

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.

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- (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 uses¹

$$f = c - p + 2$$

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 written³

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

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.

Acknowledgment. I would like to acknowledge support of this work from the National Science Foundation Grant No. DMR 76-19488 and from the National Institutes of Health for a Research Career Award.

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- (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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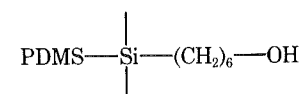
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Reactive and in particular functionally terminated (telechelic) polymers present a growing interest in the production of homogeneous as well as heterophase materials. For instance, "liquid rubbers" (carboxyl- or hydroxyl-terminated (co)polydienes) 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 polyurethanes² and multiblock copolymers, together with a polycarbonate³ or a polyether⁴ 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 Greber⁶ and Marvel⁷ illustrate the complexity of the multisteps synthetic routes and the poor control of both molecular weight and functionality.

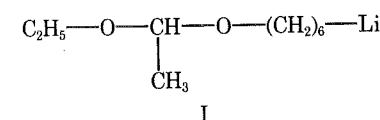
Generally, the best controlled telechelic polymers are obtained by living anionic methods implying the use of functionally substituted initiators. An excellent example is the preparation of dihydroxyl terminated polybutadiene starting from a lithioalkylacetal initiator.⁸

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:



Experimental Section

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



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

Hexamethylcyclotrisiloxane (D₃) Polymerization. A suitable amount of lithioacetal in benzene is added to a solution of D₃ (20%) in the same solvent. After 16 h, dry tetrahydrofuran (THF) is added (benzene/THF ≈ 1) and the temperature is raised to 50 °C. Four hours later, the living acetal PDMS is deactivated with (CH₃)₃SiCl, or coupled with (CH₃)₂SiCl₂, and finally precipitated in methanol. The hydrolysis of the acetal end group takes place in a toluene/H₂O solvent (3/1) with dichloroacetic acid as catalyst following Schulz's procedure.⁸

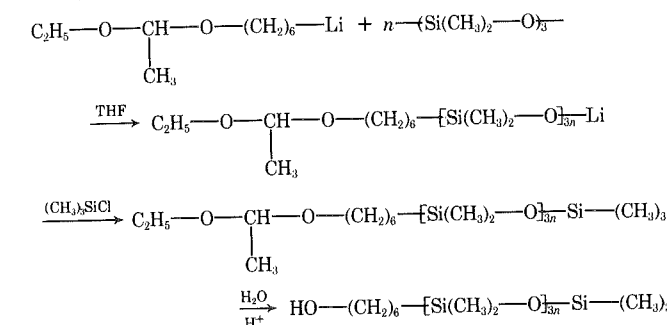
Molecular Weight Determinations. The mean number molecular weights \bar{M}_n are measured by vapor pressure osmometry (VPO) in toluene at 37 °C with a 5% accuracy. The polydispersity index is evaluated by gel permeation chromatography (GPC) in THF at 25 °C. The polystyrene calibration is used (corrections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

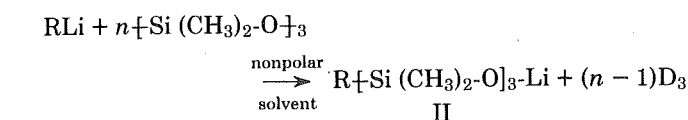
Consequently, it was very attractive to evaluate the lithioacetal (I) as an initiator of the D₃ polymerization in THF:



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-known¹¹ that in a nonpolar solvent an organolithium can attack only one D₃ molecule:

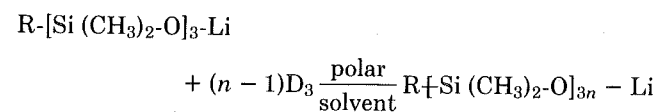


Once the medium is made more polar (i.e., by adding THF),

Table I

M_{calcd}	$\bar{M}_n(VPO)$	\bar{M}_w/\bar{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.



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 D₃ 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 (\bar{M}_w/\bar{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 D₃ 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 Schulz⁸ in the case of a hydroxyl polybutadiene.

The coupling of living acetal PDMS with (CH₃)₂SiCl₂ 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 D₃ polymerization. They offer an attractive route to the synthesis of ω -hydroxyalkyl polydimethylsiloxanes, CH₃-[Si(CH₃)₂-O]_n-Si(CH₃)₂-(CH₂)₆-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 silicon atom (six carbons) ensure the remarkable hydrolytic stability of such telechelic polymers. Their polydispersity is reduced and their functionality quasi-ideal.

Acknowledgment. P.L. is also indebted to I.R.S.I.A. for a fellowship.

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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 occasions²⁻⁵ 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.

