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Preparation of Telechelic Polysilylenes: A General Methodology for the Synthesis of Polysilylene-Based Triblock Copolymers

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ABSTRACT: Telechelic polysilylenes have been developed involving the chemical degradation of poly(di-*n*-hexylsilylene) with bromine. The molecular weight of the newly formed telechelic PDHS depends on the ratio of bromine to the starting PDHS. The percentage of end groups increases as the molecular weight of the telechelic PDHS is lowered, reaching a maximum of 99% difunctionality. Polystyrene−PDHS−polystyrene triblock copolymers have been prepared by coupling polystyryllithium to the telechelic PDHS in the presence of cryptand [2.1.1]. The effect of molecular weight on the disordering transition of PDHS into a columnar mesophase has been studied, and temperature and enthalpy have been shown to decrease by the presence of the PS end groups and eventually became unobservable at high fractions of PS. The morphologies of the triblock copolymers were studied by atomic force microscopy.

Introduction

Polysilylenes, which consist of linear chains of silicon atoms bearing two organic substituents, continue to attract attention due to their unique electronic and thermochromic properties.[1−3] These properties make the polysilylenes potential candidates for such applications as photoresists, electrooptical materials, and nonlinear optical materials. The polysilylenes have also been used as initiators for the radical polymerization of vinyl monomers and as precursors to silicon carbide.[4] One disadvantage of the polysilylenes is that they generally possess poor mechanical properties.[5] The mechanical properties can be improved by incorporation of the polysilylene unit into a block copolymer.[6] The latter method has already received some attention and will be the focus of this paper.[4,5,7,8]

Polysilylenes have been prepared by several methods including (i) the reductive coupling of dichlorosilanes,[1−3] (ii) dehydrogenative coupling of hydridosilanes,[9] (iii) anionic polymerization of masked disilylenes,[8] and (iv) ring-opening polymerization of cyclotetrasilanes.[10,11] Successful synthesis of block copolymers has been reported by the ring-opening polymerization method and by polymerization of masked disilylenes. Other approaches have used polysilylenes to initiate the radical polymerization of vinyl monomers and the coupling of polystyryllithium to chloride end-terminated poly(methylphenylsilylenes).[4,5] Both of the latter methods resulted in relatively poorly defined materials.

To prepare a series of block copolymers that are reasonably well-defined, it is necessary to develop a synthetically simple procedure, e.g., coupling of the living ends of anionically prepared polymers to halide-capped polysilylenes.[5] The chemical constitution of the end groups of polysilylenes cannot be controlled strictly in the Wurtz-coupling synthesis. Degrading high molecular weight poly(di-*n*-hexylsilylene) with halogens provides an alternative approach to prepare α,ω-dihalogen polysilylene telechelics. The chemical degradation of high molecular weight poly(methylphenylsilylene) with iodine in methylene chloride has been reported to yield the corresponding lower molecular weight polymers.[12] Similarly, photochemically degrading of high molecular weight poly(2-methylbutyl(methyl)silylene) has been reported by Fujiki in carbon tetrachloride to afford the chloride end-terminated polymer.[13]

This paper describes the synthesis of a series of different molecular weights of telechelic PDHS and the subsequent formation of triblock copolymers by condensation reaction with polystyryllithium. Bromine was chosen as the chemical degradation reagent on the basis of two factors. First, a silyl bromide is more stable than a silyl iodide with regard to hydrolysis. Second, the relative rates of nucleophilic substitution of a silyl bromide, silyl iodide, and silyl chloride are approximately 10^4, 10^9, and 1, respectively.[14] The effect of the molecular weight and also the presence of the polystyrene end groups on the disordering temperature of PDHS will be discussed along with the results of morphology studies.

Experimental Part

Telechelic PDHS (Br−PDHS−Br). In a typical experiment 0.114 g of PDHS ($M_n = 500\,000$, $M_w/M_n = 2.4$), prepared by convential Wurtz coupling of dichlorodihexylsilane with Na in refluxing toluene and subsequent polymer fractionating,[1] was placed in a 50 mL round-bottom flask and dissolved in 25 mL of benzene (distilled from K under argon). The flask was wrapped in aluminum foil to prevent photodegradation and free radical halogenation of the hexyl side chains. After the polymer had dissolved completely, 0.55 μL of a 0.1 M Br_2 solution in benzene was added by means of a syringe. The solution became dark yellow and was allowed to stir overnight. Afterward, a 1 mL sample was taken and reacted with phenylmagnesium bromide in order to convert the bromide end groups to phenyl groups. GPC analysis showed a reduced molecular weight of $M_n = 21\,000$ and $M_w/M_n = 1.6$ vs linear polystyrene standards.

