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Synthesis of Amphiphilic Poly(alkyl methacrylate-*b*-methacrylic acid) by Group Transfer Polymerization and Selective Hydrolysis

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Several poly(alkyl methacrylate-*b*-*t*-butyl methacrylate) diblock copolymers were synthesized by group transfer polymerization. The molecular weight of poly(*t*-butyl methacrylate) segments and the composition of the resulting block copolymers were controlled by the monomer feed ratios and mole ratios of monomer to initiator. The poly(*t*-butyl methacrylate) block was quantitatively hydrolyzed to poly(methacrylic acid) block by refluxing with a catalytic amount of *p*-toluenesulfonic acid in dioxane at 100°C for 12 hrs. The thermogravimetric analysis of poly(alkyl methacrylate-*b*-*t*-butyl methacrylate) exhibited the loss of isobutylene and subsequent anhydride formation in the range of 205-310°C.

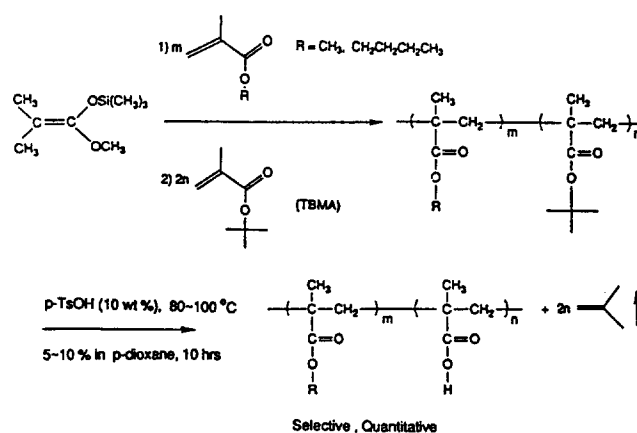
Introduction

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 superiority to other polymerization methods.¹ We had reported a difunctional initiator for GTP and the novel synthesis of acrylic based triblock copolymers.²

Block copolymers containing hydrophobic and hydrophilic segments are of interest as amphiphilic materials which are used as detergent, compatibilizer, and surface modifier etc.⁴⁻⁶ Direct synthesis of polymers with well-defined structure containing hydroxyl or carboxyl group functionality is quite difficult because the termination in anionic polymerization was caused by the active hydrogen of related monomers. One of the possible means of circumventing this difficulty is to introduce a protecting group to the monomer, masking reactive site. One of the synthetic methods for amphiphilic block copolymer is to copolymerize a protected monomer and a hydrophobic monomer and hydrolyze the resulting block copolymer selectively. Although various block copolymers had been reported,⁴⁻⁷ there is little report on acrylic based amphiphilic block copolymer. Recently, we reported the synthesis and properties of the novel amphiphilic triblock copolymers.³

This article deals with the preparation of poly(alkyl methacrylate-*b*-*t*-butyl methacrylate) (PAMA-*b*-PTBMA) by GTP and amphiphilic poly(alkyl methacrylate-*b*-methacrylic acid)

(PAMA-*b*-PMAA) by selective hydrolysis of the block copolymer. The characterization of the resulting amphiphilic block copolymer will be discussed.



Scheme 1.

Experimental

Materials and Instruments. Solvents were purified by normal procedure and handled under moisture free atmosphere. The polymerization solvent, tetrahydrofuran (THF) was distilled over sodium and benzophenone immediately prior to use.

Methyl methacrylate (MMA) and *n*-butyl methacrylate (BMA) (Aldrich) were purified by distillation over calcium hydride. TBMA was prepared from the reaction of methacry-

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Table 1. Synthesis of PMMA-*b*-PTBMA by GTP with 1-methoxy-1-trimethylsiloxy-2,2-methylprop-1-ene (TMS)^a

Sample	Alkyl	TBMA mol%		$\bar{M}_n \times 10^{-3}$		\bar{M}_w/\bar{M}_n^c
		calcd.	obsd. ^b	calcd.	obsd. ^b	
5	Methyl	19.1	19.2	9.1	10.1	1.31
2	Methyl	41.4	43.2	12.5	13.2	1.34
3	Methyl	58.6	60.2	5.9	6.6	1.37
4	Methyl	80.2	78.1	7.2	8.1	1.40
5	Butyl	20.0	22.1	8.7	9.7	1.30
6	Butyl	50.0	47.5	10.4	11.9	1.34
7	Butyl	66.6	69.2	5.2	5.5	1.39
8	—	100	100	6.6	7.2	1.42

^aPolymerization was carried out in THF at 25°C (Catalyst; TASHF₂, first addition; 0.5 mole% of TMS, second addition; 0.05 mole% of TBMA). ^bDetermined by the ratio of *t*-butyl protons to protons attached to methyl or *n*-butyl ester in ¹H-NMR spectra. ^cCalculated by GPC with PMMA standard calibration.

