Synthesis and use of a surface-active initiator in emulsion polymerization under AGET and ARGET ATRP conditions†

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A novel surface-active ATRP initiator disodium 4-(10-(2-bromo-2-methylpropanoyloxy)decyloxy)-4-oxo-2-sulfonatobutanoate (**1a**) has been designed and synthesized efficiently in three steps. The controlled radical emulsion polymerizations of methyl methacrylate (MMA) were realized in one step without any added surfactant under AGET and ARGET ATRP conditions, in which the initiator **1** functioned as both an ATRP initiator and a latex stabilizer.

Introduction

Living/controlled radical polymerization (L/CRP) methods have developed rapidly in the past decades due to their unique advantages over conventional radical polymerizations.[1] These methods mainly include atom transfer radical polymerization (ATRP),[2] reversible addition–fragmentation chain transfer (RAFT),[3] nitroxide-mediated living free-radical polymerization (NMP),[4] and iodine transfer polymerization (ITP).[5] Among them, atom transfer radical polymerization (ATRP) has attracted much interest due to its characteristics such as controllable polymer molecular weight, narrow molecular weight distribution, adaptability to most monomers, designable molecular structures (*e.g.* comb-like, star-like, telechelic and gradient polymers, *etc.*), and the many commercially-available ATRP initiators.[6] Moreover, many functional groups are tolerant to ATRP conditions, and highly chain end-functionalized polymers from ATRP can undergo post-polymerization reactions.[7] However, direct ATRP reactions catalyzed by Cu(I) or other low-valent metal ions are sensitive to air, and sometimes pretreatment of Cu(I)X (X = Cl, Br) is required to remove possible Cu(II)X_2 impurities before the reactions. This problem has been partially solved by reverse ATRP (RATRP) which uses Cu(II) or other high-valent metal ions as the catalysts, but the necessity for traditional initiators in RATRP has limited its use because block copolymers are always difficult to prepare.[8] Simultaneous reverse and normal initiation (SR&NI) ATRP was then developed to allow the preparation of block or other topological polymers, in which, however, the block copolymers are usually contaminated by a fraction of homopolymers formed through direct initiation from the added traditional initiator.[9] Recently, "activator generated by electron transfer" (AGET) ATRP allows the preparation of pure block copolymers, which applies high-valent metal ions together with appropriate reducing agents, and has overcome the disadvantages of both RATRP and SR&NI ATRP.[10] Based on AGET ATRP techniques, the further development of the "activators regenerated by electron transfer" (ARGET) ATRP method, has realized the use of ppm amounts of metal catalysts in ATRP reactions. The ARGET ATRP approach undoubtedly represents significant progress in ATRP development because the presence of metal residues such as copper(I) halide or copper(II) halide in the final products is an important drawback of the ATRP method and the removal of metal residues at the end of the polymerization is not easy, thus limiting the use of ATRP products for many purposes such as biomedical materials, drug encapsulation and food packaging materials.[11]

Due to the economic and environmental advantages of products from water-borne systems, ATRP under emulsion polymerization conditions has been widely studied and great progress has been made in recent years. Research has indicated that miniemulsion polymerization was the most appropriate method among various dispersed systems.[12] However, common ATRP emulsion polymerizations were mostly carried out in the presence of traditional emulsifiers, and the presence of these small molecular emulsifiers in the final polymers caused negative influences on the electrical, optical, surface, water-resistance and film-forming performances of the products. Therefore, emulsifier-free emulsion polymerization methods and methods involving reactive emulsifiers were developed in recent years.[13]

Recently, Stoffelbach *et al.* have reported a cationic surface-active ATRP initiator which was successfully used in soap-free miniemulsion polymerization of methyl methacrylate (MMA).[13c] Li and coworkers applied a PEO-based nonionic surface-active ATRP macroinitiator to emulsifier-free mini-emulsion polymerizations of butyl acrylate (BA).[13b] Yildiz *et al.* also described the use of PEO-based azo-type macro-monomeric initiators in emulsifier-free miniemulsion polymerizations of styrene.[9f] However, miniemulsion polymerization always required high shear tools, as well as co-surfactants such as cetane, which limited its wide use in large-scale production. The use of ATRP techniques in emulsion systems is still challenging, though an *ab initio* process based on an initial microemulsion polymerization has been developed.[12a,14]

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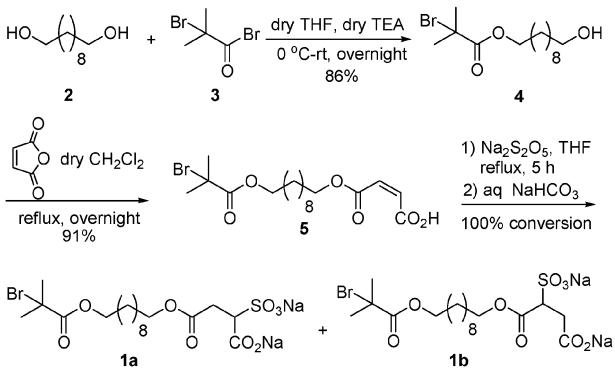
Herein, we have designed and synthesized a new surface-active ATRP initiator, which functions as both an anionic surfactant and an initiator in the emulsion polymerization of methyl methacrylate (MMA) under AGET ATRP and ARGET ATRP conditions. At least four aspects reveal the significance of our study: (1) the design and efficient synthesis of an anionic surfactant/initiator for the first time, compared with the previous cationic one by Wu *et al.*;[7d,13c] (2) the implementation of surfactant-free emulsion polymerizations in one step under AGET ATRP conditions using a molecule (containing isomers) playing both initiator and surfactant roles simultaneously; (3) the ATRP emulsion polymerization method in our work has advantages over previous miniemulsion polymerizations in being easy to perform and having the potential for large-scale production; (4) the use of ppm amounts of $CuBr_2$ catalyst in ARGET ATRP emulsion polymerizations further makes the case for potential applications of our research in industrial production.

