Synthesis of Poly(methylphenylsiloxane)-*block*-poly(dimethylsiloxane) Block Copolymers by Interfacial Polymerization

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Introduction

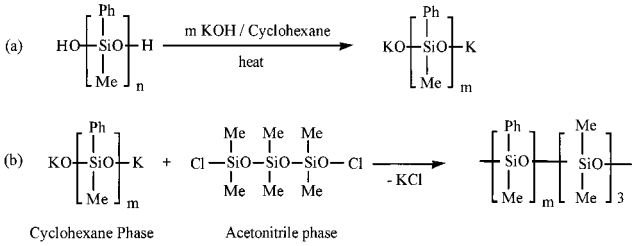
Interfacial polymerization has been used to prepare various condensation polymers, particularly polyamides,[1,2] polyesters,[3] polyurethanes, and polyureas.[4,5] Interfacial polymerization allows the synthesis of condensation polymers,[4] at low temperature with limited side reactions, and avoids the use of a catalyst or phase transfer agent. Interfacial polymerization can directly generate finished products, such as films, fibers, membranes, etc., and has seen widespread acceptance in many fields, ranging from microencapsulation of pharmaceutical products[6] to conducting polymer films.[7]

We have prepared siloxane copolymers containing phenyl groups by interfacial polymerization. Polysiloxanes are known to possess a remarkable range of properties exhibiting high stability to heat and UV exposure and low surface tension as well as being relatively insensitive to temperature changes over the range −50 to 250 °C.[8] The presence of methylphenylsiloxane segments in a poly(dimethylsiloxane) (PDMS) backbone is known to disrupt the low-temperature crystallization of PDMS, and the incorporation of phenyl groups into the siloxane backbone backbone can also enhance the thermal and radiation stability of PDMS. These enhanced properties would be very useful in new commercial products.

Siloxane copolymers of this type are usually prepared by living polymerization or under equilibrium conditions in a single medium excluding emulsion polymerization; however, interfacial polymerization has not been used to prepare alternating siloxane block copolymers. Riffle et al.[9] have prepared organofunctional siloxane block copolymers containing organic polycarbonate blocks using interfacial polymerization; however, this work required the addition of a phase transfer catalyst. Poly(alkoxysilane)s were synthesized by Carraher[10,11] using a modified interfacial polymerization technique employing two organic solvents in the two-phase system. Earlier reports by Iskenderov et al.[12] make poly(alkoxysilane)s by interfacial polymerization with an organic solvent−water system.

While others have produced siloxane block copolymers previously, using equilibrating catalysts,[13,14] our aim in this study was to prepare and characterize (^{29}Si NMR, GPC, and FT-IR) block copolymers containing methyl- and phenylsiloxane segments using interfacial polymerization, without the use of a phase transfer catalyst.

Scheme 1



Experimental Section

Materials. Methylphenylsiloxane hydrolyzate (D^{Ph}, $\bar{M}_n$ = 1352) was obtained from Dow Corning. This material is used commercially for the synthesis of poly(methylphenylsiloxane), by either acid or base catalysis, and is obtained from controlled hydrolysis of methylphenyldichlorosilane. Hydrolysis results in a blend of cyclic and hydroxyl-terminated, oligiomeric linear methylphenylsiloxanes. This low cost, commercial siloxane monomer reacts in a manner similar to tetramethyltetraphenylcyclotetrasiloxane (D_4^{Ph}), which is commonly used in academic studies; hence, extensive further characterization, of the monomer, was not considered necessary. 1,5-Dichlorohexamethyltrisiloxane was also obtained from Dow Corning. Potassium hydroxide, cyclohexane, and acetonitrile were purchased from Fischer. All solvents were stored over molecular sieves.

Characterization. ^{29}Si NMR analyses were obtained on a Varian VXR 400S NMR spectrometer at 79.46 MHz with 5000 scans at a pulse width of 45° with gated decoupling and a repetition rate of 10 s. Chemical shifts were referenced relative to tetramethylsilane internal reference. Ten mg (0.02 M) of $Cr(acac)_3$ relaxation reagent was added to each of the samples before ^{29}Si NMR spectra were obtained to effectively remove nuclear Overhauser enhancement and reduce the effects of relaxation time (T_1) on peak intensities and area.

