al.[18] showed that these monomers and their derived-polymers can be protonated ("switched on") by bubbling CO_2 in their water solution, thus becoming highly hydrophilic. Removing of CO_2 from the solution, simply by air-bubbling, then allows recovery of the neutral and more hydrophobic form of the monomers or polymers. Taking advantage of the CO_2-switchability of these monomers, Cunningham et al. found they could considerably increase the solids content of their surfactant-free emulsion polymerization of styrene from 7%[3] to 27%.[19] Copolymers of stearyl methacrylate and DMAEMA, poly(SMA-*co*-DMAEMA), were used as polymeric surfactants in the miniemulsion polymerization of styrene.[20] Diblock copolymers containing PDMAEMA or PDEAEMA as a pH-sensitive block can be used as polymeric surfactants in emulsion polymerization. Zhang et al.[21,22] synthesized CO_2-switchable PMMA latexes using PDMAEMA-*b*-PMMA as a polymeric surfactant in the emulsion polymerization of MMA. Poly(DEAEMA-*co*-PEGMA) was used as a pH-sensitive polymeric stabilizer in tetradecane-in-water emulsions.[23]

Compared to ATRP and RAFT, NMP has a fairly simple mechanism since it requires only the use of an alkoxyamine, which acts as an initiator and controlling agent at the same time.[24] Block copolymers comprised of hydrophilic and hydrophobic blocks are of high interest.[25,26,27] Sequential addition of monomers (i.e. synthesis of the first block and then extension of the second block) is the general strategy for the preparation of diblock copolymers.[28] Charleux's group developed the polymerization-induced self-assembly (PISA) process which is based on the in *situ* chain extension of a hydrophilic block (prepared by LRP techniques) with a hydrophobic block and then the subsequent self-assembly of the resultant diblock copolymer in water.[29] One of the main advantages of this process is the absence of surfactants that can alter the properties of the final product especially in film-based applications. Interestingly, while DMEAMA, DEAEMA, or their (co)polymers are of interest to reversibly stabilize latexes, to the best of our knowledge they have never been employed for the synthesis of latexes by NMP using the PISA technique.

We have synthesized DEAEMA and DMAEMA-based macroalkoxyamines via nitroxide-mediated polymerization and used them as stimuli-responsive stabilizers and initiators for the nitroxide-mediated surfactant-free emulsion copolymerization of methyl methacrylate, according to the PISA process. In the first stage, poly(DEAEMA-*co*-S)-SG1 or poly(DMAEMA-*co*-S)-SG1 macroinitiators were synthesized via NMP using 2,2'-azobis[2-(2-imidazolin-2-yl)propane] (VA-061) as initiator and SG1 as nitroxide at 100 ºC or using n-hydroxysuccinimidyl BlocBuilder (NHS-BlocBuilder) as alkoxyamine at 80 ºC. In the second stage the protonated macroinitiator is chain extended with methyl methacrylate in a surfactant-free emulsion polymerization. The polymerization kinetics, livingness of the polymer chains, control over molecular weight and molecular weight distribution, colloidal characteristics of the latex particles, pH-responsiveness, and CO_2-switchability of the final latexes are described in detail.

Experimental

Materials

All chemicals, monomers, and inhibitor removal columns were purchased from Aldrich unless otherwise stated. 2-(diethylamino)ethyl methacrylate (DEAEMA, 99%) was passed through a column of basic aluminum oxide (~150 mesh) prior to use. Styrene (S, >99%) and methyl methacrylate (MMA, 99%) were purified by passing through columns packed with inhibitor remover. The 2-((tert-butyl-(1-(diethoxyphosphoryl)-2,2-dimethylpropyl) amino) oxy)-2-methylpropanoic acid initiator (BlocBuilder) and the N-tertbutyl-N-(1- diethylphosphono-2,2-dimethylpropyl) nitroxide (SG1, 85%) were supplied by Arkema. 2,2'-azobis[2-(2-imidazolin-2-yl)propane] (VA-061) was purchased from Wako Pure Chemical Industries and used without further purification. Sodium hydroxide (NaOH, >97%), tetrahydrofuran (THF, >99%), methanol (>99.8%), hexane (>98.5%), hydrochloride acid (38 wt %), and carbon dioxide (CO_2, Praxair, medical grade) were used as received. All aqueous solutions were prepared with deionized water (DIW). *N*-hydroxysuccinimide BlocBuilder (NHS-BlocBuilder) was synthesized according to the reported procedure.[30]

SG1-mediated copolymerization of DEAEMA and styrene in bulk using VA-061 as the initiator and SG1 as the nitroxide

In a typical experiment, a mixture of DEAEMA (25.0 g, 0.135 mol), styrene (1.56 g, 0.015 mol) (initial molar fraction of styrene in the monomer mixture: f_{s0}= 0.1), VA-061 (0.18 g, 0.72 mmol), and SG1 (0.31 g, 1.08 mmol) were introduced into a 50 mL three-neck round-bottom flask immersed in an ice-water bath and the mixture was deoxygenated with a nitrogen stream for 20 min. The mixture was then introduced into a preheated oil bath at 100 ºC and fitted with a reflux condenser, a nitrogen inlet and a thermometer. Time zero of the polymerization was taken when the flask was immersed in the oil bath. The reaction mixture, while remaining under N_2, was stirred at a speed of 300 rpm and allowed to react for up to 2 h with samples withdrawn periodically for kinetic studies and raw polymer analysis. Samples were quenched by immersion in an ice-water bath and then dried under air flow for 24 h. At the end of the reaction, the flask was cooled in an ice-water bath to stop the polymerization reaction and then the polymer was purified by precipitation in 20-fold volume of cold hexane (after precipitation, the solution was kept in the freezer for 6 h and then it was decanted to leave the precipitated polymer as a paste).