loyl chloride and *t*-butyl alcohol in the presence of triethylamine. The obtained TBMA was first distilled over calcium hydride, followed by distillation over triethyl aluminium and diisobutyl aluminium hydride as described in the literature.⁹

The polymerization catalyst and GTP initiator, tris (dimethylamino)-sulfoniumbifluide (TASHF₂) and 1-methoxy-1-trimethylsiloxy-2-methylprop-1-ene (MTS) were prepared by the procedures elsewhere.¹

¹H-NMR spectra were recorded on Bruker AM-300 Spectrometer. Infrared spectra were taken on a Bomem Michelson MB-100 Spectrometer in KBr pellet. Molecular weights and molecular weight distributions of the polymers were determined by gel permeation chromatography (GPC) using a Waters 150C with refractive index detector and μ -styragel columns (pore size of 10⁵, 10⁴, 10³, and 500 Å). Poly (methyl methacrylate) (PMMA) was used as standard for the calibration curves. Thermogravimetric analysis (TGA) was performed with a Du Pont 951 TGA in nitrogen atmosphere at a rate of 10°C/min.

Polymerization Procedure. The polymerization was carried out under argon atmosphere at room temperature. Typical polymerization procedure was as follows. A 50 ml reactor fitted with an argon inlet, a magnetic stirrer, and a thermometer was charged with THF (10 ml), TASHF₂ (0.1 M in CH₃CN, 0.5 mol% of initiator), and a GTP initiator (1) (0.2 ml). Then a given amount of MMA or BMA was added dropwise *via* syringe at a rate of 1 ml/min. After 30 min, 0.2 ml of the reaction mixture was withdrawn for gel permeation chromatography (GPC) analysis. Then TBMA was added *via* syringe. After this addition, an additional TASHF₂ (0.05 mol% of TBMA) was added very slowly. The mixture was stirred for 2 hrs and the polymerization was quenched with 2 ml of methanol. After additional stirring for 1 hr, THF and methanol were evaporated. The polymer collected was dried at 60°C for 24 hrs under reduced pressure.

Hydrolysis of PTBMA Segment into PMAA Segments. *p*-Toluenesulfonic acid (*p*-TsOH) was used as a catalyst [5 mol% of poly (TBMA) content].⁵ PAMA-*b*-PTBMA was dissolved in dioxane (polymer/dioxane = 1/20 by weight),

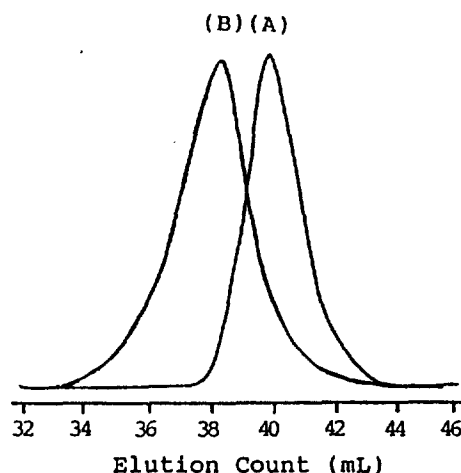


Figure 1. GPC chromatogram of PBMA and PBMA-*b*-PTBMA (sample 6 in Table 1); (A) PBMA, \bar{M}_n (obsd.)=5,580 \bar{M}_w/\bar{M}_n = 1.15, (B) PBMA-*b*-PTBMA, \bar{M}_n (obsd.)=11,860 (\bar{M}_w/\bar{M}_n = 1.34).

added with the catalyst, and heated to 100°C for 12 hrs. The resulting polymer solution was poured into a mixture of water/methanol (90/10 by volume) to precipitate the hydrolyzed polymer. The polymer was filtered, and freeze dried in benzene.¹⁰

Titration of PAMA-*b*-PMAA. Titration of methanol solution of the given weight of polymer with methanolic potassium hydroxide (0.1 N) using phenolphthalein as an indicator was carried out to determine the degree of hydrolysis.

Results and Discussion

Polymerization. The precursor polymer was prepared by a sequential GTP of MMA (or BMA) and TBMA. After initial feed of MMA (or BMA) had been polymerized completely, a second feed of TBMA was added. It was found that the GTP of TBMA lead to incomplete polymerization due to the deactivation of catalyst as reported by Müller.¹¹ To surmount this phenomena a second catalyst was added. After the feed of TBMA, additional TASHF₂ was lead to complete polymerization of TBMA. The results of the polymerization are summarized in Table 1.