Infrared spectra were obtained for the prepared dipotassium siloxanediolate samples and the prepared polysiloxane copolymer samples using a Perkin-Elmer 1000 infrared spectrophotometer. Samples were applied to NaCl plates and then analyzed using 16 scans.

Gel permeation chromatography was used to determine average molecular weight data for the polysiloxane copolymer samples. A Waters 600E GPC equipped with PL gel 5 m columns fitted with a Waters 410 differential refractometer was used for this analysis. The eluent solvent used was THF (degassed and filtered through a 0.45 μm filter). Polystyrene standards (0.02% w/v in THF; $\bar{M}_n$ ranges from 970 to 1 570 000) were used to calibrate the samples. Molecular weight data were calculated using PE Nelson Access SEC software (version 1.8) via a MicroVAX 3400 minicomputer.

Synthesis. a. Preparation of Dipotassium Poly(methylphenylsiloxanediolate) (Scheme 1). A positive nitrogen pressure was applied to a three-necked 1 L round-bottom flask equipped with a thermometer, mechanical stirrer, and a two-outlet adapter supporting a Dean-Stark reflux condenser and a dropping funnel. To the flask was added 157.76 g (1.16 mol) of methylphenyl hydrolyzate in 46.7 g of cyclohexane. An 18.6 g aliquot of potassium hydroxide (45% solution in water) was slowly dropped into the solution at a constant rate, and the solution refluxed until all the water was collected. Further aliquots of potassium hydroxide were added, during reflux, to obtain the required potassium-to-silicon ratio (see Table 1), which ensured formation of dipotassium poly(methylphenylsiloxanediolate) with the requisite average chain length. The solution was then cooled and the solvent removed, in vacuo at 50 °C, to leave the viscous telechelic potassium poly(meth-

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Table 1. Potassium Content of Dipotassium Poly(methylphenylsiloxanediolate)s

siloxane-diolate no.	structure (from experimental data)	potassium content (% w/w) expected	potassium content (% w/w) found	appearance
I	$KO[(C_6H_5)(CH_3)SiO]_{3.4}K$	12.2	13.9	clear, crystalline
II	$KO[(C_6H_5)(CH_3)SiO]_{5.5}K$	10.1	9.2	opaque, waxy
III	$KO[(C_6H_5)(CH_3)SiO]_{8.3}K$	6.6	6.4	opaque, waxy

Table 2. Interfacial Polymerization Reaction Conditions (Siloxanediolates I, II, and III); All Reactions Were Carried Out at 50 °C under Nitrogen with No Stirring and Left To Stand for 2 h

siloxanediolate no.	polymer type
I (unstirred)	clear, viscous elastomer
II (unstirred)	clear, viscous elastomer
III (unstirred)	clear, viscous oil
III (stirred)	low viscosity, clear oil

ylphenylsiloxanediolate) oligiomer in high yield (>90%).[15,16] Potassium elemental ratios were determined in duplicate from atomic absorbance spectrometry from which the average chemical structure was obtained (see Table 1).

FTIR (NaCl) ν cm^{-1}: 3050 m, (Ph); 2960 m, (CH_3); 2890 m, (CH_3); 1590 w, (Si−Ph); 1260 m, (Si−CH_3); 1120 s, (Si−Ph); 1100 s, (Si−O−Si).

