Novel Starlike Amphiphilic Graft Copolymers with Hydrophilic Poly(acrylic acid) Backbone and Hydrophobic Poly(methyl methacrylate) Side Chains

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It is well-known that star polymers have different properties compared with linear polymers of similar composition due to their branched architecture and high degrees of chain end functionality.[1,2] In recent years, many efforts were paid for the synthesis and characterization of well-defined star polymers, which was significant for the exploration of the relationships between structure and property.[3−9]

In general, two strategies, including "arm first" and "core first", were used to synthesize star polymers. For the "arm first" approach,[4−6] monofunctional arms are initially synthesized and then connected to the multifunctional core molecule. By this strategy, separation techniques are used to isolate stars from uncoupled linear polymers, and the products usually have structure defects considering of the efficiency of connecting reaction. For the "core first" approach,[3,7] multiinitiation groups of the core molecule initiated the polymerization to form arms. With the development of atom transfer radical polymerization (ATRP), this method was widely used to synthesize well-defined star polymers with controllable arm number and length.[8] Moreover, with the combination of ATRP and grafting-from techniques, a kind of star-graft copolymer was synthesized, which showed the strong power of ATRP in preparation of copolymers with complex architecture.[10]

In this study, we report the first preparation of starlike amphiphilic graft copolymers with hydrophilic backbone totally free from ester group (Scheme 1) by ATRP[11,12] and grafting-from[13] techniques as well as their self-assembly behaviors in water. As is known, the molecular architecture played an important role in the self-assembly behavior.[2,14−18] So, this study will give us more information about the relationship between structure and self-assembly properties as compared with amphiphilic linear-graft copolymers.

We selected methoxymethyl acrylate (MOMA) as the monomer to synthesize the backbone due to its mild acidic hydrolysis conditions. Poly(methoxymethyl acrylate) (PMOMA) can be synthesized by ATRP of MOMA initiated by methyl 2-bromopropionate monoinitiator. In this work, a kind of four-functional initiator, pentaerythritol tetrakis(2-bromopropionate) (4BrPr), was used to initiate ATRP of MOMA to form four-arm PMOMA backbone. From the results in Table 1, we found that the molecular weight distributions were kept very low ($M_w/M_n < 1.20$). However, a shoulder peak appeared in the GPC curve of **1a**, which resulted from side reactions at high conversion. When the conversion was kept below 40%, symmetrical and narrow dispersed peaks were obtained (**1b** and **1c**).

Figure 1 showed ^{1}H NMR spectrum of four-arm PMOMA, ATRP mechanism of polymerization was confirmed by the peaks "a" , "e" and "f" belonged to the protons of the initiation groups and the chain end groups, respectively. As we know, the molecular weight of star polymer is usually underestimated by GPC due to the lower hydrodynamic radius. We calculated the molecular weight of PMOMA ($M_{n,NMR}$) from ^{1}H NMR according to $4 \times [S_g/S_e] \times 116$ (S is the peak area). For PMOMA **1b** and **1c**, every arm has 28 and 36 MOMA repeating units, respectively.

To retain ester groups on the backbone so that they can be hydrolyzed to hydrophilic carboxylic groups, ATRP initiation groups were connected to the α-carbon of the ester groups of PMOMA backbone using LDA and α-bromoisobutyryl bromide, as shown in Scheme 1. This reaction has been successfully used to prepare macroinitiators in the synthesis of linear-graft copolymers in the previous work.[19] The bromine content of macroinitiator **2** ($M_n = 8200$, $M_w/M_n = 1.35$) which was prepared from PMOMA **1c** increased from 2.13% to 10.49% after reaction. Additionally, the obvious increase of peak area at $\delta = 1.89$ ppm (protons of $COC(CH_3)_2Br$ of ATRP initiation groups) in ^{1}H NMR and the appearance of a new peak at $\delta = 206.4$ ppm (the keton carbon of $-CO(CH_3)_2Br$) in ^{13}C NMR indicated the successful synthesis of four-arm macroinitiator **2**. From the result of %Br of macroinitiator **2**, we can obtain that the approximate graft efficiency was $^1/_5$, which means ATRP initiation groups were introduced to one-fifth of repeating units of PMOMA backbone. Because every arm of PMOMA **1c** has 36 MOMA repeating units, PMOMA-Br macroinitiator **2** has about 28 ATRP initiation groups.

