Preparation and properties of poly(dimethylsiloxane-2-ethyl-2-oxazoline) diblock copolymers

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Poly(dimethylsiloxane-2-ethyl-2-oxazoline) (PDMS-PEOX) diblock copolymers with narrow molecular weight distributions were prepared in two steps. The first involved living anionic ring-opening polymerization of hexamethyltrisiloxane and functional termination to afford monofunctional poly(dimethylsiloxane) oligomers with benzyl chloride endgroups. The second step involved the cationic ring-opening polymerization of 2-ethyl-2-oxazoline initiated by the activated halide on the monofunctional poly(dimethylsiloxane) oligomers. The well defined structure of these copolymers has allowed a fundamental investigation of structure–property relationships, which has included a study of solid, solution, and surface behaviour of these materials.

(Keywords: poly(dimethylsiloxane); poly(2-ethyl-2-oxazoline); block copolymer; micelle; surface activity)

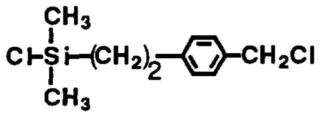
INTRODUCTION

The synthesis and applications of poly(dimethylsiloxane)-containing copolymers have been a prominent subject of research in recent years. The sustained interest in poly(dimethylsiloxane)s is due to their unique properties[1], among which, low surface energy and hydrophobicity pertain particularly to this research. The synthesis of poly(2-alkyl-2-oxazoline) materials has been studied since the 1960s[2–5]. Investigation of the polymerization of 2-ethyl-2-oxazoline using activated halides, such as benzyl iodide or benzyl chloride/NaI, as initiators indicates that these polymerization systems are living in solvents such as chlorobenzene[6]. The resultant materials are water soluble, amorphous polyamides with a strong propensity for hydrogen bonding with proton donors. Copolymers of these two components have many interesting solution and solid-state properties and are of great practical interest. It is well established that low levels of poly(dimethylsiloxane) blocks incorporated into composite polymer solids will modify the air surfaces of these systems to make them hydrophobic. This is of importance for biomaterials because of the decreased thrombogenicity of blood in the presence of these types of polymer surfaces. Less technically demanding industrial applications, such as release properties of film and anti-soiling fibre surfaces, are also of importance. These types of copolymers in solution are interesting because of their potential uses as surfactants or stabilizers for emulsion or suspension polymerization, or for their use as particle stabilizers for pigments or inorganic particles in concentrated suspensions. The poly(dimethylsiloxane-2-ethyl-2-oxazoline) diblock copolymers have been designed as model materials for studying aspects of the above-mentioned applications. Both block lengths can be controlled over a wide range and the molecular weight distributions of each block are narrow. Thus, the solution and solid-state behaviour can be studied as a function of the copolymer structure.

EXPERIMENTAL

Materials

Cyclohexane (Fisher reagent grade), tetrahydrofuran (THF) (Fisher certified grade), hexamethylcyclotrisiloxane (D_3) (Petrarch Systems), chlorobenzene (Aldrich), sodium iodide (Aldrich), and 2-ethyl-2-oxazoline (Aldrich) were purified as previously reported[7]. The sublimed D_3 was diluted with purified cyclohexane (45 wt/vol%) to obtain a stock solution and then stored under nitrogen. The benzyl chloride-containing chlorosilane terminating agent (**1**) was prepared by the hydrosilation of vinyl benzyl chloride (Dow Chemical Company) with dimethylchlorosilane (Petrarch Systems) using chloroplatinic acid hydrate (Aldrich) as a catalyst, by the method reported previously[7]. Sec-butyl lithium (1.4 M



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in cyclohexane, Lithco Division of FMC), and KOH/MeOH (0.1 N, Fisher) were used as received.

Preparation of monofunctional benzyl chloride-termininated poly(dimethylsiloxane) oligomers

The stock solution of D_3, and the calculated amount of sec-butyl lithium were charged into a reaction vessel and stirred at room temperature for approximately 2 h to initiate the polymerization. Then, THF (10 vol%) was added and propagation was allowed to proceed for 45 h at room temperature. The living siloxanolate endgroups were terminated by adding a slight excess of **1** to the system at room temperature. LiCl salts were removed by washing the oligomers with methanol in a separating funnel and the resultant materials were dried at approximately 60°C under vacuum, and then stored under nitrogen.

