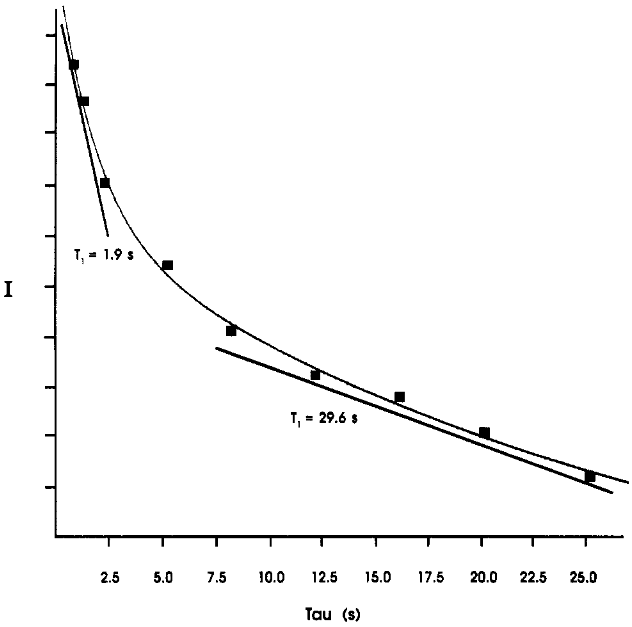

Figure 4. ^{15}N spin-lattice relaxation of nylon 6. Plot of intensity of ^{15}N resonance at 87.2 ppm versus τ. The biexponential fit is plotted along with individual T_1 components showing two-component decay.

Table I

sample	% xtal	param	amorphous phase (87.2 ppm), s		crystalline phase (84.2 ppm), s
in situ	23	T_{1N}	[a]	26	111
melt quenched	29	T_{1N}	2.7	19	230
annealed (160 °C)	45	T_{1N}	1.9	29.1	416

[a] The short T_1 component was not observed for this sample.

observe the amorphous fraction. An MAS spectrum of the ^{15}N-labeled nylon 6 was obtained without cross-polarization. By using a recycle delay of 5–10 s, the ^{15}N magnetization in the crystalline regions is quickly saturated. The nuclei in the amorphous region with shorter T_{1N} can then be observed directly. When this method was used, the spectrum of the amorphous region was obtained (Figure 5, lower trace). This spectrum is nearly identical with the deconvoluted peak from the CP/MAS spectrum shown in Figure 4; i.e., the resonance is broad and downfield of the α crystal peak but upfield from the observed position of the γ crystal peak. Spectral subtraction gives the center trace in Figure 5. Now the resonance for the α crystal form is clearly seen as a symmetrical Lorentzian line with contributions from the noncrystalline region removed.

^{15}N T_1 measurements are also reported in Table I for the in situ prepared sample as well as methanol-extracted samples that were quenched from the melt. The amorphous regions in all samples have shorter relaxation times than the crystalline regions, a fact consistent with ^{13}C relaxation studies of these materials.[5] In addition, the in situ prepared samples have shorter T_{1N} values than any of the methanol-extracted samples. Since the T_{1N} values are associated with motions of the polymers, a shorter T_{1N} value for the in situ sample indicates more rapid motion, due either to plasticization by residual caprolactam in the sample or differences in the crystalline regions. We are continuing our relaxation studies to confirm the proposed phase morphology and correlate the effects of plasticizers and thermal history on ^{15}N relaxation times.