Graft copolymerization of methyl methacrylate (MMA) initiated by macroinitiator **2** in bulk with CuBr/dhbpy as catalyst gave starlike PMOMA-*g*-PMMA with low molecular weight distributions either at 50 or 80 °C, as listed in Table 2. The molecular weights increased with the polymerization time (**3b**−**3d**), and all graft copolymers showed unimodal and symmetrical GPC curves, which are characteristic of ATRP.[11] In the synthesis of linear-graft copolymer,[10,13,20−23] a high feed ratio of monomer to initiator and a low conversion of monomer were necessary to suppress intermolecular coupling reactions, which was same in the present study.

^{1}H NMR signals of the corresponding protons of both backbone and side chains convinced us of the structure of starlike PMOMA-*g*-PMMA, as shown in Figure 2A. With the value of $[S_g/2]/[(S_{d+h} - 1.5S_g)/3]$ (S is the peak area), we can get the ratios of repeating units of backbone to the side chains (N_{MOMA}/N_{MMA} in Table 2). From the values of N_{MOMA}/N_{MMA} and the molecular weights of PMOMA, the molecular weights of graft copolymers ($M_{n,NMR}$) were also obtained from ^{1}H NMR, which were much higher than those determined by GPC due to the branched architecture.

Hydrolysis of PMOMA backbone with HCl was carried out at room temperature for 2 h. From ^{1}H NMR of the purified product (Figure 2B), the disappearance of the signals of the protons of methoxymethyl assured the complete hydrolysis of PMOMA backbone. The appearance of a broad peak of $-COOH$ at 3438 cm^{-1} in the FT-IR spectrum indicated the formation of PAA backbone. Because the arms were connected to the center core with ester groups, the effect of hydrolysis conditions on these ester groups should be studied. The obtained PAA-*g*-PMMA was reprotected by CH_2N_2 to PMA-*g*-PMMA

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Scheme 1. Synthesis of Starlike Amphiphilic Graft Copolymers

