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Versatile Initiators for Macromonomer Syntheses of Acrylates, Methacrylates, and Styrene by Atom Transfer Radical Polymerization

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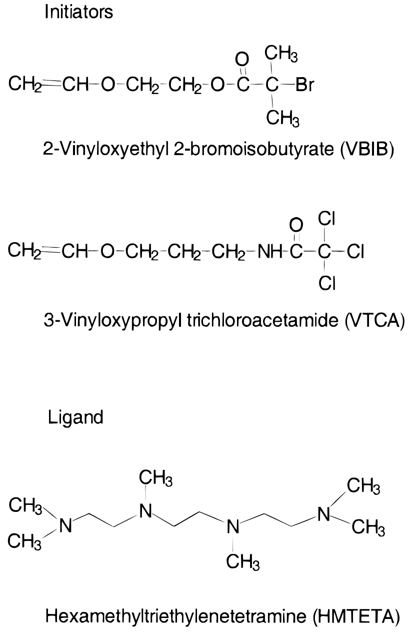
ABSTRACT: Novel vinyl-containing initiators 2-vinyloxyethyl 2-bromoisobutyrate (VBIB) and 3-vinyloxylpropyl trichloroacetamide (VTCA) were synthesized for the preparation of vinyl-terminated macromonomers of different monomers by atom transfer radical polymerization (ATRP). Catalyzed by CuBr/hexamethyltriethylenetetramine (CuBr/HMTETA), the ATRP processes initiated by VBIB (for MMA, DMAEMA, and styrene) and VTCA (for MMA and DMAEMA) followed a first-order kinetics with respect to the monomer concentration. The molecular weights of the resulting polymers were very close to their calculated values and increased with the conversion. The GPC traces showed that the vinyl moiety in the initiators did not participate the polymerization at conversions below 80% during the ATRP processes of DMAEMA in bulk and those of MMA and styrene in γ-butyrolactone (γBL). VBIB also initiated methyl acrylate (MA) and butyl acrylate (BA) with first-order kinetics in the early stage of the polymerization; however, the process deviated from the first-order kinetics at high conversions due to reactions of the vinyl moieties. By terminating the ATRP of MA and BA at the early stage, the corresponding macromonomers were also obtained. ^{1}H NMR confirmed that all polymer chains contained vinyl terminal groups derived from initiators.

Introduction

Macromonomers are important precursors for supermolecular construction such as synthesis of well-defined graft copolymers, polymer brushes, and star polymers.[1] Various methods have been developed for the synthesis of macromonomers.[2] The synthesis strategies include the direct initiation method using a functional initiator,[2] living polymer deactivation,[2,3] functional polymer endcapping,[2] and free radical chain transfer reaction.[4] The direct initiation method by living polymerization using a functional initiator is of special interest since every polymer chain produced has initiator's functional group. In addition, living polymerization has good control of the polymer structure and molecular weight. However, living polymerizations based on anionic, cationic, or group transfer are very sensitive to moisture and impurities and thus very difficult to operate. Recently, a new living radical polymerization process, atom transfer radical polymerization (ATRP), has succeeded in methacylates, acrylates, and styrene[5] and in functional monomers such as 2-hydroxyethyl methacrylate[6] and (dimethylamino)ethyl methacrylate (DMAEMA).[7] The advantage of ATRP over the traditional living processes is its great tolerance to protonic reagents.[7,8]

Scheme 1. Structures of Used Initiators and Ligand



ATRP is very useful for synthesizing functionalized polymers, such as polymers with terminal hydroxyl group.[9−11] However, there has been little study on the synthesis of macromonomers by ATRP. Matyjaszewski et al. first reported the syntheses of polystyrene macromonomers using vinyl chloroacetate[12] and allyl bromide[13] as initiators, but these initiators were in lack of activity for methacrylates. Allyl 2-bromoisobutyrate[14] was used for synthesizing DMAEMA macromonomer, but the ally group was not a good copolymerizable unit for later uses. In this paper, we report two new initiators, vinyloxyethyl 2-bromoisobutyrate (VBIB) and vinyloxypropyl trichloroacetamide (VTCA), for the preparation of macromonomers of methacrylates, acrylates, and styrene. VBIB is versatile for the well-controlled polymerizations of styrene, methyl methacrylate (MMA), DMAEMA, methyl acrylate (MA), and butyl acrylate (BA). VTCA is a good initiator for polymerizations of DMAEMA and MMA. These polymerizations produced macromonomers with controlled molecular weights and narrow molecular weight distributions. The molecular structures of these initiators and the ligand used in this work are shown in Scheme 1.

