Master of Chemical Engineering Thesis

Nitroxide-Mediated Controlled Surfactant-Free Copolymerization of n-BMA and Styrene Using Poly(HEMA)-Based Macroalkoxyamine Initiator

Wenwen Mei

260663831

Department of Chemical Engineering
McGill University
Montréal, Québec, Canada

A Thesis submitted to McGill University in partial fulfillment
of the requirements of the degree of Master of Engineering

August 2016

Abstract

N-tert-butyl-N-1-diethylphosphono-2,2-dimethyl propyl (SG1)-capped poly(2-hydroxyethyl methacrylate-*ran*-acrylonitrile) macroalkoxyamines were synthesized in 50wt% DMF solution using nitroxide-mediated polymerization (NMP) with a initial molar feed composition of acrylonitrile $f_{AN,0}$ = 0.14 for use in suspension polymerization. Narrow molecular weight distribution (Đ <1.35) was observed with a range of number average molecular weights *Mn* from 4 000 g·mol^{-1} to 19 000 g·mol^{-1}. A separate experiment was carried out using the same reaction conditions to follow the kinetics of NMP of 2-hydroxyethyl methacrylate (HEMA) and acrylonitrile (AN). A linear growth of M_n with conversion was observed, indicating a good control for the NMP of HEMA/AN. The SG1-capped HEMA-based macroinitiators were used both as initiators and surfactants in the copolymerization of n-butyl methacrylate and styrene with a small amount of triethylamine, which depronated hydroxyl groups and solubilized the HEMA-based polymer in water. The weight ratio of triethylamine to macroinitiator was adjusted from 0.28 to 0.9 accordingly. Using water as the continuous phase, the polymerization is in-between an emulsion polymerization and a suspension polymerization, in the absence of surfactant. The latex obtained was characterized by dynamic light scattering (DLS) and gives *Z*-average particle size ranging from 150-200 nm. Feasibility of this method was confirmed by the successful chain extension of the poly(HEMA-*ran*-AN) macroinitiator, yielding block polymer with *Mn* ranging from 18 000 g·mol^{-1} to 55 000 g·mol^{-1} according to gel permeation chromatography. Molar composition of the recovered block polymers was determined by ^{1}H NMR analysis, confirming the successful incorporation of the second block.

Résumé

Poly((2-hydroxyéthyl) méthacrylate-*ran*-acrylonitrile) P(HEMA-*ran*-AN) macro-alkoxyamines terminés par le nitroxide N-*tert*-butyl-N-1-diéthylphosphono-2,2-diméthyl propyl (SG1) furent synthétisés en solution dans 50 masse% de DMF en utilisant la polymérisation radicalaire contrôlée en présence de radicaux nitroxydes (NMP). La composition molaire initiale d'acrylonitrile fut de $f_{AN,0}$ = 0.14 et la polymérisation en suspension fut appliquée. Une étroite distribution moléculaire fut observée (Đ <1.35) avec une masse molaire moyenne en nombre (M_n) variant de 4 000 g·mol^{-1} à 19 000 g·mol^{-1}. Une expérience en parallèle fut menée se basant sur les mêmes conditions expérimentales afin de suivre la cinétique de copolymérisation du monomère HEMA avec le monomère AN. Une augmentation linéaire de M_n avec la conversion X fut mesurée, indiquant un bon contrôle de la copolymérisation HEMA/AN par NMP. Les macro-amorceurs à base d'unités répétitives HEMA et terminés par SG1 furent utilisés en tant qu'amorceurs et surfactants pour la copolymérisation du n-butyl méthacrylate avec le styrène. Une petite quantité de triéthylamine fut ajoutée dans le mélange réactionnel afin de déprotoner les groupes hydroxyles et solubiliser le polymère à base d'HEMA dans l'eau. Le rapport massique de triéthylamine par rapport au macro-amorceur fut ajusté de 0.28 à 0.90. En utilisant l'eau en tant que phase continue, cette polymérisation se situe entre la polymérisation en émulsion et la polymérisation en suspension, en l'absence de surfactant. Le latex obtenu fut caractérisé par diffusion dynamique de la lumière (DLS) et donna une taille moyenne de particule allant de 150 à 200 nm. La faisabilité de cette technique fut confirmée par l'extension de chaîne concluante du macro-amorceur P(HEMA-*ran*-AN), produisant un copolymère à blocs avec M_n variant de 18 000 g·mol^{-1} à 55 000 g·mol^{-1}, selon les mesures GPC. La composition molaire du copolymère à blocs purifié fut évaluée par ^{1}H NMR, confirmant l'incorporation du second bloc.

Acknowledgement

Foremost, I would like to thank my supervisor, Prof. Milan Marić, for his continuous and valuable guidance, mentoring and support throughout the whole project. His patience and generous help for guiding a novice into the wonderful world of polymers are greatly appreciated. His rigorous scholarship, intellectual curiosity, self-discipline, as well as diligence and integrity set a good example for what a scholar should be like, and will continuously motivate me in my personal development.

I would like to thank all of my current and past colleagues at McGill University, for all the great discussions we had. I'm grateful for their generous sharing of their experience both in their research and in life. Without them, the great environment for research could not be formed. Specially, I want to thank Adrien for his generous sharing of his lab experiences and translation for the abstract in French, I also want to thank Royal who helped me a lot in editorial work.

I would to thank the Department of Chemical Engineering of McGill University, which offers a great platform for exploring the fantastic world of Chemical Engineering. I'm grateful for all of the kind help provided by all the staff. I want to thank the Chemistry Department for the use of their NMR facility, and I'm extremely grateful for Robin Stein, who gave us a lot of instructions and was always willing to help. Without her enthusiasm for students, the analytic work provided from NMR would not go that smoothly.

Finally, I want to thank the Department of Chemical Engineering for financial support through the Eugene Ulmer Lamothe scholarship and NSERC grant. Without all the help provided by others, this project would not be possible. It's impossible to list all the help I got from others, but for all the help I received, I earnestly appreciate it.

Thank you.

Contribution of Authors

This thesis is a manuscript-based thesis, which contains one manuscript where I am the first author and have done the majority of the work. As a contribution to the manuscript, I performed all of the polymer synthesis, characterization and interpretation of the results. All writing, including tables and figures, were produced by me. Prof. Milan Marić performed the editing and aided with some of the writing.

Table of Contents

1. General Introduction

The demand for materials with specific functionalities has long been the driving force for modern technologies. Often, impact on the environment, processing technology and cost are key concerns for practical application of new materials. Polymers have long been accepted as suitable alternatives to metals and ceramics due to their light weight and ease of fabrication [1]. To achieve desired functionalities, copolymers are designed, which combine the properties of the constituent co-monomers. Copolymers can be classified according to microstructure, which describes the arrangement of monomers throughout the polymer chain: alternating, block, graft, star and statistical [1]. Each of these microstructures can lead to dramatically different properties.

Polymers can also be classified according to the mechanism of reaction used in their synthesis: 1) step-wise polymerization 2) free radical (addition) polymerization 3) living polymerizations (eg. ionic)[1-3]. Step-wise polymerization occurs when monomers or polymers can react with one another at any time without forming active species (the functional groups on the monomer/polymer ends serve as the linkers), which distinguishes itself from the latter two. Examples of products derived from step-wise polymerization are nylons, polyesters, polyurethanes and polycarbonates. Free radical polymerization, as its name suggests, requires free radicals for initiation and chain propagation. Typical polymers produced using this method are poly(ethylene) or poly(styrene), which are derived from vinyl-containing monomers. Similarly, ionic polymerization requires active ionic species that initiate the monomer instantaneous by a highly reactive initiator[1] (eg. organometallic species such as butyl lithium).

Conventional radical polymerization has been effective for statistical and graft copolymerization; however, it has long been a target of the polymer synthesis community to combine the ease of radical polymerization with the control of architecture enabled by living polymerizations [4-7]. Over the last 25 years, such a polymerization has been developed [4, 5,

8-15]. This kind of polymerization is known as Reversible-Deactivation Radical Polymerization (RDRP, which is the term recommended by IUPAC to replace the formerly widely-used “controlled radical polymerization”), and it includes variants such as stable-free radical- polymerization (SFRP), atom transfer radical polymerization (ATRP), and degenerative transfer radical polymerization (RAFT). Conceptually, SFRP is the simplest [9, 13, 16-19]. One of the most developed methods in SFRP is nitroxide-mediated radical polymerization (NMP), which is our main interest here.

One of the most desirable features of conventional radical polymerization is that it can be performed in dispersed aqueous media such as emulsion polymerization [20]. With RDRP, this can be still done while also synthesizing (co)polymers with the desired architecture. Such polymerizations in an aqueous continuous phase are not possible by living polymerization [17]. There are numerous advantages for conducting polymerizations in dispersed aqueous media. Besides the obvious control of heat transfer, handling of the latex is simple and environmentally friendly, as volatile organic content (VOC) is dramatically reduced. The latter is particularly important in the coatings and paint industries. One issue that does remain with conventional radical emulsion polymerization is the use of surfactants, which can negatively impact some properties of the film once dried. In the following thesis, I aim to develop a stable surfactant-free polymerization in dispersed aqueous media using NMP, which is in-between emulsion polymerization and suspension polymerization, without the use of surfactants. Both suspension and emulsion polymerization are widely applied in industry. Suspension polymerization is a typical process for producing important polymers like polystyrene, poly (vinyl chloride), polyacrylates and poly (vinyl acetate) while emulsion polymerization has been the dominant process for synthesis of poly(vinyl actate), poly (chloroprene) and poly (acrylic ester) copolymers [17, 21]. This combination of NMP with heterogeneous process will contribute to the development of new coating varnishes using greener processes. In this thesis, Chapter 2 consists of a literature review of CRP and its application in dispersed media. Chapter 3 describes the synthesis of poly(hydroxyethyl methacrylate-*ran*-acrylonitrile) (HEMA-*ran*-AN) macro alkoxyamines by NMP and its

application in surfactant-free copolymerization of n-butyl methacrylate/styrene (BMA/S) mixture in aqueous media.

2. Literature Review

2.1 Controlled Radical Polymerization

Polymer chemists have long sought to alter and tune the properties of the materials they synthesize through methods such as copolymerization or changing the polymerization mechanism. One of the greatest contributions made in polymer chemistry was the development of living polymerization, which greatly facilitates the synthesis of tailored polymers with desirable and predictable molar masses, compositions, topologies and functionalities. The term 'living polymerization' was introduced as early as 1956 [22], and refers to a chain polymerization that proceeds without irreversible chain breaking events, such as chain transfer and chain termination. However, living polymerization requires strict control over both reagent purity and reaction conditions, which hinders its wide-spread industrial application beyond niche products. [18]. In contrast to living polymerization, CRP superficially mimics the features of living polymerization: linear growth of degree of polymerization with conversion, narrow molecular weight distribution (dispersity < 1.5) and ability of active chain ends to re-initiate a second batch of monomers.

Among all of the different CRP (controlled radical polymerization) methods, nitroxide-mediated polymerization (NMP; also know as stable free radical polymerization (SFRP)) stands out for its simplicity and for the lack of extensive post-polymerization clean-up required, such as the removal of metal ligands like its counterpart ATRP (Atom Transfer Radical Polymerization) [4, 16]. Both NMP and ATRP rely on a reversible termination step to control the radical species concentration, thus minimizing the possibility of irreversible chain termination events. A brief illustration of NMP is shown in Figure 1.

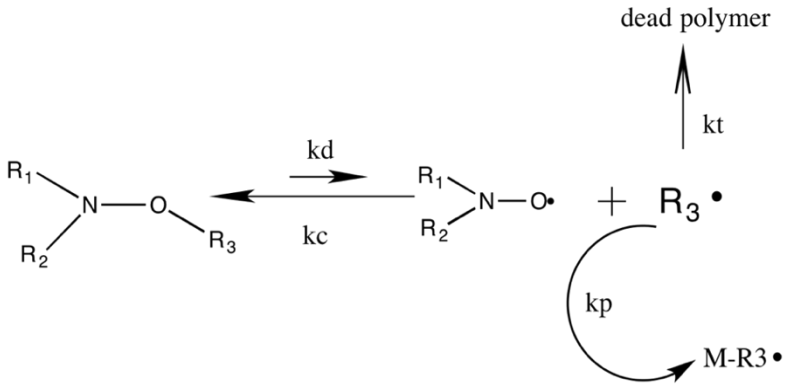


Figure 1: Simplified kinetic scheme for nitroxide mediated polymerization

In NMP, a stable nitroxide radical is used to "control" polymerization of the propagating free radicals [23]. Commonly used nitroxides for NMP are TEMPO, SG1, TIPNO. TEMPO is used for controlling styrenics while SG1 and TIPNO are capable of controlling polymerization of styrenics, alkyl acrylates, acrylic acid, acylamides and dienes[16]. Unimolecular alkoxyamines, such as BlocBuilder-MAMA, which is commercially available, can also be used (Figure 2) [24]. The availability of the MAMA-BlocBuilder is particularly relevant as it is more labile, thereby drastically reducing polymerization times and it can be used at much lower temperatures compared to first-generation nitroxides such as TEMPO[25]. In particular, BlocBuilder is very promising where dispersed media is concerned, due to the water-solubility of the carboxylic acid functional group, when neutralized with a base [25].