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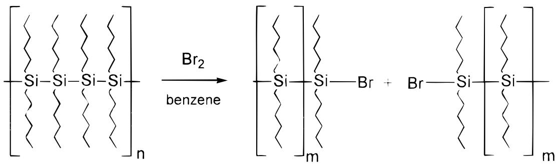
Table 1. Control of the Percentage of Reactive End Groups in the Synthesis of Telechelic PDHS and Transition Temperatures/Enthalpies of T_1 for Different Molecular Weights Samples As Determined by DSC

no. of Si−Si bonds cleaved[a]	mol % difunctional PDHS[b]	new M_n[c] [g/mol]	M_w/M_n[c]	T_{onset}[d] [°C]	T_{peak}[d] [°C]	enthalpy ΔH[d] [J/g]
0	0	500 000	2.4	43.0	37.9	72.1
2	33	170 000	2.2	46.6	40.1	74.2
4	60	90 000	1.9	43.4	39.7	68.2
7	75	61 000	1.8	44.1	39.2	70.5
15	88	32 000	1.7	43.7	39.5	69.3
24	92	21 000	1.6	42.7	39.1	69.5
49	96	12 000	1.6	44.6	39.2	62.6

[a] $n = (M_{no} - M_n) - 1$. [b] Equal to $(n - 1)/(n + 1)$. [c] M_n after reaction; determined by SEC relative to polystyrene standards. [d] Determined by DSC.

Scheme 1



Polystyryllithium. A 0.9 g sample of styrene were dissolved in 10 mL of dry benzene. A solution of *sec*-BuLi was added dropwise until a light yellow color appeared. Afterward, 150 μL of 1.6 M *sec*-BuLi was added by means of a syringe, and a dark orange color appeared. The solution was stirred for 4 h, and a sample was taken for GPC and terminated with methanol. GPC analysis showed $M_n = 4000$ with $M_w/M_n = 1.08$.

PS−PDHS−PS Triblocks. The condensation of polystyryllithium with α,ω-dibromo-PDHS was carried out by titrating a solution of Br−PDHS−Br in benzene with polystyryllithium until a dark orange color appeared. This usually required a 4−5-times excess of polystyryllithium. Then, 0.2 mL of a 0.15 mol/L solution of cryptand [2.1.1] in toluene was added, and the solution became dark red. After 1 h a sample was taken for GPC analysis in order to check the conversion by the increase in molecular weight. The reaction mixture was quenched with a few drops of methanol and precipitated twice in acetone to remove homopolystyrene. The samples were separated by filtration and dried under vacuum at 80 °C.

Methods. *GPC* was performed in THF using Waters μ-Styragel columns. Molecular weights were determined by the use of a RI and an UV detector in parallel and using narrow polystyrene standards.

Calorimetry. A Perkin-Elmer DSC-7 instrument was used to monitor the thermal transitions at scanning-rates of 10 K/min. Sample weights amounted to about 5 mg. Cyclohexane, cylopentane, gallium, and water were used as calibration standards.

Samples for *AFM* studies were prepared by putting a drop of a dilute solution (0.02 wt %) of the triblock copolymers in toluene on a piece of mica substrate and allowing the solvent to evaporate. The samples were annealed at 120 °C for 24 h. AFM investigations were performed on a Nanoscope IIIa atomic force microscope (Digital Instruments) under ambient conditions in tapping mode.

Results and Discussion

Telechelic α,ω-dibromopolysilylenes were prepared according to Scheme 1. High molecular weight PDHS was dissolved in benzene and then reacted with varying percentages of bromine. To measure the resulting molecular weight, samples were taken and terminated with phenylmagnesium bromide. This way hydrolysis of the end groups and subsequent formation of siloxane linkages were prevented, which could result in the observation of higher molecular weights than were actually present. The molecular weight of the new, telechelic PDHS was dependent on the ratio of $[PDHS]_0/[Br]_0$ and the reaction time. Figure 1 shows the number-average molecular weight M_n of samples as a function of the reaction time. Initial degradation of the molecular weight is relatively fast, leveling off after 3 h.