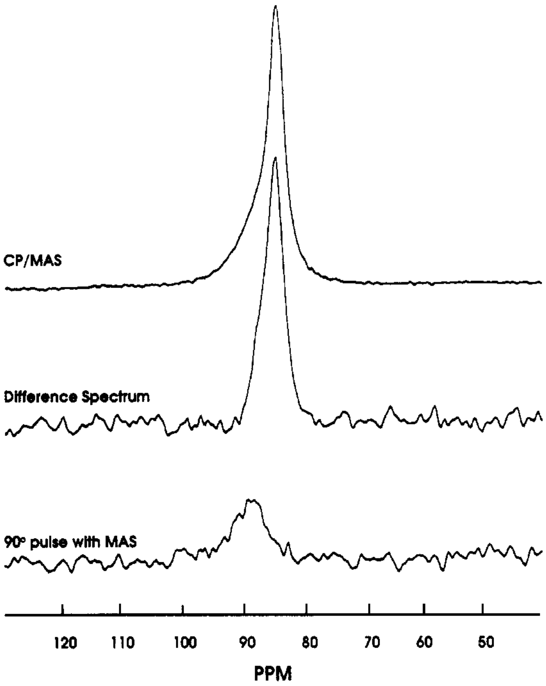

Figure 5. ^{15}N MAS spectra of nylon 6 at 300 K. Upper trace: Spectrum with cross-polarization; main peak for α crystal form is seen along with overlapping resonance downfield. Lower trace: ^{15}N spectrum obtained using a 90° ^{15}N pulse (no CP) showing only the noncrystalline region with shorter T_{1N}. Center trace: Spectral subtraction of upper and lower traces showing the symmetrical resonance line for the α crystal form of nylon 6.

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Registry No. Nylon 6, 25038-54-4.

References and Notes

(1) Kitamaru, R.; Fumitaka, H.; Murayama, K. *Macromolecules* **1986**, *19*, 1943.
(2) Powell, D. G.; Sikes, A. M.; Mathias, L. J. *Macromolecules* **1988**, *21*, 1533.
(3) Mathias, L. J.; Powell, D. G.; Sikes, A. M. *Polym. Commun.* **1988**, *29*, 192.
(4) Powell, D. G.; Sikes, A. M.; Mathias, L. J., submitted for publication.
(5) Weeding, T. L.; Veeman, W. S.; Guar, H. A.; Huysmans, W. G. B. *Macromolecules* **1988**, *21*, 2028.
(6) Kubo, K.; Takeshi, Y.; Tadashi, K.; Ando, I.; Shiibashi, T. *J. Polym. Sci.: Part B* **1989**, *27*, 929.
(7) Torchia, D. A. *J. Magn. Reson.* **1978**, *30*, 613.

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Oligo(trichlorosilyl)styrenes: Highly Functionalized Silicone Precursors[1]

Silicon-based materials have a special place in polymer chemistry, being used as cross-linking agents, as components in copolymers (e.g., poly(styrene)–poly(dimethylsiloxane) block copolymers), and in their own right as

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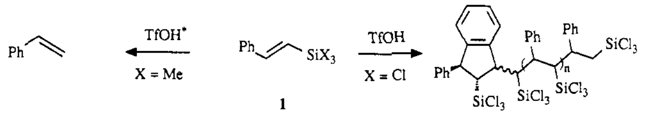
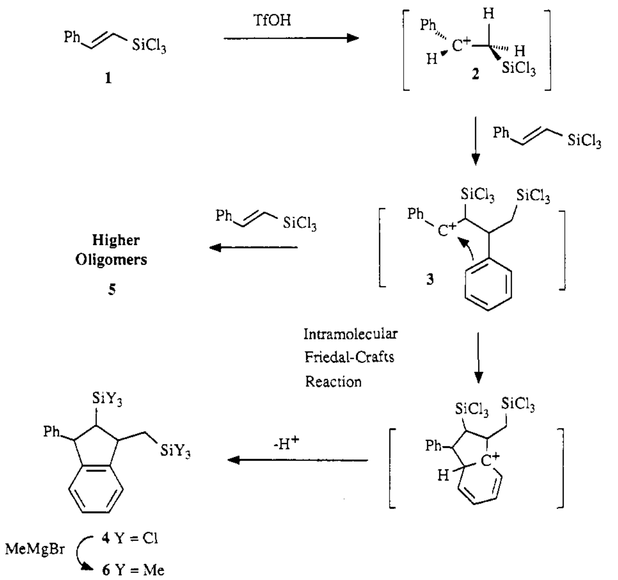
Scheme I



*Triflic acid, F_3CSO_3H

Scheme II



polymers (silicones, polysilanes). The former application generally takes advantage of the fact that, upon hydrolysis, functionalized silicon atoms undergo condensation to form stable Si–O–Si (disiloxane) linkages. We have discovered a route that leads to oligostyrenes, which contain a high degree of functionalized silicon groups that may be useful as cross-linking agents or in "moisture cure" bonding applications. In this letter, we describe the preparation and properties of these materials.