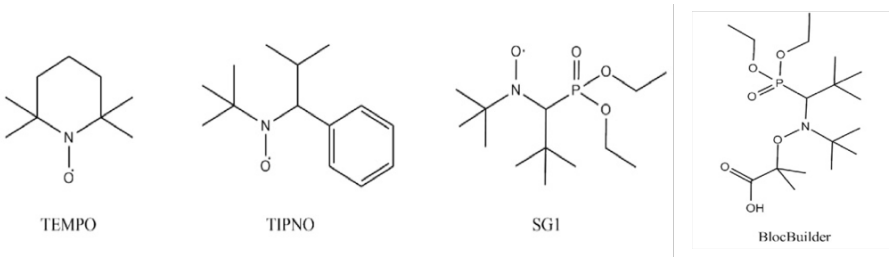


Figure 2: Common nitroxides used for NMP and commercially available alkoxyamine initiator

2.2 Controlled Radical Polymerization in Dispersed Aqueous Media

Heterogeneous polymerization processes are readily applicable for radical polymerization in dispersed aqueous media. Here, a brief introduction will be given to distinguish between the different types of heterogeneous polymerization systems.

Table 1 gives several parameters for different dispersion systems. A short description of heterogeneous polymerization processes, including suspension, emulsion, and miniemulsion is given below. Some work related to NMP with these polymerization processes are also

presented, which give insights into our work which is based on applying NMP techniques in dispersed media.

Table 1 The Different Types of Heterogeneous Polymerization System [17]

type	Typical particle size	Droplet size	initiator	Continuous phase	Discrete phase
emulsion	50-300nm	~1-10nm	Water-soluble	Water	Initially absent, monomer-swollen polymer particles form
Suspension	>1um	~1-10um	Oil-soluble	Water	Monomer + formed polymer in pre-existing droplets
Mini emulsion	30-100nm	~30nm	Water or oil soluble	Water	Monomer, co-surfactant + formed polymer
Inverse emulsion	100-1000nm	~1-10um	Water-or-oil soluble	oil	Monomer, co-surfactant + formed polymer

In suspension polymerization, an oil-soluble initiator is used, generally yielding relatively large particle sizes of the dispersed phase. The particle size of suspension polymerization varies from about 100 nm up to about 1-2 mm, depending on the stirring speed, volume ratio of monomers to suspension medium, concentration of stabilizer and viscosities of both phases [21]. The reaction is carried out in the dispersed droplet phase, on the surface where stabilizers are adsorbed to prevent colloidal coalescence.

For emulsion polymerization, in contrast, the water-soluble initiator resides solely in the aqueous phase and thus the monomer droplets serve only as monomer reservoirs. Another feature of emulsion polymerization is the use of a surface-active agent (surfactant or emulsifier), which is used at a concentration above the critical micelle concentration (cmc) to form micelles. The formed micelles provide polymerization loci and are swelled with monomers (a small concentration is present that is sufficient to be water-soluble). However, due to the complexity of the kinetics of emulsion polymerization, a miniemulsion system is often studied, since it avoids the complex nucleation [25]. The complex nucleation mechanism could be either micellar or homogeneous, while in both cases initiator decomposes in aqueous phase and form oligoradicals which yield final particles.

The central feature of miniemulsion polymerization is that particles are generated from polymerization taking place within monomer droplets (usually 50− 500 nm in diameter; monomer droplet nucleation) [1]. The particle generation can be accomplished by using a strong shear force, for example by applying an ultrasonicator [26, 27]. Low energy alternatives have also been developed recently to avoid the high-energy mixing that is required for ultrasonication. One of them is an *in-situ* surfactant technique based on the *in situ* formation of surfactant at the oil–water interface during (low-energy) mixing of the two phases[28-31].

Another key difference between miniemulsion and other dispersion systems is the addition of a 'co-surfactant' such as hexadecanol or an ultra-hydrophobe such as hexadecane[32]. Since a miniemulsion system is a thermodynamically unstable but kinetically stable system, the total interfacial area reduces to minimize the interfacial energy, either by coalescence or Ostwald ripening [17, 33-36]. By building up an osmotic pressure within the monomer droplets, the diffusion of monomers from small particles to large ones (Ostwald ripening) is prevented. This is the mechanism by which the hydrophobe behaves, and hence enhanced stabilization of tiny monomer droplets is achieved[37].

Considering the particle size of miniemulsion, the effect of compartmentalization cannot be neglected. Compartmentalization refers to the physical isolation of reactants in discrete confined spaces (polymer particles and/or monomer droplets), and comprises two separate effects: the segregation effect and the confined space effect [38]. However, no experimental data has been provided to confirm this effect for SG1, and this could be due to the following reasons: 1) the relatively high water solubility of SG1, which counteracts the confined space effect on deactivation, 2) the particle size not being sufficiently small, as the higher equilibrium constant of SG1 leads to a higher concentration, which requires smaller particles for compartmentalization to be manifested, comparing with TEMPO mediation [39, 40]. For TEMPO, several studies have investigated the compartmentalization effect either through simulations or experiments [28, 37-39, 41-43].

There is no clear consensus about how the compartmentalization effect would influence the polymerization in small particles. Charleux used a Smith-Ewart approach to predict that the decrease in particle size would lead to faster polymerization rates and a broader molecular weight distribution [44] , while Zetterlund and Okubo predicted that this would lead to a

decrease in polymerization rate and a lower dispersity, based on their simulation results[38]. Maehata et al. [45] observed a lower polymerization rate in smaller particles when they performed TEMPO-mediated styrene miniemulsion, and they attributed the reduction of polymerization rate to a combination of factors. For TEMPO-mediated styrene miniemulsion, a generally accepted factor is the geminate termination of thermally generated radicals, which is addressed by Butte [46], Zetterlund and Okubo [38] and Pan *et al* [47]. For the three dispersed systems mentioned above, elaborate choice of a suitable stabilizer, surfactant and hydrophobe would be important factors influencing the system stability and hence the successful polymerization.

2.3 Water-soluble SG1-based Alkoxyamine in Dispersed Media

Although applying controlled radical polymerization in dispersed media has obvious advantages, there are also several concerns. For instance, this method requires effective initiation in aqueous media if the polymerization is conducted in emulsion; the polymerization temperature should be relatively low since conducting polymerization reactions at higher temperature (>100°C) in aqueous media requires more costly pressurized reactors. Finally, control of the polymerization will be affected by the partition of the nitroxide mediator between aqueous phase and oil phase. Since TEMPO has a lower activation rate than SG1, it is favorable to use SG1 in dispersed media since the temperature is lower (~90°C). Examples of using SG1 and a water-soluble initiator like potassium persulfate (KPS) can be found in several reviews [20, 28, 37, 48]. In the following section, the application of water-soluble SG1-based alkoxyamines in dispersed media will be the focus.

Nicolas et al. [49, 50] first reported the use of SG1-based water-soluble alkoxyamines, called A-H in the acid form, to polymerize n-butyl acrylate and styrene in miniemulsion. Investigation into the use of SG1-based water soluble alkoxyamines was greatly promoted by the BlockBuilder-MAMA which was originally synthesized by Tordo's research group at Aix-en-Marseilles and developed by Arkema. This novel SG1-based alkoxyamine has a very high dissociation rate, leading to a fast and quantitative initiation step. This not only lowers the reaction temperature but also waives the extra addition of free SG1 to efficiently control the polymerization of styrene (and?) even n-butyl acrylate in bulk [50]. It exhibits surface activity in aqueous media resulting from the hydrophilicity of the carboxylic acid function

and hydrophobicity of SG1 group. It was also observed that MAMA has a cmc of 0.065mol/L, which is above the concentration of initiator used for a typical recipe [25].

Based on these initial results, the same group went a step further to report the use of poly(methacrylic acid)-based macroalkoxyamine initiator in surfactant-free emulsion polymerization of methyl methacrylate [51]. Compared to its counterpart, the water-soluble poly(acrylic acid)-SG1 alkoxyamine macroinitiator, this methacrylate-based macroinitiator exhibited improved initiating efficiencies (close to 100%) while still maintaining a good control of the polymerization. Since then, more studies based on the polymerization-induced self-assembly method have been reported, using water-soluble macroinitiator based on poly(ethylene oxide) methyl ether methacrylate macromonomers [52] or 2-(dimethylamino)-ethyl methacrylate (DMAEMA) [53].

Based on the previous work on applying NMP in dispersed media, I will develop a stable surfactant-free polymerization in dispersed aqueous media using NMP, the methology of which is in-between suspension polymerization and emulsion polymerization.

3. Nitroxide-Mediated Surfactant-free Polymerization of n-butyl Methacrylate Using a Poly (2-hydroxyethyl methacrylate)-based Macroalkoxyamine Initiator

3.1 Abstract

Poly(2-hydroxyethyl methacrylate-*ran*-acrylonitrile) (poly(HEMA-*ran*-AN)) macroinitiators were synthesized first in 50wt% DMF solution using nitroxide-mediated polymerization (NMP) with different number average molecular weights (M_n) ranging from 4 000 g·mol^{-1} to 19 000 g·mol^{-1}with dispersities (Đ) between 1.25 and 1.45 (table 3). The macroinitiator, after solubilization with triethylamine, were further used in surfactant-free copolymerization of n-butyl methacrylate/styrene mixtures (initial molar fraction of styrene $f_{s,0}$ = 0.11-0.12), yielding block polymer with BMA composition ranges from with broaden dispersity (1.40-1.70).

3.2 Introduction

Heterogeneous radical polymerization in aqueous media is one of the most important industrial processes for producing polymers. Consequently, applying controlled radical polymerization in aqueous media is even more desirable as it permits control of microstructure and composition not possible with conventional radical polymerization; such polymerizations have been done in emulsion [54-56] and miniemulsion [32, 47, 50, 57, 58]. Several reviews have given a detailed description of the progress made in this area[17, 20, 28, 37, 40, 48]. Here, the focus is given to the application of water-soluble SG1-based alkoxyamines, due the simplicity of nitroxide-based initiators [25]. Relying on the use of an active hydrophilic precursor (namely macroinitiator) prepared by controlled radical polymerization (CRP) will permit it to extend it with a hydrophobic block in aqueous media. To prepare a hydrophilic macroalkoxyamine, water-soluble monomers were considered. Typical water-soluble monomers are listed in Table 2.

Based on this method, various water-soluble monomers have been applied for the macroinitiating species; monomers such as acrylic acid (AA) [59], methacrylic acid (MAA) [51], 2-(diethyl) aminoethyl methacrylate (DEAEMA) [53], poly (ethylene oxide) methyl

ether methacrylate (PEO) [60] have been reported. However, the use of an acid requires the adjustment of pH because SG1 is unstable at low pH [25]; tertiary amine methacrylate-based monomers undergo hydrolysis at elevated tempearatures [61]. For macromonomer such as poly-(ethylene)oxide methacrylate, an incomplete shift in the GPC chromatograms indicated the existence of dead chains, either formed in the synthesis of macroinitiator or in the reinitiation step, which remains unclear currently[60].

Table 2. Typical Water-Soluble Monomers [17]

Monomers with acidic fuctions	Monomers with basic functions	Monomers with heterocyclic functions	Monomers with neutral hydroxyl functions
Acrylic acid	Acrylamide	2-Vinylpyridine	Allyl alcohol
Methacrylic acid	Methacrylamide	3-Vinylpyridine	2-Hydroxyethyl acrylate
Itaconic acid	N-hydroxymethylacrylamide	4-Vinylpyridine	2-Hydroxyethyl methacrylate
2-sulfoethyl methacrylate	N,N-dimethylacrylamide	4-Methylenehydantatoin	2-Hydroxypropyl methacrylate
Styrenesulfonic	N-isopropylacrylamide	4-Vinyl-3-morpholine	
Ethylenesulfonic acid	N-acetamidoacrylamide	N-vinyl-2-pyrrolidone	
Allenesulfonic acid	2-Aminoethyl methacrylate	1-Vinyl-2-methyl-2-imidazoline	

Changes in pH and ionic strengths will exert a pronounced influence on the polymerization of basic and acidic monomers [17]. In that case, it becomes more complicated to polymerize them in aqueous media. Their stability as a water-structuring center makes them better candidates for preparing hydrogels in biomedical applications [17].