Synthesis of poly(dimethylsiloxane-2-ethyl-2-oxazoline) diblock copolymers

To make 20 g of poly(dimethylsiloxane-2-ethyl-2-oxazoline) block copolymer containing 20 wt% of poly(dimethylsiloxane), 2 molar equivalents of NaI per functional oligomer, 16 g of 2-ethyl-2-oxazoline, 4 g of functional poly(dimethylsiloxane), and 60 ml of chlorobenzene were added, in that order, to a flame-dried 250 ml round-bottom flask, equipped with a Teflon-coated magnetic stirring bar and a rubber septum secured with copper wire. The reaction mixture was stirred at room temperature for approximately 1 h and then heated to about 110°C until the monomer was depleted, as monitored by ^1H n.m.r. spectroscopy. Weight compositions of these reactions designed to be high in the polyamide are miscible throughout the reaction. By contrast, weight compositions which are low in 2-ethyl-2-oxazoline (high in siloxane) are immiscible at the beginning of the reactions and become miscible as reaction proceeds. The diblock copolymers were terminated by adding a slight excess of 0.1 N methanolic potassium hydroxide to the system at room temperature, yielding diblock copolymers with a hydroxyl terminal group on the polyamide end. The solution was then diluted with $CHCl_3$ and washed with a 10% $Na_2S_2O_3$ solution, followed by three washings with water. After evaporation of the solvent the white to light-yellow powdery materials that were obtained were dried to a constant weight at 40–60°C under vacuum. To remove any unreacted poly(dimethylsiloxane) oligomers the dry copolymers were then extracted using hexane as a solvent.

Characterization

^1H n.m.r. spectroscopy measurements were performed on a Bruker WP 270 spectrometer using either $CDCl_3$ or other solvents as indicated. Elemental analysis was performed at the Spang Microanalytical Laboratory (Eagle Harbor, MI, USA). A CAHN DCA-322 dynamic contact-angle analyser was used to measure the surface tension of aqueous solutions of the poly(dimethylsiloxane-2-ethyl-2-oxazoline) block copolymers at various concentrations (0.0019 to 5%), with these measurements being used for calculation of the critical micelle concentration of the copolymers in water. The operation of this instrument is based on the Wilhelmy-plate method. A ferro-type plate was used, with dimensions of $0.46 \times 10.91 \times 25.55$ mm, and was flamed prior to the measurements in a Bunsen burner to clean the surfaces, and then handled with tweezers to avoid further contamination. The speed of the stage displacement was 94 $\mu m\ s^{-1}$, and all measurements were carried out at room temperature. A Perkin-Elmer DSC-7 was used for the d.s.c. measurements. The normal heating programme that was used first involved heating of the sample from room temperature up to about 40°C above the expected upper transition temperature, using a heating rate of 10°C min^{-1}. Then the sample was cooled slowly, at a rate of 10°C min^{-1}, followed by a second heating cycle at a rate of 10°C min^{-1}. The T_g and T_m obtained during this second cycle are reported in this work. A KRATOS XSAM 800 X-ray photoelectron spectrometer was used to investigate PDMS enrichment at the surface of films fabricated from the poly(dimethylsiloxane-2-ethyl-2-oxazoline) block copolymers. Films were prepared by the casting of chloroform solutions of the copolymers (5 wt/vol%) onto ferro-type metal plates, which were then covered with glass petri dishes to allow slow evaporation of the solvent. The films were then dried in a vacuum oven at room temperature for approximately 48 h. The instrument uses a Mg Kα X-ray source operating at 13 kV and 20 mA, with the hemispherical analyser being used in the fixed retardation ratio (FRR) mode. Angular-dependent measurements were performed by rotating the sample probe, thereby changing the angle between the sample surface plane and the analyser.

RESULTS AND DISCUSSION

Synthesis

It is well known that hexamethylcyclotrisiloxane (D_3) can be polymerized in the presence of alkyl-lithium initiators and low concentrations of a polar solvent to produce polymers with narrow molecular weight distributions[8–15]. We have utilized this technique to prepare a series of monofunctional benzyl chloride-terminated poly(dimethylsiloxane)s with number-average molecular weights which systematically vary between 500 and 20 000 g mol^{-1} (see *Figure 1*). Gel permeation chromatographs of these materials confirm the excellent molecular-weight control and the 'nearly-Poisson' distributions that were achievable. As previously reported[7], the progress of initiation and propagation can be monitored by using ^{29}Si n.m.r. spectroscopy. The absence of appreciable amounts of propagation product during the initiation stage, as well as the absence of the redistribution product, octamethylcyclotetrasiloxane (D_4), toward the end of the propagation stage, makes a positive contribution to low polydispersities, even at relatively low values of the molecular weight.