In contrast to β-(trimethylsilyl)styrene, which undergoes loss of the silyl group under acidic conditions (Scheme I; X = Me),[3] the corresponding trichlorosilyl-substituted compound undergoes oligomerization (Scheme I; X = Cl). Thus, to a mixture of β-(trichlorosilyl)styrene[4] (1) in chloroform (CH_2Cl_2 may also be used) was added triflic acid (trifluoromethanesulfonic acid, TfOH, 5 mol %) under a nitrogen atmosphere at −23 °C.[6] The red solution was allowed to stir for 4 h at which time all starting material had reacted as determined by ^{1}H NMR. The solvents were removed to leave a viscous yellow oil, which is soluble in most organic solvents. Triflic acid may be neutralized by the addition of NEt_3.[7]

In order to determine the structure of the material, it was first necessary to convert the chlorosilanes **4**,**5** into the corresponding trimethylsilyl groups (which are air and water stable) using MeMgBr or MeLi (Scheme II). These were separated into crude fractions using flash chromatography.

The dimeric product **4** predominates. Increasing the concentration of the monomer, however, leads to larger proportions of the higher oligomers. Relative distributions of the oligomers at two different concentrations are as follows: [1] = 8.43 mM, >90% dimer **4**; [1] = 4.2 M, 50% dimer **4**, 25% trimer and tetramer, 25% higher oligomers. Although it was possible to perform the reaction at higher concentrations, this did not lead to a molecular weight distribution favoring higher oligomers. Using a lower quantity of catalyst led only to slower reaction times and did not affect the molecular weight distribution.[8]

Subsequently, ^{1}H, ^{13}C, and ^{29}Si NMR were used in conjunction with mass spectroscopy to confirm that the products were the indan-terminated oligomers shown in Scheme II. GPC confirmed only that the materials were of low molecular weight. Dimer **6**: ^{29}Si NMR δ −0.61, 0.40; ^{1}H NMR δ 0.0 (s, 9 H), 0.14 (s, 9 H), 1.03 (dd, 1 H, J = 12.0, 14.3 Hz), 1.14 (dd, 1 H, J = 3.0, 14.3 Hz), 2.00 (dd, 1 H, J = 6.5, 11.5 Hz), 3.63 (ddd, 1 H, J = 3.0, 6.5, 12.0 Hz), 4.50 (d, 1 H, J = 11.5 Hz); MS 352 (M^+). Higher oligomers (the highest DP yet found is a nonamer): MS 1511 (nonamer$^+$ − 73 (TMS)), 1335 (octamer$^+$ − 73), 1159 (heptamer$^+$ − 73), 983 (hexamer$^+$ − 73), 807 (pentamer$^+$ − 73).

The mechanism of formation is, presumably, similar to that for the cationic polymerization of styrene with triflic acid as an initiator.[9] Silicon is known to stabilize a carbonium ion in the β-position (β-effect).[3,10] Thus, the addition of a proton takes place on the carbon bearing the silicon leading to the doubly stabilized benzylic cation **2**. In contrast to the trimethylsilyl group, which is reasonably labile, the trichlorosilyl group remains on the compound and the cation reacts with another monomer leading to **3**, rather than losing the $SiCl_3$ group. A partition is then established between further oligomerization, giving **5**, and termination via an intramolecular Friedel–Crafts reaction, giving **4**. This type of ring closure has precedent with TfOH as the cationic initiator of styrene polymerization.[9] As the concentration of monomer decreases, intramolecular termination becomes more important. Increasing the initial concentration of the monomer, or continuously adding monomer during the reaction, leads to an increase in the DP of the oligomer formed.

Upon exposure to moist air, the oligo(chlorosilyl)styrenes **4**,**5** cross-link to form a brittle resin. Performing this in the presence of a surface bearing hydroxyl groups, for example, glass or silica, leads we believe, to chemically bound films on the surface. The films are pale yellow to off-white; the clarity and degree of crazing depends on the solvent from which the film was formed.

