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(19) Randall, J. C. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 2083.
(20) Lindeman, L. P.; Adams, J. Q. *Anal. Chem.* **1971**, *43*, 1245.
(21) Kissin, Y. V. *Isospecific Polymerization of Olefins*; Springer-Verlag: New York, 1985.
(22) Boor, J., Jr. *Zieglar–Natta Catalysts and Polymerizations*; Academic: New York, 1979.
(23) Atarashi, Y. *Chem. High Polym.* (*Jpn.*) **1964**, *21*, 257.
(24) Atarashi, Y. *Chem. High Polym.* (*Jpn.*) **1964**, *21*, 409.
(25) Burfield, D. R. *J. Polym. Sci., Polym. Chem. Ed.* **1978**, *16*, 3301.
(26) Ray, G. J.; Johnson, P. E.; Knox, J. R. *Macromolecules* **1977**, *10*, 773.
(27) Cheng, H. N. *Polym. Bull.* (*Berlin*) **1985**, *14*, 347.
(28) Asakura, T.; Nishiyama, Y. *Macromolecules* **1987**, *20*, 616.

Comblike Polysiloxanes with Oligo(oxyethylene) Side Chains. Synthesis and Properties

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ABSTRACT: Comb polysiloxanes with oligo(oxyethylene) side chains of the type $-O(CH_2CH_2O)_nCH_3$ were synthesized from poly(methylsiloxane) and zinc octanoate as catalyst. The comb polymers, abbreviated as PMMS (followed by a number indicating the number of oxygen atoms in the side chain), were characterized by FTIR, NMR (^1H and ^{29}Si), and GPC. Thermal properties were studied by DSC. A considerable fraction of cyclics was found to be present in the polymers, and redistribution reactions result in comb polymers containing branched trisiloxy units. Side-chain crystallization is observed in all polymers except PMMS-5. Polymers with 5, 12, 16, and 22 oxygen atoms in the side chain are water-insoluble, but PMMS-8 was soluble enough to carry out cloud-point measurements in the presence of salts.

Introduction

We recently reported on the conductivity of solid complexes of lithium perchlorate with poly{[ω-methoxyhexakis(oxyethylene)ethoxy]methylsiloxane}, a comblike polysiloxane with pendant oligo(oxyethylene) groups containing an average of seven oxyethylene units.[1,2] Conductivities of $7 \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$ at 25 °C and between 10^{-4} and $10^{-3}\ \Omega^{-1}\ cm^{-1}$ at higher temperatures were found depending on the salt content of the polymer and the degree of cross-linking. While the importance of siloxane–oxyethylene block and graft copolymers has been known since the 1950s,[3] it is only recently that polysiloxane comb polymers with oligo(oxyethylene) side chains have been synthesized. Bannister et al.[4,5] synthesized such comb polymers because of their potential application in cryobiology while the conducting properties of their salt complexes were also investigated.[6] The polymers can be synthesized from poly(methylsiloxane) (PHMS) and a methoxypoly(ethylene glycol) (MPEG) with the aid of a basic catalyst. The reaction results in the elimination of hydrogen gas and the formation of the $Si-O(CH_2CH_2O)_nCH_3$ group. Kohama et al. have investigated a number of catalysts for the reaction of low molecular weight alcohols with PHMS.[7] Bannister used 2 mol of triethylamine/mol of Si–H and a reaction time of approximately 30 days. Our synthesis was carried out in THF with zinc octanoate as catalyst (*about 0.2% of available Si–H groups*) and a reaction time of 48 h to 1 week depending on the length of the MPEG. Metal octanoate catalysts have previously been employed in the preparation of model elastomeric polysiloxane networks.[8]

Because of their potential application in areas such as solid polymer electrolytes, foam stabilizers,[3] and biocompatible materials,[4,9] it is desirable to have definitive structural assignments for the comb polymers and to address the problem of chemical redistribution, an inherent property of polysiloxanes. In this paper the details of the synthesis and characterization of poly{[ω-methoxyoligo(oxyethylene)ethoxy]methylsiloxane}s by ^1H and ^{29}Si NMR, FTIR, elemental analysis, and GPC studies are reported.

Experimental Section

Materials. Poly(methylsiloxane) (PHMS), zinc octanoate (in poly(dimethylsiloxane)), and 1,3,5,7-tetramethylcyclotetrasiloxane (D4H) were purchased from Petrarch. The number average molecular weight of PHMS was determined by 100-MHz ^1H NMR by comparing the trimethylsiloxy end groups with the internal methyl group. Its value was found to be 2650. Methoxypoly(ethylene glycol)s (MPEG) of molecular weight 250, 350, 550, and 750 were Sigma products. MPEG-1000 was obtained by hydrolysis of methoxypoly(ethylene glycol) monomethacrylate (Polysciences) with a reported MPEG ester group of 1000. The hydrolysis was carried out in 0.1 N NaOH at 25 °C for 16 h. The MPEG-1000 was extracted into chloroform, the extract washed with water and dried, and the solvent removed. The final product and MPEG-750 were freeze-dried from benzene, while MPEG 250, 350, and 550 were dried by repeated azeotropic distillation with benzene on a rotary evaporator at reduced pressure.