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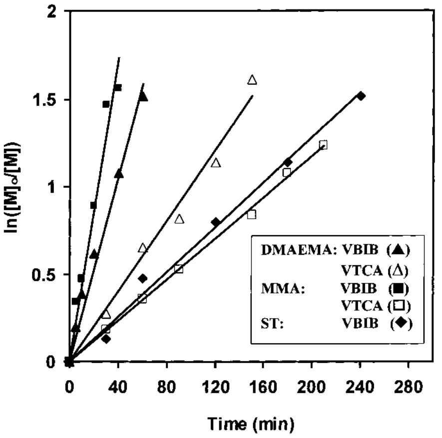


Figure 1. DMAEMA bulk polymerization and MMA and St solution polymerization in γBL with VBIB and VTCA as initiator mediated by CuBr−HMTETA. [CuBr]/[HMTETA]/[initiator] = 1/1/1; [DMAEMA] = 5.93 mol/L, [VBIB] or [VTCA] = 0.0593 mol/L, 60 °C; [MMA] = 6.66 mol/L, [VBIB] or [VTCA] = 0.066 mol/L, 60 °C; [St] = 6.23 mol/L, [VBIB] = 0.0623 mol/L, 100 °C.

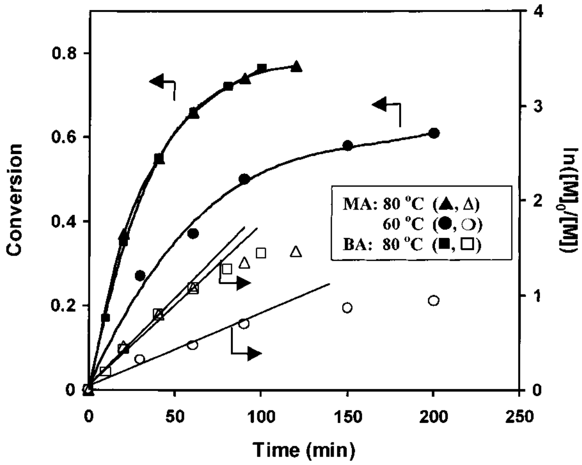


Figure 3. MA and BA solution polymerization in γBL with VBIB as initiator mediated by CuBr−HMTETA at 80 and 60 °C. [CuBr]/[HMTETA]/[VBIB] = 1/1/1 [MA] = 7.86 mol/L, [VBIB] = 0.0786 mol/L, [BA] = 5.0 mol/L, [VBIB] = 0.05 mol/L.

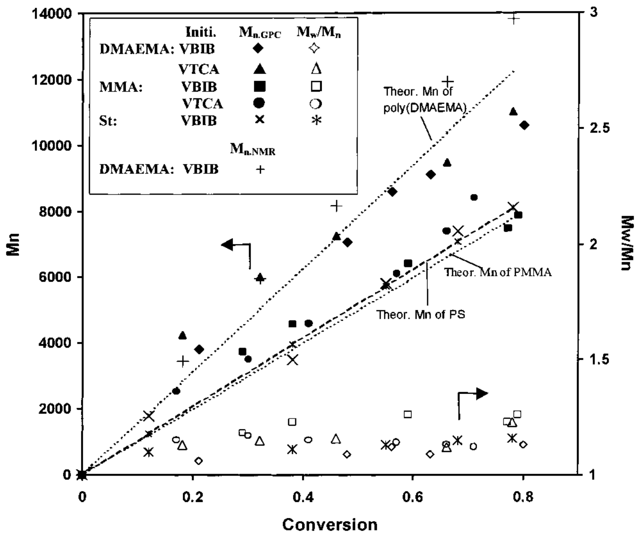


Figure 2. Dependence of polyDMAEMA, PMMA, and PS molecular weight and molecular weight distribution on conversion. See Figure 1 for conditions.

