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Nitroxide-Mediated Polymerization of 2-Hydroxyethyl Methacrylate (HEMA) Controlled with Low Concentrations of Acrylonitrile and Styrene

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Abstract: Nitroxide mediated controlled radical polymerization of 2-hydroxyethyl methacrylate (HEMA) was achieved using the copolymerization method with a small initial concentration of acrylonitrile (AN, 5-16 mol %)) or styrene (S, 5-10 mol%). The polymerization was mediated by N-*tert*-butyl-N-(1-diethyl phosphono-2,2-dimethyl propyl) nitroxide (SG1)-based BlocBuilder unimolecular alkoxyamine initiator modified with an N-succinimidyl ester group (NHS-BlocBuilder). As little as 5% molar feed of acrylonitrile resulted in a controlled polymerization, as evidenced by a linear increase in number average molecular weight M_n with conversion and dispersities (Đ) as low as 1.30 at 80% conversion in N,N-dimethylformamide (DMF) at 85 °C. With S as the controlling co-monomer, higher initial S composition (~ 10 mol%) was required to maintain the controlled copolymerization. Poly(HEMA-*ran*-AN)s with M_n ranging from 5-20 kg · mol^{-1} were efficiently chain extended using n-butyl methacrylate/styrene mixtures at 90.0 °C in DMF, thereby showing a route to HEMA-based amphiphilic block copolymers via nitroxide-mediated polymerization.

1. Introduction

The demand for polymers with specific functionalities is a key driver for many next-generation plastic materials. Traditionally, living polymerization has been the synthetic route towards tailored polymers with predictable molar masses, compositions, topologies and functionalities[1, 2], but over the past two decades, controlled radical polymerization (CRP) techniques have emerged such as nitroxide mediated polymerization (NMP), atom transfer radical polymerization (ATRP) and reversible addition fragmentation transfer polymerization (RAFT)[3-6]. These superficially possess features associated with truly living polymerizations such as exhibiting a linear relationship of degree of polymerization versus conversion, relatively narrow molecular weight distributions (dispersities Đ = 1.2-1.5) and high chain end fidelity (eg. ability to make block copolymers). Of these, NMP was the first developed but lagged considerably behind ATRP and RAFT in that first-generation nitroxides like TEMPO ((2,2,6,6-teramethylpiperidinyl-1-oxy) could only control styrenic polymerizations well[7]. However, NMP is relatively simple to apply, needing only heat and the nitroxide to initiate polymerization, and does not require extensive post-polymerization procedures to remove residual catalysts and other reagents.

The major advance of NMP arrived with the development of second-generation acyclic nitroxides like N-*tert*-butyl-N-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide, known as SG1. This enabled a broader range of monomers to be well-controlled via NMP at a much lower temperature, compared to TEMPO. Not only styrenics could be polymerized as previously demonstrated with TEMPO but also acrylates, acrylamides and dienes[7, 8]. Methacrylate homopolymerizations have been more problematic and their NMP still remains a challenge with commercially available nitroxides. The copolymerization approach reported by Charleux and co-

workers (adding ~5 mol% of a monomer that is well-controlled by NMP such as a styrenic) was quite useful with *N-(*2-methylpropyl)-*N*-(1-(diethylphosphono-2,2-dimethylpropyl)-O-(2-carboxylprop-2-yl)hydroxylamine) (BlocBuilder) type unimolecular initiators and has been widely adopted. For example, it has been used in the polymerization of methyl methacrylate (MMA)[9], methacrylic acid (MAA)[10], benzyl methacrylate (BzMA)[11], (dimethylamino) ethyl methacrylate (DMAEMA)[12-15], and poly(ethylene glycol) methyl ether methacrylate[16-20]. The most widely used co-monomers via this approach are styrene or styrenic derivatives [21-23], 9-(4-vinylbenzy)-9H-carbazole (VBK) [24, 25], and acrylonitrile [26].

2-Hydroxyethyl methacrylate (HEMA) has long been applied in coating materials, contact lenses and tissue engineering[27, 28]. HEMA-based resins containing crosslinking agents were reported to have better mechanical properties while reducing water absorption and solubility [27]. In tissue engineering, HEMA was used for its hydrophilic and hydrogel-like properties imparted into polymers [28]. CRP of HEMA using ATRP or RAFT has been investigated widely but NMP of HEMA is limited [29-31]. Bian et al. reported the controlled polymerization of the related 2-hydroxyethyl acrylate (HEA) by NMP using MONAMS initiator with SG1 in bulk and in DMF solution[32]. Clement et al. reported the homopolymerization of HEMA using a SG1-based aliphatic polyester macro-alkoxyamines[33]. Not surprisingly, the homopolymerization was not controlled, with no chain extension observed.

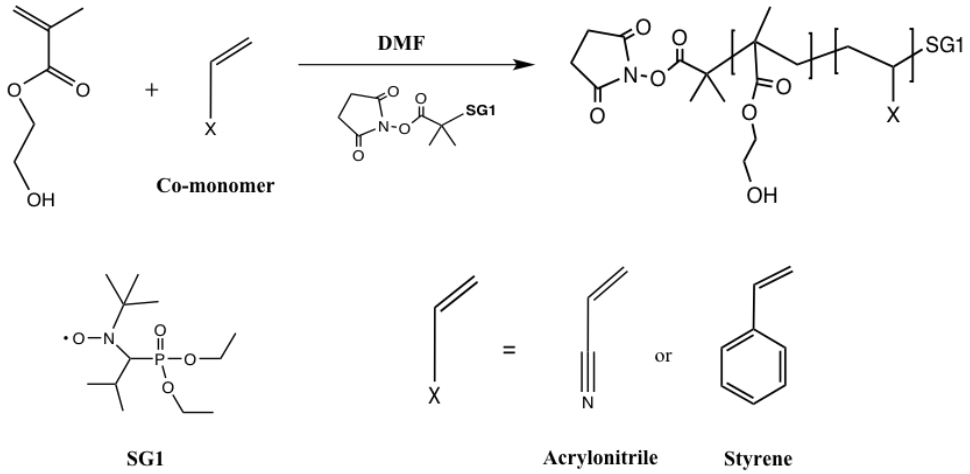
Thus, we decided to use the copolymerization method to realize the controlled polymerization of HEMA. The choice of the controlling co-monomer can have a secondary purpose; it can impart functionality. For example, it can be used to add water-solubility (eg. styrene sulfonic acid,

sodium salt) or fluorescent properties (VBK) [13, 19, 23, 34, 35]. In some cases, the media used for the polymerization may prevent usage of a monomer. For example, styrene and most of its derivatives are highly hydrophobic, which would make homogenous aqueous polymerization infeasible. For biomedical applications, use of styrene as a co-monomer might introduce toxic effects[36].

