

Synthesis and surface activity of novel ABA type triblock cationic amphiphiles

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Summary

Different amphiphilic triblock copolymers of n-butyl methacrylate (BMA) and 2-methacryloyloxyethyltrimethyl ammonium iodide were prepared by the reaction of precursor polymer and iodomethane. The precursor polymers were obtained by Group-Transfer Polymerization (GTP) of BMA with 2-(dimethylamino)ethyl methacrylate (DMAEMA) using a difunctional initiator at room temperature. Their molecular weight and composition could be controlled by regulating the monomer to initiator ratio and the feed ratio of two monomers. From quantitative quaternization of poly(DMAEMA) segments of precursor polymers by iodomethane, the target polymers were prepared. These amphiphilic triblock copolymers exhibited excellent surface activity and lowered the surface tension of their aqueous solutions. The lowest surface tension (γ) value reached to 27.4 dyn/cm.

Introduction

Since Webster *et al.*, have announced a new method of a living polymerization termed "group transfer polymerization (GTP)", it has been a considerable interest to many research groups due to its superiority to other polymerization methods (1). GTP is a living process of (meth)acrylic monomers; hence the block copolymers of well defined structure can be prepared by sequential addition of monomers even at room temperature.

Polymers with pendant quaternary ammonium salts are applicable to a wide scope such as water soluble polymer, polyelectrolyte, polyampholyte, hydrogel, etc (2). Up to now, however, there is few report on the synthesis of polyquaternary ammonium salts of controlled molecular weight and narrow molecular weight distribution (3). Recently, we have reported the synthesis and property of the novel acrylic based amphiphilic di- and triblock copolymers(4).

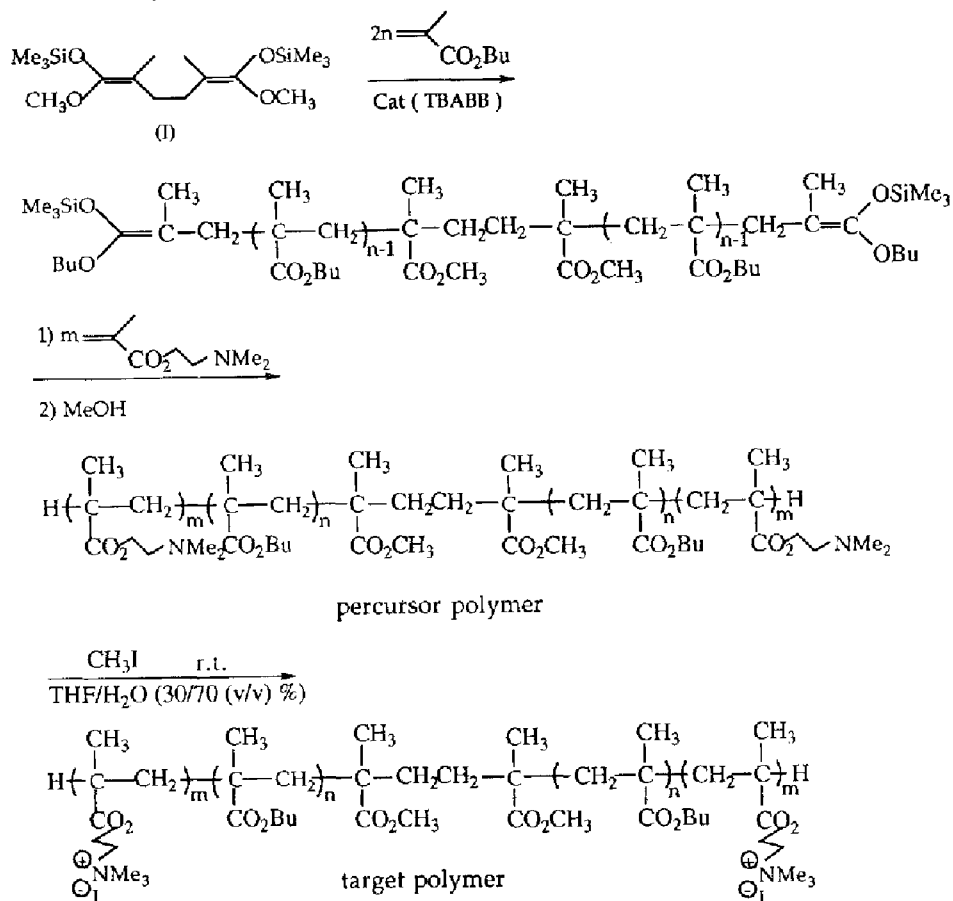
In this study, we report the synthesis and quaternization reaction of the triblock copolymers of BMA and DMAEMA by GTP with the difunctional initiator (I), and the surface activity of the resulting amphiphilic triblock copolymers.