Synthesis. Poly{[ω-methoxyoligo(oxyethylene)ethoxy]methylsiloxane}s, abbreviated as PMMS-*n*, were synthesized by adding a slight excess of the appropriate MPEG compound to a THF solution of PHMS (1 g/50 mL) and zinc octanoate as catalyst (*about 0.002 mol/mol of Si–H groups*). The temperature was kept at 60 °C, and the reaction times were 48 h for MPEG-250 and MPEG-350, 72 h for MPEG-550, and 7 days for MPEG-750 and MPEG-1000. After removal of solvent the polymers were purified by repeated precipitation into a 90/10 (v/v) mixture of hexane and THF to remove unreacted MPEG. The purity of the polymers was checked by 100-MHz ^1H NMR, ^{29}Si NMR, IR, GPC, and elemental analysis. The five polymers have been abbreviated as PMMS-5, -8, -12, -16, and -22, the number referring to the average number of oxygen atoms in the oligo(oxyethylene) side chain of the comb polymer.

The model cyclic tetramer 1,3,5,7-tetrakis[ω-methoxyhexakis(oxyethylene)ethoxy]-1,3,5,7-tetramethylcyclotetrasiloxane or D4G-8 was made from D4H and MPEG-350 in THF under conditions similar to those outlined for the corresponding polymer

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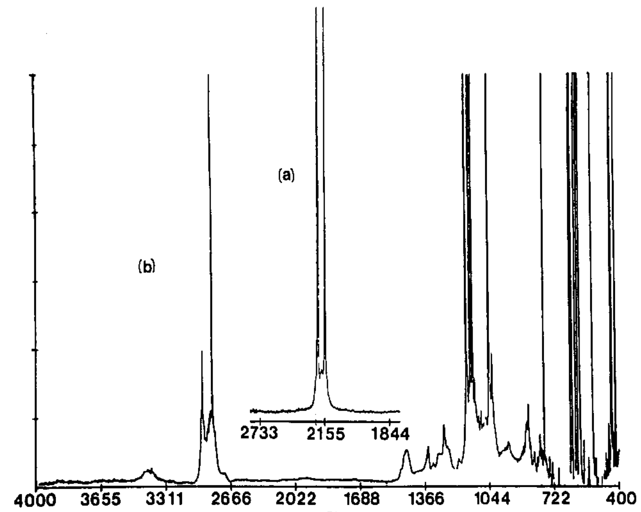
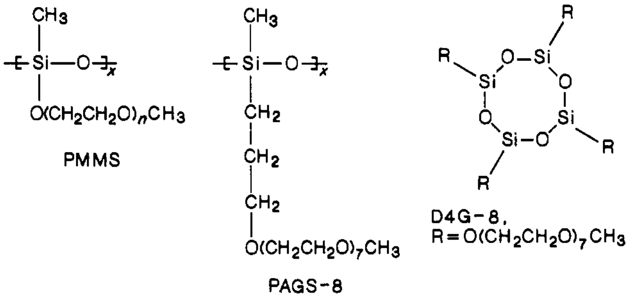


Figure 1. FT-IR of (a) Si–H stretching band of poly(methylsiloxane) and (b) PMMS-8 in CCl_4.

Chart I



PMMS

PAGS-8

D4G-8, R = $O(CH_2CH_2O)_7CH_3$

PMMS-8. The product was purified on a silica gel column with toluene as eluant. A sample of PMMS-8 was also fractionated on this column.

Measurements. Viscosities of the polymers were measured in water, THF, and toluene at 30 ± 0.1 °C by means of a conventional Ubbelohde viscometer. Thermal properties were studied on a Perkin-Elmer DSC-4 differential scanning calorimeter at a heating rate of 20 °C/min. The glass transition temperature (T_g) was taken at the inflection point, and the melting point (T_m) at the maximum of the melt peak.

Routine ^1H NMR spectra were run on a Varian XL-100 spectrometer, and ^{29}Si NMR spectra were recorded on a GN-500 spectrometer, using a flip angle of 45° and a pulse delay of 4 s. The long T_1 relaxation times typical for ^{29}Si nuclei were reduced by adding 0.02 M $Cr(Acac)_3$.[10] The NMR spectra were simulated by LAB ONE NMR 1, spectroscopic data analysis system.[11] Infrared spectra were recorded by using a Nicolet DX FTIR, and gel permeation chromatograms were obtained in THF with a Waters GPCIA instrument with 10^4-, 500-, and 100-Å ultrastyragel columns. Elemental analyses were kindly performed by the Dow Corning Corp.