Experimental Section

Initiator Synthesis. *Vinyloxyethyl 2-Bromoisobutyrate (VBIB).* A 10 g (0.113 mol) sample of ethylene glycol vinyl ether (EGVE) and 19 mL (0.136 mol) of triethylamine were dissolved in 250 mL of THF. The solution was cooled in an ice−water bath. To this solution was added dropwise 14.0 mL of 2-bromoisobutyryl bromide (BIBB) (0.113 mol) in 50 mL of THF. The mixture was stirred for another 2 h at room temperature (EGVE reacted with BIBB to yield VBIB and HBr; HBr was absorbed by triethylamine). Triethylamine hydrogen bromide salt was filtered out. THF in the filtrate was removed under vacuum at room temperature. The residual was dissolved in $CHCl_3$ and washed with 50 mL of water three times. The aqueous parts were combined and shaken with 50 mL of fresh $CHCl_3$. The total $CHCl_3$ solution was then dried over anhydrous $CaCl_2$ for overnight. After filtering off the drying agent, $CHCl_3$ was distilled out under vacuum. A brown liquid was obtained. A further distillation under high vacuum gave a colorless liquid; yield 20.8 g. ^{1}H NMR: 6.47 ppm (q, 1H, $=CH-$); 4.23−4.00 ppm (m, 2H, $CH_2=$); 4.38 ppm (t, 2H, $OCH_2CH_2-OC(O)-$); 3.91 ppm (t, 2H, $=CH-O-CH_2CH_2$); 1.92 ppm (s, 6H $-CH_3$). ^{13}C NMR: 171.2 ppm ($O=C$), 151.3 ppm ($=CH$), 87.1 ppm ($CH_2=$), 65.4 ppm ($COOCH_2$), 63.9 ppm ($=CHOCH_2CH_2$), 55.4 ppm ($C-COO$), 30.6 ppm (CH_3).

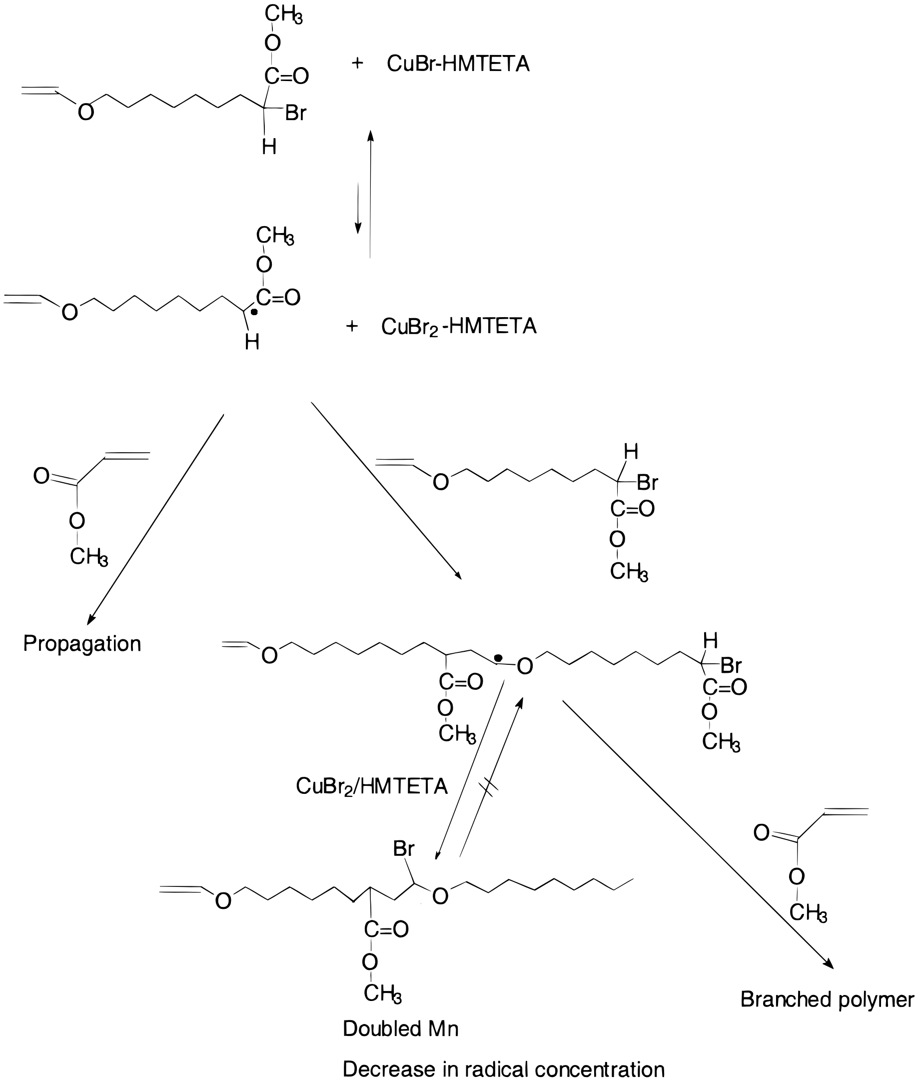
3-Vinyloxypropyl Trichloroacetamide (VTCA). A 10.1 g (0.1 mol) sample of 3-aminopropyl vinyl ether and 17 mL of triethylamine mixture in 250 mL of THF reacted with 11.2 mL (0.1 mol) of trichloroacetyl chloride by the same procedure as VBIB synthesis. A brown solid was obtained. The solid was purified by dissolving in THF and passing silicon gel. After removing THF by vacuum at room temperature, a yellowish viscous liquid was obtained; yield 12.8 g. ^{1}H NMR: 6.4 ppm (q, 1H, $=CH-$); 4.24−4.01 ppm (m, 2H, $CH_2=$); 3.81 ppm (t, 2H, $-OCH_2$); 3.50 ppm (q, 2H, $-CH_2NHC(O)-$); 2.0−1.9 ppm (m, 2H, $-CH_2CH_2CH_2-$,); 7.32 ppm (broad, $-NHC(O)-$). ^{13}C NMR: 161.7 ppm ($O=C$), 150.9 ppm ($=CH$), 92.5 ppm (CCl_3), 87.0 ppm ($CH_2=$), 66.1 ppm ($=CHOCH_2CH_2$), 39.4 ppm (CH_2-NH), 27.6 ppm ($CH_2CH_2CH_2$).

