levels, contamination can be a serious problem and care must be exercised in the handling of materials.

Proton-induced x-ray emission spectrometry is well-suited to the quantitative analysis of trace elements in thin polymer films. This is because of the technique's high sensitivity and because trace element analyses of thin films of low atomic number material are not significantly affected by errors associated with x-ray absorption and proton energy loss.

References and Notes

(1) (a) National Bureau of Standards; (b) University of Maryland.
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(10) Certain commercial equipment, instruments, or materials are identified in this paper in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

Interpretation of the Gibbs Phase Rule in the Presence of a Block Copolymer

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It is known that most block copolymers, even if quite monodisperse, form domains or microphases in bulk samples or films. In an A–B block copolymer, these domains or microphases exhibit many of the properties of bulk phases of homopolymers A and B, for example, glass transition temperatures or crystalline melting points. One is therefore inclined to attribute *all* properties of macroscopic bulk phases to these domains. This, however, is not always possible, and is particularly inappropriate in considerations involving the Gibbs Phase rule.

When using the Gibbs Phase rule, one considers phases that are in equilibrium with each other, whether these be bulk phases or surface phases. In the absence of chemical reactions or of surface phases, one uses[1]

$$f = c - p + 2$$

where f is the number of degrees of freedom or independent variables which may describe the system, c is the number of independent components in the system, and p is the number of phases in equilibrium. If the system consists solely of a monodisperse A–B block copolymer which exhibits microphase separation, the number of phases, p, in equilibrium with each other must be considered to be *one*, not two. This is because the presence of microphases of type A and of type B represents a minimum in the possible free energy of the system; it does *not* represent two phases in equilibrium.[2] In such a system, $c = p = 1$, and $f = 2$. In other words, microphase separation may be observed at a variety of temperatures and pressures. If an equilibrium should be possible between a condition in which the A and B blocks of the block copolymer are uniformly mixed and a condition in which both A and B domains exist, then $c = 1$, $p = 2$, and $f = 1$. At a fixed pressure, therefore, such an equilibrium can only exist at a single temperature.

When a second component, polymer or solvent, is added to an A–B block copolymer, the same considerations apply. For example, if the second component is homopolymer A, it may mix completely with the block copolymer domains of type A. Then again only a single "phase" is present as far as the phase rule is concerned and $c = 2$, $p = 1$, and $f = 3$. This means that such complete mixing of homopolymer A with the A domains of the block copolymer may be observed over a range of temperature, pressure, and weight fraction of homopolymer A in the block copolymer. When macroscopic phases of homopolymer A are present in equilibrium with block copolymer which may or may not contain homopolymer A mixed with its A domains, then $p = 2$, $c = 2$, and $f = 2$, that is, this condition may be observed over a range of temperatures and pressures, but the weight fraction of homopolymer A in the A domains will be fixed at any particular T and P.

If the second component in the system is a solvent that may partition between the A and B domains of the block copolymer, $c = 2$, $p = 1$, and $f = 3$. This condition is similar to that in which homopolymer A enters only the A domains. If, however, sufficient solvent is present that it cannot all enter the microphases, then there will probably be an equilibrium between block copolymer solution and micelles. Now $p = 2$ and $c = 2$, and $f = 2$, that is, at any fixed temperature and pressure the concentration of solvent in both solution and micelles is fixed when these phases are in equilibrium. Presumably, the concentration of block copolymer in the solution phase would be equal to the critical micelle concentration at that T and P.

One might continue these arguments with more and more components in the system, but it is of greater interest to consider the phase rule in a case in which the block copolymer acts as a surface active agent between two macroscopic phases made up of two other components. We now have $c = 3$ and $p = 2$ but must use the phase rule as modified for considerations of surface phases. If the interface between macroscopic phases is curved and if there are no chemical reactions between components, then the phase rule may be written[3]

$$f = c - \psi + s + 1$$

where ψ is the number of surface phases present and s is the number of types of surface present. Between two macroscopic phases, there is only one type of surface, so that $s = 1$. The surface phase may have a gas-like, a liquid-like, or a solid-like character, and several of these may be present on any type of surface. Assuming that only a single such surface phase is present, $\psi = 1$, and then $f = 4$. Presumably, the block copolymer could act as a surface active agent at a range of temperature, pressure, radius of curvature of the interface, and concentration of block copolymer at the interface. Again, in this last consideration, the block copolymer is treated as a single entity, and the different domains inhabited by the A and B blocks are not treated as if they were different phases.

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References and Notes

(1) J. W. Gibbs, "The Scientific Papers of J. Willard Gibbs", Vol. I, Dover Publications, New York, N.Y., 1961, Chapter III.
(2) The use of the word "phase" for this condition of minimum free energy of the block copolymer may be somewhat confusing since this condition in-

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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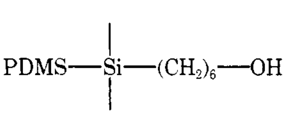
Reactive and in particular functionally terminated (telechelic) polymers present a growing interest in the production of homogeneous as well as heterophase materials. For instance, "liquid rubbers" (carboxyl- or hydroxyl-terminated (co)polydienes) provide by now a new technique of producing rubber products 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]

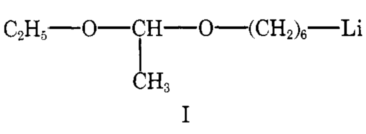
In this note, we report the use of such an organolithium initiator in the synthesis of hydroxyalkyl terminated and hydrolytically stable PDMS, characterized by narrow molecular weight distributions and carrying the following end group:



$$\mathrm{PDMS{-}\overset{|}{\underset{|}{Si}}{-}(CH_2)_6{-}OH}$$

Experimental Section

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



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

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]

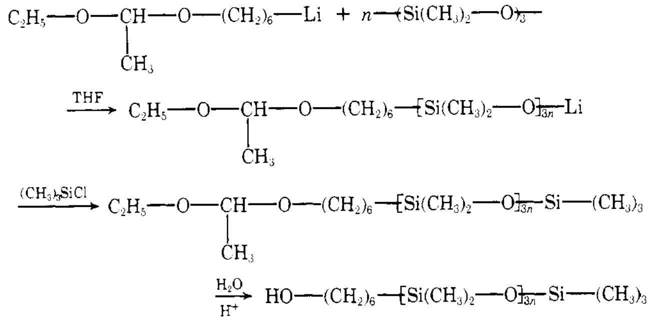
Molecular Weight Determinations. The mean number molecular weights $\overline{M}_n$ are measured by vapor pressure osmometry (VPO) in toluene at 37 °C with a 5% accuracy. The polydispersity index is evaluated by gel permeation chromatography (GPC) in THF at 25 °C. The polystyrene calibration is used (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:



$$\mathrm{C_2H_5{-}O{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}O{-}(CH_2)_6{-}Li} + n\,\mathrm{{-}[Si(CH_3)_2{-}O]_3{-}}$$
$$\xrightarrow{\mathrm{THF}} \mathrm{C_2H_5{-}O{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}O{-}(CH_2)_6{-}[Si(CH_3)_2{-}O]_{3n}{-}Li}$$
$$\xrightarrow{\mathrm{(CH_3)_3SiCl}} \mathrm{C_2H_5{-}O{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}O{-}(CH_2)_6{-}[Si(CH_3)_2{-}O]_{3n}{-}Si{-}(CH_3)_3}$$
$$\xrightarrow[\mathrm{H^+}]{\mathrm{H_2O}} \mathrm{HO{-}(CH_2)_6{-}[Si(CH_3)_2{-}O]_{3n}{-}Si{-}(CH_3)_3}$$

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:

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

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