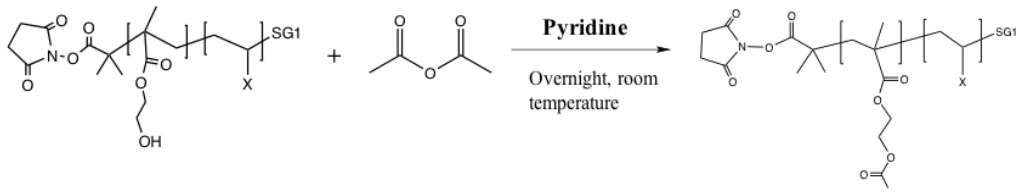
In this work, two different co-monomers, acrylonitrile and styrene, were used for the nitroxide-mediated copolymerization of HEMA-rich compositions. We chose the SG1-based alkoxyamine bearing succinimidyl ester groups (NHS-BlocBuilder) because of its high dissociation constant (~15 times higher than that of BlocBuilder) [37]. Thus, it is not required to add more free nitroxide to push the equilibrium so that the polymer is in the dormant state more often, resulting in a more controlled polymerization. This rapid dissociation mimics the persistent radical effect (PRE)[37-39]. NHS-BlocBuilder was reported to successfully control the following copolymerizations of methacrylate-rich mixtures: glycidyl methacrylate (GMA)/styrene[40], 2-(diethyl) aminoethyl methacrylate (DEAEMA)/styrene [12]; *tert*-butyl methacrylate (t-BMA)/acrylonitrile[41]; and poly(ethylene glycol) methyl ether methacrylate (PEGMA)/acrylonitrile[18, 42]. Also, it should be noted that the first peptide/protein PEGylation with functional polymers was performed using NHS-BlocBuilder[40], indicating the potential of this alkoxyamine, particularly when used with HEMA, in biomedical applications.

In this study, effects of temperature, initial molar feed composition of the co-monomer, and type of co-monomer on the copolymerization kinetics were investigated. Comparison between the copolymerization of HEMA with styrene and that of HEMA with acrylonitrile is specifically

presented. HEMA-based copolymer was synthesized (Scheme 1) and was further used as a macroinitiator in chain extension reaction with n-butyl methacrylate/styrene mixtures. The obtained copolymer was also used in the acetylated form to enable a direct injection of samples in GPC to find if unreacted macroiniator was still present (Scheme 2). Appropriate experimental conditions for NMP of HEMA were identified and a facile way to construct HEMA-based block polymers was proposed.



Scheme 1. (SG1-mediated copolymerization of HEMA and AN or S in DMF solution using NHS-BlocBuilder)



Scheme 2. (Acetylation reaction performed for HEMA-based copolymer using acetic anhydride at room temperature overnight in pyridine solution to transform the hydroxyl groups into esters, making the copolymer soluble in THF for GPC analysis. X indicates acrylonitrile or styrene.)

2. Experimental Section

2.1 Materials

2-Hydroxyethyl methacrylate (HEMA, 99%), acrylonitrile (AN, 99%), styrene (S, 99%) and n-butyl methacrylate (BMA, 99%) were purchased from Sigma-Aldrich 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 purification, monomers are sealed in separate round flasks under nitrogen and stored in refrigerator for further use. Hexane (98.5%), diethyl ether (99%), N,N-dimethylformamide (DMF, 95%), tetrahydrofuran (THF, 99.5%, HPLC grade), and pyridine (99%) were obtained from Fisher Scientific and used as received. Acetic anhydride (97%) was obtained from ACP Inc. and used as received. 2-((tert-butyl-(1-(diethoxyphosphoryl)-2,2-dimethylpropyl)amino)oxy)-2-methylpropanoic acid initiator (BlocBuilder, 99%) was kindly supplied by Arkema (N. Macy). N-hydroxysuccinimide (NHS, 98%), and N,N'-dicyclohexylcarbodiimide (DCC, 99.9%) were purchased from Sigma-Aldrich. N-Hydroxysuccinimide BlocBuilder (NHS-BlocBuilder) was synthesized according to the reported procedure [32]. For ^{1}H NMR spectroscopy, Deuterated chloroform ($CDCl_3$, >99%) was obtained from Sigma–Aldrich and dimethyl sulfoxide-d_6 (DMSO, >99%) was obtained from Cambridge Isotopes Laboratory.

2.2 SG1-Mediated Copolymerization of HEMA and Acrylonitrile or Styrene in DMF Solution

Copolymerization of HEMA and AN or S were all performed in a 15 ml three-neck round bottom glass flask equipped with a condenser, thermal well and a magnetic Teflon stir bar. The flask was placed inside a heating mantle on a magnetic stirrer. Table 1 gives the experimental conditions for the copolymerization for the studied HEMA/AN and HEMA/S copolymerizations. All the copolymerization reactions were performed in DMF solution with a low nitrogen purge. A typical procedure (E2, Table 1) is as follows: The NHS-BlocBuilder initiator (0.0795 g, 0.17 mmol) was first dissolved in DMF (3.0442 g, 42 mmol). The solution was then introduced to the

prepared monomer mixture of HEMA (2.1456 g, 16.49 mmol) and AN (0.1673 g, 3.15 mmol, molar fraction $f_{AN,0} = 0.16$). The so-formed homogeneous solution was further introduced into the reactor, which was sealed with rubber septa. This solution was further deoxygenated with nitrogen for 30 minutes. After that, the reactor was heated to 85°C at a rate of approximately 10°C min^{-1}. Time zero was taken when the reactor temperature reached 65°C. Samples were taken periodically to monitor the kinetics. For ^{1}H NMR, samples were directly dissolved in DMSO while for GPC measurements, polymers were precipitated in diethyl ether first. The recovered polymer was then acetylated using acetic anhydride and pyridine according to a reported procedure[32]. The acetylated polymers were fully dried to remove solvent and excess acetic anhydride before performing GPC characterization. The same procedure was also applied in the copolymerization of HEMA with S. For the synthesis of macroinitiator used for chain extension, the same procedure was followed. Experimental conditions were kept the same as E1, but the reaction was stopped at different conversions to give copolymers differing in chain length. Polymers were then precipitated twice in excess diethyl ether and were dried under vacuum at room temperature for two days to remove any solvent and remained monomer. The yield for macroinitiator (ID: C, Table 3) was 85%. Characterization of the macroinitiators is listed in Table 3. Details about ^{1}H NMR characterization is provided in the *Analytical Techniques* section.

For the synthesis of macroinitiator used for chain extension, the same procedure was followed. Experimental conditions were kept the same as E1, but the reaction was stopped at different conversion to give copolymers differing in chain length. Polymers were precipitated twice in excess diethyl ether and were dried under vacuum at room temperature for two days to remove any solvent and remained monomer.

Table 1. (Experimental Conditions Used for Copolymerization of HEMA and Acrylonitrile or Styrene in 43wt% DMF Solution)

Expt	[HEMA] [mol · L^{-1}]	[X][a)] [mol · L^{-1}]	[NHS-BB] [mol · L^{-1}]	[DMF] [mol · L^{-1}]	T [°C]	f_0[b)]	Mn[c)]$_{target}$ [Kg · mol^{-1}]
E1	3.08	0.16	0.031	7.6	90	0.16	18.0
E2	3.04	0.16	0.031	7.7	85	0.16	17.8
E3	3.08	0.16	0.031	7.6	78	0.16	18.0
E4	3.05	0.10	0.031	7.9	85	0.10	17.6
E5	3.05	0.05	0.032	8.0	85	0.053	17.2
E6	3.05	0.10	0.031	7.7	85	0.10	17.4
E7	3.04	0.075	0.031	7.8	85	0.075	17.4
E8	3.07	0.054	0.031	7.8	85	0.054	17.3

[a)] (For E1-E5, X represents AN; for E6-E8, X represents S)); [b)] (Initial molar feed of co-monomer (AN or S) in HEMA/X mixture) [c)] (Theoretical molar molecular weight at full conversion. Note that this is the theoretical value for acetylated copolymers calculated as follows: $Mn, target = Mn, initiator + \frac{Mx+MHE(ac)MA}{Minitiator} \times Mn, initiator$, $M_{x,0}$ represents the mass of co-monomer (AN or S) and $M_{HE(ac)MA,0}$ is the mass of the acetylated HEMA monomers assuming a full transformation of hydroxyl groups and $M_{initiator}$ is the moles of NHS-BlocBuilder initiaton.)

