Reactions of Silyl Ketene Acetal-Functionalized Polysiloxanes. Synthesis of Sulfonated Polysiloxanes

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ABSTRACT: Treatment of silyl ketene acetal-functionalized polysiloxanes with (trimethylsilyl)sulfonyl chloride, followed by hydrolysis in sodium bicarbonate, affords sulfonated polysiloxanes in high yield. The precursors are prepared by hydrosilation of poly(hydromethylsiloxane) or copolymers of dimethyl and hydromethyl units with silyl ketene acetals bearing a terminal olefin. Polysiloxanes having between 30 and nearly 100% sulfonate groups have been easily prepared. The sulfonated polysiloxanes are water-soluble and amphiphilic and are able to solubilize hydrophobic molecules such as pyrene as suggested by fluorescence spectra. Potential uses for these new polymers include surfactants and anionic dopants for conducting polymers.

Introduction

Polysiloxanes are typically hydrophobic, and it is expected that introduction of ionic groups will afford amphiphilic derivatives with interesting properties. However, the preparation of such materials has received limited attention. Recently, Smid et al. reported a convenient method for the preparation of polysiloxanes with pendant oligo(ethylene oxide) and sulfonate groups which were examined as cation-conducting polymer electrolytes.[1] The sulfonates were prepared via sulfonation of appended epoxy groups. However, this approach necessitates a water-soluble precursor as aqueous sodium bisulfite was employed as the sulfonating agent. We wish to report a new approach to the sulfonation of polysiloxanes which takes place in organic solutions, affording a route to a wide range of initially water-insoluble polysiloxanes. Advantage is taken of the reaction of silyl ketene acetal-modified siloxanes,[2,3] developed in our laboratory, with (trimethylsilyl)sulfonyl chloride.[4] The trimethylsilyl sulfonate is then converted to the corresponding ionic sulfonate by hydrolysis in a mild base such as sodium bicarbonate. The chemistry is summarized in Scheme 1.

The trisiloxanes **1a** and **2a** were used as model compounds to establish reaction conditions. The silyl ketene acetal-modified tri- and polysiloxanes in Scheme 1 are easily prepared[2,3] by hydrosilation of the corresponding hydromethyl derivatives with silyl ketene acetals bearing terminal olefins. As copolymers of methylhydro- and dimethylsiloxane are commercially available, it is also possible to readily prepare polysiloxanes with varying degrees of sulfonation as indicated in Scheme 1. Two different silyl ketene acetal derivatives (**1** and **2** in Scheme 1) were employed. The ketene acetal **1** is ultimately derived from ethyl 2-methyl-4-pentenoate, which is commercially available. The more symmetric ketene acetal **2** is derived from the more expensive 3-buten-1-ol, although it is less sterically hindered and thus is expected to react more rapidly with electrophiles. This is particularly useful when the ketene acetal is to be employed as an initiator for group transfer polymerization (GTP),[5] as it helps to ensure that initiation is faster than propagation to afford low polydispersities. Cyclic siloxanes functionalized with this type of silyl ketene acetal can be used as initiators for the GTP synthesis of PMMA star polymers.[3] We describe here the details of the preparation and characterization of the new sulfonated polysiloxanes.[6]

Experimental Section

A. Materials. Poly(methylhydrosiloxane) (PMHS) ($M_n \approx$ 4500–5000), 50–55% methylhydrosiloxane/45–50% dimethylsiloxane copolymer ($M_n \approx$ 900–1000), and 30–35% methylhydrosiloxane/65–70% dimethylsiloxane copolymer ($M_n \approx$ 2000–2100) were acquired from Petrarch. Platinum divinyltetramethyldisiloxane complex (3% in xylene) (Petrarch) was stored in a refrigerator. Bis(trimethylsiloxy)methylsilane (BTMS) was a gift from GE Silicones and distilled from calcium hydride. Trimethylsilyl chloride (TMSCl), ethyl 2-methyl-4-pentenoate, methyl trimethylsilyl dimethylketene acetal (MTDA), methyl isobutyrate, and 3-buten-1-ol were acquired from Aldrich and distilled prior to use. (Trimethylsilyl)sulfonyl chloride, lithium diisopropylamide (in heptane/tetrahydrofuran/ethylbenzene), sodium bicarbonate, potassium carbonate, anhydrous dichloromethane, and anhydrous ether were acquired from Aldrich and used as received. Pyrene was acquired from Aldrich and recrystallized twice from ethanol. Poly(styrenesulfonate) was obtained from Aldrich (M_n = 70 000). Toluene and THF were distilled from sodium benzophenone. Spectra/Por dialysis membranes were acquired from Polysciences and had a molecular weight cutoff of approximately 1000 Da.

