Nitroxide-Mediated Living Radical Polymerization of 2-Hydroxyethyl Acrylate and the Synthesis of Amphiphilic Block Copolymers

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ABSTRACT: Nitroxide-mediated radical polymerizations of 2-hydroxyethyl acrylate (HEA) were performed in bulk, in organic solvent (*N*,*N*-dimethylformamide), and in aqueous media at 100−120 °C, using an alkoxyamine initiator based on *N*-*tert*-butyl-*N*-(1-diethyl phosphono-2,2-dimethylpropyl) nitroxide, SG1. By the addition of free nitroxide (6−12 mol% with respect to the initiator), the polymerizations were controlled, exhibiting a linear relationship of $\ln([M]_0/[M])$ vs time and M_n vs conversion up to 50−60% conversion. Poly(HEA) with $M_n \approx 90\,000$ and $M_w/M_n < 1.3$ can be obtained by bulk polymerization. Solution polymerizations of HEA in *N*,*N*-dimethylformamide and in water exhibit comparable kinetics to those of HEA bulk polymerizations at the same temperature. Chain transfer to polymer produced up to 1.7 mol% branches for poly(HEA) depending on the reaction conditions, with a trend of increasing long chain branching with conversion. Amphiphilic block copolymers of poly(BA-*b*-HEA) with different molecular weights and block composition were synthesized from a poly(*n*-butyl acrylate) (pBA) macroinitiator.

Introduction

In recent years, significant advances have been made in the field of living/controlled free radical polymerization (LRP/CRP). A variety of well-controlled polymers with complex architectures have been made by several CRP methods, including nitroxide-mediated radical polymerization (NMRP),[1] atom transfer radical polymerization (ATRP),[2] and reversible addition−fragmentation chain transfer (RAFT).[3] Free-radical polymerization is of particular interest for some functional monomers because it can tolerate functional groups and polar solvents including water. This is in contrast with ionic living polymerizations, which require strictly pure conditions and cannot tolerate some functional groups nor aqueous media.

2-Hydroxyethyl acrylate (HEA) is a functional monomer whose copolymers are useful as biomaterials and coatings.[4] The CRP synthesis of poly(2-hydroxyethyl acrylate) (pHEA) and amphiphilic block copolymers based on HEA with well-defined structure is of special importance for both their application and the applicability of this living polymerization method. ATRP was the first reported CRP method for direct synthesis of pHEA.[5] In that work, using halogenated initiators and CuBr/bipy as catalyst, the controlled polymerization of HEA was obtained in bulk and in aqueous solution, with the polydispersities typically 1.2−1.5. In another report of the controlled synthesis of pHEA using ATRP, the hydroxyl group in HEA was protected and hydrolyzed after polymerization.[6] However, this is less practical as multistep reactions are needed. NMRP has not been previously used in the CRP synthesis of pHEA. The *N*-*tert*-butyl-*N*-(1-diethyl phosphono-2,2-dimethylpropyl) nitroxide, called SG1, a trademark of Atofina, has proven to be more effective for the CRP of acrylates[7a−d] and acrylic acid[8] than TEMPO ((2,2,6,6-tetramethylpiperidinyl-1-oxy)nitroxide). In this work, we report a direct synthesis of pHEA by SG1-mediated radical polymerization initiated by MONAMS, an SG1-based alkoxyamine derived from methyl acrylate. Amphiphilic block copolymers of *n*-butyl acrylate and HEA were also synthesized.

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Experimental Section

Materials. *n*-Butyl acrylate (BA, Aldrich, 99+ %) was purified by passage through a basic alumina column prior to use. 2-Hydroxyethyl acrylate (HEA, Aldrich, 96%) was purified according to the literature[5] and stored in a refrigerator (−20 °C). The *N*-*tert*-butyl-*N*-(1-diethyl phosphono-2,2-dimethylpropyl) nitroxide (SG1, 89% purity) and SG1-based alkoxyamine $CH_3-O-C(=O)-CH(CH_3)-$SG1, (MONAMS, 96% purity) were supplied by Atofina. Azo initiator V_{azo} 67 was supplied by Dupont Canada. All other reagents were used as received.

Polymerization of HEA. The polymerization was conducted in a dry Schlenk tube. Monomer HEA, alkoxyamine MONAMS, a small fraction of free SG1 with respect to the MONAMS, and solvent (if applicable) were weighed into the reaction tube, which was sealed with a rubber septum. The air was removed by three freeze−vacuum−thaw cycles, and the tube was then immersed in a preheated oil bath. Samples were taken by syringe in a predetermined time interval for NMR analysis and for SEC measurement after modification.

In an example, monomer HEA (9.64 g, 0.083 mol), initiator MONAMS (183 mg, 0.480 mmol), and nitroxide SG1 (17 mg, 0.0578 mmol) were weighed into a Schlenk tube and sealed with a rubber septum. Deoxygenation was performed by three freeze−vacuum−thaw cycles, and the tube was then immersed in a 110 °C oil bath. Samples were taken by syringe at times: 0.4, 1, 1.75, 2.75, 3.75, 4.75, 6.25, 7.8, and 9.3 h. One to two drops of sample were directly dissolved in deuterated dimethyl sulfoxide (DMSO-d_6) for ^{1}H NMR analysis, giving conversions of 7.3%, 13.9%, 21.1%, 31.4%, 41.0%, 48.7%, 59.2%, 69.1%, and 78.4%, respectively. The rest of the samples were measured by SEC after acetylation (for the method, see below), giving M_n/PDI values of 3600/1.18, 3800/1.25, 5600/1.20, 7000/1.19, 9200/1.15, 11 500/1.17, 14 200/1.13, 17 800/1.17, and 23 200/1.26, respectively.