SG1-mediated copolymerization of DEAEMA and styrene in bulk using NHS-BlocBuilder

A mixture of DEAEMA (20.0 g, 0.108 mol), styrene (1.12 g, 10.7 mmol) (initial molar fraction of styrene in the monomer mixture: f_{s0}= 0.09), NHS-BlocBuilder (1.0 g, 2.1 mmol), and SG1 (62.0 mg, 0.21 mmol) were mixed in a 50 mL three-neck round-bottom flask immersed in an ice-water bath and the mixture was deoxygenated with a nitrogen stream for 20 min. The mixture was then introduced into a preheated oil bath at 80 ºC and fitted with a reflux condenser, a nitrogen inlet and a thermometer. Time zero of the polymerization was taken when the flask was immersed in the oil bath. The reaction mixture, while remaining under N_2, was stirred at a speed of 300 rpm and continued to react for up to 2 h with samples withdrawn periodically for kinetic studies and raw polymer analysis. Samples were quenched by immersion in an ice-water bath and then dried under the flow of air for 24 h. At the end of the reaction, the polymerization medium was first cooled in an ice-water bath to stop the polymerization and then, the polymer was purified by precipitation in 20-fold volume of cold hexane (after precipitation the solution was kept in the freezer for 6 h and then it was decanted to leave the precipitated polymer as a paste).

Surfactant-free emulsion polymerization of MMA

In a typical experiment (experiment 1, Table 1), in a 50 mL three-neck round-bottom flask fitted with a reflux condenser, a nitrogen inlet and a thermometer, poly(DEAEMA-*co*-S)-SG1 macroalkoxyamine (0.2 g, 0.034 mmol) was mixed with deionized water (22 mL), and pH was adjusted to 6.0 by addition of HCl 1M. The solution was deoxygenated by nitrogen bubbling for 20 min at room temperature. MMA (4.65 g, 0.045 moles) and St (0.53 g, 5.0 mmoles) were added to the flask and N_2 bubbling continued for 10 minutes more. The flask was then immersed in a preheated oil bath at 90 ºC. Time zero of the polymerization was taken when the flask was immersed into the oil bath. The reaction mixture, while remaining under N_2, was stirred at a speed of 300 rpm and the polymerization was allowed to proceed for 5 h. Samples were periodically withdrawn and quenched by immersion in an ice-water bath and the dried under the flow of air for 24 h to follow monomer conversion gravimetrically.

Characterization

Monomer conversion was determined gravimetrically. To determine conversion, 0.5 mL samples were removed from the reaction flask via syringe, quenched in an ice-water bath to stop polymerization, and were allowed to dry under a flow of air for 24 h. Size exclusion chromatography (SEC) was used to determine molecular weight and polydispersity index (Đ) of the polymer samples. The SEC was equipped with a Waters 2960 separation module containing three Styragel columns coupled with the separation limits between 400 and 1×10^6 g mol^{-1}. THF was used as the eluent with a flow rate of 0.3 mL min^{-1}. A differential refractive index detector (Waters 2960) was used and the average molar masses (M_n and M_w) and molar mass dispersity (Đ) were derived from a calibration curve based on polystyrene (PS) standards from Polymer Standard Service. For the reactions under CO_2 atmosphere, samples were dried under air at least for 24 h to make sure that all the amine groups became deprotonated and poly(DEAEMA-*co*-S) became soluble in THF. For the reactions performed in the presence of HCl, at the end of the reaction all the amine groups were neutralized with base (1M sodium hydroxide) before running SEC. Particle size, size polydispersity (PDI), and zeta-potential were determined for the stable latexes using the Zetasizer Nano ZS. Before measurements of the latex particle diameters, the latex samples were diluted in deionized water. Measurements were taken in a disposable capillary cuvette. Particle size and polydispersity were taken from intensity average values.

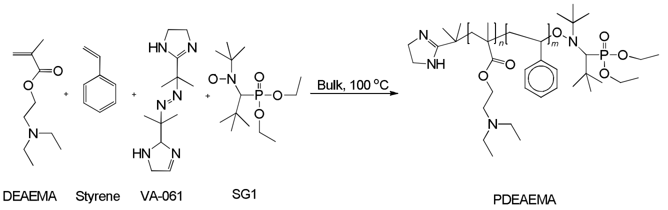
Results and discussion

DEAEMA has a tertiary amine group that makes this monomer pH sensitive. This monomer is water-soluble (hydrophilic) in its protonated form and essentially water-insoluble (hydrophobic) in its neutral form. Before performing emulsion polymerizations with MMA, the kinetics of the nitroxide-mediated aqueous solution polymerization of DEAEMA was studied in different systems to compare the blocking efficiency of poly(DEAEMA) macroinitiators.

In all experiments 8-10 mol% styrene was used in the monomer mixture to reduce the irreversible deactivation of propagating radicals and increase the livingness of the polymer chains.[31] The most convenient approach to making the poly(DEAEMA) block would be to polymerize DEAEMA in water. MMA could then be added to yield a one pot process. Therefore in the first set of experiments we conducted polymerizations in water by protonating DEAEMA with bubbling of CO_2 into the water solution at atmospheric pressure. In most of these experiments, the reaction was neither controlled nor living. The main problem was the very low solubility of CO_2 in water at high temperatures, and as a result a biphasic system existed since the monomer was not sufficiently protonated to make it water soluble. Lowering the temperature to 60 ºC increased the CO_2 solubility but gave a very slow reaction with poor control. Based on these observations, it was decided to prepare the poly(DEAEMA) based macroinitiator in bulk under a nitrogen atmosphere thereby allowing the reaction to be performed at higher temperatures with the neutral form of DEAEMA.

