Preparation and Properties of Functionalized Polyorganosiloxanes

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ABSTRACT: A series of linear functionalized polyorganosiloxanes of the type $Me_3SiO[MeSiO(CH_2)_nR]_x(Me_2SiO)_ySiMe_3$, where $n = 2$, $R = —(CH_2)NMe_2$; $n = 1$, $R = —(CH_2)OEt$; $n = 4$, $R = —(CH_2)COOEt$; $n = 3$, $R = —(CH_2)Me$, have been prepared and characterized. Functional group loadings of ~4 mol % ($x = 1$, $y = 25$), ~11 mol % ($x = 3$, $y = 23$), and ~30 mol % ($x = 8$, $y = 18$) were obtained by reacting commercially available copolymers $Me_3SiO(MeSi\{H\}O)_x(Me_2SiO)_ySiMe_3$ with the appropriate ratios of $_{x:y}$, with the required quantities of $HO(CH_2)_nR$, using dichloro(1,5-cyclooctadiene)-platinum(II) as catalyst. Amine, ether, ester, and alkyl functionalized siloxanes were obtained in good yields after purification, and each fluid polymer has been characterized by ^1H and ^{13}C-nuclear magnetic resonance (NMR), and Fourier transform infrared (FTIR) spectral measurements, elemental analysis, viscosity, surface tension, and density measurements. The functionalized polymers exhibit Newtonian behavior over the range of shear rates 0.4–79.4 s^{-1}, and significant viscosity enhancements were observed for all functionalized polymers compared with poly(dimethylsiloxane) fluids of similar chain lengths. The functionalized siloxanes exhibited in almost all cases an increase in both viscosity and density as the functional group loading increased. The surface tensions of the polymers have also been determined and lie within the range 18.8–22.3 mN m^{-1}. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 808–817, 2001

Key words: functionalized polyorganosiloxanes; synthesis; spectral characterization; viscosity and surface tension

INTRODUCTION

Linear poly(organosiloxanes) containing pendant functional groups have recently attracted considerable interest[1–16] because of the many applications for which such materials are suitable as a result of the inherently flexible siloxane backbone, low glass-transition temperature, thermooxidative stability, low surface tension, and chemical and biological inertness of the parent polymer.[17,18] As a result of their hydrophobic nature, these fluid polymers also exhibit viscosification properties similar to those observed for much higher-molecular-weight organic polymers, such as hydrophobically modified polyvinyl alcohol (PVA).[19,20] Thus, this class of materials is of potential interest for important commercial applications, which include flocculation, emulsification,
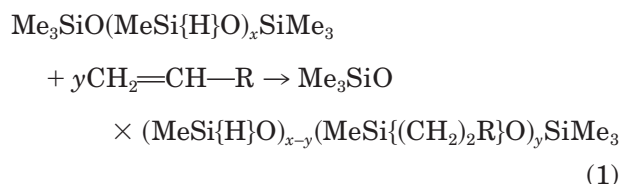
drag reduction, superabsorbency, latex paints, hydraulic fluids, surface active agents, coatings, and enhanced oil recovery operations (if the polymers can be made water soluble).

Poly(methylhydridosiloxanes), ($Me_3SiO(MeSi\{H\}O)_x(Me_2SiO)_ySiMe_3$), exhibit unique reactivity among the commercially available organosiloxanes. They undergo three basic types of synthetically useful reaction involving the Si—H group: (1) hydrosilylation reaction with unsaturated organic linkages, particularly 1-alkenes, to afford new Si—C linkages; (2) reaction with hydroxyl groups to yield new Si—O bonds; and (3) reactions in which they act as mild, selective reducing agents toward organic and inorganic substrates. To date, hydrosilylation reactions have been widely applied for the preparation of organofunctional siloxanes.[8,13,15] These reactions are catalyzed by a range of platinum, rhodium, palladium, ruthenium, nickel, and cobalt complexes, as well as various organic radical initiators, ultraviolet (UV) and γ-radiation. The choice of catalyst depends on many factors, including the type and nature of the silane, the solvent, and the organic substrate.[10]

$$Me_3SiO(MeSi\{H\}O)_xSiMe_3$$

$$+ yCH_2\!\!=\!\!CH\!-\!R \rightarrow Me_3SiO$$

$$\times (MeSi\{H\}O)_{x-y}(MeSi\{(CH_2)_2R\}O)_ySiMe_3$$

$$(1)$$

A variety of different functional groups R, including ester, crown-ether, amine, alkyl, and aryl,[8] may be incorporated as side-arm substituents on the polymer backbone using this methodology. Some of the resultant organofunctional fluids, including $Me_3SiO(Me_2SiO)_x[MeSi(CH_2)_n$—crown-ether]$_yOSiMe_3$, have used as selective extractants.[7,9,14] The main drawbacks in using this hydrosilylation reaction include difficulty in preparing the required 1-alkenylated organic precursor; introducing reactive groups that "poison" the metal catalyst; maximizing anti-Markownikow addition to afford a linear spacer chain, and obtaining complete replacement of all Si— H groups.