Experimental

Materials. Solvent, THF, was purified by distillation over sodium and benzophenone before use. BMA and DMAEMA (Aldrich) were purified by distillation over calcium hydride at least twice prior to use. The polymerization catalyst, tetrabutyl ammonium bibenzoate (TBABB), was prepared as described in the literature(1). A difunctional initiator, 1,6-[bis(trimethylsilyloxy)-dimethoxy]-2,5-

dimethyl-1,5-hexadiene (I), was prepared as described earlier(5).

Scheme 1 Synthesis of triblock copolymer



Polymerization Procedure. A typical triblock copolymerization procedure was as follows: a 50 mL reactor fitted with an argon inlet, a magnetic stirrer, and a thermocouple was charged with THF (12 mL), TBABB (0.26 mL, 0.1M in THF), and an initiator (2) (2.0 mmol). Then BMA (0.39 mL) was added dropwise via syringe at a rate of 0.5 mL/min. After 30 min, DMAEMA (3.7 mL) was added via syringe at a rate of 1.0 mL/min. The mixture was stirred for 3 hrs and then quenched with methanol (2.0 mL). After 1 hr of stirring, THF and methanol were evaporated. The polymer collected was dried at 40 °C/1 torr for 24 hrs.

Conversion of Amine pendant into Quaternary Ammonium salt. A precursor polymer (2.0 g) was dissolved in 30mL of THF-H₂O (70/30 (v/v) %) co-solvent, and 1.1 equivalent of CH₃I was added slowly not to exceed the temperature 40 °C. The solution was stirred for 3 hrs, and poured into large volume of hexane. The

Table 1. Synthesis of Triblock Copolymer by GTP with I^a

exp. no.	THF (mL)	monomer feed (mL)	content, mol%		Mn/10 ³		Mw/Mn ^d	quaternized sample no.	cmc ^c	γ_{\min}^f
			calcd. ^b	obsd. ^c	calcd.	obsd. ^d				
1	6	BMA(0.62) DMAEMA(1.3)	67	67	2.0	2.1	1.10	1a	8	35.1
2	6	BMA(0.19) DMAEMA(1.7)	90	89	2.0	2.0	1.15	2a	10	31.1
3	6	BMA(0) DMAEMA(1.9)	100	100	2.0	1.9	1.19	3a	10	30.8
4	12	BMA(1.3) DMAEMA(2.8)	67	65	4.0	4.3	1.23	4a	6	37.1
5	12	BMA(0.4) DMAEMA(3.7)	90	91	4.0	3.8	1.19	5a	30	36.9
6	12	BMA(0) DMAEMA(4.1)	100	100	4.0	3.6	1.17	6a	50	37.1
7	18	BMA(2.0) DMAEMA(4.3)	67	66	6.0	6.4	1.20	7a	9	41.9
8	18	BMA(0.6) DMAEMA(5.6)	90	88	6.0	6.0	1.21	8a	60	36.7
9	18	BMA(0.3) DMAEMA(5.9)	95	95	6.0	5.6	1.26	9a	120	36.2
10	18	BMA(0) DMAEMA(6.2)	100	100	6.0	5.6	1.28	10a	80	40.1
11	18	BMA(0) DMAEMA(0.86)	100	100	1.0	0.9	1.31	11a	140	27.4

^a Initiator ; 2.0 mmol, catalyst ; TBABB (0.5 mol % relative to initiator), Yields of the polymers were all quantitative.

^b mol % of DMAEMA.

^c Determined by ¹H-NMR.

^d Obtained by GPC using poly(MMA) standards.

