Macromolecules **2000,** *33,* 451−456

Synthesis and Solution Properties of Dimethylsiloxane−2-(Dimethylamino)ethyl Methacrylate Block Copolymers

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Received October 1, 1999; Revised Manuscript Received November 15, 1999

ABSTRACT: A series of novel well-defined dimethylsiloxane−2-(dimethylamino)ethyl methacrylate diblock and triblock copolymers were synthesized in various solvents at or above ambient temperature. This was achieved by the oxyanion-initiated polymerization of 2-(dimethylamino)ethyl methacrylate (DMA) using either monofunctional or bifunctional low molecular weight poly(dimethylsiloxane) (PDMS) as macroinitiators. Provided that the terminal hydroxyl groups of the PDMS macroinitiators are carefully titrated to the corresponding potassium alcoholates, reasonably good control over the DMA chain length was achieved. ^{1}H NMR characterization of these DMS−DMA diblock copolymers proved unexpectedly problematic since micellization generally occurred even in solvents such as $CDCl_3$ or d_8-toluene, which are good solvents for both DMS and DMA homopolymers. Electron microscopy and dynamic light scattering studies confirmed the formation of spherical, polydisperse micelles of 200 nm. Presumably micellization is driven by a demixing term: the PDMS block prefers to be less solvated in order to avoid interacting with the DMA residues. Reliable block compositions were eventually obtained by NMR analysis of dilute solutions of the diblock copolymers in 3:1 d_8-IPA−D_2O mixtures. These DMS−DMA diblock copolymers were highly surface active, particularly at pH 9 where the degree of protonation of the DMA block was low. Dynamic light scattering studies indicated micellization in aqueous solution, as expected.

Introduction

Poly(dimethylsiloxane) [PDMS] chains are very flexible, and the homopolymer exists as a liquid at room temperature. PDMS-based surfactants are widely used in industry since they confer low cohesive energy, which in turn leads to excellent wetting properties.[1] In particular, dimethylsiloxane−alkylene oxide copolymers have been used in the manufacture of polyurethane foams for many decades.[2] Other applications for this class of materials include use as antifoam agents, additives in paint and cosmetic formulations, lubricants, emulsifying agents, etc.[3−6] Generally, such copolymers are prepared by condensation chemistry, i.e., by the coupling of end-functionalized low molecular weight poly(ethylene oxide) and PDMS chains as described by Kiraly and Vincent.[7]

PDMS-based block copolymers have also been prepared using so-called "living" polymerization techniques and subsequently used as steric stabilizers for dispersion polymerizations in nonaqueous media. For example, Dawkins and Taylor have utilized poly(styrene-*block*-dimethylsiloxane) to prepare poly(methyl methacrylate) latexes in *n*-alkanes.[8] PDMS is one of the few polymers that is soluble in supercritical carbon dioxide, and it can act as the solvated buoy block in this medium. Thus, Canelas and DeSimone[9] have used poly(styrene-*block*-dimethylsiloxane) as a stabilizer for polystyrene latex syntheses, and Webber and co-workers[10] have used poly(methacrylic acid-*block*-dimethylsiloxane) as a stabilizer for the preparation of poly(methyl methacrylate) particles.

Riffle and co-workers[11] synthesized a series of 2-ethyl-2-oxazoline−dimethylsiloxane diblock copolymers via the ring-opening cationic polymerization of 2-ethyl-2-oxazoline using a PDMS macroinitiator. The same group subsequently studied the micellization of selected copolymers in aqueous and aqueous alcohol mixtures by dynamic light scattering.[12] It was found that these copolymers dissolved molecularly in 2-propanol (IPA) but formed micelles on addition of water, which is a nonsolvent for the hydrophobic PDMS block. These hydrophilic−hydrophobic copolymers are rather similar to the diblock copolymers prepared in the present study, and later we discuss our observations in the context of this earlier work.

In 1997, Nagasaki and co-workers reported[13] the synthesis of 2-(diethylamino)ethyl methacrylate-based macromonomers using the potassium alcoholate salt of 4-vinylbenzyl alcohol as a functional initiator. Such oxyanionic initiators do not normally polymerize methacrylate monomers: the Japanese group attributed their unexpected success to complexation of the potassium counterion with the nitrogen heteroatom of the 2-(diethylamino)ethyl methacrylate. However, this explanation remains speculative; the precise mechanism for this polymerization has not yet been established. Nevertheless, polymerization of the tertiary amine methacrylate monomer proceeded at or above ambient temperature to produce well-defined macromonomers ($M_w/M_n < 1.30$) containing a single polymerizable styrenic group per chain. Recently, we extended[14] these macromonomer syntheses to include other tertiary amine methacrylates, via 2-(dimethylamino)ethyl methacrylate [DMA], 2-(*N*-morpholino)ethyl methacrylate [MEMA], and 2-(diisopropylamino)ethyl methacrylate [DPA]. It was shown that these macromonomers can act as reactive polymeric stabilizers for polystyrene latex syntheses under both aqueous emulsion and alcoholic dispersion polymeriza-