Block Copolymerization of BA and HEA. Block copolymers were prepared by the macroinitiator method. Poly(*n*-butyl acrylate) (pBA) capped with SG1 was prepared by the polymerization of BA at 115 °C, initiated by azo initiator V_{azo} 67, and mediated with excess SG1. The pBA macroinitiator, after removal of excess monomer, was directly heated with HEA at 105 °C to give block copolymers.

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Thus, for a specific example (experiment # 2 in Table 4), BA (15.75 g, 0.123 mol), V_{azo} 67 (68 mg, 0.354 mmol) and SG1 (234 mg, 0.796 mmol) were weighed into a Schlenk flask. The flask was immersed in a 115 °C oil bath after deoxygenation by three freeze−vacuum−thaw cycles. Samples were taken and directly dissolved in deuterated chloroform ($CDCl_3$) to determine the conversion by ^{1}H NMR. After 7.5 h, the polymerization was stopped with a monomer conversion of 50%. The excess monomer was removed in a vacuum at 38 °C for 1 day. SEC analysis of polymer gave an M_n of 12 750 and a PDI of 1.07.

The above pBA macroinitiator (1.28 g, 0.1 mmol) was mixed with HEA (4.30 g, 0.0370 mol) in a Schlenk tube, degassed by three freeze−vacuum−thaw cycles, and heated in a 105 °C oil bath. Samples were taken by syringe at times 1.25, 2.5, and 5 h. A drop of each sample was directly dissolved in DMSO-d_6 for ^{1}H NMR analysis, giving the conversions 17%, 33%, and 51%, respectively. The rest of the sample (~1.5 mL) was purified before other measurements. The block copolymers were purified by stirring with water. The aqueous parts were removed by centrifugation. The copolymers were again mixed with fresh water, and supernatant was discarded by centrifugation (5 cycles). The final block copolymers were dried in a vacuum at 60 °C overnight. The purified block copolymers were measured by ^{1}H NMR to give the mole percent of the HEA block as 35.9%, 54.6%, and 65.5%, respectively. SEC analysis gave M_n/PDI as 31 100/1.30, 40 650/1.41, and 53 600/1.70, respectively. Differential scanning calorimeter (DSC) measurements for the second and third samples gave glass transition temperatures as −46.8, −4.2 °C; and −52.2, −10.2 °C, respectively.

Acetylation of (Co)Polymers. For size exclusion chromatography, the polymers were modified by acetylation of the hydroxyl groups using acetic anhydride. In a typical example, 0.2 g of pHEA was dissolved in 5 mL pyridine and stirred with 1 mL of acetic anhydride at room temperature overnight. The acetylated pHEA (pAcHEA) was obtained after removing excess reagent and solvent using a rotary evaporator and then being placed in a vacuum at 60 °C overnight. The pAcHEA can also be purified by precipitation in methanol and then decanting the solvent and drying at vacuum. For all the kinetic studies of HEA polymerization, pAcHEAs were measured by SEC, without further precipitation in methanol.

Analytical Techniques. Analytical size exclusion chromatography (SEC) was performed in a Waters 2690 separation module equipped with five Waters Styragel HR columns (HR5.0, HR4.0, HR3.0, HR1.0, HR0.5) in series. Two detectors set at 40 °C were used: a Waters 410 differential refractometer as the refractive index (RI) detector and a Wyatt Technology DAWN EOS laser photometer as the light scattering (LS) detector. Tetrahydrofuran (THF) was used as eluent at a flow rate of 1 mL/min. Narrowly distributed polystyrene samples were used as calibration standards for the RI detector. The absolute molecular weight and molecular-weight distribution were calculated using ASTRA for Windows (Version 4.90.08) with known specific refractive index increment (dn/dc) and known RI detector calibration constant. Except as specified, we report the number-average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity (as measured by M_w/M_n) from the LS detector. The dn/dc of pAcHEA was determined in THF at room temperature using a Precision Instruments differential refractometer with light that passed a band-pass filter centered on 633 nm. The dn/dc of 0.062 was obtained from the slope of plot $\Delta n \sim$ concentration. The dn/dc values of block copolymers p(BA-*b*-AcHEA) were calculated on the basis of the weight percent of each block, adopting the reference value of 0.065 as the dn/dc of pBA.[9]

The monomer conversion was determined by ^{1}H NMR in DMSO-d_6 or $CDCl_3$, using either a Bruker AV-300 or AV-400 MHz FT spectrometer. The ^{13}C NMR analysis of pAcHEA was performed in $CDCl_3$ by a Bruker AV-600 spectrometer, operating at a frequency of 150.9 MHz. The spectra were recorded in a 5 mm tube at room temperature using standard conditions: pulse interval of 0.91 s, flip angle of 30°, and no relaxation delay. The chemical shifts were referenced to the solvent resonance (peak at 77.0 ppm). Two selected samples were recorded again in a 10 mm tube using a Bruker DRX-400 spectrometer operating at 100.6 MHz. The conditions used are as follows: acquisition time 0.5s, the flip angle 45°, relaxation time 10 s, and nuclear Overhauser enhancement (NOE) suppressed by inverse gated decoupling.