Results and discussion

1. Synthesis of the initiator/surfactant disodium 4-(10-(2-bromo-2-methylpropanoyloxy)decyloxy)-4-oxo-2-sulfonatobutanoate (1a and 1b)

Three steps are involved in the synthesis of initiator/surfactant **1**. The first step is an esterification reaction which applies 1,10-decanediol (**2**) and 2-bromoisobutyryl bromide (**3**) as the starting materials (Scheme 1). The anhydrous solvent plays an important role in this step as the reaction is very sensitive to water. Initially, we tried to use dry CH_2Cl_2 as the solvent, but the solubility of 1,10-decanediol (**2**) in CH_2Cl_2 is very poor, thus seriously limiting the large-scale synthesis and giving a very low yield of monoester **4**. Fortunately, 1,10-decanediol (**2**) can be easily dissolved in THF which was then selected as the solvent. Temperature is another important factor that affects the rate of the reaction and the purity of the product, **4**. At relatively low temperatures (*e.g.* 0 °C to room temperature), the reaction is slow, but provides relatively pure product; at reflux temperature, the reaction can be accomplished within an hour, but the amount of bi-esterification side product is increased. Therefore, the esterification reaction was carried out at relatively low temperatures (0 °C to room temperature). The molar ratio of decanediol (**2**) to 2-bromoisobutyryl bromide (**3**) was adjusted to 2 : 1, and **3** in THF was added dropwise to **2** in THF solution in order to avoid the formation of the bi-esterification side product. Thus, under the above optimized conditions, the intermediate **4** can be obtained in 86% yield (based on 2-bromoisobutyryl bromide).

In the second step, the monoester **4** undergoes another esterification reaction using maleic anhydride as the acylation reagent. The reaction is conducted with excess cheap maleic anhydride (2 molar equivalents) under refluxing conditions to improve the yield. Dry CH_2Cl_2 solvent is necessary for the reaction as the presence of water can decrease the yield of the esterification reaction. We have failed to remove excess maleic anhydride by saturated aqueous $NaHCO_3$ during workup, because the intermediate **5** is an amphiphilic species (especially in basic medium) which caused serious emulsification in the



Scheme 1 Synthesis of the surface-active ATRP initiator **1**.

separation procedure. Therefore, excess maleic anhydride had to be removed by water extraction.

The last step is a sulfonation reaction at the double bond position of maleic acid moiety. Both sodium metabisulfite and sodium sulfite can be used as the sulfonation reagent in the reaction. Mild conditions of 0 °C to room temperature have been tried in the reaction to avoid possible hydrolysis of the ester, but the reactant remained intact even for 48 h. Fortunately, quantitative conversion was observed by thin layer chromatography (TLC) under reflux for a few hours. Then, the reaction mixture was neutralized with a base to obtain a clear colorless aqueous solution which was applied directly to the subsequent ATRP emulsion polymerizations.

For the purpose of analysis, a little portion of the reaction mixture was worked up, and almost quantitative total yield of crude **1** was obtained. Although the crude initiator/surfactant (**1**) prepared in the third step can be used directly for ATRP emulsion polymerizations without purification, its purity must be evaluated because an accurate quantity of initiator/surfactant (**1**) is required to determine the molar mass of the PMMA produced. Therefore, the purity of crude **1** was evaluated by acquiring a ^1H NMR spectrum of the product before silica gel chromatography (Fig. 1). The peak at the chemical shift 6.45 ppm has disappeared, indicating that the maleic acid moiety has been sulfonated completely and no carbon–carbon double bond exists. In the ^1H NMR spectrum, the singlet peak at the chemical shift 1.93 ppm is from the six protons (labeled as H_a) of the two CH_3 groups and the integral value is therefore designated as six. Thus, the integral value of the multiplet peak at 1.29–1.43 ppm should be twelve as it represents the twelve protons (labeled as H_d) of the middle six CH_2 groups of the carbon chain. But the real integral value is 12.9 and the redundant 0.9 is caused by some impurities. Thus, 12 divided by 12.9 affords an approximate purity of 93%. The impurities may be the hydrolysis byproducts of the third step of the reaction.

2. Emulsion polymerization of methyl methacrylate (MMA) initialized and stabilized by initiator/surfactant 1 under AGET ATRP and ARGET ATRP conditions

Scheme 2 shows the process of surfactant-free emulsion polymerization of MMA, in which **1a** (and **1b**) functions as both an ATRP initiator and a latex stabilizer. The initiator **1**, $CuBr_2$ catalyst, 2,2′-bipyridine (BPY) ligand and methyl