B. Measurements. ^{1}H, ^{13}C, and ^{29}Si NMR and ^{13}C–^{1}H chemical shift correlation spectra were obtained on a Varian XL-200 spectrometer. Solvent peaks were used as the internal standards. FT-IR spectra of the reactions between silyl ketene acetal-functionalized siloxanes and (trimethylsilyl)sulfonyl chloride in a gastight IR cell were recorded on a Perkin-Elmer 1850 instrument. Emission spectra of pyrene (excitation wavelength at 263 nm) were obtained with a Perkin-Elmer LS-5 fluorescence spectrometer. Melting points were determined on a Mel-Temp melting point apparatus and were uncorrected.

C. Preparation of Silyl Ketene Acetal-Functionalized Siloxanes 1a, 1b, 2a, and 2b. We employed our previously reported procedure for the preparation of the necessary 3-butenyl trimethylsilyl 2,2-dimethylketene acetal and the silyl ketene acetal-modified trisiloxane **2a**[3] and applied it to the synthesis of the related compound **1a**. Polysiloxane **1b** was prepared earlier using ethyl trimethylsilyl 2-methyl-2-allylketene acetal (ETMA),[2] although in the present work we modified the hydrosilation conditions by employing the platinum divinyltetramethyldisiloxane complex rather than chloroplatinic acid as the catalyst. The following is a detailed description for the modified procedure for the preparation of **1b**. (Polymer **2b** was prepared in a similar manner.) A 500-mL three-neck round-bottom flask was fitted with a reflux condenser, magnetic stirring bar, and rubber septum. The reflux condenser was connected to a drying tube. After the flask was flame-dried, it was charged with 6 g of PMHS (0.1 mol),

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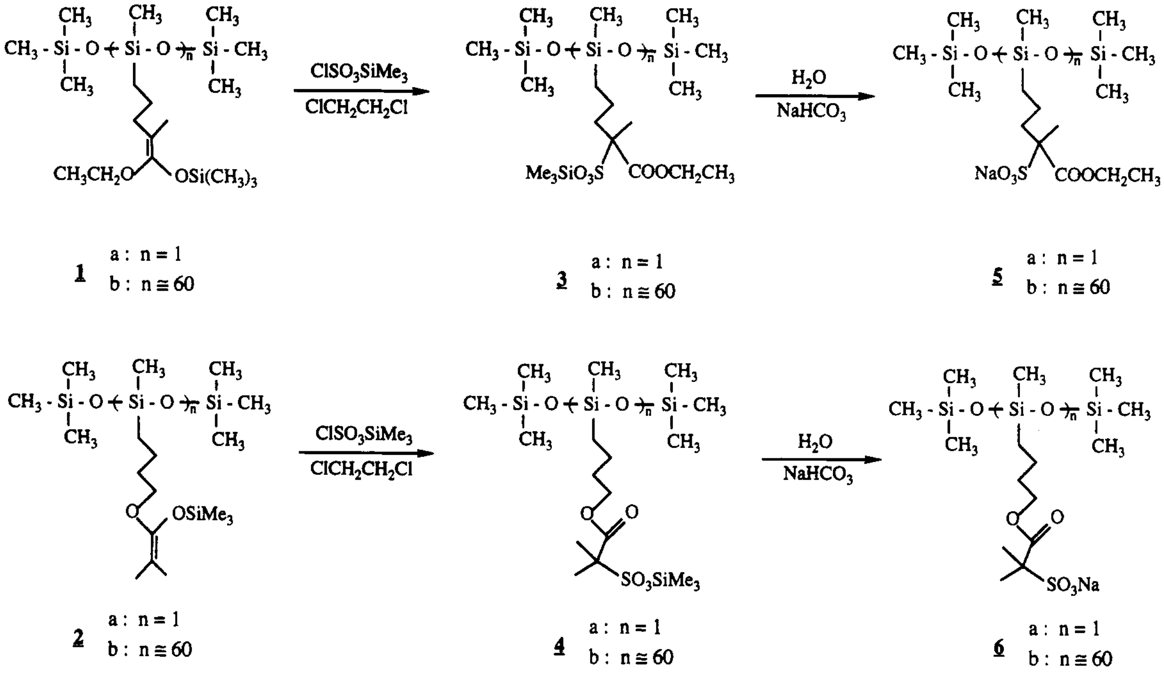
Scheme 1



