SYNTHESIS AND CHARACTERIZATION OF POLYCARBONATE-POLYDIMETHYLSILOXANE BLOCK COPOLYMERS

by

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Chapter I

INTRODUCTION

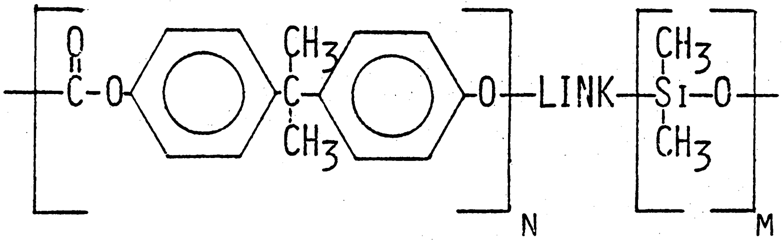
Block copolymers are generally characterized by long sequences of each of two dissimilar structures chemically combined at their terminal segments. The architectures within this class of polymers ~~varies~~ vary from A-B to A-B-A and to $(A{-}B)_N$ structures wherein A and B denote different chemical components. If the physical properties of these A and B blocks differ sufficiently and the block segments are of sufficient length (1-4), these polymers tend to phase separate on a microscopic scale. Thus, small domains of one type of block tend to be dispersed in a continuous matrix of the complimentary structure. The covalent bonds linking these block structures prevent them from the separation on a macroscopic scale characteristic of incompatible physical blends.

Thermoplastic elastomers are probably the most industrially important class of materials resulting from this microscopic phase separation behavior developed to date. These linear materials are characterized by the mechanical properties of a crosslinked rubber and the processibility of a thermoplastic. These polymers are normally of either A-B-A or $(A{-}B)_N$ architecture wherein A is a high Tg glassy or crystalline structure and B is a softer, low Tg (Tg well below room temperature) segment. Bulk composition must be high in the percentage of the soft block in order to provide the necessary continuous elastomeric matrix. The domains composed of the more rigid blocks provide physical sites which serve the same function as both chemical crosslinks and filler particles in crosslinked rubber (5-8).

Random copolymers are generally defined as polymers in which there is a random or statistical coupling of the types of monomers. This normally produces short sequence lengths which in turn produces a one phase system possessing properties intermediate between the corresponding homopolymers. It is possible, however, to produce copolymers intermediate in structure between the normal conceptions of block and random copolymers. For example, Vaughn et al. (9) solution synthesized polycarbonate-polydimethylsiloxane copolymers by reacting a preformed bisphenol-A terminated polydimethylsiloxane with bisphenol-A and phosgene. Although a minimum length of the siloxane block corresponding to the preformed oligomer length was insured, the length of the polycarbonate block formed in situ was much less defined. In the event of extreme dissimilarity of the two chemical structures involved as in the case of the bisphenol-A carbonate-polydimethylsiloxane somewhat random copolymers just described (the solubility parameter of bisphenol-A polycarbonate is 9.9 while the solubility parameter for polydimethylsiloxane is 7.3) (10-11), microphase separation may occur even in these less tailored systems.

The thermal behavior of multiphase block copolymers also reflects their phase separation. Two distinct transition temperatures separately characterizing each microphase occur. Their positions in the case of good phase separation are close to the positions of the respective homopolymer transitions and are not dependent on bulk compositional changes. In contrast, one-phase random copolymers exhibit only one Tg intermediate between the transitions of the homopolymers involved (12).

Thermoplastic elastomers based on polycarbonate-polysiloxane block copolymers display some intrinsic properties which may be of interest as biomaterials (12). The foremost intent in the research discussed herein was to prepare polymers of the generalized structure shown below which may prove suitable for such uses. There are at least two basic requirements for materials which one might consider for biological end-uses. First, the polymers should be "compatible" (e.g. not coagulate) with blood, and secondly, the materials must also be very stable in the physiological environment. The latter requirement specifically requires that the copolymers possess good hydrolytic stability.



Earlier publications from this laboratory (13-15) and elsewhere (12, 16-18) demonstrate that the subject block copolymers and related structures easily undergo a microphase separation above segment molecular weights of a few thousand. This was recognized as being a function of the inherent immiscibility of bisphenol-A polycarbonate and polydimethylsiloxane block structures. Such phenomena even affect the melt rheology of these systems (11, 18-20). Quantification of this immiscibility has been probed by inverse gas chromatography (21-22). Moreover, in polystyrene-polydimethylsiloxane block copolymer systems (23-25), in our preliminary work (13, 26), and earlier work by Gaines and LeGrand (27), it was demonstrated that the polydimethylsiloxane component migrates to the surface of films of these materials in preference to the other component domains. This phenomenon was attributed (12, 23-26) to the fact that the polydimethylsiloxane component has a considerably lower surface free energy relative to polystyrene or polycarbonate. The pure polydimethylsiloxane homopolymer surface is known to be quite "compatible" with blood (28). The fact that surfaces of the films of these copolymers could be tailored to be composed predominantly of siloxane (13-14) suggested that the surfaces and, hence, the materials, could be tailored to be biologically "compatible" in the sense defined earlier.

In view of the requirement for good hydrolytic stability, block copolymers with two different types of bonds between the block structures have been investigated:

1. $\equiv$Si-O-C$\equiv$ links
2. Direct $\equiv$Si-C$\equiv$ links.

The relative hydrolytic stabilities of the $\equiv$Si-O-C$\equiv$ bond versus the $\equiv$Si-C$\equiv$ bond in some siloxane copolymers has been extensively studied and it is generally agreed that the $\equiv$Si-C$\equiv$ bond is much better, even though the $\equiv$Si-O-C$\equiv$ bond (28) is the link of choice when thermal stability is required.

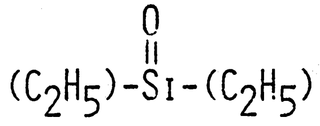
Chapter II

LITERATURE REVIEW

This section contains a general review of the syntheses and properties of both polysiloxanes and polycarbonates. Each section, however, emphasizes those aspects considered most pertinent to the specific research described herein. Consequently, in the polysiloxane section, emphasis will be placed on the synthetic polymerization of cyclic monomers and on biological aspects. A separate section will be devoted to surface properties of siloxane copolymers. The polycarbonate section will be both more brief and more general. Finally, a section covering previous syntheses of polycarbonate-polysiloxane copolymers and their observed properties will be included.

Siloxanes: Introduction

The first syntheses of the major types of the polyalkylsiloxanes were performed by Friedel, Ladenburg, and Crafts in 1865-1871 (29-34). Ladenburg probably obtained the first alkylsiloxane polymer when he saponified either diethyldichlorosilane or diethyldiethoxysilane but he erroneously assumed the structure of his polysiloxane products to be ketones, **1**. The first pure cyclic siloxane, hexaphenylcyclotrisiloxane



$$(C_2H_5)-\overset{\overset{O}{\|}}{Si}-(C_2H_5)$$

1

was prepared and characterized in 1904 by Dilthey (32). Although Ladenburg first prepared siloxane polymers in 1872, it was not until the early 1900's that F. S. Kipping and his group proved the siloxane polymeric structure (31). This group prepared a large number of linear and cyclic polymers of type $(R_2SiO)_N$ and $HO(R_2SiO)_NH$, and also crosslinked architectures $(RSiO_{3-N}H_{3-2N})_M$. Kipping's studies disclosed for the first time that the Si-O-Si group differs dramatically from the C-O-C group in its reactivity and that the Si-O-Si group could be particularly easily cleaved by acids, bases, or Lewis acids. He was the first to observe the catalytic effect of acids and bases for the now commercially important siloxane redistribution and ring opening polymerization reactions. Following this period, commercial production of siloxane polymers was restrained by the absence of convenient methods for monomer synthesis. In the 1930's, Eugene G. Rochow at General Electric (28, 32, 35) and the German, R. Müller (nine months later), apparently independently discovered what is known as the "direct process" (36) and, in so doing, pioneered an industry via the economical manufacture of the family of methylchlorosilanes necessary for siloxane production. Controlled hydrolysis of the various organohalosilanes then provided the cyclic trimers and tetramers used for polymerization.

Today, there are four major producers of the various forms of siloxane products in the United States: Dow-Corning Corporation, General Electric Company, Stauffer-Wacker Chemical Company, and Union Carbide Corporation. The products include a variety of fluids, resins, elastomers (including the important RTV formulations) and copolymers of silicones with organic polymers.

Siloxanes: Physical/Chemical Characteristics

The sigma silicon-oxygen bond in siloxanes is formed through the interactions of the electrons in $3s3p^3$ hybrid orbitals on silicon with electrons in the 2p orbitals on oxygen. Although there is now some question as to the nature of an additional form of bonding contribution, physical characteristics of the Si-O bond have led to the general agreement that some type of additional bond component does exist.