In this thesis, HEMA is copolymerized with acrylonitrile to give hydrophilic polymers with different chain length. These hydrophilic polymers were further used in deprotonated form to initiate the copolymerization of n-butyl methacrylate with styrene, where the poly(HEMA-*ran*-AN) serves as both surfactant and initiator. Three factors: 1) Chain length of macroinitiator; 2) macroinitiator concentration; 3) initial monomer content have been

examined for their influence on polymerization kinetics, control of the polymerization, and colloidal characteristics.

3.3 Experimental

3.3.1 Materials

The monomers 2-hydroxyethyl methacrylate (HEMA, 99%), acrylonitrile (AN, 99%), st yrene (S, 99%) and n-butyl methacrylate (BMA, 99%) were purchased from Sigma-Al drich and purified by passing through a column of basic alumina (Brockmann, Type 1, 150 mesh) mixed with 5% calcium hydride (90-95%, reagent grade). After purificat ion, monomers are sealed in separate round flasks under nitrogen and stored in the re frigerator for further use. Hexane (98.5%), diethyl ether (99%), N,N-dimethylformamid e (DMF, 95%), tetrahydrofuran (THF, 99.5%), tetrahydrofuran (THF, 99.5%, HPLC gr ade), and pyridine (99%) were obtained from Fisher Scientific and used as received. Acetic anhydride (97%) was obtained from ACP Inc. and was used as received. For ^{1}H NMR spectroscopy, deuterated chloroform ($CDCl_3$, >99%) was obtained from Sig ma–Aldrich and dimethyl sulfoxide-D_6 (DMSO, >99%) was obtained from Cambridge Isotopes Laboratories. The 2-((tert-butyl-(1-(diethoxyphosphoryl)-2,2-dimethylpropyl)amin o)oxy)-2-methylpropanoic acid initiator (BlocBuilder,99%) was supplied by Arkema. N-hydroxysuccinimide (NHS, 98%), and N,N'-dicyclohexylcarbodiimide (DCC, 99.9%) w ere purchased from Sigma-Aldrich. Succinimidyl-functionalized BlocBuilder (NHS-Bloc Builder) was synthesized according to the reported procedure [62]. Deionized water w as used for all experiments.

3.3.2 Copolymerization of 2-Hydroxyethyl Methacrylate with Acrylonitrile

Syntheses of poly(HEMA-*ran*-AN) macroinitiator were all performed in a 25 ml three-neck round-bottom glass flask equipped with a condenser, thermal well and a magnetic Teflon stir bar. The flask was placed inside of a heating mantle on a magnetic stirrer. The copolymerization reaction was carried out in dimethylformamide (DMF) solution at 85 °C with a small nitrogen purge. A typical procedure is as follows: a mixture of HEMA (4.815 g, 3.74 mol·L^{-1}) and AN (0.324 g, 0.616 mol·L^{-1}, the initial molar fraction of AN in the comonomer mixture $f_{AN,0} = 0.14$). The NHS-BlocBuilder initiator (0.12 g, 2.6×10^{-2} mol·L^{-1}) was then dissolved in dimethylformamide (5 mL) and were further added to monomer mixture and introduced into a 25 ml three-neck round-bottom reactor all together. The

mixture was deoxygenated with nitrogen for 30 minutes and the reactor was then heated to 85°C at a rate of 10°C·min^{-1}. Time zero for the reaction is taken when the reactor temperature reached 70°C. Reaction time was dependent on the desired chain length. Before using the copolymers as macroinitiators, polymers were precipitated in diethyl ether and further dried under vacuum at room temperature for one day to remove unreacted monomers and solvent. The purified copolymers were measured by GPC after acetylation (the procedure is reported by Bian el. [63]).

3.4 Chain Extension of Poly(HEMA-*ran*-AN) Macroinitiator in 50%wt DMF

Chain extension of poly(HEMA-*ran*-AN) macroinitiator was carried in 50%wt DMF solution for all the macroinitiators prepared. Experimental conditions for the chian extension in 50wt% DMF solution can be found in table 4.

A typical procedure is given: a mixture of n-butyl methacrylate (0.903 g, 2.99 mol·L^{-1}) and styrene (0.087 g, 0.35 mol·L^{-1}, the initial molar fraction of styrene in the comonomer mixture $f_{s,0}$ = 0.11). The poly(HEMA-*ran*-AN) macroinitiator (0.181 g) was then dissolved in dimethylformamide (1.2 g) and were further added to the monomer mixture and introduced into a 15 ml three-neck round-bottom reactor all together. The mixture was deoxygenated with nitrogen for 30 minutes and the reactor was then heated to 90.0°C at a rate of 10.0°C min^{-1}. Time zero for the reaction is taken arbitrarily when the reactor temperature reached around 60.0-70.0°C. Samples were taken periodically and precipitated in hexane and further dried under vacuum at room temperature for one day to remove unreacted monomers and solvent. Before the GPC measurement, all the block polymers were acetylated using the same procedure mentioned above.

3.5 Surfactant-free Copolymerization of n-Butyl Methacrylate and Styrene Using poly(HEMA-*ran*-AN) Macroinitiator in Dispersed Media

Chain extension of poly(HEMA-*ran*-AN) macroinitiator in aqueous media was carried at 85.0°C for all the macroinitiator prepared. A typical procedure is followed: The poly(HEMA-*ran*-AN) macroinitiator MaI-A (MaI-A, 0.118g), water (2.49 g) and triethylamine (0.0579 g) were mixed together in vial and left overnight at room temperature to enable sufficient dissolving of macroinitiator. A mixture of n-butyl methacrylate (0.835 g, 5.875×10^{-3} mol·L^{-1}) and styrene (0.0703 g, 0.675×10^{-3} mol·L^{-1}, the initial molar fraction of

styrene in the comonomer mixture $f_{s,0} = 0.11$) was then introduced to previous mixture. The biphasic system was then introduced into a 15 ml reactor and was deoxygenated with nitrogen for 30 minutes. The reactor was then heated to 85.0°C at a rate of 10.0°C min^{-1}. Time zero for the reaction is taken when the reactor temperature reached 70.0°C. Samples were taken periodically. The apparent molecular weight and particle size were measured by GPC and DLS respectively and described below. Before the GPC measurement, all the block polymers were acetylated using the same procedure mentioned above.

3.6 Analytical Techniques

Gel permeation chromatography (GPC) was used to determine the number average molecular weight (M_n), weight average molecular weight (M_w) and dispersity (M_w/M_n) with HPLC grade THF as the mobile phase. The flow rate was 0.3mL min^{-1} during analysis. The GPC is equipped with 3 Waters Styragel HR columns with the molecular weight ranges are given: (HR1: 10^2 -5× 10^3 g·mol^{-1}, HR2: 5 × 10^2-2 × 10^4 g·mol^{-1}, HR3: 5 × 10^3-6 × 10^5 g·mol^{-1}) and a guard column. The GPC is also equipped with a differential refractive index detector (RI 2410). The molecular weights were determined by calibration against linear, nearly monodisperse poly(methyl methacrylate) (PMMA) standards supplied by Varian.

^{1}H NMR was performed using an Agilent 300 MHz Varian VNMRS with DMSO-d_6 as solvent. For kinetic study for the synthesis of poly(2-hydroxyethyl methacrylate-ran-acrylonitrile) macroalkoxyamines, samples were directly diluted in DMSO-d6 while the recovered block polymer was acetylated before NMR analysis. For the kinetic study of polymerization of HEMA and AN, the molar conversion of HEMA and AN (XHEMA and XAN, respectively) were determined by integration of vinly proton at δ = 6.35 ppm, δ = 6.20 ppm (vinly proton for AN) and δ = 6.05 ppm δ = 5.65 ppm (vinly proton for HEMA) based on -OH proton (δ = 4.7-4.9 ppm) and COOCH2-protons at 3.7-4.1ppm. The overall conversion was molar conversion calculated from monomer conversion as follows: $X_{mol}=X_{AN} \times f_{AN,0} + X_{HEMA} \times f_{AN,0}$ ($f_{AN,0}$ and $f_{AN,0}$ are initial molar fractions of AN and HEMA in monomer mixture).

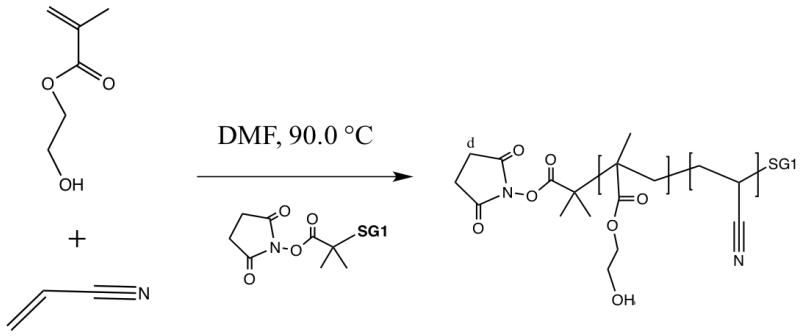
Particle size and dispersity of the particles from the surfactant-free copolymerization were measured using dynamic light scattering (DLS). All DLS measurements were performed with a Malvern Zetasizer Nano equipped with He-Ne laser operating at 633 nm and an avalanche

photodiode detector. The samples were drawn periodically and analyzed using disposable cuvettes. Before performing the measurement, samples were diluted with deionized water.

4. Results and Discussion

4.1 Synthesis of Poly (HEMA-*ran*-AN) Macroinitiator

Scheme 1. Schematic representation of the synthesis of poly(HEMA-*ran*-AN)-SG1 macroalkoxyamine initiators



In NMP, methacrylates have an elevated activation–deactivation equilibrium constant K which makes their polymerization hard to control [64, 65]. For TEMPO, this is a result of the disproportionation reaction between the nitroxide and the growing radical, which yields an alkene chain-end along with a hydroxylamine, which dominates over the reversible combination with the nitroxide. For SG1, despite the absence of a disproportionation reaction between the nitroxide and the growing radicals, the excessively high activation-deactivation equilibrium constants leads to a high concentration of propagating macroradicals, which favors their irreversible self-termination [66]. To address this problem, using a controlling monomer which has a lower K is used with BlocBuilder mediated systems. It has been reported that styrene [66], acrylonitrile [67] and 9-(4-vinylbenzyl)-9H-carbazole (VBK) [68] can all be used as a controlling comonomer at low fractions ~ 1-10 mol% in the initial mixture for polymerizing methacrylates in a controlled manner. For the polymerization of HEMA, acrylonitrile was chosen to try to make the resulting macroinitiator as water-soluble as possible. Synthesis of the poly-(HEMA-*ran*-AN)-SG1 macroalkoxyamine initiators was carried out in DMF solution at 90.0°C, using NHS-BlocBuilder [62] as an alkoxyamine initiator (see Scheme 1) in presence of approximately 15 mol% of acrylonitrile. The polymerizations were quite rapid at 90.0^{o}C for all the reaction conditions used. Reactions were stopped within one hour. The final target M_n for the polymer vary from 8 000 g·mol^{-1}to 20 000 g·mol^{-1}in order to get macroinitiator with a wide range of chain length to eventually study the effect on the subsequent suspension polymerization. Table 1 gives the experimental formulations and main characterization of the macroinitiator prepared.

Table 3. Experimental Conditions used for Synthesis of the Poly(HEMA-*ran*-AN)-SG1 Macroalkoxyamine Initiators at 90.0 °C in DMF Solution

Macro ID	[HEMA] (mol·L^{-1})	[AN] (mol·L^{-1})	[NHS-BB] (mol·L^{-1})	$f_{AN,0}$[a]	M_n (target)[b]	M_n[c] (acetylated)	M_w/M_n	F_{AN}[d]
A	3.74	0.62	0.0359	0.14	14 400	10 000	1.33	0.17
B	3.74	0.62	0.0260	0.14	2 0000	18 100	1.29	0.16
C1	2.66	0.44	0.0461	0.14	8 200	6 300	1.34	0.18

a. initial molar fraction of acrylonitrile in monomer mixture

b. number average molecular weight expected at complete conversion

c. Experimental molecular weight determined by GPC for acetylated polymers in THF at 40°C based on PMMA standards

d. composition of AN in the macro alkoxyamines determined by ^{1}H NMR

The average molecular weight (M_n) was measured after acetylating the raw polymer without further recalculation for HEMA units. Synthesis of poly(HEMA-*ran*-AN) exhibits controlled manner with comparably low dispersities (M_w/M_n ~ 1.3).