In view of these difficulties, we have investigated the reaction of primary alcohols $HO(CH_2)_nR$ with poly(methylhydridosiloxanes), $[Me_3SiO(MeSi\{H\}O)_x(Me_2SiO)_ySiMe_3]$, with various $x{:}y$ ratios, to produce Si—$O(CH_2)_nR$-containing compounds as an alternative means of attaching specific functional groups to polysiloxanes. As a wider range of primary alcohols containing other functionalities are readily available, and the reaction between Si—H and primary alcohols is facile, this procedure should expand the range of receptors that can be introduced into siloxane fluids. Many metal species, notably dialkyltin carboxylates and zinc carboxylates, catalyze the elimination of H_2O from silanols; these and other metal salts can be used to effect coupling of Si—H and ROH species:

$$\equiv Si\!-\!OH + HO\!-\!Si\!\equiv \rightarrow$$

$$\equiv Si\!-\!O\!-\!Si\!\equiv + H_2O \quad (2)$$
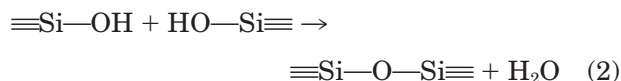
Our interest in organofunctional siloxane fluids is centered on their use as integrated solvent/carrier supported liquid membrane (SLM) systems,[8,11,14,21] which can be used to effect the separation of organic compounds from the aqueous phase. Consequently, we wished to generate a general procedure that could be used to synthesize linear materials with different loadings of various functional groups. In this article, we describe the preparation and characterization of amine, —$(CH_2)_3NMe_2$, ether, —$(CH_2)_2OEt$, ester, —$(CH_2)_5COOEt$, and alkyl, —$(CH_2)_4Me$ functionalized, linear poly(organosiloxanes) of the type $Me_3SiO(MeSiO(CH_2)_nR)_x(Me_2SiO)_y SiMe_3$.

EXPERIMENTAL

Materials

The three types of Si—H containing polyorganosiloxanes used in the syntheses—(3–4%)-methylhydrido-(96–97%)-dimethylsiloxane copolymers (M_r 1900–2000 and also ~13,300 daltons), (15–18%)-methylhydrido-(82–85%)-dimethylsiloxane copolymer (M_r 1900–2500 daltons), and (30–35%)-methylhydrido-(65–70%)- dimethylsiloxane copolymer (M_r of 1900–2100 daltons)—were supplied by Fluorochem. The four functional alcohols used—3-dimethylamino-1-propanol, ethyl-2-hydroxyhexanoate, 2-ethoxyethanol, and n-pentanol—were supplied by Aldrich and were dried over molecular sieves. Dichloromethane and methanol were supplied by E.M. Science and dried by standard procedures. The catalyst, dichloro(1,5-cyclooctadiene)platinum(II) was synthesized by a modification of a literature method.[22] All other reagents and solvents used
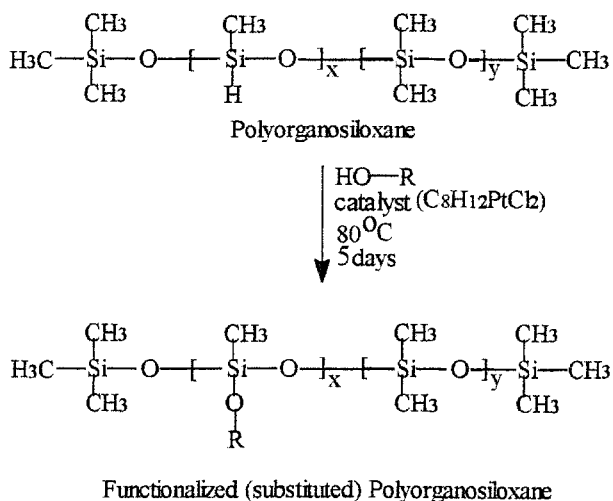
Figure 1 Reaction scheme and molecular structure of functionalized polyorganosiloxanes.

in the preparations were obtained from Aldrich or E.M. Science.

General Procedure

Fluid, functionalized polysiloxanes containing three different concentrations (i.e., 4, 11, and 30 mol %) of each of the four organofunctional groups—amine [-$(CH_2)_3NMe_2$], ether [-$(CH_2)_2Oet$], ester [-$(CH_2)_5COOEt$], and alkyl [-$(CH_2)_4Me$]—were prepared as shown in Figure 1. Each of the functional alcohols used in the synthesis was treated with the catalyst, dichloro(1,5-cyclooctadiene)platinum(II) before being added to the appropriate quantity of poly(organohydridosiloxane) in a flask fitted with a reflux condenser and stirrer. As the reaction is sensitive to moisture, all reagents and solvents were dried before use, and each reaction was carried out under an atmosphere of dry N_2 gas (*CARE*: H_2 evolved).