21.9 g of ETMA (0.1 mol), 250 mL of dry toluene, and 10 drops of platinum divinyltetramethyldisiloxane solution. The flask was immersed in an oil bath at 60 °C and the solution was continuously stirred. The reaction was kept at 60 °C for 24 h, during which time IR spectroscopy was used to follow the reaction. A small amount (<5%) of Si–H groups remained after 24 h and were reacted in a similar fashion for another 6 h with dried 1-hexene (0.5 mL). Solvent, unreacted ETMA, and 1-hexene were removed by rotary evaporation, and the resulting liquids were kept under 0.7 mmHg for 24 h. ^1H NMR ($CDCl_3$, δ (in ppm from $CHCl_3$)): **1a** 3.65 (m, 2H, OCH_2), 1.93 (m, 2H, allyl, CH_2), 1.50 (double singlet, 3H, methyl, $CH_3C{=}C$), 1.33 (m, 2H, CH_2), 1.19 (m, 3H, methyl, CH_3CH_2), 0.42 (m, 2H, CH_2Si), 0.17 (s, 9H, $OSi(CH_3)_3$), 0.09 (s, 18H, $OSi(CH_3)_3$), –0.02 (s, 3H, $Si(CH_3)$; **1b**, 3.82 (q, 2H, OCH_2), 2.38 (m, 2H, allyl, $CH_2C{=}$), 1.84 (double singlet, 3H, methyl, CH_3), 1.80 (overlapping, 2H, $SiCH_2CH_2$), 1.23 (m, 3H, methyl, CH_2CH_3), 0.92 (br, 2H, $SiCH_2$), 0.46 (s, 9H, $Si(CH_3)_3$), 0.34 (s, 3H, $SiCH_3$); **2a**, 3.66 (t, 2H, OCH_2), 1.57 (m, overlapping, CH_2CH_2), 1.52 (d, 6H, methyl, CH_3), 1.38 (m, 2H, $SiCH_2CH_2$), 0.44 (t, 2H, $SiCH_2$), 0.17 (s, 9H, methyl, $Si(CH_3)_3$), 0.07 (s, 18H, $2Si(CH_3)_3$), –0.02 (s, 3H, $SiCH_3$); **2b**, 3.71 (t, 2H, OCH_2), 1.60 (m, overlapping $CH_2CH_2CH_2$), 1.51 (d, 6H, methyl, CH_3), 1.34 (m, 2H, $SiCH_2CH_2$), 0.47 (t, 2H, $SiCH_2$), 0.20 (s, 9H, methyl, $Si(CH_3)_3$), 0.04 (s, 3H, $SiCH_3$).

D. Reactions of Silyl Ketene Acetal-Modified Polysiloxanes with (Trimethylsilyl)sulfonyl Chloride and Hydrolysis to the Sulfonates. Representative examples with the heptamethyltrisiloxane **1a** and polysiloxane **1b** follow. Sulfonations of methyl trimethylsilyl dimethylketene acetal,[5] **2a**, **2b**, and partially silyl ketene acetal-functionalized polysiloxanes derived from the hydrosilation of copolymers of dimethyl and hydromethylsiloxane with either vinyl-bearing silyl ketene were carried out in a similar manner.