Quenching of the dipotassium poly(methylphenylsiloxanediolate)s with trimethylchlorosilane for further detailed characterization was attempted; however, extensive base-catalyzed redistribution of the quenched siloxanediolates occurred which invalidated this characterization work.

b. Interfacial Polymerization. Preparation of Poly(methylphenylsiloxane)-*block*-poly(dimethylsiloxane) Block Copolymers (Scheme 1). Freshly prepared dipotassium poly(methylphenylsiloxanediolate) was added to 60 mL of cyclohexane to prepare a 0.2 mol/L solution. This was added, through a septum sealed opening, to a 500 mL round-bottom flask equipped with a nitrogen inlet. This solution was heated to 50 °C, and then 40 mL of dry acetonitrile was added, via syringe, under a positive pressure of nitrogen. An equimolar solution of 1,5-dichlorohexamethyltrisiloxane in 20 mL of acetonitrile was then slowly added to the reaction mix. A polymer immediately formed at the acetonitrile/cyclohexane interface and potassium chloride salt precipitated from the interface. The polymerization reaction was exothermic. The reaction mix was then allowed to stand for 2 h without stirring, after which it was poured into 200 mL of cyclohexane. The precipitated polymers were either viscous oils or elastomers and were separated by filtration, washed with water to remove potassium chloride, and dried under vacuum at 50 °C to give polymer in good yield (70%). The final properties of the siloxane copolymer have been given in Table 2.[15,16]

FTIR (NaCl) ν cm^{-1}: 3050 m, (Ph); 2960 m, (CH_3); 2890 w, (CH_3); 1590 m, (Si−Ph); 1260 s, (Si−CH_3); 1120 s, (Si−Ph); 1100 s, (Si−O−Si).

Results and Discussion

Three dipotassium poly(methylphenylsiloxanediolate) materials (I, II, and III) were prepared (see Table 1), and three block copolymers were prepared by reacting these with 1,5-dichlorohexamethyltrisiloxane using interfacial polymerization (see Table 2). However, only the copolymers prepared from dipotassium poly(methylphenylsiloxanediolate)s II and III were extensively characterized by GPC and ^{29}Si NMR. The GPC results (see Figures 1 and 2) have been given in Table 3. The ^{29}Si NMR analysis (see Figures 3 and 4) has been given in Table 4. Also included in Table 4 are ^{29}Si NMR results for copolymer from dipotassium poly(methylphenylsiloxanediolate), III, where the interfacial polymerization reaction was subjected to vigorous mechanical stirring (see Figure 5).

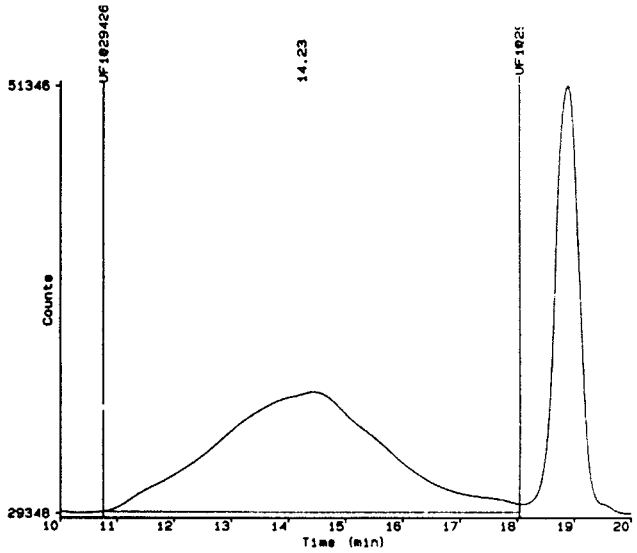

Figure 1. GPC of poly(methylphenylsiloxane)-*block*-poly(dimethylsiloxane) block copolymer prepared from siloxanediolate II using unstirred interfacial polymerization.

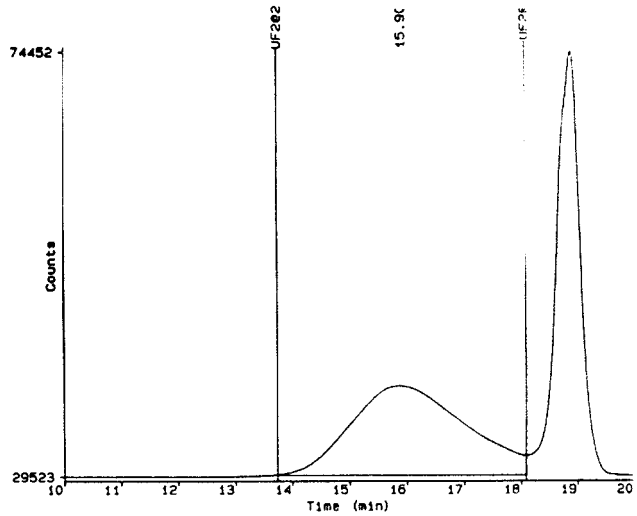

Figure 2. GPC of poly(methylphenylsiloxane)-*block*-poly(dimethylsiloxane) block copolymer prepared from siloxanediolate III using unstirred interfacial polymerization.