Results and Discussion

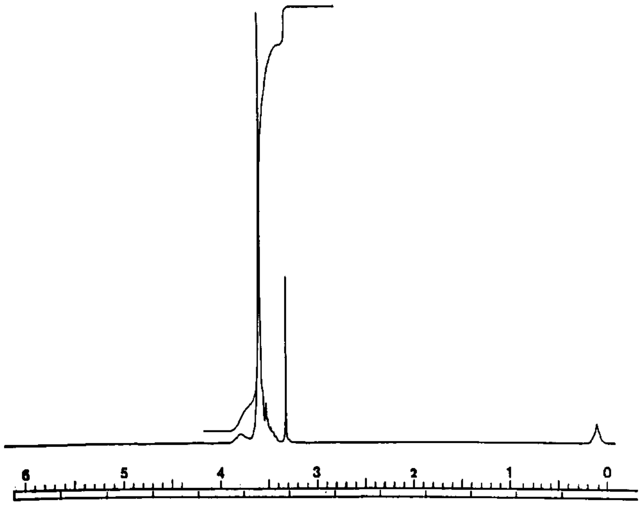


Figure 2. 100-MHz ^1H NMR spectrum of PMMS-8.

Table I
Substitution Yields and Si Analysis of Comb Polysiloxanes with Oligo(oxyethylene) Side Chains. Reaction of PHMS with Methoxypoly(ethylene glycol)s

polymer[a]	reactn time, h	% subst	% Si found	% Si calcd
PMMS-5	48	>99	8.50	8.46
PMMS-8	48	>99	7.54	7.50
PMMS-12	72	95	5.23	5.30
PMMS-16	168	90	3.54	3.60
PMMS-22	168	70		
PHMS			47.7	46.6

[a] Number following PMMS refers to the average number of oxygen atoms in the oligo(oxyethylene) side chains.

The reaction between MPEG and PHMS with zinc octanoate as catalyst results in a comb copolymer, the expected structure of which is depicted in Chart I. The progress of the reaction can be monitored by ^1H NMR or IR. From NMR the percent substitution can be calculated by comparing unreacted Si–H protons (4.60 ppm) with the Si–CH_3 protons at 0.20 ppm. Alternatively, the sensitive Si–H infrared doublet at 2200 and 2137 cm^{-1} can be monitored (Figure 1a). These bands are absent in the product PMMS-8 (Figure 1b), indicating an essentially quantitative substitution when methoxypoly(ethylene glycol) of MW 350 is used. The origin of the Si–H doublet in the PHMS FTIR spectrum is not well-understood. Neither the IR nor the ^{29}Si NMR reveal the presence of any D4H cycles in PHMS (*D4H has a single Si–H band at 2173 cm^{-1}*). It is possible that a peculiar backbone conformation causes the IR doublet, but more information is needed to pinpoint its origin. The Si–O–Si stretching band in PMMS-8 can be seen at 1050–1100 cm^{-1}, but there appears to be no Si–OH absorption at 3700 cm^{-1}.[12] Some absorbed moisture is the probable cause of the small OH band centered at 3500 cm^{-1}. The 100-MHz ^1H NMR spectrum of PMMS-8 (Figure 2) also lacks the 4.60 ppm peak characteristic for Si–H. The Si–CH_3 protons appear at 0.15 ppm. The width of this peak is probably due to overlap of the resonances from different microstructures (e.g., tacticity and end group) of the polymer backbone. The OCH_3 protons can be seen at 3.3 ppm and the bulk of the oligo(oxyethylene) protons at 3.6 ppm. The area of the peak at 0.15 ppm includes the trimethylsiloxy end group and is, therefore, slightly larger than the peak at 3.3 ppm. The methylene protons β to the Si atom are slightly downfield from the rest of the oxyethylene protons. The integration is consistent with a nearly quantitative substitution.

The results obtained with methoxypoly(ethylene glycol)s of different average length are collected in Table I. Longer reaction times are needed to achieve high conversions for the longer glycols. The substitution yields calculated from IR and NMR data agree well with those derived from elemental Si analysis. For longer glycols (i.e., n = 16 and 22) the substitution yield was only 70%. This result is in contrast to observations by MacFarlane et al. who reported nearly quantitative substitution with very long side chains using triethylamine as catalyst and reaction times of 30 days.[5]

Although the comb polymers were synthesized through a condensation reaction, the possibility of chemical redistribution and the formation of cyclic siloxanes should

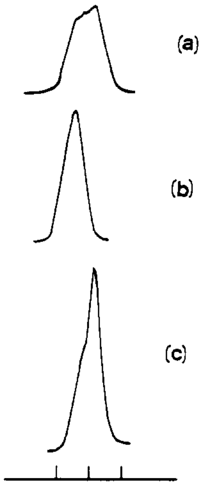


Figure 3. Gel permeation chromatogram of (a) PMMS-8, (b) fractionated PMMS-8, and (c) D4G-8 in THF.