A typical preparation for an 11-mol % functionalized polymer is given below. Other polymers with ~4 and 30 mol % functionalization were made by an analogous procedure, using measured quantities of (3–4%)-methylhydrido-(96–97)-dimethylsiloxane and (30–35%)-methylhydrido-(65–70%)-dimethlylsiloxane copolymers. A summary of the syntheses and process conditions are given in Table I.

Preparation of 11 mol % Functionalized Polyorganosiloxanes

The four functional alcohols were each in turn treated with (15–18%)-methylhydrido-(82–85%)-dimethylsiloxane copolymer of molecular weight 1900–2500 daltons and viscosity 25–35 counts per second (cps). Typically, a measured quantity (30 g, 13.6 mmol) of the (15–18%)-methylhydrido-(82–85%)-dimethylsiloxane copolymer was charged into a flame-dried 150-mL single neck round-bottomed reaction flask fitted with a reflux condenser. A measured quantity of the amine functionalized alcohol, 3-dimethylamino-1-propanol (4.5 g, 40.8 mmol) was treated with 30 mg (8×10^{-5} moles) of dichloro(1,5-cyclooctadiene)platinum(II), and the mixture was added to the flask. The flask was placed in a hot oil bath and the contents held at 80°C, while being stirred under an atmosphere of dry N_2 gas. The reaction was continued for 24 h, after which a further 30 mg of catalyst was added, and the heating process continued for ~72 h at 80 ± 5°C.

The progress of the reaction was monitored in a qualitative manner using infrared (IR) spectroscopy. The Si—H bond produces a characteristic peak at 2166 cm^{-1}, and the intensity of this peak decreases as S—H addition occurs. The reaction was deemed to have reached completion when the intensity of the S—H peak was reduced to zero, or very close to zero, which was normally after ~4 days.

When reaction was complete, the reaction mixture was cooled, washed several times by decantation with 30-mL portions of methanol to remove the catalyst, soluble impurities and unreacted reactants. Dichloromethane (60 mL) was then added to dissolve the residual oil. The resulting solution was filtered and transferred to a rotary evaporator, and the solvent was removed under vacuum. Final traces of unreacted volatiles were removed under high vacuum (~0.05 mbar) at 50°C until the characteristic IR signal of the OH group of methanol (at 3000–4000 cm^{-1}) disappeared, leaving the product as a colorless oil. This was weighed and the yield determined by simple mass balance, after confirming that the product consisted solely of functionalized polysiloxane.

Typically, for the ether functionalized material, 2-ethoxyethanol (3.5 g, 38.1 mmol) was treated with 30 mg (8×10^{-5} moles) of the catalyst and then reacted with 28 g (12.7 mmol) of (15–18%)-methylhydrido-(82–85%)-dimethylsiloxane copolymer. For the ester functionalized material, ethyl-2-hydroxylhexanoate (6.6 g, 40.8

Table I   Summary of Polyorganosiloxane Syntheses, Process Conditions, Product Yields, and Functionalities*

Polymer[a]	Precursor[b]	Quantities Charged g (mmol)		Yield (%)	Functionality (%)
		Polymer	Precursor		
11 mol % Functionalized Polyorganosiloxanes					
1	A	30 (13.6)	4.5 (3 × 13.6)	83	11.4
2	B	28 (12.7)	3.5 (3 × 12.7)	97	11.3
3	C	30 (13.6)	6.6 (3 × 13.6)	48	10.4
4	D	30 (13.6)	3.6 (3 × 13.6)	86	12.2
30 mol % Functionalized Polyorganosiloxanes					
5	A	30 (14.6)	13.6 (9 × 14.6)	93	29.7
6	B	30 (14.6)	9.7 (9 × 14.6)	95	30.5
7	C	20 (9.8)	14 (9 × 9.8)	87	33.6
8	D	20 (9.8)	7.8 (9 × 9.8)	86	30.0
4 mole % Functionalized Polyorganosiloxanes					
9	A	30 (2.3)	1.7 (9 × 2.3)	95	3.6
10	B	30 (2.3)	1.5 (9 × 2.3)	96	3.7
11	C	30 (2.3)	2.7 (9 × 2.3)	91	3.8
12	D	30 (2.3)	1.5 (9 × 2.3)	81	4.0

* Reaction time for each of the above reactions: 120 h. Total quantity of catalyst normally added to each reaction: 60 mg (1.6 × 10^{-4} mol).

[a] 1–4: (15–18%)-methylhydrido-(82–85%)-dimethylsiloxane copolymer; 5–8: (30–35%)-methylhydrido-(65–70%)-dimethylsiloxane copolymer; 9–12: (3–4%)-methylhydrido-(96–97%)-dimethylsiloxane copolymer.