(a) Reaction of 1a with (Trimethylsilyl)sulfonyl Chloride. To a solution of **1a** (20 mmol) in 100 mL of anhydrous dichloroethane in a drybox was added dropwise (trimethylsilyl)sulfonyl chloride (20 mmol). The reaction was allowed to proceed for 2 h. The reaction was followed by IR spectroscopy using a gastight IR cell. Dichloroethane and the trimethylsilyl chloride byproduct were removed using a rotary evporator and then by pumping at 70 °C (ca. 4 mmHg) for another 2 h. The product **3a** was a colorless liquid. ^1H NMR ($CDCl_3$, δ (in ppm from TMS)): 4.15 (q, 2H, OCH_2CH_3), 2.24–1.72 (two double triplets, 2H, CH_2CSO_3), 1.41 (s, 3H, methyl CH_3), 1.18 (t, 3H, OCH_2CH_3) ~1.10 (overlapping, 2H, $SiCH_2CH_2$), 0.59 (br, 2H, $SiCH_2CH_2$), 0.27 (s, 9H, $SO_3Si(CH_3)_3$), 0.11 (s, 18H, $OSi(CH_3)_3$), –0.02 (s, 3H, $SiCH_3$).

(b) Hydrolysis of 3a to Obtain 5a. **3a** was added dropwise with continuous stirring to a saturated sodium bicarbonate aqueous solution until the pH reached 7. Most of the water was removed by a rotary evaporator, and then the residues dried under vacuum at 60 °C overnight. The product was a pale yellow solid. ^1H NMR (D_2O, δ (in ppm from TMS)): 4.01 (q, 2H, OCH_2), 2.18, 1.53 (two double triplets, 2H, CH_2CSO_3), 1.28 (s, 3H, methyl, CH_3), 1.14 (t, 3H, methyl CH_2CH_3), ~1.06 (overlapping, 2H, $SiCH_2CH_2$), 0.39 (t, 2H, $SiCH_2$), 0.07 (s, 18H, $2Si(CH_3)_3$), –0.04 (s, 3H, $SiCH_3$).

(c) Reaction of 1b with (Trimethylsilyl)sulfonyl Chloride. A 100-mL one-neck round-bottom flask was flame-dried, flushed with dry argon, transferred to a drybox, and equipped with a magnetic stirring bar. The flask was charged with 50 mL of anhydrous dichloroethane and polysiloxane **1b** (20 mmol). Next, (trimethylsilyl)sulfonyl chloride (5.0 g, 26.5 mmol) was added dropwise with continuous stirring over 30 min. The solution was stirred for an additional 4 h. Solvent and unreacted (trimethylsilyl)sulfonyl chloride were removed by distillation at reduced pressure. The resulting polymer **3b** was a light brown, viscous liquid. ^1H NMR ($CDCl_3$, δ (in ppm from TMS)): 4.25 (q, 2H, OCH_2CH_3), 2.39, 192 (two triplets, 2H, CH_2CSO_3), 1.69 (s, 3H, methyl, CH_3CSO_3), 1.28 (t, 3H, OCH_2CH_3), 1.10 (br, 2H, $SiCH_2CH_2$), 0.85 (b, 2H, $SiCH_2CH_2$), 0.38 (s, 9H, $SO_3Si(CH_3)_3$), 0.12 (s, 3H, $SiCH_3$).

(d) Hydrolysis of 3b to Obtain 5b. **3b** was added dropwise with continuous stirring to a 200-mL saturated aqueous sodium bicarbonate solution. After addition, the solution was concentrated on a rotary evaporator. The product was purified by repeated dialysis using a 1000 MW cutoff membrane over 10 days and then dried by azeotroping with benzene followed by storage in a vacuum oven at 60 °C for 4 days. ^1H NMR (D_2O, δ (in ppm from TMS)): 4.11 (q, 2H, OCH_2CH_3), 2.18, 1.65 (two triplets, 2H, CH_2CSO_3), 1.57 (s, 3H, methyl, CH_3CSO_3), 1.15 (t, 3H, methyl, CH_2CH_3), 1.07 (br, 2H, $SiCH_2CH_2$), 0.48 (t, 2H; $SiCH_2$), 0.00 (s, 3H, $SiCH_3$).