Differential scanning calorimeter (DSC) measurements were carried out on a TA Instruments Q100 DSC accessorized with an autosampler and refrigerated cooling system. The sample was first heated at 60 °C for 2 min, cooled to −80 °C, and held there for 1 min. Then the sample was heated at 10 °C/min to 60 °C. Glass transition temperature (T_g) of the polymer was calculated by Universal Analysis 2000 software from TA Instruments, Inc.

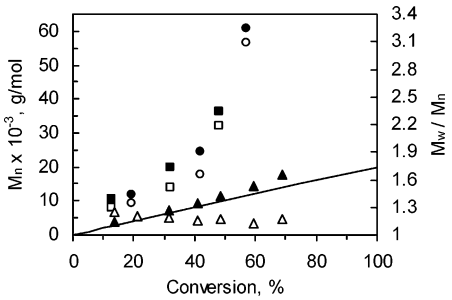

Figure 1. Effect of different monomer purification methods on bulk NMRP of HEA at 110 °C. $[HEA]_0/[MONAMS]_0 = 172$; $[SG1]_0/[MONAMS]_0 = 0.12$; (■□) monomer used as received; (●○) monomer passed through alumina column; (▲△) monomer washed with hexane and then distilled; (—) theoretical M_n; filled symbol: M_n; void symbol: M_w/M_n.

Results and Discussion

Monomer Purification. The homopolymerization of HEA was initiated by MONAMS, with a small portion of excess SG1 added. Figure 1 shows the effect of HEA purification methods on the HEA polymerization. When the HEA was not purified, the polydispersity index (PDI) remains relatively low only in the early stage of polymerization (conversion <30%), and control is lost completely when the conversion approaches 50%. This is also the case when HEA was purified only by passage through alumina column. In both cases, some degree of cross-linking was found when the conversion is very high. As can be seen from Figure 1, the M_n's show much higher values than theoretical, indicating loss of control. Therefore, the monomer was thoroughly purified for all subsequent experiments. An HEA aqueous solution was extracted with hexane to remove diacrylate, which is the primary cause of cross-linking. It should be noted that the acrylic acid impurities are not harmful to NMRP, though they may deactivate transition metal complex catalysts in ATRP. The HEA thus purified gave well-controlled polymerizations with very low PDI.

Effect of the Initial Concentration of Free SG1. SG1-mediated polymerization of acrylates is usually undertaken with addition of a slight excess of free nitroxide with respect to the alkoxyamine initiator.[10] Because the acrylate monomers have a high propagation rate constant, k_p, the excess free nitroxide is used to reduce the polymerization rate and maintain good control of the polymerization. As HEA is expected to have a higher k_p than BA,[11] we performed the polymerization of HEA at 100 °C, a relatively low temperature for NMRP, with free SG1 from 6 to 12 mol% with respect to the alkoxyamine MONAMS. The results are shown in Figure 2.The two plots of $\ln([M]_0/[M])$ versus time are linear, indicating first-order kinetics. The evolution of M_n with conversion has a linear relationship below 50%

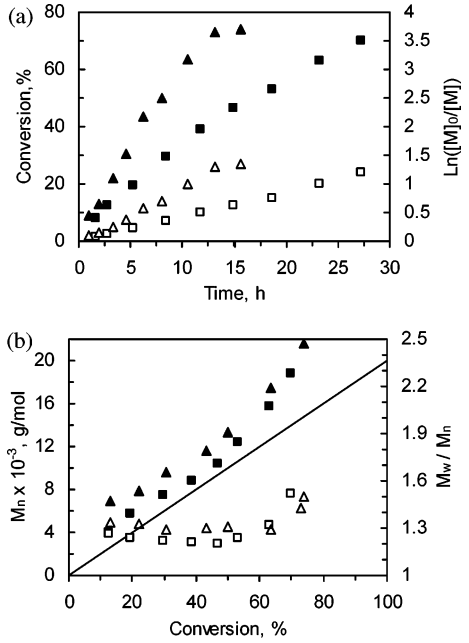

Figure 2. Kinetic plot (a) and evolution of M_n and M_w/M_n with conversion (b) for bulk NMRP of HEA at 100 °C. $[HEA]_0/[MONAMS]_0 = 172$; (■□) $[SG1]_0/[MONAMS]_0 = 0.12$; (▲△) $[SG1]_0/[MONAMS]_0 = 0.06$; (—) theoretical M_n; filled symbol: conversion (a) or M_n (b); void symbol: $Ln([M]_0/[M])$ (a) or M_w/M_n (b).