Table II
Intrinsic Viscosities of Comb Polysiloxanes with Oligo(oxyethylene) Side Chains in Toluene and THF at 30 °C

	$10^2[\eta]_0$, dL/g	
polymer[a]	toluene	THF
PHMS		10.7
PMMS-8	5.6	5.15
PMMS-12	6.5	6.85
PMMS-16	7.0	7.5
PMMS-22	8.0	8.35
MPEG-350	3.0	3.0
MPEG-550	3.7	3.6
MPEG-750	3.8	3.8

[a] PHMS is the starting poly(methylsiloxane) of MW 2600. MPEG denotes methoxypoly(ethylene glycols) (Carbowax) of average MW 350, 550, and 750, respectively.

be considered especially since small cycles can adversely affect the properties of the comb polymers. In the ring-opening polymerization of substituted cyclic siloxanes, the formation of small cycles is favored when the substituents are large. For example, the cyclic content of bulk polymerized (3,3,3-trifluoropropyl)methylsiloxane at 100 °C is 82.7%, most of it in the form of cyclic tetramer and pentamer.[13,14] Hence, any redistribution in our system is likely to favor the formation of small cyclic species. This can be checked by GPC and ^{29}Si NMR. The gel permeation chromatogram of PMMS-8 given in Figure 3 displays a rather broad molecular weight distribution. Generally the molecular weight and broadness of its distribution relative to polystyrene standards are severely underestimated for comb polymers.[15] For example, the GPC of PMMS-8 of M_n = 17 500 had a higher retention volume (lower hydrodynamic volume) and a narrower peak profile than the PHMS of MW 2600 from which it was synthesized. This is also consistent with the higher intrinsic viscosity of PHMS in THF as compared to PMMS-8 (Table II). A comparison of the GPC of PMMS-8 and that of the cyclic tetrasiloxane D4G-8 (Chart I and Figure 3c) implies the presence of a significant amount of D4G-8 in the polymer (*the estimate is 25–30%*). A fractionated sample of PMMS-8 gave a much sharper GPC peak (Figure 3b) with apparently most of the cycles being removed.

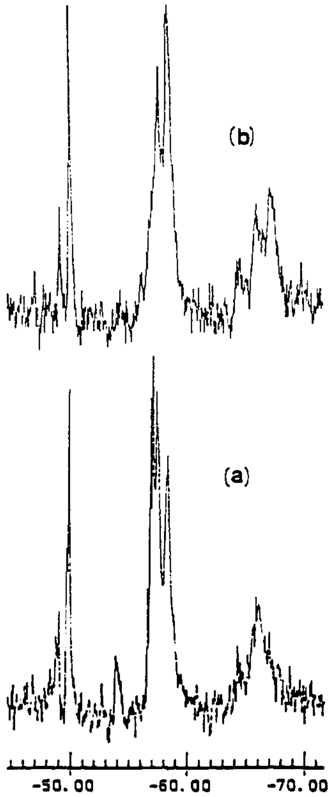


Figure 4. 100-MHz ^{29}Si NMR spectra of (a) D4G-8 and (b) PMMS-12.

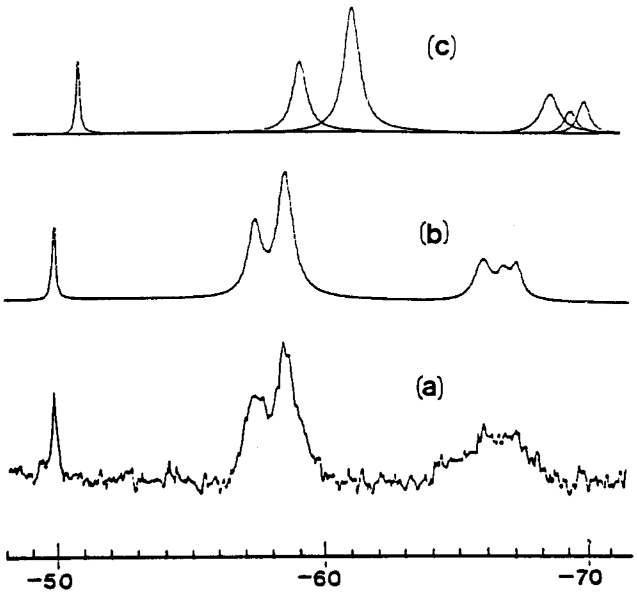


Figure 5. 100-MHz ^{29}Si NMR spectrum of PMMS-8: (a) experimental spectrum, (b) simulated (Lorentzian) spectrum, and (c) individual peaks of simulated spectrum (scale different from a and b).

In poly(dimethylsiloxane) ^{29}Si NMR is readily able to distinguish between the linear PDMS chain and the cycles D3, D4, and D5.[10] In Figure 4 the ^{29}Si NMR spectra of the cycle D4G-8 and of PMMS-12 are reproduced. The ^{29}Si NMR spectrum of PMMS-8 together with the simulated[11] (*Lorentzian line shape*) spectrum and individual simulated peaks are shown in Figure 5. D4G-8 has a triplet between −56.6 and −58 ppm that can be assigned to the cyclic tetramer. The triplet reflects stereochemical resolution due to isotactic, syndiotactic, and atactic resonances. A similar 1:2:1 triplet between −32.0 and −33.0 ppm is observed for D4H.[16] This absorption can also be found in the spectrum of the two polymers (*the amount of D4G-8 cycle is estimated to be about 25–30%*).