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10.1021/ma991665s CCC: $19.00

Table 1. Summary of Synthetic Details and Molecular Weight Data for the Oxyanionic Polymerization of DMA Using the Monocarbinol and Dicarbinol PDMS Macroinitiators

		polymerization		theoretical		NMR	GPC	
copolymer ID[a]	solvent	time (h)	temp (°C)	Dp of DMA	M_n (g mol^{-1})	M_n (g mol^{-1})	M_n (g mol^{-1})	M_w/M_n
D1[b]	*i*Pr$_2$O	12.0	30	30	5800	6100	6600	1.39
D2	THF	3.0	50	45	8200	9400	12200	1.41
D3	toluene	20.0	50	50	9000		8700	1.49
D4[b]	*i*Pr$_2$O	12.0	30	59	10400	11300	8300	1.33
D5	toluene	20.0	25	75	12900	13800	17000	1.34
D6	THF	20.0	50	98	16500	14300	16700	1.37
T1[b]	*i*Pr$_2$O	12.0	50	33	6300	8200	7500	1.38
T2[b]	*i*Pr$_2$O	12.0	50	59	10400	10300	9200	1.40

[a] D1−D6 are diblock copolymers prepared using the monocarbinol PDMS. T1 and T2 are triblock copolymers prepared using the dicarbinol PDMS. [b] Triphenylmethane was used as indicator for quantitative alcoholate formation.

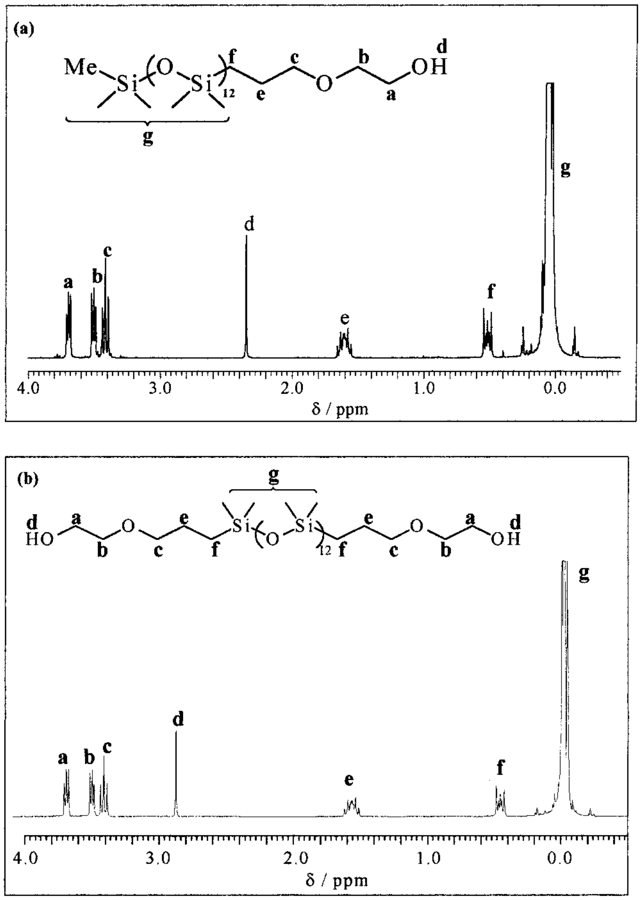

Figure 1. Assigned ^{1}H NMR spectrum for the (a) monocarbinol-functionalized PDMS and (b) the dicarbinol-functionalized PDMS used in this work.

tion conditions. In a separate study, a poly(ethylene oxide)-based macroinitiator was used to polymerize various tertiary amine methacrylates and hence obtain novel poly(ethylene oxide-*block*-tertiary amine methacrylates).[15] These hydrophilic diblock copolymers undergo reversible self-assembly in aqueous solution to form micelles, with the tertiary amine block forming the micelle core.

In the present work the potassium alcoholate salts of low molecular weight monocarbinol- and dicarbinol-functionalized PDMS were prepared in situ, and these macroinitiators were utilized in turn to polymerize DMA. Thus, a range of novel DMS−DMA diblocks were produced, in which the DMS block length was fixed and the DMA block length was varied (see Table 1). Comonomer composition studies using ^{1}H NMR spectroscopy brought to light a surprising anomaly: the diblock copolymers generally formed aggregates with the PDMS block forming the desolvated micelle core *even in solvents that are good solvents for the PDMS block*. Finally, the aqueous solution properties of these block copolymers were assessed using surface tensiometry and dynamic light scattering.