As shown in Table 1, the polydispersities of block copolymers are in the range of 1.30-1.42 and increased as the mole ratio of PTBMA increased. This may be due to the deactivation of catalyst by *t*-butyl moieties.¹¹ The compositions in all block copolymers were determined from the integration value ratio of *t*-butyl proton to *n*-butyl or methyl proton in ¹H-NMR spectra and were found to be about the same as those calculated from the monomer feed ratios in the polymerization. The observed \bar{M}_n s of the polymers were reasonably in agreement with those calculated from the mole ratios of monomer to initiator. The polymerization yields are quantitative.

The GPC curves of the representative samples are shown in Figure 1.

As can be seen, the GPC curves show that the peak of starting poly(butyl methacrylate) (PBMA) is shifted toward the higher molecular weight side after addition of TBMA and that the resulting block copolymer still possess a single

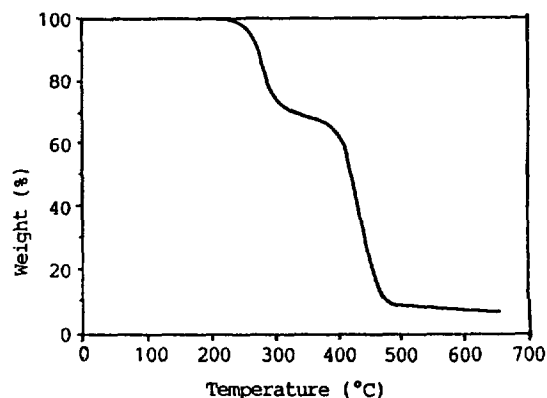


Figure 2. TGA thermogram of sample 7 in Table 1.

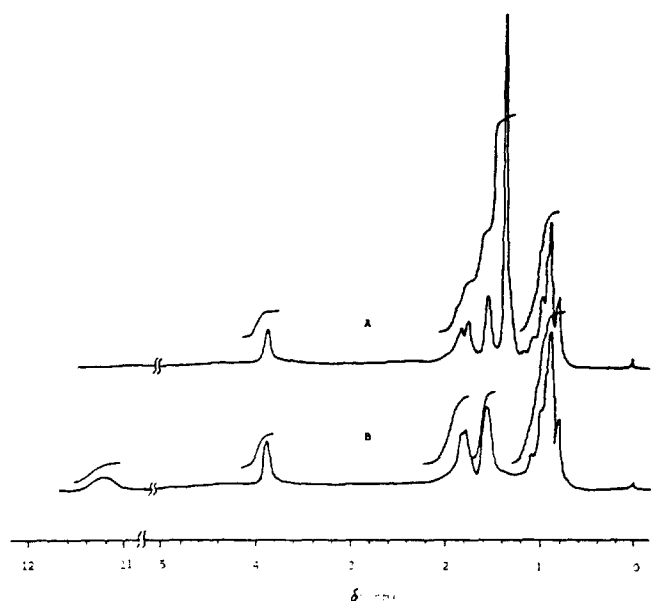


Figure 3. $^1\text{H-NMR}$ spectra of PBMA-*b*-PTBMA (A; Sample 6 in Table 1, chloroform- d_3) and PBMA-*b*-PMAA (B; hydrolyzed sample 6 in Table 1, dimethyl sulfoxide- d_6).

peak without shoulder. These results indicate that the block copolymerization is efficiently performed and the starting PBMA has a livingness.

The TGA thermogram of a precursor block copolymer (sample 7 in Table 1) is shown in Figure 2.

Thermal loss of isobutylene and subsequent anhydride formation¹² is responsible for the first weight loss at the range of about 205-310°C. The observed amount of weight loss of sample 7 in Table 1, 34.25% is well in agreement with calculated one from the TBMA content in the block copolymer, 33-54%.

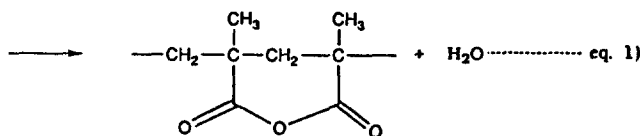
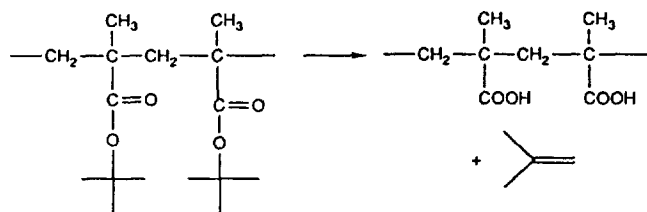


Table 2. Acid-base Titration of Hydrolyzed PBMA-*b*-PTBMA by KOH in Toluene/methanol Mixture (50/50, by volume)

Exp. No.	Content of PTBMA (mol%)	Weight of hydrolyzed polymer(mg)	COOH(mmol)		Yield of hydrolysis (%)
			Titrated	Theoretical	
1	20.0	500	0.75	0.76	98.7
2	50.0	500	2.17	2.19	99.1
3	66.7	500	3.18	3.19	99.7
4	100.0	500	5.79	5.81	99.7
5	50.0	250	1.08	1.10	98.2

Hydrolysis of *t*-Butyl Ester to Carboxylic Acid.