Polymerization. A typical run of the polymerization was as follows: 5 g of DMAEMA (31.8 mmol), 45.8 mg of CuBr (0.318 mmol), and 73.2 mg of HMTETA (0.318 mmol) were added to a tube. The tube was sealed with a rubber septum and cooled in ice water. The solution was bubbled with ultrahigh-purity nitrogen for 10 min. Then 75 mg (0.318 mmol) of VBIB previously purged with nitrogen was added with a syringe. The flask was then immersed into an oil bath at 60 °C. After 40 min, the polymerization was stopped by cooling the tube in ice and immediately diluted with 15 mL of THF. About 50 μL of this mixture was taken for the GPC measurement directly. The contents in the tube were divided in two parts: one part used for determining conversion by weight and the other for purification. For the conversion measurement the solution was poured into petroleum ether (for MMA, DMAEMA, and St polymerization). The polymer was precipitated and dried in a vacuum and then weighed to give conversion. In the BA and MA cases, the polymer solution was dried directly without adding petroleum ether. The other portion of the solution was passed silicon gel using toluene as eluent to remove the catalyst. The polymer solution was concentrated, and then the polymer was precipitated in petroleum ether and dried in a vacuum until constant weight. More than 90% polymer was recovered. The samples for determining terminal end group by NMR were further purified by reprecipitation. No monomer traces were detected (by NMR) in the samples after dried. A similar procedure was used to synthesize large-scale (50 g) macromonomers.

Results and Discussion

Copper bromide−hexamethyltriethylenetetramine (CuBr−HMTETA) was a good catalyst for the ATRP of DMAEMA,[14] MMA, MA, and St.[15] Therefore, CuBr−HMTETA was used to evaluate the initiation efficiency and survival of the vinyl moieties in VBIB and VTCA

Scheme 2. Reaction of Terminal Vinyl Group of the Polymer during ATRP of MA with VBIB as Initiator



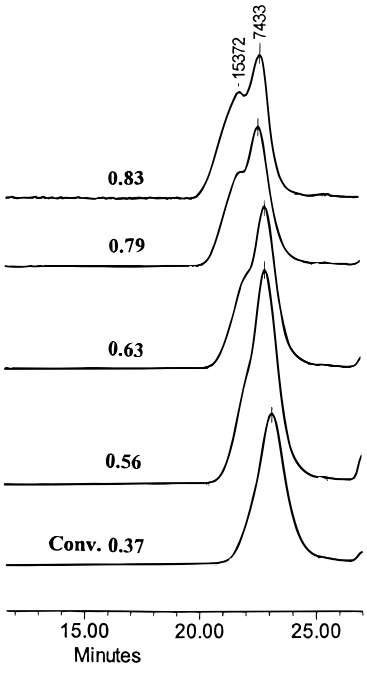


Figure 4. GPC traces of PMA initiated by VBIB in γBL at 80 °C. See Figure 3 for the experimental conditions.