In the majority of silicon compounds, the length of the Si-O bond is $\cong 1.64$ Å (32). This value is substantially smaller than the 1.83 Å sum of the atomic radii (1.17 Å for silicon and 0.66 Å for oxygen). The polar nature of the bond serves as a partial rationalization for the shortness of the bond. On Pauling's electronegativity scale silicon is assigned a value of 1.8 which is in large contrast to the value of 3.5 assigned to oxygen (28). The percent ionic character of the bond has been estimated to be 40-50% (32, 37). Evidently, however, the polar bond component does not account for the extent of bond shortening existing in these compounds. The abnormally large $Si\overset{O}{\diagup\diagdown}Si$ bond angles also testify to an additional type of bonding. The valence angle between oxygen bonds increases in the following order: $CH_3\overset{O}{\diagup\diagdown}CH_3$ (111.43^o) < $H_3Si\overset{O}{\diagup\diagdown}CH_3$ (120.6^o) < $H_3Si\overset{O}{\diagup\diagdown}SiH_3$ (144^o) (32). It varies between 130-145^o in cyclosiloxanes containing more than three siloxane units and in linear and branched siloxanes (32). The relative base strength of silyl ethers as compared to their carbon analogs declines in the order R_3COCR_3 > R_3COSiR_3 >> $R_3SiOSiR_3$ (thereby paralleling the bond angle "deformation" pattern)(38). Silylamines are weak bases compared to alkylamines and silanols are stronger acids than the corresponding alcohols (29). The prevailing explanation of the abovementioned phenomena lies in the possible existence of backbonding between the filled p orbitals on oxygen and the empty $3d_{z}2$ and $3d_{x}2_{-y}2$ orbitals of silicon (29, 32, 39). Recently, it has been suggested that hyperconjugation effects involving σ^* orbitals would also explain the physical properties observed (40).

In contrast to the polar nature of the Si-O bond, the Si-C bond is basically covalent. Electronegativities of silicon and carbon on Pauling's scale are 1.8 and 2.5 respectively. Using equation 1 as a first approximation to calculate the % ionic character of the Si-C bond reveals it to be 88% covalent and 12% ionic (28).

Equation 1

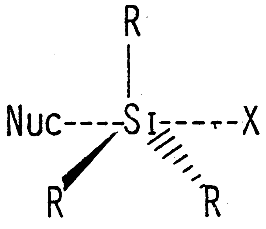
$$\text{Polar Bond Contribution (\%)} = 100\ [1 - e^{0.25}(X_A - X_B)^2]$$

X_A and X_B = Electronegativities of Elements A and B

On the basis of electron diffraction and X-ray structure methods, a helical shape has been proposed for the polyorganosiloxane molecule (32). In such a conformation, the siloxane bonds would be oriented towards the screw axis with the organic substituents protruding outwards to form a nonpolar organic sheath around the molecule. Flory, Crescenzi, and Mark (41) attributed this type of structure to the intramolecular dipole stabilization offered through the positioning of an Si-O bond opposite an O-Si group in immediately adjacent turns of the helix (and vice versa). This helical structure helps explain the unusually low intermolecular forces existing in the siloxanes which is in turn responsible for many of their unique properties. Undoubtedly, however, the "additional bond component" existing in the Si-O bond in conjugation with the σ bond also contributes to this phenomenon.

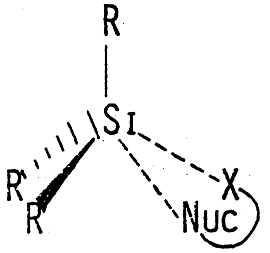
It is generally agreed that the polar nature of the Si-O bond together with the relative ease of substitution on silicon renders the $Si^{\diagup O \diagdown}C$ group relatively labile hydrolytically in most organosilicon compounds (28,32).

Hydrolytic substitutions on silicon probably proceed by either an S_N2 or "S_N2-Si" mechanism (42). Both involve pentacoordinate transition states as illustrated below (**2**, **3**, **4**).



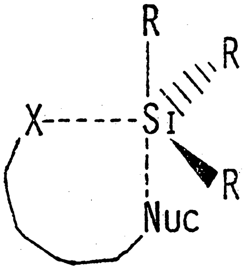
S_N2 TRANSITION STATE

2



S_N2-Si TRANSITION STATE (TETRAGONAL PYRAMID)

3



S_N2-Si TRANSITION STATE (TRIGONAL BYPYRAMID)

4

The S_N2 mechanism proceeds as usual with inversion of configuration. However, the cyclic transition state involved in the "S_N2-Si" mechanism results in retention of configuration. The increased reactivity of silicon as opposed to carbon toward these mechanisms can be attributed to less steric strain in the five-coordinate species. Also, these transition states may be stabilized through 3d orbital participation (43).

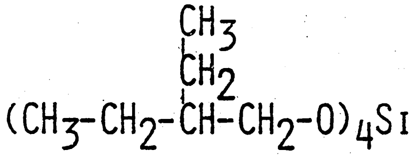
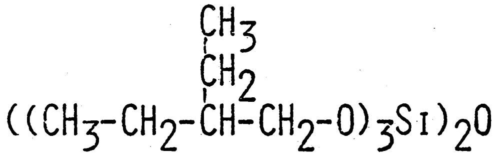
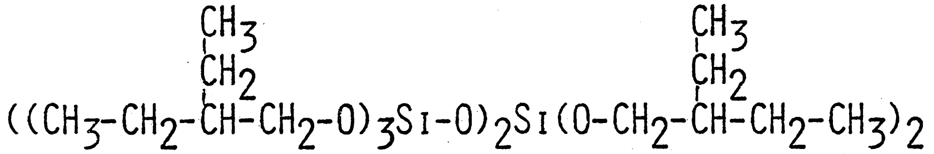
In keeping with analogous carbon mechanisms involving 5-coordinate intermediates, the rate of hydrolysis of silyl ethers is dramatically dependent on steric factors. Whereas tetraphenoxysilane hydrolyzes in the presence of atmospheric moisture, phenylphenoxysilanes remain practically unchanged under such conditions (32). Abbott et al. systematically studied the relative rates of hydrolysis of various alkoxy substituted silanes and siloxanes in boiling water (44). Table 1 lists some of their results. The results demonstrate that all of the alkyl groups which impart any degree of steric hindrance render those molecules more resistant to hydrolysis than the n-alkyl cases. Increasing from a silane to a siloxane produced a small decrease in hydrolysis rate but not nearly as large an effect as changes in alkyl groups produced.

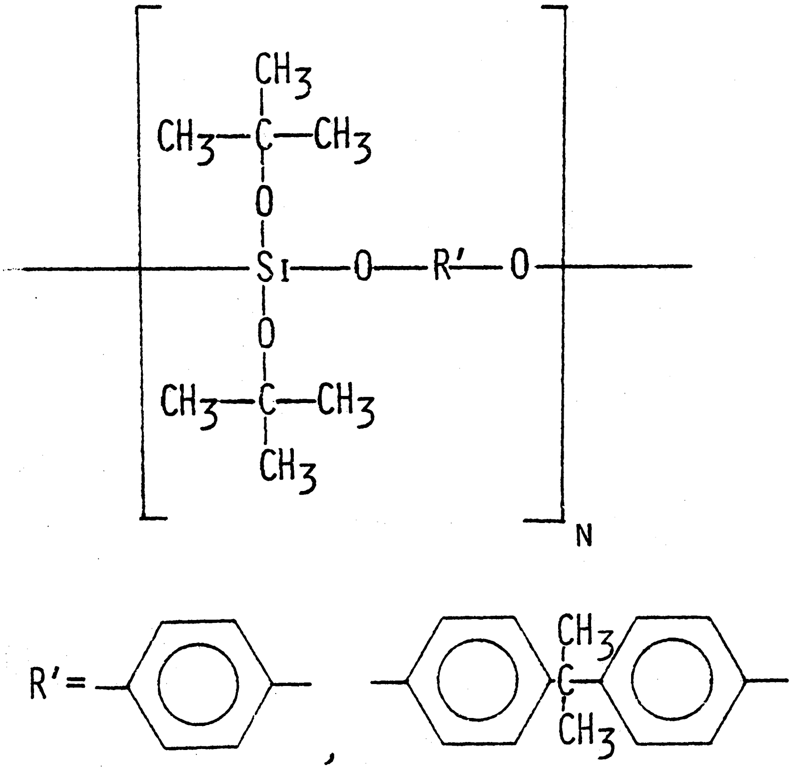
Not surprisingly, hydrolysis is greatly facilitated in a homogeneous medium. For example, hydrolysis of alkyl-2,3-epoxypropoxysilanes in heterogeneous media proceeded at a noticeable rate only when heated, while in a homogeneous medium decomposition proceeded rapidly at room temperature (32).