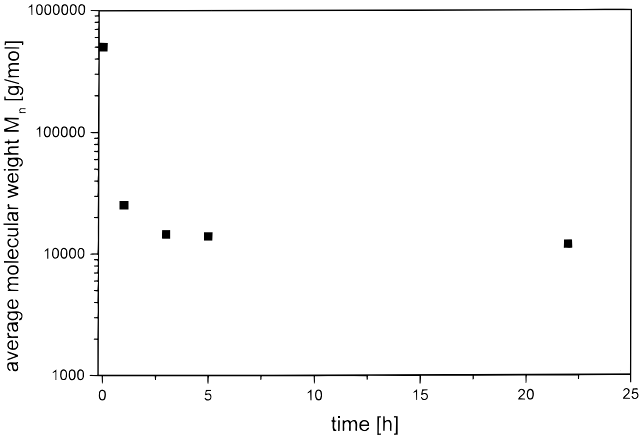


Figure 1. Plot of M_n versus time for the reaction of 0.11 g of PDHS (2.0×10^{-7} mol), with $M_n = 500\,000$ g/mol in 15 mL of benzene and 1.1 μL of bromine (2.1×10^{-5} mol).

Table 1 lists the molecular weights and the calculated fraction of α,ω-dibromo telechelic PDHS prepared from stock polymer with $M_n = 500\,000$. Experimental determination of the end groups, for example by NMR spectroscopy, has not been possible in view of the rather high molecular weight.

Transition temperatures are generally molecular weight dependent; thus, it was necessary to determine the mesophase transition temperature for each of the new molecular weight samples, to be able to compare the effect of end groups for the various molecular weights and compositions of the triblock copolymers. The results of DSC measurements performed on the phenyl-terminated telechelic polymer samples are listed in Table 1. The disordering transition temperatures remain constant even down to $M_n = 12\,000$, but enthalpies tend to decresase for polymers with lower molecular weights. This is in agreement with a report by Sakurai et al., who analyzed the solution properties of a variety of different molecular weights of PDHS prepared by photochemical degradation.[15] The solution UV absorption maxima of PDHS with molecular weights ranging from 2000 to 300 000. The maxima reached a limiting value at a molecular weight of 10 000, and the critical temperature T_c for the thermochromic transition in solution was found to decrease considerably at molecular weights below 10 000.

Synthesis of Triblock Copolymers. Triblock copolymers were synthesized by condensing polystyryllithium solutions with telechelic PDHS (α,ω-bromide PDHS) in benzene as depicted in Scheme 2.

Table 2. Molecular Weight Data and Thermal Properties for a Series of Triblock Copolymers Prepared by the Condensation of Polystyryllithium with Telechelic PDHS

no.	Br−PDHS−Br M_n [g/mol] (M_n/M_w)	polystyrene (PS) M_n [g/mol] (M_n/M_w)	PS−PDHS−PS M_n [g/mol] (M_n/M_w)	$T_{1,\text{onset}}$ [°C]	$T_{1,\text{peak}}$ [°C]	ΔH_1 [J/g]
1	11 000 (1.6)	1500 (1.08)	12 500 (1.6)	35.3	38.5	51.2
2	12 000 (1.6)	2000 (1.09)	16 000 (1.5)	35.7	39.2	48.6
3	20 000 (1.8)	2000 (1.09)	22 500 (1.6)	36.4	42	54.7
4	32 000 (1.7)	2000 (1.09)	36 000 (1.7)	40.4	45.4	62.1
5	31 000 (1.6)	2500 (1.07)	36 000 (1.6)	31.9	37.0	69.4
6	21 000 (1.6)	4000 (1.08)	28 000 (1.3)	34.3	36.0	19.4

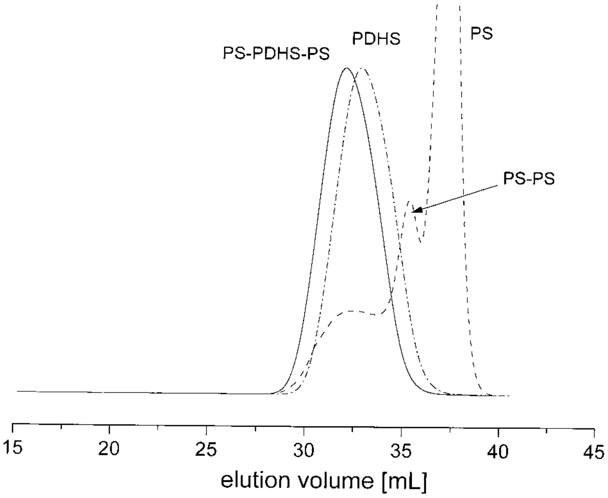
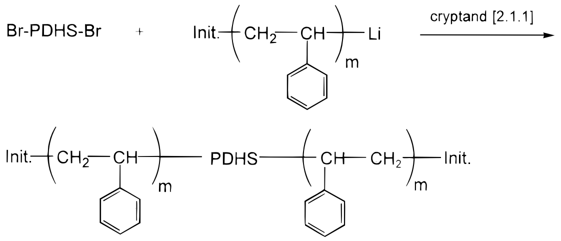


