volves microphase separation in which each microphase exhibits some properties of macroscopic phases. Nevertheless, for thermodynamic purposes a phase must necessarily contain complete molecules, not just one type of block out of a block copolymer molecule. This is necessary in the derivation of the phase rule. Surface phases as well as bulk phases must fulfill this criterion.

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Anionic Synthesis of Thermally and Hydrolytically Stable Telechelic Polysiloxanes

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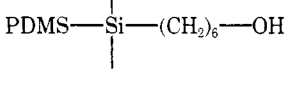
Reactive and in particular functionally terminated (telechelic) polymers present a growing interest in the production of homogeneous as well as heterophase materials. For instance, "liquid rubbers" (carboxyl- or hydroxyl-terminated (co)polydienes) provide by now a new technique of producing rubber products utilizing lightweight and less expensive equipment. Telechelic polymers (mainly hydroxylated ones) are also largely involved in the synthesis of multiblock and heterophase copolymers; well-known examples are elastomer thermoplastics such as polyurethanes and segmented polyesters (Hytrel).[1]

The interest of a telechelic polymer is essentially dependent on its nature and its functionality. At the present time, only a few examples of synthesis and use of telechelic polydimethylsiloxanes (PDMS) have been reported, in spite of the attractive thermal and elastomeric properties of these polymers. Introduction of PDMS in polyurethanes[2] and multiblock copolymers, together with a polycarbonate[3] or a polyether[4] sequence, has been described. However, the functional end group is generally linked through a hydrolytically unstable Si–O–C bond to PDMS.[5] Obviously, a Si–C linkage, with at least three carbon atoms between the siloxane chain and the first heteroatom (N, O, S), is much more interesting in this respect but also more difficult to obtain.[4] Methods described by Greber[6] and Marvel[7] illustrate the complexity of the multisteps synthetic routes and the poor control of both molecular weight and functionality.

Generally, the best controlled telechelic polymers are obtained by living anionic methods implying the use of functionally substituted initiators. An excellent example is the preparation of dihydroxyl terminated polybutadiene starting from a lithioalkylacetal initiator.[8]

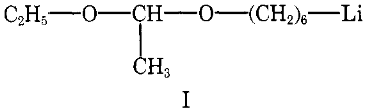
In this note, we report the use of such an organolithium initiator in the synthesis of hydroxyalkyl terminated and hydrolytically stable PDMS, characterized by narrow molecular weight distributions and carrying the following end group:



$$\text{PDMS}\text{—}\overset{|}{\underset{|}{\text{Si}}}\text{—}(CH_2)_6\text{—OH}$$

Experimental Section

Lithioacetal Synthesis. Ethyl 6-lithiohexyl acetaldehyde acetal is prepared in 80% yield in accordance to Schulz's procedure.[8] Ether



$$C_2H_5\text{—O—}\underset{\displaystyle CH_3}{\underset{|}{\text{CH}}}\text{—O—}(CH_2)_6\text{—Li}$$

I

is eliminated under vacuum and dry benzene is added to the solid initiator to form a 0.5 N solution.

Hexamethylcyclotrisiloxane (D_3) Polymerization. A suitable amount of lithioacetal in benzene is added to a solution of D_3 (20%) in the same solvent. After 16 h, dry tetrahydrofuran (THF) is added (benzene/THF $\simeq$ 1) and the temperature is raised to 50 °C. Four hours later, the living acetal PDMS is deactivated with $(CH_3)_3SiCl$, or coupled with $(CH_3)_2SiCl_2$, and finally precipitated in methanol. The hydrolysis of the acetal end group takes place in a toluene/H_2O solvent (3/1) with dichloroacetic acid as catalyst following Schulz's procedure.[8]

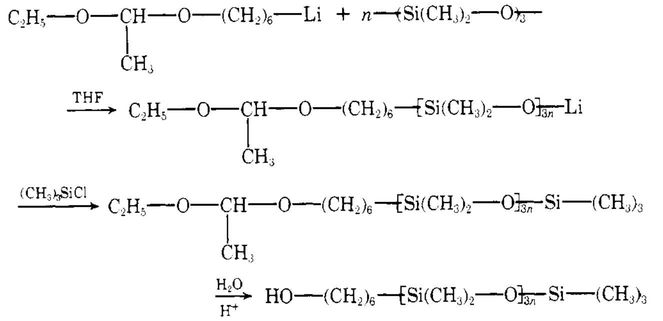
Molecular Weight Determinations. The mean number molecular weights $\overline{M}_n$ are measured by vapor pressure osmometry (VPO) in toluene at 37 °C with a 5% accuracy. The polydispersity index is evaluated by gel permeation chromatography (GPC) in THF at 25 °C. The polystyrene calibration is used (corrections for skewing and diffusion were not applied).