Since steric and solubility effects might be altered for the cases of Si-O-C bonds occurring in polymeric siloxane molecules, a consideration of hydrolytic stability in molecules of these types must also be made. Yoshimoto et al. (45) prepared polymers 5 which were shown to be hydrolytically stable in neutral aqueous media. In contrast, corresponding polymers of structure 6 hydrolyzed at room temperature (32). Polymeric siloxanes 7 were also prepared and analyzed (46-48). In the case of R equaling the cycloalkylene structure, these polymers were reportedly

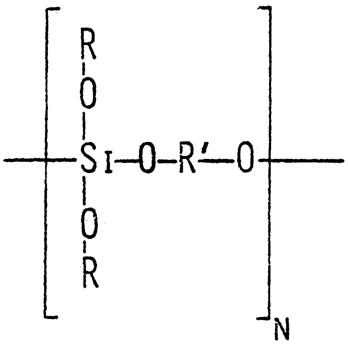
TABLE 1 (44)

Hydrolytic Stability of Tetraalkoxysilanes (Siloxanes) in a Heterogeneous Neutral Boiling Water Medium

Formula	Hydrolysis time up to gel formation (hrs.)
$(C_2H_5O)_4Si$	2
$(n\text{-}C_4H_9O)_4Si$	32
$(CH_3(CH_2)_6O)_4Si$	25
 $(CH_3\text{-}CH_2\text{-}\overset{\substack{CH_3\\|\\CH_2\\|}}{CH}\text{-}CH_2\text{-}O)_4Si$	75
$(n\text{-}C_4H_9O)(t\text{-}C_4H_9O)_3Si$	236
$(sec\text{-}C_4H_9O)_4Si$	500
$((sec\text{-}C_4H_9O)_3Si)_2O$	300
$((sec\text{-}C_4H_9O)_3SiO)_2Si(sec\text{-}C_4H_9O)_2$	1600
 $((CH_3\text{-}CH_2\text{-}\overset{\substack{CH_3\\|\\CH_2\\|}}{CH}\text{-}CH_2\text{-}O)_3Si)_2O$	120
 $((CH_3\text{-}CH_2\text{-}\overset{\substack{CH_3\\|\\CH_2\\|}}{CH}\text{-}CH_2\text{-}O)_3Si\text{-}O)_2Si(O\text{-}CH_2\text{-}\overset{\substack{CH_3\\|\\CH_2\\|}}{CH}\text{-}CH_2\text{-}CH_3)_2$	126

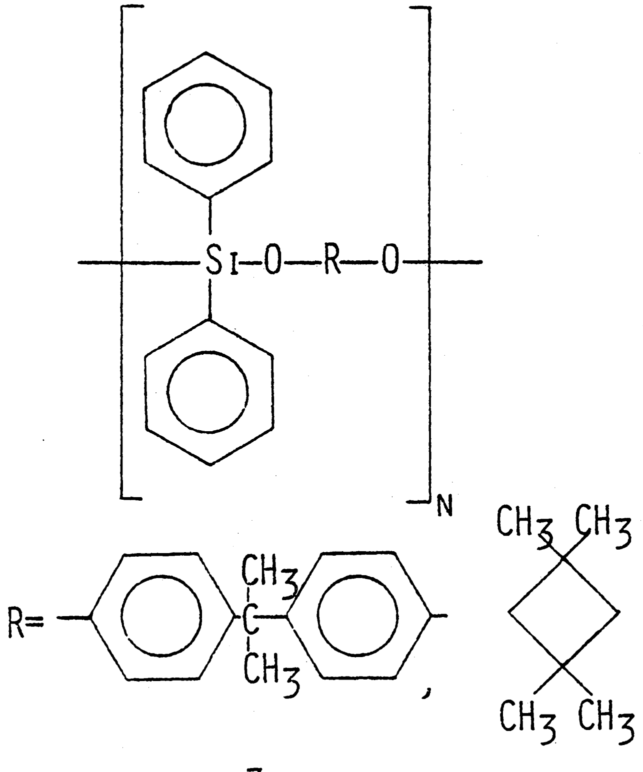


5



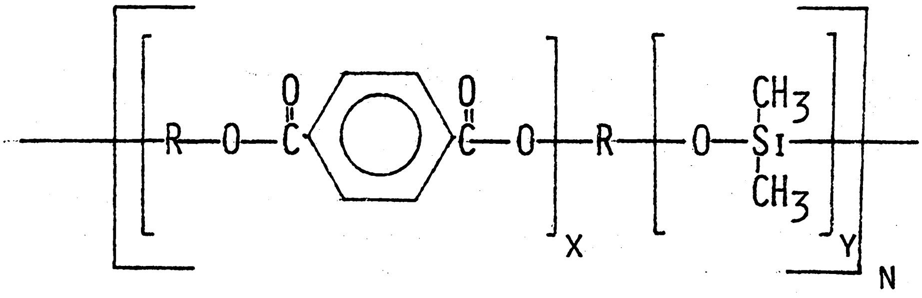
R= CH_3, C_6H_5

6



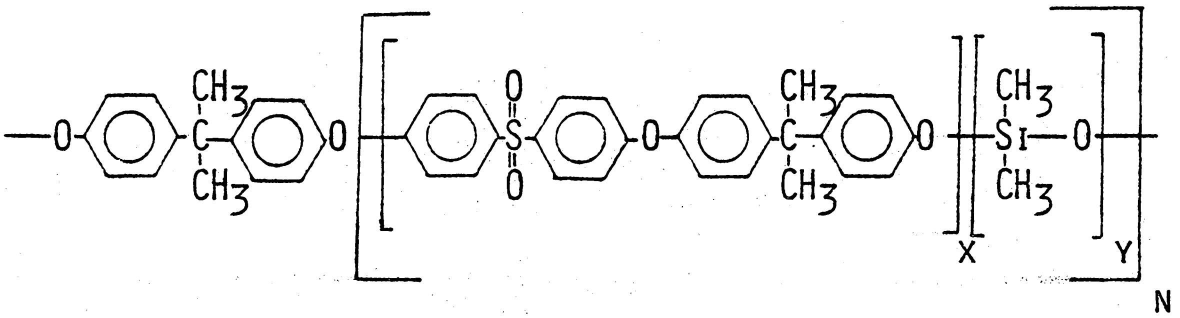
7

"relatively stable to hydrolysis." However, the polymer prepared with bisphenol-A "underwent rapid hydrolytic degradation." The hydrolytic stability of block copolymers, 8, was investigated by Metkin et al. (49) by subjecting the polymers to water vapor (160-220°C) under an argon

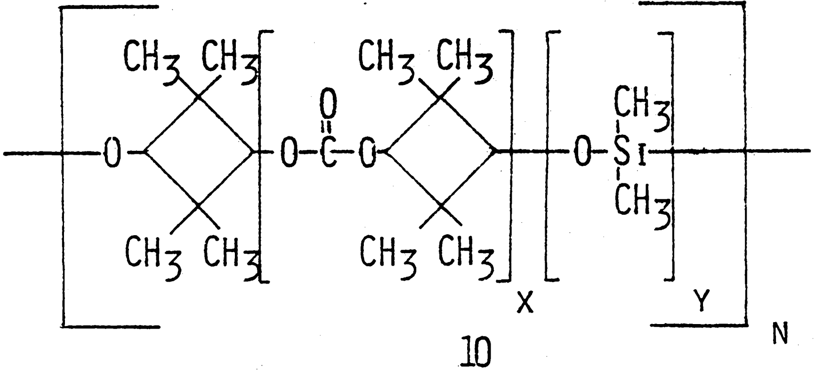


8

atmosphere. Under these conditions, the Si-O-C bond hydrolyzed while the Si-O-Si bonds reportedly remained intact. On the other hand, Noshay and Matzner (48) prepared block copolymers 9 and 10 wherein the blocks were linked through Si-O-C bonds. Solution cast films of 9 retained



9



10

80% of their initial reduced viscosity after exposure to boiling water for two weeks. Block copolymer 10 showed no change in reduced viscosity after being subjected to boiling water for 8 weeks. The superior hydrolytic stability of these polymers as opposed to literature data on low molecular weight compounds was attributed to three factors (48):

"1. Hydrophobicity due to the presence of long siloxane segments.
2. Steric shielding of the Si-O-C linkages by the long adjacent segments.
3. Low concentration of Si-O-C linkages in the polymer backbone."

Madec and Marechal compared the hydrolytic stability of poly(ethylene-co-maleate)/polydimethylsiloxane block copolymers containing the Si-O-C bond between the blocks with poly(hexamethylene) adipate/polydimethylsiloxane block copolymers not containing any Si-O-C bonds (50-51). The polymers were placed in plain water for a period of 10 weeks. A decrease in <Mn> for the polymers containing the Si-O-C link was observed in all cases whereas no change occurred for the polymer not containing these bonds. The extent of degradation decreased as the <Mn> of the hydrophobic siloxane block increased from 350 to 1000 g/mole.