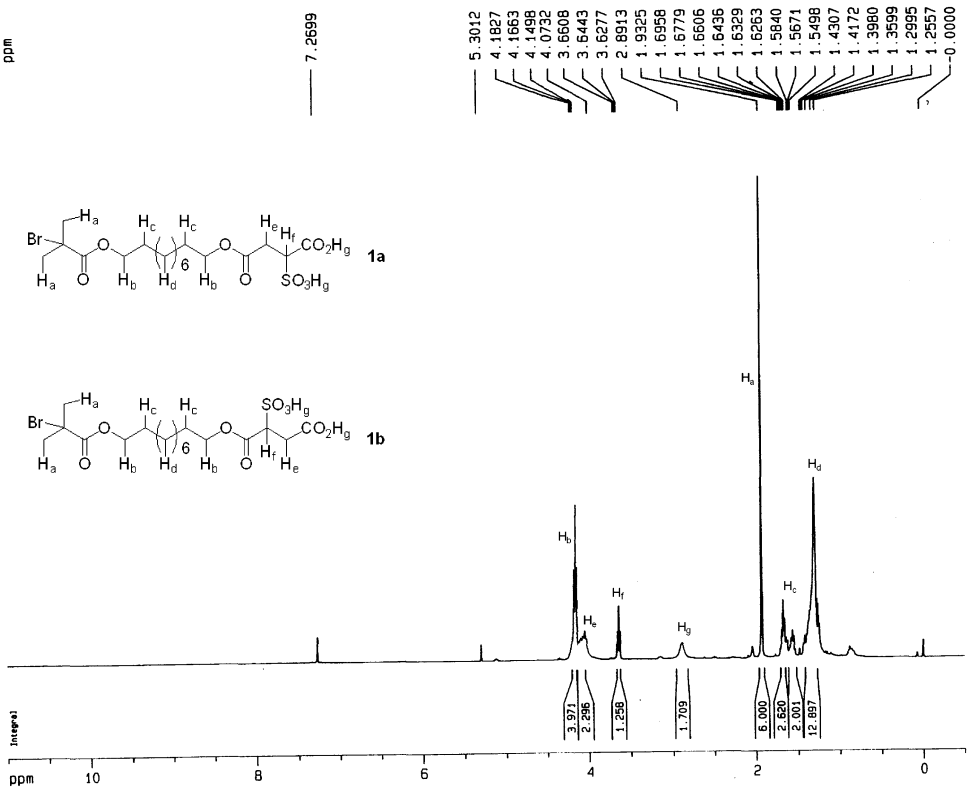


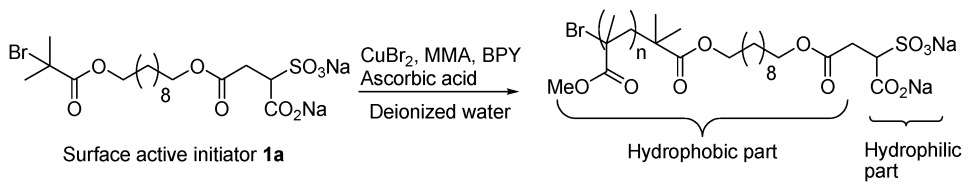
Fig. 1 The ^{1}H NMR spectrum in $CDCl_3$ of the crude initiator/surfactant (**1**) before purification by silica gel chromatography.

methacrylate (MMA) monomer were emulsified in deionized water, then the addition of ascorbic acid (AA) as a reducing agent facilitated the AGET ATRP emulsion polymerization reactions. A typical procedure for the polymerization is as follows: the catalyst $CuBr_2$, 2,2′-bipyridine (BPY) ligand and MMA monomer were stirred to form the Cu(II) complex, followed by the addition of an aqueous solution of initiator **1** and deionized water to lead to a stable latex. The emulsion was bubbled with nitrogen for 30 min at room temperature and then placed in a Schlenk flask, immersed in an oil bath thermostated at 80 °C. Aqueous ascorbic acid (AA) was added dropwise to the flask to initiate the reaction.

Table 1 lists the concentrations and ratios of reaction materials. The emulsion polymerizations can be conducted easily to form stable latex at solid contents of 18–22%. Table 2 gives detailed results of the experiments. All the emulsion polymerizations proceeded rapidly with high monomer conversions obtained within several hours. The high reaction rate is a large improvement over a previous report that utilized an amphiphilic diblock copolymer as both a macroinitiator and a stabilizer, and always required dozens of hours to reach high conversions.[9b]

Fig. 2a indicates the dependence of experimental number-average molar mass ($M_{n,exp}$) and polydispersity index (PDI) on MMA conversions. Throughout the polymerization reactions, the experimental M_n values ($M_{n,exp}$) determined by gel permeation chromatography (GPC) became higher with increasing MMA conversions, and were close to their corresponding theoretical ones, indicating the high efficiency of the initiator, **1**. Moreover, the polydispersity indices (PDI) were very low in most polymerizations. As shown in Fig. 2b, the linear relationship of $\ln([M]_0/[M])$ and the reaction time indicates that the first-order kinetic plot is linear. The straight line fit does not pass the origin point with an intercept on the time axis, indicating a short inhibition period of about a dozen minutes. Therefore, nearly linear relationship of $\ln([M]_0/[M])$ *versus* reaction time and MMA conversions *versus* $M_{n,exp}$ values, together with relatively low PDI, prove the living/controlled features of the emulsion polymerizations (exp. A_1, Table 2).

All the experiments gave very stable latex even with a low content of initiator **1** (exp. A_3, A_6 and A_{3R} in Table 1), compared with experiment A_0 which is a common ATRP emulsion polymerization using common SDS and OP-10 as emulsifiers and ethyl 2-bromoisobutyrate (EBiB) as an



Scheme 2 Surfactant-free emulsion polymerization of MMA *via* AGET ATRP.

Table 1 Atom transfer radical emulsion polymerization of MMA at 80 °C using **1** as both an initiator and a stabilizer and ascorbic acid (AA) as a reducing agent[a]

Exp.	MMA (wt%)	$[\mathbf{1}]_0$[c]	$[EBiB]_0$	$[CuBr_2]_0$	$[MMA]_0/[initiator]_0$	$[AA]_0$
A_0[b]	21.64	0	11.82	9.73	185	1.65
A_1	18	4.74	0	4.92	452	1.38
A_2	19.44	2.76	0	3.04	757	1.14
A_3	19.47	1.59	0	1.86	807	1.04
A_4	19.64	3.96	2.78	7.08	358	1.23
A_5	20.65	2.87	4.55	7.69	369	1.43
A_6	20.3	1.69	6.61	6.64	296	1.21
A_{1R}	19.98	4.79	0	0.50	423	1.48
A_{2R}	20.57	1.98	0	0.32	1056	1.25
A_{3R}	20.90	1.51	6.76	0.78	365	1.58

[a] The molar ratio of ligand BPY to $CuBr_2$ was 1 : 1 for the AGET ATRP experiments (A_0–A_6) and 10 : 1 for the ARGET ATRP experiments (A_{1R}–A_{3R}). Concentrations are given in mmol L_{latex}^{-1}. [b] With the surfactants [SDS] = 4.38 mmol L_{latex}^{-1} (SDS = sodium 1-dodecanesulfonate), [OP-10] = 2.19 mmol L_{latex}^{-1} (OP-10 = octylphenol polyoxyethylene ether-10). [c] Concentration of **1** in the experiments was calculated from the intermediate **5** which was quantitatively converted to **1**.