The assignments of the respective peaks can be made by a comparison with literature data.[17,18] Alkoxy and especially siloxy substituents bound to a Si atom result in

Chart II

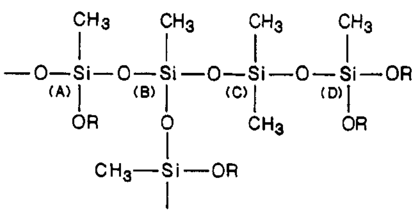


Table III
Glass Transition and Melt Temperatures of Comb Polysiloxanes with Oligo(oxyethylene) Side Chains

polymer	T_g, °C obsd	T_g, °C calcd[a]	T_m, °C
PMMS-5	−93	−94	
PMMS-8	−78	−75	−1
PMMS-8 (fract)[b]	−68	−75	−10
D4G-8	−72		−1
PMMS-12	−74	−73	15
PMMS-16			30
PMMS-22			39
PAGS-8[c]	−73	−73	−1

[a] From the Gordon–Taylor relationship. [b] Cycles removed by column chromatography. [c] Side chain is $-(CH_2)_3O-(CH_2CH_2O)_7CH_3$; see ref 2.

large upfield ^{29}Si NMR shifts. The spectrum of PMMS-8 has a dominant peak at −56 to −59 ppm that can be assigned to a Si atom with two siloxy and one OR substituent where in the comb polysiloxane R is the methoxypoly(ethylene glycol) branch (A unit, see Chart II). The peak around −57 ppm suggests that a considerable fraction of PMMS-8 consists of cyclic D4G-8 (the curve fit integration of this peak being about 25% of the total Si), an observation confirmed by our GPC data. A relatively strong absorption is found at −64 to −69 ppm and can be traced to a Si atom with three siloxy substituents (*B unit*). Integration indicates that about 20% of Si atoms are of this branched type. Branching can develop when in the redistribution process a silanolate anion attacks the reactive Si–OR bond to form a trisiloxy unit and RO^-. The latter species then can react with the siloxane backbone to form a chain with a terminal Si atom containing two OR and a siloxy substituent (D unit). This absorption is found at −49 ppm (Figure 4 and ref 17 and 18). A small peak at −22 ppm (not reproduced in Figure 4) can be traced to the presence of a small amount of dimethylsiloxane units (C). These can be incorporated into the backbone via redistribution reactions since the zinc octanoate catalyst is dissolved in dimethylsiloxane oligomer. The comb polymer remains completely soluble in toluene and THF, indicating that the branching does not cause the polymer to gel. None of the ^{29}Si NMR spectra show any quaternary $Si \equiv (OSi)_4$ which should appear at −100 ppm, and the absence of a peak at 35 ppm implies that the conversion of Si–H is essentially quantitative. The combined results suggest that the structure of the PMMS copolymers is considerably more complex than that represented by Chart I. For comb polymers made by hydrosilylation in which a $(CH_2)_3$ spacer separates the polysiloxane backbone from the $-(OCH_2CH_2)_nOCH_3$ side-chain branching and cyclization reactions are practically absent. Their ^{29}Si spectra resemble those of linear poly(dimethylsiloxane).[2]

Thermal Properties

The comb polysiloxanes PMMS-5, -8, and -12 are clear, viscous liquids at room temperature, while PMMS-16 and -22 are waxy solids. DSC scans for some of the materials are given in Figure 5 and the data collected in Table III.

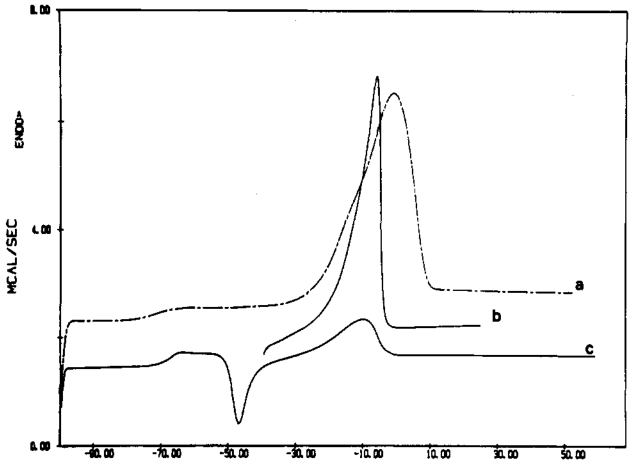


Figure 6. DSC thermograms of (a) PMMS-8, (b) PMMS-8 made with fractionated MPEG-350, and (c) PMMS-8 after removal of low molecular weight materials.

The T_g values for the respective polymers, starting with −93 °C for PMMS-5, are close to those calculated from the Gordon–Taylor relationship $T_g = N_1T_{g1} + N_2T_{g2}$ where N_1 and N_2 were taken as the mole fractions of siloxane and oxyethylene units, respectively. For T_{g1} the T_g = −123 °C of PDMS was used and for T_{g2} the value −66 °C of MPEG-350.