Experimental Section

Materials. Unless otherwise stated, materials were obtained from Aldrich and used without further purification. Monocarbinol-terminated and dicarbinol-terminated poly(dimethylsiloxane) (PDMS), each with a nominal molecular weight of 1000, were purchased from Gelest Inc., Germany. ^{1}H NMR studies in CDCl$_3$ (see Figure 1) indicated a number-average molecular weight of 1100 for the monocarbinol PDMS (corresponding to a Dp of 13) and a number-average molecular weight of 1100 for the dicarbinol PDMS (corresponding to a Dp of 13). GPC analyses gave polydispersities of 1.16 and 1.25 for the monocarbinol- and dicarbinol-terminated PDMS, respectively.

2-(Dimethylamino)ethyl methacrylate (DMA) was passed through a basic alumina column. The monomer was stirred over CaH$_2$ for 12 h, and an inhibitor, 2,2-diphenyl-1-picrylhydrazyl hydrate, was added. It was stored at −9 °C and distilled prior to use. THF was dried first with sodium wire and then by refluxing for 3 days over potassium metal and was freshly distilled before each polymerization.

All polymerizations were conducted under anhydrous conditions under an inert atmosphere using glassware that had been previously baked at 200 °C for 24 h and flamed out after assembly. Liquid reagents were handled using standard Schlenk techniques.

Preparation of Potassium Methylsulfinyl Carbanion (DMSO$^-$K$^+$). KH suspension in mineral oil (typically 12.5 mmol) was placed in a preweighed Schlenk tube along with a magnetic stirrer bar and was washed three times with anhydrous *n*-pentane. THF was then added, and the solution was stirred for 5 min at 0 °C using an ice bath before addition of a 2-fold molar excess of DMSO based on KH. After warming to 20 °C the suspension was stirred until all the KH had reacted. This solution was then titrated under anhydrous conditions against 2-naphthol, using triphenylmethane as indicator. The latter was used due to the deep red color of the triphenylmethyl anion that immediately appears in the presence of excess methylsulfinyl carbanion.[16]

Preparation of Potassium PDMS Alcoholate. The monocarbinol or dicarbinol PDMS (1.00 g) was dissolved to give a 0.01 M solution in THF, toluene, or diisopropyl ether (*i*Pr$_2$O) before the required amount of DMSO$^-$K$^+$ was added via a double-tipped needle at 25−35 °C to form the PDMS macroinitiator. Triphenylmethane was used as an indicator in most experiments to ensure complete formation of the potassium alcoholate chain ends (see Figure 2).

Oxyanionic Polymerization. Freshly distilled DMA monomer was added to the PDMS macroinitiator solution at the desired polymerization temperature (25−50 °C). The reaction was stirred for 12 h before quenching with methanol (see Figure 3). Solvent was removed under vacuum, and the

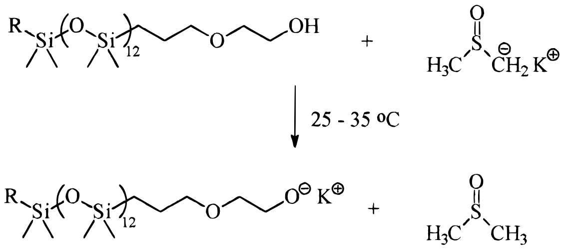

Figure 2. Formation of potassium alcoholate end groups on the monocarbinol-functionalized PDMS used in this work.

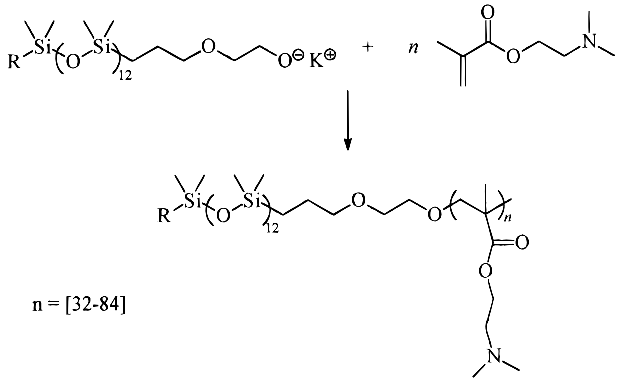

Figure 3. Reaction scheme for the oxyanionic polymerization of 2-(dimethylamino)ethyl methacrylate (DMA) using the monocarbinol PDMS macroinitiator.

copolymer was dissolved in water and extracted with *n*-hexane in order to remove any PDMS homopolymer contamination. The copolymer was then salted out of the aqueous phase using NaCl, and the water/*n*-hexane extraction was repeated. The copolymer was dissolved in dichloromethane and dried using $MgSO_4$, and the solvent was removed under vacuum to leave the pure copolymer (>95% yield). The six diblock copolymers prepared using monocarbinol PDMS are denoted D1 to D6, and the two triblock copolymers prepared using the dicarbinol PDMS are denoted T1 and T2 (see Table 1).