^e cmc (critical micellar concentration) ; wt % X 10³.

^f Surface tension of quaternized polymer samples, the surface tension of aqueous solution (1.0 wt %) was measured at 25 °C; dyn/cm.

precipitate was filtered and dried at 40 °C/1 torr for 24 hrs. The degree of quaternization determined by $^1\text{H-NMR}$ spectra was quantitative.

Measurement. Molecular weights and molecular weight distributions of the polymers were determined by GPC using a Waters 150C with refractive index detector and four μ -styragel columns (10^5 , 10^4 , 10^3 , and 500\AA) connected in series. Poly(MMA) standards were used for the construction of a calibration curve. $^1\text{H-NMR}$ characterizations were accomplished using a Bruker AM-300 Spectrometer. The surface tension of aqueous polymer solutions was measured by a Fisher Surface Tensiometer Model 21 at 25 °C.

Results and discussion

As shown in Scheme 1, the precursor triblock copolymer was prepared by sequential addition of BMA and DMAEMA using a difunctional initiator (I). Poly(BMA) was employed as a hydrophobic segment because our preceding study showed that poly(BMA) was more efficient hydrophobic segment than that of poly(MMA) (4a).

Table 1 represents the results of the triblock copolymerization. When DMAEMA was added to the solution of poly(BMA) prepared by GTP, the living poly(BMA) polymerize DMAEMA to produce triblock copolymers. The polydispersities of triblock copolymers are in the range from 1.10 to 1.31. Figure 1 shows the GPC chromatogram of a triblock copolymer and its precursor (exp. no. 7 in Table 1). After the addition of the second monomer, the GPC chromatogram shifts toward the higher molecular weight side, while maintaining its narrowness.

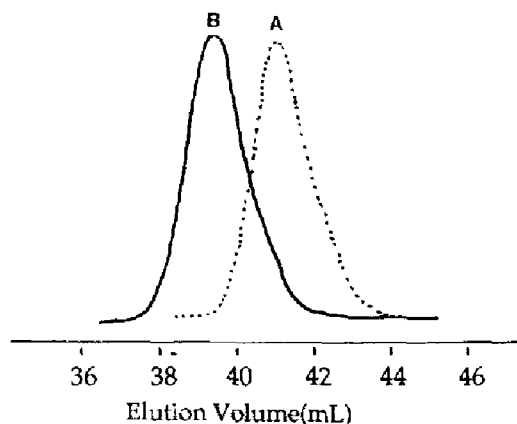


Figure 1. GPC chromatogram of BMA-DMAEMA triblock copolymer (exp. no. 7 in Table 1): (A) poly(BMA) precursor, $M_n(\text{obsd}) = 2010$, $M_w/M_n = 1.09$; (B) triblock copolymer, $M_n = 6380$, $M_w/M_n = 1.20$.

The quaternization of a precursor polymer was achieved with iodomethane at r.t. in THF- H_2O (70/30 (v/v) %) co-solvent for 3 hrs. The degree of quaternization determined by $^1\text{H-NMR}$ spectrum was quantitative. Figure 2 shows the $^1\text{H-NMR}$ spectra of the starting precursor polymer and the quaternized products. The methyl proton peak of amino group appears at 2.3 ppm (a) in precursor polymer. This peak disappears completely at that position and shifted 3.3 ppm (b) in quaternary ammonium salt.