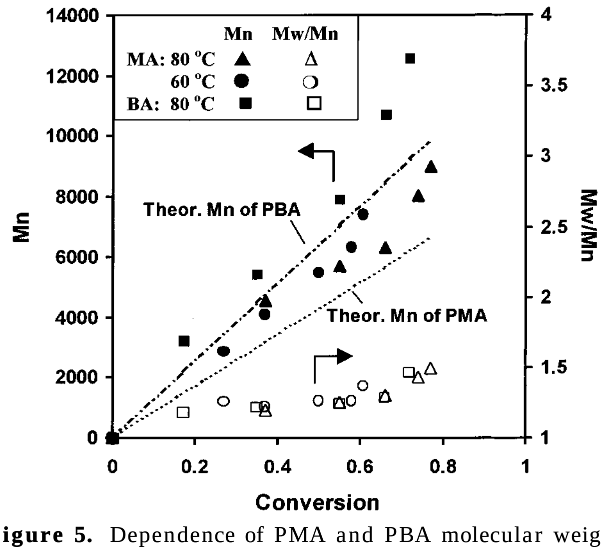


Figure 5. Dependence of PMA and PBA molecular weight and molecular weight distribution on conversion. See Figure 3 for conditions.

during the ATRP process. The CuBr−HMTETA complex was soluble in DMAEMA but only slightly soluble in MMA, MA, BA, and St. Therefore, the polymerization was carried out in bulk for DMAEMA but in γ-butyrolactone (γBL) for the other monomers.