[b] A: 3-dimethylamino-1-propanol; B: 2-ethoxylethanol; C: ethyl-2-hydroxy-hexanoate; D: n-pentanol.

mmol) was treated with 30 mg (8 × 10^{-5} mol) of the catalyst and reacted with 30 g (13.6 mmol) of (15–18%)-methylhydrido-(82–85%)-dimethylsiloxane copolymer. For the alkyl functionalized polymer, 3.7 g (40.8 mmol) of n-pentanol was treated with the same amount of catalyst and then reacted with the same quantity of the polysiloxane polymer as noted above (Table I).

Preparation of Dichloro(1,5-Cyclooctadiene)-Platinum(II) Catalyst

The catalyst was prepared after a modification of the procedure reported in the literature.[22] A sample of 4.0 g (6.72 mmol) of hydrated chloroplatinic acid was dissolved in 12 mL of glacial acetic acid at 75°C in a 100-mL Erlenmeyer flask. 1,5-Cyclooctadiene (5.2 g, 6.72 mmol) was added to the warm solution, and the reaction mixture was swirled gently and then allowed to cool slowly to room temperature. The solution was diluted with 40 mL of distilled water to yield a black suspension. The mixture was stored for 1 h and then filtered using a Buchner funnel. The black solid

was collected, washed with 40 mL of distilled water and 80 mL of diethyl ether. The crude product was suspended in 1.6 l of dichloromethane and the mixture was heated at boiling for 5 min and then cooled to room temperature.

Chromatographic grade silica gel (100–200 mesh) (6.0 g) was then added and the mixture allowed to settle. The mixture was filtered and the solid residue washed with 200 mL of dichloromethane; the washings were added to the filtrate. The dichloromethane solution was evaporated until the product started to crystallize (~200 mL). The hot solution was then poured into 800 mL of petroleum ether (40–60°C) to yield the product as a white solid which was filtered and washed with 80 mL of diethyl ether and then dried at room temperature. The yield was 2.5 g (62.5%).

Experimental Measurements and Instrumentation

Each of the functionalized polyorganosiloxane polymers was characterized by elemental analysis, ^{1}H-NMR, and ^{13}C-NMR, and Fourier trans-

Table II   ¹H-NMR, ¹³C-NMR and FTIR Spectral Analyses

| ¹H-NMR Spectrum		¹³C-NMR Spectrum		FTIR Data (cm⁻¹)
H Atom	Peak Position (ppm)	C Atom	Peak Position (ppm)	
Amine Functionalized Polyorganosiloxanes (3.6, 11.4, and 29.7 mol %)				
Si—CH₃, singlet	0.09	Si—C	−2.80	2963, 2905
O—C—CH₂—C—N, multiplet	1.70	O—CH₂—C—CH₂—N	31.7	2822, 2785, 1446, 1412
N(CH₃)₂, singlet	2.23	—N(C)₂	46.7	1261, 1092
CH₂—N, multiplet	2.32	C—N	57.7	1022, 800
O—CH₂—, multiplet	3.72	O—C	61.7	688
Ether Functionalized Polyorganosiloxanes (3.7, 11.3, and 30.5 mol %)				
Si—CH₃, singlet	0.08	Si—C	2.20	2963, 2905
O—C—CH₃, triplet	1.20	O—CH₂—C	16.7	2872, 1445, 1414,
O—CH₂; O—CH₂, overlapping, multiplet	3.50	O—C—CH₃	62.7	1261,
Si—O—CH₂, multiplet	3.82	O—CH₂—C; O—C—CH₂	67.7; 72.7	1094, 1026, 801 and
				688 cm⁻¹
Ester Functionalized Polyorganosiloxanes (3.8, 10.4, and 33.6 mol %)				
Si—CH₃, singlet	0.09	Si—C	(−2.8)−2.2	2963, 2905
O—C—CH₂CH₂CH₂—C—C=O, overlapping, multiplet	1.10–1.85	O—CH₂CH₂—C—CH₂CH₂—C=O	14.7	2872, 1740, 1447, 1412
C—CH₃, triplet	1.24	CH₂—C	25.2	1261, 1093, 1022, 800
—CH₂—C=O, triplet	2.30	—C—CH₂—C=O	26.5	688
O—CH₂—, multiplet	3.69	O—CH₂—C	32.7	
O=C—O—CH₂—, quartet	4.13	O—CH₂CH₂—CH₂CH₂—C—	34.7	
		O—C	61.2	
		O=C—O—C	62.7	
Alkyl Functionalized Polyorganosiloxanes (4.0, 12.2, and 30.0 mol %)				
Si—CH₃, singlet	0.10	Si—C	(−3.3)−2.20	2963, 2907
—C—CH₃, triplet	0.90	—CH₂—C	14.7	2872, 1447
O—C—C—CH₂CH₂—C, overlapping, multiplet	1.35	O—CH₂CH₂—CH₂—C—CH₃	23.4	1412, 1261, 1095, 1023
O—C—CH₂, multiplet	1.55	O—CH₂CH₂—C—CH₂CH₃	28.7	800, 701
O—CH₂—, triplet	3.70	O—CH₂—C—CH₂CH₂CH₃; O—C	33.2	
			63.2	
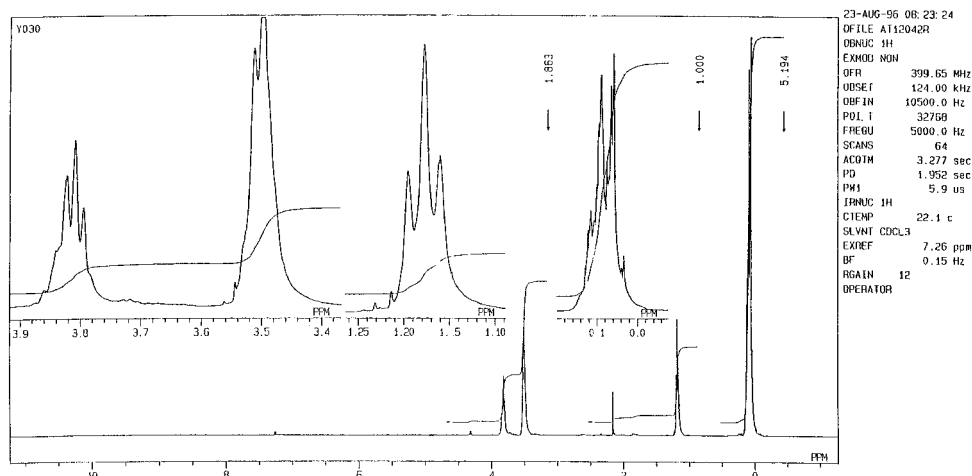
Figure 2 ^{1}H-NMR spectrum of 30 mol % ether functionalized polyorganosiloxane.