2.3 Chain Extension of HEMA-Based Alkoxyamine Using n-Butyl Methacrylate and Styrene

To confirm the chain end fidelity of the HEMA-based copolymers, chain extension was performed using n-butyl methacrylate (BMA)/styrene (S) mixtures in DMF solution. Experimental conditions for the chain extension can be found in Table 2. A typical procedure (H1) is given: The poly(HEMA-*ran*-AN) macroinitiator (Macro ID A, 0.183 g, 0.020 mmol) was dissolved in DMF (1.2 g, 16.5 mmol) and BMA (0.903 g, 6.35 mmol) and S (0.087 g, 0.84 mmol, $f_{S,0}$ = 0.11) were mixed with the macroinitiator solution. The so-formed homogeneous solution was further introduced into a 15 ml three-neck round-bottom reactor, fitted with a condenser and purge escape, sealed with rubber septa. The solution was deoxygenated with nitrogen for 30 minutes. After that, the reactor was heated to 90.0°C at a rate of 10.0°C min^{-1}.

Time zero for the reaction was taken arbitrarily when the reactor temperature reached 65.0°C. The reaction was stopped after approximately 45 minutes, and the reactor contents were precipitated in hexane twice. The recovered crude block polymer was dried under vacuum at room temperature for one day to remove residual monomers and solvent. The acetylated block polymers were characterized by GPC to give the apparent molecular weight (based on PMMA standard in THF) and by ^{1}H NMR to determine composition. The yield for the block polymers from H3 (chain extended from macroinitiator ID C, Table 3) was 60%. Characterization results for block polymers can be found in Table 3. Details about ^{1}H NMR peak indexes were provided in the *Analytical Techniques* section.

Table 2. (Experimental Conditions for Synthesis of Poly(HEMA-*ran*-AN)-SG1 Macroalkoxyamine for Chain Extension in DMF Solution at 90°C)

Expt	**Macro ID**	**Mn of Macro[a)] [Kg · mol^{-1}]**	**[Macro] [mmol · L^{-1}]**	**[BMA] [mol · L^{-1}]**	**[S] [mol · L^{-1}]**	$f_{S,0}$	**Target Mn[c)] [Kg · mol^{-1}]**
H1	A	10.0	8.3	2.7	0.35	0.12	60.3
H2	B	18.1	6.0	2.5	0.32	0.12	83.2
H3	C	6.3	7.2	2.6	0.37	0.12	63.8
H4[b)]	Acetylated-C	13.1	15.4	2.7	0.36	0.12	40.8

a)(Experimental Mn measured after acetylation based on PMMA standards (THF solvent ,40°C);) [b)](Chain extension using the acetylated poly(HEMA-*ran*-AN) copolymer;) [c)](Theoretical molecular weight calculated at full conversion.)

Chain extension using the acetylated macroinitiator (H4, Table 2) followed a similar procedure described above. This is intended to further confirm the fraction of 'living' chains in macroinitiator samples. To perform the chain extension with the acetylated copolymer, the macroinitiator was first added in a 20 ml vial and was acetylated using pyridine and acetic anhydride. The mixture was then put in the fume hood to evaporate most of the solvent and excess acid and further dried under vacuum at room temperature for one day. DMF was added directly into the 20 ml vials to dissolve the acetylated macroinitiator (poly(HE(ac)MA-*ran*-AN)).

Monomer mixtures of BMA and S were further introduced into the same vial and the so-formed homogeneous solution was then introduced to a 15 ml three-neck round-bottom reactor. All the other procedures were the same as described above. Samples were taken periodically and directly diluted with THF for GPC analysis.

Table 3. (Characteristics of the Copolymerization of HEMA and AN or S in DMF Solution)

expt[a)]	**reaction time [min]**	**$\langle k_p \rangle\langle K \rangle$**[b)] **[$s^{-1}$]**	**Conversion**[c)] **[X_{wt}]**	**M_n**[d)] **[kg · mol^{-1}]**	**M_w/M_n**
E1	80	3.37×10^{-4}	0.85	16.2	1.28
E2	120	1.80×10^{-4}	0.74	13.0	1.29
E3	160	0.95×10^{-4}	0.62	11.7	1.30
E4	120	1.92×10^{-4}	0.82	13.4	1.33
E5	135	1.83×10^{-4}	0.83	14.5	1.37
E6	120	1.82×10^{-4}	0.76	13.9	1.34
E7	120	---	0.71	40.4	1.84
E8	120	---	0.79	37.5	1.88

[a)](Experimental conditions can be found in Table1; [b)] Extracted from the slope of the ln[(1/1-X_{wt})] versus time plot (sample calculation is provided in supporting information));) [c)] (Overall weight conversion;) [d)] (Experimental M_n measured after acetylation based on PMMA standards (THF solvent, 40°C).)

2.4 Analytical Techniques

Gel permeation chromatography (GPC) was used to determine the number average molecular weight (M_n), weight average molecular weight (M_w) and dispersities Đ (M_w/M_n) with HPLC grade THF as the mobile phase. Before injecting the samples, the same acetylation reaction (Scheme 2) was performed to convert the hydroxyl groups into esters [32]. The flow rate was 0.3 mL 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 estimated by calibration against linear, nearly monodisperse poly(methyl methacrylate) (PMMA) standards supplied by Varian

(Agilent Technologies, molecular weight range 875 g mol^{-1} to 1,677,000 g mol^{-1}). In all the figures displaying M_n as a function of conversion and all the M_n values listed in all of the Tables, the M_n values correspond to those of acetylated polymers.

Conversion for copolymerization of HEMA and AN or S was determined by ^{1}H NMR using an Agilent 300 MHz Varian VNMRS. Samples taken periodically were directly dissolved in DMSO-d_6 for ^{1}H NMR. The individual conversion of each monomer were determined by taking the average value of the integration of vinyl protons (δ = 6.35 ppm and δ = 6.20 ppm for AN; δ = 6.05 ppm and δ = 5.65 ppm for HEMA; δ = 6.05 ppm and δ = 5.65 ppm for S), relative to the peaks of two protons of ester groups (-$COOCH_2$-, δ = 3.7-4.1ppm) from HEMA. The overall conversion was calculated from monomer conversion according to the relationship $X_{wt} = X_x \times W_{x,0} + X_{HEMA} \times W_{HEMA,0}$ where $W_{x,0}$ and $W_{HEMA,0}$ were the initial weight fractions of controlling co-monomer (x = AN or S) in monomer mixture and that of HEMA; X_x and X_{HEMA} were the conversion of co-monomer (x = AN or S) and that of HEMA.

The compositions of the macroinitiator and the block copolymers were determined using an Agilent 500 MHz Varian VNMRS. Before performing ^{1}H NMR, samples were acetylated and dried sufficiently to remove solvents and excess acetylating agent. For the macroinitiators used for chain extension (Macro ID A, B and C), the composition was determined by integrating the proton at δ = 2.3-2.7 ppm for acrylonitrile (1H, –CH-) and the protons at δ = 3.7-4.6 ppm (4H, COO-CH_2-CH_2-COO) for HE(ac)MA. For the composition of poly(HEMA-*ran*-AN)-b-poly(BMA-*ran*-S) block polymers, composition was determined as follows: the composition of BMA units was determined by the integration of COO-CH_2- protons (2H, δ = 3.7-4.1 ppm), the

composition of HEMA units was determined by COO-CH_2-CH_2-COO protons (4H, δ = 4.1-4.5 ppm), and the composition of S units was determined by the aromatic protons (5H, δ = 6.8-7.4 ppm). The composition of AN was determined using the resonances described for the macroinitiator (δ = 2.3-2.7 ppm).