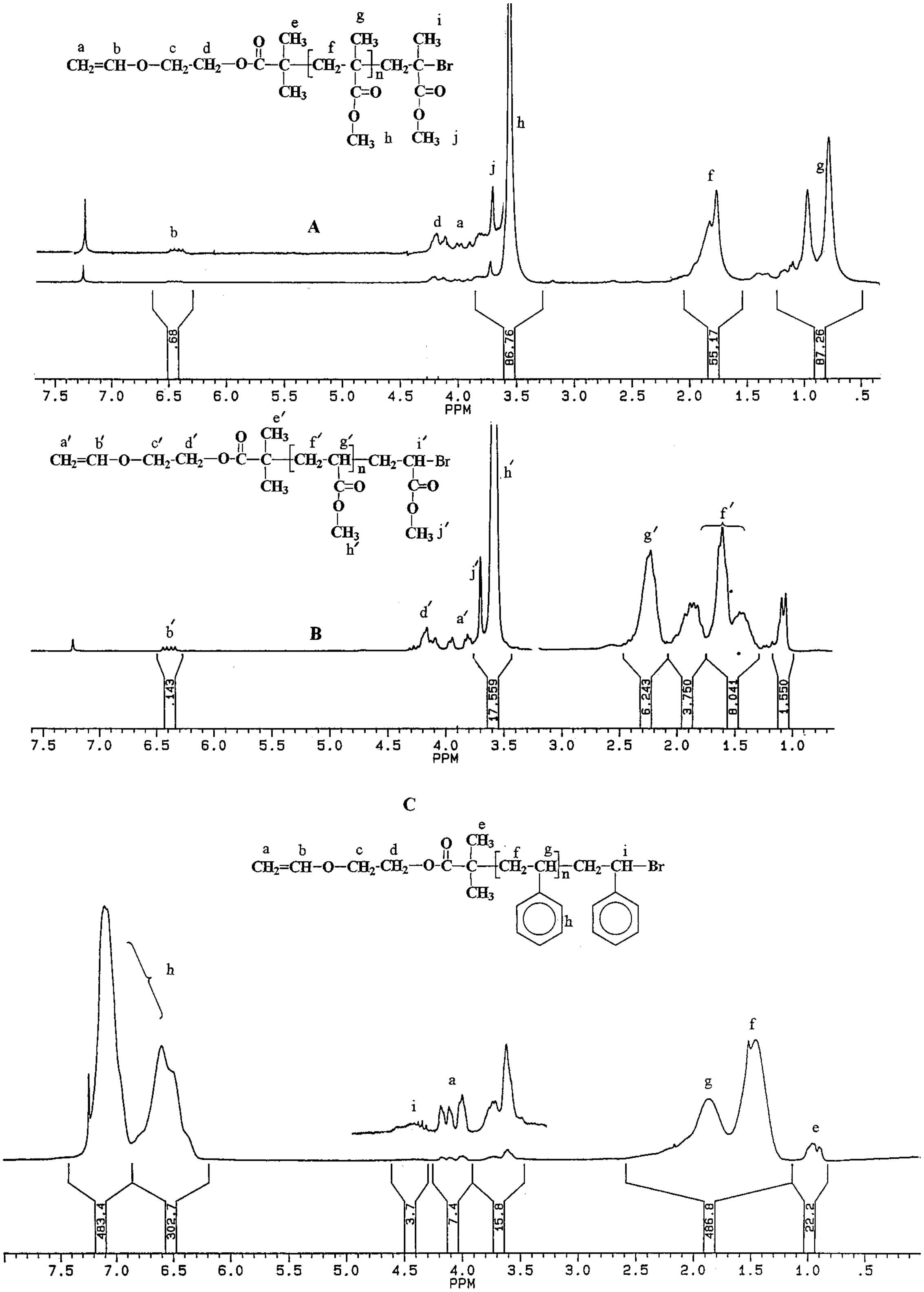


Figure 6. ^{1}H NMR spectra of prepared macromonomer. PMMA: [MMA] = 6.66 mol/L, [VBIB] = 0.066 mol/L, 60 °C, reaction time 10 min. PMA: [MA] = 7.86 mol/L, [VBIB] = 0.0786 mol/L, 80 °C, reaction time 20 min. PS: [St] = 6.23 mol/L, [VBIB] = 0.0623 mol/L, 100 °C, reaction time 60 min. [CuBr]/[HMTETA]/[VBIB] = 1/1/1.

Figure 1 shows the polymerizations of DMAEMA, MMA, and St with the two initiators. The ln([M]$_0$/[M])–time plots of all the reactions are linear, suggesting first-order kinetics with respect to monomer and constant radical concentrations during the reactions. With VBIB as initiator, DMAEMA and MMA polymerized rapidly to 80% in less than 1 h at 60 °C, while the St polymerization was much slower in the rate even at 100 °C. The slower polymerization rate of St was also observed in other ATRP catalyst/initiator systems.[5] The MMA and DMAEMA polymerizations with VTCA were slower than those with VBIB. For example, the k_{app} value of DMAEMA polymerization with VTCA was 2.6 times lower than that with VBIB at the same conditions.

This slower polymerization with VTCA is probably due to a low radical concentration because the C−Cl bond is stronger than C−Br.[5] VTCA was found not to be able to initiate St polymerization at 100 °C.

The GPC traces of the resulting DMAEMA, MMA, and St polymers were typical Gaussian distributions. Figure 2 shows the molecular weight (M_n) and polydispersity (M_w/M_n) of the polymers as a function of conversion. The molecular weights of all the polymers increased linearly with the conversion and were close to their theoretical values. The molecular weights of polyDMAEMA measured by NMR ($M_{n,NMR} = M_{monomer}r$, where r is the intensity ratio of the polymer backbone to terminal vinyl group; see discussion below) were also plotted in the figure and were agreeable with the GPC data. It was reported that the trichloroacetate was a multifunctional initiator.[16] Therefore, the polymers prepared with VTCA may not have linear but three-armed star structure with the vinyl moiety in the center. The molecular weight distributions of all the polymers were around 1.2. The initiator efficiencies ($M_{n,theor}/M_{n,GPC}$) were about 90%. These results clearly indicate that the vinyl group in the initiators did not influence the polymerizations of MMA, DMAEMA, and St.

Figure 3 shows the polymerizations of MA and BA initiated by VBIB at 80 and 60 °C. In contrast to the linear plots in Figure 1, both MA and BA polymerization showed a strong curvature. In the early stage of the polymerization, the $\ln([M]_0/[M])$−time plots were linear, i.e., a first-order reaction in monomer. However, these reactions began to deviate from the first-order kinetics and slowed down at about 60% conversions, suggesting that there was a rapid decrease in the radical concentration.