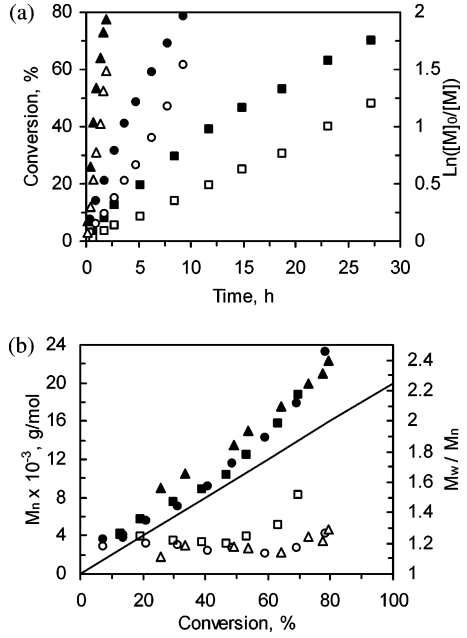

Figure 3. Kinetic plot (a) and evolution of M_n and M_w/M_n with conversion (b) for bulk NMRP of HEA at different temperatures. $[HEA]_0/[MONAMS]_0 = 172$; $[SG1]_0/[MONAMS]_0 = 0.12$; (■□) 100 °C; (●○) 110 °C; (▲△) 120 °C; (—) theoretical M_n; filled symbol: conversion (a) or M_n (b); void symbol: $Ln([M]_0/[M])$ (a) or M_w/M_n (b).

conversion, with the PDI remaining low up to 70% conversion. The upward trend of M_n versus conversion in the high conversion region may be from the chain transfer reaction and/or intermolecular termination. Both polymerizations with different initial concentrations of free SG1 can be considered to be controlled, as they give low PDI. As expected, with a lower concentration of free SG1, the polymerization is faster and PDI is slightly higher.

Effect of Polymerization Temperature. The alkoxyamine MONAMS is easy to decompose, with a cleavage temperature of 75 °C and decomposition constant k_d $(1.0-3.0) \times 10^{-3}$ s^{-1} (120 °C).[12] The SG1-mediated polymerization of HEA at 100 °C is in good control (Figure 2). This temperature is lower than that for most reported NMRP experiments. However, the reaction time is somewhat long. To shorten the reaction time, we performed the polymerization at higher temperature, keeping the initial amount of free SG1 at 12 mol% with respect to MONAMS. Figure 3 gives a comparison of HEA polymerization at 100, 110, and 120 °C. As shown in Figure 3, the plots of $ln([M]_0/[M])$ versus time show an almost linear relationship, with polymerization rate increasing with temperature. More than 27 h are required to reach 70% conversion at 100 °C, about 9 h to get 78% conversion at 110 °C, and only 2 h for 80% conversion at 120 °C. All the polymerizations give relatively low PDI, typically below 1.3. Low temperature does not guarantee very low PDI at high conversion (PDI 1.52 for 70% conversion at 100 °C), while at 110 and 120 °C, the PDI still remains <1.3 for conversion near 80%. This indicates that the control of polymerization will be reduced when too long a reaction time is applied.

Synthesis of pHEA with High M_n. The good control achieved with the SG1-mediated polymerization of HEA encouraged us to pursue the synthesis of high-M_n pHEA with narrow molecular-weight distribution. A series of bulk polymerizations of HEA were undertaken by changing the $[HEA]_0/[MONAMS]_0$ ratio. Conversions were kept below 50−55% to maintain good control of the polymerization. Table 1 lists the experimental results. It can be seen that pHEA having an M_n near 90 000 can be obtained with a low PDI of 1.27. The pHEA with an M_n of 127 000 has a PDI of 1.64, with a shoulder peak seen in the molecular-weight distribution. The M_n's measured by SEC with the LS detector are higher than the theoretical values. This is probably due to the formation of branched structures caused by chain transfer, which will be discussed in a later section.

Table 1. Synthesis of pHEA by NMRP (Nitroxide-Mediated Radical Polymerization) in Different Initial Molar Ratios of HEA and MONAMS[a]

$[HEA]_0/[MONAMS]_0$	conv %	$M_{n,calc} \times 10^{-3}$	$M_{n,SEC} \times 10^{-3}$	M_w/M_n
262	44.4	13.5	15.2	1.18
372	47.7	20.6	20.8	1.22
474	53.3	29.3	32.2	1.27
608	55.7	39.3	45.8	1.26
740	52.6	45.2	56.8	1.27
873	51.6	52.3	62.7	1.31
1137	49.0	64.7	81.1	1.22
1915	33.5	74.5	88.2	1.27
1637	52.2	99.2	127.1	1.64
2155	48.4	121.1	180.8	1.81

[a] Conditions: bulk polymerization with ramp temperature, 110 °C (1 h), 115 °C (1.75 h); $[SG1]_0/[MONAMS]_0 = 0.12$.

