Polymerization of Acrylates by Atom Transfer Radical Polymerization. Homopolymerization of 2-Hydroxyethyl Acrylate

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ABSTRACT: The application of atom transfer radical polymerization (ATRP) to the homopolymerization of 2-hydroxyethyl acrylate, a functional monomer, is reported. The polymerizations exhibit first-order kinetics, and molecular weights increase linearly with conversion. Polydispersities remain low throughout the polymerization ($M_w/M_n \approx 1.2$). Reactions were conducted in bulk and in 1 : 1 (by volume) aqueous solution; the latter demonstrates the resilience of ATRP to protic media. Analysis of poly(2-hydroxyethyl acrylate) by MALDI-MS and ^{1}H-NMR shows $M_{n,exp}$ to be much closer to $M_{n,th}$ than those observed by SEC using polystyrene standards. © 1998 John Wiley & Sons, Inc. J Polym Sci A: Polym Chem 36: 1417–1424, 1998

Keywords: 2-hydroxyethyl acrylate; poly(2-hydroxyethyl acrylate); atom transfer radical polymerization (ATRP); controlled free radical polymerization; MALDI-MS

INTRODUCTION

Controlled polymerization resulting in polymers with well-defined molecular weights, mass distributions, end groups, and chain topologies is of great scientific and commercial importance. Until relatively recently, such control had only been achieved for anionic and cationic polymerizations. Although free radical polymerization is of great commercial importance and is much more tolerant to traces of impurities (moisture, etc.), methods of "living" free radical polymerization have proved to be more elusive. This is because, in radical polymerization, the deactivation of growing polymer chains by bimolecular termination is fast and limits control. Over recent years, however, significant advances have been made in the field of controlled free radical polymerization and numerous systems have been reported in the literature. In order for such methods to be truly versatile it is necessary that they be compatible with a variety of protic solvents and a broad range of functionalized monomers.[1]

Living polymerizations were defined by Szwarc in 1956[2] as chain growth polymerizations which do not undergo either chain transfer or termination. If initiation is fast, the molecular weight of such polymers increases linearly with conversion; hence, the degree of polymerization (DP) is directly related to the mass of monomer consumed and the concentration of initiator used. The resulting end functionalities of the polymers produced are, therefore, clearly defined, and the products show characteristically narrow polydispersities approaching the Poisson distribution.

To date the literature shows a variety of controlled free radical processes and a plethora of monomers which they polymerize. These processes are rendered "living" by the reversible activation of dormant polymer chain ends which are then free to propagate in the presence of mono-

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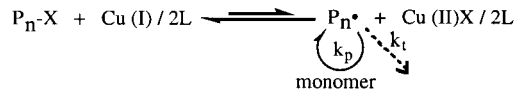


Scheme 1.

mer. Rizzardo,[3] Georges,[4] Hawker,[5] Gnanou,[6] and our group[7] have shown that nitroxides, such as TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy radical), are efficient in the controlled polymerization of styrene[3,4a,5,7] and acrylates.[4b,6] Such polymerizations involve the homolytic cleavage of the dormant chain end group, to give a propagating radical chain and a stable free radical which is unable to efficiently initiate further polymerization but which can then deactivate the growing polymer chain. Georges has demonstrated that little or no termination occurs in this system, and the polydispersities of such systems are maintained well below $M_w/M_n < 1.5$.[4a] Iniferters, described by Otsu et al.,[8,9] are similar in nature; many have the stable radical centered on a sulfur atom and can be used for the polymerization of styrenes[8] and alkyl methacrylates.[9] Cobalt porphyrin complexes have been used to polymerize acrylates[10,11] and as efficient transfer agents for methacrylates.[12]

Recently, transition metal-mediated polymerization systems using atom transfer have been growing in importance. Cu complexes are becoming well-known for their use in atom transfer radical polymerization (ATRP).[13] Other transition metal catalysts have also been described; Sawamoto and co-workers reported the use of Ru-mediated systems for alkyl methacrylates.[14] Ni complexes have been discussed by Teyssié et al.[15a] and Sawamoto,[15b] also for the polymerization of alkyl methacrylates.

ATRP[13a] employs a Cu(I) halide, which is complexed with ligands (often bidentate), to form a "CuX/2L" complex. Halogenated initiators are used for polymerization. The Cu(I) complex reversibly activates dormant polymer chains (and the initiator) by transfer of the halogen end group as shown in Scheme 1.