In contrast to the understanding which has been developed over past years concerning the anionic living polymerization process of poly(dimethylsiloxane), correlations between reaction conditions and molecular weight distributions in the cationic polymerization of 2-ethyl-2-oxazoline are less well understood. Studies have shown that poly(dimethylsiloxane) oligomers with tosylate endgroups produced poly(dimethylsiloxane-2-ethyl-2-oxazoline) diblock copolymers with broad molecular weight distributions[16]. We have previously shown that benzyl chloride α,ω-functionally terminated

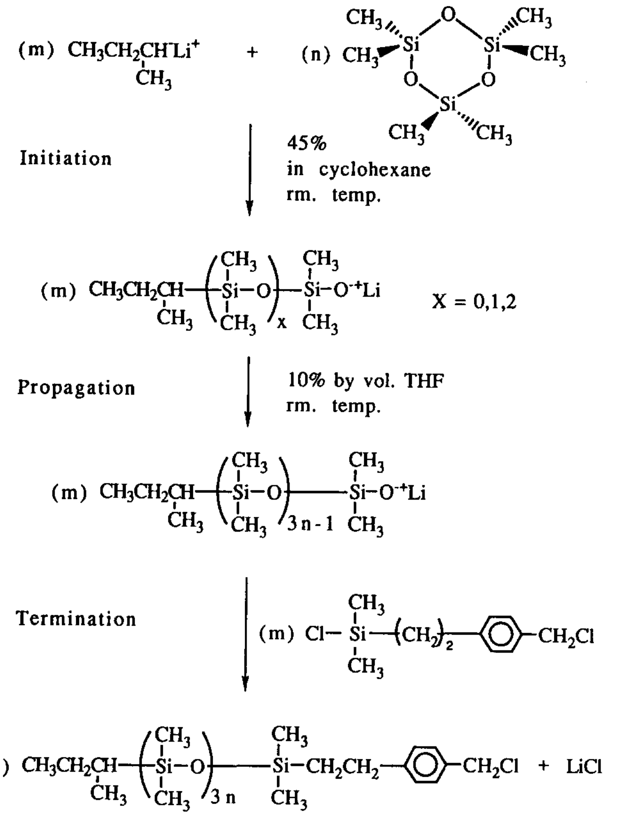

Figure 1 Synthesis of monofunctional benzyl-chloride-terminated poly(dimethylsiloxane)s

poly(dimethylsiloxane) oligomers, prepared by the equilibrium ring-opening polymerization of D_4, are effective macroinitiators for the melt polymerization of 2-ethyl-2-oxazoline in the presence of catalytic amounts of sodium iodide, yielding triblock copolymers (PEOX-PDMS-PEOX)[17]. The objective of the present research is to prepare well defined diblock copolymers comprised of these two components in order to study their structure–property relationships.

Recently we have demonstrated that polymerization of 2-ethyl-2-oxazoline in chlorobenzene, initiated by benzyl chloride in combination with sodium iodide (2 moles of NaI per mole of benzyl chloride) is living[6]. Therefore, it is possible to prepare well defined diblock materials by polymerizing 2-ethyl-2-oxazoline using monofunctional benzyl chloride-terminated poly(dimethylsiloxane), together with sodium iodide as the macroinitiator system (see *Figure 2*). The function of the sodium iodide is to convert benzyl chloride to the more reactive benzyl iodide *in situ*. A model study of the exchange reaction between benzyl chloride and NaI indicates that this reaction is complete within 1–2 h, even at room temperature. Thus, it is assumed that exchange is completed early in the copolymerization process. When the reaction mixture is heated at 110°C, a pale yellow colour, characteristic of the 2-ethyl-2-oxazoline polymerization reaction, develops. When the 2-ethyl-2-oxazoline monomer is depleted (as confirmed by the ^1H n.m.r. spectra), the reaction is terminated by adding KOH/MeOH at room temperature, and immediately after this addition, the pale yellow solution becomes colourless.

A series of poly(dimethylsiloxane-2-ethyl-2-oxazoline) diblock copolymers were synthesized, covering a range of structural compositions (10–66 wt% of PDMS) and block lengths (500–20 000 g mol^{-1} PDMS). Although gel permeation chromatography (g.p.c.) does not yield absolute molecular weights for these materials, the results shown in *Figure 3* for the poly(dimethylsiloxane) precursor and some selected copolymers do show a shift of the g.p.c. traces toward the higher-molecular-weight region of the block copolymers, and indicate fairly narrow molecular weight distributions. It should be noted that these copolymers were rigorously extracted with hexane following their isolation, to ensure the quantitative removal of any residual PDMS, prior to performing any detailed investigations of their structure–property relationships.