To further comfirm that the polymerization yielding the family of poly(HEMA-*ran*-AN) was in a controlled manner, a kinetic study of the NMP of HEMA and AN was followed at the same temperature with the initial molar feed of acrylonitrile $f_{AN,0}$=0.14 in 50wt% DMF solution. The NHS-BB concentration is 0.0314 mol·L-1 with a target molecular weight $M_{n,target}$ (calculated by the M_n at full conversion) of 13 800 mol·L^{-1}. Detailed experimental results are in Figure 3.

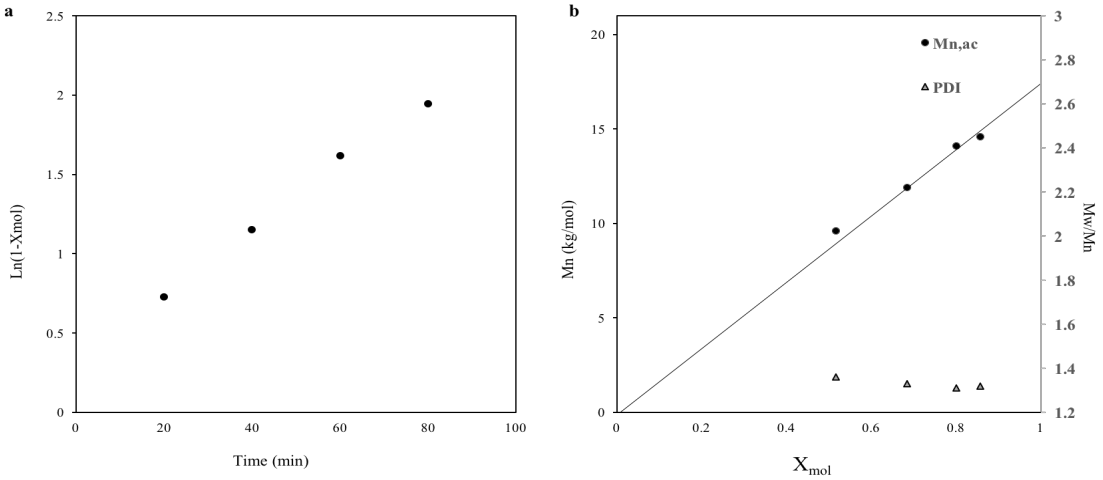


Figure 3. (a) ln[1/(1-Xmol)] vs time plot and (b) evolution of M_n and M_w/M_n (determined by GPC in THF, PMMA calibration) with conversion X_{mol} . The $M_{n,ac}$ is the experimental molecular weight for acetylated polymers. The stragight line in (b) corresponds to the theoretical evolution, note that the theoretical value for the polymers was transformed to acetylated polymers in correspondence to the the experimental results based on acetylated polymers.

The first order plot of ln[1/(1-x)] vs time (figure 3a) shows a linear evolution, and the M_n data points fall close to the theoretical line. These prove that preparation of poly(HEMA-*ran*-AN) family using NHS-BB is in good control with high initiator efficiency.

^{1}H NMR analysis was used to determine the conversion as well as the composition of the macro alkoxyamines. The conversion of monomer was calculated separately by integration of vinly protons (Figure 4), and overall molar conversion was determined by $X_{mol}=X_{AN} \times f_{AN,0} + X_{HEMA} \times f_{AN,0}$ ($f_{AN,0}$ and $f_{AN,0}$ are initial molar fractions of AN and HEMA in monomer mixture).

To determine the composition of the SG1-capped macro alkoxyamines, the sample taken when the reaction was stopped was used. The composition was calculated by the final conversion of monomers (indicated by the vinly peaks from 5.5-6.5 ppm) based on the initial molar fraction of monomers mixture. This gives a ratio between the HEMA and AN in the obtained polymer as below : F_{AN}: $F_{HEMA} = X_{AN} \times f_{AN,0}$ ： $X_{HEMA} \times f_{HEMA,0}$. An example isshown in Figure 5. The composition of the macro alkoxyamines were provided in table 3.

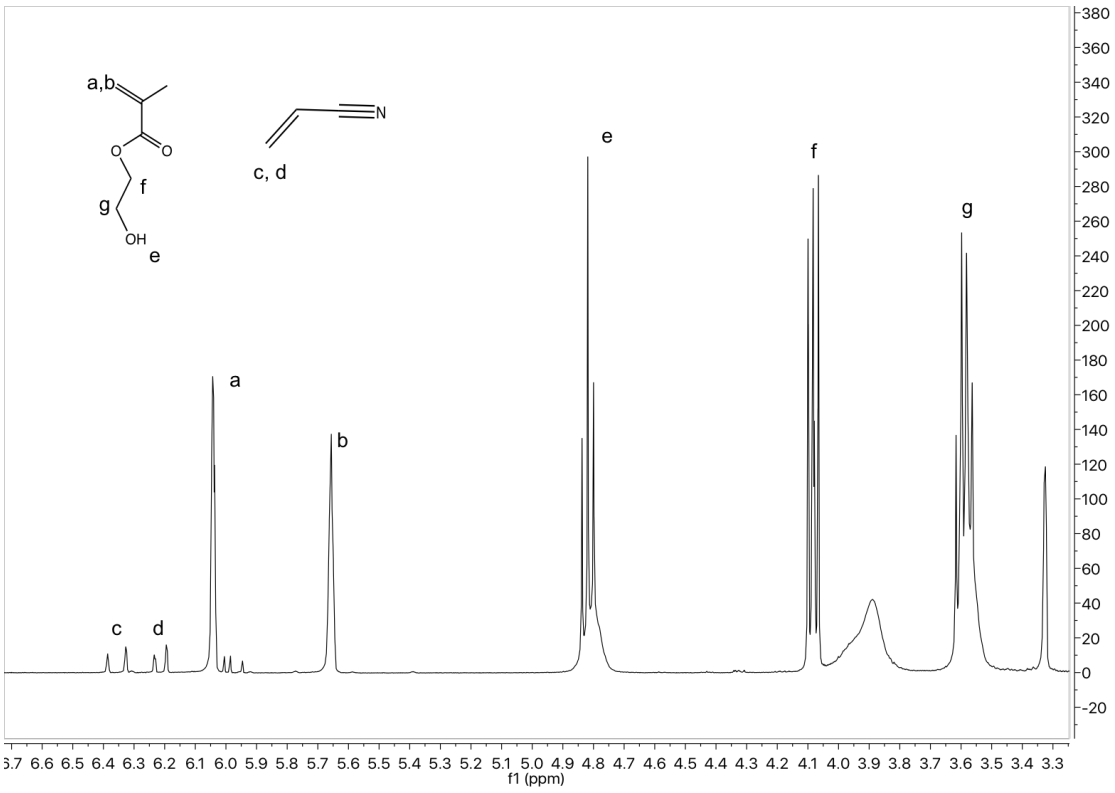


Figure 4. Samples for kinetic study of synthesizing SG1-capped poly(HEMA-*ran*-AN) macro alkoxyamines

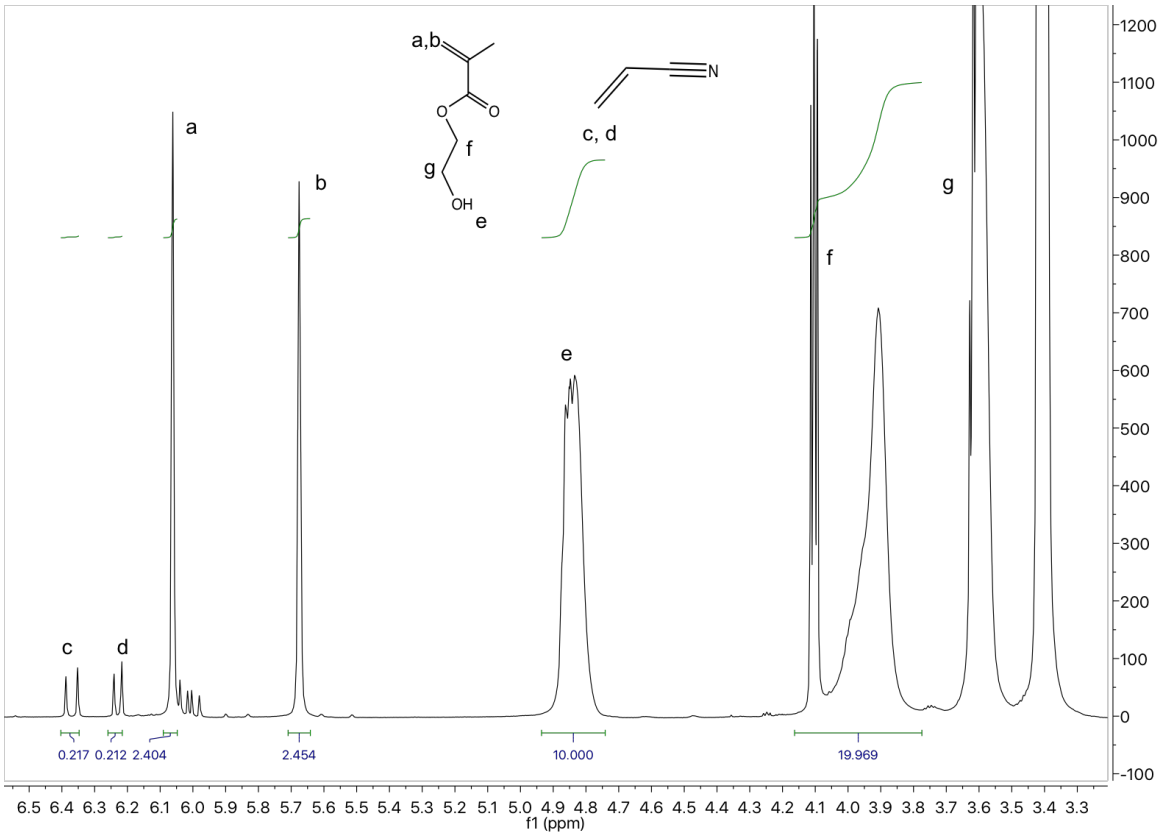


Figure 5. Example of calculation of the composition for SG1-capped poly(HEMA-*ran*-AN) macro alkoxyamine based on monomer conversion determined by ^{1}H NMR

4.2 Chain Extension of Poly(HEMA-*ran*-AN) Macroinitiator in 50%wt DMF

To confirm that the macroinitiators prepared were capped with SG1 and can further initiate a new batch of monomers, chain extension experiments were carried out in DMF solution at 90.0 °C for copolymerization of n-butyl methacrylate with approximately 10 mol% styrene. All the reactions were stopped at 40 minutes while the time zero was set arbitrarily when temperature reached 65.0 °C. Polymers were purified by precipitation in hexane and further dried in a vacuum oven overnight at room temperature. To perform the GPC measurement, the obtained block polymers were acetylated using the same method mentioned above. For all the macroinitiators tested, a complete monomodal shift of GPC chromatograms was observed (see Figure 6).

Table 4. Experimental Conditions used for Chain Extension of the Poly(HEMA-*ran*-AN)-SG1 Macroalkoxyamine Initiators at 90.0 °C in 50wt% DMF Solution

Macro ID	[BMA](mol·L^{-1})	[S](mol·L^{-1})	[Macro](kg·L^{-1})	$f_{s,0}$	$M_n^{a,b}$	M_w/M_n
A	2.99	0.35	0.077	0.12	31 800	1.53
B	2.88	0.33	0.039	0.12	33 600	1.58
C1	2.68	0.41	0.084	0.12	27 700	1.51

a Experimental molecular weight measured after acetylation based on poly (methyl methacrylate) standards
b. All the measurements were performed using THF as solvent at 40°C

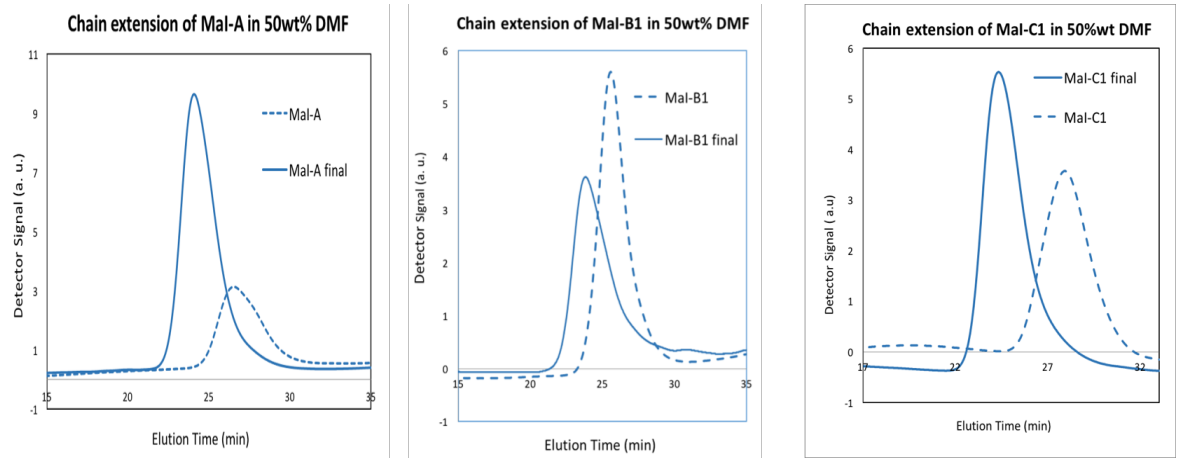


Figure 6. Gel permeation chromatograms of chain extension of macroinitiator performed at 90 °C in 50 wt % DMF solution.

