

ORIGINAL PAPER

Synthesis of a photoactive gemini surfactant and its use in AGET ATRP miniemulsion polymerisation and UV curing

Chuan-Jie Cheng^{*}, Xiong-Xiong Bai, Wu-Qin Fan, Hai-Ming Wu, Liang Shen^{*}, Qing-Hua Huang, Yuan-Ming Tu

Jiangxi Key Laboratory of Organic Chemistry, Jiangxi Science & Technology Normal University, Fenglin Street, Nanchang, Jiangxi 330013, China

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A novel photoactive gemini surfactant was easily synthesised in high yields. The multi-functional molecule can be used as a gemini surfactant, a benzophenone type photoinitiator, and as an ATRP initiator. Poly(methyl methacrylate) (PMMA) and poly(methyl methacrylate)-*block*-poly(allyl methacrylate) (PMMA-*b*-PAMA) were prepared using the photoactive gemini surfactant as an ATRP initiator under soap-free miniemulsion polymerisation conditions. Kinetic results of the miniemulsion polymerisation of methyl methacrylate (MMA) indicate that the reaction has controlled/living characteristics. UV curing was performed by irradiation of the linear PMMA-*b*-PAMA polymer, in which PMMA-*b*-PAMA containing a benzophenone moiety functioned as a macromolecular photoinitiator.

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Introduction

Controlled/living radical polymerisation (L/CRP) has drawn great attention in recent years due to its significant academic value and promising industrial applications (Braunecker & Matyjaszewski, 2007; Chu et al., 2012; Zhang et al., 2009; Destarac, 2010). Many functional polymers and materials were prepared by this versatile technique, e.g. polymer brushes (Tsujii et al., 2006), telechelic polymers (Tasdelen et al., 2011), stimuli-responsive polymers (Yan et al., 2011), photoelectric functional molecules (Zhu et al., 2011; Shen et al., 2009), functional biomacromolecules (Benoit et al., 2011), etc. Among various L/CRP methods, atom transfer radical polymerisation (ATRP) and a recently developed activator generated by electron transfer for atom transfer radical polymerisation (AGET ATRP) are prominent due to their advantages such as easy manipulation, absence of conventional radical initiator, adaptability to most vinyl monomers and reaction systems, tolerance to many functional groups, etc. (Matyjaszewski, 2012; Jiang et al., 2012; Zhai et al., 2012; Lou & Shipp, 2012; Bai et al., 2011, 2012; Jakubowski & Matyjaszewski, 2005; Miao et al., 2012).

With the increasing global environmental protection pressure on chemical industries, people are seeking safer and environmentally friendly reagents as well as solvents or media to meet the demand of "green chemistry". The most preferable reaction medium is water which is safe, nontoxic, cheap, and eco-friendly (Lindström, 2007). For ATRP reactions in aqueous systems, the miniemulsion polymerisation approach is preferred; its controlled/living characteristics are best compared with those of emulsion polymerisation and microemulsion polymerisation methods (Mincheva et al., 2009; Oh et al., 2009; Cheng et al., 2011a). However, to stabilise the dispersion system in conventional emulsion polymerisation, small molecular emulsifiers are usually used, these are only physically ad-

^{*}Corresponding author, e-mail: chengcj530@gmail.com; shenliang00@tsinghua.org.cn

sorbed on the particle which can desorb from the polymer product or migrate to the polymer surface thus affecting the surface and electrical properties of the final polymer product. To overcome the disadvantages of small molecular emulsifiers, reactive and macromolecular emulsifiers have been developed in recent years (Cheng et al., 2011b; Basinska & Slomkowski, 2012). Reactive or polymeric emulsifiers can act as a macromonomer, inimer, or a transfer agent in the L/CRP reactions. For example, Li et al. (2009) used amphiphilic poly(ethylene oxide)-blockpoly(butyl methacrylate) with a chloro end group (PEO-b-PBMA-Cl) to polymerise butyl methacrylate (BMA) and ethylene glycol dimethacrylate (EGDMA) to obtain a shell-crosslinked nanocapsule. Recently, our research group introduced the synthesis and application of an anionic surface-active ATRP initiator of emulsion polymerisation of MMA, in which no other emulsifiers were needed (Cheng et al., 2010).