Nitroxide-mediated copolymerization of DEAEMA and styrene in bulk

Bicomponent system: VA-061 as initiator and SG1 as nitroxide. DEAEMA and VA-061 are pH-responsive and CO_2-switchable monomer and initiator, respectively.[3] Using VA-061 as initiator in the nitroxide-mediated polymerization of DEAEMA causes both the head and the body of the polymer chains to become pH-sensitive (Scheme 1).



Scheme 1 A schematic representation of the bulk copolymerization of DEAEMA and styrene initiated by VA-061 as initiator and SG1 as nitroxide.

VA-061 is not soluble in DEAEMA at room temperature, but at elevated temperatures it becomes soluble after decomposition and addition to DEAEMA. For the NMP of DEAEMA using VA-061 as the initiator and SG1 as the nitroxide, three different temperatures were investigated: 90, 100, and 110 ºC. While at 90 ºC complete solubilisation of VA-061 in DEAEMA took about one hour, at 110 ºC it took less than 10 minutes. However the polymerization rate was very fast with poor control and high molar mass dispersity. At 100 ºC, the initiator was dissolved in the monomer phase in about 20 minutes and better control was obtained. At the start of the reaction after bubbling CO_2 for about 30 minutes, the pH drops to 7 and DEAEMA becomes soluble in water. However when the flask is inserted into an oil-bath at high temperatures, most of the CO_2 escapes from the solution and pH increases. Therefore, depending on the specific reaction conditions, pH changes during the course of reaction.

Thus, the temperature was set to 100 ºC for the rest of the experiments. According to our observations, at $[SG1]_0/[VA\text{-}061]_0$ ratios higher than ~ 1.2, control of the reaction was improved. Also, the polymerization should not be continued beyond approximately 35% conversion since viscosity increases and irreversible termination reactions begin to noticeably affect the dispersity and chain livingness. Reactions exhibited all the features of well-controlled and living polymerizations (Figures 1 and 2): a linear increase of M_n with monomer conversion; linear increase of ln[1/(1-x)] versus time; relatively narrow molecular weight distribution; and complete shifts in the molecular weight distributions (MWD) to higher molar masses (Number average molecular weights (M_n) were calculated based on polystyrene standards). An induction period is observed in Figure 1a, showing the time required for the reaction to consume free excess SG1 present at the start of the reaction. The intercept of the M_n versus conversion is higher than zero probably because of the time required for the establishment of the activation-deactivation cycles of the alkoxyamine. Some experiments were also performed using DMAEMA as the pH-sensitive monomer and the results showed similar behaviour in terms of control and livingness of the reactions.

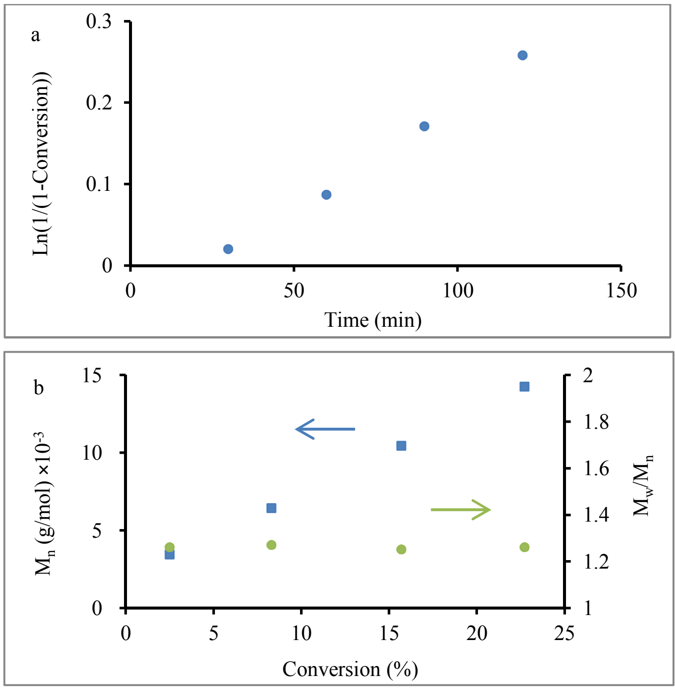


Figure 1 Bulk copolymerization of DEAEMA and styrene (initial molar fraction of styrene: f_{s0}=0.1) at 100 ºC in the presence of VA-061 and SG1 ($[SG1]_0/[VA\text{-}061]_0$=1.5). (a) ln[1/(1-x)] vs time plot (x= conversion) (b) number-average molar mass, M_n, and polydispersity index, PDI, vs conversion.

To test the CO_2-switchability of the final polymer, after precipitating the polymer in cold hexane, it was dissolved in a small amount of methanol and then water was added to the solution. The poly(DEAEMA-*co*-S) precipitated in water but after CO_2 bubbling through the solution for a few minutes, the polymer completely dissolved in water and the solution became transparent (Figure 3).

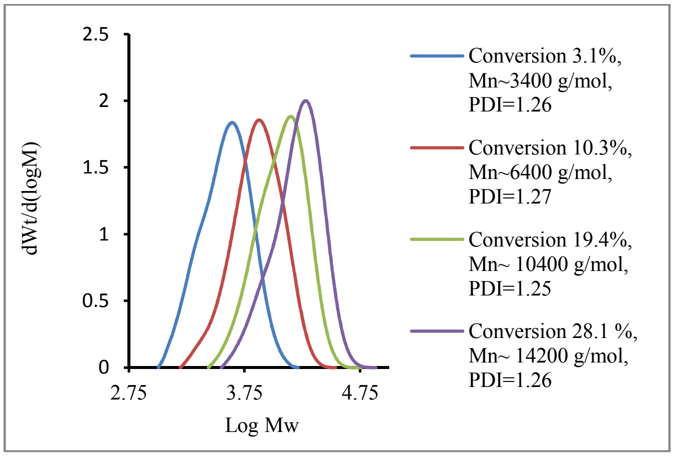


Figure 2 Size exclusion chromatograms at various monomer conversions for the copolymer of the DEAEMA and St in bulk at 100 ºC with f_{s0}=0.1 and $[SG1]_0/[VA\text{-}061]_0$=1.5.