4.3 Surfactant-free Copolymerization of n-butyl Methacrylate and Styrene Using Poly(HEMA-*ran*-AN) Macroinitiator in Dispersed Media

After using the macroalkoxyamine for the chain extension of n-butyl methacrylate with styrene in 50%wt DMF solution and confirming their ability to reinitiate a second batch of monomer, the macroalkoxyamine was further used both as an initiator and a surfactant in polymerizing n-butyl methacrylate and styrene in water. One of the challenges of doing that is poly(HEMA) is merely swellable in water, which makes it hard to distribute in the aqueous phase and stabilize the monomer droplets. To address this problem, triethylamine was used to deprotonate the proton on hydroxyl functional groups. Scheme 2 demonstrated the deprotonation process. Triethylamine is a mild organic base with pKa=10.75. The feasibility of depronating our macroinitiators was tested in vials with various weight ratios of triethylamine and macroinitiator, from 1-0.3. For the macroinitiator with shorter chain length, a sufficient dissolution was reached within several hours, while it takes longer for the macroinitiator with longer chains to reach sufficient dissolution. Also, it is not surprising that the more triethylamine was used, the less time it took for a sufficient dissolution. After deprotonating the macroinitiator in water using triethylamine, the mixture was further used in

surfactant-free copolymerization of n-butyl methacrylate/styrene mixtures, all the experimental conditions can be found in table 5.

Scheme 2. Schematic representation of the deprotonation of poly(HEMA-*ran*-AN)-SG1 macroalkoxyamine initiators

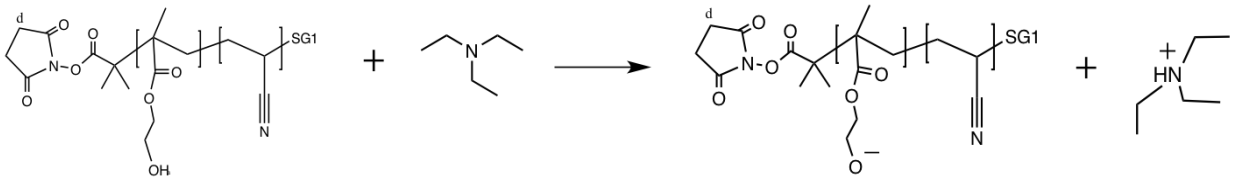


Table 5. Experimental Conditions used for Surfactant-free Copolymerization of n-Butyl Methacrylate and Styrene Using Poly(HEMA-*ran*-AN)-SG1 Macroalkoxyamine Initiators at 85.0 °C

Exp	Macro ID	Concentration ($g \cdot L^{-1}$)[a]	Monomer content[b]	TEA weight ratio[b]	$f_{s,0}$	Reaction time (min)	$M_n/(M_n/M_w)$[c]	*Zave*[d] (nm)
1	C1	45.3	0.338	0.85	0.12	150	18 200/1.61	176 (0.45)
2	C1	45.6	0.343	0.58	0.12	135	23 800/1.40	198 (0.57)
3	C1	42.2	0.346	0.39	0.12	80	25 500/1.57	-
4	C1	48.8	0.331	0.28	0.11	20	9 600/2.0	744 (0.84)
5	A	47.6	0.338	0.50	0.12	130	36 600/1.44	153 (0.25)
6	A	47.6	0.442	0.50	0.12	60	25 200/1.54	154 (0.35)
7	B	42.2	0.397	0.51	0.12	200	51 500/1.64	-

a. weight concentration, calculated by weight of macroinitiator divided by volume of aqueous phase

b. based on the weight of macroinitiator (W_{TEA}/W_{MaI})

c. Experimental molecular weight measured after acetylation based on poly (methyl methacrylate) standards using THF as solvent at 40°C

d. Determined by DLS by diluting samples with deionized water

4.4 Influence of the Concentration of Triethylamine Used

The influence of concentration of triethylamine (TEA) used has been investigated by experiment 1-3. In these experiments, other factors were kept the same while the weight ratio of TEA to water was varied from 0.85 to 0.34. For experiments 1 and 2, the reaction time was 150 minutes while for experiment 3, the experiment was stopped at 80 min due to large aggregation. In all cases, the solution appeared transparent. Improved latex stability could be attributed to a better distribution of macroinitiator in water when the weight ratio of TEA to water was raised. As molecular weight grows, the hydrophobic block increasingly gets longer, leading to aggregation.

In experiment 4, the TEA being used was further lowered with 33%wt TEA (based on weight of macroinitiator). However, despite the aqueous solution of the macroinitiator being transparent (Figure 7), noticeable coagulum occurred within 20minutes, and bimodal peak was observed from the GPC chromatogram. Therefore, the following discussion were only given to experiment 1-3.

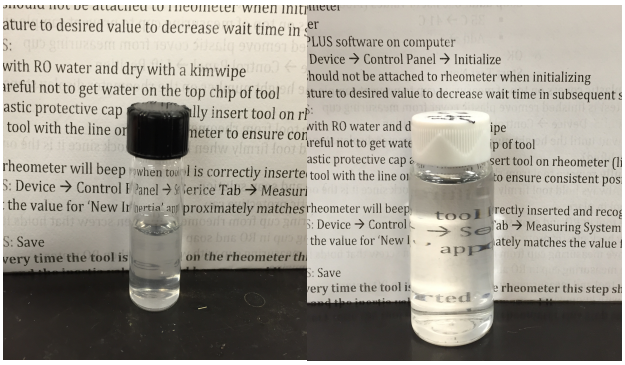


Figure 7. Picture of the MaI-C1 aqueous solution for experiment 4 (left), experiment 2 (right)

For experiment 1, the samples were directly dissolved in THF for GPC measurement. The shift of GPC chromatograms (Figure 8) demonstrated the successful synthesis of block polymer in aqueous media with a small amount of TEA. Tails were observed in all the chromatograms, indicating the existence of uninitiated macroinitiator and/or the oligomers since no fractionation was performed for GPC samples. Furthermore, it should be noted that the interaction between the hydroxyl groups and the GPC columns could not be easily excluded, which may also contribute to the existence of tails in chromatograms. Fracture of the crude product using hexane was able to get rid of the tail, which is demonstrated in Figure 8.

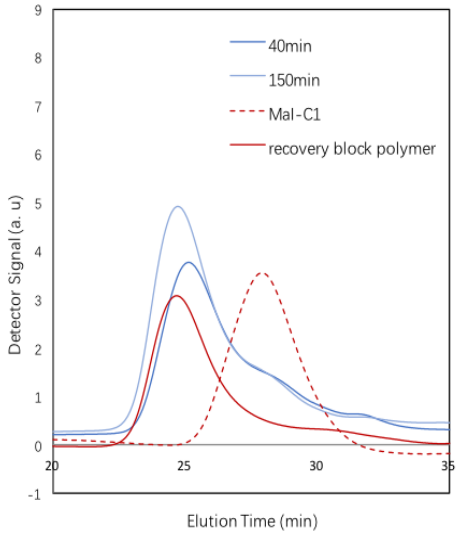


Figure 8. Gel permeation chromatograms of chain extension of MaI-C1 performed at 85 °C in aqueous media. Refer to table 5 for experimental conditions.

To further confirm the cause, particularly to know whether the macroinitiator prepared was capped with SG1, another chain extension experiment was performed using the acetylated MaI-C1. In this way the samples could be directly diluted in THF and used for GPC characterization, without fractionation and the acetylation step in which dead macroinitiators could be easily removed. The reaction was performed in 50wt% DMF at 90.0 °C using n-butyl methacrylate and styrene. A complete shift of the GPC chromatograms (Figure 6) confirmed a high initiating efficiency of MaI-C1. Hence the tails observed in Figure 9 could not be attributed to dead macroinitiator formed in the synthesis process.

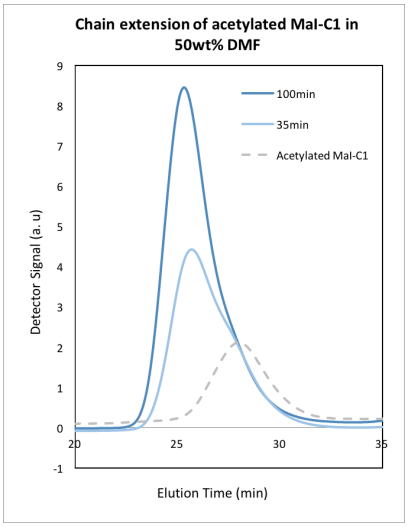


Figure 9. Gel permeation chromatograms of chain extension of acetylated MaI-C1 performed at 90 °C in 50wt% DMF

Experiment 2 was performed with a lower TEA weight ratio. The reaction was stopped at 135 minutes due to a noticeable colloidal aggregation. A lower molecular weight (M_n) for the recovered block polymer was observed from Figure 10, comparing with the block polymer obtained in Experiment 1.

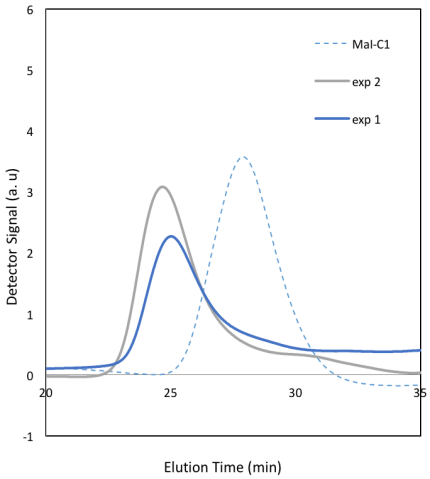


Figure 10. Gel permeation chromatograms of recovered block polymer for experiment 1 and experiment 2, samples were acetylated before performing GPC measurement, The grey line represents the recovered block polymer from experiment 1, and blue line represents the recovered polymer from experiment 2, the dotted line represents the macroinitiator used. Refer to table 5 for experimental conditions.

The plot of molecular weight vs. time (Figure 11) indicates that in both experiments, the molecular weight reached a plateau, which suggests the occurrence of irreversible termination after a certain reaction time. However, more experiments are needed to identify the causes. It seems possible to reach a higher molecular weight when better stirring is applied. More vigorous stirring is expected to give a better distribution of radicals in heterogeneous media, hence decrease the possibility for aggregation of growing radicals, which favors termination resulting from high concentration of radicals in a limited region.

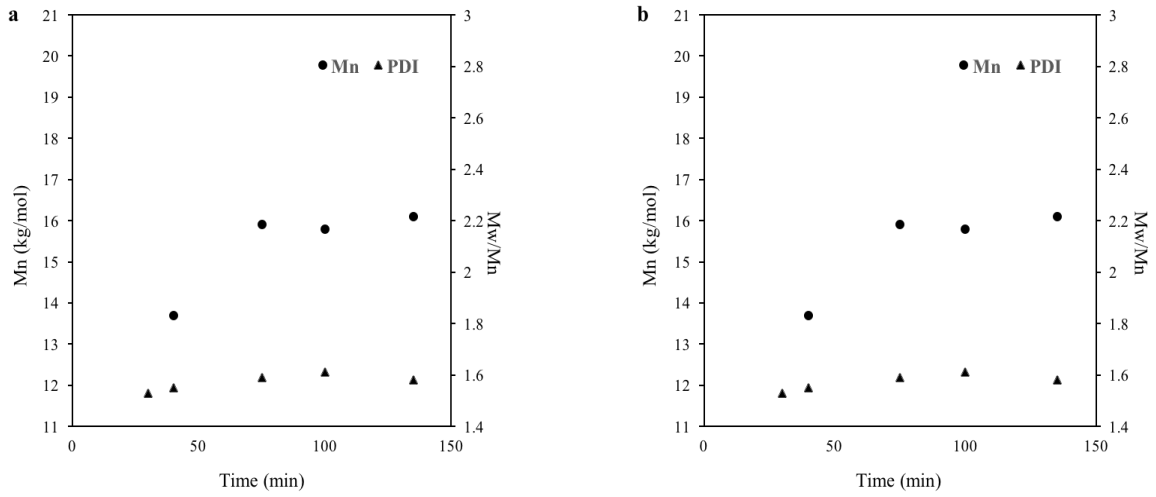


Figure 11. Evolution of M_n and M_w/M_n with time for experiment 1 (a) and experiment 2 (b) (experimental conditions are listed in table 5)

To confirm the assumption that better stirring might increase the molecular weight reached, experiment 3 was performed with a bigger reactor using a bigger stir bar, which gives a better stirring by increasing the contacting area between the stirring bar and reaction medium. In this case, other conditions were kept similar. Reaction was stopped at 80 minutes and the final molecular weight was higher (M_n=25.5 kg·mol^{-1}, M_w/M_n=1.57). Figure 12a shows the GPC chromatogram and Figure 12b gives the plot of molecular weight versus time.