Table I
Organization of Mesomorphic Monomers and Their Polymers

Monomer	Polymer ^a					
	Molecular structure	Transition °C ^b	d , Å	D , Å	Organization	Ref
1. CH ₂ =CHPhN=CHPhC≡N		K 113 N 140.5 I		4.9	Nematic	9
2. CH ₂ =CHPhN=CHPhCH=NPhCH=CH ₂		K 180 N polymer		5.1	Nematic	7
3. CH ₂ =CHCOOPhCH=N-N=CHPhOOCCH=CH ₂		K 140 N polymer		5.3	Nematic	7
4. CH ₂ =CHPhN=CHPhOC ₄ H ₉		K 88.3 N 120.6 I	26 (b, i)	5.0	Intermediate $l \sim 19$ Å	6
5. CH ₂ =CHPhN=CHPhOC ₆ H ₁₃		K 94.5 S 97.5 N 116 I	28.5 (b, i)	5.0	Intermediate $l \sim 22$ Å	
6. CH=CHCOOC ₂₇ H ₄₅		K 118.7 I 127 (78 C)	33.4 (b, i)	6.4	Intermediate $l \sim 18$ Å	13
7. CH ₂ =CHCOOPhCH=NPhOC ₂ H ₅		K 78 N 136 I	32 (s, i)	4.9	Smectic $l \sim 18$ Å	11
8. CH ₂ =CHCOOPhCH=NPhN=CHPhOOCCH=CH ₂		K 180 S polymer	22.2 (s, i)	5.0	Smectic $l \sim 22$ Å	7
9. CH ₂ =CHCOOPhPh		K 65 I	23.2 (s, i)	5.2	Smectic $l \sim 11$ Å	12
10. CH ₂ =C(CH ₃)COOC ₂₇ H ₄₅		K 109 I (103 C 85 K)	36.5 (s, i)	6.3	Smectic $l \sim 18$ Å	13
11. CH ₂ =CHCOOPhCOOC ₂₇ H ₄₅		K 128 C polymer	45.2 (s, i)	6.1	Smectic $l \sim 23$ Å	13
12. CH ₂ =CHCOOPhCOOH		K 201 I	17.7 (vs, i)	4.7; 5.1	(Form II) $l \sim 11$ Å	8
13. CH ₂ =C(CH ₃)COOPhCOOH		K 182 I	19 (vs, i)	4.4	Smectic (C) $l \sim 11$ Å	6
14. CH ₂ =C(CH ₃)COOPhCH=NPhCOOH		K ₁ 182 K ₂ 201 S 205 N polymer	32 (s, i)	5.1	Smectic $l \sim 16.5$ Å	15

^a Structural information: d = low-angle spacing; D = wide-angle spacing; vs = very sharp; b = broad; i = intense; l = approximate length of the side group (from molecular models). ^b Transition temperatures: I = isotropic; N = nematic; C = cholesteric; K = crystal; () = monotropic transition; polymer = polymerization ensues.

From a phenomenological point of view one can qualitatively explain these effects by extending to the case of polymers some simple structural considerations initially developed by Gray for low molecular weight thermotropic liquid crystals.¹⁴ Nematic phases are as a rule obtained through strong terminal and weak lateral interactions between molecules. Smectic phases are the result of weak terminal and stronger lateral attraction forces. Thus, one can state very schematically that dipoles operating across the long molecular axes (transverse dipoles) enhance smectogenic tendencies, while dipoles operating along these axes weaken these tendencies through mutual electrostatic repulsion. One should, however, beware of oversimplification and keep in mind that the precise part of a given dipole in the establishment of the mesophase depends on the overall balance of terminal to lateral interactions. For example, a terminal dipole acting at an angle can have a nematogenic effect by strengthening the terminal attraction between molecules. Removed from the end of the molecule the same dipole will strengthen the lateral attractions. This is the pattern of behavior of many homologous series in which lower members display nematic behavior whereas the higher members (long paraffinic chains) are smectogenic. If a structural element weakens the cohesion of molecules in the smectic layers, a nematic or isotropic phase results. Thus, branching weakens lateral cohesion and also weakens the smectogenic tendencies.

These considerations are still qualitatively valid in the case of polymers in which the mesomorphic side groups are placed in the vicinity of each other by their attachment to the backbone of the macromolecule.

It is apparent from Table I that the presence of two strong transversal dipoles (carboxy group) leads in the overwhelming majority of cases to polymers with a well-defined lamellar (smectic) organization. Acrylic and diacrylic derivatives are good examples of this tendency. Polymers prepared from acrylic or methacrylic esters of benzoic acids give well defined smectic arrangements.^{6,8} Conversely, the absence of strong transversal dipoles and the presence of one or several strong longitudinal dipoles in a rigid and polarizable side group will decrease the tendency of the polymer to organize into well-defined layered arrangements, possibly by pushing the mac-

romolecular backbone out of the confining planes. Poly[*N*-(*p*-cyanobenzylidene)-*p*-aminostyrene] and poly[*p*-phenylenebis(*N*-methylene-*p*-aminostyrene)] are examples of such exclusively nematic structures (monomers 1 and 2).

In all cases, the presence in the side group of a long linear paraffinic chain or a cholesterol moiety increases the tendency to form layered structures.

Some polymers given in Table I develop arrangements of side groups intermediate between a well-defined lamellar organization and a nematic organization. Monomers 4, 5, and 6 give polymers characterized by such an intermediate structure. The x-ray patterns of this group of polymers have in common a rather broad but intense low-angle reflection and a diffuse ring at 4-5 Å. This is compatible with a more fluid layered structure of side groups and can perhaps be considered as a special case of nematic arrangements of higher order. It is possible to see from the table that the corresponding monomers have a structure intermediate between that of smectic and exclusively nematic monomers. For example, the replacement of the strong longitudinal terminal C≡N dipole in monomer 1 by the weak, transverse dipole of an alkoxy group in monomer 4 produces a polymer with such an intermediate structure. Similarly, the replacement of one or more transverse dipoles (carboxy group) by a longitudinal dipole may impair the well-defined smectic organization in the polymer.

Di(*N*-*p*-acryloyloxybenzylidene)hydrazine (monomer No. 3) gives a polymer with a nematic organization of side groups in spite of two strong transverse dipoles. This apparent discrepancy can be rationalized: the relatively free rotation around the =N-N=hydrazine bond unsettles the rigidity of the side group. This point was confirmed experimentally by x-ray measurements of the average distance D between side groups. This distance was found to be substantially larger in polymer 3 than for other polymers with a Schiff-base structure (see Table I).

This last example shows the danger of predicting the nature of the order in polymers with mesomorphic side groups from qualitative structural considerations. The combined influence of geometry, polarizability of structural elements, and distribution of polar interactions in the side group on the balance