Photocuring technology utilises light (e.g., UV or visible light) to initiate and promote radical or ionic polymerisation. This method is advantageous over thermal curing in energy saving, safety, high reaction rate, etc. (Yagci et al., 2010; Yilmaz et al., 2011; Eriksson et al., 2010). Thus, the technology is extensively studied and applied in photocured coatings (Chen et al., 2011), photocured printing inks (Lin et al., 2012), and dental materials (Brandt et al., 2011).

Gemini surfactant is a special surfactant with two hydrophilic "heads" and two hydrophobic hydrocarbon "tails"; its symmetrical structure provides it with some unique properties such as low critical micelle concentration (CMC) and high capability of lowering surface tension (Wang, et al., 2012; Jahan et al., 2009; Zana, 2002). In our recent work, a gemini surface-active ATRP initiator was synthesised and used in miniemulsion polymerisation of MMA without any other emulsifier involved, and the resulting latex was stable enough to stand for at least half a year (Cheng et al., 2013). Herein, a facile synthesis of a photoactive gemini surfactant is reported. To the best of our knowledge, there are no reports on such a multi-functional molecule or similar ones except in our previous work (Cheng et al., 2013). There are three aspects concerning the application of the new surfactant: i) gemini surfactant that can be used in miniemulsion polymerisation; *ii*) ATRP initiator of the corresponding polymers formation; *iii*) reactive benzophenonetype photoinitiator in UV curing for the preparation of UV cured resins.

Experimental

Materials and methods

Bis(4-methylphenyl)methanone (4,4'-dimethylbenzophenone), carbamide peroxide (urea hydrogen peroxide, UHP), 2-bromo-2-methylpropanoyl bromide, N, N-dimethylethanolamine, dichloromethane, copper (II) bromide, ascorbic acid (AA), N,N-dimethyldodecylamine (DMDA), and 6-(prop-2-enoyloxy)hexyl prop-2-enoate (1,6-hexanediol diacrylate, HDDA) of AR grade were used directly as received from Sinopharm Chemical Reagent Co. (SCRC, China). Tetrahydrofuran (THF) (SCRC, China) of AR grade purity used as an eluent for neutral Al₂O₃ column separation and of chromatographic purity used for gel permeation chromatography (GPC), respectively, was used as received. Methyl methacrylate (MMA) monomer was purified by stirring with a 5 mass % aqueous NaOH solution for 30 min, washing with deionised water, and distillation under reduced pressure to remove the inhibitor prior to use. Allyl methacrylate (AMA) monomer was purified analogously but its instability and higher boiling point were considered. Therefore, it was finally purified on a neural Al₂O₃ column instead of distillation.

 1 H (400 MHz) and 13 C (100 MHz) NMR spectra of the intermediates were recorded on a Bruker AV 400 MHz spectrometer using $CDCl_3$ (unless specified otherwise) as a solvent and tetramethylsilane (TMS) as an internal standard. FTIR spectra (in KBr pellet) were measured on a Bruker V70 FTIR spectrophotometer. Critical micelle concentration (CMC) of the gemini surfactant was determined on a BZY-2 surface tension meter. 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 mm \times 7.5 mm columns (packed with 5 mm particles of different pore size). The column packing allowed the separation of polymers over a wide molecular mass range of 500-1000000 Da. THF was used as the eluent at the flow rate of 1 mL min⁻¹ at 40 °C. PMMA standards were used as the reference. Monomer conversion was determined by gravimetry. UV curing tests were performed on an RW-UV AH400a UV curing meter.