Figure 2. (- - -) GPC trace of the products of a polycondensation reaction of polystyryllithium with α,ω-dibromo-PDHS; (- · -)PDHS precursor; (—) copolymer after ppt.

Scheme 2



α,ω-Dibromopoly(dihexylsilylene) with molecular weights below $M_n \leq 30\,000$ were employed, ensuring a high degree of difunctionality. The molecular weight of the polystyrene block was kept low in order to ease the separation of homopolystyrene from the block copolymer. The condensation reaction was more efficient in the presence of a small amount of cryptand [2.1.1] whereas the reaction was very slow without the addition of cryptand. This is not unexpected as the Si−Br end groups are sterically screened, and additionally, polystyryllithium tends to aggregate in nonpolar solution. However, after addition of the cryptand the condensation reactions were completed in less than 1 h. In all cases a large excess of polystyryllithium (4−5 equiv) was used to ensure complete coupling. Excess polystyrene was removed by precipitation in acetone which yielded the triblock copolymers as the precipitate. The triblock copolymers were additionally purified by extracting the triblock copolymers with hexane, which did not dissolve styrene homopolymer.

Figure 2 displays representatively the GPC trace of a sample taken from a completed condensation reaction in comparison to the GPC trace of the α,ω-phenyl-terminated PDHS segment.

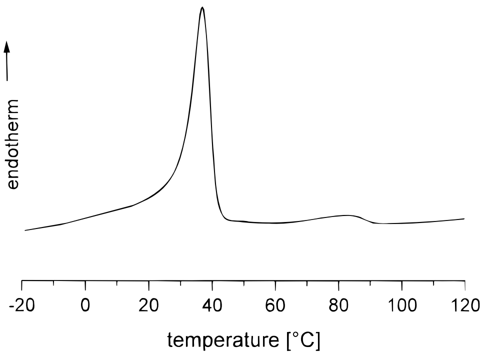


Figure 3. DSC traces for a PS(4000)−PDHS(21 000)−PS-(4000) triblock copolymer.

Table 2 contains the molecular weight data and compositions for a series of triblock copolymers. In all cases a decrease in the elution volume corresponding to an increased molecular weight was found compared to the α,ω-dibromo-PDHS, demonstrating a successful coupling.

Thermal Analysis. The triblock copolymers were analyzed by DSC to determine the effect of the polystyrene end groups on the mesophase formation of the PDHS center block. A representative DSC trace for a sample with a $M_n = 4000$ polystyrene block and a $M_n = 21\,000$ PDHS central segment is shown in Figure 3. The T_1 transition is shifted to lower temperatures, 36.0 vs 42 °C, and the enthalpy of the transition is also considerably lower, 19.4 vs ca. 70 J/g for the telechelic PDHS block. The lower enthalpy can only be explained in part by the composition of the sample which contains only 71% of PDHS. However, the observed enthalpy is 2.5 times lower than this, indicating that the presence of polystyrene affects the transition into the mesophase.

Table 2 lists the thermal properties for the triblock copolymers. The effect of the polystyrene end groups became more pronounced as the polystyrene chain length increased and the relative fraction of polystyrene was higher. For the samples 2 and 6, which had the highest polystyrene content, broad and barely detectable endotherms were observed. No glass transitions were observed for the polystyrene segments. The reduced ability to crystallize indicates disturbance of the PDHS chains by the presence of polystyrene end groups.