Alternatively, the chlorosilanes can be first converted to alkoxysilanes [using alcohols with chemical removal of HCl (an amine base or $HC(OMe)_3$)]. The alkoxylated oligomers also undergo cross-linking and related reactions but more slowly than the chlorosilanes.

One limitation of the oligomeric silylstyrenes may be the relatively low DP. The question of the detailed mechanism must be further investigated in light of this fact. In order to increase the DP, it will be necessary to increase the β-effect of the silyl group but maintain the poor leaving group ability. Studies directed toward this goal and to the examination of these materials as cross-linking agents are currently under way.

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Registry No. 1 (homopolymer), 121988-00-9; 1 (dimer), 121987-99-3; 1 (trimer), 121988-01-0; 1 (tetramer), 121988-02-1; TfOH, 1493-13-6.

References and Notes

(1) Brook, M. A.; Jefferson, E.; Sebastian, T. Polytrihalosilylstyrenes: Exploiting the β-Effect for Polymer Synthesis. *Ab-*

stracts of Papers, North American Chemical Congress, Toronto, Canada, June 1988; American Chemical Society: Washington, DC, 1988; Abstract ORGN-50.

(2) NSERC University Research Fellow, 1985–1990.

(3) Koenig, K. E.; Weber, W. P. *J. Am. Chem. Soc.* **1973,** *95,* 3416.

(4) This material is readily prepared by the H_2PtCl_6-catalyzed hydrosilation of phenylacetylene with $HSiCl_3$ in THF.[5]

(5) Tamao, K.; Yoshida, J.; Yamamoto, H.; Kakui, T.; Matsumoto, H.; Takahashi, M.; Kurita, A.; Murata, M.; Kumada, M. *Organometallics* **1982,** *1,* 355 and references cited therein. Benkeser, R. A.; Burrous, M. L.; Nelson, L. E.; Swisher, J. V. *J. Am. Chem. Soc.* **1961,** *83,* 4385.

(6) The reaction was performed in a flame-dried glass vessel under a nitrogen atmosphere. Syringe techniques were used for the transfer of reagents.

(7) Emde, H.; Domsch, D.; Feger, H.; Frick, U.; Götz, A.; Hergott, H. H.; Hofmann, K.; Kober, W.; Krägeloh, K.; Oesterle, T.; Steppan, W.; West, W.; Simchen, G. *Synthesis* **1982,** 1–26.

(8) In principle, lower reaction temperatures should facilitate a higher degree of polymerization. Unfortunately, problems with compatible solvents and catalyst solubility precluded confirming this result. At lower temperatures, no polymerization was observed, as shall be reported in due course.

(9) Moreau, M.; Matyjaszewski, K.; Sigwalt, P. *Macromolecules* **1987,** *20,* 1456–1464. Higashimura, T.; Hiza, M.; Hasegawa, H. *Macromolecules* **1979,** *12,* 217–222; **1979,** *12,* 1058–1061. Kunitake, T.; Takarabe, K. *Ibid.* **1979,** *12,* 1061–1067. Hiza, M.; Hasegawa, H.; Higashimura, T. *Polym. J.* **1980,** *12,* 379–385.

(10) Colvin, E. W. *Silicon in Organic Synthesis*; Butterworths: London, 1981. Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer: Berlin, 1983. Fleming, I. In *Comprehensive Organic Chemistry*; Neville Jones, D., Ed.; Pergamon: Oxford, 1979; Vol. 3, Chapter 13.

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Preparation of Poly(methacrylic acid-*g*-ethylene oxide) Microspheres

Introduction. Poly(methacrylic acid-*g*-ethylene oxide) (P(MAA-*g*-EO)) is a copolymer that has been shown to exhibit unique properties due to its ability to form reversible hydrogen-bonded complexes.[1,2] This complexation results in changes in the swelling characteristics upon a change of pH or temperature of the surrounding environment. At acidic pH values, the ethylene oxide chains associate with the poly(methacrylic acid) backbone of the copolymer to form a highly compact network. Upon raising the pH to alkaline values, this complexation reverses and the network swells.[1] This behavior presents a potential for use of such polymers in biosensors or as carriers for controlled drug delivery systems.[3]

P(MAA-*g*-EO) has been synthesized by means of a free-radical bulk polymerization.[1,2] However, for use in the physiological environment, this copolymer would be more feasible in the form of microspheres.

