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Synthesis and properties of well-defined poly (dimethylsiloxane)-b-poly(2-hydroxyethyl methacrylate) copolymers

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Abstract

Block copolymers containing dimethyl siloxane and 2-hydroxyethyl methacrylate sequences were synthesized by group transfer polymerization (GTP) of 2-trimethylsilyloxyethyl methacrylate (TMS-HEMA) using silyl ketene acetal terminated poly(dimethylsiloxane) (PDMS) as macroinitiator, followed by hydrolysis of TMS-HEMA to HEMA. The block copolymers were obtained with controlled molecular weight and narrow molecular weight distribution. Trimethylsilyl groups in the P(TMS-HEMA) block could be selectively hydrolyzed without cleaving Si-O bond in PDMS block. The block copolymers formed micelles in methanol, the effective diameters (R_h) of which were in the range of 78 − 110 nm with narrow distribution by dynamic light scattering (DLS). The TEM image showed micelles with a spherical shape.

Introduction

Block copolymers composed of hydrophobic and hydrophilic segments show an interesting morphology, unique surface properties, and an unusual solution behavior [1-3]. They self-assemble into well-defined structures when placed in a medium that is a good solvent for one of the segments (the hydrophilic segment) and a poor solvent for the other segment (the hydrophobic segment) [4-11]. These surfactants are typified by micelle or more complex aggregates in which the hydrophobic segments form a core surrounded by a shell of hydrophilic segments that extend into the continuous phase. The core regions of such micelles are technologically useful, as they are capable of emulsifying otherwise insoluble materials into a microphase-separated environment within a preferred continuous solvent phase. This ability may be taken into account in various separation and drug delivery technology [7-11]. Thus, the synthesis of hydrophilic-hydrophobic block copolymers with well-defined chain structure is of importance for understanding the morphology in solution [6].

While much attention has been attracted to the PHEMA based block copolymers due to their biomedical applications [12-14], few synthetic methods for PDMS-*b*-PHEMA with controlled molecular weight have been published in the literature [15]. Recently, we reported the synthesis of PDMS-poly[alkyl(meth)acrylate] block copolymers by GTP using silyl ketene acetal terminated PDMS as macroinitiator [16]. The esters of alkyl(meth)acrylate were hydrolyzed into corresponding acids to give a novel amphiphilic polymer of PDMS-*b*-PMA and PDMS-*b*-PAA, which were utilized to stabilize water-in-CO_2 emulsions as an ionic surfactant [17]. It is known to be difficult to prepare the block copolymers of dimethyl siloxane and α,β-unsaturated esters directly by sequential addition of the monomers due to the limited copolymerizabilities of both monomers in the anionic polymerization [1]. Therefore, this polymerization technique could be useful in the synthesis of well-defined block copolymers of those types.
In this article, we describe the synthesis of PDMS-*b*-PHEMA with controlled molecular weight and narrow molecular weight distribution. In addition, the micellar characteristics of the amphiphilic polymers are investigated by dynamic light scattering and TEM.

Experimental Section

Materials

Tetrahydrofuran (THF) was distilled from sodium naphthalide under reduced pressure prior to use. 2-(Trimethylsilyloxy)ethyl methacrylate (TMS-HEMA) (Aldrich) were first distilled from CaH_2, followed by distillation from triethyl aluminium.
The GTP catalyst, tetrabutyl ammonium bibenzoate (TBABB) was synthesized according to the procedure in the literature [18]. Poly (dimethyl siloxane) monomethacrylate (M_n = 10K from Aldrich) was degassed under high vacuum for 24 hours before using. Ethyl dimethyl silane (United) and tris (triphenyl phosphine) rhodium(I)chloride (Wilkinson catalyst) (Aldrich) were used as received.
The GTP macroinitiator, silyl ketene acetal functional PDMS was prepared by reacting poly (dimethyl siloxane) monomethacrylate with a slightly molar excess of ethyl dimethyl silane in the presence of Wilkinson catalyst as previously described [16].