initiator. This indicates the efficient stabilization function of initiator **1** in the whole process of emulsion polymerizations. The average diameters of the latex particles ranged from 254 to 655 nm with relatively broad particle size distributions (PSD), indicating the submicrometer size of the particles. We deduce that both micelle nucleation and monomer droplet nucleation existed in the emulsion polymerizations because the surfactant/initiator **1** distributed in the periphery of micelles and monomer droplets could simultaneously initiate the polymerization reactions. And this can explain the relatively large particle size as well as the broad particle size distributions (PSD): droplet nucleation where there were sufficient monomers provided big particles while micelle nucleation gave small ones. The average particle diameter increased with greater proportion of initiator **1**, which may be attributed to the higher proportion of monomer droplet nucleation. The high initiating efficiency and very good latex stability demonstrate that (a) the surfactant/initiator **1** was mainly distributed at the surface of both monomer droplets and micelles, and still remained there after reaction to maintain the stability of the latex by electrostatic repulsion, and (b) that no free surfactant/initiator **1** existed at the end of the polymerization reactions.[13c]

The kinetics research for the emulsion polymerization of MMA under AGET ATRP conditions is illustrated in Fig. 3. The monomer conversions increased linearly with reaction time, indicating a relatively stable reaction rate. The polymerization rate was accelerated with the increasing concentration of initiator **1** when the ratio of initiator **1**, $CuBr_2$, BPY and AA remained unchanged. The result is very reasonable because a greater amount of initiator means more initiating sites.

Fig. 4 gives the dependence of experimental number-average molar mass ($M_{n,exp}$, kg mol^{-1}) on MMA conversions. The approximate linear increase of $M_{n,exp}$ value with monomer conversion is another proof for the controlled features of the emulsion polymerizations under AGET ATRP conditions. At the same conversion, the $M_{n,exp}$ values decreased with the increasing amount of initiator **1**.

The role of ethyl 2-bromoisobutyrate (EBiB) as a co-initiator in the emulsion polymerizations was also researched according to the previous report by Li *et al.* to reduce the amount of initiator **1** while keeping the latex stability (exp. A_4–A_6 in Table 1). The polymerization rate decreased when the ratio of initiator **1** to EBiB ranged from 3.96 : 2.78 to 1.69 : 6.61, indicating that initiator **1** has a greater initiating efficiency than EBiB. Moreover, the average particle diameter (D_z) as well as particle size distribution (PSD) was improved when the ratio of EBiB to initiator **1** was increased (exp. A_0, A_4–A_6 in Table 2). This result can be explained as follows: the EBiB-initiated-polymerization dominated the reactions when more EBiB was present than initiator **1** in the reaction system, in which initiator **1** mainly functioned as a stabilizer. In this case, the latex particle was not stable enough to effectively avoid particle collision and combination because of the presence of less surface active initiator **1**, thus causing relatively large average particle diameter (D_z) as well as broad particle size distribution (PSD). The emulsion polymerizations followed the pattern discussed for exp. A_1–A_3 in Table 1, when initiator **1** dominated the polymerizations while EBiB was only a co-initiator.

Based on the above research results, we further studied emulsion polymerization of MMA initialized and stabilized by initiator/surfactant **1** under ARGET ATRP conditions (A_{1R}–A_{3R} in Table 1 and Table 2). The ARGET ATRP method is advantageous over AGET ATRP in that the amount of metal catalyst was greatly reduced, to a ppm grade. For example, the initial concentration of $CuBr_2$ was decreased from 4.92 mmol L_{latex}^{-1} in exp. A_1 to 0.50 mmol L_{latex}^{-1} in exp. A_{1R}, while retaining an acceptable control (Fig. 5). In fact, the latex made by the ARGET ATRP method was almost white, while that by AGET ATRP looked blue—the colour of Cu(II) hydrate. However, the concentration of BPY ligand was 10× that of the Cu (II) catalyst in order to achieve complex formation.[15]

Kinetics studies of ARGET ATRP (exp. A_{1R}) are illustrated in Fig. 5. The monomer conversion was linear with reaction time for ARGET ATRP as shown in Fig. 4a, with the PDI less than 1.4. The reaction rate of exp. A_{1R} was slower than that of exp. A_1, which may be ascribed to there being less copper catalyst and a lower activator concentration. Fig. 5b provides the dependence of experimental number-average molar mass ($M_{n,exp}$, kg mol^{-1}) on MMA conversions. In the three experiments A_{1R}, A_{2R} and A_{3R}, all the $M_{n,exp}$ values increased linearly with

Table 2 Characteristics of the polymer latex prepared by emulsion polymerizations of MMA with **1** acting as both an ATRP initiator and a latex stabilizer

Exp.	t/min	Conversion (%)	$M_{n,th}$[a]/g mol^{-1}	$M_{n,exp}$[b]/g mol^{-1}	PDI	D_z[c]/nm (PSD)
A_0	20	13	2530	2570	1.10	—
	40	29	5630	6480	1.08	—
	60	44	8290	8350	1.18	—
	80	59	11100	11600	1.29	—
	100	71	13360	14840	1.31	788 (0.33)
A_1	20	14	7530	7160	1.05	—
	40	30	15220	15190	1.21	—
	60	50	24750	23650	1.19	—
	80	67	33270	37670	1.21	—
	100	82	40420	39320	1.25	629 (0.28)
A_2	20	14	11820	12120	1.16	—
	40	30	24690	24210	1.25	—
	60	45	37320	34360	1.13	—
	80	62	51010	49600	1.16	—
	100	77	63560	60120	1.22	483 (0.23)
A_3	20	10	8990	10520	1.10	—
	40	23	20200	19620	1.12	—
	60	35	31060	30860	1.15	—
	120	57	50430	49010	1.20	366 (0.20)
A_4	20	12	5170	5310	1.24	—
	40	32	13230	12140	1.19	—
	60	48	19190	16750	1.10	—
	80	64	25400	24250	1.28	—
	160	93	36500	35240	1.34	254 (0.18)
A_5	20	11	5020	4950	1.12	—
	40	22	9630	7140	1.22	—
	60	44	18170	17540	1.14	—
	180	96	38990	36650	1.32	355 (0.21)
A_6	20	9	3680	3600	1.28	—
	40	24	8480	9470	1.33	—
	60	45	14960	12520	1.18	—
	120	75	24770	25930	1.31	655 (0.27)
A_{1R}	20	11	5710	7300	1.13	—
	40	24	11270	12340	1.13	—
	80	43	20110	16110	1.40	—
	160	76	35030	37990	1.23	562 (0.26)
A_{2R}	20	7	8980	10370	1.08	—
	60	22	26030	25330	1.22	—
	100	38	43190	42780	1.27	—
	240	75	85600	83630	1.37	367 (0.21)
A_{3R}	20	12	5530	5800	1.30	—
	40	27	11460	12100	1.26	—
	80	49	19980	20560	1.20	—
	160	84	33620	34790	1.24	449 (0.25)