Characterization

To determine the effect of molecular weight on their properties, copolymers with the same theoretical compositions (20 wt% of PDMS) were evaluated. The compositions of the purified and isolated block copolymers were determined by elemental analysis, and the wt% of PDMS for each copolymer is shown in *Table 1*. In all cases, the experimental compositions, after careful extraction with hexane, were very close to the theoretical values. This reflects the quantitative nature of the poly(dimethylsiloxane) functionalization as well as a quantitative initiation of 2-ethyl-2-oxazoline. Since the second copolymer block could only have been initiated by the PDMS oligomer, this data also strongly suggests that only diblock copolymer is formed and that the systems are essentially free of homopolymers of either of the components.

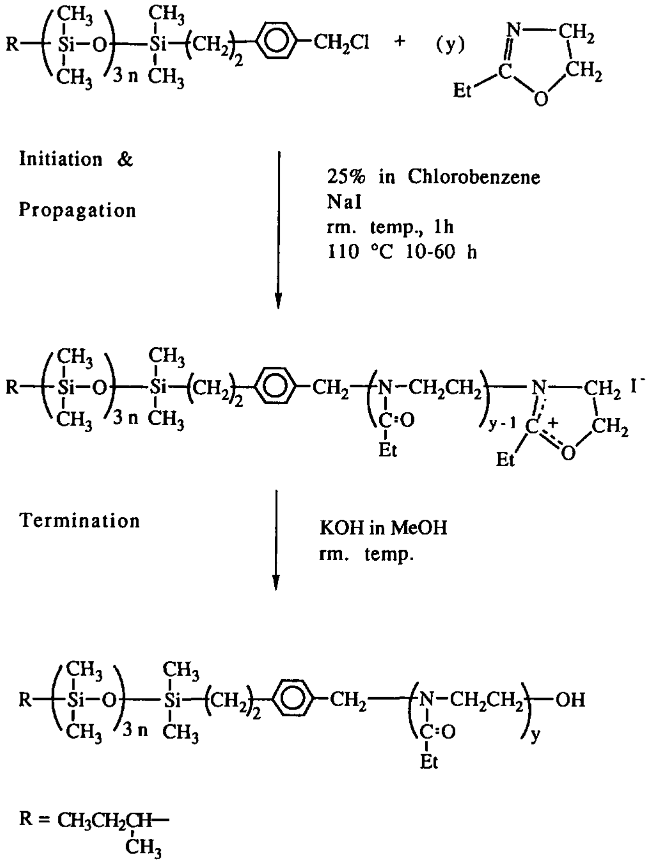

Figure 2 Synthesis of poly(dimethylsiloxane-2-ethyl-2-oxazoline) diblock copolymers