Characterization. Molecular weights and molecular weight distributions were obtained using a Viscotek gel permeation chromatography setup equipped with a Polymer Laboratories PL gel 3 μm mixed "E" column. The mobile phase was THF (1.0 mL min^{-1} flow rate) and a Knauer UV detector K-2501 ($\lambda = 254$ nm) was used in series with a Knauer refractive index detector K-2301. The calibration standards were four near-monodisperse PMMA homopolymers in the 400−29 400 g mol^{-1} range.

Block copolymer compositions were investigated using a Bruker AC-P 250 or 300 MHz spectrometer and either $CDCl_3$, d_8-toluene, d_6-benzene, a 1:1 CCl_4:d_6-benzene mixture, or various d_8-IPA:D_2O mixtures.

The hydrodynamic size of the block copolymers in aqueous solution was measured using a Malvern PCS 4700 spectrometer equipped with a 80 mV argon ion laser operating at 632.8 nm and a series 7032 Multi-8 correlator. The measurements were performed at a fixed angle of 90°, and the data were fitted using monomodal cumulants analysis. All measurements were carried out on 0.50 w/v % solutions. The polydispersity is a model-independent estimate of the width of the size distribution, which is equal to the normalized second moment from a cumulant analysis of the scattered light autocorrelation function. For relatively narrow size distributions the polydispersity may be equated to the variance of the distribution.

Transmission electron microscopy studies were carried out using a Hitachi 7100 instrument operating at 75 kV. Negative staining using uranyl acetate was employed in order to improve the contrast between the micelles and the background.

The surface tension measurements were carried out using a Kruss K10ST surface tensiometer equipped with a platinum ring either as a function of copolymer concentration or by varying the solution pH.

Results and Discussion

The assigned NMR spectra for the monocarbinol and dicarbinol PDMS precursors are shown in Figure 1. These materials were selected since there is some literature evidence that "backbiting" (i.e., degradation of the PDMS backbone via chain scission) can occur with conventional PDMS if the silanol end groups are converted into SiO^-K^+.[2] No evidence for this side reaction was found in the present study.

$DMSO^-K^+$ was selected for converting the PDMS carbinol groups to potassium alcoholate chain ends for several reasons. First, it is a strong base.[17] Second, it can be easily titrated using triphenylmethane as indicator[16] to enable its exact concentration to be determined. Third, $DMSO^-K^+$ solutions can be stored for long periods without decomposition.[18] Finally, DMSO, its conjugate acid, is an aprotic, polar solvent, so it is ideal for nucleophilic reactions.

It was suspected that the nucleophilic nature of the DMSO anion might cause unwanted initiation in the anionic polymerization of DMA. To explore this possibility, double the stoichiometric amount of $DMSO^-K^+$ was deliberately added in one particular synthesis (not shown in Table 1). Subsequent GPC analysis indicated a bimodal distribution due to the presence of DMSO-initiated DMA homopolymer. Thus, it is very important to achieve precise stoichiometry during the in situ preparation of the PDMS macroinitiator. Too little $DMSO^-K^+$ may lead to PDMS homopolymer contamination, whereas too much leads to the formation of DMA homopolymer. Control experiments with diblock copolymers deliberately contaminated with PDMS homopolymer confirmed that, if this impurity is present, it is readily removed (>97%) by extraction of an aqueous solution of the crude diblock copolymer with *n*-hexane. However, diblock copolymers purified in this manner were generally obtained in high overall yield (>90%), indicating minimal homopolymer formation in most cases.

Potassium alcoholate formation was complete within 3 h in THF at 30 °C, as judged by titration against $DMSO^-K^+$ using triphenylmethane as indicator. Shorter times and lower reaction temperatures led to incomplete alcoholate formation. It was noted that the reaction solution became turbid in the early stages of DMA polymerization, indicating reduced solubility of the PDMS macroinitiator in THF. Since toluene and iPr$_2$O are much less polar than THF, these solvents required longer reaction times and/or higher reaction temperatures for quantitative alcoholate formation. However, the solubility of the PDMS macroinitiator is much improved in these solvents. Unfortunately, accurate detection of the titration end point in toluene is rendered difficult due to the development of a competing yellow coloration in this medium. This problem is not encountered with iPr$_2$O, which is therefore recommended as the preferred solvent in these particular PDMS-based block copolymer syntheses. However, THF is perfectly acceptable for the synthesis of all-methacrylate block copolymers by oxyanion-initiated polymerization.[19]