form infrared (FTIR) spectral measurements. Viscosity, surface tension, and density were also measured.

FTIR spectra were measured in the region 400–4000 cm^{-1}, using a Nicolet 20SXB FTIR with a deuterated triglycerine sulfate (DTGS) detector, or in some cases with a Perkin–Elmer 599b spectrophotometer. Proton and ^{13}C {^{1}H}-NMR spectra were recorded in CDCl$_3$, using a JNM-GX270 instrument equipped with a 5.0-mm carbon/hydrogen probe or, in some cases, with JEOL

PS 100 and GX 270 instruments. Between 12 and 64 scans were obtained for the proton spectra and 2000–4000 scans for ^{13}C spectra. Chemical shifts are given in ppm downfield from internal SiMe$_4$. IR and NMR data are summarized in Table II. Elemental analyses for carbon, hydrogen and nitrogen were performed using a Carlo Erba model 1106 Elemental Analyzer. Viscosity measurements were performed using Brookfield digital rotational viscometers at shear rates ranging within 0.4–79.4 s^{-1}. Surface tension measure-
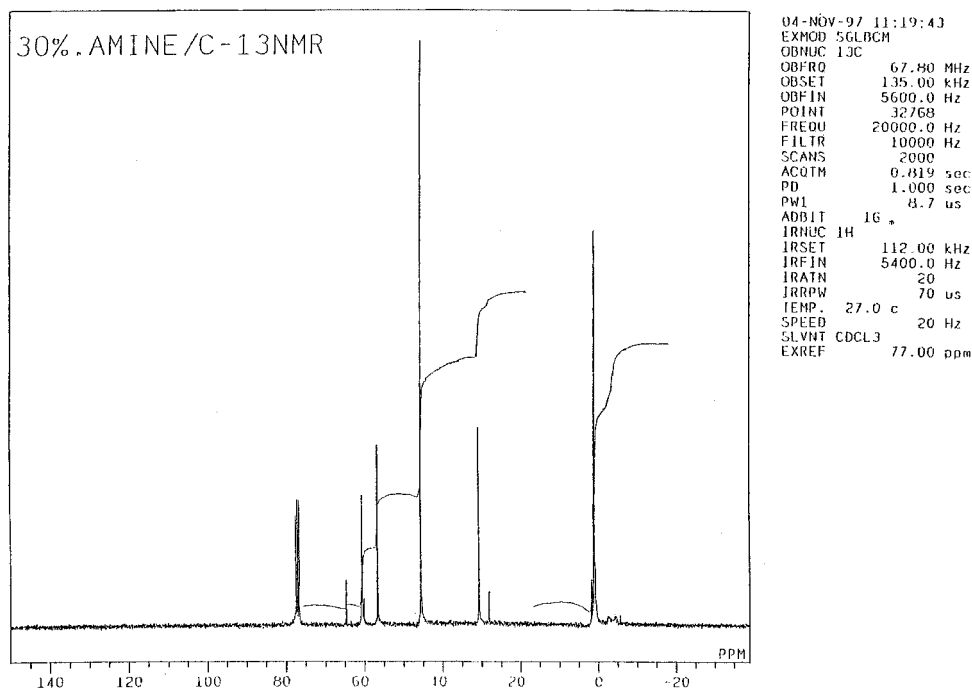
Figure 3 ^{13}C-NMR spectrum of 30 mol % amine functionalized polyorganosiloxane.
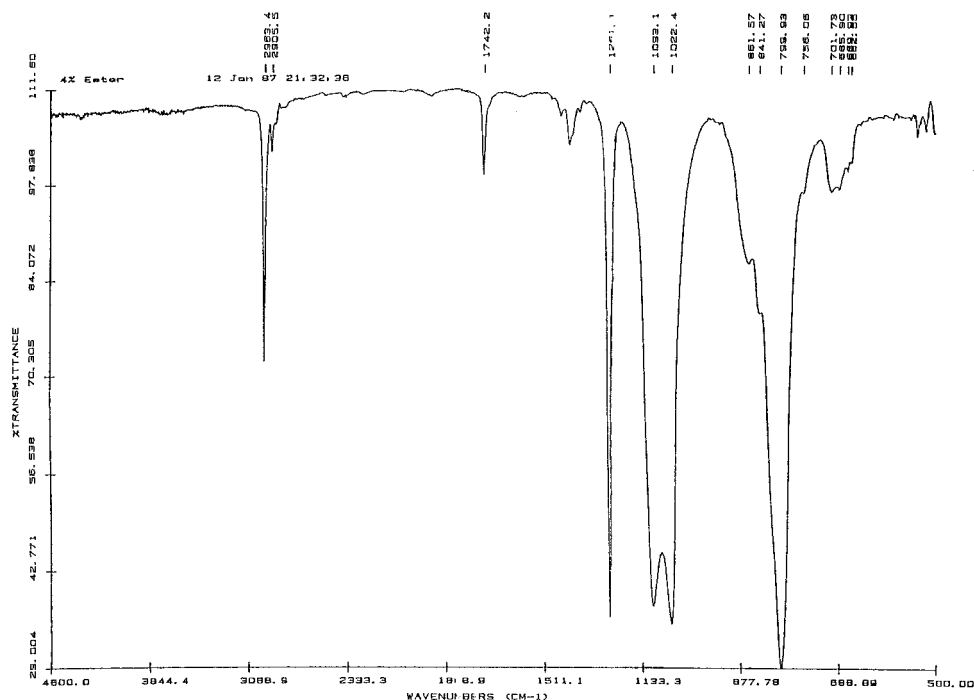
Figure 4   FTIR spectrum of 4 mol % ester functionalized polyorganosiloxane.