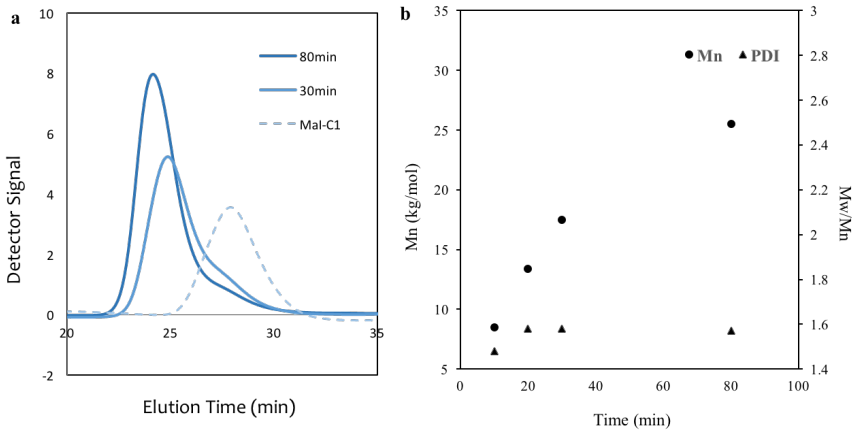


Figure 12. GPC chromatograph (a) and evolution of M_n and M_w/M_n with time (b) for experiment 7 (experimental conditions are listed in table 5)

Hence, the amount of TEA used should be considered if a stable latex is desired. It seems that increasing the amount of TEA used could improve the colloidal stability. However, to further

identify the influence of the amount of TEA used on the kinetics and colloidal properties, more experiments with better stirring conditions are expected, which will give more insights for applying this method to a larger scale.

4.5 Influence of the Monomer Content

To investigate the influence of monomer content, experiments 5 and 6 were carried with all the other factors kept the same. Monomer content was increased from 0.338 to 0.442 (based on water). Experiment 6 was stopped at 60 minutes due to noticeable coagulum. For both reactions, a complete shift of GPC chromatogram was observed (Figure 13), indicating a successful reinitiation step using this method.

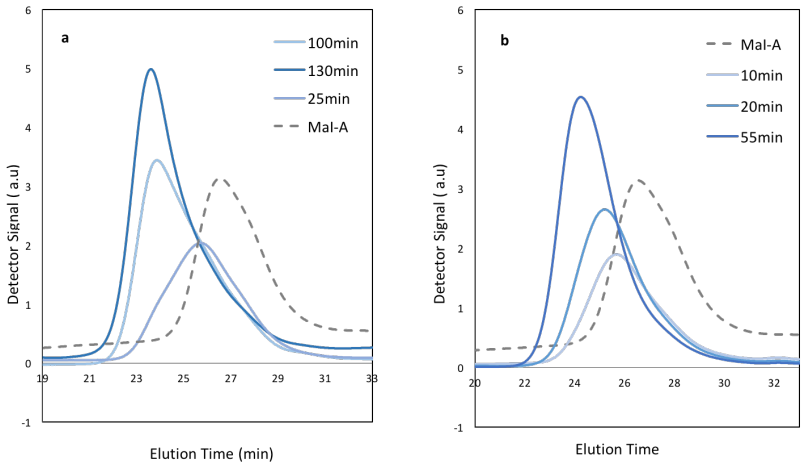


Figure 13. Evolution of the gel permeation chromatograms for experiment 5 (a) and experiment 6 (b) , samples were acetylated before performing GPC measurement. (experimental conditions are listed in table 5)

Figure 14 demonstrates the evolution of molecular weight with time, indicating a linear relationship of M_n and time in both experiments. Since both reaction were carried with the exactly same experimental conditions, it is sensible to conclude that increasing the monomer content increase the polymerization rate, since the slope is higher for experiment 5 (0.228 kg $\cdot mol^{-1} \cdot min^{-1}$) compared with experiment 6 (0.247 kg $\cdot mol^{-1} \cdot min^{-1}$).

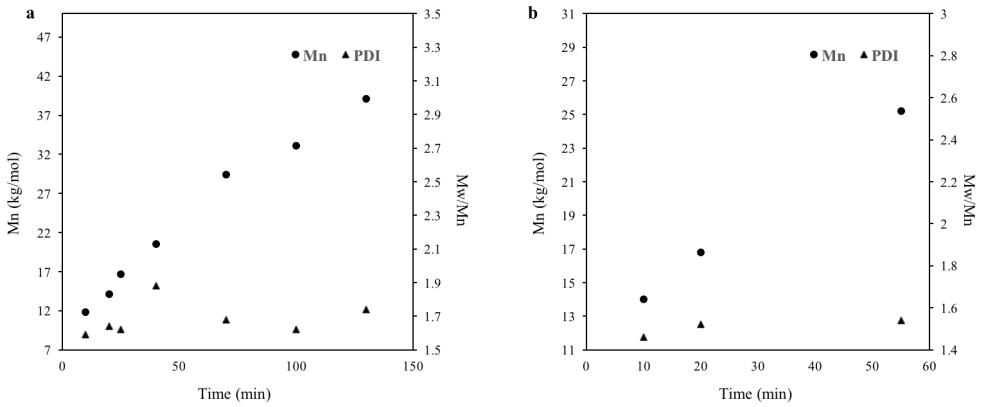


Figure 14. Evolution of M_n and M_w/M_n with time for experiment 5 (a) and experiment 6 (b) (experimental conditions are listed in table 3)

For the recovered block polymer, experiment 5 gave block polymers with Mn = 36.6 kg ·mol^{-1} *and* M_w/M_n=1.44; experiment 6 gave block polymers with Mn=25.2 kg ·mol^{-1} and M_w/M_n=1.54. The higher molecular weight and lower value of M_w/M_n of the block polymer for experiment 5 was attributed to a slower polymerization rate, which enable a better control. Comparison of GPC chromatograms for the final block polymer was demonstrated in Figure 15.

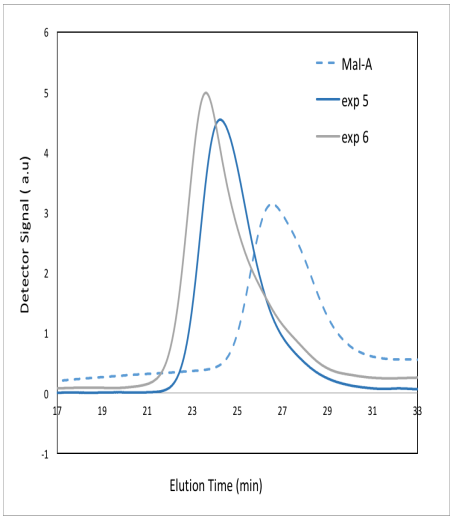


Figure 15. Gel permeation chromatograms of recovered block polymer for experimental 5 and 6, samples were acetylated before performing GPC measurements (experimental conditions are listed in table 3)

4.6 Influence of the Macroinitiator Chain Length

To identify the versatility of this method, three kinds of macroinitiators have been prepared (Mn=6 300 g·mol^{-1} , Mn=10 000 g·mol^{-1} , Mn=18 100 g·mol^{-1} respectively). Experiment 2, 5, 7 were performed using these three kinds of macroinitiator with the approximately same

weight concentration (~45 g·L^{-1}). TEA weight ratio (based on the weight of macroinitiator) was controlled around 0.55. A complete shift of GPC chromatograph for all the experiments confirmed that this process could be used for poly(HEMA-*ran*-AN) macroalkoxyamine with a wide range of molecular weight (from 5 000 g·mol^{-1} to 20 000 g·mol^{-1}). From the plot of molecular weight versus time for all the three experiments (Figure 11, 13, 15), a linear growth of molecular weight with time was observed. A much slower polymerization rate was observed for MaI-B, since the molar concentration is the lowest.

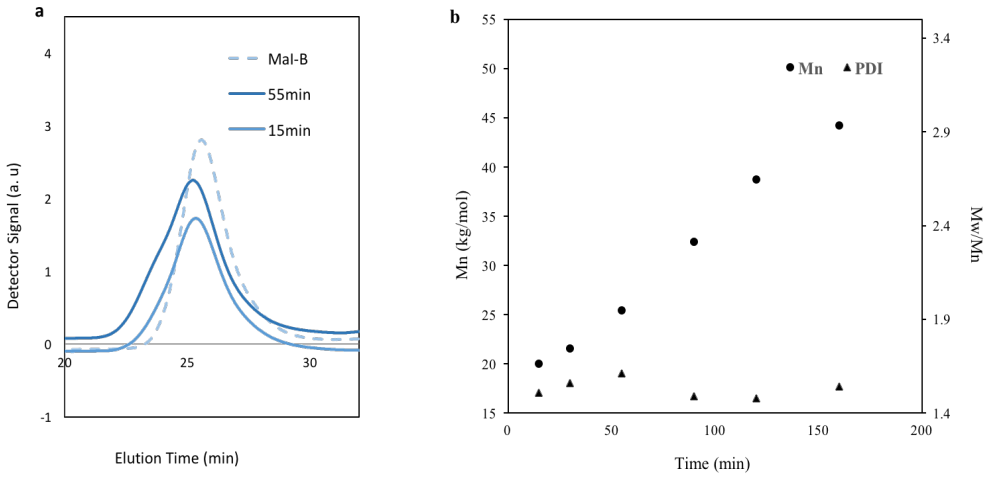


Figure 15. GPC chromatograph (a) and evolution of M_n and M_w/M_n with time (b) for experiment 7 (experimental conditions are listed in table 3)

4.7 Determination of the Composition of Recovered Block Polymer

After stopping the reaction, polymers were precipitated in hexane and dried under vacuum at room temperature overnight. Despite the fact that the recovered polymer could dissolve in CDCl3, it appeared impossible to determine the composition in this way, since the characteristic peaks (COOCH2-) for n-BMA and HEMA overlapped all together at δ = 4.0-4.5 ppm. Hence the block polymer was acetylated using the same procedure mentioned above, and after removing the pyridine and anhydrous acid used for the acetylation reaction, the acetylated block polymer was dissolved in CDCl3 for ^{1}H NMR analysis. Determination of the composition of the recovered block polymer was calculated by measuring the integrals of protons for styrene units (δ =7.0-7.5 ppm), protons for HEMA units(COO-CH2CH2-COO, δ =4.0-4.4 ppm) and protons for n-BMA units(COOCH2-, δ =3.75-4.0 ppm). For the

composition of AN units, it was determined previously in the characterization of the macro alkoxyamines. Hence the composition was determined using ^{1}HNMR and composition of the macroalkoxyamine already identified. Molar composition for the recovered block polymer for experiment 3, 5 and 7 are listed in table 6. Example of the using the ^{1}HNMR to determine the composition of acetylated poly(HEMA-*ran*-AN)-b-(n-BMA-*ran*-S) was shown in Figure 16 (the grey line represents the corresponding macroalkoxyamine).