Preparation of photoactive gemini surfactant I

2-(Dimethylamino)ethyl 2-bromo-2-methylpropanoate (II) was synthesised using the previously described method (Cheng et al., 2013). Bis[4-(bromomethyl)phenyl]methanone (4,4'-di(bromomethyl)benzophenone, III) was prepared by a known procedure (Zheng et al., 2011) as follows: Bis(4-methylphenyl) methanone (1.50 g, 7.1 mmol) and UHP (1.47 g, 7.1 mmol)15.7 mmol) were dissolved in CH_2Cl_2 (20 mL) and the solution was heated to reflux under the irradiation of visible light (100 W of electric lamp). Aqueous HBr (48 mass % solution, 2.9 mL, 14.3 mmol) was then added dropwise within about 20 min and the reaction mixture was refluxed for additional 50 min followed by the addition of water (20 mL). The organic phase was separated, washed with brine, dried with anhydrous Na_2SO_4 , filtered and the solvent was



Fig. 1. Synthesis of the photoactive gemini surfactant *I*. Reaction conditions: *i*) Et₃N, CH₂Cl₂, rt, overnight, 86 %; *ii*) 48 % aq. HBr, UHP, CH₂Cl₂, light irradiation, reflux, 50 min, 46 %; *iii*) acetone, rt, 15 h, 86 %.

evaporated to give a white solid. Recrystallisation from CH₂Cl₂/EtOH afforded pure product *III* (1.20 g, 46 %). M.p. 120–122 °C; IR, $\tilde{\nu}/\text{cm}^{-1}$: 3051, 1670, 1602, 1587, 1410, 850, 609; ¹H NMR (400 MHz, CDCl₃): δ 7.77 (d, 4H, J = 8.00 Hz), 7.50 (d, 4H, J = 7.92 Hz), 4.53 (s, 4H); ¹³C NMR (100 MHz, CDCl₃): δ 195.5, 142.7, 137.6, 130.9, 129.5, 32.6.

Intermediate III (2.20 g, 6 mmol) was dissolved in acetone (20 mL), followed by the addition of II (3.33 g, 14 mmol) and stirring the mixture at ambient temperature for 15 h in N₂ atmosphere. The reaction mixture was filtered, the filter cake (white solid) was triturated in anhydrous diethyl ether and the resulting solid was dried in a vacuum drying oven at 60 °C to give the photoactive gemini surfactant I (4.37 g, 86.4 %). M.p. 109–111 °C; IR, $\tilde{\nu}$ /cm⁻¹: 3002, 2975, 1740, 1660, 1611, 1464, 1419, 1275, 1162, 1110, 934, 872; ¹H NMR (400 MHz, DMSO): δ 7.89 (d, 4H, J =7.80 Hz), 7.81 (d, 4H, J = 7.84 Hz), 4.82 (s, 4H), 4.70 (m, 4H), 3.83 (m, 4H), 3.13 (s, 12H), 1.95 (s, 12H); ¹³C NMR (100 MHz, D₂O): δ 199.1, 172.9, 138.8, 133.7, 132.2, 131.2, 68.9, 63.2, 60.0, 56.4, 51.1, 30.0.

Complete NMR spectra of compounds I, II, and III are available in the Supplementary data file.

Soap-free miniemulsion copolymerisation of MMA and AMA using the photoactive gemini surfactant I

Gemini surfactant I (1.287 g, 1.5 mmol), CuBr₂ (catalyst) (0.223 g, 1 mmol), DMDA (ligand) (0.854 g, 4 mmol), MMA (14.02 g, 140 mmol), and deionised water (50 mL) were mixed in a 100 mL three-necked flask and the mixture was ultrasonicated for 30 min to form a pre-emulsion. The pre-emulsion was purged with N₂ for 15 min and the flask was sealed and heated to 60 °C on an oil bath. Ascorbic acid (0.396 g, 2 mmol) dissolved in deionised water (5 mL) was then added by a syringe to initiate the reaction, and samples were withdrawn periodically during the reaction. After 5 h, an additional portion of monomer AMA (7.57 g, 60 mmol) was introduced into the reaction mixture and the reaction was run for another 4 h to complete the polymerisation. The resulting latex

was dried in a ventilation oven at $40 \,^{\circ}$ C until constant mass was achieved. The crude polymer product was dissolved in THF and purified on a neutral Al₂O₃ column to remove possible copper residues.