3. Results and Discussion

3.1 Selection of Appropriate Experimental Conditions for the Copolymerization of 2-Hydroxyethyl Methacrylate with a Small Proportion of Controlling Monomers.

The polymerization of methacrylic esters has long been a difficult task for NMP. Early attempts performing NMP of methyl methacrylate were not satisfactory concerning the chain growth with conversion and dispersities Đ [43]. For TEMPO, a disproportionation reaction between TEMPO and the growing radical dominated over reversible combination, which prevented a high conversion and the formation of nitroxide-terminated polymers [44]. Early research by Fischer and co-workers reported an absence of a disproportionation reaction between SG1 and 1-phenyl-ethyl (PhEt) radicals in contrast with TEMPO-PhEt[44, 45]. SG1-mediated polymerization of methacrylic esters was still not successful. This was attributed to an excessively high equilibrium constant K, which strongly favored the production of propagating radicals, thus leading to irreversible termination[46]. Notwithstanding the limited success from homopolymerization of methacrylic esters via NMP, the copolymerization approach was proven applicable for NMP of many methacrylates [9-13, 15, 16, 19, 20, 23, 24, 26, 35, 40, 47]. A preliminary experiment copolymerizing HEMA with AN in 1,4-dioxane failed due to lack of solubility and thus the solvent was switched to DMF. The copolymerization performed above 95.0 °C suffered from an excessively rapid polymerization rate, and the reaction media became excessively viscous quickly. Therefore, the

temperatures were set below 90.0 °C, in the range of 78 - 90.0 °C, in DMF solution.

In a subsequent model experiment, the copolymerization of HEMA with AN was performed at 90.0 °C with an initial molar feed of AN $f_{AN,0} = 0.16$ (E1, Table 1). The polymerization was still quite fast, and the conversion reached 80% in one hour. The polymerization was assessed to be controlled, based on the following observations: 1) linear plot of $\ln[1/(1-X_{wt})]$ versus time; 2) M_n grew linearly with conversion and correlated well to the theoretical value; 3) continuous decrease of Đ with conversion and a complete, monomodal shift of gel permeation chromatograms (Figure 1a, Figure 1b); High initiating efficiency of the initiator used and an absence of irreversible chain transfer reactions to solvent was indicated by M_n value falling close to the theoretical line. The Đ was 1.28 even at 85% conversion.

Based on that, experiments were performed at different temperatures (E1, E2, E3), various initial molar feed fractions of co-monomer (E2, E4, E5 for AN; E6, E7, E8 for S) while keeping all other conditions the same (solution concentration). Characterization results and kinetic data for all the experiments are summarized in Table 3.

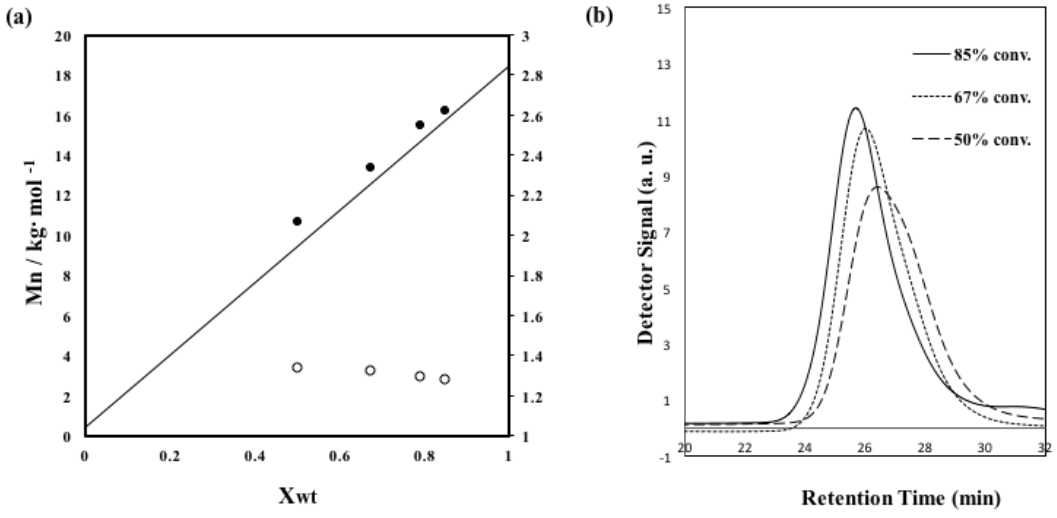


Figure 1. **(**Copolymerization of HEMA and AN (E1, Table 1): (a) evolution of M_n and M_w/M_n versus conversion. The straight line corresponds to the theoretical evolution (note that the

theoretical value was transformed to acetylated polymers); (b) gel permeation chromatograms as a function of monomer conversion.)

3.2 Influence of the Temperature on the Copolymerization of HEMA with Acrylonitrile

HEMA/AN copolymerizations (E1, E2 and E3) were performed with temperatures ranging from 90.0 °C -78.0 °C to investigate their influence on the copolymerization. Controlled copolymerization was observed at each temperature studied, indicated by the linear relationship of $\ln[(1/1-X_{wt})]$ versus time; the linear evolution of M_n with X_{wt}; and continuous decrease of Đs with X_{wt} (Figure 2).

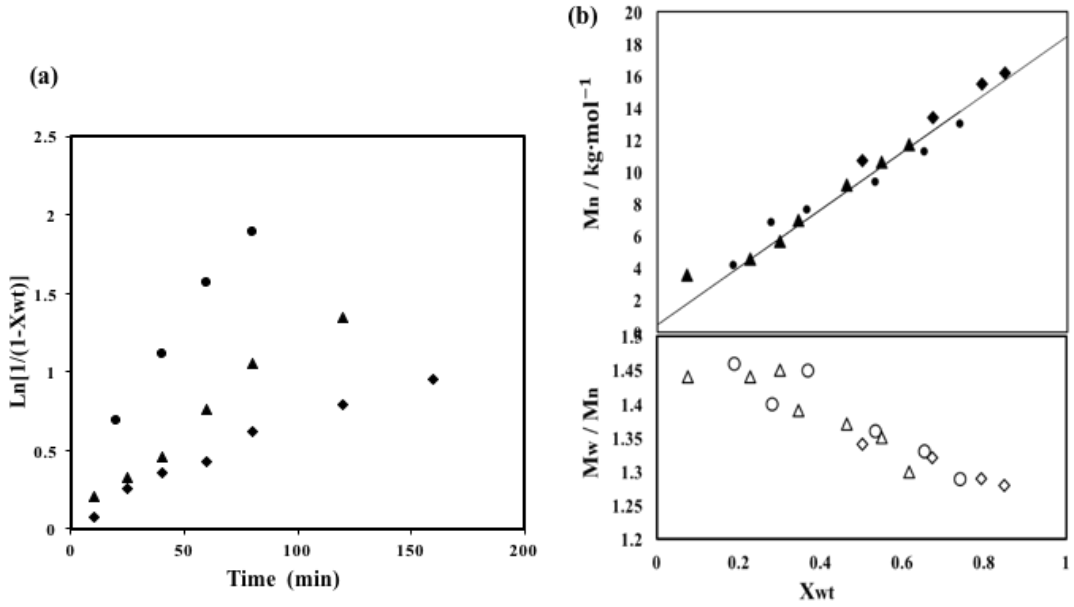


Figure 2. (Effect of temperature on the copolymerization of HEMA and AN (E1, E2, E3, Table 1: (a) $\ln[1/(1-X_{wt})]$ versus time plot; (b) evolution of M_n and M_w/M_n with conversion. The straight line in (b) corresponds to the theoretical evolution based on the acetylated value (○/● : E1, 78.0 °C, $f_{AN,0}$=0.16; △/▲: E2, 85.0 °C, $f_{AN,0}$=0.16; ◇/◆: E3, 78.0 °C, $f_{AN,0}$=0.16).)