Except for PMMS-5 all the PMMS comb copolymers exhibit a melt endotherm close to that found for the MPEG methoxypoly(ethylene glycol) used as the side chain. For PMMS-8 and 12 the endotherms are quite broad. This may in part be due to the rather wide molecular weight distribution of the commercial MPEG glycols. To check this, a sample of MPEG-350 was carefully fractionated and a narrow fraction selected which by ^{1}H NMR gave a structure $HO(CH_2CH_2O)_{7.2}CH_3$. The GPC trace showed one main peak and small amounts of the higher and lower homologue. The PMMS-8 polymer made from this purified MPEG-350 has a much narrower melt peak than the regular PMMS-8 (Figure 6). The melt endotherm of PAGS-8 (Chart I), a polysiloxane comb polymer made by hydrosilylation of PHMS and a column-chromatographed allylmethylpoly(ethylene glycol ether), also is narrow.[2] Whether the presence of cycles in the PMMS polymers contributes significantly to the melt peak broadening is not clear. The cyclic siloxane D4G-8 (*a structure similar as PMMS-8 but a cyclic tetramer*) has a DSC scan very similar to PMMS-8. When the regular PMMS-8 is fractionated with removal of low molecular weight cycles (*see GPC results*), the melt endotherm does not appear to have narrowed (Figure 6), but its center has moved to lower temperature (Table II). The ^{29}Si spectrum of the fractionated PMMS-8 shows a higher fraction of branched siloxane units than in the nonfractionated sample, presumably because the removed D4G-8 cycle has less branched units than PMMS-8 (compare parts a and b of Figure 4). Increased branching may well contribute to the lower melt temperature of the fractionated sample. In general, our T_m values are lower than those reported by MacFarlane et al.[6] Different synthetic procedures with resulting differences in the fraction of cycles or other redistribution products may be the cause of this discrepancy.

It is noteworthy that PMMS-8 has a melt endotherm at all, since the comb polymethacrylate PMG-8 (MW ≈ 10^5) with the same pendant oligo(oxyethylene) chain is a viscous melt with a T_g of −58 °C but no melt peak.[19-21] Apparently the flexible polysiloxane backbone facilitates side-chain crystallization. As discussed in the next section, this appears to have important ramifications as to the water solubility of oligo(oxyethylene) comb copolymers as a function of the structure of the backbone.

Side-chain crystallization of the comb polymers is prevented when small amounts of salt in which one of the ions chelates with the oligo(oxyethylene) chain are present. For example, addition of lithium perchlorate at ratios of oxyethylene unit to $Li^+ \approx 20$ completely eliminates the melt endotherms in polymers such as PMMS-8 and PAGS-8.[1,2] Why the removal of cyclics in fractionated PMMS-8 caused a slowdown in the crystallization process (Figure 6) is not clear. Its DSC scan clearly shows a crystallization exotherm centered at −47 °C when a liquid nitrogen quenched sample in the DSC was reheated. This behavior was not found in the other polymers, although it is a common phenomenon when salts are solubilized in these polymers.[1,2,20]

Solution Properties

The PMMS comb polysiloxanes are soluble in most common organic solvents, for example, chloroform, aromatic hydrocarbons, tetrahydrofuran, and methanol. They are not soluble in aliphatic hydrocarbons. The small hydrodynamic volume of the comb polymers as implied from GPC data is confirmed by their low intrinsic viscosity values that were measured in toluene and THF (Table II). In the latter solvent the $[\eta]_0$ is higher for the starting polymer PHMS than for any of the comb copolymers, even PMMS-22. As expected, $[\eta]_0$ increases with the length of the oligo(oxyethylene) side chain, but the values are only 1.7–2.2 times higher than those of the corresponding methoxypoly(ethylene glycol)s. As far as their hydrodynamic volume is concerned comb polymers somewhat resemble the compact globular proteins which have $[\eta]_0$ values of 0.03–0.04 dL/g for molecular weights ranging from 14 000 to 250 000.[21]

The solubility behavior of the PMMS polymers in water is surprising. The only polymer for which we were able to carry out cloud-point measurements was PMMS-8 for which a 3% aqueous solution yields a cloud point, T_p, of 39 °C. PMMS-5, as expected, was not soluble in water, but so were PMMS-12, -16, and -22. This is peculiar since graft copolymers of polysiloxanes with oligo(oxyethylene) side chains are known to become more water-soluble when the oxyethylene content is increased.[3,22] We also found this to be the case for comb polymers with oligo(oxyethylene) chains anchored to a polymethacrylate backbone.[20] For example, the respective cloud points for comb polymethacrylates with an average of 4, 8, or 22 oxyethylene units in the side chain are 54, 83, or 102 °C, respectively.[21] Comb polymers synthesized from a styrene derivative containing a chain of seven oxyethylene units as para substituent are also water-soluble.[24] It is interesting to note that the PMMS-8 comb polysiloxane synthesized from the fractionated methoxypoly(ethylene glycol) of MW 350 (see thermal properties section) did not dissolve in water, while PMMS-8 made from the commercial product had a water solubility of at least 3%. The insolubility of the PMMS polymers cannot be attributed to the hydrolysis of the Si–O–C bond which would form insoluble structures of the type $CH_3SiO_{3/2}$. This bond in our comb polymers is hydrolytically quite stable in water. For example, PMMS-8 was left in water for several days, the water removed by evaporation and the polymer reprecipitated from hexane–THF (9/1 v/v). The polymer remained soluble in THF and toluene, and the IR and NMR spectra were identical with the original polymer. The observation of hydrolytic stability is consistent with that reported by MacFarlane for similar polymers.[6] Also, phase separation at the cloud point (vide infra) is a reversible process. The hydrolytic stability of the PMMS comb polymer may be due to steric interference of water molecules on approaching the polymer backbone.