Inspecting Table 1, it is clear that reasonably good control over the DMA block length is obtained, even at relatively short block lengths. (The selection of the most suitable solvent medium for the NMR analysis is

Table 2. Apparent Copolymer Compositions for DMS−DMA Diblocks As Determined by ^{1}H NMR Spectroscopy in Various Solvents

copolymer ID	NMR solvent	theor PDMS (mol %)	PDMS by NMR (mol %)
D2	$CDCl_3$	22.4	3.7
	d_6-benzene		6.3
	CCl_4:d_6-benzene (1:1)		6.8
	d_8-IPA:D_2O (3:1)		19.7
D5	d_8-toluene	14.8	5.7
	d_6-benzene		6.6
	d_8-IPA:D_2O (3:1)		13.8
D6	C_6D_6	11.7	8.1
	d_8-IPA:D_2O (3:1)		13.4

discussed in more detail below.) Polydispersities range from 1.33 to 1.49, which is a little higher than those reported by Vamvakaki et al. for PEO−DMA diblock copolymers.[15] There was usually no evidence of residual DMA monomer in the GPC chromatograms. Clearly oxyanionic polymerization of DMA using a PDMS-based macroinitiator is a suitable method for obtaining reasonably well-defined PDMS−DMA block copolymers without significant homopolymer contamination.

Although ^{1}H NMR spectroscopy is usually a reliable and convenient method for determining block compositions, results can occasionally be erroneous, especially when the nature of the constituent blocks is markedly different. In particular, Liu et al.[11] studied dimethylsiloxane−2-ethyl-2-oxazoline diblock copolymers and reported unexpected difficulties in characterizing these materials by ^{1}H NMR. It is noteworthy that the poly(2-ethyl-2-oxazoline) block is highly hydrophilic and contains basic nitrogen atoms in its monomer residues, so it is structurally rather similar to the DMA blocks of interest in the present study. Three deuterated solvents, $CDCl_3$, d_8-toluene, and D_2O, were examined by Liu et al. in their ^{1}H NMR studies. In D_2O, the siloxane content of the diblock copolymer was substantially underestimated. This was expected because D_2O is a poor solvent for the PDMS block; thus, the copolymer forms micelles in this solvent. On the other hand, $CDCl_3$ is a good solvent for both blocks, so micellization would not normally be expected in this solvent. However, peak integral analyses of the NMR spectra obtained from a series of five 2-ethyl-2-oxazoline−siloxane diblock copolymers dissolved in $CDCl_3$ suggested much lower PDMS contents than the theoretical values in each case (by at least a factor of 2 and up to a factor of 5). In d_8-toluene (a selective solvent for the PDMS block) the calculated siloxane content was either lower or higher than the expected values, depending on the copolymer molecular weight. In summary, Liu et al. were unable to identify a suitable solvent for satisfactory ^{1}H NMR analysis and instead relied on silicon microanalyses for the determination of block copolymer compositions.

In the present study, numerous NMR solvents and solvent mixtures were evaluated for the DMA−DMS diblocks, and the results are summarized in Table 2 and Figure 4. In each case block compositions were determined by comparing the signal due to the methyl protons of the siloxane chains, (δ −0.4 to δ 0.4) to the oxyethylene proton signal due to the DMA residues (singlet at δ 4.0 to δ 4.3). The first NMR solvent investigated was $CDCl_3$, which gave an anomalously low PDMS content of 3.7 mol % for sample D2 (see Table 2). This suggests the formation of micelles with siloxane cores in this solvent, which is surprising since both DMA homopolymer and PDMS are soluble in $CDCl_3$. Similar problems were encountered with a wide range of common deuterated solvents, including d_6-benzene, d_8-toluene, and a 1:1 mixture of CCl_4 and d_6-benzene. However, these observations are consistent with those reported by Liu et al. for DMS−2-ethyl-2-oxazoline diblocks, as discussed above. To test the micelle hypothesis, one of the DMA−DMS diblock copolymers (D2) was examined by dynamic light scattering in toluene at 25 °C. This experiment confirmed the existence of polydisperse aggregates, with a major population characterized by an intensity-average diameter of around 135 nm and a minor population of larger aggregates. Similar results were obtained in $CHCl_3$. Thus, these NMR and light scattering observations support the idea that, even in good solvents for PDMS such as $CHCl_3$ or toluene, these DMS−DMA copolymers have a very strong tendency for forming organized micellar structures, with the siloxane block being located within the micelle core. A typical transmission electron micrograph of a grid prepared from a dilute solution of the DMS_{13}−DMA_{53} diblock copolymer (D2) dissolved directly in $CHCl_3$ at 20 °C is shown in Figure 5. Spherical, polydisperse micelles are clearly observed, with diameters which are broadly comparable to those indicated by dynamic light scattering (allowing for polydispersity and drying effects).