Solution Polymerization of HEA. To explore the general applicability of this SG1-mediated HEA polymerization, two solvents, *N*,*N*-dimethylformamide (DMF) and water, were chosen for the solution polymerization of HEA. Figure 4 demonstrates a comparison of HEA polymerization in bulk, in 50 wt% DMF, and in 50 wt% water. The polymerization in DMF gave similar behavior as that in bulk polymerization. The M_n and PDI are largely agreeable for the two polymerizations. However, the solution polymerization in DMF is a little faster

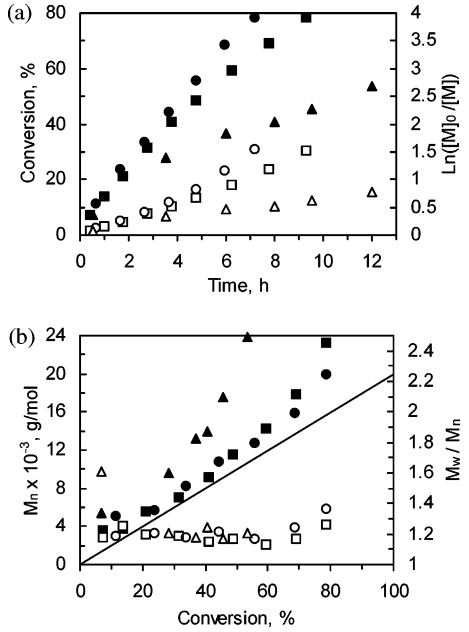

Figure 4. Kinetic plot (a) and evolution of M_n and M_w/M_n with conversion (b) for solution NMRP of HEA at 110 °C. $[HEA]_0/[MONAMS]_0 = 172$; $[SG1]_0/[MONAMS]_0 = 0.12$; (■□) bulk polymerization as comparison; (●○) in 50 wt% DMF; (▲△) in 50 wt% H_2O; (—) theoretical M_n; filled symbol: conversion (a) or M_n (b); void symbol: $Ln([M]_0/[M])$ (a) or M_w/M_n (b).

than in bulk, indicating a slight accelerating effect by the polar solvent DMF.

For the aqueous polymerization, the plot of $ln([M]_0/[M])$ versus time is linear up to 70% conversion, though the apparent polymerization rate is lower. However, although the temperature of oil bath was 112 °C, the real temperature in solution was ~100 °C. While the aqueous polymerization rate is slower than bulk polymerization at 110 °C, it is slightly faster than bulk at 100 °C. The kinetics will be discussed in the next section. The M_n versus conversion for the aqueous polymerization is linear and PDI remained very low, below 1.2. However, the M_n's deviate from theoretical values at higher conversion, indicating a loss of control and possibly caused by chain transfer to polymer. The ^1H NMR confirms that the hydroxyl group in the polymer is not affected by the reaction. All these results show that the aqueous polymerization of HEA is a controlled process.

Polymerization Kinetics. Scheme 1 illustrates the key steps of the SG1-mediated polymerization of HEA. Following the discussion previously reported on SG1 polymerization,[8] the activation−deactivation equilibrium relationship that controls the polymerization kinetics is

$$K = [P\cdot][SG1]/[[P{-}SG1] \quad (1)$$

Where K is the equilibrium constant, [SG1] is the concentration of free nitroxide, and [P−SG1] is the concentration of pHEA-based alkoxyamine. The decomposition rate of MONAMS is high, giving the polymerization a fast initiation. The chain concentration can be considered to be constant and equal to the initial alkoxyamine concentration; therefore, $[P{-}SG1] = [MONAMS]_0$. Because a large concentration of initial free SG1 was used, $[SG1] = [SG1]_0$. Then,

$$k_pK = k_p[P\cdot][SG1]_0/[[P{-}SG1]_0 = k_p[P\cdot]r \quad (2)$$

Here, r is the initial molar ratio of free SG1 to MONAMS. The $k_p[P\cdot]$ can be calculated from the slope of plot $ln([M]_0/[M])$ versus time for the linear region. (In the linear portion of the plot, [P−SG1] is assumed to be constant. The curvature observed in conversion plots at high conversions indicates this assumption is not valid throughout the polymerization.) Table 2 lists the calculated k_pK values for all the HEA homopolymerizations.

The k_pK increases with temperature. As the reaction time is long at 100 °C, adopting a low r value (0.06) seems to be a good means to shorten the time, while still keeping a narrow molecular weight distribution. At 120 °C with an r value of 0.12, both fast rate and low PDI are achieved. Compared to k_pK values of BA (1.8×10^{-5} s^{-1} at 120 °C)[7] and acrylic acid ($1.1{-}1.8 \times 10^{-5}$ s^{-1} at 120 °C),[8] HEA gives a k_pK of 2.6×10^{-5} s^{-1} at 120 °C, which is slightly higher than those of these two monomers. Worthy of mention is that the aqueous polymerization of HEA exhibits similar behavior as bulk polymerization; the k_pK value is comparable (slightly higher) to that of the bulk polymerization at 100 °C. This suggests a direction for further experiments of aqueous HEA polymerization at higher temperature under pressure, which may provide a good compromise of fast rate and good control in aqueous media.