Hydroxyl Functionality Determinations. RMN and/or IR spectra of the acetylated hydroxyl PDMS enable the calculation of the OH functionality knowing the $\overline{M}_n$ value. The results are reproducible (±10%) in accordance with the acetic/pyridine method of Ogg et al.[9] A mixture of acetic acid anhydride, pyridine, and benzene (30/30/40) has been used to acetylate the hydroxyl end groups (3 days at 50 °C).

Results and Discussion

Schulz and co-workers have described the synthesis of lithioalkyl initiators containing a mixed acetal as an hydroxyl protecting group.[8] The initiator is synthesized in high yield (80–90%) in diethyl ether, while its low or even null solubility in hexane is mentioned. So, polybutadienes with the theoretical functionality values (±10%) have been reported, dihydroxyl polybutadienes being prepared by deactivation of the living macromolecules with ethylene oxide or by coupling them with dichlorodimethylsilane. The initiator being used in ether solution, the microstructure of telechelic polybutadiene is therefore characterized by 36 to 52% of vinyl units.

Consequently, it was very attractive to evaluate the lithioacetal (I) as an initiator of the D_3 polymerization in THF:



$$C_2H_5\text{—O—}\underset{\displaystyle CH_3}{\underset{|}{\text{CH}}}\text{—O—}(CH_2)_6\text{—Li} + n\text{—}\!\left(Si(CH_3)_2\text{—O}\right)_3\text{—}$$

$$\xrightarrow{\text{THF}} C_2H_5\text{—O—}\underset{\displaystyle CH_3}{\underset{|}{\text{CH}}}\text{—O—}(CH_2)_6\text{—}\left[Si(CH_3)_2\text{—O}\right]_{3n}\text{—Li}$$

$$\xrightarrow{(CH_3)_3SiCl} C_2H_5\text{—O—}\underset{\displaystyle CH_3}{\underset{|}{\text{CH}}}\text{—O—}(CH_2)_6\text{—}\left[Si(CH_3)_2\text{—O}\right]_{3n}\text{—Si—}(CH_3)_3$$

$$\xrightarrow[H^+]{H_2O} HO\text{—}(CH_2)_6\text{—}\left[Si(CH_3)_2\text{—O}\right]_{3n}\text{—Si—}(CH_3)_3$$

the α-ethoxy ethyl ether end group being further hydrolyzed in dilute acid medium to obtain the hydroxyl PDMS. As established by GPC measurements before and after hydrolysis, the PDMS chains are essentially unmodified by that treatment. However, the molecular weight distribution is rather large, about 1.6.

It appeared interesting to lower the polydispersity index, since, in fact, it had been shown that the narrower the molecular weight distribution and the faster the curing the lesser the tendency toward network defects upon chain extension.[10]

On the other hand, it was well-known[11] that in a nonpolar solvent an organolithium can attack only one D_3 molecule:

$$RLi + n\left[Si\,(CH_3)_2\text{-}O\right]_3 \xrightarrow[\text{solvent}]{\text{nonpolar}} \underset{\text{II}}{R\left[Si\,(CH_3)_2\text{-}O\right]_3\text{-}Li} + (n-1)D_3$$

Once the medium is made more polar (i.e., by adding THF),

Table I

M_{calcd}	$\overline{M}_n$(VPO)	$\overline{M}_w/\overline{M}_n$	No. OH/chain
3.100	3.200	1.10	0.97
5.060	5.000	1.12	1.04
9.100	8.500	1.16	1.08

the propagation takes place and a living monodisperse PDMS is obtained.

$$\text{R-[Si (CH}_3)_2\text{-O]}_3\text{-Li} + (n-1)\text{D}_3 \xrightarrow[\text{solvent}]{\text{polar}} \text{R-[Si (CH}_3)_2\text{-O]}_{3n} - \text{Li}$$

Thus, it was necessary to prepare a solution of the lithioacetal I in a nonpolar solvent. Unfortunately, the synthesis of I in hexane was unsuccessful and its solubility in such a nonpolar solvent was even claimed doubtful.[8] In fact, the lithioacetal I is only formed in polar medium, but a simple solvent exchange allows it to be obtained in benzene or toluene solution.