Not surprisingly, increasing the temperature accelerated the polymerization rate. At 90.0 °C, 85% conversion was reached at about 80 mins while at 78.0 °C, 62% conversion was reached at about 160 mins using a similar initial composition. The parameter $<k_p><K>$ ($<k_p>$ is the average propagation rate constant and <K> is the average equilibrium constant) was estimated by

extracting the slope from the ln[(1/1-X_{wt})] versus time plot in the linear range and assuming that the concentration of macroradicals is the same as the concentration of initiator initially added (sample calculation was provided in Supporting *Information*). For the copolymerization of HEMA with AN in DMF solution, a higher $\langle k_p \rangle \langle K \rangle$ value was observed (~10^{-4} s^{-1}), compared to the copolymerization of MMA with AN in bulk, the $\langle k_p \rangle \langle K \rangle$ value being 2.60×10^{-6} s^{-1} ($f_{AN,0}$ = 0.088, 90°C) [26]. The result is not surprising because HEMA has a higher k_p compared to that of MMA, which exhibits still a relatively high polymerization rate even at lower temperature (78.0 °C) [48].

With respect to the M_n versus conversion for the HEMA/AN copolymerizations (Figure 2b), the M_n values increased linearly with conversion, and fall close to the theoretical line. This indicates again a high initiating efficiency of NHS-BlocBuilder (also, the acetylated copolymers are structurally similar to PMMA). Đ decreased steadily with the increase of conversion, and was below 1.30 at even over 60% conversion.

3.3 Influence of the Initial Concentration of Acrylonitrile

In the next step, polymerizations were fixed at 85.0 °C based on the previous section's results, with various initial molar fractions of AN. The initial molar feed of AN, $f_{AN,0}$ ranged from 0.05 to 0.16. As little as 5% molar of AN was sufficient to keep the polymerization controlled (Figure 3b). Noticeable effect of initial molar feed of AN on the Đ was observed (Figure 3b). Lower Đs were observed with higher $f_{AN,0}$, as the Đ value was 1.46 for $f_{AN,0}$ = 0.053, 1.38 for $f_{AN,0}$ = 0.10, 1.32 for $f_{AN,0}$ = 0.16 (all at ~65% conversion). The same effect was also observed for the MMA/AN system in bulk using BlocBuilder [26]. However, for the parameter $\langle k_p \rangle \langle K \rangle$, the influence of $f_{AN,0}$ was not that obvious. The calculated experimental values were all very close to each other, in the range of 1.8 - 2.0 $\times 10^{-4}$ s^{-1} (Table 3). This is agreement with other systems

employing the copolymerization method, with the <k_p><K> increasing sharply at only very low controlling co-monomer compositions.

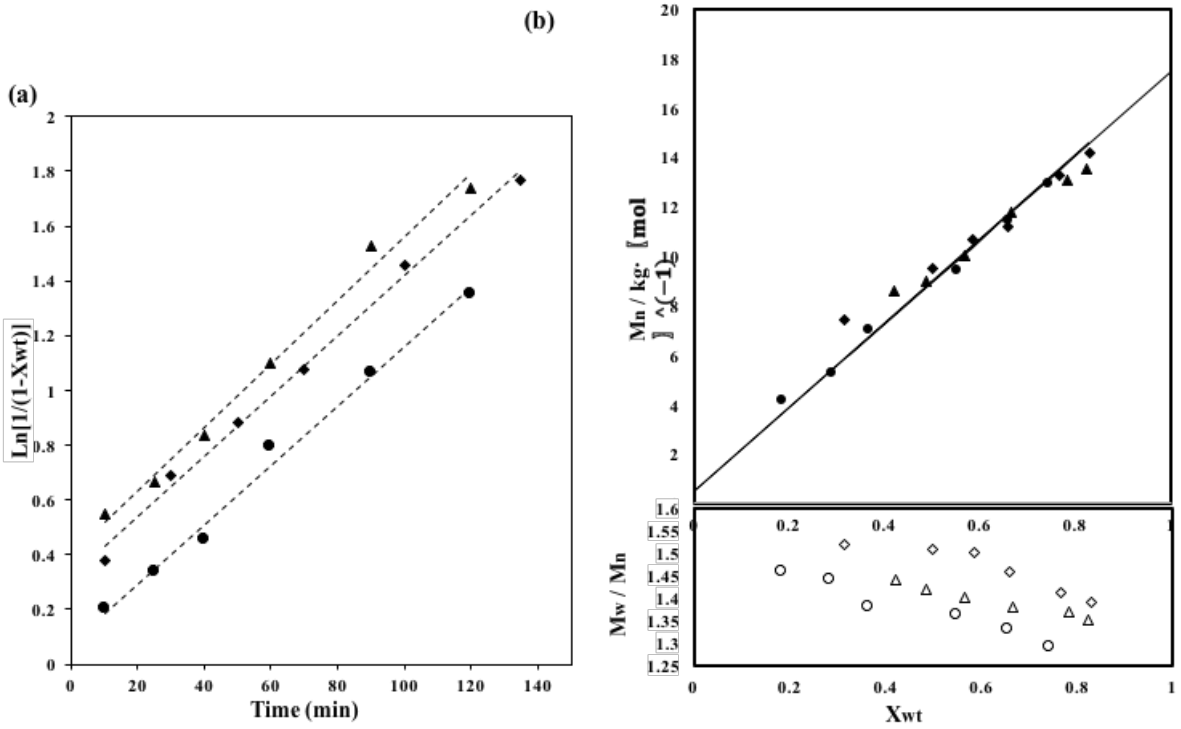


Figure 3. (Effect of initial composition of acrylonitrile on the copolymerization of HEMA with AN (E2, E4, E5, Table 1. (a) ln[1/(1-X_{wt})] versus time plot (●: E2, 85.0 °C, $f_{AN,0}$ = 0.16; ▲: E4, 85.0 °C, $f_{AN,0}$ = 0.10; ◆: E5, 85.0 °C, $f_{AN,0}$ = 0.053) and (b) evolution of M_n and M_w/M_n with conversion X_{wt}. The straight line in (b) corresponds to the theoretical evolution of M_n versus conversion for acetylated samples (○/●: E2, 85.0 °C, $f_{AN,0}$ = 0.16; △/▲: E4, 85.0 °C, $f_{AN,0}$ = 0.10; ◇/◆: E5, 85.0 °C, $f_{AN,0}$ = 0.053).

3.4 Influence of the Type of Co-Monomer

Our next step was replacing AN with S in the experimental formulation as the controlling co-monomer. This was aimed to give a straightforward comparison of the influence of co-monomer type. However, a detailed theoretical explanation for the differences is limited by the lack of corresponding kinetic data, as the more comprehensive implicit penultimate unit effect (IPUE) model did not have enough available parameters. For the same reason, in this work, we are not

aiming to give a detailed explanation, but rather a straightforward description of the differences between the two types of co-monomers for HEMA that were used.

Experiment conditions for copolymerization of HEMA with S were kept the same as that for the HEMA/AN system. An initial molar feed fraction $f_{S,0}$ = 0.10 was able to turn the HEMA/S copolymerization into a controlled one (Figure 4). However, the control was readily lost when the $f_{S,0}$ was decreased to 0.053. No linear relationship of ln[(1/(1-X_{wt})) versus time was observed, and the conversion reached a plateau within one hour. The M_n obtained from GPC deviated strongly from the theoretical value, and the Đ was increasing steadily throughout the entire course of the reaction, with all above 1.5.