The equilibrium which is established between active and dormant chain ends results in a low steady-state concentration of radicals which suppresses termination. Activation is fast, ensuring that all chain ends grow at the same rate. This system is proving to be a very versatile polymerization process, and to date, it has been shown to polymerize styrene,[16] methyl methacrylate,[17] acrylates,[18] and acrylonitrile.[19] ATRP has also been used to produce a variety of polymer architectures and copolymers.[20–23]

In this paper we report the homopolymerization of 2-hydroxyethyl acrylate (HEA), a functionalized monomer. We also show that the polymerization system is resilient to protic media and in particular to water, thus demonstrating the robustness of the ATRP technique. The controlled nature of the HEA polymerization is described, and end functionalities are discussed. Controlled polymerization of such monomers is of immense importance, since applications of functionalized polymers require well-defined products. Commercially, copolymers of poly(2-hydroxyethyl acrylate) (PHEA) are applied in the fields of coatings[24,25] and biomaterials.[26]

EXPERIMENTAL

Materials

2-Hydroxyethyl acrylate (HEA) (Aldrich) was purified by first dissolving the monomer in water (25% by volume). Hydroquinone (0.1%) was then added to the solution to inhibit thermal polymerization. The solution was extracted with hexane (10 times) to remove diacrylate, and the aqueous solution was salted (250 g/L NaCl). The monomer was then separated from the aqueous phase by ether extraction (4 times) to remove acrylic acid. Hydroquinone was added to the ether solution. $CaSO_4$ drying agent was used to remove traces of water before evaporation of the ether phase. The purified monomer was subsequently kept over molecular sieves and distilled under reduced pressure immediately prior to use.

Methyl 2-bromopropionate (MBP) (Aldrich), diethyl 2-methyl-2-bromomalonate (DEMBM) (Aldrich), CuBr (98%, Aldrich), and 2-2′-bipyridine (bpy) (Aldrich) were used as received.

Polymerization Procedures

Bulk Polymerizations

These polymerizations were conducted in sealed glass tubes. Typical ratios of the reactants were M : I : Cu : L = 100 : 1 : 1 : 2. The initiators used were either MBP or diethyl 2-methyl-2-bromomalonate (DEMBM). All reagents were added to the glass tube, and the mixture was degassed three times before sealing tubes under vacuum. Reac-

tions were conducted in an oil bath regulated at 90°C. Tubes were removed at regular intervals for kinetic experiments, the resulting polymer was dissolved in DMF, and samples were injected directly into the SEC. The solution was additionally passed over alumina to remove the catalyst and dried in a vacuum oven overnight to remove monomer and DMF to isolate the polymer for NMR (d_6-DMSO) and MS analysis.

For example, in a reaction tube, 0.0337 g (0.2 mmol) of bpy, 0.0154 g (0.1 mmol) of CuBr, 12 μL (0.1 mmol) of MBP and 0.5 mL (4.3 mmol) of HEA were combined and degassed via three freeze–pump–thaw cycles. The tube was then sealed under vacuum and placed in an oil bath at 90°C for 2 h. The tube was then immediately frozen in liquid nitrogen and broken open. Part of the contents was dissolved in d_6-DMSO, and the rest, in DMF. The deuterated sample was used to determine conversion by ^{1}H-NMR. About 0.5 mL of the DMF solution was filtered through a 0.2 μm filter with one drop of diphenyl ether as an internal standard and injected directly into the GPC. The remaining DMF solution was passed over alumina and dried in a vacuum oven at 60°C overnight. Part of the remaining sample was dissolved in d_6-DMSO to determine molecular weight from NMR by end group analysis and the residual concentration of DMF, and the rest was used for preparation of MALDI samples (discussed below): M_n = 3800 (NMR); conversion = 91%; M_w/M_n = 1.15 (SEC).

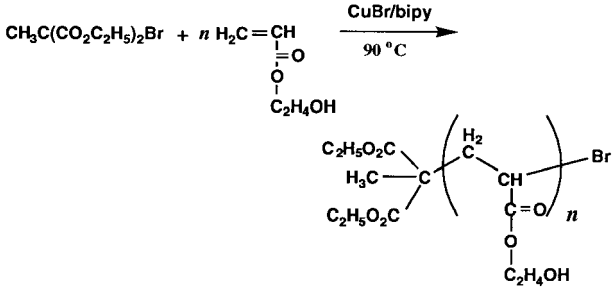
Polymerizations Using Water as Solvent

These polymerizations were conducted in a 1 : 1 (v/v) ratio of HEA/H_2O. The ratio of reactants was M : I : Cu : L = 100 : 1 : 1 : 3. The reaction mixture was degassed twice to remove traces of oxygen before tubes were sealed. Polymerization was carried out at 90°C, and the reaction was terminated after 12 h. The tube contents were dried over $MgSO_4$ and dissolved in DMF.