Morphology Studies. The morphology of different triblock copolymers was studied by atomic force microscopy (AFM). According to the fractions of polystyrene which were between 15% and 30%, for all samples except sample 4, which has a slightly lower polystyrene content (11%), the formation of cylindrical domain structures was expected. Figures 4 and 5 show atomic force micrographs of the PS(2000)−PDHS(20 000)−PS-(2000), (no. 3) and the PS(2500)−PDHS(31 000)−PS-(2500) (no. 5) triblock copolymers, which both formed distinct cylindrical surface structures after annealing above 120 °C. Assuming a chain length of ≈5 nm for a

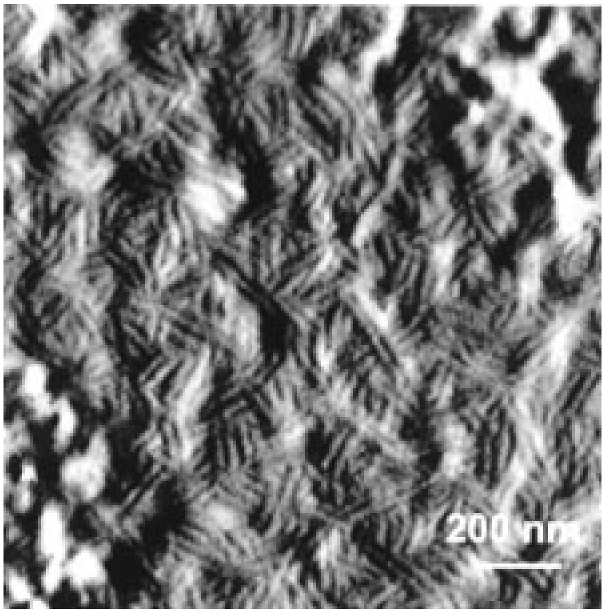


Figure 4. AFM picture of a PS(2000)−PDHS(20 000)−PS(2000) (no. 3) triblock copolymer.

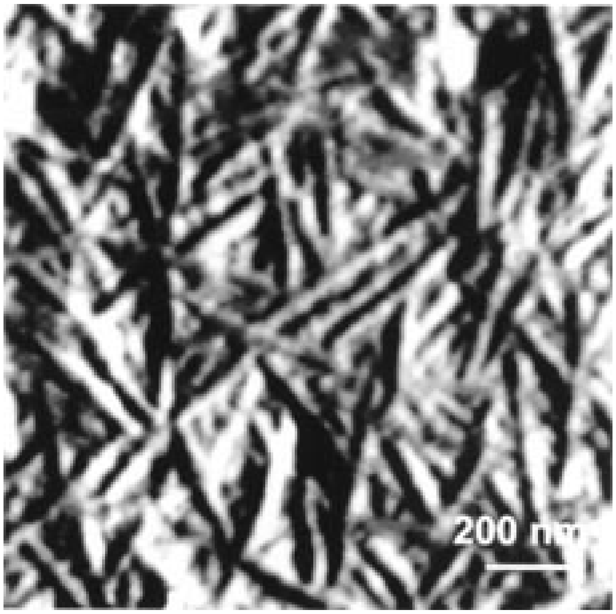


Figure 5. AFM picture of a PS(2500)−PDHS(31 000)−PS(2500) (no. 5) triblock copolymer.

polystyrene chain with $M_n = 2000$, and a chain length of ≈15 nm for a PDHS segment with $M_n = 20\,000$, the expected diameters for the cylinders amounted to 25−30 nm for no. 3 and 35−40 nm for no. 5. From AFM images the experimental values of 30−35 nm (no. 3) and 40−50 nm (no. 5) were obtained, which were in agreement with the calculated data regarding the fact that lateral structures are exaggerated in width due to the convolution with the apex of the tip. The fact that the cylinders are packed in high disorder might be explained by the formation of cylindrical micelles in solution, which could not order or rearrange during the fast evaporation of the solvent. Phase separation could also be observed by TEM.

Conclusions

A simple, but versatile, method has been developed for the synthesis of telechelic poly(di-*n*-hexylsilylene), PDHS. The functionalities consist of bromide end groups introduced by the chemical degradation of high molecular weight PDHS with bromine in benzene solution. The molecular weight of the degraded polymer and the percentage of difunctional and monofunctional chains can be controlled by the ratio of bromine to polymer. The disordering transition temperature to the mesophase for α,ω-diphenyl-terminated PDHS was found to be independent of molecular weight for a series of samples with molecular weights as low as $M_n = 10\,000$.

The telechelic PDHS chains were employed as the central block for the synthesis of triblock copolymers which were prepared by the condensation reaction of polystyryllithium with the telechelic PDHS. The composition of the triblock copolymers could be controlled by changing the length of either block. The T_1 transition of the PDHS central block was found to be decreased in temperature, and also the enthalpy of the transition was decreased as the polystyrene content was increased. Both TEM and AFM studies showed that the triblock copolymer samples are phase-separated. AFM studies of the triblock copolymers showed cylindrical structures for annealed samples.

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