Siloxanes: Properties

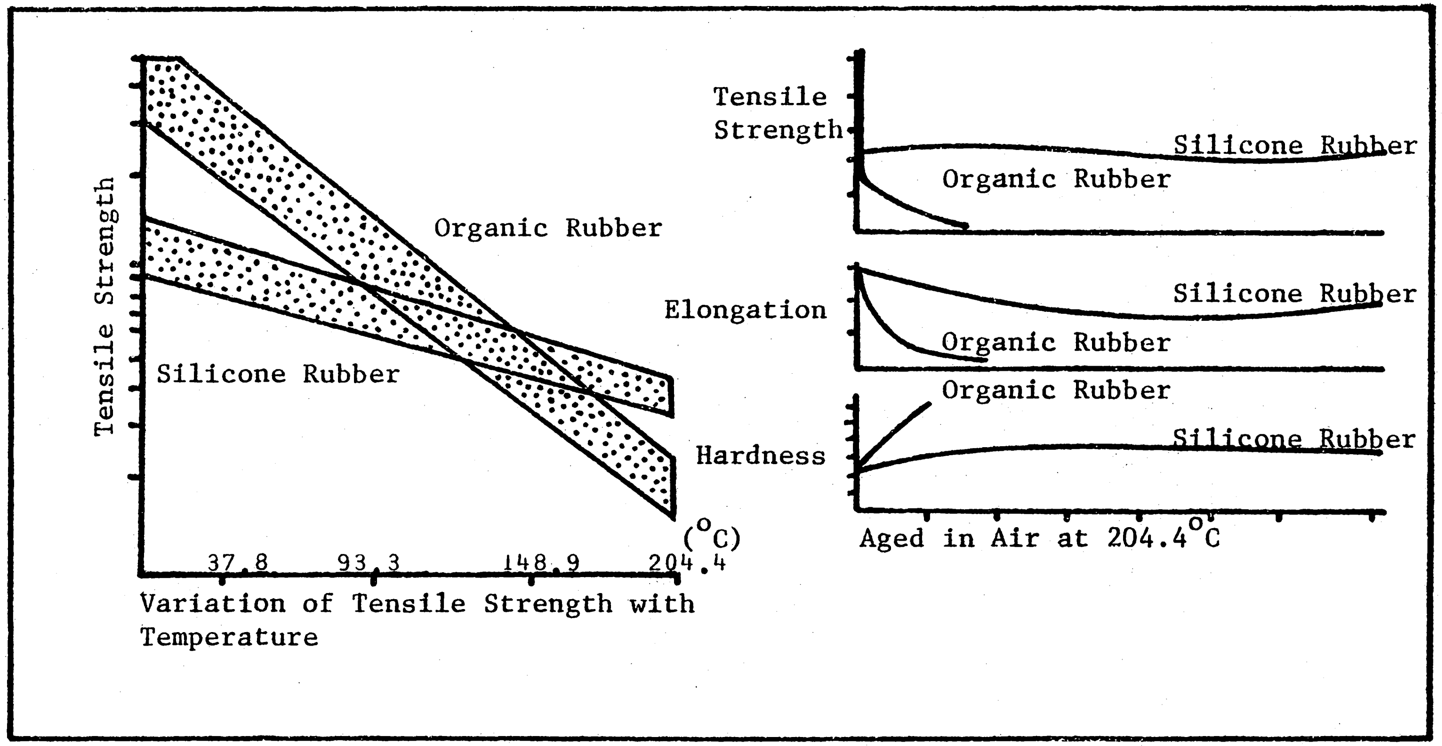
Chief in importance among the properties of the siloxanes is the dramatic thermal stability exhibited accompanied by an unusually mild dependence of physical properties on temperature. For example, general purpose silicone rubber compounds reportedly (35) perform at temperatures ranging from -100 to 260°C without undergoing physical property deterioration. Stability at high temperatures probably results mainly from the high bond energies of Si-O bonds. Representative single bond energies are offered in Table 2 for comparison. These bond energies reflect both the polar nature of the Si-O bond together with additional types of interactions between the atoms. Intramolecular dipole stabilization made possible by the spiral conformation also probably adds to the thermal stability. The wide use range at low temperatures of polydimethylsiloxane elastomers can be interpreted mainly through the unusually weak intermolecular forces. Polydimethylsiloxane rubber has a glass transition temperature of -123°C and crystallizes at a rapid rate at $\sim -54^{\circ}$C (32). Although rotation of the Si-O bond is restricted somewhat, the siloxane backbone is considerably more flexible than that of most other polymers (41). Methyl groups reportedly rotate around the Si-O bonds with unusual ease thereby forcing the siloxane molecules further apart. Undoubtedly, the larger size of silicon as opposed to carbon contributes to the wide spacing between the backbone of the polymer and the organic groups and thereby enhances free rotation. Flexibility of the siloxane chain decreases with increasing steric effects due to organic substituents. The replacement of methyl groups by phenyl substituents appears to induce a particularly marked effect (52).

In comparison with most organic rubbers, unfilled polydimethylsiloxanes have poor mechanical properties in the vicinity of room temperature and below (28, 32). However, the polymers show a substantially smaller decrease in mechanical properties as the temperature is raised (see Figure 1).

Table 2 (28)

SINGLE BOND ENERGIES ($^{KCAL}/_{MOLE}$)

Si-O	88.2, 106, 117, 101
C-O	84.0, 80.9
Si-C	69.3, 75.0, 64, 52-76
C-C	83.1, 84.9



Variation of Tensile Strength with Temperature

Figure 1: Silicone Rubber vs. Organic Rubber (35)

The viscosity of low molecular weight linear and cyclic polydimethylsiloxanes is lower than that of hydrocarbons of comparative molecular weights. As in the cases of other siloxane properties, the temperature coefficient of the viscosity is also extremely low. The poor mechanical properties and low viscosity result from the weak intermolecular forces in these molecules. The siloxane helices tend to straighten out with increases in temperature which leads to a strengthening of intermolecular forces (leading, in turn to more chain entanglement and, hence, to higher viscosity and better mechanical properties). This increase in intermolecular forces compensates somewhat for the usual decreases in these forces with temperature. This compensation allows many of the physical properties of the siloxanes to remain relatively constant with temperature.

A property of siloxanes which has recently gained importance is that of the relatively low surface free energies. This property too is a result of the weak intermolecular forces involved. For linear polydimethylsiloxane, the surface tension increases from $\sim 15 \frac{\text{dynes}}{\text{cm}}$ for hexamethyldisiloxane to $\sim 22 \frac{\text{dynes}}{\text{cm}}$ for a high molecular weight polydimethylsiloxane oil (32). Comparably, the surface tension of cyclodimethylsiloxanes (n=3-7) increases with increase in the size of the ring from ~ 17.3 to $\sim 18.3 \frac{\text{dynes}}{\text{cm}}$ at 25°C (32). This renders the siloxanes useful as additives for applications wherein high surface activity or great spreading power is necessary. Included among these applications are uses as foaming and antifoaming agents and uses as pore structure regulators in foamed materials. They also aid the flow of paints and varnishes and act as mold release agents.

It has been known for some time that siloxanes are surface active in the sense that they are enriched in the surface of liquid phases in which they are soluble (28). There is now growing evidence that the surfaces of films of organic block copolymers containing siloxane blocks are also siloxane rich. This phenomenon has been attributed to the fact that the siloxane block has a lower surface free energy than the other block component (details of these cases will be discussed further on in this thesis).

Due to the somewhat polar siloxane bond, these materials tend to resist homolytic cleavage. This factor and the fact that these molecules contain no double bonds renders them generally resistant to oxidative degradation.

The silicones exhibit a host of additional desirable properties. Inclusive among these are high gas permeabilities, good insulating properties, good resistance to corona discharge and hydrophobicity. For a discussion of these aspects, the reader is referred mainly to Noll (28).

Siloxanes: Biological Aspects

The striking physiological inertness of the high molecular weight polymeric methyl and/or phenyl silicones is well documented. Various studies on animals (23,53-54) and on man (55-57) demonstrate a common lack of pathogenic tissue response to systemically or orally administered silicones. The only problem found has been in the area of eye irritation (28,58). In rabbits, transitory eye irritation reportedly develops within a few hours after contact with these polymers but usually disappears within 24 hours. According to Noll (28), the human eye reacts to contact with a "painful burning sensation." In contrast, however, polydimethylsiloxane (PDMS) fluids have been injected into the eyes of both animals and man as a replacement for aqueous and vitreous humor (58) with no inflammatory response. The silicones are not absorbed through the skin nor do they produce skin irritations when applied to the skin (59). They are not absorbed through the intestinal tract upon ingestion (59-60). Implantation of silicone rubber subcutaneously in man for up to 18 months gave no indication of any carcinogenic effect (59).