Polymerization

The group transfer polymerization was carried out under argon atmosphere in a previously flamed glass reactor. A typical example is as follows: 7 g (7.0×10^{-4} mol) of dried 10K macroinitiator was introduced into the reactor. Then 20 mL of THF and 7 mg TBABB (2 mol % based on silyl ketene acetal functionality) were transferred into the reactor by means of a cannula. After 5 minutes of stirring, 5 g (2.5×10^{-2} mol) of TMS-HEMA was added slowly via syringe and the polymerization proceeded for 2 hrs under argon. The polymerization was quenched with degassed methanol (1 mL). After an additional half hour of stirring, the THF and methanol were removed by evaporation. The polymer collected was dried at 10^{-3} Torr for 24 hrs. For deprotecting

trimethylsilyl group, to the solution of polymer in 20 mL of THF were added a few drops of 1.5 N HCl. The solution was stirred for two hours at room temperature, and precipitated into excess water. The polymer was collected and dried under vacuum. The unreacted PDMS macroinitiator was extracted with hexane to give 6.4 g of PDMS-*b*-PHEMA. The Si-CH_3 peak (0.07 ppm) of TMS-HEMA disappeared in ^{1}H NMR spectrum after deprotection. The molecular weight of PHEMA block was determined to be 9900 by ^{1}H NMR analysis. To obtain copolymer with different block ratio, the amount of TMS-HEMA was varied.