The PTBMA segment was easily hydrolyzed to PMAA segment by a catalytic amount of *p*-TsOH in dioxane⁵ at 100°C for 12 hrs. In $^1\text{H-NMR}$ spectrum of hydrolyzed PBMA-*b*-PTBMA, the disappearance of the peak at 1.38 ppm originated from *t*-butyl groups indicates that *t*-butyl ester is hydrolyzed completely. Furthermore, the integration value ratios of the peaks except for the peak at 1.38 ppm is in well agreement before and after hydrolysis.

In FT-IR spectra of the hydrolyzed sample, a broad absorption band between 3400 and 2400 cm^{-1} and a new one in carbonyl region, 1705 cm^{-1} which are assigned to O-H and carbonyl stretching band of carboxylic acid, respectively, are exhibited. They are resulted from the hydrolysis of *t*-butyl ester in PBMA-*b*-PTBMA. These factors suggest that the hydrolysis was carried out selectively and completely.

The titration of the hydrolyzed polymers with different composition are summarized in Table 2. The quantitative hydrolysis of the *t*-butyl ester was conformed by the results of titrations, which were consistent with the calculated values of the carboxyl groups within experimental error (Table 2).

When the hydrolyzed sample was stirred for 24 hrs in diethyl ether which was a solvent of homo-PBMA, no soluble fraction was obtained. Consequently the polymer is considered to consist of only block copolymer of MAA and BMA.

In summary, amphiphilic diblock copolymers, PMAA-*b*-PMMA and PMAA-*b*-PBMA were easily prepared by GTP and selective hydrolysis.

The studied on the potential of these polymers and their neutralized ones as detergent, compatibilizer, surface modifier etc. are in progress.

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Electron-Impact Ionization Mass Spectroscopic Studies of Acetylene and Mixed Acetylene-Ammonia Clusters as a Structure Probe

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Ion-molecule reactions of acetylene and mixed acetylene-ammonia cluster ions are studied using an electron impact time-of-flight mass spectrometer. The present results clearly demonstrate that $(C_2H_2)_n^+$ cluster ion distribution represents a distinct magic number of $n=3$. The mass spectroscopic evidence for the enhanced structural stabilities of $[C_6H_4 \cdot (NH_3)_m]^+$ ($m=0-8$) ions is also found along with the detection of mixed cluster $[(C_2H_2)_n \cdot (NH_3)_m]^+$ ions, which gives insight into the feasible structure of solvated ions. This is rationalized on the basis of the structural stability for acetylene clusters and the dissociation dynamics of the complex ion under the presence of solvent molecules.

Introduction

In recent years, the so-called intracluster ion-molecule reactions¹⁻⁹ have become a subject of great interest in the cluster ion chemistry due to its unique position between bimolecular gas-phase reaction dynamics and ionic solution chemistry. The study of a specific chemical reaction within a cluster ion is especially interesting since it is possible to directly observe how chemical reactivity changes as a function of stepwise solvation by simple monitoring the changes in reaction channel versus the cluster size.¹⁰ A considerable amount of experimental and theoretical attention¹¹ has been also given to cluster systems in which small number of solvent molecules are bound to a solute molecule. The investigation of solvent effects provides knowledge of the mechanisms of "internal ion-molecule reaction" in clusters, giving direct information on the influence of solvation and insight into the structure of solvated ions.

It has been known that for small hydrogen-bonded cluster ions the stabilities of mixed cluster ions, based on the thermochemical data¹² and relative cluster ion intensity studies,¹³

can be often well correlated to the complete solvation shell structures with chain-like hydrogen-bonding such as for $(NH_3)_4 \cdot NH_4^+$, $(H_2O)_4 \cdot ((CH_3)_3N)_6H^+$, and $(CH_3OCH_3)_3 \cdot H_3O^+$. This intriguing result makes it possible to investigate how the nature of a solvating component may affect the subsequent dissociation reaction and the stability of mixed cluster ion.

The acetylene clusters have been widely studied by the molecular beam mass spectroscopy incorporating VUV photoionization^{14,15} and electron-impact ionization.¹⁶ Recently, Shinohara *et al.*¹⁷ have found the unprotonated acetylene cluster ions, $(C_2H_2)_n^+$ ($n=2-4$), using the near-threshold photoionization method, showing that these ions are produced from the mixed cluster ions followed by loss of the argon or helium used as a carrier gas through evaporation process. For unprotonated acetylene cluster ions, however, very little information is known about the pronounced magic number and whether or not "stable structures" exist in the binary system containing polar solvent molecules.

In this paper, we report an electron impact ionization of acetylene clusters and acetylene/ammonia heteroclusters. In