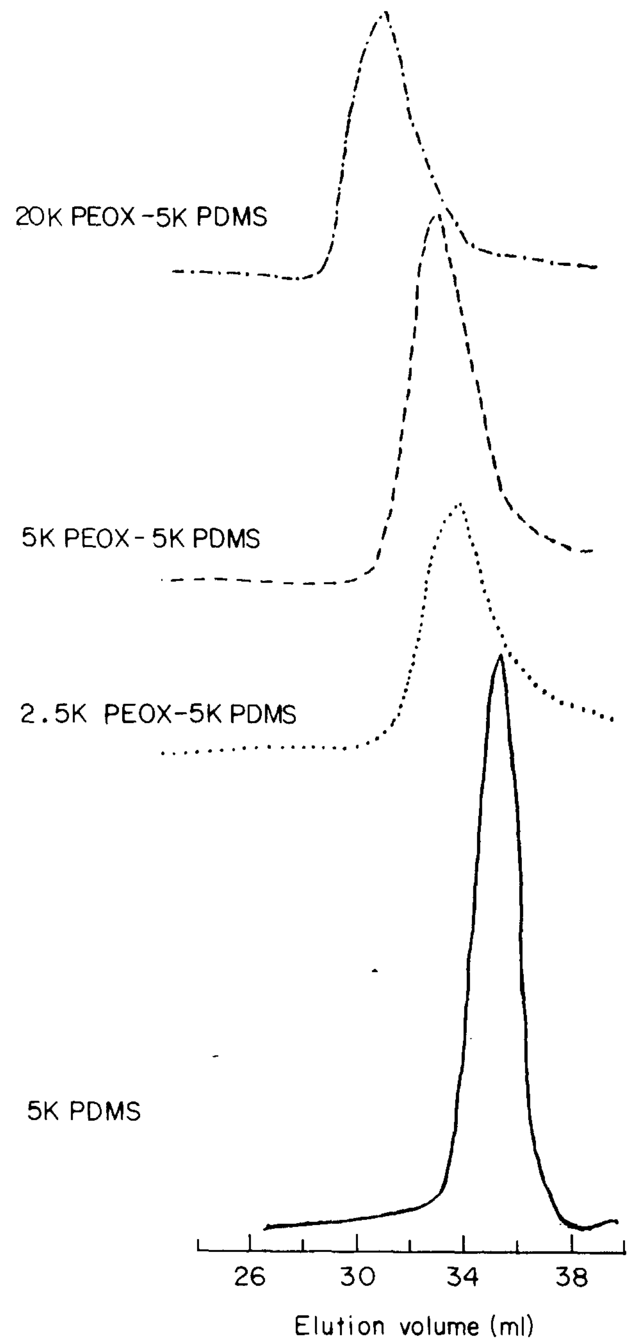

Figure 3 Gel permeation chromatograms of a poly(dimethylsiloxane) (PDMS) precursor and various poly(dimethylsiloxane-2-ethyl-2-oxazoline) (PDMS-PEOX) diblock copolymers (column: Ultrastyragel; solvent: toluene; temperature: 30°C)

Table 1 Compositions of several PDMS-*b*-PEOX copolymers obtained from elemental analysis[a]

Copolymer sample (kg mol^{-1})	PDMS[b] (wt%)
0.5K PDMS-2K PEOX[c]	17.21
1K PDMS-4K PEOX	18.24
2K PDMS-8K PEOX	16.95
5K PDMS-20K PEOX	19.78
20K PDMS-80K PEOX	15.18

[a] All samples have the same theoretical composition of 20 wt% PDMS
[b] Results obtained by Spang Microanalytical Laboratory
[c] For example, 0.5K PDMS-2K PEOX≡0.5 kg mol^{-1} PDMS-*b*-2 kg mol^{-1} PEOX

^{1}H n.m.r. spectroscopy is often a convenient method for determining the chemical compositions of copolymers. However, the calculated weight percentage of PDMS in these block copolymers, based on ^{1}H n.m.r. measurements in $CDCl_3$, and particularly for the longer block lengths in the copolymers (e.g. as in the 20K PDMS-80K PEOX material), suggested much lower PDMS contents than the theoretical value of 20 wt% (*Table 2*). One possible explanation of these results is the existence of micelles. It has been known for some time, but not well appreciated, that aggregated structures can cause the relaxation time (T_1) of the poorly solvated component to be quite long and, hence, the signal intensity of that component is dramatically reduced. Due to the great dissimilarity between the two block structures, formation of micelles would be expected, especially in certain solvents. *Figure 4* shows the ^{1}H n.m.r. spectra obtained for one of these block copolymers, measured in $CDCl_3$, toluene-d_8 and D_2O. In toluene, a poor solvent for poly(2-ethyl-2-oxazoline), the peak at 3.5 ppm, due to