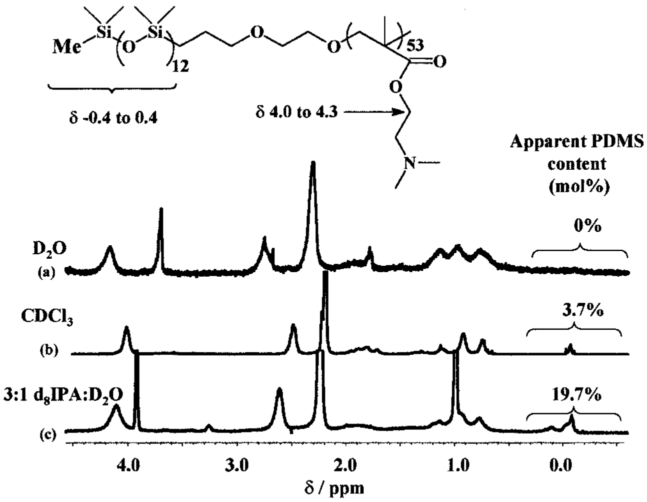

Figure 4. Assigned ^{1}H NMR spectra for DMS_{13}−DMA_{53} diblock copolymer (D2) in (a) D_2O, (b) $CDCl_3$, and (c) 3:1 d_8-IPA:D_2O. In each case the copolymer concentration was 1.0 w/v %.

Presumably micellization is driven by an enthalpic demixing term: the PDMS block prefers to pay the entropic penalty of becoming less solvated in order to avoid enthalpically unfavorable interactions with the DMA residues. This unusual behavior is apparently confined to nitrogen-based hydrophilic blocks since, according to the literature and also our own recent experience, accurate copolymer compositions can be readily obtained for PDMS blocked with a wide range of hydrophobic monomers (styrene,[8,20] various methacrylates,[21] etc.) and also hydrophilic oligo(ethylene oxide)-based chains.[7,22]

It is also noteworthy that attempts were made to calculate the block composition of D2 by comparing the total peak integral for the three pairs of oxymethylene protons at δ 3.20−3.45 originating from the PDMS macroinitiator (and now located at the block junction point) with that of the oxymethylene protons due to the DMA residues at δ 4.00−4.30. Since the former protons are directly attached to the solvated DMA block, it was

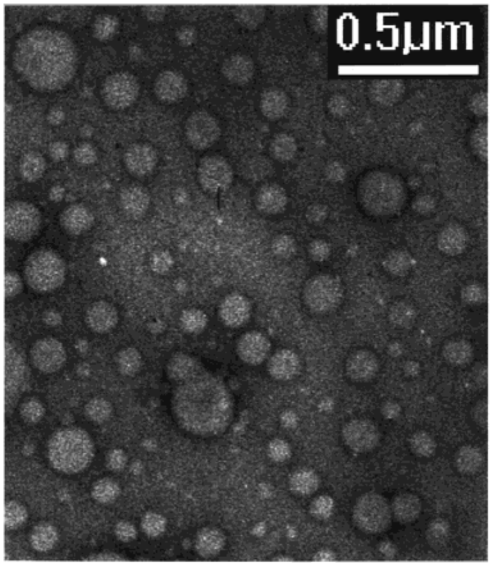

Figure 5. Typical transmission electron micrograph of micelles prepared by dissolving a DMS_{13}−DMA_{53} diblock copolymer (D2) in $CHCl_3$ at 20 °C.

Table 3. Apparent Copolymer Compositions for DMS_{13}−DMA_{81} (D5, Theoretical PDMS Content = 14.8 ± 0.7 mol %) in Various d_8-IPA:D_2O Mixtures, As Determined by ^1H NMR Spectroscopy

solvent	PDMS (mol %) by NMR
d_8-IPA	4.5
1:1 d_8-IPA:D_2O	6.7
2:1 d_8-IPA:D_2O	7.0
3:1 d_8-IPA:D_2O	13.8

hoped that this might allow realistic NMR compositions to be calculated even if the PDMS block itself was poorly solvated due to micelle formation. However, this approach gave disappointing results with all solvents tested.