Because of the low tissue reaction invoked and the non-allergenic properties demonstrated by these materials, polydimethylsiloxane fluids have been widely used as soft tissue substitutes administered through injections. The reader is referred to several reviews for a listing of laboratory and clinical experiences using these liquids (55,61-63). Used under controlled conditions, the use of these materials is generally considered advantageous as a fat substitute in soft tissue contour restorations. Injections for augmentation of the breast are not recommended because the large doses required interfere with the normal mammary gland architecture (64). Severe complications (formation of mammary granulomas, multiple silicone cysts and lymphatic blockages) have been reported in cases of silicones being used for such purposes (65-66). It is the opinion of several authors (64), however, that the deluge of complications which arose in this area were mainly a result of clinical misuse and were not a result of tissue responses to silicones under optimized conditions.

Heat vulcanized solid silicone rubbers are now widely used for various types of implants and prosthetic devices. Major uses of the materials include hydrocephalus shunts, facial restorations, breast augmentations and reconstructions, and artifical joints (these do not include major load-bearing joints due to problems associated with the mechanical properties of the silicones) (64).

Tissue response to silicone injections and implantations is similar. Initial response is the formation of a granulation tissue layer on the plastic. The amount formed is directly related to the amount of irritation caused by the physical presence of the prosthesis (which will, in turn, be partially related to the amount of motion between the prosthesis and the adjacent tissue). This granulation tissue later converts to fibrous tissue. In the uncomplicated implant, a thin, fibrous capsule will be formed.

Additional established uses of the silicones include incorporation into ointments for skin protection and as additives for cosmetics (nail polish, lipstick). Because of their low surface energy, silicones are used in burn treatments to prevent dressings from sticking.

Although the structural requirements for the non-thrombogenic synthetic plastics are not well understood, it has been established that the polymeric medical grade silicones generally belong to this class (67-76). This factor has led to the use of silicones in synthetic heart valves and various extracorporeal assist devices (e.g. membrane and bubble oxygenators) wherein non-thrombogenicity is essential. Blood compatibility requirements appear stringent, however, as compared to the requirements for low tissue response in the implants previously described. In addition, mechanical property performance requirements for materials comprising prostheses with moving parts (e.g. heart valves) make strenuous demands on silicone (which are known to have relatively poor mechanical properties). Consequently, even though the silicones are considered to be one of the most promising classes of materials (along with the segmented polyether-urethanes) to be used for these types of purposes, development in this area has met with some degree of difficulty.

When synthetic surfaces come into contact with blood, they become coated with plasma proteins within ∿3 sec (68). This protein layer then influences subsequent interactions with blood platelets. The absorption of proteins from plasma is influenced by the type of polymer surface, the properties of blood components, hemorheological parameters, and possibly by ionic species present in the plasma which probably arrive at a surface prior to the proteins. When platelets adhere to proteinated surfaces, they may become activated depending on the molecular stimuli and hemorheological factors, and liberate "coagulation activators." As a consequence, irreversible platelet aggregation results which lead to thrombosis. A thrombus (blood clot) is comprised of fibrin (polymerized and crosslinked fibrinogen), platelets, and red and white cells.

Efforts to explain the compatibility of blood with the silicones and other surfaces in terms of a single parameter have not been successful. Various trends, however, have been observed in terms of parameters such as critical surface tension, intermolecular forces, wettability, ionic charge, and protein absorption isotherms. Dr. D. L. Lyman and his group have contributed a great deal toward the understanding of blood compatibility of siloxanes and other biomedically useful polymers (69-71, 73, 77-80). Early in his work, Lyman reported that an inverse relationship appeared to exist between the surface free energies of a variety of polymers (including siloxanes) and coagulation times of human and dog blood exposed to those surfaces (69). Studies of the interactions of proteins found in the blood and blood platelets with the synthetic polymeric surfaces were conducted (70). On the basis of the size of the proteins involved coupled with the measured plateau amount adsorbed onto the surfaces of the polymers, it was concluded that these proteins did not spread upon adsorption. On the basis of this data, Lyman postulated that thrombosis depended on the interactions between the surfaces and blood platelets. Investigation of this latter type of interaction revealed a qualitative relationship between critical surface tension of the polymer surfaces (siloxanes were included in this study) and platelet adsorption (similar to the relationship previously found between critical surface tension and degree of blood clotting). At this point, it was also observed (via electron microscopy) that platelet adsorption appeared to be competitive with the adsorption of plasma proteins.

Since the late sixties, there has been a growing body of evidence indicating the importance of the nature of the protein layer adsorbed on platelet adhesion (71, 73, 77-85). A direct relationship between the number of platelets adhering to polymer surfaces (including siloxanes) and the tendency of these surfaces to form a clot has been established (71). Evidence that the number of platelets adhering to these surfaces cannot be explained by simple diffusion of the platelets onto those surfaces is claimed (71). This tends to indicate that the nature of the polymer surface is important. In addition, it has been demonstrated that a pre-adsorbed layer of albumin as opposed to a layer of fibrinogen or γ-globulins tend to pacify a thrombogenic surface (71, 73, 78, 86-87) (see Table 3). This has led to the conclusion that differences in the thrombogenicity of noncoated polymers must relate to the nature of the protein layer formed in situ. This protein layer together with the rate of its formation must, in turn, be related to the chemical and physical properties of the polymer surfaces. In vivo experiments in dogs showed dramatic differences in the protein layer adsorbed (see Table 4) in situ. Note that the non-thrombogenic copolyether-urethane (PEUU 1025) showed essentially no proteins other than albumin adsorbed on its surfaces while the thrombogenic Teflon FEP showed a large amount of globulins present. The silicone rubber showed intermediate results in both thrombogenicity (see Table 3) and the percentage amount of globulins adsorbed onto its surface (see Table 4). Based on the data presented immediately above together with protein adsorption data taken under static conditions (no blood flow) (71), two trends were observed concerning the relationship between protein adsorption and the thrombogenicity of the polymer surface: 1. As the amount of protein adsorbed increases, thrombogenicity decreases, and 2, as the fibrinogen to albumin concentration increases, thrombogenicity increases (71).

Recent evidence suggests (71, 88) that the relative hydrophobicity of the polymer surface has a large effect on the amount and rate of protein adsorption. This is rationalized via the assumption that the

Table 3 (78,73)

Platelet Adhesion to Various Surfaces

Surface	Platelet Adhesion[a] 1 min.	 3 min.	 5 min.
Teflon fep	5.4	18.5	clot
Teflon fep/albumin[b]	0.1		0.1
Silastic rubber	4.6		
Silastic rubber/albumin[b]	0.2		0.5
Silastic rubber/fibrinogen[b]	1.3		3.7
Silastic rubber/γ-globulins[b]	1.3		6.1
Biomer[c]	2.2	4.3	5.7
PEUU 1025[d]	0.2	0.4	0.9
PEUU 710[e]	7.5	17.0	25.0

---

a. Mean number of platelets adhering to 20,000 μ^2 surface area after exposure to whole blood in a flow through cell (i.e. no blood came into contact with air).

b. Films were precoated with protein.

c. A segmented polyether-urethane produced by Ethicon, Inc.

d. A copolyether-urethane made by Lyman's group from polypropylene glycol (M_n = 1025 g/mole), MDI, and ethylene diamine.

e. A copolyether-urethane made by Lyman's group from polypropylene glycol (M_n = 710 g/mole), MDI, ethylene diamine.

Table 4 (73)

In Vivo Protein Adsorption on Polymer Surfaces

	Recirculation Time	% of Total Protein Present		
Polymer	min.	Albumin	γ-globulin	Other Globulins
PEUU 710 M[a]	1	0	0	0
	9	0	0	0
	45	62	30	8
PEUU 1025 M[a]	1	0	0	0
	4	100 (trace)	0	0
	45	98	0	2
Biomer	9	100 (trace)	0	0
	45	98	2	0
Silastic Rubber	4	0	0	0
	9	100 (trace)	0	0
	18	0	0	0
	30	60	10	30
	45	70	20	10
Teflon fep	9	100 (trace)	0	0
	18	10	5	85
	30	30	17	53

---

[a] Samples described in footnotes "d" and "e" of Table 3.