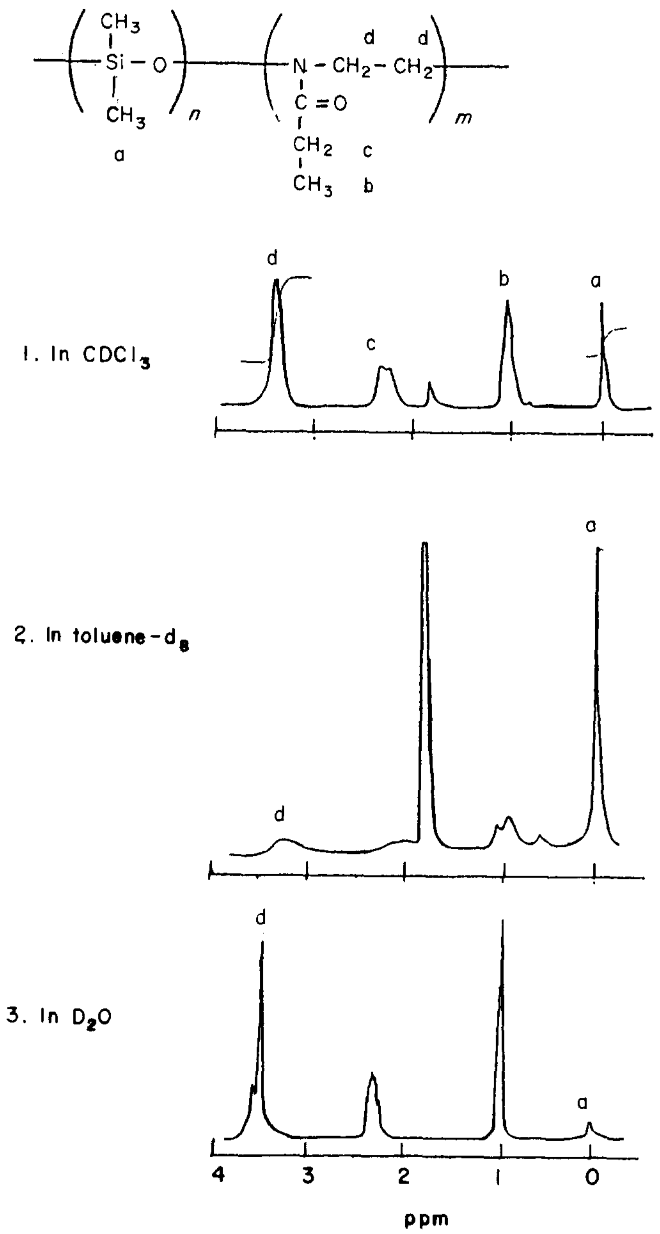

Figure 4 ^{1}H n.m.r. spectra of a poly(dimethylsiloxane-2-ethyl-2-oxazoline) diblock copolymer measured in different solvents

Table 2 Compositions of several PDMS-*b*-PEOX copolymers determined by ^1H n.m.r. spectroscopy in various solvents[a]

	Solvent		
Copolymer sample ($kg\ mol^{-1}$)	$CDCl_3$ (wt% PDMS)	Toluene-d_8 (wt% PDMS)	D_2O (wt% PDMS)
0.5K PDMS-2K PEOX[b]	10.7	16.8	13.1
1K PDMS-4K PEOX	8.9	18.3	10.7
2K PDMS-8K PEOX	9.8	36.1	6.6
5K PDMS-20K PEOX	13.4	69.2	4.6
20K PDMS-80K PEOX	3.6	71.4	2.2

[a] All samples have the same theoretical composition of 20 wt% PDMS

[b] For example, 0.5K PDMS-2K PEOX ≡ 0.5 $kg\ mol^{-1}$ PDMS-*b*-2 $kg\ mol^{-1}$ PEOX

the poly(2-ethyl-2-oxazoline) backbone, is extremely weak, when compared to the signal at 0.1 ppm, the latter being due to the poly(dimethylsiloxane) component. In great contrast, in water, which is a poor solvent for the poly(dimethylsiloxane), but an excellent solvent for the poly(2-ethyl-2-oxazoline), the peaks of the latter are prominent, while the poly(dimethylsiloxane) peaks are extremely small. Based on these spectra, the wt% of PDMS was calculated for each block copolymer, and these are given in *Table 2*. Several interesting trends are evident from these results. The wt% of PDMS measured when using toluene-d_8 as the solvent was uniformly greater than that obtained using D_2O. Moreover, for both solvents, the deviation from the theoretical value of 20 wt% of PDMS (in agreement with the elemental analysis results), consistently increased as the block lengths increased. Both of these trends support the hypothesis that micelles are present in these solutions. It was expected that when toluene-d_8 was used as the n.m.r. solvent, the PDMS blocks would be solubilized and form the outskirts of the micelle, while PEOX would be insoluble and form the core. Conversely, when D_2O was used as the solvent, the reverse would be true. As the molecular weight of each block increased, microphase separation in solution would be expected to be more complete. Thus, the block-length effect on the n.m.r. results can be understood in terms of such phase separation. This demonstrates the necessity for cautious interpretation of solution-n.m.r. data of phase-separated block copolymers in which the characteristics of the blocks differ significantly.

In order to confirm the presence of micelles for these PDMS-PEOX block copolymers, the critical micelle concentration (CMC) for the copolymer having the lowest molecular weight, i.e. 0.5K PDMS-2.0K PEOX, was determined in water. Many properties of a solution change dramatically at the CMC, for example, osmotic pressure, turbidity, surface tension and molar conductivity, and measurement of any one of these properties as a function of the concentration yields CMC values[18]. In this study, the surface tension of the copolymer was measured using a dynamic contact-angle analyser, and the values obtained were plotted against concentration (*Figure 5*). This analysis produced a surface tension *versus* concentration plot, typical of surfactant behaviour. The CMC value, obtained by the intersection of the two tangents on the curve, was approximately 0.07 $mg\ ml^{-1}$ (0.028 $mmol\ l^{-1}$). By contrast, a typical surfactant, such as sodium dodecyl sulfate, has a CMC value of 8.1 $mmol\ l^{-1}$ at 25°C[19], and it was therefore concluded that these block copolymers were very surface active.