UV curing of PMMA-b-PAMA

The PMMA-*b*-PAMA polymer (1.0 g) was dissolved in THF (10 mL) followed by an addition of HDDA (0.1 g) and DMDA (0.03 g). The solution was spin-coated on a glass plate with the rotation speed of 1500 min⁻¹ for 1 min, and the coated layer was dried at ambient temperature to form a film. After coating, the plate was irradiated for 15 s by UV light (365 nm, 400 W) at the distance of 5 cm.

Results and discussion

Synthesis and properties of photoactive gemini surfactant (I)

Synthesis of the gemini surfactant I from a tertiary amine (II) and bis[4-(bromomethyl)phenyl]methanone (III) is depicted in Fig. 1. In the first step, an esterification reaction between 2-bromo-2-methylpropanoyl bromide and N,N-dimethylethanolamine in the presence of triethyl amine gave intermediate II in a 86 % yield. Subsequently, compound III was prepared from bis(4-methylphenyl)methanone by bromination with aqueous HBr and UHP under visible light irradiation. The method is cost-effective, highly efficient, and avoids the use of toxic and corrosive bromine (Zheng, et al., 2011).

One of the functions of surfactants is to decrease the surface tension; and the higher the concentration of the surfactants, the lower the surface tension of substances. When the concentration is increased to the critical micelle concentration (CMC), the surface tension is almost constant. According to this principle, surface tension was determined by preparing aqueous solutions of I with different concentrations. The plot of surface tension versus concentration is presented in Fig. 2. As it can be seen, the surface tension decreased rapidly with the increasing concentration of I; how-

Table 1. AGET atom transfer radical miniemulsion polymerisation of MMA at 60 $^{\circ}$ C using *I* as both an initiator and a stabiliser and ascorbic acid (AA) as a reducing agent^{*a*}

Entry	Time/h	$\operatorname{Conversion}^b/\%$	$M_n(\mathrm{th})^c/(\mathrm{g} \ \mathrm{mol}^{-1})$	$M_n(\mathrm{GPC})^d/(\mathrm{g\ mol}^{-1})$	PDI	$\ln(c_0(\mathrm{M})/c(\mathrm{M}))$
1	0.5	21.1	2774	3300	1.37	0.24
2	1	40.1	4522	4900	1.35	0.51
3	1.5	55.4	5941	6800	1.35	0.81
4	2	64.3	6730	7200	1.32	1.02
5	2.5	74.0	7649	8000	1.33	1.35
6	3	82.1	8386	8800	1.30	1.71
7	3.5	84.8	8646	8900	1.29	1.89
8	4	88.1	8938	9000	1.27	2.12
9	5	90.0	9122	9300	1.27	2.30

a) No additional emulsifier was required in the whole process of miniemulsion polymerisation; b) conversion was determined by gravimetric method; c) theoretical number-average molecular mass $(M_n(\text{th}))$ was calculated from the experimentally determined conversions; d) experimental number-average molecular mass $(M_n(\text{GPC}))$ was measured by gel permeable chromatography (GPC) using PMMA standards.



Fig. 2. Dependence of surface tension on the concentration of *I*.

ever, when the concentration increased to 5 mmol L^{-1} and higher, the curve became almost smooth. So, the CMC value of I is about 5 mmol L^{-1} .

The hydrophilic–lipophilic balance (HLB) number is another important parameter of surfactants. The HLB value of a surfactant can be calculated from the corresponding CMC. For a surfactant of a quaternary ammonium salt like I, the HLB can be calculated by Eq. (1), where the c(CMC) unit is mol L⁻¹ (Zhou & Cui, 2001). As the CMC value of surfactant I is 0.005 mol L⁻¹, its calculated HLB value is 40.229, indicating highly hydrophilic properties of I. Furthermore, solubility of I in water was tested, and it was found that 27.3 g of I can be dissolved in 100 mL of deionised water at ambient temperature.

$$HLB = 1.155 \log(c(CMC)) + 42.887$$
(1)

Preparation of PMMA-b-PAMA via soap-free AGET ATRP miniemulsion polymerisation

Multi-functional compound I can act as a sur-



Fig. 3. Monomer conversion (\blacksquare) and $\ln(c_0(M)/c(M))$ (\bullet) as a function of the reaction time.