Table 3. GPC Data for Interfacial Polymerizations (Siloxanediolates II and III); All Reactions Were Carried Out at 50 °C under Nitrogen with No Stirring and Left To Stand for 2 h

siloxane-diolate no.	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_z$	polydispersity
II	16020	96520	327 100	6.0
III	4818	9455	16 400	2.0

The ^{29}Si NMR data can be used to determine the average degree of polymerization and the average branch chain length (based on the number of silicon atoms as repeat units), plus the average number of branched chains per linear chain. Integration of the methylphenylsiloxane peak (D^{Ph} occurring at −33 ppm)

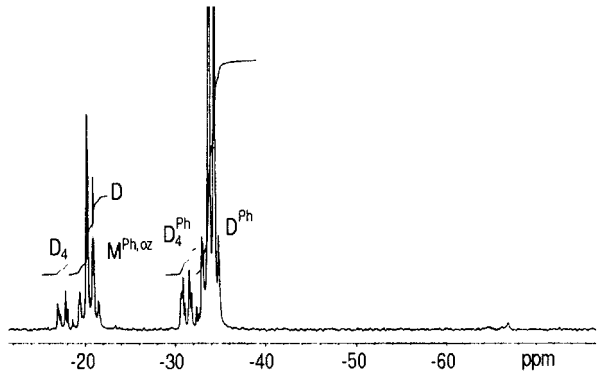

Figure 3. ^{29}Si NMR spectrum of poly(methylphenylsiloxane)-*block*-poly(dimethylsiloxane) block copolymer prepared from siloxanediolate II using unstirred interfacial polymerization.

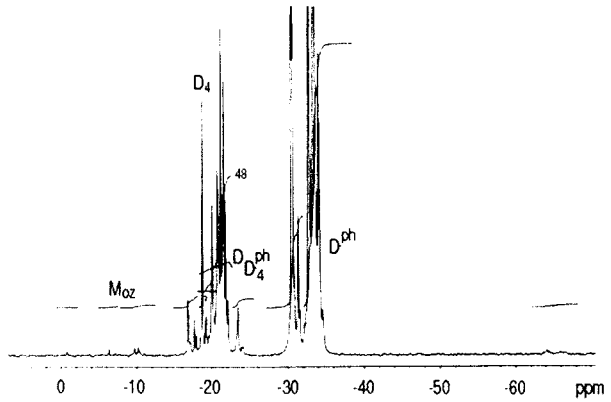

Figure 4. ^{29}Si NMR spectrum of poly(methylphenylsiloxane)-*block*-poly(dimethylsiloxane) block copolymer prepared from siloxanediolate III using unstirred interfacial polymerization.

Table 4. ^{29}Si NMR Data for Interfacial Polymerizations (Siloxanediolates II and III); All Reactions Were Carried Out at 50 °C under Nitrogen with No Stirring and Left To Stand for 2 h and Siloxanediolate III Repeated with Vigorous Mechanical Stirring

siloxanediolate no.	$\overline{DP}$	branched chain length	no. of branches per linear chain
II (unstirred)	398	55	0.24
III (unstirred)	65	38	0.47
III (stirred)	16	2.8	3.0

and the dimethylsiloxane peak (D occurring at −20 ppm) gave intensities for the linear chain absorptions. Integration of the terminal methylphenylsiloxane peak ($M^{Ph,OZ}$ occurring at −23 ppm) and the terminal dimethylsiloxane peak (M^{OZ} occurring at −10 ppm) gave intensities for the terminal end group absorptions. Integration of the branched peaks (T groups occurring at −65 ppm) gave the intensities for the branched silicon atoms.