E. Fluorescence Spectra. These were recorded with an excitation wavelength of 263 nm. All measurements were carried out at least twice at room temperature and were not corrected. Samples were prepared by adding pyrene (3 mg), pyrene (3 mg) plus poly(styrenesulfonate) (50 mg), or pyrene (3 mg) plus a 50% sulfonated polysiloxane derived from a 50:50 copolymer of diethylsiloxane and hydromethylsiloxane (5 mg) to deionized water (20 mL). The solutions were then vortexed and immersed in a 35 °C water bath overnight.

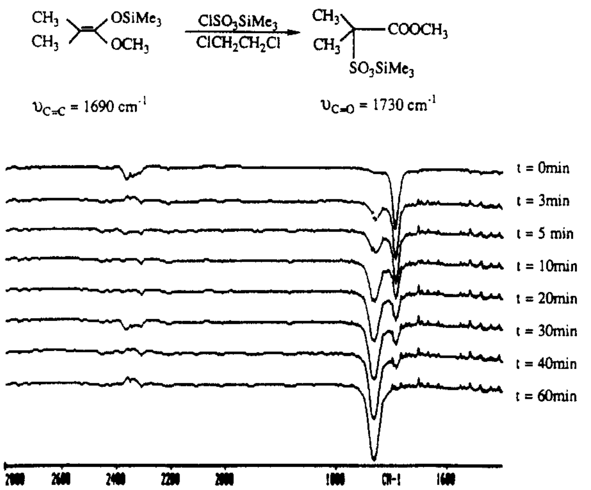


Figure 1. IR spectra of MTDA in the presence of (trimethylsilyl)sulfonyl chloride as a function of time.

Results and Discussion

Synthesis and Structure Confirmation. The silyl ketene acetal-modified siloxanes (1 and 2) were easily prepared via hydrosilation of terminal olefin-bearing ketene acetals. In the present work, a small amount of 1-hexene was added after the hydrosilations to ensure complete reaction of all Si–H groups. The polymers **1b** and **2b** therefore contain about 2–5% hexyl groups.

IR spectroscopy (Figure 1) provides a convenient means to follow the kinetics and extent of reaction of silyl ketene acetals with electrophiles such as (trimethylsilyl)sulfonyl chloride because the C═C stretch of the ketene acetal (ca. 1690 cm^{-1}) is easily distinguished from the carbonyl stretch of the resulting ester (ca. 1730 cm^{-1}). Figure 2 shows plots of the disappearance of the C═C stretch as a function of time for three silyl ketene acetals (**1a**, **2a**, and methyl trimethylsilyl dimethylketene acetal (MTDA)) during their reaction with(trimethylsilyl)sulfonyl chloride in 1,2-dichloroethane. All three react completely in under 2 h, although the one with the most sterically hindered nucleophilic carbon (**1a**) is the slowest. The derivatives can be readily hydrolyzed in aqueous sodium bicarbonate to afford the sodium sulfonates in almost quantitative yield.

NMR spectroscopy was used to confirm the structures of the sulfonated trisiloxy and polysiloxane materials. ^{1}H and ^{13}C NMR chemical shifts for these materials are summarized in the Experimental Section, and for the most part the assignments are straightfoward. We only discuss here the ^{1}H NMR data for **5a** and **5b** as these are the most complex due to the asymmetric carbon adjacent to the sulfonate. The complete ^{1}H and ^{13}C NMR spectra for **5a** are shown in Figure 3 along with the corresponding carbon–proton correlated 2D spectrum. In the ^{1}H NMR spectrum there are two "double triplet" peaks at ca. 1.6 and 2.2 ppm and integration indicates one proton is responsible for each. We tentatively assigned these resonances to the methylene proton adjacent to the sulfonated carbon. Because these methylene protons are adjacent to a chiral center, they are not chemical shift equivalent and thus are coupled with each other. The carbon–proton correlation 2D spectrum confirmed this assignment as it indicates that the two ^{1}H NMR peaks mentioned above result from protons of the same carbon. We also note that the H2 peak, which cannot be seen in the ^{1}H NMR spectrum as it is buried in the H8 peak, can be clearly seen from the 2D NMR presentation because C2 has a much different chemical shift from C8 in the ^{13}C spectrum.