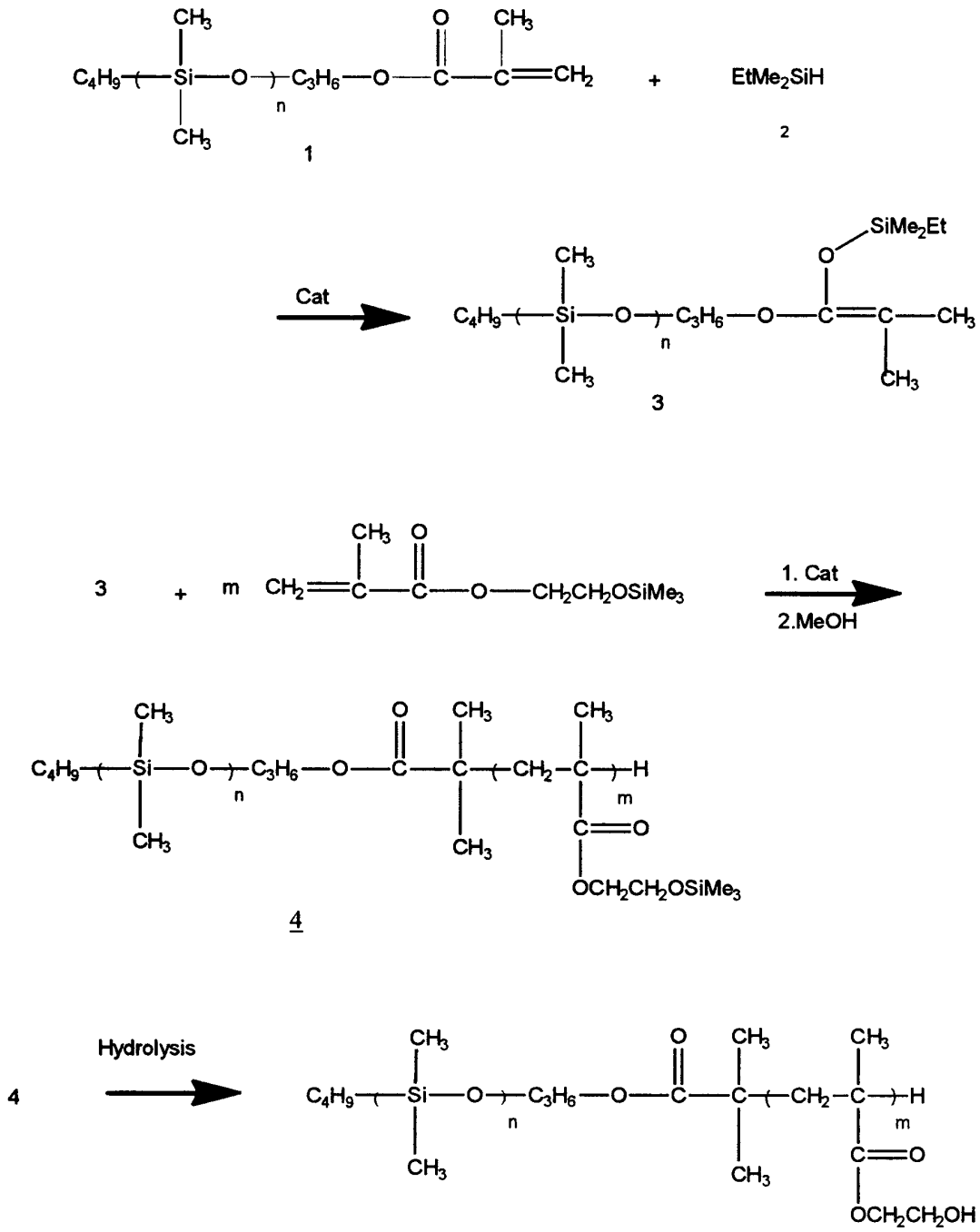
Characterization

Size exclusion chromatography (SEC) was carried out with a Waters Alliance GPC 2000 apparatus equipped with two Styragel columns (HR5E and HR4E) with THF as the eluent. Five standard polystyrene samples with molecular weights between 1060 and 182000 were used to construct the calibration curve. ^{1}H NMR spectra were obtained using a JNM-ECP 400 (JEOL). ^{29}Si NMR spectra were recorded on a Bruker AMX-500 in 0.04 M chromium (III) acetyl acetonate solution in $CDCl_3$. IR spectra were recorded on a Nicolet Avatar 360 FT-IR. The TEM image was obtained using a Hitachi H-7500 instrument operated at 80 kV. A drop of polymer solution (1 g/L) was applied onto a copper grid coated with carbon, followed by air-drying. The sample was stained with OsO_4 vapor for 48 hrs. Dynamic laser light scattering (DLS) measurements on the PDMS-b-PHEMA block copolymer micelles were carried out using a Brookhaven laser light scattering instrument (Brookhaven instruments Corporation), with diode laser (24 mV) at a wavelength of 659 nm at 20°C. The sample solution (1 g/L) was purified by passing through a 0.45 μm filter. The scattered light of a vertically polarized laser was measured at an angle of 90° and was collected on a Brookhaven BI 9000 AT autocorrelator. The hydrodynamic diameter (R_h) was calculated from the measured diffusion constant using the Stokes equation. The polydispersity of the micelle is given by μ_2/Γ^2, where μ_2 is the second cumulant of the decay function and Γ is the average characteristic line width [19].

Results and discussion

The synthesis of amphiphilic PDMS-b-PHEMA copolymers is illustrated in Scheme 1. PDMS macromer (1) was confirmed to have almost quantitative functionality by comparing the integration of silicone adjacent to the methacryloxy functional fragment (7.3 ppm) with the silicone adjacent to the terminal butyl fragment (7.5 ppm) in ^{29}Si NMR [20]. The methacryloxy functional end group of PDMS was transformed into a silyl ketene acetal (3) by hydrosilation with ethyl dimethyl silane. Confirmation of the quantitative hydrosilation of PDMS chain end was followed by ^{1}H NMR and FT-IR. As the hydrosilation proceeds, a shift in the carbonyl band (1725 cm^{-1}) is observed upon o-silylation of the carbonyl oxygen (1705 cm^{-1}). A weak absorption band at 1740 cm^{-1} was also appeared, which is attributed to the hydrolysis of the silyl ketene acetal moiety. This species is estimated to be less than 5 mole % by ^{1}H NMR, and may have resulted from moisture or protonic impurities in the PDMS. The GTP proceeded successfully by introducing TMS-HEMA to the macroinitiator (3) to give well-defined block copolymers with controlled molecular weight and narrow