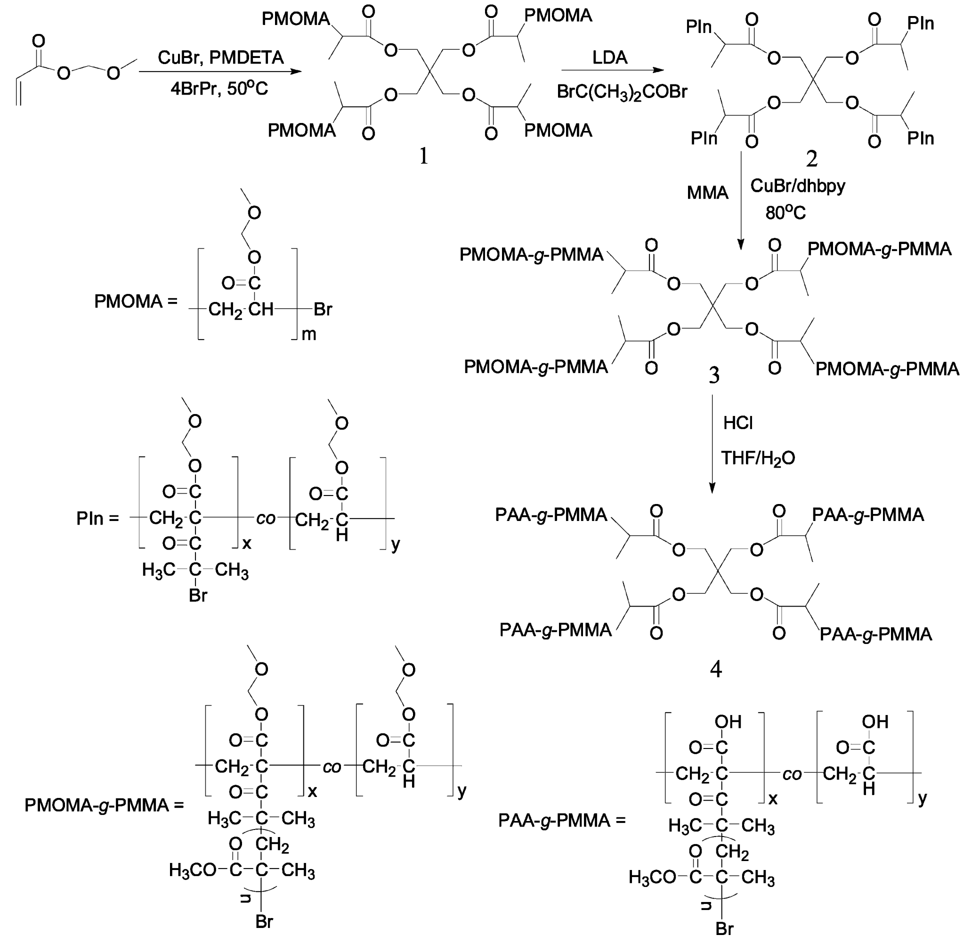


Table 1. ATRP of MOMA Initiated by 4BrPr

PMOMA	[MOMA]:[CuBr]: [PMDETA]:[In][a]	T (°C)	t (h)	M_n[b] (g/mol)	M_w/M_n[b]	$M_{n,NMR}$[c] (g/mol)	yield (%)	Br (%)[d]
1a	17:1:1:1	50	3	8 200	1.16		60	
1b	34:1:1:1	50	2	11 000	1.08	13 000	33	2.34
1c	40:1:1:1	50	3	11 000	1.17	17 000	25	2.13

[a] [In] = 4[4BrPr]. [b] Measured by GPC. [c] Obtained by ^{1}H NMR. [d] Obtained by titration with $Hg(NO_3)_2$.

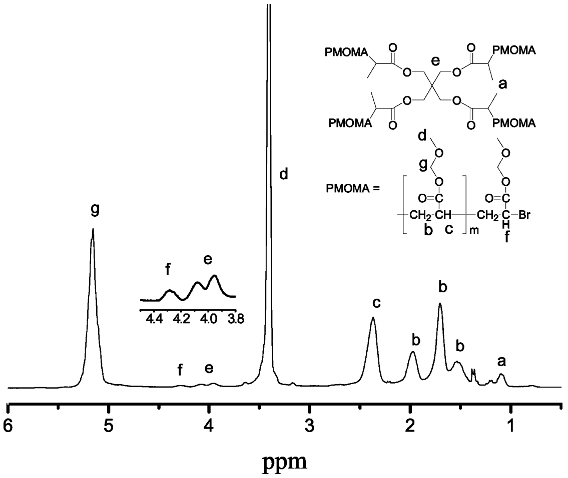


Figure 1. ^{1}H NMR spectrum of starlike PMOMA **1**.

for GPC measurement, and the molecular weight and distribution (M_n = 35 000, M_w/M_n = 1.26) were almost the same as that of PMOMA-*g*-PMMA before hydrolysis (M_n = 36 000, M_w/M_n = 1.24). These results confirmed the successful preparation of amphiphilic star-graft copolymers.

Table 2. Synthesis of Star-Graft Copolymers Initiated by Macroinitiator 2[a]

	T (°C)	time (min)	M_n[b] (g/mol)	M_w/M_n[b]	$M_{n,NMR}$[c] (g/mol)	N_{MOMA}/N_{MMA}[c]	conv[d] (%)
3a	50	20	36 000	1.24			
3b	80	10	50 000	1.38	134 000	1/8	2.6
3c	80	15	100 000	1.25	470 000	1/31	7.9
3d	80	30	110 000	1.23	484 000	1/32	9.7

[a] Initiated by **2** (M_n = 8200, M_w/M_n = 1.35, Br = 10.49%, graft efficiency: 1/5), [MMA]:[Br]:[CuBr]:[dhbpy] = 500:1:1:2. [b] Measured by GPC. [c] Obtained by ^{1}H NMR. [d] Determined by GC.

The fluorescence probe technique[24−28] was used to measure the critical micelle concentration (cmc) of amphiphilic copolymers in water. The acetone solution of pyrene (6 mg/100 mL, 2.97×10^{-4} mol/L) was added to water until the concentration of pyrene reached 5×10^{-7} mol/L. Next, different amounts of PAA-*g*-PMMA **4c** (hydrolysis product of **3c**) solutions in THF (1 mg/mL) were added to water containing pyrene. The cmc value of PAA-*g*-PMMA **4c** is 5.21×10^{-7} g/mL, which is comparable to that of linear PAA-*g*-PMMA with similar composition.[19] It seems that further star-branch would not facilitate the formation of micelles because linear-graft copolymers had a high degree of branch.