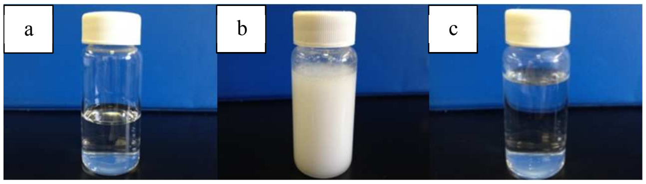
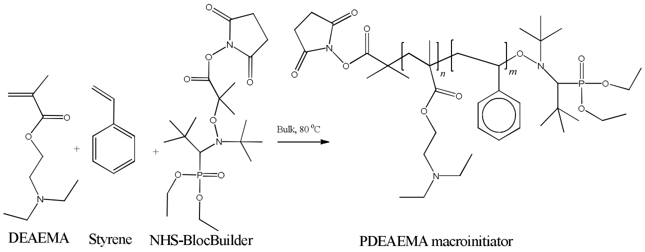


Figure 3. CO_2-switchability test of the poly(DEAEMA-*co*-S): (a) in methanol (b) after adding water (c) after bubbling CO_2 for 10 minutes at room temperature.

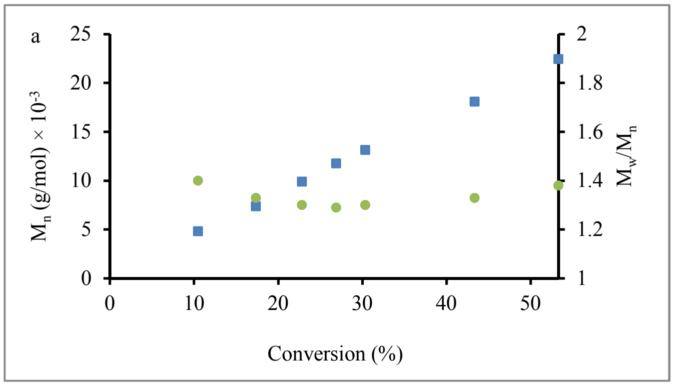
Monocomponent system: NHS-BlocBuilder

One of the disadvantages of bicomponent initiating systems (nitroxide and initiator) is difficulty in controlling and predicting initiator efficiency. Alkoxyamines are monocomponent initiating systems which produce initiator and nitroxide in an equimolar ratio after decomposition at elevated temperatures. To compare the differences between these systems, two different alkoxyamines, BlocBuilder and n-hydroxysuccinimidyl BlocBuilder (NHS-BlocBuilder), were used in the NMP of DEAEMA. BlocBuilder was used as the first choice of alkoxyamine because it is available commercially. Most of the reactions using BlocBuilder resulted in high polydispersity and poor livingness of the synthesized poly(DEAEMA-*co*-S) macroinitiator. BlocBuilder was not completely soluble in the monomer phase. Changing the ratio of SG1 to BlocBuilder and temperature did not improve the situation. The reason for the poor performance may be the presence of the carboxylic group on the BlocBuilder. It has been reported that NHS-BlocBuilder is able to polymerize DMAEMA (a similar monomer to DEAEMA with more hydrophilicity) with the small amount of styrene in the monomer feed without the need to add any free SG1.[17] Therefore; we employed this alkoxyamine instead of BlocBuilder for the NMP of DEAEMA (Scheme 2).



Scheme 2 A schematic representation of the Bulk copolymerization of DEAEMA and St initiated by NHS- BlocBuilder

The NHS-BlocBuilder is more soluble in DEAEMA at room temperature than BlocBuilder. In most experiments, reactions showed all the features of a controlled and living polymerization up to 50% conversion (Figures 4 and 5) as indicated by the low polydispersity index at these conversions. No trace of residual macroinitiator is observed on the SEC chromatograms (Figure 5), indicating a very high initiation efficiency. The clean shift of the SEC chromatograms with conversion shows the simultaneous growth of all polymer chains and indicates a good control and livingness of the polymerization.



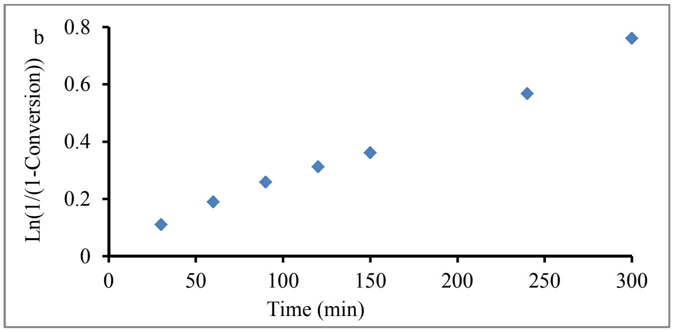


Figure 4 Kinetic plots of the bulk copolymerization of DEAEMA and styrene (initial molar fraction of styrene: f_{s0}=0.1) at 80 ºC in the presence of NHS-BlocBuilder and SG1 ([SG1]$_0$/[NHS-BlocBuilder]$_0$=0.1). (a) number-average molar mass, M_n, and polydispersity index, PDI, vs conversion. (b) ln[1/(1-x)] vs time (x= conversion).