Scheme 1



molecular weight distribution. The conversions of TMS-HEMA monomer to block copolymer were calculated to be almost quantitative by either weighing the recovered products and ^{1}H NMR analysis of the products in $CDCl_3$. Therefore, block copolymers of PDMS and P(TMS-HEMA) of various lengths could be prepared simply by varying the ratio of monomer to macroinitiator charged in the polymerization. The TMS protecting groups attached to the resulting polymer were selectively removed by acid treatment to afford PDMS-*b*-PHEMA. The hydrolysis of the ester of PDMS-*b*-

P(TMS-HEMA) was carried out under mild conditions [21] in order to avoid undesirable cleavage of siloxane bond in PDMS block which is susceptible to hydrolysis in both acidic and alkaline condition [22,23]. The complete removal of the trimethylsilyl groups was confirmed by the ^{1}H NMR spectrum of the resulting polymer in $CD_3OD/CDCl_3$ (1:2 (v/v)). The peak of trimethylsilyl protons in the P(TMS-HEMA) block at 0.07 ppm disappeared after hydrolysis. The peak was not detectable in the ^{1}H NMR spectra of the polymer either in CD_3OD or in $CDCl_3$. Thus the resulting polymer should have been in the form of PDMS-*b*-PHEMA. The wt % of PDMS incorporated was less than theoretically predicted, and the macroinitiator efficiency was calculated in the range of 0.42 ~ 0.47. A similar efficiency was found before for other (meth)acrylate in our report [15]. The unincorporated homo PDMS was simply removed by successive hexane extraction from the PDMS-*b*-PHEMA copolymer after hydrolysis. All the copolymers have identical 10 K-PDMS blocks whose M_n was measured as 17900 by GPC using PS standard but different chain lengths of PHEMA blocks.

Table 1. Molecular Weights and Compositions of Block Copolymers

Block copolymers[a]	wt % of PDMS		GPC[c]		macroinitiator efficiency[d]
	charged	incorp[b]	$M_n(\times10^{-3})$	M_w/M_n	
$PDMS_{10K}$	-		17.9	1.17	-
$PDMS_{10K}$-$PHEMA_{4.7K}$	83	68	20.5	1.23	0.42
$PDMS_{10K}$-$PHEMA_{6.2K}$	77	62	23.9	1.25	0.47
$PDMS_{10K}$-$PHEMA_{9.9K}$	69	50	28.1	1.26	0.46

[a] the molecular weight of PHEMA block is determined by ^{1}H NMR; [b] weight fraction of PDMS in the block copolymer by ^{1}H NMR analysis; [c] polystyrene standard; [d] PDMS in block copolymer / PDMS in feed.

Figure 1 shows the GPC traces of the PDMS macroinitiator and the resulting PDMS-b-PHEMA block copolymer. The elution volume is shifted towards higher molecular weight and molecular weight distribution remains narrow. When acid-catalyzed redistribution reaction has occurred in the PDMS, the molecular weight decreases with broad molecular weight distribution [16]. In order to confirm that the polymer backbone is not degraded in this condition, 10K-PDMS was treated with same

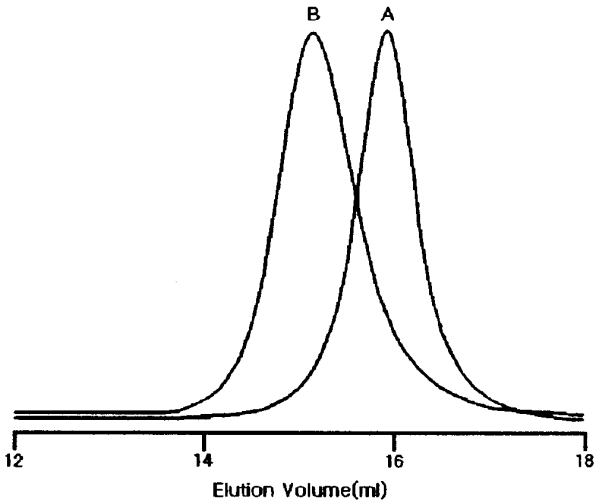


Figure 1. GPC trace of 10K-PDMS macroinitiator (A) and $PDMS_{10K}$-*b*-$PHEMA_{9.9K}$ (B).