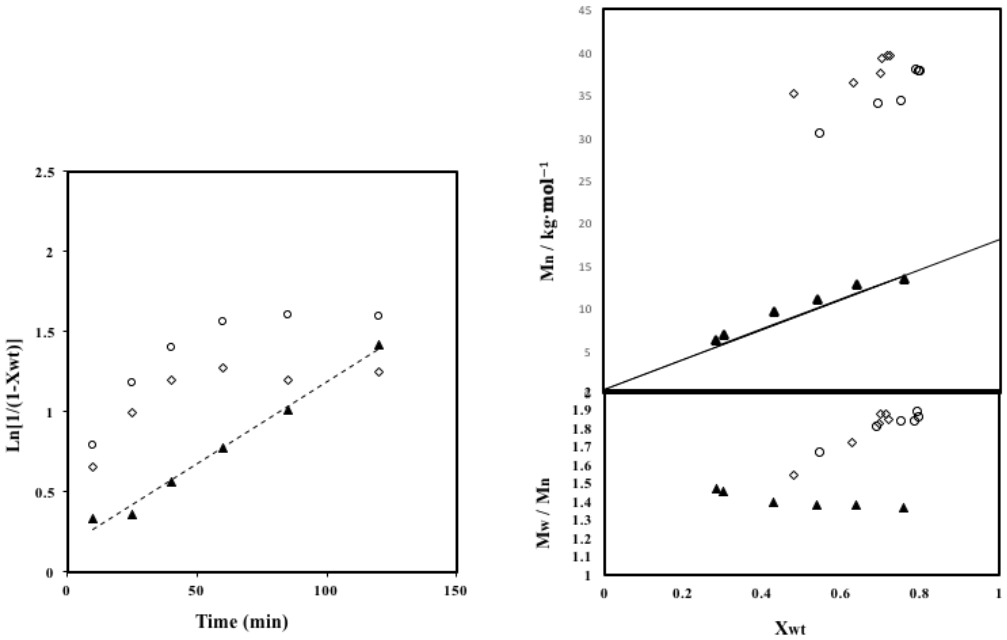


Figure 4. (Effect of the initial feed fraction of styrene, $f_{S,0,}$ on the copolymerization of HEMA and S (E6, E7, E8, Table 1) (a) ln[1/(1-X_{wt})] versus time plot and (b) evolution of M_n and M_w/M_n with conversion X_{wt}. The straight line in (b) corresponds to the theoretical evolution based on the acetylated sample (▲: E6, 85.0 °C, $f_{S,0}$ = 0.10; ◇: E7, 85.0 °C, $f_{S,0}$=0.075; ○: E8, 85.0 °C, $f_{S,0}$ = 0.054).)

A slight increase of the initial feed of styrene to 0.075 was still insufficient, indicated by the non-

linear growth of ln[(1/(1-X_{wt})) versus time. Not surprisingly, no linear relationship was observed for M_n and conversion, and a plateau of M_n was reached at an early stage. The polymerization rate was reduced when $f_{S,0}$ was increased, as shown in Figure 4a). Decrease of polymerization rate with increasing $f_{S,0}$ was also observed for the copolymerization of MMA and S in bulk, indicated by a small decrease of the <k_p><K> value[21]. Interestingly, high conversion was reached in all cases (>70%), despite the lack of control of the copolymerization when $f_{S,0}$ was below 0.10.

The evolution of GPC chromatograms versus conversion for E5 is shown in Figure 5a). The chromatograms continuously shifted to the higher molecular weight region. However, in the case of $f_{S,0}$ = 0.075 and $f_{S,0}$ = 0.054, high molecular weight (M_n > 30 kg · mol^{-1}) was reached at an early stage, deviating strongly from the theoretical prediction. Đ value was never below 1.5 throughout the entire course of the reaction, and kept increasing to 1.9 when the reaction was stopped at about 2 hours (Figure 4b). The GPC chromatograms of the final sample taken from E5, E6 and E7 indicate a poor control for E6 and E7, as a much broader molecular weight distribution was observed (Figure 5b).

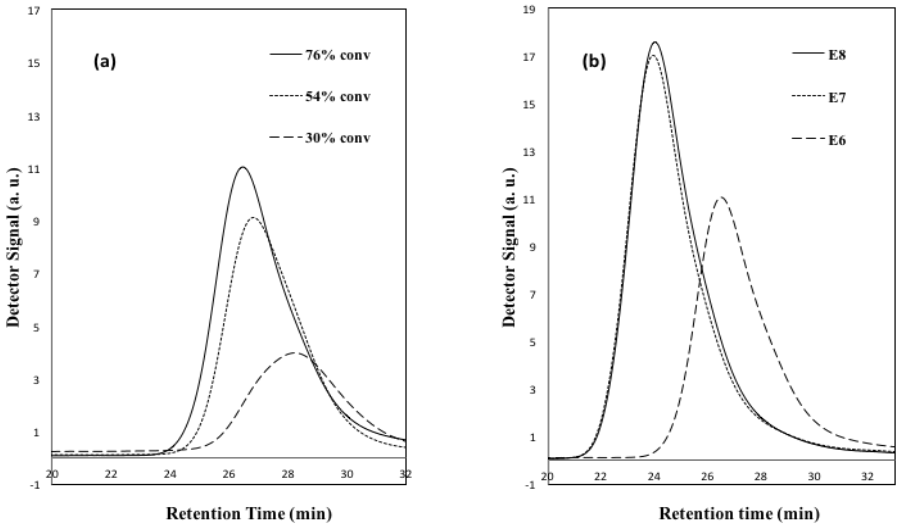


Figure 5. **(**GPC chromatograms for copolymerization of HEMA and styrene (E5, E6, E7, Table

1) (a) GPC chromatograms as a function of monomer conversion for E6; (b) gel permeation chromatograms for the final sample of E5 (~76% conversion), E6 (~71% conversion) and E7 (~80% conversion).)

As the most studied model for the copolymerization approach for the NMP of methacrylic esters, the copolymerization of MMA could be a reference to study other copolymerizations of methacrylic esters. Despite the structural differences between HEMA and MMA, those two systems share some similarities. First, better control was observed for copolymerization with AN, which could be attributed to the lower K of AN [26]. In both systems, when $f_{AN,0}$ was as low as 0.05, it was sufficient to maintain the copolymerization with linear M_n versus conversion and relatively narrow molecular weight distribution. Second, the influence of $f_{AN,,0}$ on the Đ was observed to be the same, with Đ being lower for AN compared to S at the same co-monomer initial mole fraction. Third, both systems exhibited the trend of an increase of polymerization rate when the initial molar concentration of controlling co-monomer decreased, as expected.

For copolymerizing HEMA with S, however, a higher initial molar feed concentration of S was required to achieve satisfactory control, compared to that of MMA or MAA [10, 21]. While controlled copolymerization of MAA or MMA could be obtained with as little as 5% initial molar feed of styrene, this concentration was insufficient for a controlled polymerization of HEMA here.