The initiator efficiency appeared to be very high since there is no remaining peak in the low molecular weight parts of the SEC chromatograms. The final polydispersity was less than 1.4 for a macroinitiator with M_n~ 23000 g/mol and 53 % conversion in bulk. Finally, to ensure most of the poly(DEAEMA-*co*-S)-SG1 chains were capped with an SG1 moiety, chain extension tests were performed in bulk using styrene as monomer. The temperature was chosen as 120 ºC which is suitable for the NMP of styrene. The SEC chromatogram of the PDEAEMA macroinitiator shifted to higher molecular weight without any shoulder on the low molecular side of the chromatogram, confirming a high degree of livingness of the macroinitiator (Figure 6).

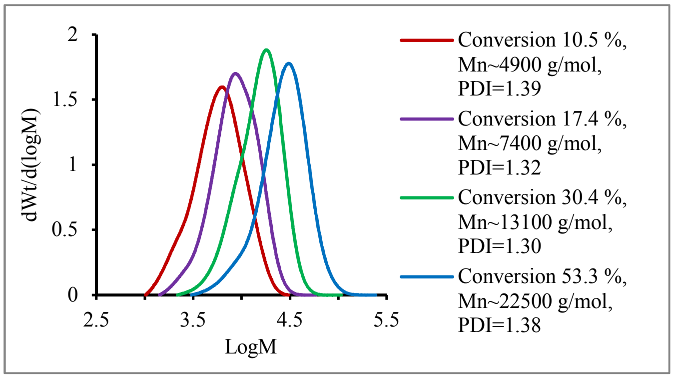


Figure 5 Size exclusion chromatograms of the DEAEMA and styrene copolymer obtained in bulk at 80 ºC with f_{s0}=0.1 and [SG1]$_0$/[NHS-BlocBuilder]$_0$=0.1 at various monomer conversions for the copolymer.

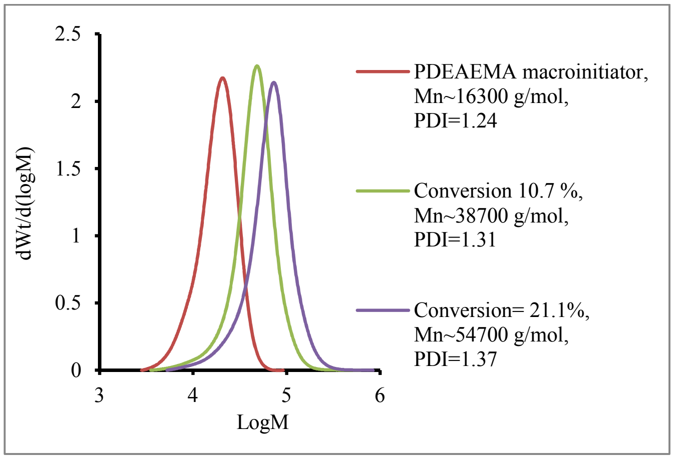
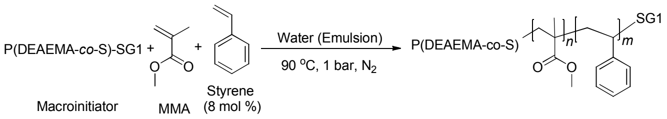


Figure 6 Chain extension of the poly(DEAEMA-*co*-S)-SG1 macroalkoxyamine via nitroxide-mediated polymerization of styrene in bulk at 120 ºC.

Surfactant-free emulsion polymerization of MMA

In its protonated form, poly(DEAEMA-*co*-S)-SG1 macroalkoxyamine is expected to be water-soluble and thus to be able to stabilize latex particles obtained by a polymerization-induced self-assembly mechanism. As such, and with the aim of preparing easily coagulatable/redispersible latexes via NMP, we first tried to use CO_2 as a protonating agent for the macroalkoxyamine. However, protonation of the poly(DEAEMA-*co*-S)-SG1 macroinitiator with CO_2 appeared challenging for different reasons. Firstly, at the higher temperatures employed for NMP (T> 80 ºC), the solubility of CO_2 in water is almost negligible and hence does not reduce the solution pH below the pK_a of the polymer (i.e. pK_a=7.4[32]). As a result, the macroinitiator protonated at room temperature reverts to its neutral form at reaction temperature and is no longer able to stabilize latex particles. Secondly, based on our observations if the concentration of DEAEMA in water exceeds ~10 wt%, protonation requires long times at room temperature. Even after a long time, complete protonation of all the amine groups in the polymer chains is not possible using only a weak acid such as carbonic acid.[33] Therefore, HCl (strong acid) was used for protonation of the macroinitiator during the emulsion polymerization experiments (Scheme 3).



Scheme 3 A schematic representation of emulsion copolymerization of MMA and styrene initiated by poly(DEAEMA-*co*-S)-SG1 macroinitiator.

Table 1 shows the experimental conditions employed in the polymerization-induced self-assembly of MMA with either poly(DEAEMA-*co*-S)-SG1 or poly(DMAEMA-*co*-S)-SG1 macroinitiators.

Table 1. Experimental conditions for the surfactant-free emulsion copolymerization of MMA with a small percentage of styrene initiated by poly(DEAEMA-*co*-S)-SG1 or poly(DMAEMA-*co*-S)-SG1 macroinitiators.

No.	Macroinitiator	M_n[a] (g.mol^{-1})	[Macroinitiator]$_0$ (mmol.L^{-1} solution)	[MMA]$_0$ (mol.L^{-1})	[S]$_0$	$f_{s,0}$[b]	Target M_n[c] at full conversion (g.mol^{-1})	Z_{ave} (nm)
1	M_1	5900	1.27	1.68	0.18	0.1	158250	90
2	M_2	17530	1.96	1.46	0.16	0.1	100380	75
3	M_3	5470	3.72	1.67	0.14	0.08	50000	61
4	M_4	3870	4.46	0.71	0.06	0.08	21740	-

[a] Experimental M_n measured by SEC, [b] Mole fraction of styrene in the monomer feed, [c] Theoretical number-average molar mass calculated according to M_n = MM(macroinitiator) + conversion × initial weight of monomers/initial mol number of macroinitiator, with conversion =1.