reaction condition. No change in the molecular weight and molecular weight distribution was observed as determined from GPC. Thus, the trimethylsilyl protective group could be readily and selectively cleaved without interfering with the Si-O linkage in the PDMS by above treatment.

The solubility behavior of typical PDMS-*b*-PHEMA copolymers was investigated with several solvents. The block copolymer was soluble in polar solvents such as THF and DMSO, and insoluble in aromatic and aliphatic hydrocarbons. When the copolymer was dissolved in methanol, the mixture was almost clear with an iridescent bluish tinge indicative of small colloidal particles. Since methanol is a poor solvent for PDMS but a good solvent for PHEMA, the block copolymer is expected to form micelles consisting a core composed of PDMS and a shell of PHEMA swollen by methanol. The effective diameters of micelles in 0.1 wt % copolymer solutions when 0.45 μm filter is used are in the range of 77 – 104 nm (Table 2). The polydispersity factors (μ_2/Γ^2) of the micelles, estimated by the cumulant method, were fairly low (0.16 – 0.24), suggesting a narrow size distribution. For the 9.9K and 6.2K-PHEMA block copolymer, the similar sized micelles were formed. However larger micelles were observed in the case of shorter PHEMA (4.7K) block copolymer. In previous reports, micelles with a hydrophilic outer shell are frequently found to form large aggregates in an aqueous phase [3,9,10]. Eisenberg et al. observed large aggregates from block copolymer of polycaprolactone and poly(ethylene oxide), and explained that the aggregates of individual micelles might form due to relatively short PEO block (~2K) which did not outweigh the hydrophobic-hydrophobic interactions or van der Waals interactions between the exposed cores of the individual micelles [10]. This explanation might also be applied to the case of $PDMS_{10K}$-*b*-$PHEMA_{4.7K}$ which generated larger micelles resulted from more aggregation between the exposed PDMS

Table 2. Characteristics of PDMS-*b*-PHEMA micelles

Exp. No.	Block copolymer	Solvent[a]	Diameter[b] (nm)	Polydispersity; μ_2/Γ^2
1	$PDMS_{10K}$-*b*-$PHEMA_{9.9K}$	methanol	77.6	0.23
2	$PDMS_{10K}$-*b*-$PHEMA_{6.2K}$	methanol	69.0	0.23
3	$PDMS_{10K}$-*b*-$PHEMA_{4.7K}$	methanol	104.2	0.17
4	$PDMS_{10K}$-*b*-$PHEMA_{6.2K}$	methanol /toluene[c]	0	-
5	$PDMS_{10K}$-*b*-$PHEMA_{9.9K}$	toluene[d]	113.6	0.17
6	$PDMS_{10K}$-*b*-$PHEMA_{6.2K}$	toluene[d]	101.6	0.19
7	$PDMS_{10K}$-*b*-$PHEMA_{4.7K}$	toluene[d]	119.0	0.20

[a] 0.1 wt % polymer solution; [b] effective diameter at 20°C; [c] methanol/toluene = 0.1 ~ 0.5 by weight; [d] a few drops of methanol are added, more drops are neccessary for higher PHEMA block copolymer.

cores. Toluene is a good solvent for PDMS and a poor solvent for PHEMA, in contrast with methanol. The copolymers were not completely soluble in toluene producing a turbid suspension. However, a few drops of methanol made the solutions clear with bluish tinge, and the reversed micelles were observed by DLS (Exp. No. 5, 6, 7 in Table 2). The solutions became clearer with increasing fraction of methanol in the mixed solvent up to ca. 0.5. No micelle was detected in the range 0.1 ~ 0.5 of methanol weight fraction in the case of $PDMS_{10K}$-*b*-$PHEMA_{6.2K}$, in which both