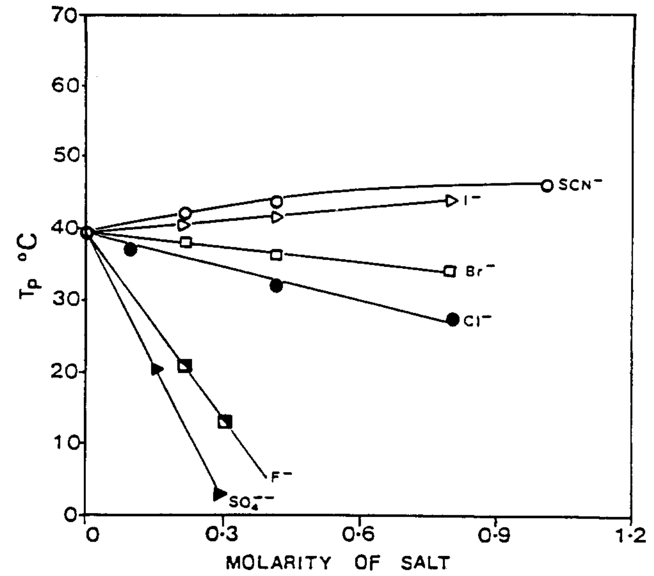


Figure 7. Change in cloud point of a 3% aqueous PMMS-8 solution on addition of sodium salts.

The cause of the peculiar behavior of PMMS polymers in aqueous media may lie in the ability of the side chains to organize in a closely packed structure. In the solid state this results in a more effective side-chain crystallization (vide supra). In aqueous solution it may hinder the penetration of water molecules, especially close to the hydrophobic polysiloxane backbone. Water-deficient regions close to the polysiloxane phases have also been reported in block copolymers of poly(dimethylsiloxane) and poly(oxyethylene) which were exposed to water.[25] The wider distribution of molecular weights in the commercial Carbowax as compared to the fractionated sample would hinder the packing of side chains in PMMS-8 and improve its water solubility as is observed. The comb polysiloxane with a $(CH_2)_3$ spacer in between the backbone and the oxyethylene units are all water-insoluble up to at least 12 units.[2] However, when the hydrosilylation reaction was carried out with a methoxypoly(ethylene glycol methacrylate) of 22 oxyethylene units, the resulting comb polymer was soluble. Apparently, the bulky and more polar $-CH_2C(CH_3)COO-$ spacer prevents close side-chain packing, at least in the backbone region.

Comb polyacrylates with long oligo(oxyethylene) side chains have been reported to form aggregates in water to the point where gels are formed.[26] The same, but to a lesser extent, has been claimed for the corresponding polymethacrylates. Our comb polymethacrylates[21] did not show any tendency to form gels in water. For comb polysiloxanes aggregation in water cannot be excluded. Some evidence for this in aqueous PMMS-8 solutions was found in the increased reduced viscosity on diluting the polymer solution. Aggregation may result from interactions between the hydrophobic polysiloxane backbones and/or between the long side chains because of their tendency to form ordered domains.

The solubility of PMMS-8 in water rapidly changes on adding salts. Figure 7 shows that the cloud point of this polymer increases or decreases depending on the nature of the salt, especially that of the anions. Fluorides or sulfates are very effective in salting out the polymer, while

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thiocyanates, and to a lesser extent, iodides slightly raise the cloud point. These results, to be discussed in more detail elsewhere, resemble those reported for the comb polymethacrylates[20] and are qualitatively similar to the behavior found in salt solutions of polymers or nonionic surfactants that are known to solubilize in water by hydrogen bonding, e.g., polymers with oxyethylene moieties.[27–29]