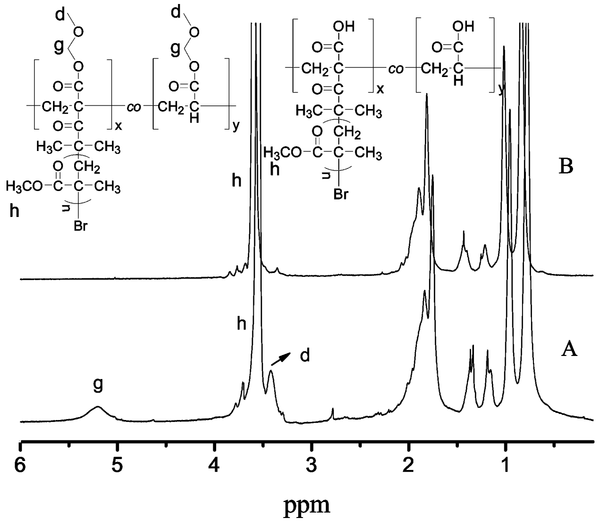
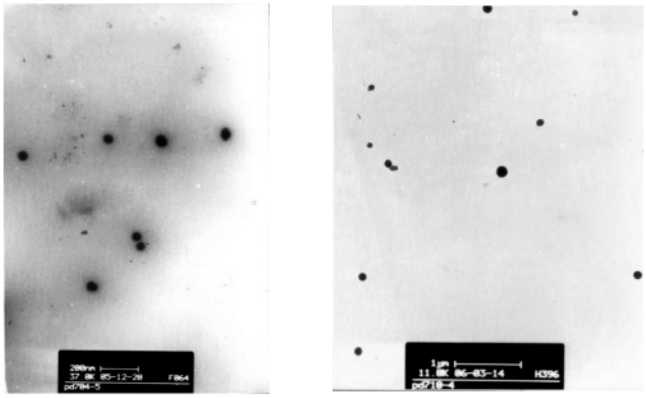


Figure 2. ^{1}H NMR spectra of starlike PMOMA-*g*-PMMA (A) and PAA-*g*-PMMA (B).



(A) (B)

Figure 3. TEM images of micelles of starlike PAA-*g*-PMMA **4c** in water (A) and in NaCl solution (B).

In the study of micellar morphologies of amphiphilic linear-graft copolymers,[19] we found PAA-*g*-PMMA with different molecular weights formed vesicles in water. It can be explained that the weak hydrophobic property of PMMA and the interactions between PMMA and water helped PMMA side chains exist in the relaxed conformation, which could benefit for the formation of vesicles. However, the micelles formed by amphiphilic star-graft copolymers PAA-*g*-PMMA **4c** were spheres (Figure 3A). These star-graft copolymers have the more confined structure and stronger repulsion among side chains than linear-graft copolymers so that PMMA side chains intended to stretch out. As a result, spheres were preferred to be formed. This study sufficiently indicated the importance of polymer architecture in the self-assembly properties of amphiphilic copolymers. The addition of electrolyte, NaCl, increased the micellar sizes from ca. 55 to 110−180 nm (Figure 3B) because Na^+ screened the electronic repulsion among the hydrophilic poly(acrylic acid) backbones and the hydrophobic side chains were easier to aggregate to form big micelles.[29]

In summary, the synthesis of well-defined amphiphilic star-graft copolymers with hydrophilic PAA backbone and hydrophobic PMMA side chains by ATRP and grafting-from techniques has been successfully carried out. It is a significant progress for synthesis of amphiphilic star-graft copolymers since the hydrophobic side chains can be extended to other polymer blocks and the arm number can be regulated by the multifunctional initiator. The micelles formed by starlike PAA-*g*-PMMA were spheres, which were different from vesicles formed by linear PAA-*g*-PMMA. This finding reflected the important role of polymer architecture on the self-assembly behavior. The addition of NaCl to water had no effect on the micellar morphology but increased the sizes.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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