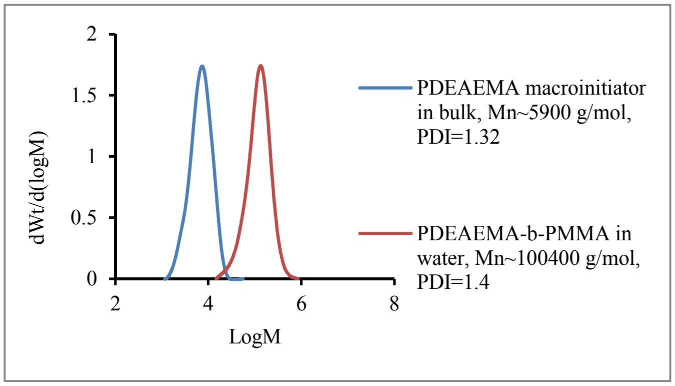


Figure 7 Size exclusion chromatograms at various monomer conversions for nitroxide-mediated emulsion copolymerization of MMA and styrene initiated with Poly(DEAEMA-*co*-S) macroinitiator at 90 ºC.

In the first experiment (exp. 1, Table 1) the suitability of the protonated poly(DEAEMA-*co*-S)-SG1 macroinitiator with M_n~ 5900 g.mol^{-1} for producing stable latex was evaluated. The reaction was stopped after 5 h and the polymer was neutralized with 1 M sodium hydroxide solution thus inducing coagulation of the latex particles that could be filtered and dried. The conversion of MMA was 40 % and the final latex was stable without any coagulum. The dried polymer had a molecular weight of 101 kDa with dispersity of 1.4. The clear shift in the SEC chromatograms (Figure 7) indicates the formation of poly(poly(DEAEMA-*co*-S)-*b*-poly(MMA-*co*-S)) amphiphilic block copolymers according to the PISA technique. To investigate the effect of the molecular weight of the macroinitiator on the pH-responsiveness of the latex, which will be discussed later, a new macroinitiator (M$_2$ in Table 1) with higher M_n was prepared. To increase the conversion, concentration of the macroinitiator was increased in order to increase the number of generated radicals in the water phase and as a result increase the number of oligoradicals which finally leads to the increase in the number of particles. Samples were taken periodically to monitor the control and livingness of the reaction. Results are shown in Figure 8. Number average molecular weights were higher than theoretical values (Figure 8a). SEC chromatograms shifted to higher molecular weights but small shoulders were observed at lower molecular weights, which indicates the macroinitiator contains some dead chains (Figure 8b). Polydispersities are higher compared to the previous experiments which indicate decrease in the control of the reaction. The livingness of the reaction decreased at conversions higher than 40%. The intensity average particle size is monomodal with the average diameter of 75 nm (Figure 8c).

To increase the polymerization rate and final conversion, the amount of styrene in the monomer mixture was reduced from 10 to 8 % (exp. 3 Table 1). In this case, conversion increased from 54% in the previous experiment to more than 63% at the same reaction time. Also, decreasing the M_n of the macroinitiator improved the control and livingness of the polymerization which can be seen from the lower PDIs and better shifts in the SEC chromatograms (Figure 9). The polydispersities decreased considerably from 1.46 to 1.23. No residuals of the macroinitiator were observed in the SEC chromatograms, indicating very efficient reinitiating ability of the polymer chains. Attempts at precipitation of poly(DEAEMA-*co*-S)

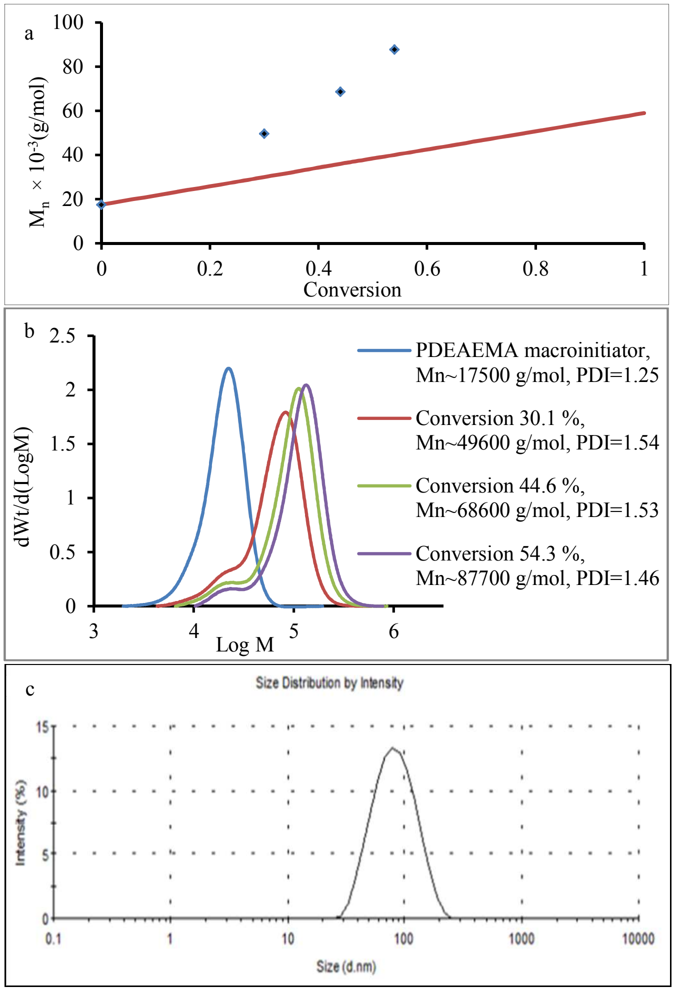


Figure 8 Nitroxide-mediated emulsion copolymerization of MMA and styrene initiated with Poly(DEAEMA-*co*-S) macroinitiator at 90 ºC (exp. 2 Table 1) (a) number average molecular weight versus conversion, (b) Size exclusion chromatograms at various monomer conversions, (c) Intensity distribution of particles size from DLS.