Note: [a] Theoretical number average molecular weights ($M_{n,th}$) were calculated from the experimentally determined conversions. [b] The experimental number average molecular weights ($M_{n,exp}$) were determined by gel permeable chromatography (GPC) using PMMA standards. [c] Average diameter (D_z) and particle size distribution (PSD) were measured by a laser particle size analyzer.

the monomer conversion. In the absence of EBiB, the $M_{n,exp}$ values decreased with increasing amount of initiator **1** at the same conversion, which is easy to understand as more initiator means more initiating sites (exp. A_{1R} and A_{2R}). As in AGET ATRP, the presence of EBiB can also save the amount of initiator **1** in ARGET ATRP reactions, while keeping the reaction characteristics. The first-order kinetics study indicated the linear relationship of $\ln([M_0]/[M])$ and reaction time (Fig. 6). Thus, the results of the kinetics studies prove the living/controlled characteristics of the emulsion polymerization of MMA under ARGET ATRP conditions.

The ^{1}H NMR spectrum of the PMMA polymer prepared by our method is shown in Fig. 7 to further prove the reliability of $M_{n,Exp}$ values determined by GPC. The number-average molecular weight can be calculated by integrating the peak at δ = 4.03 ppm which represents the six protons (3 CH_2) labeled with H_a and the reference peaks at 3.63 ppm due to the methoxy protons (H_b) in

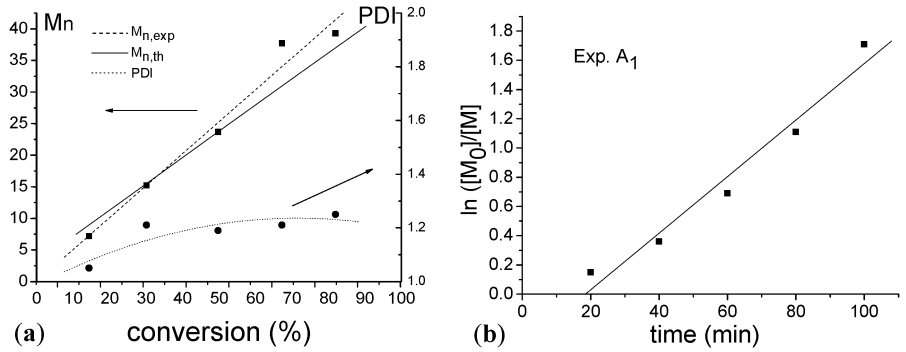


Fig. 2 (a) Experiment A_1: dependence of experimental number-average molar mass ($M_{n,exp}$, kg mol^{-1}) and polydispersity index (PDI) on MMA conversions. (b) Experiment A_1: dependence of ln([M_0]/[M]) on the reaction time (min), where [M_0] is the initial concentration of the monomer MMA, and [M] is the concentration of MMA at a certain reaction time.

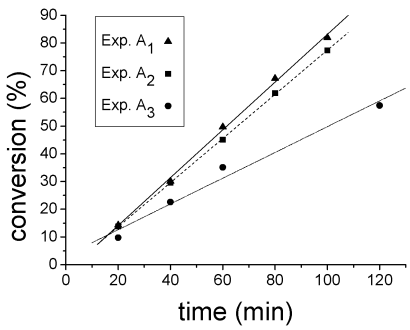


Fig. 3 Kinetics for the emulsion polymerization of methyl methacrylate at three different concentrations of initiator **1**. ▲: $[1]_0$ = 4.74 mM (Experiment A_1); ■: $[1]_0$ = 2.76 mM (Experiment A_2); ●: $[1]_0$ = 1.59 mM (Experiment A_3).

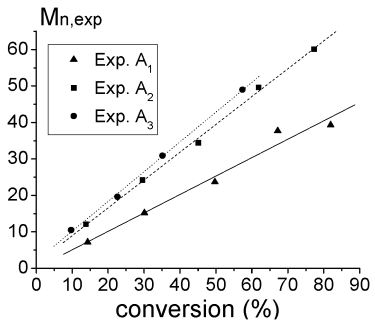


Fig. 4 Dependence of experimental number-average molar mass ($M_{n,exp}$, kg mol^{-1}) on MMA conversions.

the MMA units. The integral value at 3.63 ppm is 135 which is then divided by 3 to obtain the number of methoxy groups (*i.e.* 45). As the number of methoxy groups equals that of MMA units, the number-average molecular weight of PMMA can be calculated as follows (eqn (1)):

$$M_{n,NMR} = M_I + 100n = 525 + 100 \times 45 \approx 5030 \quad (1)$$

Thus, the experimental molecular weights ($M_{n,GPC}$ = 5310 g mol^{-1}, $M_{n,NMR}$ = 5030 g mol^{-1}) are well consistent with the theoretical one ($M_{n,th}$ = 5170 g mol^{-1}).

Conclusions

A simple surface-active ATRP initiator has been designed and synthesized efficiently for the first time, using commercially cheap reactants as the materials. The new initiator/surfactant can function as both an initiator and the sole emulsifier in AGET ATRP and ARGET ATRP emulsion polymerizations of MMA. Gel permeation chromatography (GPC) analyses showed controlled molecular weights and low polydispersity indexes (PDI), and the kinetics study showed the linear relationship of ln([M_0]/[M]) and reaction time, indicating the "living/controlled" feature of the emulsion polymerizations. This promising method has both an academic value and industrial feasibility in researching soap-free ATRP emulsion polymerizations.