It is well known that polysiloxanes are sensitive to acid- and base-catalyzed cleavage.[7] To minimize degradation, the sulfonation reactions were carried out in a drybox to minimize proton generation by premature hydrolysis of the trimethylsilyl sulfonate, and the mild base bicarbonate was employed in the hydrolysis to the ionic sulfonate. Evidence that degradation is not important under these conditions comes from gel electrophoresis and ^{29}Si NMR experiments. Regarding the former, a sample of polymer **5b** reveals a broad molecular weight distribution centered at ca. 10 000 Da vs poly(styrenesulfonate) standards,[8] and comparison with a sample of a tetrasulfonated cyclic siloxane[9] suggests that degradation to low molecular weight cyclics is negligible. Also, the presence of a single ^{29}Si NMR peak at ca. −22 ppm, typical of linear polysiloxanes,[10] argues against significant equilibration with cyclic tetramers and higher cyclics under the sulfonation and hydrolysis conditions.

Properties of Sulfonated Polysiloxanes. The heavily sulfonated polysiloxanes discussed above are completely water soluble and appear to be powerful surfactants; i.e., significant foaming is observed when dilute aqueous solutions are vigorously shaken. While these particular polymers are insoluble in nonpolar organics such as chloroform, it is possible to adjust the solubility by preparing sulfonated materials derived from copolymers

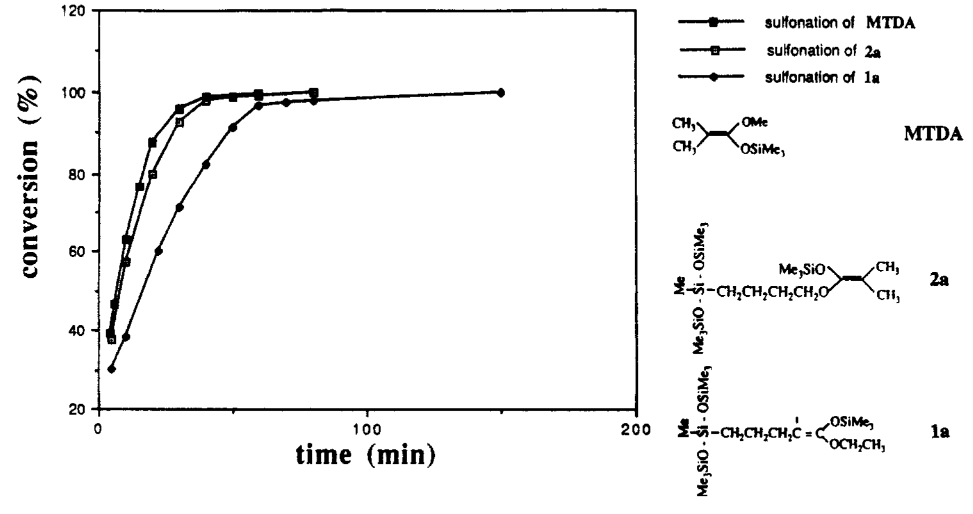


Figure 2. Plots of the disappearance of the C═C stretch of silyl ketene acetals **1a**, **1b**, and MTDA upon reaction with (trimethylsilyl)sulfonyl chloride as a function of time.