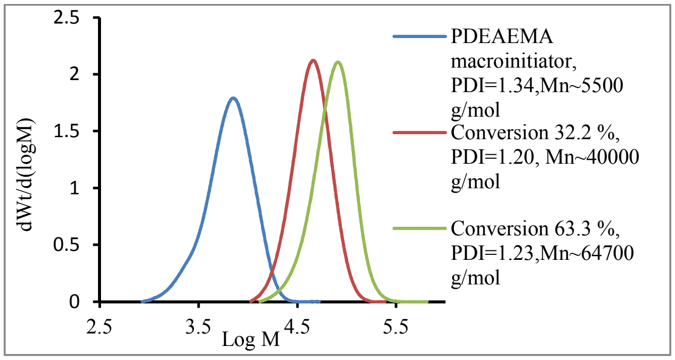
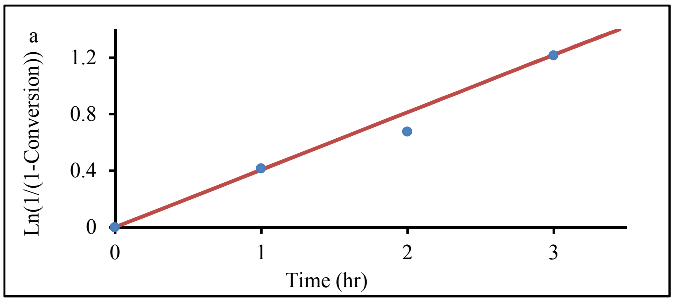


Figure 9 Size exclusion chromatograms at various monomer conversions for nitroxide-mediated emulsion copolymerization of DEAEMA and styrene at 90 ºC with f_{s0}=0.08.

with molecular weight less than 5000 g.mol^{-1} in hexane or diethyl ether were not successful.

DMAEMA is another pH-sensitive monomer with a structure similar to DEAEMA. It has higher water-solubility (more hydrophilic) which can be helpful in redispersion of a dried latex. Furthermore, its precipitation in hexane is considerably easier compared to DEAEMA. Thus, poly(DMAEMA-*co*-S)-SG1 macroinitiator with M_n=3870 g.mol^{-1} was synthesized and readily precipitated in hexane (exp. 4 Table 1). It was then used as a macroinitiator instead of poly(DEAEMA-*co*-S)-SG1. The macroinitiator concentration was increased while the length of the second block decreased. Results are shown in Figure 10. Final conversion increased to more than 70%. Ln [1/(1-conv.)] increased almost linearly with time and the polydispersity of the latex decreased to 1.18 (Figure 10). As shown in Figure 10, size exclusion chromatograms of the macroinitiator completely shifted to the right, and there was no visible shoulder which confirms that most of the macroinitiator chains were living.

In all of the synthesized latexes, coagulation occurred immediately after neutralizing the latex with sodium hydroxide. In other words, all the latexes were easily switched off. After separation of the latex particles by centrifugation, washing with DI water to remove the residual salt, drying under air for 24 h, and grinding, the dried latex powders were partially redispersible in carbonated water with CO_2 bubbling for 30 minutes and followed by sonication for 10 minutes. Increasing the period time of CO_2 bubbling and the number of sonication cycles improved the redispersibility of the latexes. Interestingly, those latexes dried under air without neutralization by NaOH, were readily redispersible by water addition with a few minutes sonication. Chain entanglements of the polymers in the particle shell may affect the CO_2-redispersibility of the latexes.



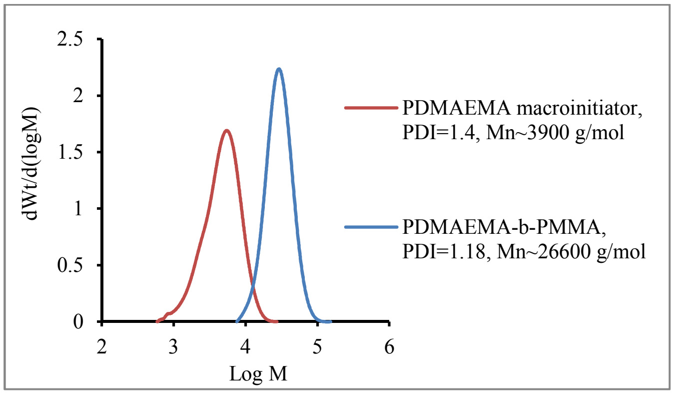


Figure 10 Emulsion copolymerization of MMA and styrene (initial molar fraction of styrene: f_{s0}=0.1) at 90 ºC initiated by poly(DMAEMA-*co*-S)-SG1 macroinitiator (exp. 4 Table 1), (a): Ln [1/(1-conversion)] vs time plot, (b): Size exclusion chromatograms at various monomer conversions.