RESULTS AND DISCUSSION

Polymer Synthesis and Spectral Characterization

The platinum-catalyzed reaction of $HO(CH_2)_nR$ with Si—H containing siloxanes [$Me_3SiO(MeSi\{H\}O)_x(Me_2SiO)_ySiMe_3$] yielded fluid, functional siloxanes $Me_3SiO[MeSiO(CH_2)_nR]_x(Me_2SiO)_ySiMe_3$ with different concentrations of amine, ether, ester, and alkyl side-chains. Yields are given in Table I.

Each of the new polymers was analyzed and characterized by ^{1}H-NMR and ^{13}C-NMR spectra. The former were used to determine the degree of functional group loading of the products, and representative ^{1}H-NMR and ^{13}C-NMR spectra of ether and amine functionalized polymers are shown in Figures 2 and 3, respectively. To determine the degree of functionality accurately, x integrations for the total number of hydrogen atoms

in the side-arm functionality were compared with the total integrated signal for the Si—CH$_3$ groups (all centered at ~0.1 ppm); thus, the degree of functional group loading for each polymer was obtained. These values are summarized in Table I. It is apparent that there is good agreement between expected and observed loadings. The ^{1}H-NMR spectra of amine functionalized polyorganosiloxanes (4, 11, 30 mol %) are all expected to exhibit 5 signals, and as shown in Table II, all five signals were detected and have been assigned. NMR studies of the ether, ester, and alkyl functionalized polyorganosiloxanes are summarized in Table II and are illustrated for the ether containing product in Figure 2. In all cases, superimposition of two resonances reduces by one the number of observed signals compared with the number expected.

Each of the polymers was also characterized by FTIR spectroscopy. Major absorptions are summarized in Table II for each of type of functional polymer, and a representative spectrum of an ester containing product is shown in Figure 4. The polymers exhibit very similar spectral features, except for the ester functionalized polymer, which has an additional strong absorption band at 1740 cm^{-1} due to the C==O stretching mode of the ester group.