None of the NMR solvents or solvent mixtures investigated proved satisfactory except for 3:1 d_8-IPA:D_2O solvent mixtures, as can be seen in Table 2. In all three cases, the block compositions obtained using this NMR solvent mixture were in good agreement (within the bounds of experimental error) with those expected from the synthesis conditions. In Table 3 the effect of varying the d_8-IPA:D_2O composition was examined. The best results were obtained with 75% d_8-IPA. At 50% d_8-IPA an anomalously low PDMS content was obtained. These findings are consistent with the work of Nagpal et al., who showed that the analogous 2-ethyl-2-oxazoline−siloxane diblock copolymers are molecularly dissolved in IPA-rich IPA:H_2O mixtures.[12]

Remarkably, the absolute copolymer concentration also proved an important parameter for reliable NMR analyses, with accurate block compositions only being obtained at copolymer concentrations of 1.0 w/v % or lower. This is illustrated in Figure 6, which shows how the apparent block composition of one of the DMA−DMS diblocks (D5) changes systematically with concentration. This behavior strongly suggests a critical micelle concentration (cmc) at approximately 1.0 w/v % for this block copolymer in a 3:1 d_8-IPA:D_2O mixture. Below this cmc, no micelles are formed and NMR analyses are satisfactory, whereas above the cmc the copolymer exists mainly in micellar form, with the siloxane block forming the desolvated micelle cores. This inevitably leads to an underestimate of the PDMS content of the copolymer by NMR.

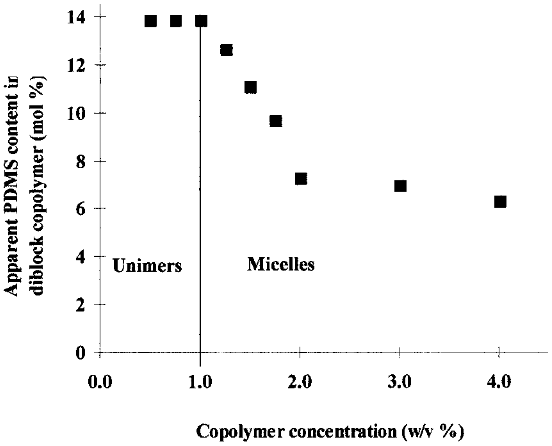

Figure 6. Apparent PDMS content of the DMS_{13}−DMA_{81} diblock copolymer (D5) as a function of copolymer concentration as indicated by ^1H NMR spectroscopy in 3:1 d_8-IPA:D_2O.

Table 4. Dynamic Light Scattering Results for DMS_{13}−DMA_{53} Diblock Copolymer (D2) Micelles in Aqueous Media

cosolvent (%)	pH	hydrodynamic diameter (nm)	polydispersity
none	9.4	110	0.40
	3.9	180	0.21
2-propanol (5.0)	9.2	15	0.71
	6.0	150	0.18
1,4-dioxane (5.0)	8.3	230	0.08
	4.5	210	0.07

Numerous dynamic light scattering experiments were carried out using D2 (DMS_{13}−DMA_{53}) in order to obtain the best conditions for producing well-defined micellar aggregates in aqueous media. All experiments were run at 25 °C between pH 3.9 and pH 9.4, at a copolymer concentration of 0.50 w/v %. The diblock copolymer was either (a) dispersed directly into water or (b) first dissolved in either IPA or 1,4-dioxane cosolvent prior to dilution with water to give a final cosolvent content of 5.0 v/v %. The addition of 0.25−0.75 M K_2SO_4 was also examined, but no significant differences in micelle size were observed. The light scattering data are summarized in Table 4. The micelles with the narrowest size distribution were obtained using 1,4-dioxane as a cosolvent: under these conditions a polydispersity less than 0.10 was obtained, and the mean intensity-average diameter was around 220 nm. Transmission electron microscopy studies (not shown) of a DMS_{13}−DMA_{53} diblock copolymer (D2), dissolved first in 1,4-dioxane cosolvent and then diluted with water to a final copolymer concentration of 1.0 w/v % at 20 °C, confirmed the existence of spherical micelles with diameters in the 100−250 nm range.

Figure 7 depicts a series of surface tension vs concentration curves at two solution pH's for two selected DMS−DMA diblock copolymers and a DMA homopolymer control. At pH 9.5 the limiting surface tension is approximately 28 mN m^{-1} for the DMS_{13}−DMA_{53} copolymer. This relatively low value is due to the strong adsorption of the hydrophobic PDMS block at the air−water interface. A significantly higher limiting surface tension of 37 mN m^{-1} is observed for a DMS_{13}−DMA_{81} copolymer. This reflects the reduced packing efficiency for the higher molecular weight DMA chains near the water surface. As a comparison, the limiting surface tension of a DMA homopolymer with a Dp of 66 is 43 mN m^{-1}. A similar trend was observed at pH 6.0, except