The Cu/bpy complex was homogeneous in both the bulk and aqueous polymerizations. In both instances the brown solution was characteristic of Cu(I) complexes.

Characterization of Materials

Monomer conversion was determined by GC using THF as an internal standard or by NMR using d_6-DMSO as a solvent. Molecular weight and molecular weight distribution were measured in DMF using a Waters 510 liquid chromatograph equipped with the following Phenogel GPC columns: guard, linear, 1000 Å and 100 Å in series with 410 differential refractometer and a Waters 991 UV detector. Analysis of polymers was achieved in comparison to polystyrene standards (range 1.1×10^3–1.3×10^6) and poly(methyl methacrylate) standards (range 1.1×10^3–1.6×10^6), though little difference was observed between the two. GC measurements were carried out using a Shimadzu GC-14A chromatograph equipped with a wide-bore capillary column. The structure of the polymers was analyzed using ^{1}H-NMR spectroscopy (300 MHz Bruker instrument) and by MALDI-MS.



Scheme 2.

MALDI-MS data were collected using a PerSeptive Biosystems Voyager Elite MALDI mass spectrometer, equipped with a nitrogen laser, wavelength 337 nm. Collection was achieved in linear mode using delayed extraction, with a delay time of 150 ns. All spectra were averaged over 128 laser shots.

MALDI-MS Sample Preparation

PHEA ($M_n \approx 3000$) solutions ($10^{-3}M$) were prepared in DMF. A 0.1M solution of *trans*-3-indoleacrylic acid (IAA) matrix was prepared in acetone and doped with sodium trifluoracetate (0.1M in THF) in a 50 : 1 ratio of matrix/salt. Matrix and salt were used as received from Aldrich. IAA and PHEA solutions were mixed in a 1 : 1 volumetric ratio prior to spotting on a gold-plated sample slide.

RESULTS AND DISCUSSION

The ligand used in all these reactions was 2,2′-bipyridine (bpy), which when complexed with Cu-

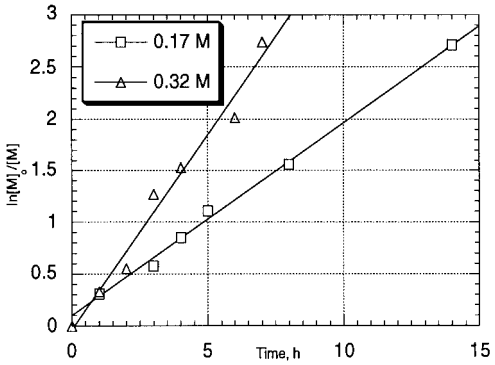


Figure 1. Effects of two different concentrations of initiator on polymerization kinetics: $[HEA]_0 = 8.57M$; $[MBP]_0 = 0.32M$; $0.17M$; $T = 90°C$.

(I)Br affords a heterogeneous catalyst system in most reaction media. In HEA, however, the catalyst was homogeneous. This was attributed to the more polar nature of the monomer. Polymerization of the purified HEA is described in reaction Scheme 2. It is essential that the HEA monomer be purified (as described in Experimental) prior to use in reactions. Purification procedures remove diacrylate and acrylic acid impurities. The presence of the diacrylate leads to crosslinking, and in the presence of large amounts of acrylic acid no polymerization is observed. Polymerizations of the unpurified or poorly purified monomer may be either slow and incomplete or lead to insoluble solids.

KINETIC DATA

The plot of $\ln([M]_0/[M])$ versus time is linear (Fig. 1), indicating first-order kinetics; hence, the number of active species is constant throughout the course of the reaction (i.e. $k_p[P^*] = \text{constant}$). This observation together with the linear evolution of molecular weight with conversion (Fig. 2.) indicates that initiation is fast and that the contribution of chain breaking, transfer, and termination reactions during the course of the polymerization is negligible; thus, the process is indeed controlled. Increasing the $[HEA]_0 : [MBP]_0$ ratio results in the expected increase in M_n. Polydispersities decrease with increasing conversion, remaining low ($M_w/M_n \approx 1.2$) even at high conversion.