factant, ATRP initiator, and a photoinitiator. First, miniemulsion polymerisation of MMA, using I as both an emulsifier and an AGET ATRP initiator, was studied. Based on our previous work, DMDA was selected as both the ligand and the co-emulsifier for the AGET ATRP miniemulsion polymerisation (Cheng et al., 2011b). Mole ratio of the reagents was optimised as n(I) : $n(CuBr_2)$: n(DMDA) : n(AA) : n(MMA)= 1.5 : 1 : 4 : 2 : 140, and the reaction was performed at 60 °C. Kinetic data of the MMA polymerisation are listed in Table 1, and the dependence of conversion, $\ln(c_0(M)/c(M))$, versus time is shown in Fig. 3. Conversion increased smoothly with the increasing reaction time, and conversion higher than 90 % was obtained within about 5 h. The linear relationship between $\ln(c_0(M)/c(M))$ and the reaction time indicates that the polymerisation followed the first-order kinetic law and the concentration of propagating radicals during the polymerisation was nearly constant (Fig. 3). Fig. 4 shows the relationship of molecular mass (M_n) , polydispersity index (PDI), and monomer conversion. M_n of PMMA increased almost linearly with the monomer conversion, indicating the controlled character of the miniemulsion polymerisation. In addition, the relatively low PDI (< 1.4) is another proof of the controlled character of the reaction (Table 1).



Fig. 4. Dependence of molecular mass $(M_n(\text{GPC}))$ (**•**) and polydispersity index (PDI) (**•**) on monomer conversion.

Then, polymerisation of AMA utilising I as both an emulsifier and an AGET ATRP initiator was attempted. AMA is a special monomer that has two types of C=C double bonds with different reactivity. The C=C double bond of methacrylate is more reactive and it is expected to undergo ATRP reactions, while the less reactive allylic C=C double bonds remain unchanged. In a control experiment, when only AMA was polymerised in emulsion, a cross-linking side-reaction occurred and the resulting polymer product was insoluble in THF as well as in other common solvents, indicating that a nonnegligible amount of allylic double bonds underwent the reactions. To solve this problem, copolymerisation of MMA and AMA was performed. After several controlled experiments (by emulsion polymerisation), the mole ratio MMA/AMA of 7 : 3 was adopted, and flocculation was neglected under these conditions. At first, MMA was polymerised to let the conversion reach about 90 % in 5 h. Then, the AMA monomer was added to the reaction system and the polymerisation was run for additional 4 h. In this way, PMMA-*b*-PAMA was prepared in one pot, and the "living" characteristics of the miniemulsion polymerisations were also proven (Fig. 5) (Shu et al., 2011).

¹H NMR spectrum confirming the formation of block copolymer PMMA-*b*-PAMA is illustrated in Fig. 6. Proton signals of both MMA and AMA units were found in the spectrum. H_a and H_b represent the protons on aryl rings of benzophenone, and their number was estimated as eight (4 H_a and 4 H_b). The number of protons of typical functional groups in the block copolymer can be determined based on the number of aryl protons. H_c and H_d represent vinyl protons of allyl groups. The number of H_c was about 65, and that of H_d 130, indicating that about 65 of AMA units



Fig. 5. One-pot preparation of PMMA-b-PAMA. Reaction conditions: i) MMA, CuBr₂, AA, deionised water, 60 °C, 5 h; ii) AMA, CuBr₂, AA, deionised water, 60 °C, 4 h.



Fig. 6. ¹H NMR spectrum of block copolymer PMMA-*b*-PAMA.

are present in the copolymer. The signal designated as H_e at $\delta = 4.40$ belongs the protons of CH₂ in allyl groups. The peak at $\delta = 3.53$ (H_f) corresponds to the proton of methoxy groups of MMA units, and the presence of about 790 protons in the spectra suggests that there are about 260 MMA units in the copolymer. Therefore, the molecular mass of PMMAb-PAMA can be estimated as $M_n(\text{NMR}) = M_n(\text{init})$ + $(65 \times M(\text{AMA})) + (260 \times M(\text{MMA})) = 844 +$ $(65 \times 126) + (260 \times 100) = 35034 \approx 35000.$

GPC spectra of PMMA and PMMA-*b*-PAMA are shown in Fig. 7 to further verify the formation of the block copolymer. The number-average molecular mass of PMMA-*b*-PAMA was higher than that of PAMA, indicating the polymerisation of the AMA monomer based on the PMMA macroinitiator to form the corresponding block copolymer. The molecular mass of PMMA-*b*-PAMA obtained from the GPC spectra is inconsistent with that obtained from ¹H NMR, which can be attributed to an integration error in NMR.