Experimental Section. A suspension polymerization technique was used to prepare microspheres of P(MAA-*g*-EO). A 500-mL three-neck flask, equipped with a reflux condenser, was employed for the suspension polymerization reaction. The suspending phase consisting of 300 mL of silicone oil (Dow 200 fluid, dielectric grade) was added to the flask and agitated at a rate of 250 rpm until its temperature reached 70 °C. The polymerizing phase solution consisted of 5 g of methacrylic acid (MAA; Aldrich Chemical Co., Milwaukee, WI) and 5 g of methoxypoly(ethylene glycol) monomethacrylate 1000 (M(1000)G; Polysciences, Warrington, PA) mixed with 2 wt % tetraethylene glycol dimethacrylate (TEGDMA; Polysciences) as a cross-linking agent, 0.2 wt % 2,2-azobis(2-methylpropionitrile) (AIBN, Aldrich) as an initiator, and 1 wt % poly(dimethylsiloxane-*b*-ethylene oxide) (P(DMS-*b*-EO) with 25% DMS; Scientific Polymer Products, Ontario, NY) as a surfactant. This mixture was added to the silicone oil, agitated at 400 rpm, and allowed to react for 3 h at 70 °C and for 2 h at 90 °C.

When the reaction was completed, the contents of the flask were poured into a 1000-mL beaker and allowed to cool for 30 min. Most of the silicone oil was decanted, approximately 1000 mL of deionized water was then added to the beaker, and the contents were stirred overnight. Subsequently, the particles were allowed to settle, and the water and remaining silicone oil were decanted. This washing procedure was repeated until no silicone oil remained.

The particle size distribution was determined by means of a Coulter Counter (Model ZM, Coulter Electronics, Luton, Bedsford, U.K.). In addition, the chemical composition of a sampling of dried particles was determined by means of a Fourier transform infrared (FTIR) spectrometer (Perkin-Elmer Model 1600, Norwalk, CT).

The equilibrium degree of swelling of the polymer microparticles was determined in buffer solutions of pH 4.75 and 7.4. Particles were isolated on microscope slides and allowed to dry for 24 h at room temperature and then for 24 h under vacuum. Their diameters were measured by examination under a microscope. The particles were then swollen in the buffer solution at 37 °C for 1 h. The particles were again examined under the microscope, and the final diameters were measured.

Results and Discussion. Developing the suspension polymerization technique involved variations in the suspending phase, the reaction temperature, the surfactant concentrations, and the agitation rate. Initially, a salting-out technique[4] was used by adding the water-soluble monomers, MAA and M(1000)G, to a saturated (26 wt %) sodium chloride solution. This two-phase mixture was agitated and allowed to react for 18 h at 60 °C. These reaction conditions were chosen because the bulk polymerization of P(MAA-*g*-EO) had successfully been completed at these conditions. The result of the suspension polymerization, however, was not the formation of microparticles but of a mass of gel.

In an attempt to understand this result, the same suspension polymerization technique was used to produce homopolymer microparticles of MAA or M(1000)G. Under these reaction conditions, M(1000)G polymerized to form microparticles; however, MAA did not polymerize. PMAA microparticles could, however, be produced if the reaction was run at 70 °C for 3 h and 90 °C for 2 h.

These reaction conditions could not be used for the polymerization of the copolymer in the presence of water, because water-swollen P(MAA-*g*-EO) underwent irreversible swelling at temperatures exceeding 70 °C, possibly due to PEG hydrolysis. Thus, the suspending phase was changed to an organic phase, and silicone oil was chosen because of its relative nontoxicity.

Suspension polymerization of P(MAA-*g*-EO) in silicone oil at the higher temperatures resulted in copolymer microspheres; however, the particles were highly agglomerated as shown in Figure 1. Performing the reaction in the presence of 1 wt % surfactant P(DMS-*b*-EO) significantly reduced this agglomeration as indicated in Figure 2.

The final adjustment made to the polymerization technique was the variation of agitation rate. Increasing the agitation rate from 250 to 400 rpm resulted in a significant

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