Using the ^{29}Si NMR peak intensity data, described above, it was possible to obtain the average degree of polymerization of the copolymer using eq 1.

$$\overline{DP} = \frac{\sum(\text{linear absorptions}) + 2}{\sum(\text{end group absorptions})/2} \quad (1)$$

The average branch chain length (based on the number of silicon atoms) for the copolymer was found from eq 2.

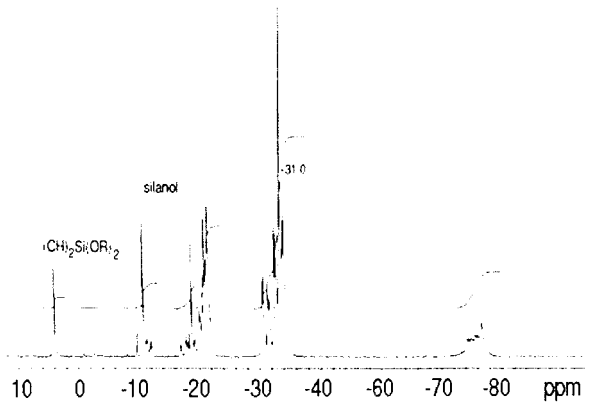

Figure 5. ^{29}Si NMR spectrum of poly(methylphenylsiloxane)-*block*-poly(dimethylsiloxane) block copolymer prepared from siloxanediolate III using stirred interfacial polymerization.

$$\overline{\text{branched chain length}} = \frac{\sum(\text{linear absorptions})}{\sum[\text{end group absorptions} + 3(\text{branched T absorptions})]/2} \quad (2)$$

The average number of branched chains per linear chain was found from eq 3.

$$\text{no. of branched chains/linear chains} = \frac{\sum(\text{branched T group absorptions})}{\sum(\text{end group absorptions})/2} \quad (3)$$

High yields of block copolymer (70−80%) were obtained by interfacial polymerization. The longer dipotassium poly(methylphenylsiloxanediolate) chains produced less viscous the polymer and the shorter siloxanediolate chains formed elastomeric products of high molecular weight (>100 000). Comparison of the relative FTIR absorbances of the methyl peak (2960 cm^{-1}) and the phenyl peak (3050 cm^{-1}) verified that 1,5-dichlorohexamethyltrisiloxane formed block copolymers with the dipotassium poly(methylphenylsiloxanediolate). The methyl absorbance was found to increase relative to the phenyl absorbances after interfacial polymerization.

The ^{29}Si NMR analysis revealed the formation of block copolymers with little or no cyclic material present. In addition, ^{29}Si NMR spectra showed the dimethylsiloxy unit Me_2SiO (D) at about −21 ppm and another absorption at about −34 ppm belonging to the phenylmethylsiloxy unit PhMeSiO (D^{Ph}). D_4 cyclics (at about −18 ppm) and D_4^{Ph} cyclics (at about −32 ppm) were less than 10%. Branching for the unstirred interfacial polymerization was found to be minor; however, a significant increase in branching and cyclic formation was observed for the stirred system, resulting in the formation of a low molecular weight, low viscosity silicone oil. Branching was attributed to cleavage of phenyl groups from the siloxane backbone.

A number of interesting features were observed for the block copolymer prepared from the shorter dipotassium poly(methylphenylsiloxanediolate) (II) compared to the longer siloxanediolate III using unstirred interfacial polymerization. First, siloxanediolate II gave a high molecular weight elastomer with high polydispersity, whereas siloxanediolate III gave a much lower weight silicone oil with a reduced polydispersity. Siloxanediolate II also had about half the branching of

siloxanediolate III, and the branch length as a ratio of average DP, for siloxanediolate II, was about one-quarter of that for siloxanediolate III.

It is appeared that high-speed stirring disrupted the interface required for reaction, and the accelerated contact of monomers with each other resulted in a variety of unwanted side reactions, such as phenyl cleavage.

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