Experimental section

Materials

Commercial 1,10-decanediol, 2-bromoisobutyryl bromide, *cis*-butenedioic anhydride, 2,2′-bipyridine (BPY), $CuBr_2$, $Na_2S_2O_5$, silica gel, neutral Al_2O_3 and triethylamine were all AR grade purity, and were used directly as received. The solvent tetrahydrofuran (THF, AR grade) was refluxed with sodium and then distilled before use; the eluant THF (AR grade) was used directly as received; the solvent CH_2Cl_2 was dried with CaH_2 and then distilled; methyl methacrylate (MMA) was washed in 5% aqueous NaOH, and then distilled under reduced pressure to remove the inhibitor.

Compound characterization

The structures of the intermediates were characterized by ^{1}H NMR and ^{13}C NMR spectroscopy on a Bruker AV 400 MHz spectrometer, with tetramethylsilane (TMS) as the internal standard. $CDCl_3$ was used as the solvent. The FTIR spectra were recorded *via* the KBr pellet method by using a Bruker V70 FTIR spectrophotometer. Elemental analyses were conducted on a FLASH EA1112 analyzer. Gel permeation chromatography (GPC) was performed on an HP 1100 HPLC, equipped with a Waters 2414 refractive index detector and three Styragel HR 2, HR 4, HR 5 of 300 × 7.5 mm columns (packed with 5 mm particles of different pore sizes).

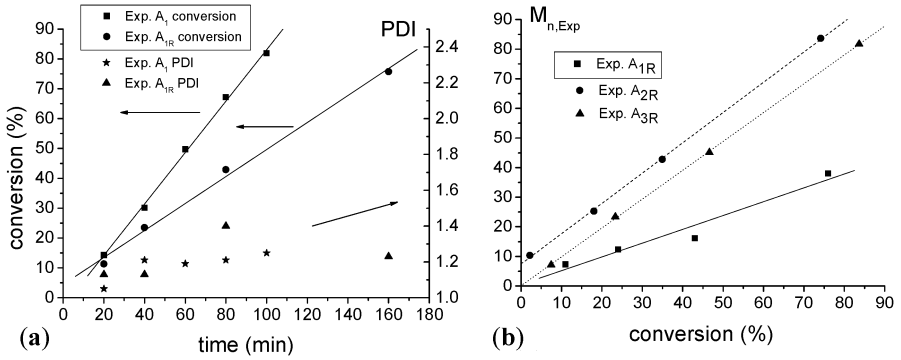


Fig. 5 (a) Comparison of the kinetics research on AGET ATRP (exp. A_1) and ARGET ATRP (exp. A_{1R}). (b) Dependence of experimental number-average molar mass ($M_{n,exp}$, kg mol^{-1}) on MMA conversions (exp. A_{1R}–A_{3R} for ARGET ATRP).

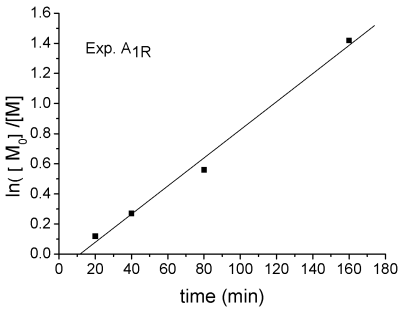


Fig. 6 Dependence of experimental number-average molar mass ($M_{n,exp}$, kg mol^{-1}) on MMA conversions.

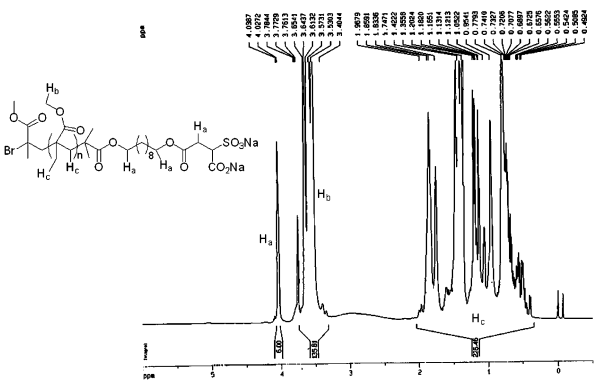


Fig. 7 ^{1}H NMR spectrum in $CDCl_3$ of PMMA prepared by AGET ATRP emulsion polymerization (exp. A_4). $M_{n,th}$ = 5170 g mol^{-1}, $M_{n,GPC}$ = 5310 g mol^{-1}, $M_{n,NMR}$ = 5030 g mol^{-1}.

The column packing allowed the separation of polymers over a wide molecular weight range of 500–1 000 000. THF was used as the eluent at a flow rate of 1 mL min^{-1} at 40 °C. PMMA standards were used as the reference. The average particle diameter (D_z) and particle size distribution (PSD) were determined on Rize-2008 laser particle size analyzer.