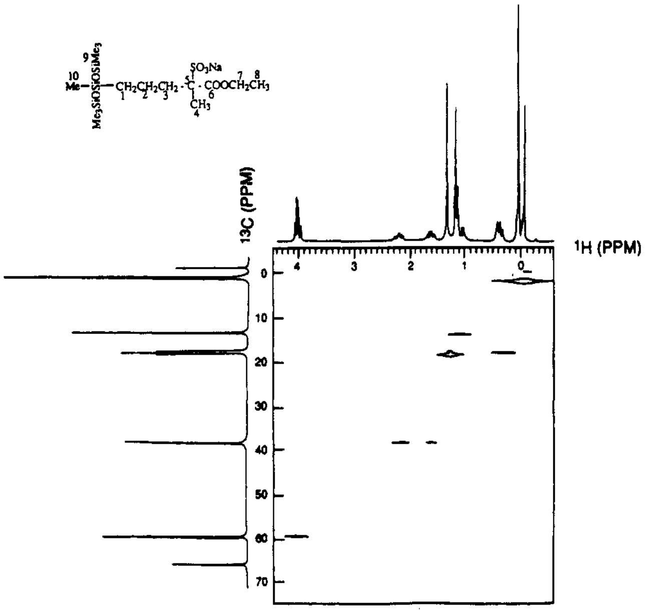


Figure 3. ^1H-^{13}C 2D NMR spectrum of sulfonate **5a** in D_2O.

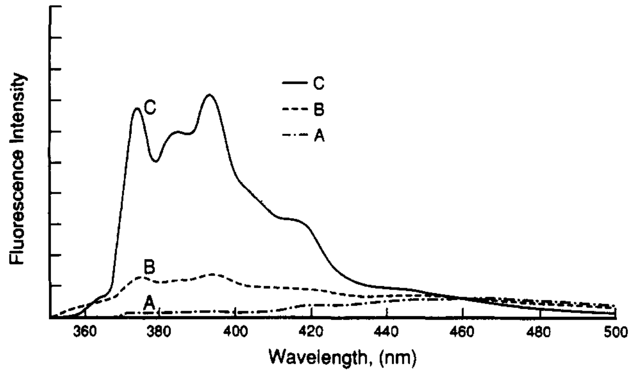


Figure 4. Fluorescence spectra of (A) pyrene, (B) pyrene plus poly(styrenesulfonate), and (C) pyrene plus 50% sulfonated polysiloxane derived from a 50:50 copolymer of dimethyl- and hydromethylsiloxane in deionized water. The concentration of the sulfonated siloxane in (C) was ca. 10 times less than that of the PSS in (B).

of methylhydro- and dimethylsiloxane. We find that 100 and 50% sulfonated silicones are very hydrophilic and dissolve in water and DMSO but not in chloroform and acetone. However, a 30% sulfonated polysiloxane is less hydrophilic, and while it still can dissolve in water, it is also able to dissolve in chloroform, acetone, and THF.

It was of interest to explore whether our sulfonated polysiloxanes in water are able to solubilize hydrophobic organic molecules such as pyrene in water.[11] The sulfonated polysiloxanes are expected to take up a confirmation in aqueous solution where the nonpolar backbone forms a core surrounded by sulfonates. Solubilization of pyrene in the core would be reflected by an increase in emission from excited, individual pyrene molecules compared with emission from pyrene dimers or aggregates (excimer emission). Figure 4A shows the fluorescence spectrum of a saturated solution of pyrene in water. Only a broad excimer-dominated emission is seen at ca. 480 nm, presumably from the small amount of solid pyrene dispersed in the water. Addition of 50 mg of poly(styrenesulfonate) (M_n = 70 000) leads to the appearance of bands due to monomer emission near 380 nm (Figure 4B). However, addition of one-tenth of that amount of a sulfonated polysiloxane derived from a 50:50 copolymer of dimethyl- and hydromethylsiloxane affords a significantly higher monomer fluorescence (Figure 4C), reflecting the greater ability of this polymer, with its nonpolar siloxane backbone and polar sulfonate pendants separated by several carbons, to act much like a surfactant with a hydrophobic core.

Conclusions

The reaction of silyl ketene acetal-modified polysiloxanes with (trimethylsilyl)sulfonyl chloride followed by hydrolysis affords a convenient route to water-soluble sulfonated derivatives. Partially sulfonated polysiloxanes can exhibit solubility in both organics and water. The properties of these new amphiphilic materials are under investigation. Of particular interest may be their use as surfactants, carriers for nonpolar drugs, and dopants for conducting polymers.[12] Finally, we note that this chemistry could in principle be applied to the preparation of sulfonate-terminated poly(methyl methacrylate) and related materials produced via group transfer polymerization.

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