Table 6. Molar Composition of Recovered Poly(HEMA-ran-AN)-b-(n-BMA-co-S) from Experiment 3, 5, 7

Exp	M_n (MaI)[a]	M_n [b]	F_{HEMA}	F_{AN}	F_S	$F_{n\text{-}BMA}$
3	6 300	25 500	0.19	0.03	0.09	0.69
5	10 000	36 600	0.21	0.04	0.08	0.67
7	18 100	44 500	0.25	0.04	0.07	0.63

a. experimental M_n (mol·g) for the acetylated macroalkoxyamine

b. experimental M_n (mol·g) for the acetylated block polymers

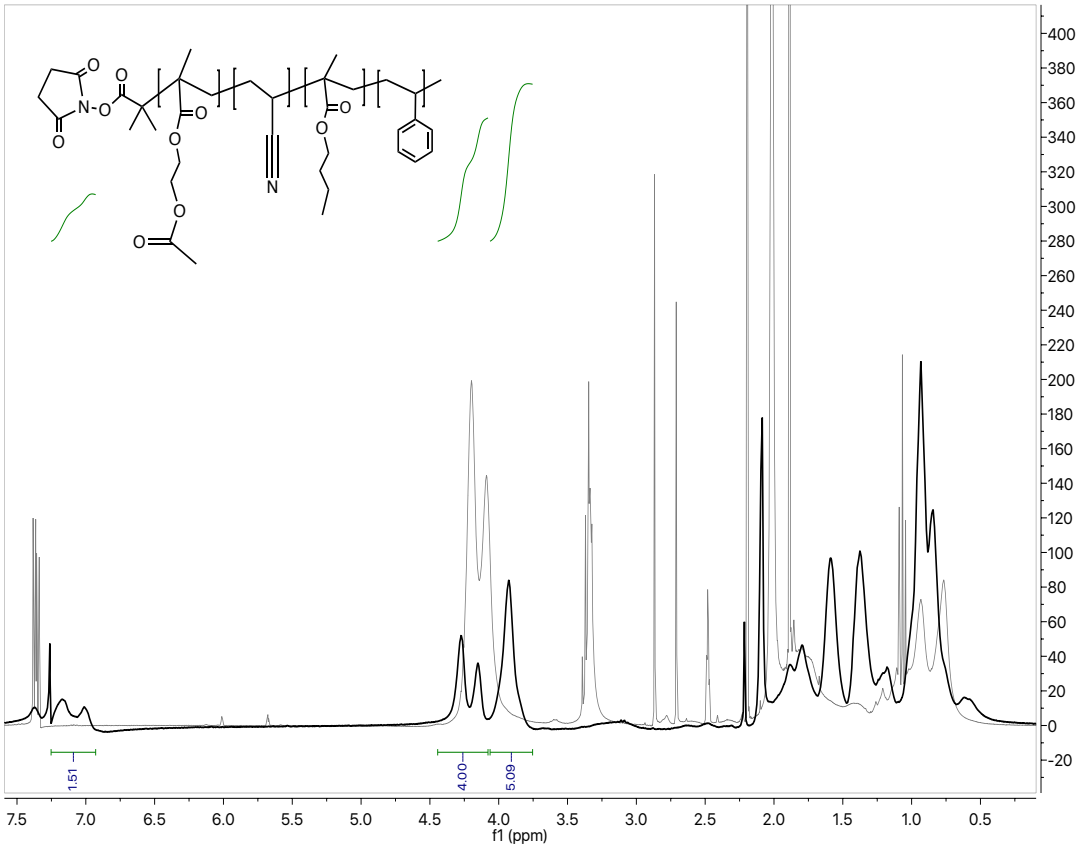


Figure 16. ^{1}H NMR for recovered block polymeri for experiment 7, the light grey line represents the ^{1}H NMR for acetylated macroinitiator in $CDCl_3$

The molar composition was further used for comparison with the molecular weight M_n given by GPC. GPC gives the M_n for both the recovered block polymer and the corresponding macroalkoxyamine, which can be used to estimate the composition of the block polymer. The estimation using GPC was in accordance with the ^{1}HNMR characterization despite a small discrepancy. Since GPC only gives the apparent molecular weight based on separation of hydrodynamic volume, and the calibration using PMMA standards might not be perfect to determine the true molecular weight, it is understandable that the results from GPC measurement and ^{1}HNMR analysis are not exactly the same [69].

Also, figure 16 clearly demonstrated the successful incorporation of the second block. In this way, the feasibility of using SG1-capped poly(HEMA-ran-AN) macro alkoxyamine in dispersed media without any use of surfactant to form HEMA-based block polymer was confirmed both by GPC and ^{1}H NMR.

4.8 Analysis of Particle Size

For all the latex examined, multi-modal size distributions were observed. Peaks were in the range of 50-100nm, 150-350nm, and >600nm. These multi-peaks might be attributed to big monomer droplets resulting from insufficient stirring, and the aggregates formed when the hydrophobic part of the block polymer increased. Also, TEA is only slightly soluble in water, which might contribute to the peaks in the range of 50-100nm. The population with large diameter (D_i>600nm) would be more likely caused by big monomer droplets, since the latex from experiment 4 has the major population with particle size Di>900nm (~70 vt%), To get rid of the extremely big particles, samples from experiment 1, 5, 6 was filtered using 0.2 μm membrane. Results were listed in table 7.

Table 7. Characteristics of Latex Particles after Filteration

Exp	M_n ($g \cdot mol^{-1}$)	*Zav* (nm)	σ	Peak 1 (nm)	Volume %	Peak 2 (nm)	Volume %
1	18 200	104	0.25	68	87	255	12
5	36 600	221	0.10	234	100	-	-
6	25 200	115	0.11	107	95	391	4

After filtration, a monomodal peak was observed for experiment 5, while in experiment 1and 6, a small second peak remained with volume percentage less than 15%. The results are listed in table 7. For a higher M_n, higher *Z*-average particle size was detected. Figure 17 gives the volume distribution of particle diameter from DLS after filteration.

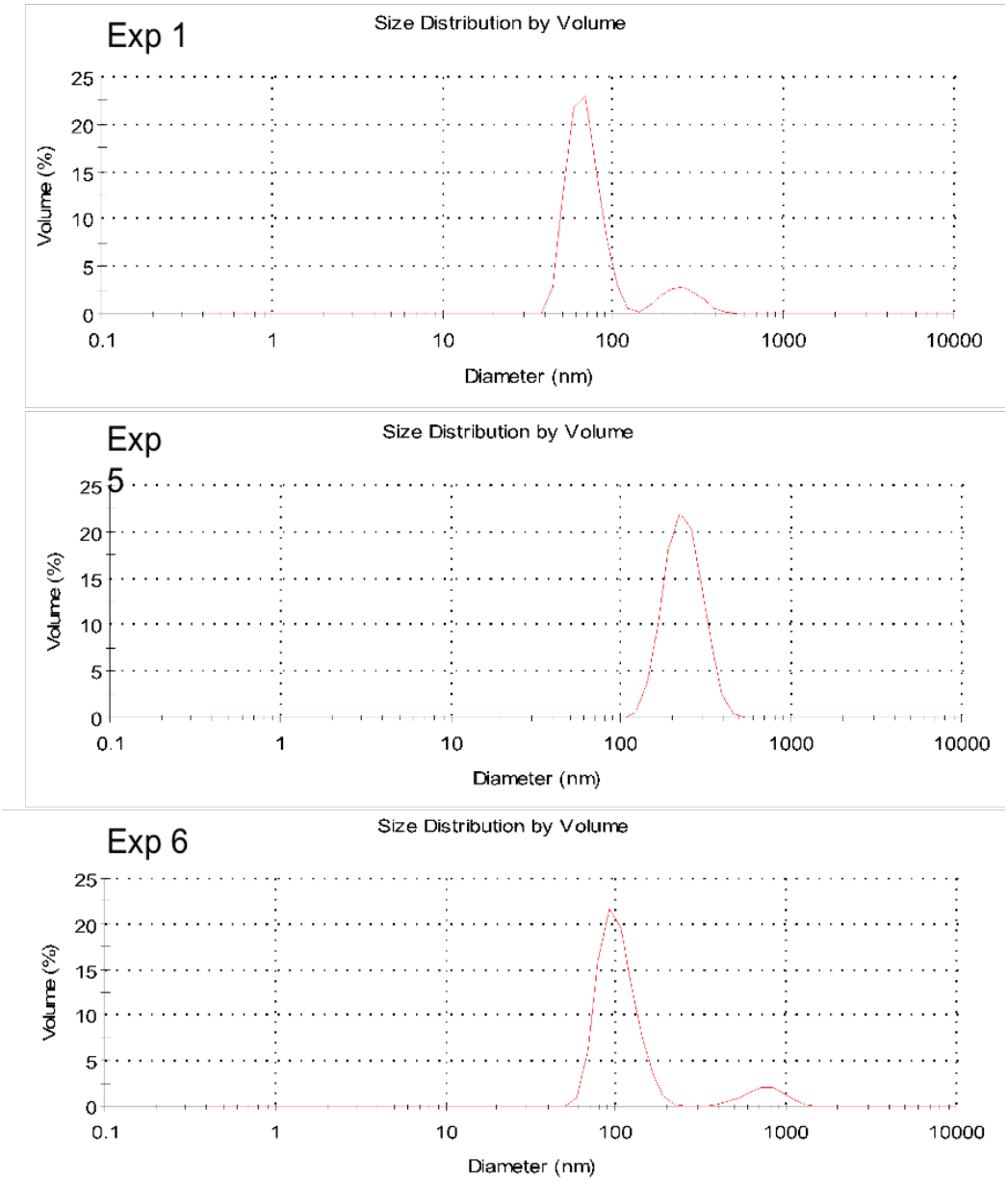


Figure 17. Volume distribution of particle diameter from DLS for experiment 1, 5, 6

5. Conclusion

SG1-capped poly(HEMA-*ran*-AN) macroalkoxyamines were synthesized by NMP using NHS-BlocBuilder initiator. The average molar molecular weight for the resulting macroalkoxyamine initiators ranged from 5 000-20 000 g·mol^{-1}with the value of M_w/M_n from 1.25-1.35. The amphiphilic macroalkoxyamine was further used in surfactant-free dispersed aqueous NMP of n-butyl methacrylate and styrene with a small amount of TEA, under low temperature conditions (90.0 ^{o}C). Reinitiation was successful for all the macroalkoxyamine preprared and stable latex with *Zave* ranging from 150-200 nm was obtained in the absence of surfactant. The feasibility of developing HEMA-based block polymer in aqueous media without the use of surfactant using the poly(HEMA-*ran*-AN) macro alkoxyamines was confirmed both by GPC and ^{1}H NMR. Thus, a versatile method for preparing HEMA-based block polymers with different composition in aqueous media was developed using NMP technique.

6. Future Work

For the process developed in laboratory scale, more studies should be employed towards the improvement of latex stability. Better stirring device with larger reactors is supposed to be used if a more detailed study is expected. With the polymerization in a large reaction medium, more insights could be provided on the kinetics and colloidal characteristics, which would be helpful for future application in industry.

Despite the successful preparation of 2-hydroxyethyl methacrylate based block polymer in aqueous media, the block polymer yielded is not that satisfactory considering the polydispersity, which might be attributed to the partition of SG1 between oil phase and aqueous phase. This might be addressed by using styrene instead of acrylonitrile as the controlling monomer when polymerizing 2-hydroxyethyl methacrylate. As styrene is much more amphiphobic, thus the partition of SG1 might be alleviated.

Also, it worth trying to use ethylamine or diethylamine in replacement of triethylamine, since they have the same chemical property with TEA in terms of deprotonation while their solubility in water are better. This might be helpful for improving colloidal stability and might even enlighten the further simplification of this process.

References

1. Ebdon, J.R., *Introduction to polymers (second edition) R. J. Young and P. A. Lovell Chapman and Hall, London, 1991. pp. 443, price £16.95. ISBN 0-412-30640-9 (PB); ISBN 0–412–30630–1 (HB).* Polymer International, 1992. **27**(2): p. 207-208.
2. Biesenberger, J.A. and D.H. Sebastian, *PRINCIPLES OF POLYMERIZATION ENGINEERING*. Princ of Polym Eng. 1983.
3. Moad, G. and D.H. Solomon, *The Chemistry of Radical Polymerization*. The Chemistry of Radical Polymerization. 2005.
4. Braunecker, W.A. and K. Matyjaszewski, *Controlled/living radical polymerization: Features, developments, and perspectives.* Progress in Polymer Science, 2007. **32**(1): p. 93-146.
5. Coessens, V., T. Pintauer, and K. Matyjaszewski, *Functional polymers by atom transfer radical polymerization.* Progress in Polymer Science, 2001. **26**(3): p. 337-377.
6. Riess, G., *Micellization of block copolymers.* Progress in Polymer Science, 2003. **28**(7): p. 1107-1170.
7. Hamley, I., *Block Copolymers in Solution: Fundamentals and Applications*. Block Copolymers in Solution: Fundamentals and Applications. 2012.
8. Hawker, C.J. and K.L. Wooley, *The convergence of synthetic organic and polymer chemistries.* Science, 2005. **309**(5738): p. 1200-1205.
9. Wang, J.S. and K. Matyjaszewski, *CONTROLLED LIVING RADICAL POLYMERIZATION - HALOGEN ATOM-TRANSFER RADICAL POLYMERIZATION PROMOTED BY A CU(I)CU(II) REDOX PROCESS.* Macromolecules, 1995. **28**(23): p. 7901-7910.
10. Muhlebach, A., S.G. Gaynor, and K. Matyjaszewski, *Synthesis of amphiphilic block copolymers by atom transfer radical polymerization (ATRP).* Macromolecules, 1998. **31**(18): p. 6046-6052.