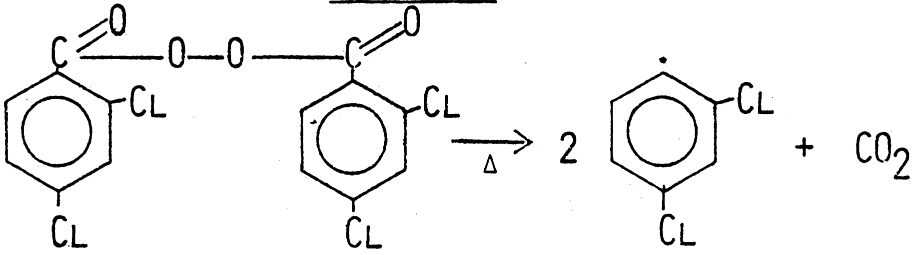
urethane surface would hydrogen bond with water, thereby giving less resistance to the approach of protein molecules as opposed to the cases involving silicones and teflon. This is supported by evidence that the rate of adsorption of proteins and the adsorption plateau is highly dependent upon the rate of blood flow across silastic and teflon surfaces while these factors show no dependence on blood flow rate in the case of "PEUU 1025" (71).

While the evidence presented sheds some light on variables affecting blood compatibility between various classes of polymers, it does not take changes within a given family into consideration. Consequently, the chemistry of various medical grade silicone rubbers presently available commercially shall first be discussed. Following this will be a discussion of experimental changes made in the compounds in order to improve blood compatibility.

The major producer of medical grade silicones is Dow Corning Corporation who markets these products under the general tradename of "Silastic." These products are based upon the chemistry involved in making all silicones as described herein. Most silicone rubbers are compounded with fillers to provide added strength, with various additives (e.g. for color, plasticizing, antioxidation, and heat stability), and with vulcanizing agents. The medical grade polymers contain fillers and a vulcanizing agent by necessity, but do not contain other additives.

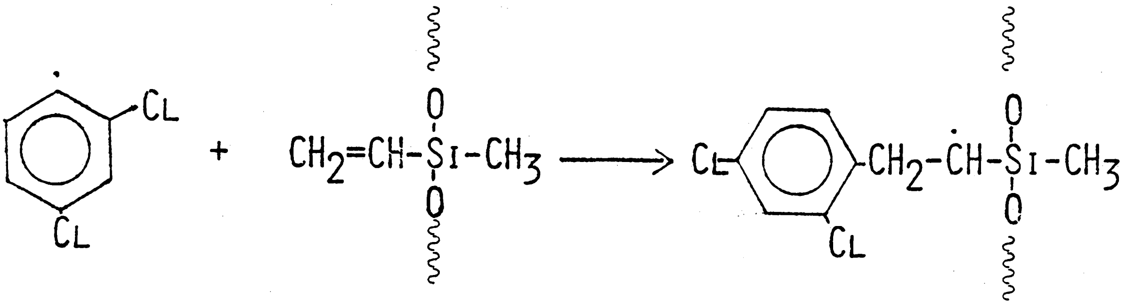
There are three types of heat vulcanized silicone rubbers (medical grade) produced by Dow which mainly differ in that they span a hardness range from soft to hard (89). The filler used in these compounds is a pure, finely divided silica (partical size ≃ 30 mμ). The medium and harder stocks are composed primarily of dimethylsiloxane units with small amounts of methylvinyl units incorporated. One type also contains small amounts of methylphenyl siloxy units in addition to the methylvinyl and dimethyl substituted structures. The vulcanizing agent in all cases is dichlorobenzoyl peroxide, 11. The first step in the crosslinking procedure involved the normal decomposition of the peroxide as shown in equation 2. This radical will then attack vinyl groups present (equation 3). The reaction shown in equation 3 is followed by hydrogen abstraction

Equation 2



11

Equation 3



from methyl groups on neighboring chains accompanied by release of the dichlorophenyl radical (equation 4). The final step involves combination of two alkyl radicals (schematically shown in equation 5 through combination of a methyl and an ethyl radical). The broken down products resulting from the peroxide are fugitive. Properties typical of these heat cured Silastics are listed in Table 5.

Table 5 (89)

Typical Properties of Heat Vulcanizing Medical Grade Silicone Rubber[a]

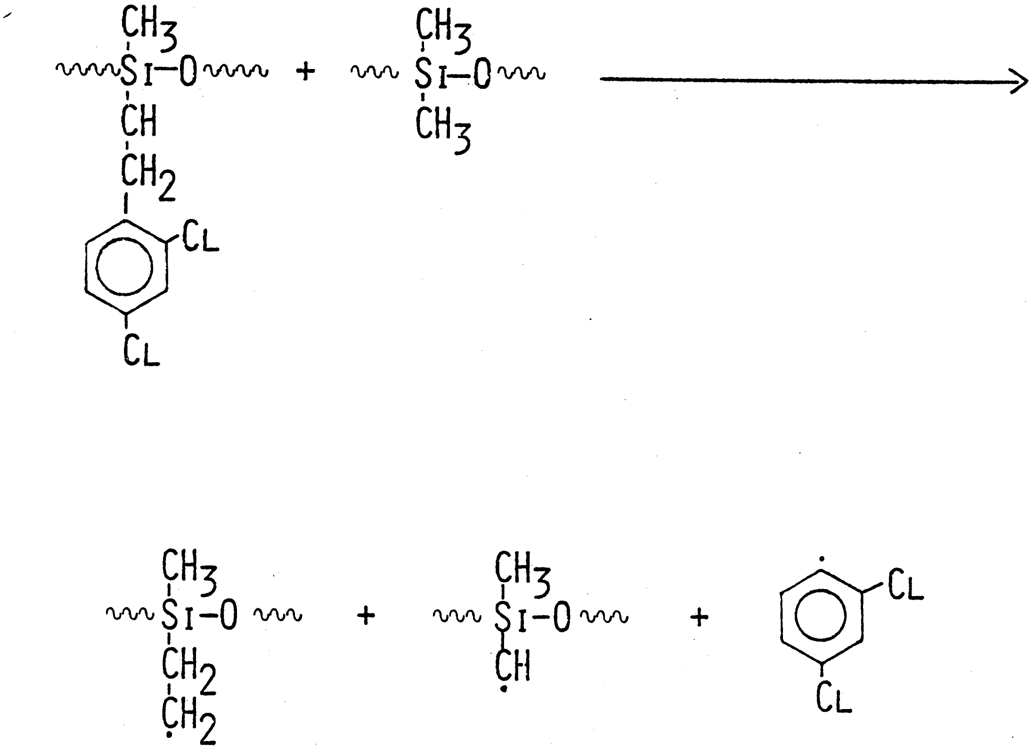
Property	Test Method	Soft	Medium	Firm
Color	---	Translucent	Translucent	Translucent
Specific gravity	---	1.12	1.14	1.23
Durometer hardness, Shore A	ASTM D676	25	50	75
Tensile strength, psi	ASTM D412	850	1200	1000
Elongation %	ASTM D412	600	450	350
Die B tear strength, pi	ASTM D624	70	75	75
Brittle point, °F	ASTM D746	-175	-100	-100
Electric strength,[b] V/mil	ASTM D149	500	540	540
Dielectric constant at 10^2, cps	ASTM D150	2.91	2.8	2.8
Dielectric constant at 10^5, cps		2.90	2.8	2.8
Dissipation factor at 10^2, cps	ASTM D150	0.0006	0.0008	0.0008
Dissipation factor at 10^5, cps		0.0006	0.0009	0.0009

---

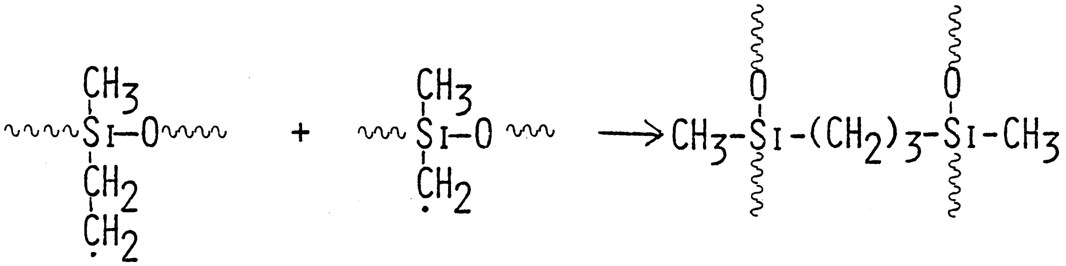
[a] All physical and electrical properties measured on 1/8 in. thick samples molded 5 min. at 240°F and oven cured 1 hr. at 480°F.

[b] Continuous voltage rise, 1/4 in. electrodes, silicone rubber samples 1/16 in. thick.