Table I demonstrates that relatively high molecular weight polymers of HEA with low polydispersities can be achieved by ATRP. A discrepancy between the values of $M_{n,th}$ and $M_{n,SEC}$ is observed ($M_{n,th} = [MW_{HEA}p([M]_0/[I]_0)]$, where MW_{HEA} is the molecular weight of the monomer, p is the conversion, and $[M]_0$ and $[I]_0$ are the initial concentrations of monomer and initiator used, respectively). This is attributed to analysis of SEC data using calibrations made with commercially available polystyrene standards. The differences in hydrodynamic volume of polystyrene and poly(2-hydroxyethyl acrylate) of the same molecular weight are evidently large in the DMF solvent phase of the SEC. Initiator efficiency is difficult to estimate from this data since the $M_{n,SEC}$ values are not accurate. Molecular weights as high as $M_{n,SEC} = 78{,}000$ have been obtained with $M_w/M_n = 1.3$. As the molecular weight increased toward 100,000, however, polydispersities also increased ($M_w/M_n > 1.6$). In the low range of $M_n < 10{,}000$, MALDI-MS and ^{1}H-NMR end group analyses indicate that $M_{n,MALDI} \approx M_{n,NMR} \approx M_{n,th}$; however, at the molecular weights mentioned above, accurate molecular weights cannot be determined using either of these methods.

^{1}H-NMR End Group Analysis

Low molecular weight samples ($M_n < 10{,}000$) are generally required for analysis of terminal groups by NMR or MALDI-MS. Two such samples were prepared, using different initiators (DEMBM and MBP), and the results of SEC and MS are summarized in Table II.

The number average molecular weight for

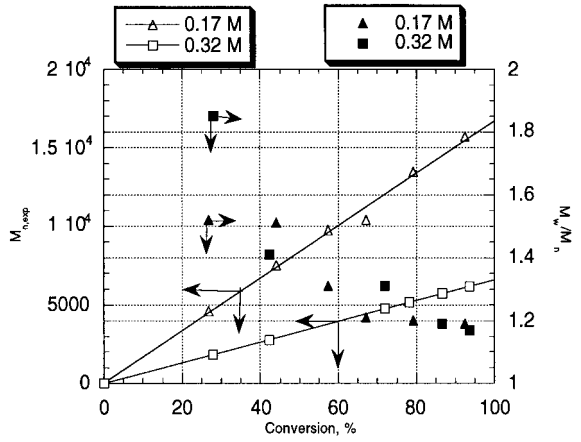


Figure 2. Effect of different $[\text{monomer}]_0/[\text{initiator}]_0$ ratios for bulk ATRP of HEA: $[HEA]_0 = 8.57M$; $[MBP]_0 = 0.32M$, $0.17M$; $T = 90°C$.

Table I. Molecular Weight Data for PHEA Samples Produced by ATRP

Expt[a]	Conversion (%)	$M_{n,th}$	$M_{n,SEC}$	M_w/M_n
1	92	3,100	6,170	1.19
2	91	15,000	30,000	1.19
3	90	18,000	36,000	1.17

[a] Conditions: extp 1, $[HEA]_0 = 8.67M$, $[MBP]_0/[CuBr]_0/[bipy]_0 = 1/1/3$, $T = 90°C$, time = 10 h; expt 2, $[HEA]_0 = 8.67M$, $[MBP]_0/[CuBr]_0/[Bipy]_0 = 1/1/3$, $T = 90°C$, time = 14 h; expt 3, $[HEA]_0 = 8.67M$, $[MBP]_0/[CuBr]_0/[bipy]_0 = 1/1/3$, $T = 90°C$, time = 14 h.

PHEA initiated by MBP has been calculated from ^{1}H-NMR spectra (Fig. 3) by comparing integrals for the $—CH_3$ of the end group with resonances corresponding to the backbone protons. Thus, a broad multiplet (g) at $\delta = 1.10$ ppm corresponds to the terminal $—CH_3$ group from the MBP initiator, whereas —CH and $—CH_2$ backbone protons (d and e) resonate at 2.25 ppm and from 1.30 to 2.00 ppm, respectively. Signals at $\delta = 4.05$ and 3.55 ppm are assigned to $—CH_2$ protons of the hydroxyethyl group (c and b), and a resonance at $\delta = 4.80$ ppm corresponds to the —OH of the hydroxyethyl group (a). The methyl ester protons of the tail end group (h) are expected to give a signal at 3.60 ppm; this is, however, masked by the resonance of one of the $—CH_2$ groups from the hydroxyethyl substituent. The methylene proton (f) from the head group is expected to resonate at 4.20 ppm, which is obscured by the other $—CH_2$ group from the hydroxyethyl substituent. When DEMBM is used as initiator, the polymer end groups are masked by resonances from the polymer chain and M_n cannot be calculated directly from the ^{1}H-NMR data.