In terms of the parameter $<k_p><K>$, which can be estimated from the apparent rate constant, the differences are interesting. A much lower $<k_p><K>$ value was observed for the MMA/AN system compared to the MMA/S system (2.6×10^{-6} s^{-1} for MMA/AN; 1.3×10^{-5} s^{-1} for MMA/S; all at 90.0 °C with 0.088 initial molar fraction of AN or S) [26]. However, such a big difference in $<k_p><K>$ value was not observed in the copolymerization of HEMA, as the experimental values were similar for HEMA/AN and HEMA/S, both ~ 10^{-4} s^{-1}. When comparing E4 and E6 (Table

1), which has the same initial composition but different type of co-monomer (AN or S), the Đ value of copolymer obtained at similar conversion did not differ much. The Đ value for copolymer obtained from E4 ($f_{AN,0}$ = 0.10) and E6 ($f_{S,0}$ = 0.10) is 1.38 and 1.38, respectively, both with a conversion approximately 65%.

Due to the scarce kinetic data related to NMP of HEMA/AN, especially the <K> for the SG1-mediated copolymerization of AN with HEMA, neither the implicit penultimate unit effect (IPUE) model nor the terminal model could be used here to determine the $<k_p><K>$ value. We have no direct comparison of K_{HEMA} with $K_{MMA,}$ although we can assume that the radicals behaved similarly. Also, radical reactivity ratios for HEMA/S and HEMA/AN pairs are needed to give a better prediction of $<k_p><K>$ using IPUE model.

For HEMA/S copolymerizations, the effect of solvent was pronounced [48-50]. In DMF solution, the monomer reactivity ratios for HEMA/S were 0.45/0.53 (r_s/r_{hema}, 90.0 °C, 50 vol% DMF) [48], compared to the values of 0.27/0.49, respectively, reported in bulk (r_s/r_{HEMA}, 50.0 °C) [50]. Table 4 summarized the related kinetic data for copolymerization of HEMA with S and of MMA with S. The $<k_p><K>$ value could be estimated from the apparent rate constant. Since the two systems HEMA/S and MMA/S compared here have different $[SG1]_0/[alkoxyamine]_0$ ratio, $<k_p><K>$ was estimated from the apparent rate constant. The $<k_p><K>$ value for HEMA/S was ~ 10^{-4} s^{-1} at 85 °C, and for MMA/S ~ 10^{-6} s^{-1}. The results indicated that a higher $k_{p,HEMA}$ compared to MMA contributes to a higher $<k_p><K>$ value at very low $f_{S,0} < 0.02$. This increase in rate constant may also correspond to the higher conversion plateau exhibited by the HEMA/S system (>70%) compared to the MMA/S (~50%) when control of both systems was not maintained [21]. Using the terminal model, the $<k_p>$ for HEMA/S and MMA/S system was estimated. With initial feed of S set as 0.075, the $<k_p>$ was calculated for both HEMA/S and MMA/S using the parameter

listed in Table 4. This gave a value of 3100 L· mol^{-1}· s^{-1} for HEMA/S [48], and a value of 1800 L· mol^{-1}· s^{-1} for the MMA/S [51, 52]. The differences became less pronounced at higher $f_{S,0}$ however since we assumed that the equilibrium constants were equal for HEMA versus MMA in our simulation comparisons using the <kp><K> expression from the terminal model presented by Charleux and co-workers. Direct measurement of K_{HEMA} was not available and a reliable value would have confirmed how sharp the decrease in $<k_p><K>$ versus $f_{S,0}$ would have been.

Table 4. (Kinetic Parameters for the SG1-Mediated Copolymerization of S and HEMA or MMA)

	Kinetic parameter	**Value**	**Ref.**
$k_{p,S}$	Propagation rate constant of styrene in 50vt% DMF (90°C, L· mol^{-1}· s^{-1})	691	48
$k_{p,HEMA}$	Propagation rate constant of HEMA in 50vt% DMF (90°C, L· mol^{-1}· s^{-1})	3763	48
r_S/r_{HEMA}	Monomer reactivity ratios for the styrene/HEMA pair at 20-60°C	0.53/0.45	48
$k_{p,s}$	Propagation rate constant of styrene in bulk (90°C, L· mol^{-1}· s^{-1})	900	51
$k_{p,MMA}$	Propagation rate constant of MMA in bulk (90°C, L· mol^{-1}· s^{-1})	1640	51
r_S/r_{MMA}	Monomer reactivity ratios for the styrene/MMA pair (90°C, 50vt% DMF)	0.4890/0.4929	52

3.5 Chain Extension of HEMA-Based Macroalkoxyamine Using n-Butyl Methacrylate and Styrene

To verify the chain end fidelity of the HEMA-based copolymer, chain extension was performed using BMA/S mixtures. Because BMA is highly hydrophobic, the block copolymer obtained would be amphiphilic and could be desirable in coatings and paints where a relatively low glass transition temperature and amphiphilic properties would be desirable. Therefore, macroinitiators (Macro ID A, B, C) were chain extended with BMA/S mixture in DMF solution at 90°C. The macroinitiator was prepared at similar experimental conditions, but a lower conversion was

chosen (~50% conversion) to avoid excessive irreversible terminating side-reactions. Only AN-functional macroinitiators were used in chain extension studies. Table 5 gives the characterization results for the various HEMA/AN copolymers used as macroinitiators for the chain extension experiments. Also, characterization of the chain extended products was summarized in Table 5.

Table 5. (Characterization of the Macroinitiator and Block Polymers from Chain Extension in DMF Solution)

		Macroinitiator					Chain extended product			
expt	**Macro ID**	**M_n[a),b)] [kg · mol^{-1}]**	**M_n[c)] [kg · mol^{-1}]**	**M_w/M_n[c)]**	**$F_{AN,th}$[d)]**	**F_{AN}[d)]**	**M_n[c)] [kg · mol^{-1}]**	**M_w/M_n[c)]**	**F_s[e)]**	**F_{BMA}[e)]**
H1	A	11.2	10.0	1.33	0.10	0.070	31.8	1.53	0.07	0.60
H2	B	17.1	18.1	1.29	0.047	0.045	35.1	1.50	0.06	0.45
H3	C	6.5	6.3	1.34	0.11	0.086	27.3	1.51	0.09	0.79

[a)] (Experimental M_n measured after acetylation; ^{1}H NMR for the acetylated copolymer in $CDCl_3$, 500 MHz) [b)] (molecular weight is calculated for the acetylated macroinitiator, assuming all HEMA units in the copolymer have been transformed); [c)] Experimental Mn measured after acetylation based on PMMA standards in THF solvent ,40°C [d)] (Average composition of AN in the copolymer was calculated from the Skeist equation using reactivity ratios for HEMA/AN pair from [53];) [e)] (Average composition of AN in the copolymer determined by ^{1}H NMR;) [d)] (Average composition of the block polymer determined by ^{1}H NMR.)

Chain extension reaction in DMF indicates the successful re-initiation of the macroinitiator. Complete shift of GPC chromatograms was observed from all of the macroinitiators (Figure 6).