Chain Transfer to Polymer. The free-radical polymerization of acrylates is subject to chain transfer to polymer by the hydrogen abstraction of tertiary C−H bonds. Consequently, a branched structure is formed. This chain transfer to polymer will not be completely suppressed when living radical polymerization is used, as has been observed for SG1-capped pBA[13] and poly(acrylic acid).[8]

^{13}C NMR spectroscopy was the best means reported to quantitatively characterize the presence of branches.[14] This is done by calculating the percent of quaternary carbon at a branch junction, together with the three adjacent CH_2 and CH. Figure 5 shows a typical ^{13}C NMR spectrum of pAcHEA in $CDCl_3$; the peak assignments followed those of pBA by Ahmad et al.[15] The pHEA was acetylated because the solvent, DMSO-d_6, we used has an absorption near the branch CH_2 and CH, and pAcHEA is very easy to purify. As the pHEA solution is very viscous, it is not suitable to put more sample in the NMR tube. Therefore, we did not try to use other solvents such as deuterated pyridine as the NMR solvent. For quantitative analysis of ^{13}C NMR, a long relaxation time and suppression of the NOE are normally needed because in the standard conditions the relative intensities do not necessarily reflect the relative abundance of each type of carbon due to different relaxation times and NOE. For example, the primary and quaternary carbons usually give lower intensities compared with those of methine and methylene carbons. However, this condition requires a much longer acquisition time and as a result is very time-consuming. Fortunately, the branch CH and CH_2 give almost the same NOE with the backbone CH and CH_2 in fast-pulse spectra. The calculation based on the branch CH and CH_2 integrals is almost equivalent to that based on the branch quaternary carbon integral, which was demonstrated in the research of pBA branching by Ahmad et al.[15]

Table 3 gives mole percent branches of selected pHEA samples prepared in different conditions. All the spectra were recorded under fast pulse conditions, except two

Scheme 1. SG1-Mediated Polymerization of HEA (Hydroxyethyl Acrylate)

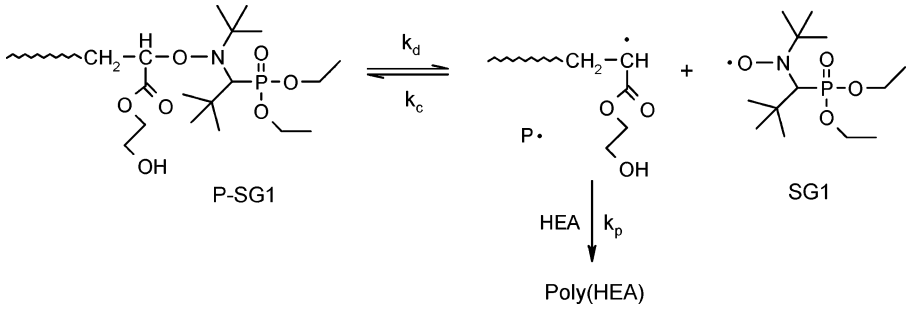

Table 2. k_pK Values for SG1-Mediated Homopolymerization of HEA

temp °C	$[SG1]_0/[MONAMS]_0$	solvent	k_pK s^{-1}
100	0.06	bulk	1.6×10^{-6}
	0.12	bulk	1.3×10^{-6}
110	0.12	bulk	4.3×10^{-6}
	0.12	50 wt% DMF	5.1×10^{-6}
	0.12	50 wt% H_2O	1.9×10^{-6}
120	0.12	bulk	2.6×10^{-5}

in which ^{13}C NMR spectra were recorded again using reverse gated decoupling to suppress the NOE and a relaxation time of 10 s to allow complete recovery of all carbons. From Table 3, it can be seen that pHEA has a branch around 1 per 100 monomer repeat units in bulk and aqueous polymerizations, and a branch about 1.5−1.7 per 100 monomer repeat units in solution polymerization (DMF). These data are equivalent to those of SG1-mediated miniemulsion polymerization of BA at 112 °C (1−1.5 mol% branches for conversion of 47−73%)[13] and much lower than those of SG1-mediated polymerization of acrylic acid in 1,4-dioxane at 120 °C (4.6−6.1 mol% branches for conversion of 85−90%).[8] From the data in Table 3, there is a higher chain transfer to polymer in solution (DMF) than in bulk or aqueous polymerization, and the mole percent branches

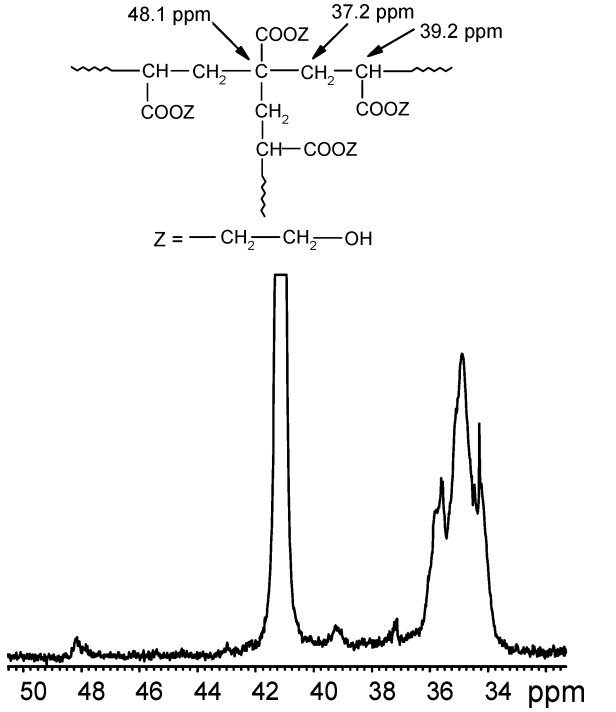

Figure 5. Representative ^{13}C NMR spectrum of p(AcHEA) between 32 and 50 ppm.