MALDI-MS Data

Both samples, PHEA1 and -2, were analyzed by MALDI-MS and gave clear spectra with good signal to noise ratios. Figure 4 shows the spectrum of PHEA1. Some distortion of the baseline is clearly visible, even though data were accumulated just above the laser power threshold for this sample. It is thought that the hydrogen-bonding interactions present in the cocrystals of PHEA analyte and the IAA matrix are stronger here than for most polar meth(acrylates) in IAA. This results in PHEA samples being difficult to ionize and explains why slightly higher than average laser powers are required. Spectra may be improved by using a different matrix. To date, however, IAA has been found to be a more compatible MALDI matrix with PHEA samples than dithranol, 2,5-dihydroxybenzoic acid (DHB), or 9-nitroanthracene.

$M_{n,MALDI}$ of both PHEA1 and PHEA2 agree well with their $M_{n,th}$. In both instances three series are observed. The primary (most intense) series corresponds to $\mathbf{A} = [CH_3CH(CO_2CH_3)_2 - \{HEA\}_n - Br + Na]^+$. A second species, **B**, corresponds to $[CH_3CH(CO_2CH_3)_2 - \{HEA\}_n - CH{=}CH(CO_2C_2H_5OH) + Na]^+$. The presence of the latter raises the question of whether the unsaturation results from the polymerization reaction or it is produced as a result of fragmentation in the MALDI mass spectrometer. Since no evidence of unsaturation is seen in the ^{1}H-NMR data (and this should be clearly visible at this molecular

Table II. Molecular Weight Data for Low Molecular Weight PHEA Samples for End Group Analysis

Sample (initiator)	$M_{n,th}$	Method	$M_{n,expt}$	M_w/M_n
PHEA1 (DEMBM)	3100	SEC	6270	1.22
		NMR		
		MALDI	3200	1.25
PHEA2 (MBP)	4100	SEC	9860	1.17
		NMR	4200	
		MALDI	4842	1.19

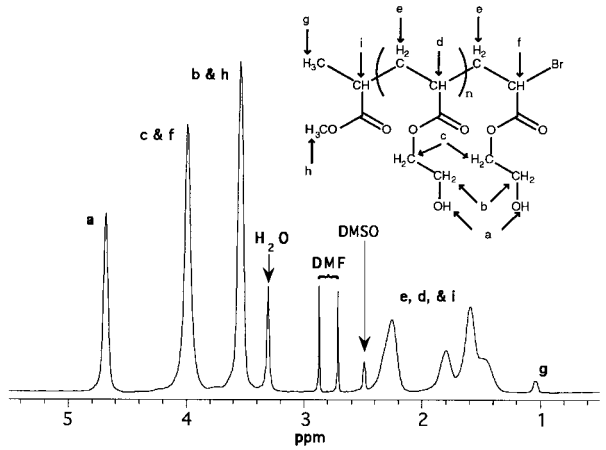


Figure 3. ^{1}H-NMR spectrum of PHEA initiated with MBP showing labeling of end groups used to determine molecular weight: $[HEA]_0 = 8.57M$; $[MBP]_0 = 0.21M$; $T = 90°C$.

weight), it is therefore proposed that this species is produced within the mass spectrometer. The loss of halides in such a manner is a known fragmentation route in MS.[27]

Finally, a third series, **C**, is seen, 61 amu below that of the primary series, **A**, and 17 amu above series **B** peaks. These mass differences are irrespective of the initiator used (PHEA1 or PHEA2). Although it could be proposed that this species corresponds to a fragmentation of the pendant group on the PHEA, the fact that only one such fragmentation is observed per oligomer (DP > 10) seems surprising. It is proposed, therefore, that species **C** corresponds to $[CH_3CH(CO_2CH_3)_2 - \{HEA\}_n - OH + Na]^+$. It is proposed that the brominated polymer end group undergoes a nucleophilic substitution reaction with H_2O (PHEA is a hydrophilic polymer, and water is associated with the polymer to some extent). It is probable that the substitution occurs in the solution phase (i.e. while the samples are being prepared for MALDI analysis), but evidence exists indicating that a gas phase reaction in the mass spectrometer is also a possibility,[28] although less likely.