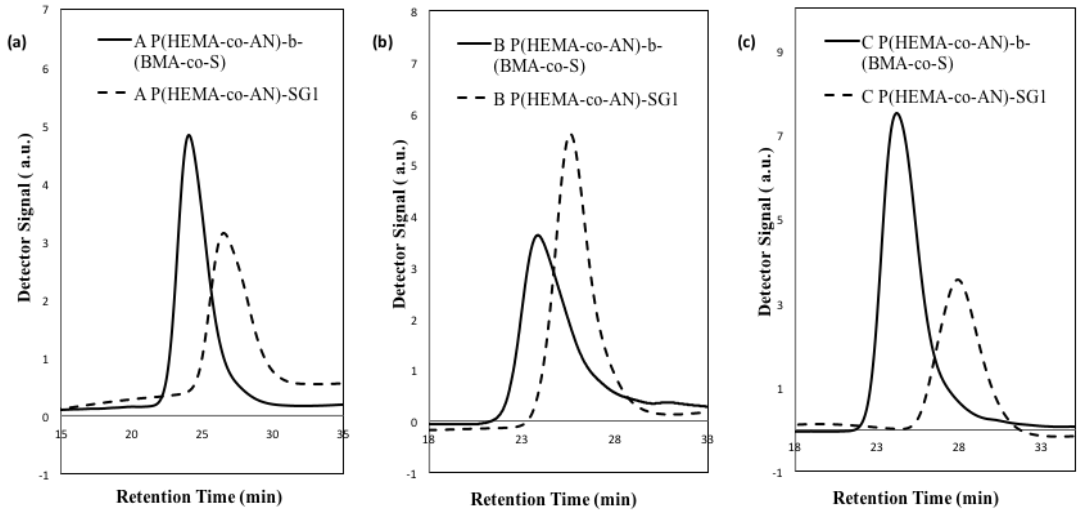


Figure 6. **(**GPC chromatograms for chain extension of poly(HEMA-*ran*-AN)-SG1 macroalkoxyamine using n-BMA/styrene mixtures (Table 5, H1, H2, H3) (a) chain extension using macroinitiator A, H1; (b) chain extension using macroinitiator B, H2; (c) chain extension was done using macroinitiator C, H3.)

The incorporation of the second block was confirmed by ^{1}H NMR, which gives the composition of the resulting block polymer based on the protons of ester group from n-BMA units (2H, -$COOCH_2$-, δ = 3.75-4.0 ppm) and aromatic protons from styrene units (δ = 7.0-7.5 ppm) (Figure 7). To distinguish the protons of the ester group of BMA units from that of HEMA units, the acetylation reaction was performed for the obtained block copolymer before ^{1}H NMR characterization.

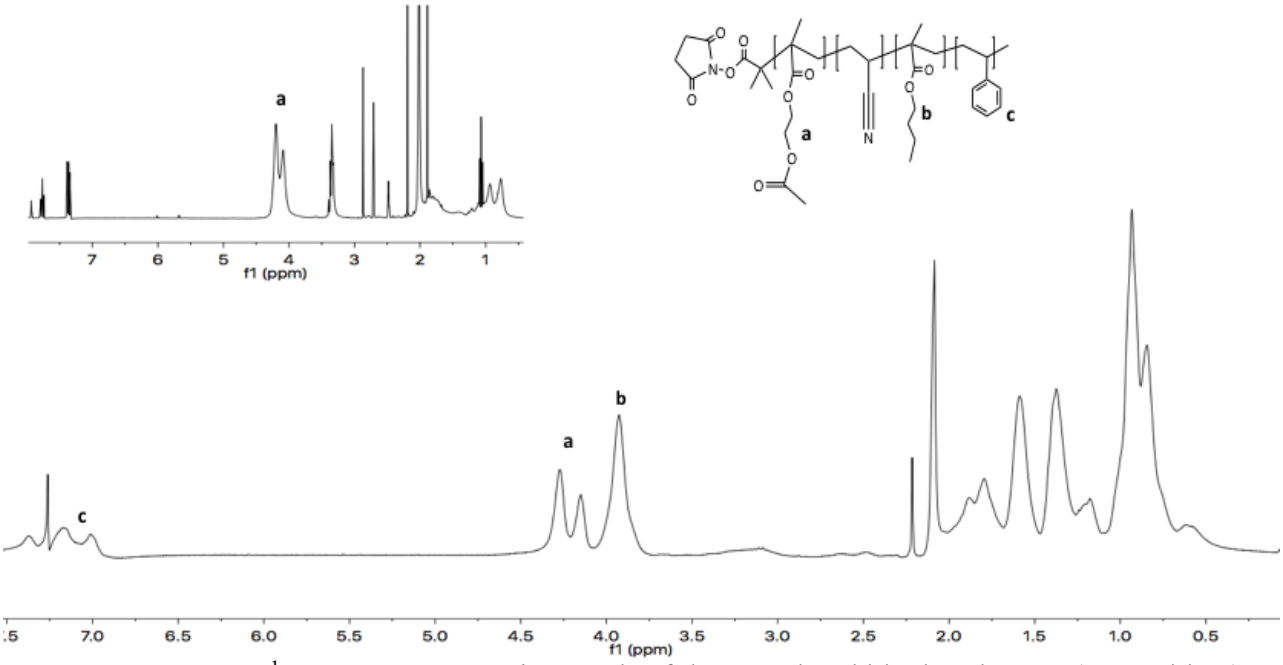


Figure 7. (500 MHz ^{1}H NMR spectrum in $CDCl_3$ of the acetylated block polymers (H3, Table 2). Inset: acetylated macroinitiator C of the 500 MHz ^{1}H NMR spectrum in $CDCl_3$.)

As the fraction of "living" chains is important for building block copolymers, identification of the fraction of "living" chains is of interest for the macroinitiator. An easy, direct way to do that is using GPC to observe the shift in the molecular weight distributions. However, this requires a direct injection of samples without any possible fractionation step, since the hexane used to precipitate the block copolymer products in experiments H1, H2, H3, partially dissolved the poly(HEMA-*ran*-AN) macroinitiators and thus would remove any inactive macroinitiators from the GPC chromatograms. Thus, direct injection of the crude product was done by a pre-treatment of poly(HEMA-*ran*-AN) samples, transforming hydroxyl groups in HEMA units to esters using the same protocol, and dried sufficiently before the chain extension. With the chain extension using acetylated macroinitiator (from Macro ID: C, Table 2), samples taken periodically from the reaction were directly diluted in THF for GPC characterization. A neat shift of GPC chromatograph from samples taken periodically indicated a high fraction of "living" chains

(Figure 8). This further confirms that we have a promising way to construct HEMA-based block copolymers with desirable chain length and composition, with little effort in purification.

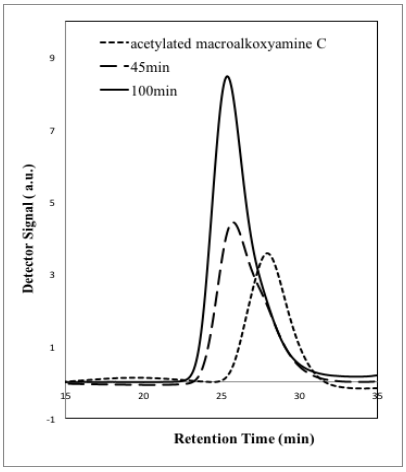


Figure 8. **(**Evolution of GPC chromatograms for chain extension using acetylated macroinitiator C (Table 2, H4), The time indicated when samples were taken during reaction after time zero were set arbitrarily.)

4. Conclusion

2-hydroxyethyl methacrylate (HEMA) was shown to be polymerized in a controlled manner via NMP with a small concentration of controlling co-monomer (~ 5-10 mol% in the initial mixture of either acrylonitrile (AN) or styrene (S)) in dimethylformamide (DMF) solution. Temperature, type of co-monomer and the initial molar fraction in the feed were investigated for their influence on the polymerization kinetics. AN works better as the controlling agent than S for polymerizing HEMA. As little as 5 mol% AN in the feed was sufficient to maintain the polymerization in a controlled manner, while for S, the initial feed should not be less than 7.5 mol%. GPC characterization of the HEMA-based copolymers showed relatively narrow molecular weight distributions (~1.3). Chain extension using the so-prepared copolymer confirmed a good re-initiation ability of the macroalkoxyamine. This marks another successful application of the copolymerization approach for NMP of methacrylic esters, and demonstrates a facile way to construct HEMA rich-based block polymers via NMP.

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