Table 3. Mole Percent Branches of pHEA by ^{13}C NMR[a]

sample	polymerization condition	conversion %	$M_{n,SEC}$	PDI	mol% branches[b]
1	110 °C in bulk	20.5	8150	1.14	1.0
2		78.4	23200	1.26	0.8 (0.8[c])
3	120 °C in bulk	26.0	9000	1.11	1.1
4		77.4	21000	1.22	1.0
5	110 °C in 50 wt% DMF	29.5	8700	1.18	1.5
6		43.5	10850	1.18	1.5
7		70.8	20000	1.52	1.6 (1.7[c])
8	110 °C in 50 wt% H_2O	27.3	12350	1.24	0.9
9		54.0	20600	1.45	0.7

[a] The mol% branches of pAcHEA (acetylated pHEA) were measured. [b] From the ratio of one-third of the sum of the branch CH and CH_2 integrals to the total integral for backbone carbon atoms in fast pulse spectra. [c] From the ratio of the branch quaternary carbon integral to half the total integral for backbone carbon atoms in quantitative conditions.

are almost unchanged or even decreased with an increase of conversion. Normally high-M_n species have a higher probability of undergoing chain transfer to polymer.[14] However, as a very high monomer concentration (>50 wt%) and accordingly a very concentrated solution are used in our experiments, intermolecular chain transfer may dominate through the polymerization process.[15] Consequently, the long-chain branches increase at higher conversion. However, both intra- and intermolecular chain transfers to polymer may make contributions, especially at the early stage of polymerization.

Block Copolymerization of BA and HEA. Using the synthesized pHEA as macroinitiator for the BA polymerization was avoided because of the insolubility of pHEA in BA, which was also observed by Muhlebach et al.[5] when they applied ATRP to prepare the same block copolymer. Other processes such as emulsion or miniemulsion polymerizations may be able to use pHEA as macroinitiator; however, this is beyond the scope of this work. Therefore, we prepared pBA first by NMRP as a macroinitiator, and then added HEA to obtain the block copolymer p(BA-*b*-HEA).

The pBA macroinitiator with terminal SG1 units was synthesized by initiation with V_{azo} 67 at 115 °C, with the addition of excess of SG1. This pBA was then used for block copolymerization with HEA after removal of excess BA under vacuum, without the addition of free SG1 since the excess SG1 was not removed from the pBA macroinitiator. In the preparation of the pBA macroinitator, the conversion was kept below 50% in order to avoid loss of livingness of the SG1-capped ends, and the temperature was kept low (<40 °C) when polymers were dried under vacuum. Unpurified block copolymers were stirred with water to give a soaplike

Table 4. Synthesis and Characterization of P(BA-*b*-HEA) by NMRP of PBA Macroinitiator and HEA (BA; *n*-butyl acrylate)[a]

expt	conv[b] %	mol% HEA[c]	$M_{n,NMR}$[d]	$M_{n,SEC(RI)}$; PDI[e]	$M_{n,SEC(LS)}$; PDI[f]	T_g °C
1−0				5300; 1.12	5200; 1.16	
−1	23	44.8	9020	8870; 1.19	9230; 1.19	−45.4; −13.6
−2	47	64.2	13650	12400; 1.26	13650; 1.26	−51.4; −15.3
−3	67	73.0	17950	16700; 1.42	19600; 1.44	−46.0; −2.5
2−0				14300; 1.12	12750; 1.07	
−1	17	35.9	19200	22700; 1.34	31100; 1.30	
−2	33	54.6	26650	28950; 1.40	40650; 1.41	−46.8; −4.2
−3	51	65.5	34700	38450; 1.78	53600; 1.70	−52.2; −10.2
3−0				22800; 1.15	21800; 1.07	
−1	12	27.4	29250	27950; 1.53	45050; 1.35	
−2	28	51.6	42850	33800; 1.45	51350; 1.41	−46.7; 9.1
−3	15	60.0	51400	41300; 1.54	58950; 1.34	−46.2; 9.9

[a] Conditions: pBA macroinitiator prepared by initiation of V_{azo} 67 at 115 °C, with M_n and PDI listed in expt 1−0, 2−0, 3−0, $[BA]_0/[V_{azo}\ 67]_0 = 172$ (expt 1−0), 347 (expt 2−0), 690 (expt 3−0), $[SG1]_0/[V_{azo}\ 67]_0 = 2.25$; block copolymerization performed at 105 °C, $[HEA]_0/[pBA]_0 = 140$ (expt 1), 370 (expt 2), 640 (expt 3−1, 3−2), and 1280 (expt 3−3), [b]by ^{1}H NMR directly sampled from reaction mixture, dissolved in DMSO-d_6, [c]by ^{1}H NMR of purified p(BA-*b*-HEA) in DMSO-d_6, [d]Calculation based on $M_{n,SEC(LS)}$ of pBA and ^{1}H NMR. [e]M_n and polydispersity index from calibration relative to linear polystyrene standards in SEC with DRI detector. [f]M_n and polydispersity index obtained by light scattering method of SEC.

solution, indicating the formation of an amphiphilic copolymer. The copolymer particles are very fine, especially when the HEA block is large; conventional filtration cannot effectively separate them. By centrifugation at a high rotation rate (>10 000 rpm) and with supernatant replacement, the block copolymers can be purified.