UV curing of the prepared PMMA-b-PAMA

In the linear PMMA-b-PAMA polymer, benzophe-



Fig. 7. GPC spectra of PMMA-b-PAMA ($M_n = 11000$ Da, PDI = 1.13) (a) and PMMA ($M_n = 9300$ Da, PDI = 1.27) (b).

none photoinitiator and many allyl groups are present; this unique structure enables further curing of the polymer under UV irradiation. Because benzophenone belongs to hydrogen-abstracting photoinitiators, tertiary amine is required for UV curing. Thus, DMDA was used as the corresponding tertiary amine, and it accounted for 3 mass % of the PMMA-b-PAMA polymer. HDDA was chosen as the diluter in the amount of 10 mass % based on PMMA-b-PAMA. After the



Fig. 8. Comparison of IR spectra of PMMA-*b*-PAMA before (a) and after UV irradiation (b).

Table 2. Effect of the HDDA amount on the properties of UVcured polymer films a

Entry	$\mathrm{HDDA}^b/\mathrm{mass}~\%$	Properties of UV cured polymer films
1	0	very brittle, light yellow
2	5	brittle, light yellow
3	10	good toughness, light yellow
4	20	too soft, low hardness

a) Amount of DMDA co-photoinitiator was 3 mass % based on compound I; UV irradiation time was 15 s; b) amount of the HDDA diluter based on compound I.

UV irradiation for 15 s, a film was obtained. Comparison of the IR spectra of PMMA-*b*-PAMA before and after the UV curing (Fig. 8) showed that there is a peak at 3086 cm⁻¹ before the UV curing, representing the signal of the vinylic C—H bond. The peak at 3086 cm⁻¹ disappeared after the UV irradiation, indicating that most allylic C—C double bonds underwent radical reactions under the UV curing conditions. Changes in the polymer's solubility also confirmed the effect of UV curing. Before UV irradiation, the PMMA-*b*-PAMA polymer (1.0 g) dissolved in THF (20 mL) in 30 min, while the cured PMMA-*b*-PAMA polymer (1.0 g) cannot be dissolved in THF (20 mL) even after 24 h.

Control experiments were performed to illustrate the role of the HDDA diluter in the UV curing of the PMMA-*b*-PAMA polymer (Table 2). During UV curing, it is usually necessary to use a diluter to adjust the curing rate, viscosity of the system, and film properties. In the control experiment, properties of the film remained almost unchanged without HDDA after the UV irradiation for 15 s, which indicated that the UV curing rate is very low in the absence of a diluter (Entry 1, Table 1). When 5 mass % of HDDA were added to the formulation, its properties improved but the film's surface was still brittle (Entry 2, Table 1). Relatively good toughness was obtained when 10 mass % of HDDA were used (Entry 3, Table 1). However, when 20 mass % of HDDA were added, the film showed very low hardness.

Conclusions

A photoactive gemini surfactant was prepared in a 86 % yield under mild conditions. This novel multifunctional molecule was successfully used as an emulsifier, ATRP initiator, and a type-II photoinitiator. Linear PMMA as well as PMMA-b-PAMA were prepared by employing the functional molecule as an ATRP initiator generated by electron transfer (AGET) for atom transfer miniemulsion polymerisation, in which no other emulsifiers were involved. The polymerisation followed the first-order kinetic law and showed controlled/living characteristics. UV irradiation of PMMA-b-PAMA within 15 s afforded the corresponding UV cured polymer which was almost insoluble in common organic solvents. The novel photoactive gemini surfactant is expected to provide more functional macromolecules.

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Supplementary data

Supplementary data associated with this article can be found in the online version of this paper (DOI: 10.2478/s11696-013-0420-y).

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