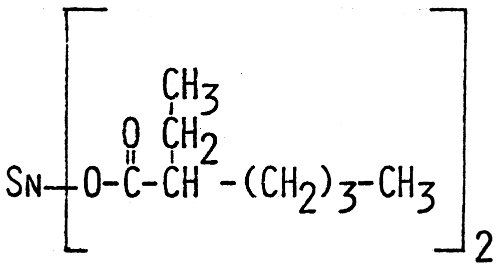
Equation 4



Equation 5



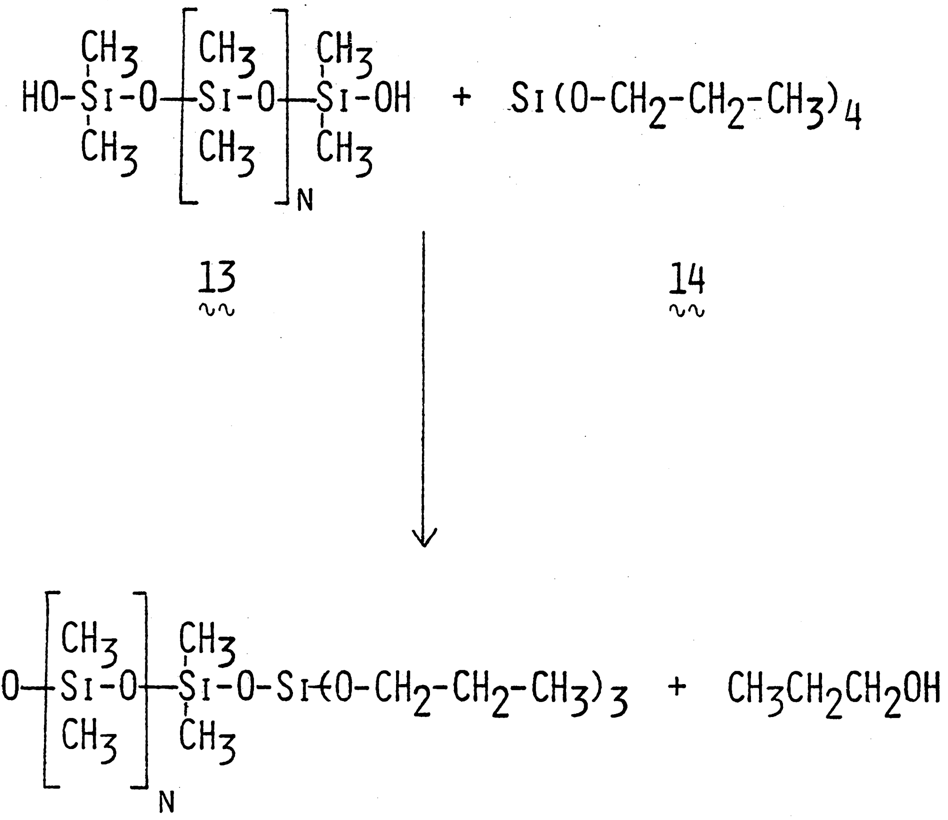
Room temperature vulcanizing (RTV) medical grade silicone rubbers can be of either the one component or two component type. In the latter types, one component is comprised of the stannous octoate catalyst **12** while the other component contains a fluid, hydroxyl terminated siloxane polymer, **13**, with a filler and propyl orthosilicate **14** (the crosslinking agent). A relatively nontoxic substance, n-propanol, is eliminated as the by-product of vulcanization (equation 6).



$$Sn\left[O-\overset{\overset{O}{\|}}{C}-\underset{}{\overset{\overset{CH_3}{|}}{\overset{CH_2}{\overset{|}{CH}}}}-(CH_2)_3-CH_3\right]_2$$

12

Equation 6



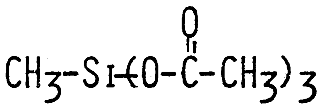
13

14

$$HO-\overset{CH_3}{\underset{CH_3}{Si}}-O\left[\overset{CH_3}{\underset{CH_3}{Si}}-O\right]_N\overset{CH_3}{\underset{CH_3}{Si}}-OH + Si(O-CH_2-CH_2-CH_3)_4 \longrightarrow HO-\overset{CH_3}{\underset{CH_3}{Si}}-O\left[\overset{CH_3}{\underset{CH_3}{Si}}-O\right]_N\overset{CH_3}{\underset{CH_3}{Si}}-O-Si(O-CH_2-CH_2-CH_3)_3 + CH_3CH_2CH_2OH$$

Because of the necessity of mixing in the catalyst, the viscosity of the polymer containing component must remain relatively low (i.e. a relatively small amount of filler can be added). Consequently, these two component RTV systems are mechanically weak relative to the heat vulcanized polymers. They are therefore normally used in static applications only.

The one component RTV materials are composed of a low molecular weight hydroxyl terminated polymer, **13**, and methyl triacetoxysilane, **15**, as the crosslinking agent. The acetoxy group quickly hydrolyzes in the



$$CH_3\text{-}Si\text{-}(O\text{-}\overset{\overset{O}{\|}}{C}\text{-}CH_3)_3$$

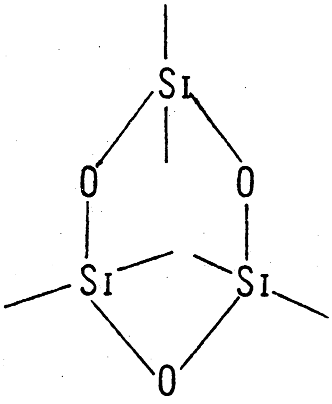
15

presence of atmospheric moisture eliminating acetic acid and producing hydrolytically unstable methylsilanes with multiple hydroxyl groups. These spontaneously condense with the hydroxyl terminated siloxane. The products are normally used as adhesives or caulking compounds. The fillers contained in them are similar to those used in the other types of medical grade silicones.

The silica fillers commonly used in medical grade silicones in order to increase their strength possess fairly high surface free energies. Unfortunately, for most biomedical uses, the extremely poor mechanical strengths of the silicones render them dependent upon usage of these fillers. Indeed, the addition of 20 to 40 wt. % of a fumed silica can increase the tensile strength of silicone rubber from less than 50 psi to more than 800 psi (90). Several authors have investigated the effects of these fillers on the blood compatibility of the siloxanes and found them to be detrimental in this respect (70, 74-76, 91). Kolobow et al. (75) investigated the use of composite membranes for membrane lungs wherein the first layer consisted of standard filled silicone rubber and the outer, blood-contacting layer was comprised of filler free silicone rubber reinforced with a totally immersed polyester fabric. Resistance to blood flow was found to be substantially lower in the cases of using the filler free silicone rubber membranes. Perfusions on lambs revealed that platelet counts of the blood fell almost immediately with the standard membranes while noticeable drops in platelet count were not observed using the filler free silicone coated membranes for 6 hours. The results of Zapol et al. (76) on the same types of systems yielded analogous results.

Gifford (91) studied the effects of tissue response to implants radiation cured without fillers, radiation cured with a filler, and peroxide cured with a filler. The intent in radiation curing was to investigate the effects on tissue response of eliminating possible occluded peroxide by-products. As in the previously described studies, effects of fillers on tissue response was also of interest. Results demonstrated no advantage in the radiation cure over the curing method used by Dow. However, in agreement with data suggesting the adverse effect of fillers on blood compatibility, the filled implants evoked more tissue response than the unfilled implants.

Due to mounting evidence that fillers adversely affect the biocompatibility of these silicones, attempts are being made to improve the mechanical properties of these materials without the addition of fillers. Chawla (74) polymerized D_3, **16**, under high vacuum with gamma



16

radiation. Reportedly, the product was considerably less brittle than commercial unfilled medical grade silicones and had a higher extensibility but comparable strength. This phenomenon was attributed to the fact that crosslinking and polymerization took place simultaneously from a dense, crystalline monomer (as opposed to the crosslinking process taking place in the presence of a relatively expanded polymer). Scanning electron microscopic slides showed the presence of domains with high crosslink density embedded in a matrix of polymer with lower crosslink density.

The high oxygen permeability which renders the silicones useful for membranes in membrane lungs also makes them potentially useful for the manufacture of contact lenses. Lenses made totally from polymethyl-methacrylate hydrogels are not permeable enough to oxygen to assure a sufficiently long contact without damage to the corneal epithelium (92). However, the highly hydrophobic character of the silicones is an obstacle to this use because good wettability by the tear film is essential both for physiological reasons and for the attainment of good vision. Wajs et al. (92) investigated the effect of grafting the relatively hydrophilic poly(vinyl pyrrolidone) onto the dimethylsiloxane backbone. Although the grafting produced an undesirable increase in the wettability by water, it was successful in stabilizing the tear film.

The biomedical utility of the siloxanes discussed up to this point has been based on their biological inactivity. In the late 1960's, Dow Corning Corporation discovered that some phenyl containing siloxanes possessed estrogenic activity (93). This rather unique activity is limited to methylaryl substituted, linear di- and trisiloxanes and cyclic tri- and tetrasiloxanes (94-96).

Siloxanes: Monomer Synthesis

The first step toward the production of siloxane polymers is the building up of elemental silicon to the silanes which are subsequently hydrolyzed to form cyclic and linear siloxanes. By far the most important reaction of this type industrially is still Rochow's "direct synthesis" (97). Although the production of the methylchlorosilanes via this reaction is its largest use, a variety of alkyl and aryl chloro and bromo silanes (28) can be made in this manner. A notable class of substituents which cannot be added to silicon using this route are the perfluorinated alkanes.