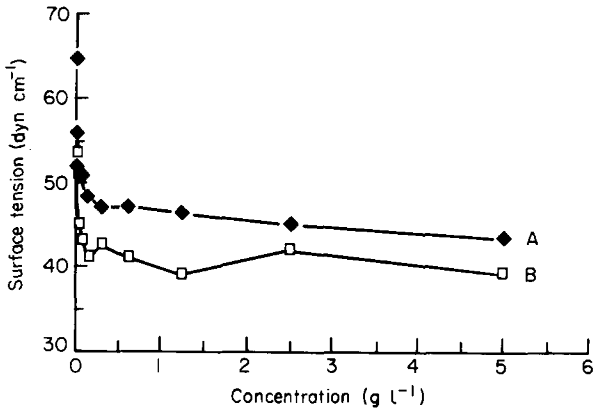

Figure 5 Surface tension *versus* concentration plot of a poly(dimethylsiloxane-2-ethyl-2-oxazoline) diblock copolymer: (A) receding; (B) advancing

For a block copolymer in the solid state, the lowest energy component will be energetically driven to concentrate at the polymer/air interface. Since poly(dimethylsiloxane) has a very low surface energy, the air surfaces of poly(dimethylsiloxane)-containing copolymers, or blends containing these copolymers, are expected to be enriched with this component. This has been demonstrated in numerous studies[20–25] through either surface tension and contact angle measurements or by more sophisticated surface chemical composition analysis techniques, such as X-ray photoelectron spectroscopy (X.p.s.), secondary ion mass spectrometry (SIMS), etc. However, relatively little work quantifying the effects of molecular weight on the chemical composition of the surface has been carried out. Among the surface analysis techniques capable of yielding this information, such as X.p.s., SIMS, Auger electron spectroscopy (A.e.s.), and ion scattering spectroscopy (ISS), X.p.s. is the method of choice for obtaining quantitative data. The probing depth of X.p.s. ranges from approximately 10 to 70 Å[26]. Since we have successfully prepared block copolymers with a wide range of molecular weights for the various components, and moreover with rather narrow molecular-weight distributions, it is possible to correlate the surface chemical compositions with the block lengths of the copolymers.

The surface chemical compositions of a series of poly(dimethylsiloxane-2-ethyl-2-oxazoline) block copolymers where the number-average molecular weight of the PDMS component varied from 500 to 20 000 $g\ mol^{-1}$ (all having essentially the same bulk composition of 20 wt% of PDMS) were determined by X.p.s. measurements. Since silicon and nitrogen are respectively

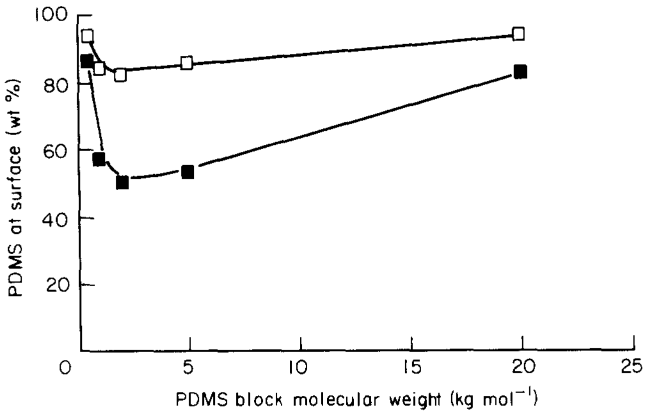

Figure 6 Surface composition, expressed as wt% of PDMS, of a series of poly(dimethylsiloxane-2-ethyl-2-oxazoline) diblock copolymers as a function of M_n of the PDMS component (bulk composition of 20 wt% PDMS for all samples): (A) 15°; (B) 90°

unique to the poly(dimethylsiloxane) and poly(2-ethyl-2-oxazoline) blocks the areas under the Si_{2p} peaks and the N_{1s} peak can be directly related to the chemical composition of the sampled depth. The weight percentages of PDMS at the copolymer surfaces were calculated using this approach, and the results are summarized in *Figure 6*. Two electron take-off angles corresponding to two sampling depths into the surface (15° angle sampling less depth into the surface, ~10–20 Å, as compared to the 90° angle) were investigated. As expected, in both cases, the weight percentage of PDMS on the surface is much higher than that in the bulk, indicating that all of the surfaces are preferentially enriched by PDMS. *Figure 6* further indicates that the weight percentages of PDMS at the 15° take-off angle are greater than those at the 90° angle, indicating the presence of thin PDMS-rich overlayers on the copolymer films. A second observation was a non-linear dependence of the surface concentration of PDMS on the molecular weight of the block. In the higher-molecular-weight range (M_n of PDMS >2000 g mol^{-1}), the surface concentration of PDMS increased with increasing PDMS block length. This agrees with observations made on polycarbonate-PDMS-containing block copolymers[27], and can be rationalized by the general phase-separation behaviour of block copolymers. An increasing block length of the PDMS component would lead to better phase separation and an increased PDMS-phase thickness. Many studies[25] have shown an overlayer coverage of PDMS on the surface of various PDMS-containing copolymers. If this is the case, then increasing the thickness of the PDMS layer should increase the surface concentration of PDMS as measured by X.p.s., which gives a weighted average value of the top layer between approximately 10 and 70 Å in depth.