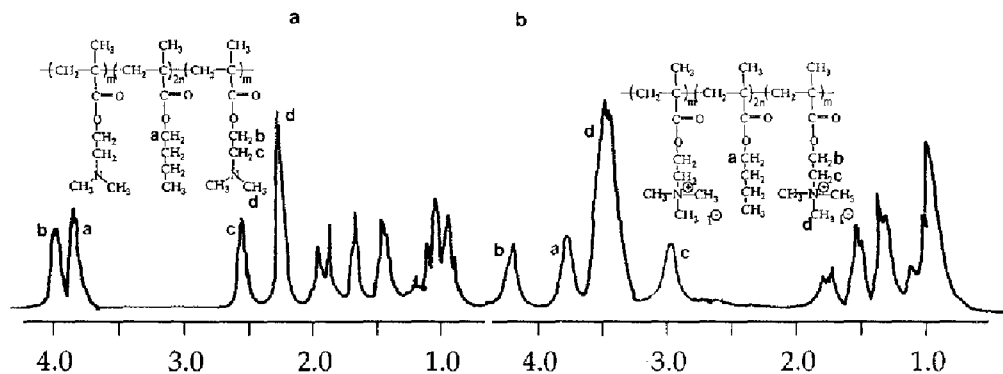


Figure 2. $^1\text{H-NMR}$ spectra of (a) precursor triblock copolymer and (b) quaternized triblock copolymer (exp. no. 7 in Table 1) (CDCl_3 , 300MHz).

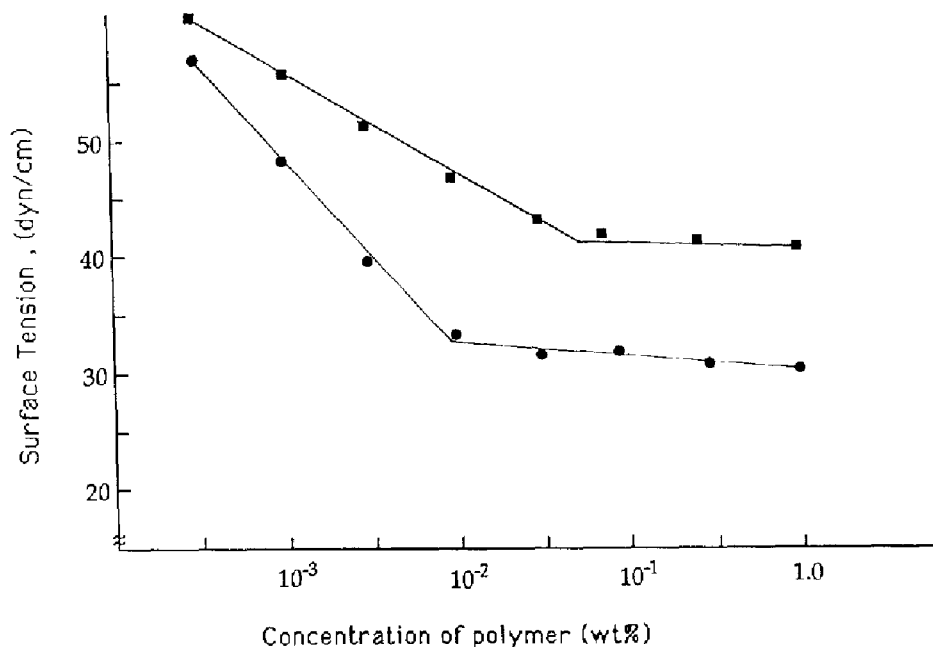


Figure 3. The relationship between polymer concentration and surface tension : (●) quaternized sample no. 3a; (■) quaternized sample no. 10a.

The structure of all block copolymers was confirmed by $^1\text{H-NMR}$ spectroscopy (cf. Figure 2) and the compositions of all block copolymers were determined from the integration ratio of the $^1\text{H-NMR}$ spectra, which were in good agreement with the monomer feed ratio. The observed molecular weights of the polymers were reasonably in agreement with those expected from the ratios of monomer to initiator

in each sample. When the quaternized sample was stirred for 24 hrs in hexane which is a good solvent of homo-poly(BMA) and non-solvent of the quaternized block copolymer, no detectable amount of soluble fraction was obtained. Thus the polymer is considered to be only a block copolymer.

The surface activities of the quaternized triblock copolymers were evaluated by measuring the surface tension (γ) of their aqueous solutions. The γ values were obtained with aqueous solutions of 1.0 wt %, which was higher than the critical micellar concentration (cmc), as shown in Figure 3. All samples were soluble in water and showed excellent surface activity. Among the quaternized polymers prepared, polymer no. 11a exhibited the lowest γ value of 27.4 dyn/cm. In this case, bifunctional initiator, by itself, acts as hydrophobic segment.

Figure 3 shows the γ value of quaternized sample no. 3a, 10a as a function of their concentration. The cmc values were smaller than 1.0 wt % in all cases.

Acknowledgement

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