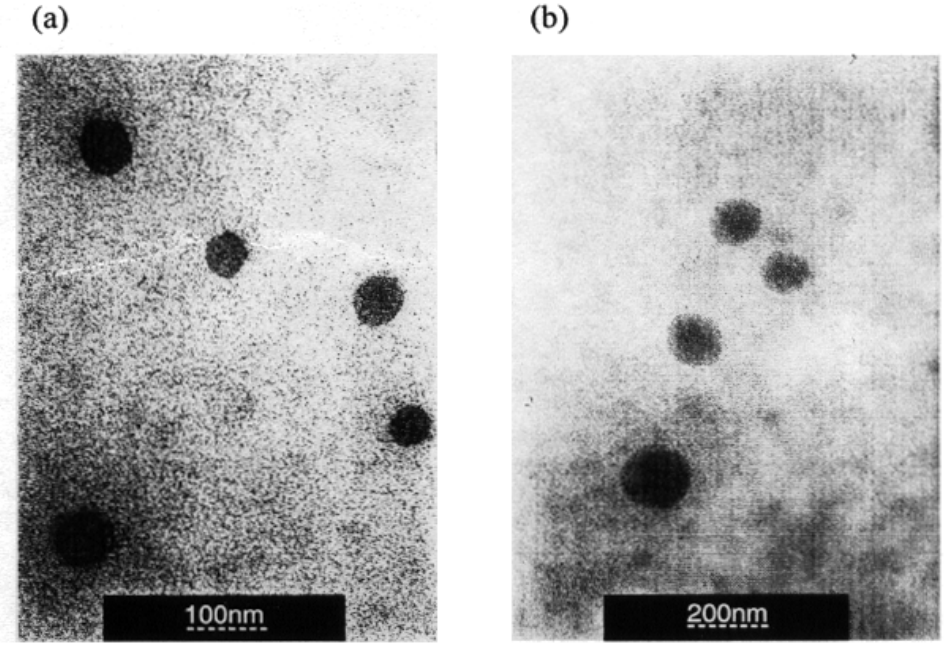


Figure 2. TEM images of spherical micelles of $PDMS_{10K}$-*b*-$PHEMA_{6.2K}$ (a) and $PDMS_{10K}$-*b*-$PHEMA_{4.7K}$ (b) in methanol.

PHEMA and PDMS blocks might be soluble. A further increase of methanol reduced the solubility of the non-polar chain (PDMS) and the micelles formed again. Similar behavior has been investigated for the poly (1,1-diethylsilabutane)-*b*-PHEMA block copolymer in methanol and methanol/toluene mixed solvents using Small-angle X-ray scattering (SAXS) technique. The copolymer formed spherical micelles in methanol, and in the mixed solvent was found to have different morphology depending on the mixing ratio of the solvent; i.e., micelle-unimer-reversed micelle transition with increasing toluene content [24].

The micelles of $PDMS_{10K}$-*b*-$PHEMA_{6.2K}$ and $PDMS_{10K}$-*b*-$PHEMA_{4.7K}$ observed by TEM were generally spherical as shown in Figure 2. The TEM diameters of the copolymers are similar to the effective diameters (R_h) from DLS.

Conclusions

Well defined PDMS-*b*-p(TMS-HEMA) copolymers were successfully synthesized by GTP using silyl ketene acetal terminated PDMS as initiator. The TMS protecting groups were almost quantitatively hydrolyzed to give a novel amphiphilic polymer of PDMS-*b*-PHEMA. DLS measurements were performed for these copolymers in methanol and toluene. They might form micelles in methanol and reverse micelles in toluene, which corresponds to the previous report [24]. No micelle structure was detected in the solvent mixture of 0.1 ~ 0.5 weight percent of methanol with toluene.

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