Synthesis of the initiator/surfactant 1

1,10-decanediol (**2**) (34.86 g, 200 mmol) was dissolved in dry THF (200 mL), then excess triethylamine (TEA) was added to the solution as an acid-trapping agent. At 0 °C to room temperature, 2-bromoisobutyryl bromide (**3**, 23.0 g, 100 mmol) in THF (30 mL) was added dropwise over 30 min. The reaction mixture was stirred at room temperature overnight. The reaction mixture was filtered to remove the solid part, and the filtrate was evaporated on a rotavapor. The oily residue was dissolved in CH_2Cl_2, then the resulting solution was washed with water and saturated aqueous sodium bicarbonate, and dried over anhydrous sodium sulfate. When the solvent was removed by evaporation on a rotavapor, a pale yellow oil was obtained as the mono-ester intermediate **4** (28.1g, 86%), which can be used directly as a reactant in the second step without further purification. Column chromatography on silica gel with hexane–ethyl acetate (4/1, v/v) as the eluant afforded the pure colorless **4** for identification. IR: ν 3368, 2930, 2856, 1734, 1396, 1279, 1166 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.17 (t, 2H, J = 6.61 Hz, OCH_2), 3.63 (t, 2H, J = 6.64 Hz, CH_2OH), 2.05 (s, 1H, OH), 1.93 (s, 6H, $2CH_3$), 1.70–1.66 (m, 2H, CH_2), 1.58–1.54 (m, 2H, CH_2), 1.36–1.28 (m, 12H, $6CH_2$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.7, 66.1, 62.9, 56.0, 32.7, 30.8, 29.5, 29.44, 29.36, 29.1 (2C), 28.3, 25.74, 25.71 ppm. Anal calcd for $C_{14}H_{27}BrO_3$: C, 52.02; H, 8.42. Found: C, 52.07; H, 8.39.

cis-Butenedioic anhydride (9.8 g, 100 mmol) and a catalytic amount of tosylic acid (0.4 g, 2 mmol) were dissolved in dry CH_2Cl_2 (100 mL). Mono-ester intermediate **4** (16.4 g, 50 mmol) in dry CH_2Cl_2 (40 mL) was added dropwise to the above solution under refluxing conditions over half an hour. The reaction mixture was then refluxed overnight. The mixture was washed with water three times to remove excess maleic anhydride. The organic phases were combined and then dried over anhydrous sodium sulfate. The oily crude product was obtained after removing CH_2Cl_2 solvent on a rotavapor. Further purification on silica gel chromatography with hexane–ethyl acetate (1/1, v/v) as the eluant gave the pure product **5** as a pale yellow crystal (19.1 g, 91%). Mp: 29–31 °C. IR: ν 3446, 3222, 2927, 2856, 1735, 1462, 1379, 1277, 1165 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.5 (br s, 1H), 6.49–6.40 (m, 2H, CH=CH), 4.29 (t, 2H, J = 6.59 Hz, OCH_2), 4.17 (t, 2H, J = 6.50 Hz, OCH_2), 1.94 (s, 6H, $2CH_3$), 1.74–1.65 (m, 4H, $2CH_2$), 1.32–1.28 (m, 12H, $6CH_2$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.8, 167.9, 164.7, 136.4, 129.8, 67.3, 66.1, 56.2, 30.7, 29.3, 29.2, 29.1, 29.03, 28.96, 28.3, 28.1, 25.70, 25.67 ppm. Anal calcd for $C_{18}H_{29}BrO_6$: C, 51.31; H, 6.94. Found: C, 51.36; H, 6.91.

Compound **5** (10.5 g, 25 mmol) was dissolved in THF (20 mL). Sodium metabisulfite (9.5 g, 50 mmol) in water (20 mL) was added slowly at room temperature. The reaction mixture was then refluxed for 5 h. The disappearance of substrate **5** and the appearance of a very polar component by thin layer chromatography (TLC) (EtOH–CH_2Cl_2 (v/v 1/1) as the eluant) indicated the end of the sulfonation reaction. Removal of THF solvent on a rotavapor provided a white mixture of solid and liquid as the crude product **1**. Most of the crude **1** was neutralized with aqueous sodium bicarbonate to give a clear colorless solution, which was used directly as both an initiator and a surfactant in AGET ATRP emulsion polymerizations. For analytic purposes, a little portion of the crude **1** was acidified with dilute aqueous HCl, then evaporation of water *in vacuo* afforded a light yellow oil, and the subsequent purification on silica gel chromatography yielded the pure acid form of product **1** as a viscous oil. IR: ν 3440 (br), 2930, 2856, 1733, 1637, 1400, 1275, 1227, 1166, 1045, 691cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.04 (t, 4H, J = 10.88 Hz, 2OCH_2), 3.99–3.97 (m, 2H, CH_2), 3.57 (t, 1H, J = 6.62 Hz, CH), 1.86 (s, 6H, 2CH_3), 1.62–1.49 (m, 4H, 2CH_2), 1.48–1.18 (m, 12H, 6CH_2) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.6, 171.8, 169.0, 66.1, 65.9, 63.0, 56.0, 30.8 (2C), 29.44, 29.35, 29.10, 28.56, 28.52, 25.84, 25.75, 25.71 ppm. Anal calcd for $C_{18}H_{31}BrO_9S$: C, 42.91; H, 6.24. Found: C, 42.95; H, 6.21.

Typical procedure for AGET ATRP of MMA in emulsion with compound 1 as both an initiator and a surfactant

A mixture of $CuBr_2$ (0.056g, 0.25 mmol), bpy (0.039g, 0.25 mmol) and MMA (10.0 g, 100 mmol) was stirred in a three-necked flask (100 mL) for 15 min to form a gray mixture. An aqueous solution of initiator **1** (1.2 g, 10 wt% concentration, 0.22 mmol) was added to the above mixture together with deionized water (35 mL). The resulting blue mixture was vigorously stirred for 30 min to form a stable latex, during which N_2 gas was bubbled through to remove O_2. Then the temperature was raised to 80 °C, and an aqueous solution of ascorbic acid (0.012 g, 0.12 mmol) was injected into the reaction mixture to initiate the reaction. Samples were withdrawn periodically to monitor the average particle diameter and to determine the monomer conversion by gravimetry.

Before GPC analysis, the polymer products were chromatographed with neutral alumina to remove the undesired Cu^{2+}, using THF as the eluant.