Table III   Elemental Analyses for Functionalized Polyorganosiloxanes

Polymer (mol %)	Found			Calculated		
	%C	%H	%N	%C	%H	%N
Amine Functionalized Polyorganosiloxane						
3.6	33.0	8.2	[a]	34.3	8.4	0.7
11.4	36.9	8.9	2.5	36.0	8.6	1.8
29.7	38.6	8.7	5.1	38.8	8.8	4.0
Ether Functionalized Polyorganosiloxane						
3.7	33.5	8.2	—	33.9	8.3	—
11.3	33.6	8.2	—	34.8	8.3	—
30.5	36.3	8.2	—	36.7	8.3	—
Ester Functionalized Polyorganosiloxane						
3.8	33.7	8.2	—	35.1	8.3	—
10.4	36.0	8.3	—	37.6	8.3	—
33.6	41.4	8.2	—	42.2	8.3	—
Alkyl Functionalized Polyorganosiloxane						
4.0	32.4	8.2	—	34.5	8.4	—
12.2	36.9	8.7	—	36.5	8.6	—
30.0	40.5	8.9	—	40.6	8.9	—
Dichloro(1,5-cyclooctadiene)platinum(II) catalyst ($C_8H_{12}PtCl_2$)						
	26.5	3.4	—	25.7	3.2	—

[a] Too low for accurate microanalysis on the instrumentation available.

Elemental analyses for the C and H and, where relevant, N, content of each functionalized polymer are presented in Table III. Calculated data are based upon the chemical structure of each of the polymers as obtained from the ^{1}H-NMR spectral analysis. Experimental and calculated results are generally in close agreement, thus confirming the identity and constitution of the products.

Material Properties

The viscosity and surface tension of each functionalized polymer were measured under varying conditions. Viscosity measurements were carried out at room temperature at shear rates ranging within $0.4–79.4$ s^{-1}, with the results summarized in Table IV. All polymers exhibited Newtonian behavior over the range of shear rates monitored, as the solution viscosity of each of the polymers was found to be constant within that range (Table IV). In addition, all the functionalized polymers exhibited higher viscosity than poly(dimethylsiloxane) analogues.

The incorporation of functional groups onto the backbone of the polyorganosiloxane is expected to promote intermolecular side-chain association, leading to an increase in hydrodynamic volume, and consequently an increase in the viscosity of the functionalized polymers. The enhancements observed in this study are consistent with reports in the literature for other hydrophobically associating polymers.[23,26–30] Furthermore, as the functional loading on the polymers increases from 4 to 30 mol %, most of the functionalized polyorganosiloxanes exhibit a sharp increase in viscosity consistent with the formation of large aggregates with a high hydrodynamic volume, and high resistance to shear and flow.[23–25,28,29] A small number of the polymers depart from this behavior, however. Measurements on these exceptions were repeated several times on freshly prepared samples, but with the same results. The figure for the 30 mol % alkyl functionalized polyorganosiloxane appears to be anomalously low, but we can offer no immediate explanation.

Table IV   Solution Viscosity, Surface Tension, and Density of Functionalized Polyorganosiloxanes

	Viscosity (cps)	Surface Tension (mN/m)	Density (g/cm^3)
Unfunctionalized Polyorganosiloxane			
(3–4%) methylhydrido copolymer	37.7	18.8	0.93
(15–18%) methylhydrido copolymer	34.9	19.3	0.94
(25–30%) methylhydrido copolymer	42.6	19.3	0.95
Amine Functionalized Polyorganosiloxane			
3.6 mol %	46.2	19.8	0.94
11.4 mol %	69.2	20.5	0.95
29.7 mol %	138	21.0	0.97
Ether Functionalized Polyorganosiloxane			
3.7 mol %	46.6	19.8	0.95
11.3 mol %	68.0	20.4	0.97
30.5 mol %	100.2	20.7	0.99
Ester Functionalized Polyorganosiloxane			
3.8 mol %	53.7	20.2	0.95
10.4 mol %	148.5	20.8	0.98
33.6 mol %	146	22.3	1.00
Alkyl Functionalized Polyorganosiloxane			
4.0 mol %	46.1	19.7	0.93
12.2 mol %	235	20.0	0.81
30.0 mol %	90.0	21.3	0.79

The surface tension of all functionalized and unfunctionalized polymers was determined, and these data are reported in Table IV. All polymers exhibit a high surface activity as the surface tension obtained for each of the polymers is low, ranging within 18.8–22.3 mN m^{-1}, at room temperature. These figures are in a similar range to the reported room temperature values of 16–21 mN m^{-1} for PDMS of various molecular weights.[31] This behavior can be attributed to the amphiphilic structure of the polymer, which also accounts for the tendency of the polymer to accumulate/adsorb at the interfaces between phases.

The results of the density measurements are given in Table IV. The functionalized polymers exhibit a greater density than that of unfunctionalized PDMS, and the density of the new polymers also increases as the functional loading increases, with the exception of the alkyl functionalized polymers which contain nonpolar side-arm substituents.