11. Carlmark, A. and E.E. Malmstrom, *ATRP grafting from cellulose fibers to create block-copolymer grafts.* Biomacromolecules, 2003. **4**(6): p. 1740-1745.
12. Chiefari, J., et al., *Living free-radical polymerization by reversible addition-fragmentation chain transfer: The RAFT process.* Macromolecules, 1998. **31**(16): p. 5559-5562.
13. Perrier, S. and P. Takolpuckdee, *Macromolecular design via reversible addition-fragmentation chain transfer (RAFT)/Xanthates (MADIX) polymerization.* Journal of Polymer Science Part a-Polymer Chemistry, 2005. **43**(22): p. 5347-5393.
14. Müller, A.H.E. and K. Matyjaszewski, *Controlled and Living Polymerizations: From Mechanisms to Applications*. Controlled and Living Polymerizations: From Mechanisms to Applications. 2010.
15. Barner-Kowollik, C., *Handbook of RAFT Polymerization*. Handbook of RAFT Polymerization. 2008. 1-543.
16. Nicolas, J., et al., *Nitroxide-mediated polymerization.* Progress in Polymer Science, 2013. **38**(1): p. 63-235.
17. Qiu, J., B. Charleux, and K. Matyjaszewski, *Controlled/living radical polymerization in aqueous media: homogeneous and heterogeneous systems.* Progress in Polymer Science, 2001. **26**(10): p. 2083-2134.
18. Gaynor, S., et al., *CONTROLLED RADICAL POLYMERIZATION.* Journal of Macromolecular Science-Pure and Applied Chemistry, 1994. **A31**(11): p. 1561-1578.
19. Wang, J.S. and K. Matyjaszewski, *CONTROLLED LIVING RADICAL POLYMERIZATION - ATOM-TRANSFER RADICAL POLYMERIZATION IN THE PRESENCE OF TRANSITION-METAL COMPLEXES.* Journal of the American Chemical Society, 1995. **117**(20): p. 5614-5615.
20. Cunningham, M.F., *Living/controlled radical polymerizations in dispersed phase systems.* Progress in Polymer Science, 2002. **27**(6): p. 1039-1067.
21. Arshady, R., *Suspension, emulsion, and dispersion polymerization: A methodological survey.* Colloid and Polymer Science, 1992. **270**(8): p. 717-732.
22. Swarc, M., Nature (London), 1956. **178**: p. 1168.

23. Hawker, C.J., J. Am. Chem. Soc., 1994. **116**: p. 11185.

24. Grubbs, R.B., *Nitroxide-Mediated Radical Polymerization: Limitations and Versatility.* Polymer Reviews, 2011. **51**(2): p. 104-137.

25. Charleux, B. and J. Nicolas, *Water-soluble SG1-based alkoxyamines: A breakthrough in controlled/living free-radical polymerization in aqueous dispersed media.* Polymer, 2007. **48**(20): p. 5813-5833.

26. Alam, M.N., P.B. Zetterlund, and M. Okubo, *TEMPO-mediated radical polymerization of styrene in aqueous miniemulsion: Macroinitiator concentration effects.* Polymer, 2008. **49**(16): p. 3428-3435.

27. Alam, M.N., P.B. Zetterlund, and M. Okubo, *Network formation in nitroxide-mediated radical copolymerization of styrene and divinylbenzene in miniemulsion: Effect of macroinitiator hydrophilicity.* Polymer, 2009. **50**(7): p. 1632-1636.

28. Zetterlund, P.B., et al., *Controlled/Living Radical Polymerization in Dispersed Systems: An Update.* Chemical Reviews, 2015. **115**(18): p. 9745-9800.

29. Cheng, S., Y. Guo, and P.B. Zetterlund, *Miniemulsion Polymerization Based on Low Energy Emulsification with Preservation of Initial Droplet Identity.* Macromolecules, 2010. **43**(19): p. 7905-7907.

30. Guo, Y., J. Liu, and P.B. Zetterlund, *Nitroxide-Mediated Radical Polymerization in Miniemulsion On the Basis of in Situ Surfactant Formation without Use of Homogenization Device.* Macromolecules, 2010. **43**(14): p. 5914-5916.

31. Guo, Y. and P.B. Zetterlund, *Particle formation mechanism in radical polymerization in miniemulsion based on in situ surfactant formation without high energy homogenization.* Polymer, 2011. **52**(19): p. 4199-4207.

32. Farcet, C., et al., *Mechanistic Aspects of Nitroxide-Mediated Controlled Radical Polymerization of Styrene in Miniemulsion, Using a Water-Soluble Radical Initiator.* Macromolecules, 2000. **33**(23): p. 8559-8570.

33. Burguiere, C., et al., *Amphiphilic block copolymers prepared via controlled radical polymerization as surfactants for emulsion polymerization.* Macromolecular Symposia, 2000. **150**: p. 39-44.

34. Guyot, A. and K. Tauer, *Reactive surfactants in emulsion polymerization*, in *Polymer Synthesis*. 1994, Springer Berlin Heidelberg: Berlin, Heidelberg. p. 43-65.

35. Chern, C.S., *Emulsion polymerization mechanisms and kinetics.* Progress in Polymer Science, 2006. **31**(5): p. 443-486.

36. Garnier, S. and A. Laschewsky, *New Amphiphilic Diblock Copolymers: Surfactant Properties and Solubilization in Their Micelles.* Langmuir, 2006. **22**(9): p. 4044-4053.

37. Zetterlund, P.B., Y. Kagawa, and M. Okubo, *Controlled/living radical polymerization in dispersed systems.* Chemical Reviews, 2008. **108**(9): p. 3747-3794.

38. Zetterlund, P.B. and M. Okubo, *Compartmentalization in Nitroxide-Mediated Radical Polymerization in Dispersed Systems.* Macromolecules, 2006. **39**(26): p. 8959-8967.

39. Zetterlund, P.B., J. Wakamatsu, and M. Okubo, *Nitroxide-Mediated Radical Polymerization of Styrene in Aqueous Microemulsion: Initiator Efficiency, Compartmentalization, and Nitroxide Phase Transfer.* Macromolecules, 2009. **42**(18): p. 6944-6952.

40. Save, M., Y. Guillaneuf, and R.G. Gilbert, *Controlled radical polymerization in aqueous dispersed media.* Australian Journal of Chemistry, 2006. **59**(10): p. 693-711.

41. Zetterlund, P.B., *Nitroxide-Mediated Radical Polymerization in Dispersed Systems: Compartmentalization and Nitroxide Partitioning.* Macromolecular Theory and Simulations, 2010. **19**(1): p. 11-23.

42. Zetterlund, P.B., *Controlled/living radical polymerization in nanoreactors: compartmentalization effects.* Polymer Chemistry, 2011. **2**(3): p. 534-549.

43. Sugihara, Y. and P.B. Zetterlund, *Synergistic Effects of Compartmentalization and Nitroxide Exit/Entry in Nitroxide-Mediated Radical Polymerization in Dispersed Systems.* Acs Macro Letters, 2012. **1**(6): p. 692-696.

44. Charleux, B., *Theoretical aspects of controlled radical polymerization in a dispersed medium.* Macromolecules, 2000. **33**(15): p. 5358-5365.

45. Maehata, H., et al., *Compartmentalization in TEMPO-mediated styrene miniemulsion polymerization.* Macromolecules, 2007. **40**(20): p. 7126-7131.

46. Butte, A., M. Storti, and M. Morbidelli, DECHEMA Monogr., 1998. **134**: p. 497.

47. Pan, G.F., et al., *Thermal self-initiation of styrene in the presence of TEMPO radicals: Bulk and miniemulsion.* Journal of Polymer Science Part a-Polymer Chemistry, 2004. **42**(19): p. 4921-4932.

48. Cunningham, M.F., *Controlled/living radical polymerization in aqueous dispersed systems.* Progress in Polymer Science, 2008. **33**(4): p. 365-398.

49. Nicolas, J., et al., *Nitroxide-mediated controlled free-radical emulsion polymerization of styrene and n-butyl acrylate with a water-soluble alkoxyamine as initiator.* Angewandte Chemie - International Edition, 2004. **43**(45): p. 6186-6189.

50. Nicolas, J., et al., *Novel SG1-Based water-soluble alkoxyamine for nitroxide-mediated controlled free-radical polymerization of styrene and n-butyl acrylate in miniemulsion.* Macromolecules, 2004. **37**(12): p. 4453-4463.

51. Dire, C., et al., *Nitroxide-Mediated Controlled/Living Free-Radical Surfactant-Free Emulsion Polymerization of Methyl Methacrylate Using a Poly(methacrylic acid)-Based Macroalkoxyamine Initiator.* Macromolecules, 2009. **42**(1): p. 95-103.

52. Guo, Y. and Y. Luo, *Controlled synthesis and properties of gradient copolymers.* Huagong Xuebao/CIESC Journal, 2016. **67**(1): p. 218-230.

53. Darabi, A., et al., *Nitroxide-mediated surfactant-free emulsion copolymerization of methyl methacrylate and styrene using poly(2-(diethyl)aminoethyl methacrylate-co-styrene) as a stimuli-responsive macroalkoxyamine.* Polymer Chemistry, 2014. **5**(21): p. 6163-6170.

54. Bon, S.A.F., et al., *Controlled Radical Polymerization in Emulsion.* Macromolecules, 1997. **30**(2): p. 324-326.

55. Marestin, C., et al., *Nitroxide Mediated Living Radical Polymerization of Styrene in Emulsion.* Macromolecules, 1998. **31**(12): p. 4041-4044.

56. Cao, J., et al., *Nitroxide-mediated radical polymerization of styrene in emulsion.* Polymer Journal, 2001. **33**(1): p. 75-80.

57. Maehata, H., et al., *TEMPO-Mediated Emulsion Polymerization.* Macromolecular Rapid Communications, 2008. **29**(6): p. 479-484.

58. Zetterlund, P.B., N. Alam, and M. Okubo, *Effects of the oil-water interface on network formation in nanogel synthesis using nitroxide-mediated radical copolymerization of styrene/divinylbenzene in miniemulsion.* Polymer, 2009. **50**(24): p. 5661-5667.

59. Delaittre, G., et al., *Aqueous suspension of amphiphilic diblock copolymer nanoparticles prepared in situ from a water-soluble poly(sodium acrylate) alkoxyamine macroinitiator.* Soft Matter, 2006. **2**(3): p. 223-231.

60. Qiao, X.G., et al., *Nitroxide-Mediated Polymerization-Induced Self-Assembly of Poly(poly(ethylene oxide) methyl ether methacrylate-co-styrene)-b-poly(n-butyl methacrylate-co-styrene) Amphiphilic Block Copolymers.* Macromolecules, 2013. **46**(11): p. 4285-4295.

61. Darabi, A., et al., *Nitroxide-Mediated Polymerization of 2-(Diethylamino)ethyl Methacrylate (DEAEMA) in Water.* Macromolecules, 2015. **48**(1): p. 72-80.

62. Vinas, J., et al., *SG1-based alkoxyamine bearing a N-succinimidyl ester: A versatile tool for advanced polymer synthesis.* Polymer, 2008. **49**(17): p. 3639-3647.

63. Bian, K. and M.F. Cunningham, *Nitroxide-mediated living radical polymerization of 2-hydroxyethyl acrylate and the synthesis of amphiphilic block copolymers.* Macromolecules, 2005. **38**(3): p. 695-701.

64. Ananchenko, G.S., et al., J. Polym. Sci., Part A: Polym. Chem., 2002. **40**: p. 3264.

65. Guillaneuf, Y., et al., Macromol. Chem. Phys., 2006. **207**: p. 1278.

66. Charleux, B., J. Nicolas, and O. Guerret, *Theoretical expression of the average activation-deactivation equilibrium constant in controlled/living free-radical copolymerization operating via reversible termination. Application to a strongly improved control in nitroxide-mediated polymerization of methyl methacrylate.* Macromolecules, 2005. **38**(13): p. 5485-5492.

67. Nicolas, J., S. Brusseau, and B. Charleux, *A Minimal Amount of Acrylonitrile Turns the Nitroxide-Mediated Polymerization of Methyl Methacrylate into an Almost Ideal*

Controlled/Living System. Journal of Polymer Science Part a-Polymer Chemistry, 2010. **48**(1): p. 34-47.

68. Lessard, B., et al., *Nitroxide-Mediated Radical Copolymerization of Methyl Methacrylate Controlled with a Minimal Amount of 9-(4-Vinylbenzyl)-9H-Carbazole.* Journal of Polymer Science Part a-Polymer Chemistry, 2011. **49**(4): p. 1033-1045.
69. Guillaneuf, Y. and P. Castignolles, *Using apparent molecular weight from SEC in controlled/living polymerization and kinetics of polymerization.* Journal of Polymer Science Part a-Polymer Chemistry, 2008. **46**(3): p. 897-911.