Table 4 lists the experimental results of the block copolymerizations and the properties of p(BA-*b*-HEA). Beginning from pBA macroinitiators with different M_n's, a series of p(BA-*b*-HEA)s were synthesized. The molecular weights of the block copolymers listed are readjusted since only acetylated p(BA-*b*-HEA) was analyzed by SEC. The PDI of copolymers are low, typically less than 1.5. When pBA macroinitiators with higher M_n (>12 700) were used, and a higher mole percent HEA block was targeted, the PDI increased accordingly. The block copolymers exhibit two T_g's: one is the pBA block at −52 to −45 °C, the other is the pHEA block at −15 to 10 °C. The formation of block copolymers is also illustrated by the SEC elution curves of copolymers in Figure 6. As can be seen from Figure 6, block copolymers were formed with the M_n increasing with polymerization time, without evidence of a shoulder peak.

Three sets of molecular-weight data are listed in Table 4: M_n estimated from NMR and M_n's from SEC with the RI and LS detectors, respectively. For pBA with low molecular weight (M_n 5200), the three groups of M_n data are in good agreement. However, for pBA with a higher M_n (>12 700), M_n from SEC with the LS detector exhibited much higher values. There are a few possible reasons for these discrepancies. (1) Not all pBA macroinitiator chains are capable of reinitiation. The higher the M_n of pBA, the lower is the percent activated end groups of pBA for reinitiation. This may bring about some errors for the estimation of M_n by NMR. (2) The $M_{n,SEC(RI)}$'s are from the universal calibration equivalent to linear polystyrene, based on the hydrodynamic size of polymers, while $M_{n,SEC(LS)}$'s use the light scattering principle, giving an absolute molar mass. When the block copolymers are branched, their hydrodynamic size decreased, thereby giving lower $M_{n,SEC(RI)}$ values. (3) Bimolecular termination or even slight cross-linking may not be completely suppressed, especially when the solution is very thick. The temperature might not be controlled inside the medium when the viscosity increases. Comparing expt 2-3 with expt 3-3, the latter had a higher initial concentration of monomer to macroinitiator and hence lower viscosity; the difference between $M_{n,NMR}$ and $M_{n,SEC(LS)}$ was also smaller (42.8% versus 13.7%).

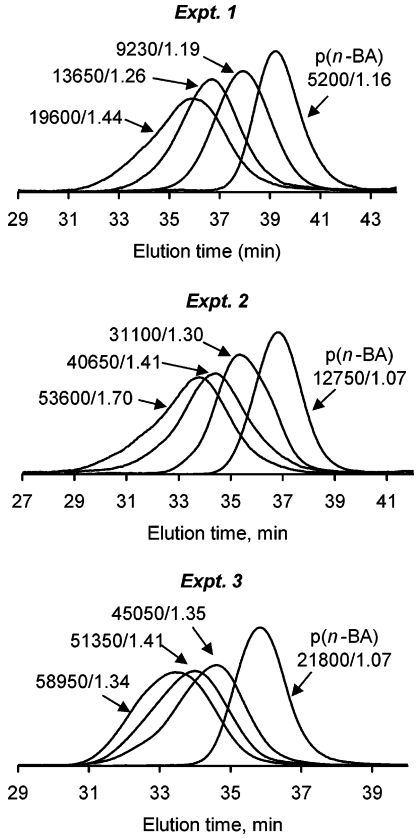

Figure 6. SEC elution curves of block copolymer p(BA-*b*-AcHEA). The first curve from right in each experiment is from pBA macroinitiator. The rest of curves are from block copolymers prepared in different times. The values shown are M_n/PDI from SEC with light scattering detector.

Conclusion

NMRP of HEA was carried out at 100−120 °C using an alkoxyamine initiator based on the *N*-*tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl)nitroxide, SG1. By the addition of free nitroxide (6−12 mol% with respect to the initiator MONAMS), the polymerizations were performed in a controlled manner. Fast rate and

good control can be achieved by polymerization at 120 °C for 2 h, giving a conversion of about 80% and a PDI of less than 1.3, as determined by light scattering. The $\ln([M]_0/[M])$ versus time and M_n versus conversion profiles exhibit a linear relationship up to 50−60% conversion. pHEA with a high molecular weight (up to 90 000) can be synthesized by bulk polymerization. The polydispersity indexes are less than 1.3. Solution polymerization in 50 wt% DMF gives similar polymerization behavior as in bulk polymerization, exhibiting a slight rate accelerating effect. The SG1-mediated polymerization of HEA is also applicable to aqueous media; the polymerization rate and molecular-weight distribution are comparable to those of bulk polymerization at 100 °C. Chain transfer to polymer gives rise to ∼1 mol% branches in bulk and aqueous polymerizations and 1.5−1.7 mol% branches for polymerization in DMF, remaining unchanged or even decreasing with conversion, which may result from increased long-chain branching at higher conversion. From a pBA macroinitiator capped with SG1, amphiphilic block copolymers p(BA-*b*-HEA) can be synthesized via SG1-mediated polymerization.

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