CONCLUSIONS

A series of novel, functionalized, hydrophobic, fluid polyorganosiloxanes of the type Me$_3$SiO-[MeSiO(CH$_2$)$_n$R]$_x$(Me$_2$SiO)$_y$SiMe$_3$ has been prepared in good yield by the reaction of Si—H-containing poly(methylhydridosiloxanes)dimethylsiloxane copolymers, [Me$_3$SiO(MeSi{H} O)$_x$ (Me$_2$SiO)$_y$SiMe$_3$], with primary alcohols containing terminal amine, ether, ester and alkyl functional groups using a dichloro(1,5-cyclooctadiene)platinum(II) catalyst. The products have been characterized by ^{1}H-NMR, ^{13}C-NMR, and FTIR spectra, and elemental analysis, and their viscosity, surface tension, and densities measured. Each of the polymers was found to exhibit Newtonian behavior over the range of shear rates 0.4–79.4 s^{-1} and also enhanced viscosity compared with poly(dimethylsiloxane) fluids. The functionalized polyorganosiloxanes also exhibit very low surface tension and an increase in viscosity and density as the functional group loading increases in almost all cases. The new polymers were found to be stable for a period of in excess of six months at room temperature as indicated by unchanging FTIR and ^{1}H-NMR spectra over that period.

REFERENCES

1. Spindler, R.; Shriver, D. F. Macromolecules 1988, 21, 648.
2. Zeldin, M.; Fife, W. K.; Tian, C.-X.; Xu, J.-M. Organometallics 1988, 7, 470.
3. Cabrera, I.; Kronganz, V.; Ringsdorf, H. Angew Chem Int Ed Engl 1987, 26, 1178.
4. Kaiser, A.; Schmidt, H.; Bottner, H. J Membr Sci 1985, 22, 257.
5. Duczmal, W.; Urbaniak, W.; Marciniec, B. J Organomet Chem 1986, 85, 317.
6. Ohyanagi, M.; Kanai, H.; Katayama, Y.; Ikeda, K.; Sekine, Y. Polym Commun 1985, 26, 249.
7. Abed-Ali, S. S.; Brisdon, B. J.; England, R. J Chem Soc Chem Commun 1987, 1565.
8. Abed-Ali, S. S.; Brisdon, B. J.; England, R. Macromolecules 1989, 22, 3969.
9. Ashworth, A. J.; Brisdon, B. J.; England, R.; Reddy, B. S. R.; Zafar, I. J Membr Sci 1991, 56, 217.
10. Barton, T. J.; Boudjouk, P. In Silicon-Based Polymer Science: A Comprehensive Resource, Advances in Chemistry Series 224; Zeigler et al., Eds.; American Chemical Society: Washington, DC; 1990; Chapter 1.
11. Brisdon, B. J. J Chem Technol Biotechnol 1993, 58, 303.
12. Brisdon, B. J.; England, R.; Reza, K.; Sainsbury, M. Tetrahedron 1993, 49, 1103.
13. Brisdon, B. J.; Watts, A. M. J Chem Soc Dalton Trans 1985, 2191.
14. England, R.; Abed-Ali, S. S.; Brisdon, B. J. Biotechnol Prog 1990, 6, 93.
15. Yilgor, I.; J. McGrath, E. In Polysiloxane Copolymers/Anionic Polymerization, Yilgor et al., Eds.; Advances in Polymer Science 86; Springer-Verlag: New York, 1988; p 1.
16. Bennett, M.; Brisdon, B. J.; England, R.; Field, R. W. J Membr Sci 1997, 137, 63.
17. Gill, J. S.; Marwah, U. R.; Misra, B. M. J Membr Sci 1993, 76, 157.
18. Noll, W. Chemistry and Technology of Silicones; Academic Press: New York, 1968.
19. Yahya, G. O.; Asrof Ali, S. K.; Al-Naafa, M. A.; Hamad, E. Z. J Appl Polymer Sci 1995, 57, 343.
20. Yahya, G. O. M.S. Thesis, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia, 1994.
21. Yahaya, G. O. Ph.D. Thesis, University of Bath, Bath, UK, 1998.
22. Drew D.; Doyle, J. Inorg Synth 1942, 13, 47.
23. Wang, K. T.; Illipoulos, I.; Auderbert, R. Polym Bull 1988, 20, 577.
24. Candau, A. H. F.; Selb, J. Macromolecules 1993, 26, 4521.
25. Kaczmarski , J. P.; Glass, J. E. Macromolecules 1993, 26, 5149.
26. McCormick, C. L.; Nandaka, T.; Johnson, C. B. Polymer 1988, 29, 731.
27. Landoll, L. M. J Polym Sci 1982, 20, 443.
28. Shulz, D. N.; Kaladas, J. J.; Maurer, J. J.; Bock, J.; Pace, S. J.; Shulz, W. W. Polymer 1987, 28, 2110.
29. Valint, P. L.; Bock, J. Macromolecules 1988, 21, 175.
30. L. M. Landoll, Neth. Pat. 8003, 241 (1989).
31. Owen, M. J. In Silicon-Based Polymer Science: A Comprehensive Resource, Zeigler et al., Ed.; Advances in Chemistry Series 224; American Chemical Society: Washington, DC, 1990; Chapter 40; p 705.