Figure 4 shows the GPC traces of PMA prepared at 80 °C. At low conversions, the GPC traces were normal and relatively narrow, with polydispersity about 1.2. The molecular weights of PMA and PBA increased linearly with conversion at this stage (Figure 5). However, a high molecular weight shoulder peak began to appear at a medium conversion (about 60%), and its intensity increased with the conversion (see Figure 4). The molecular weight at the high molecular weight shoulder peak was twice of that at the low molecular weight peak. Correspondingly, the overall molecular weight showed a sharp increase. The molecular weight distribution also became broader after this point (Figure 5).

The dramatic difference in the polymerization behavior of acrylic from methacrylic monomers was caused by the reaction of terminal vinyl group with the acrylate propagating radical. At high conversions, the latter might attack the $CH_2{=}CH{-}O{-}$ group and form the $-CH_2-\dot{C}H-O-$ radical (Scheme 2). This radical either propagated with monomers to produce a branched polymer or reacted with $CuBr_2$ to form a CH−Br bond ($CH_2{-}C(O{-})H{-}Br$). This carbon−bromide bond is too stable to be reactivated by Cu(I)Br to generate propagating radical (Scheme 2). This conclusion was confirmed by polymerizing (dimethylamino)ethyl vinyl ether and 2-hydroxylethyl vinyl ether using the same catalyst system.[17] This radical reaction actually became radical termination, resulting in a decrease in radical concentration and producing polymers with doubled molecular weight. Consequently, to obtain well-defined polyacrylic macromonomers, the polymerization should be stopped at a conversion before this side reaction becomes significant.

The prepared polyDMAEMA, PMMA, PS, PMA, and PBA macromonomers were characterized by NMR. Typical spectra for PMMA and PMA with VBIB are shown in Figure 6. In PMMA and PMA spectra, there were tetrad signals at 6.50−6.30 ppm attributed to the methine proton of the vinyl group ($CH_2{=}CH{-}O{-}$). The methylene proton ($CH_2{=}CH{-}O{-}$) signals appeared at 3.9−4.2 ppm. In PS, the methine signals were overlapped by those of benzene ring, but the tetrad signal of the methylene proton appeared clearly at 3.9−4.2 ppm. The vinyl group signals were also found in polyDMAEMA and PBA prepared with VBIB, as well as the polymers prepared with VTCA. These observations confirmed the survival of the vinyl groups during the ATRP process.

The polymer molecular weights were also measured from the signal intensity ratios of $-COOCH_2-$ (for polyDMAEMA and PBA) or $-COOCH_3$ (for PMMA and PMA) to the vinyl methine proton ($CH_2{=}CH{-}O{-}$). For PS, the intensity ratios of the benzene ring to the methylene proton ($CH_2{=}CH{-}O{-}$) were used. The NMR calculated molecular weights of polyDMAEMA prepared with VBIB are shown in Figure 2. They were slightly higher than the theoretical values and those by GPC. The PMMA and PS molecular weights by NMR were also agreeable with those by GPC. The molecular weights of PMA and PBA obtained at low conversions were comparable with their corresponding GPC results. The good agreement between the NMR data and their theoretical values strongly indicated that most terminal vinyl groups survived from the macromonomer preparation process. Our preliminary experiments showed that these macromonomers were copolymerizable with other vinyl monomers such as acrylamide and vinylformamide. We will report the copolymerization results elsewhere.

Conclusion

With CuBr/HMTETA as catalyst/ligand, VBIB was an effective ATRP initiator for preparing PMMA, polyDMAEMA, PMA, PBA, and PS macromonomers. In the MMA, DMAEMA, and St polymerization, the vinyl groups in the initiator moieties were stable up to high conversions. But, in the acrylate polymerization (MA and BA), the initiator's vinyl groups started to be consumed at medium conversions. The acrylate macromonomers can thus only be achieved at low conversion. VTCA also initiated the MMA and DMAEMA polymerization and yielded very narrow-distributed macromonomer samples. The survival of the terminal vinyl groups during the macromonomer preparation was also confirmed by NMR study.

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(17) The polymerization of 2-(dimethylamino)ethyl vinyl ether was tried with the same catalyst system. 19.8 mg of CuBr, 31.6 mg of HMTETA, 2 mL of (dimethylamino)ethyl vinyl ether, 1 mL of γ-BL, and 20 μL of ethyl 2-bromoisobutyrate were charged to a tube and degassed by nitrogen. The mixture was heated to 60 °C for 24 h. No polymer was isolated. Then 1.5 mL of degassed MA was injected to the polymerization media. No polymer was found either. The same result was obtained using 2-hydroxylethyl vinyl ether as a monomer.

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