Then, by adding this benzene solution of I to D_3 in the same solvent, the lithium silanolate II (where R is an acetal group) is obtained. Once the initiation step has occurred, THF is added to the reaction medium and an acetal PDMS with a low polydispersity is formed and finally hydrolyzed into the expected hydroxyl PDMS. Table I summarizes the values of molecular weight, polydispersity index ($\overline{M}_w/\overline{M}_n$), and hydroxyl functionality for different functionally terminated PDMS.

The molecular weights, calculated on the basis of the monomer over catalyst molar ratios, are in excellent agreement with the observed values, while the polydispersity is now satisfying, 1.13 ± 0.03. These results confirm the living character of D_3 anionic polymerization as well as the similar values of the initiation and propagation rate constants. The functionality observed is as good as that mentioned by Schulz[8] in the case of a hydroxyl polybutadiene.

The coupling of living acetal PDMS with $(CH_3)_2SiCl_2$ followed by the hydrolysis of the acetal end groups leads to α–ω dihydroxyl PDMS.

Moreover, thanks to the solubility of the lithioacetal I in benzene, it is also now possible to synthesize hydroxyl polybutadiene with a high 1–4 microstructure.

Conclusions

Lithioalkylacetal derivatives in benzene solution are excellent initiators of D_3 polymerization. They offer an attractive route to the synthesis of ω-hydroxyalkyl polydimethylsiloxanes, $CH_3\text{–}[Si(CH_3)_2\text{–}O]_n\text{–}Si(CH_3)_2\text{–}(CH_2)_6\text{–}OH$ where $n \geq 3$; the coupling of the corresponding living chains leads to dihydroxyl macromolecules. The absence of any Si–O–C bond as well as the distance between the hydroxyl group and the first silicium atom (six carbons) ensure the remarkable hydrolytic stability of such telechelic polymers. Their polydispersity is reduced and their functionality quasi-ideal.

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Mesomorphic Order in Polymers with Side Groups Containing Elements of Mesogenic Structure

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Recent industrial developments in the field of high modulus fibers have generated a lively interest in polymers with liquid crystalline organization. Such polymers can be roughly divided into three categories: polymers in which the mesogenic element of structure is contained in the backbone of the macromolecule, polymers in which such elements are in the side group, and block and graft copolymers.

The correlation between molecular structure and nature of the liquid crystalline order has been a subject of intensive study in the case of block and graft copolymers.[1] However, such correlations have been little discussed for the first two categories of polymers mentioned above. The object of this note is to discuss such correlations for polymers in which the side groups contain elements of mesogenic structure. This discussion will be based on existing literature data.

It has been pointed out on several occasions[2–5] that the molecular organization of a mesomorphic monomer can be "locked in" if rapid polymerization were accompanied by extensive cross-linking of the polymer. In such cases the molecular organization prevailing within the mesophase of the monomer was found preserved in the polymeric network down to the minute detail of textural disclinations.[5] The situation is, however, entirely different in the absence of cross-linking at lower polymerization rates. Under such circumstances relaxation occurs and this often leads to phase separation and formation of an amorphous polymer. In some cases a directional (nematic) or layered (smectic) order is developed in the polymer. Rapid precipitation from dilute solution in good solvents of such ordered polymers leads invariably to an amorphous polymer, whereas skillful annealing, swelling, and casting bring back the mesomorphic order.[6–8] This order is not necessarily identical with the order of the initial monomeric mesophase.

A sizable body of information concerning the molecular organization of polymers derived from mesogenic monomers has recently emerged. Statements found in the literature are often confusing and not always reliable. A critical albeit qualitative discussion of well-established data appears to be justified at this point in providing some understanding of correlation between the structure of the mesogenic monomer and the nature of the order in the polymer.

A compendium of monomers and polymers for which the nature of molecular and segmental order has been reliably established by x-ray diffraction is given in Table I. As one can easily see from this table, the majority of polymers assume layered arrangements. In most cases bilayers of macromolecules are formed in which the "mesomorphic" side group is oriented at an angle to the plane of the stratum containing the convoluted backbone. The side group may or may not be arranged into a regular array.