At the lower end of the molecular-weight scale (M_n of PDMS <2000 g mol^{-1}), the surface concentration of PDMS increased with decreasing PDMS block length. Repeated experiments and rigorous extraction procedures confirmed that this result is reproducible and that it was not due to homopolymer impurities in the sample. This behaviour cannot be explained by the theory of phase-separation dependence on the molecular weight. According to the traditional bulk-phase separation theory, a decreasing molecular weight would lead to less phase separation, and therefore, less PDMS at the surface. One possible explanation is that these low-molecular-weight block copolymers behave differently at a surface. The block lengths of both the PDMS and PEOX components are probably too short to behave as random coils. In addition, the very low surface tension of PDMS should serve as an extra driving force for phase separation to occur at the surface. These speculations emphasize the need for further research to be carried out in this area.

The solid-state phase-separation behaviour of these block copolymers (20 wt% PDMS) was evaluated by examining the glass-transition temperatures of the two component blocks by d.s.c., and the results are summarized in *Table 3*. By using this technique, no transition could be detected around −124°C, the glass transition temperature of PDMS, while transitions occurred between 25 and 75°C, corresponding to the T_gs of PEOX. As expected, the T_g increased with increasing molecular weight. Only one copolymer, namely the 20K PDMS-80K PEOX material, showed a T_m corresponding to that of 'pure' PDMS, which occurs at around −48°C. These observations, in general, agreed with those found for another set of PDMS-containing copolymers with similar weight percentages and molecular weights of the PDMS component, namely the PDMS-*g*-poly(1-butene sulfone) series[28]. The fact that no T_g corresponding to the PDMS component could be detected is probably due to the low weight percentage of the latter. The increase in the PEOX T_g with increasing block length is probably caused by a combination of the molecular-weight dependence of this transition point, together with the increasing level of phase separation as the block lengths were increased. Comparison of the PEOX-block T_gs with those found for PEOX homopolymers of similar molecular weights (using identical d.s.c. heating–cooling cycles) suggests that essentially complete phase separation was probably achieved for block copolymers with molecular weights of PDMS larger than 1000 and PEOX and 4000 g mol^{-1}, respectively.

CONCLUSIONS

Well defined poly(dimethylsiloxane-2-ethyl-2-oxazoline) diblock copolymers have been successfully prepared by the living ring-opening polymerization of hexamethyl cyclotrisiloxane and 2-ethyl-2-oxazoline in two steps. These diblock copolymers show microphase separation

Table 3 D.s.c. results obtained for several PEOX and PDMS homopolymers and a number of PDMS-*b*-PEOX copolymers

(Co)polymer sample (kg mol^{-1})	T_g (°C) PEOX	T_g (°C) PDMS[a]	T_m (°C) PDMS[a]
5K PEOX	50	–	–
10K PEOX	54	–	–
30K PEOX	56	–	–
17K PDMS	–	−124	−48, −37
0.5K PDMS-2K PEOX[b]	38	ND	ND
1K PDMS-4K PEOX	47	ND	ND
2K PDMS-8K PEOX	57	ND	ND
5K PDMS-20K PEOX	55	ND	ND
20K PDMS-80K PEOX	56	ND	−42

[a] No transitions detected in some samples (ND)
[b] For example, 0.5K PDMS-2K PEOX≡0.5 kg mol^{-1} PDMS-*b*-2 kg mol^{-1} PEOX

in the bulk, form micelles in solution (especially aqueous solution) and are enriched in polydimethylsiloxane at the air surface of the copolymers. The formation of micelles of these block copolymers in various solvents indicates the necessity for careful interpretation of solution-n.m.r. data of phase-separated block copolymers in general. The unexplained surface activity of the low molecular weight block copolymer (0.5K PDMS-2K PEOX) and the applications of these block copolymers as ceramic particle steric suspension stabilizers are currently under investigation.

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