Conclusions

The nitroxide-mediated polymerization of DEAEMA and DMAEMA using either a bicomponent system of VA-061 as initiator and SG1 as nitroxide, or a monocomponent system of NHS-BlocBuilder led to excellent results in terms of control and livingness of the polymerization reactions. The synthesized poly(DEAEMA-*co*-S)-SG1 and poly(DMAEMA-*co*-S)-SG1 macroalkoxyamines were used for the first time as stabilizers and macroinitiators in their protonated form in the nitroxide-mediated surfactant-free emulsion polymerization of MMA and small amount of styrene based on the polymerization-induced self-assembly (PISA) mechanism. The polymerizations showed the features of controlled and living polymerizations. The final latex displayed a monomodal particle size distribution with particle sizes between 70 and 90 nm, was pH-responsive and was easily coagulated by neutralization with NaOH. Redispersion of those NaOH-neutralized and dried latexes in carbonated water was difficult; however, latexes dried under air were easily redispersed.

Author Information

Corresponding Author
*E-mail: Michael.cunningham@chee.queensu.ca

Acknowledgment

We thank National Sciences and Engineering Research Council of Canada, and the Ontario Research Chairs Program (Cunningham) for financial support and Arkema Inc. for providing BlocBuilder.

Notes and references

1. S. Lin and P. Theato, *Macromol. Rapid Commun.*, 2013, **34**, 1118–33.
2. M. H. Li and P. Keller, *Soft Matter*, 2009, **5**, 927.
3. J. Pinaud, E. Kowal, M. Cunningham, and P. Jessop, *ACS Macro Lett.*, 2012, **1**, 1103–1107.
4. B. Yan, D. Han, O. Boissière, P. Ayotte, and Y. Zhao, *Soft Matter*, 2013, **9**, 2011.

5. E. G. Kelley, J. N. L. Albert, M. O. Sullivan, and T. H. Epps, *Chem. Soc. Rev.*, 2013, **42**, 7057–71.
6. M. J. Manganiello, C. Cheng, A. J. Convertine, J. D. Bryers, and P. S. Stayton, *Biomaterials*, 2012, **33**, 2301–9.
7. Y. Tang, S. Y. Liu, S. P. Armes, and N. C. Billingham, *Biomacromolecules*, 2003, **4**, 1636–45.
8. X. Zhang, J. Xia, and K. Matyjaszewski, *Macromolecules*, 1998, **31**, 5167–9.
9. F. Zeng, Y. Shen, and S. Zhu, 2002, 1113–1117.
10. L. Gan, P. Ravi, B. A. O. W. E. I. Mao, and K. Tam, *J. Polym. Sci., Part A Polym. Chem.*, 2003, **41**, 2688–2695.
11. A. E. Smith, X. Xu, and C. L. McCormick, *Prog. Polym. Sci.*, 2010, **35**, 45–93.
12. Q. Xiong, P. Ni, F. Zhang, and Z. Yu, *Polym. Bull.*, 2004, **53**, 1–8.
13. M. Sahnoun, M.-T. Charreyre, L. Veron, T. Delair, and F. D'Agosto, *J. Polym. Sci., Part A Polym. Chem.*, 2005, **43**, 3551–3565.
14. A. Goto, A. Ohtsuki, H. Ohfuji, M. Tanishima, and H. Kaji, *J. Am. Chem. Soc.*, 2013, **135**, 11131–9.
15. J. Lokaj, P. Vlcek, and J. Kriz, *Macromolecules*, 1997, 7644–7646.
16. K. Bian and M. F. Cunningham, *J.Polym. Sci., Part A Polym. Chem.*, 2006, **44**, 414–426.
17. C. Zhang and M. Maric, *Polymers*, 2011, **3**, 1398–1422.
18. D. Han, X. Tong, and Y. Zhao, *ACS Macro Lett.,* 2012, **1**, 57-61.
19. X. Su, P. G. Jessop, and M. F. Cunningham, *Macromolecules*, 2012, **45**, 666–670.
20. M. Zhang, J. He, J. Mao, C. Liu, H. Wang, Y. Huang, and P. Ni, *Colloids Surfaces A Physicochem. Eng. Asp.*, 2010, **360**, 190–197.
21. Q. Zhang, G. Yu, W.-J. Wang, B.-G. Li, and S. Zhu, *Macromol. Rapid Commun.*, 2012, **33**, 916–21.
22. Q. Zhang, G. Yu, W. Wang, H. Yuan, B. Li, and S. Zhu, *Macromolecules*, 2013, **46**, 1261–1267.
23. S. Shahalom, T. Tong, S. Emmett, and B. R. Saunders, *Langmuir*, 2006, **22**, 8311–8317.
24. M. F. Cunningham, *Prog. Polym. Sci.*, 2008, **33**, 365–398.
25. J. Gohy, *J. Adv. Polym. Sc*i. 2005, **190**, 65–136
26. G. Riess and C. Labbe, *Macromol. Rapid Commun.*, 2004, **25**, 401–435.
27. A. Lavasanifar, J. Samuel, and G. S. Kwon, *Adv. Drug Deliv. Rev.*, 2002, **54**, 169–90.
28. G. Odian, *Principles of Polymerization*, John Wiley & Sons, Hoboken, New Jersey, Fourth Edi., 2004.
29. B. Charleux, G. Delaittre, J. Rieger, and F. D'Agosto, *Macromolecules*, 2012, **45**, 6753–6765.
30. J. Vinas, N. Chagneux, D. Gigmes, T. Trimaille, A. Favier, and D. Bertin, *Polymer*, 2008, **49**, 3639–3647.
31. J. Nicolas, L. Mueller, C. Dire, K. Matyjaszewski, and B. Charleux, *Macromolecules*, 2009, **42**, 4470–4478.
32. N. C. B. V. Butun, S. P. Armes, *Polymer*, 2001, **42**, 5993–6008.
33. P. Cotanda, D. B. Wright, M. Tyler, and R. K. O'Reilly, *J. Polym. Sci., Part A Polym. Chem.*, 2013, **51**, 3333–3338.