Although it is known that MALDI-MS data are subject to discrimination effects due to detector bias and ionization effects,[29] unlike SEC, the hydrodynamic volume and other physical properties do not influence the determination of molecular weight in MS and values obtained by the latter can be more accurate for less polydisperse samples. The low polydispersities obtained by SEC and MALDI-MS methods agree well. Table II shows that the MALDI-MS and ^{1}H-NMR M_n values are similar. Both are also much closer to the theoretical M_n than those obtained by SEC; this adds credence to the MS data. For PHEA, MALDI-MS gives a better estimate of M_n than SEC; however, MS analysis cannot be conducted over M_n = 10,000 since the polymers cannot be ionized efficiently.

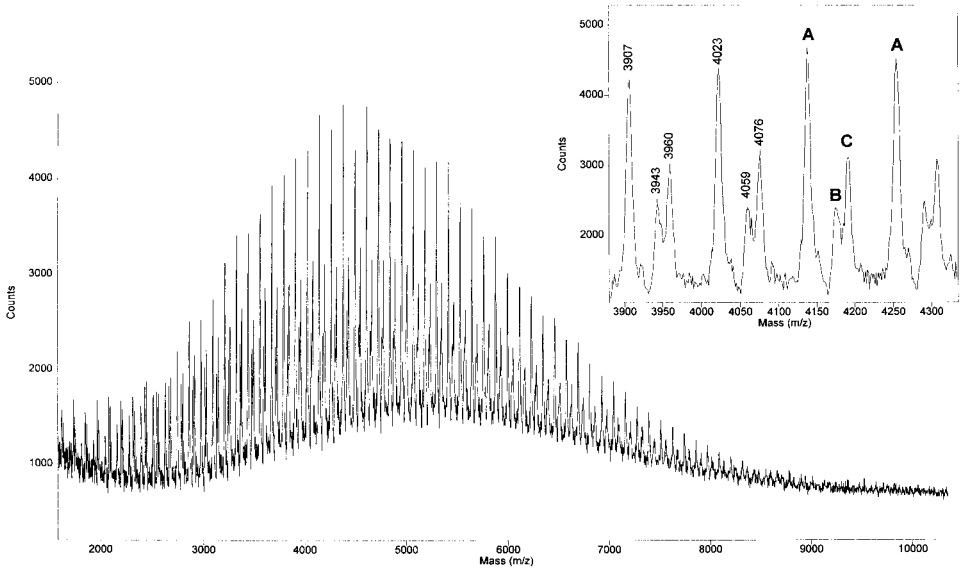


Figure 4. MALDI-TOF spectrum of PHEA initiated with MBP ($M_{n\,(NMR)} = 4200$): $[HEA]_0 = 8.57M$; $[MBP]_0 = 0.24M$; $T = 90°C$.

Polymerization in the Presence of Water

As stated earlier, in order for a controlled free radical polymerization system to be truly versatile it must not only be applicable to a wide range of monomers but must also be tolerant to protic media. In order to further test this criterion, the HEA polymerization was conducted in aqueous solution, since both monomer and polymer dissolve in water. After 12 h at 90°C in an aqueous medium (50 vol. %), the resulting polymer reached high conversion (87% by GC) with $M_{n,SEC}$ = 14,700 and M_w/M_n = 1.34. The ^{1}H-NMR confirms that the hydroxyl group is unaffected by the reaction and that unsaturated acrylic monomer is still present. Although the polymerization was slower, the value of M_n is comparable to the data listed in Table I. Polydispersity has remained relatively low, although it is slightly higher than in experiments conducted without the presence of water.

CONCLUSION

This paper shows that controlled/"living" polymerization of 2-hydroxyethyl acrylate by ATRP has been successfully achieved. Polymerization of this functional monomer using halogenated initiators and CuBr/bipy as catalyst leads to polymers with molecular weights controlled by the ratio $\Delta[M]_0/[I]_0$ and which possess low polydispersities. We have demonstrated that ATRP of 2-hydroxyethyl acrylate is effective in bulk polymerizations and is also robust in aqueous solution.

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