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References

1 (*a*) H. F. Gao and K. Matyjaszewski, *Prog. Polym. Sci.*, 2009, **34**, 317–350; (*b*) V. Sciannamea, R. Jrme and C. Detrembleur, *Chem. Rev.*, 2008, **108**, 1104–1126; (*c*) M. Ouchi, T. Terashima and M. Sawamoto, *Acc. Chem. Res.*, 2008, **41**, 1120–1132.
2 (*a*) K. Matyjaszewski and J. H. Xia, *Chem. Rev.*, 2001, **101**, 2921–2990; (*b*) T. Meng, X. Gao, J. Zhang, J. Y. Yuan, Y. Z. Zhang and J. S. He, *Polymer*, 2009, **50**, 447–454; (*c*) X. F. Sui, J. Y. Yuan, M. Zhou, J. Zhang, H. J. Yang, W. Z. Yuan, Y. Wei and C. Y. Pan, *Biomacromolecules*, 2008, **9**, 2615–2620.
3 (*a*) C. Barner-Kowollik, *Handbook of RAFT Polymerization*, 1st ed., Wiley-VCH, Weinheim, 2008; (*b*) M. J. Monteiro, *J. Polym. Sci., Part A: Polym. Chem.*, 2005, **43**, 3189–3204; (*c*) J. W. Chan, B. Yu, C. E. Hoyle and A. B. Lowe, *Chem. Commun.*, 2008, 4959–4961.
4 (*a*) C. J. Hawker, A. W. Bosman and E. Harth, *Chem. Rev.*, 2001, **101**, 3661–3688; (*b*) G. Delaittre, C. Dire, J. Rieger, J. L. Putauxb and B. Charleux, *Chem. Commun.*, 2009, 2887–2889.
5 (*a*) G. David, C. Boyer, J. Tonnar, B. Ameduri, P. Lacroix-Desmazes and B. Boutevin, *Chem. Rev.*, 2006, **106**, 3936–3962; (*b*) J. Tonnar and P. Lacroix-Desmazes, *Angew. Chem., Int. Ed.*, 2008, **47**, 1294–1297; (*c*) J. Tonnar, P. Lacroix-Desmazes and B. Boutevin, *Macromolecules*, 2007, **40**, 6076–6081.
6 (*a*) T. E. Patten, J. Xia, T. Abernathy and K. Matyjaszewski, *Science*, 1996, **272**, 866–868; (*b*) N. V. Tsarevsky and K. Matyjaszewski, *Chem. Rev.*, 2007, **107**, 2270–2299; (*c*) K. Fries, S. Samanta, S. Orski and J. Locklin, *Chem. Commun.*, 2008, 6288–6290.
7 (*a*) L. Shen, C. Ma, S. Z. Pu, C. J. Cheng, J. K. Xu, L. Li and C. Q. Fu, *New J. Chem.*, 2009, **33**, 825–830; (*b*) X. P. Chen and K. Y. Qiu, *New J. Chem.*, 2000, **24**, 865–869; (*c*) W. M. Wan and C. Y. Pan, *Chem. Commun.*, 2008, 5639–5641; (*d*) D. X. Wu, Y. F. Yang, X. H. Cheng, L. Liu, J. Tian and H. Y. Zhao, *Macromolecules*, 2006, **39**, 7513–7519; (*e*) X. J. Lu, S. L. Gong, L. Z. Meng, C. Li, F. Liang, Z. Q. Wu and L. F. Zhang, *Eur. Polym. J.*, 2007, **43**, 2891–2900.
8 J. S. Wang and K. Matyjaszewski, *Macromolecules*, 1995, **28**, 7572–7573.
9 (*a*) J. Gromada and K. Matyjaszewski, *Macromolecules*, 2001, **34**, 7664–7671; (*b*) M. Li, N. M. Jahed, K. Min and K. Matyjaszewski, *Macromolecules*, 2004, **37**, 2434–2441.
10 W. Jakubowski and K. Matyjaszewski, *Macromolecules*, 2005, **38**, 4139–4146.
11 (*a*) W. Jakubowski, K. Min and K. Matyjaszewski, *Macromolecules*, 2006, **39**, 39–45; (*b*) W. Jakubowski and K. Matyjaszewski, *Angew. Chem., Int. Ed.*, 2006, **45**, 4482–4486; (*c*) Y. Kwak and K. Matyjaszewski, *Polym. Int.*, 2009, **58**, 242–247.
12 (*a*) M. F. Cunningham, *Prog. Polym. Sci.*, 2008, **33**, 365–398; (*b*) M. Save, Y. Guillaneuf and R. G. Gilbert, *Aust. J. Chem.*, 2006, **59**, 693–711; (*c*) K. Min, H. F. Gao, J. A. Yoon, W. Wu, T. Kowalewski and K. Matyjaszewski, *Macromolecules*, 2009, **42**, 1597–1603; (*d*) J. K. Oh, *J. Polym. Sci., Part A: Polym. Chem.*, 2008, **46**, 6983–7001; (*e*) B. Charleux and J. Nicolas, *Polymer*, 2007, **48**, 5813–5833; (*f*) L. Q. Xu, F. Yao, G. D. Fu and L. Shen, *Macromolecules*, 2009, **42**, 6385–6392.
13 (*a*) F. Stoffelbach, B. Belardi, J. M. R. C. A. Santos, L. Tessier, K. Matyjaszewski and B. Charleux, *Macromolecules*, 2007, **40**, 8813–8816; (*b*) W. W. Li, K. Min, K. Matyjaszewski, F. Stoffelbach and B. Charleux, *Macromolecules*, 2008, **41**, 6387–6392; (*c*) F. Stoffelbach, N. Griffete, C. Buiab and B. Charleux, *Chem. Commun.*, 2008, 4807–4809; (*d*) S. Fréal-Saison, M. Save, C. Bui, B. Charleux and S. Magnet, *Macromolecules*, 2006, **39**, 8632–8638; (*e*) X. J. Cui, S. L. Zhong and H. Y. Wang, *Polymer*, 2007, **48**, 7241–7248; (*f*) U. Yildiz and K. Landfester, *Polymer*, 2008, **49**, 4930–4934.
14 (*a*) K. Min and K. Matyjaszewski, *Macromolecules*, 2005, **38**, 8131–8134; (*b*) K. Min, H. F. Gao and K. Matyjaszewski, *J. Am. Chem. Soc.*, 2006, **128**, 10521–10526.
15 K. Min, H. F. Gao and K. Matyjaszewski, *Macromolecules*, 2007, **40**, 1789–1791.