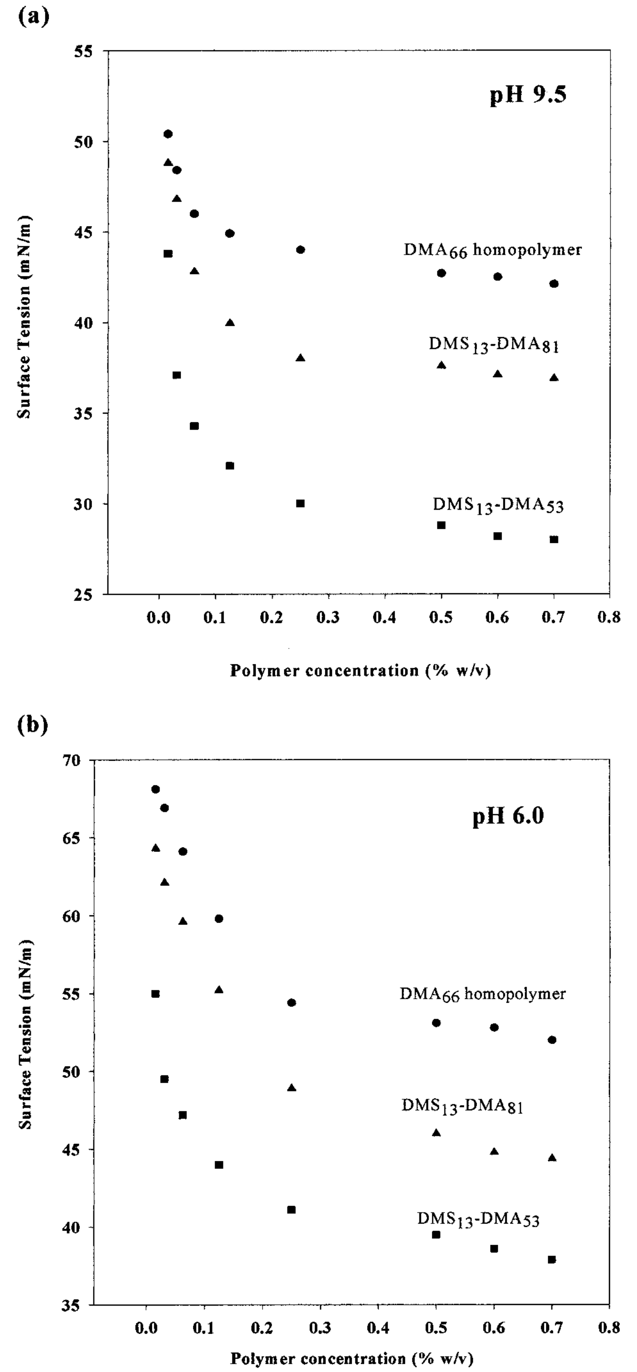

Figure 7. Surface tensiometry curves as a function of copolymer concentration for two selected DMS−DMA diblock copolymers (D2 and D5) compared with DMA homopolymer (a) at pH 9.5 and (b) at pH 6. Subscripts denote the degrees of polymerization of the DMS and DMA chains determined by NMR in each case.

that all three curves were shifted upward by 7−10 mN m^{-1}. This is because at this pH the DMA chains are partially protonated and therefore somewhat expanded, again leading to inefficient packing at the air−water interface. In summary, DMS−DMA copolymers can be strongly surface-active provided that the solution pH is alkaline and the Dp of the hydrophilic DMA block is not too high relative to the hydrophobic siloxane block.

Conclusions

Oxyanionic polymerization has been utilized to prepare novel DMS−DMA diblock and triblock copolymers. Provided that the terminal hydroxyl groups of a PDMS macroinitiator are carefully titrated to their alcoholate form, reasonably good control over the DMA chain length was achieved. ^{1}H NMR characterization of these DMS−DMA diblock and triblock copolymers proved problematic, since micellization generally occurred even in solvents that are good solvents for both blocks. Dynamic light scattering and transmission electron microscopy studies in toluene and $CHCl_3$ confirmed the existence of these aggregate structures for the first time. Reasonable block compositions were eventually obtained by NMR using IPA-rich d_8-IPA:D_2O mixtures, but even here it was important to keep the copolymer concentration relatively low (<1.0 w/v %) in order to avoid anomalous results. These DMS−DMA diblock copolymers were highly surface active in aqueous media, particularly at pH 9 where the charge density (degree of protonation) of the DMA block was low. As expected, polydisperse micelles were formed under these conditions, since water is a nonsolvent for the highly hydrophobic PDMS block. Micelles with narrower size distributions were obtained using cosolvents such as 1,4-dioxane, rather than by direct dissolution in water.

Acknowledgment. La Universidad de Huelva is thanked for a postdoctoral visiting fellowship for M.V.P.B. The EPSRC is acknowledged for a PhD project studentship (GR/M03351) for K.L.R., and Avecia (formerly Zeneca Specialities) is thanked for additional financial support.

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MA991665S