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References and Notes

(1) Fish, D.; Khan, I. M.; Smid, J. *Makromol. Chem., Rapid Commun.* **1986**, *7*, 115.
(2) Fish, D.; Khan, I. M.; Wu, E.; Smid, J. *Br. Polym. J.* **1988**, *20*, 281.
(3) Noll, W. *Chemistry and Technology of Silicones*; Academic: New York, 1968.
(4) Hall, P. G.; Davies, G.; McIntire, J. E.; Ward, I. M.; Bannister, D. J.; LeBrocas, K. M. F. *Polym. Commun.* **1986**, *27*, 98.
(5) Bannister, D. J.; Doyle, M.; MacFarlane, D. R. *J. Polym. Sci., Polym. Lett. Ed.* **1985**, *23*, 465.
(6) MacFarlane, D. R.; Bannister, D. J.; Barry, W. R.; Forsyth, M.; Jeffery, R. L. *Polym. Prepr., (Am. Chem. Soc., Div. Polym. Chem.)* **1987**, *28*(1), 405.
(7) Kohama, S.; Umeki, J. *J. Appl. Polym. Sci.* **1977**, *21*, 863.
(8) MacKnight, W. J.; Chundury, D. *Polym. Prepr., (Am. Chem. Soc., Div. Polym. Chem.)* **1983**, *24*(2), 67.
(9) Nagaoka, S.; Mori, Y.; Takiuchi, H.; Yokota, K.; Tanzawa, H.; Nishiumi, S. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1983**, *24*(1), 67.
(10) Williams, E. A. *Annu. Rep. NMR Spectrosc.* **1979**, *9*, 221.
(11) LAB ONE NMR 1, Spectroscopic Data and Analysis System, Syracuse University, 1986.
(12) Andersen, D. R. *Chem. Anal. (N.Y.)* **1974**, *41*, 247.
(13) Wright, P. V.; Semylen, J. A. *Polymer* **1970**, *11*, 462.
(14) Wright, P. V. In *Ring Opening Polymerization*; Ivin, K. J., Saegusa, T., Eds.; Elsevier: New York, 1984; Vol. 2, p 1058.
(15) Grubisic, Z.; Rempp, P.; Benoit, H. *J. Polym. Sci., Polym. Lett. Ed.* **1967**, *5*, 753.
(16) Harris, R. K.; Kimbler, B. J.; Wood, M. D. *J. Organomet. Chem.* **1976**, *116*, 291. Unpublished results from this laboratory.
(17) Marsmann, H. In *NMR, Basic Principles and Progress*; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer-Verlag: Berlin, 1981; Vol. 17, p 65.
(18) Smith, K. A. *Macromolecules* **1987**, *20*, 2054.
(19) Xia, D. W.; Smid, J. *J. Polym. Sci., Polym. Lett. Ed.* **1984**, *22*, 173.
(20) Fish, D.; Xia, D. W.; Smid, J. *Makromol. Chem., Rapid Commun.* **1985**, *6*, 761.
(21) Nwankwo, I.; Xia, D. W.; Smid, J. *J. Polym. Sci., Polym. Phys. Ed.* **1988**, *26*, 581.
(22) Tanford, C. *Physical Chemistry of Macromolecules*; Wiley-Interscience: New York, 1961; p 394.
(23) Dow Corning Corp. U.S. Patent 2,846,458, 1958.
(24) Sinta, R.; Smid, J. *Macromolecules* **1980**, *13*, 339.
(25) Haesslin, H. W.; Eicke, H. F. *Makromol. Chem.* **1984**, *185*, 2525.
(26) Gramain, P.; Frere, Y. *Polym. Commun.* **1986**, *27*, 16.
(27) Bailey, J.; Callard, R. H. *J. Appl. Polym. Sci.* **1959**, *1*, 56.
(28) Garvey, M. J.; Robb, I. D. *J. Chem. Soc., Faraday Trans. 1* **1979**, *75*, 993.
(29) Florin, E.; Kjellander, R.; Ericksson, J. C. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 2889.

Surface and Bulk Phase Separation in Block Copolymers and Their Blends. Polysulfone/Polysiloxane

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ABSTRACT: The relationship between bulk phase separation and surface segregation was elucidated in a series of polysulfone/polysiloxane alternating block copolymers and their blends with polysulfone. X-ray photoelectron spectroscopy (XPS) with angular dependence was used to obtain the compositional information from the top ~6 nm of the surfaces, and transmission electron microscopy (TEM) was used to characterize the bulk morphologies. In general, solvent-cast neat block copolymers had a layer (>6 nm) at the surface enriched in siloxane and the bulk had 10–50-nm microphase-separated domain structures. In the case of blends, siloxane surface enrichment was relatively high, even at bulk concentrations as low as 0.05% w/w siloxane. The surface siloxane concentration showed a rapid increase between 1 and 10% w/w bulk siloxane concentration, corresponding to the appearance of 0.1–10-μm diameter *macro*phases of block copolymer in the bulk. The blend surfaces attained surface compositions equivalent to pure copolymer at bulk concentrations above 10% siloxane, where phase inversion occurred in the bulk. XPS results indicated that the polysiloxane block length controlled the level of surface enrichment of siloxane, while the polysulfone block length influenced the *gradient* of surface composition, or the degree of phase mixing.

Introduction

Block or segmented copolymers have long sequences (blocks) of one chemical structure type of repeat unit, A, joined at one or both ends to long sequences of an another type, B. The dissimilar nature of the two blocks combined with the fact that they are chemically linked to each other manifests in a variety of surface and bulk properties quite different from those of the corresponding homopolymeric systems.[1] An attractive feature of these copolymers is their flexible molecular design parameters that can be controlled to tailor systems for specific applications. Some of those parameters are the chemical nature of the blocks, the architecture of the copolymer, diblock, triblock, or multi-

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