The "direct method" involves the reaction of organic halides (e.g. methyl chloride or chlorobenzene) with silicon and silicon alloys in a gas–solid reaction. Reactions of the following types (equations 7-10) occur.

Equation 7: $2RX + Si \longrightarrow R_2SiX_2$

Equation 8: $3RX + Si \longrightarrow RSiX_3 + 2R\cdot$

Equation 9: $3RX + Si \longrightarrow R_3SiX + X_2$

Equation 10: $2X_2 + Si \longrightarrow SiX_4$

A complex mixture of products is yielded: Various organohalosilanes, tetraalkylsilanes, organo-H-halosilanes, silicon tetrachloride, and small amounts of hydrocarbons (generated through the combination of two alkyl radicals). Organic free radicals formed as shown in equation 8 are also responsible for the formation of the hydride substituted silanes formed. Although the composition of the product mixture can be modified by such parameters as the choice of suitable catalysts, controlling the temperature or the use of diluent gases, a typical industrial product mixture is given in Table 6.

Copper is the classic catalyst for the reaction of CH_3Cl with Si. Silver is often used for reactions with chlorobenzene. Optimum catalytic amounts usually vary from between 5-10% of the silicon used (28). Other factors such as the nature and amount of surface area on the silicon, temperature, pressure, types and amounts of promoters, and the composition of the gas phase also affect the reaction. Evidently, a

Table 6 (29)

TYPICAL YIELDS OF CHLOR~~I~~OSILANES FROM THE DIRECT REACTION

COMPOUND	%	Bp, °C
Me_2SiCl_2	75	70
$MeSiCl_3$	10	66
Me_3SiCl	4	58
$MeSiHCl_2$	6	41
$SiCl_4$	5	58
Me_4Si		26
$HSiCl_3$		32
DISILANES		

variance in any one of the aforementioned parameters is likely to necessitate changes in others.

There are a variety of routes available for siloxane production. These include:

1. Hydrolytic processes mainly based on hydrolysis of organohalosilanes produced in the direct process or organoalkoxysilanes.
2. Redistribution reactions involved in the anionic or cationic polymerization of cyclic monomers or low molecular weight linear species.
3. Non-hydrolytic processes based on reaction of organohalosilanes or organoalkoxysilanes with alcohols or acids. Noll (28) offers an excellent discussion of these reactions.
4. Anionic polymerization of D_3 using Li^+ as the counterion.
5. Thermal polymerizations.

Of these processes, only "1" and "2" are commercially important. In our laboratory, we have used only the redistribution type anionic or cationic ring opening polymerizations. Consequently, a discussion of these types follows herein. For further information on the remaining types of processes, the reader is referred to Noll (28) and to The Siloxane Bond (32).

Siloxanes: Polymerization of Cyclosiloxanes

The cyclic monomers for process "2" are normally produced in a ring-chain equilibrium reaction by the alteration of various parameters in the hydrolysis of organochlorosilanes (process "1"). The principles applicable to the equilibrium are identical to those concerning the polymerization of the cyclics.

Linear polysiloxanes can be synthesized by both the anionic and cationic polymerization of cyclic siloxanes. Molecular weight is regulated through the incorporation of controlled amounts of monofunctional endblockers into the system (28, 98). As a result of the nature of the configurations of siloxane chains coupled with the similar reactivity of siloxane bonds in the linear as compared to cyclic species, the anionic or cationic catalysts attack both the rings and chains during the polymerization. These so called "redistribution" or "equilibration" polymerizations involve reactions such as those listed in equations 11-14 occurring throughout the process. At thermodynamic equilibrium

Equation 11: $-D_X- + D_4 \longrightarrow -D_{(X+4)}-$

Equation 12: $-D_X- + MM \longrightarrow MD_XM$

Equation 13: $MD_XM + MM \longrightarrow MD_{(X-5)}M + MD_5M$

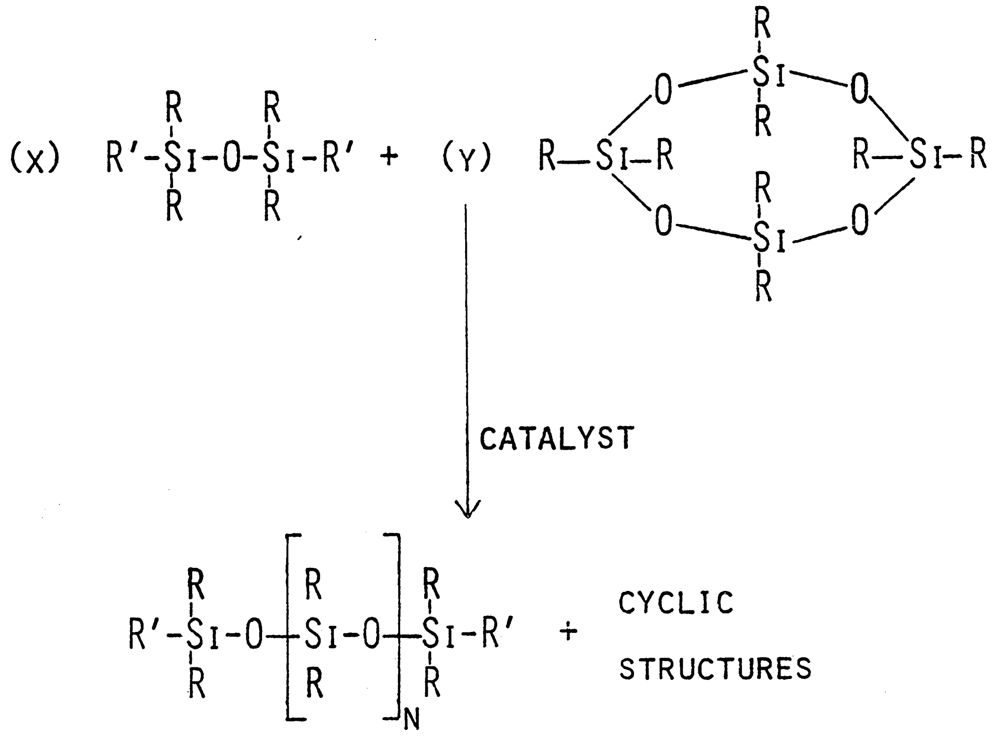
Equation 14: $MD_XM + MD_YM \longrightarrow MD_{(X+W)}M + MD_{(Y-W)}M$

"M" denotes a monofunctional siloxane unit whereas "D" refers to a difunctional siloxane unit. "D_4" therefore represents the cyclic siloxane tetramer while "MM" is the linear dimer. "D" nomenclature is normally associated with dimethylsiloxy units. This is standard nomenclature among siloxane chemists.

(at least in the absence of endblocking units) these reactions result in a Gaussian distribution of molecular weights among the chain molecules together with an approximately monotonically decreasing distribution of ring species as ring size increases (99-105). Rates of the various processes depend upon factors such as catalyst type and concentration, temperature, pressure, and the use of various types and amounts of promoters and can undoubtedly be controlled to some extent. With the exception of using organolithium catalysts in conjunction with the D_3 monomer (106-107), however, significant amounts of redistribution evidently cannot be avoided.

The technique involved in these types of polymerizations is normally quite facile. The general method potentially lends itself well to the laboratory synthesis of di-organofunctional siloxanes through variance of the structures of "R" and "R'" shown in equation 15.

Equation 15



In order to accurately synthesize difunctional siloxanes of varied but controlled molecular weights by this method, an understanding of the mechanisms and ring-chain equilibria must be considered. Jacobson and Stockmayer published their now classic paper (99) describing the theory of molecular weight distributions in linear/cyclic equilibrated polymer systems in 1950. Up to that time, theories describing molecular weight distributions had not considered the presence of cyclic structures. Jacobson and Stockmayer's theory is based on the premise that the proportion of a macrocyclic species of units in equilibrium with linear components is related to the probability of coincidence of the terminal atoms of the sequence of x units. In development of this theory, the following processes were considered:

$$\text{Process 1:}\quad -M_y- \rightleftharpoons -M_{y-x}- + -M_x-$$

$$\text{Process 2:}\quad -M_x- \rightleftharpoons C\text{-}M_x$$

M = monomer unit
C-M = cyclic form of the monomer unit
x and y = degrees of polymerization

Process 3 denotes the sum of processes 1 and 2.

$$\text{Process 3:}\quad -M_y- \rightleftharpoons -M_{y-x} + C\text{-}M_x$$

An equilibrium constant, K_x, for ring formation (for process 3) was derived from entropy relationships (written in equations 16, 17, and 18 for processes 1, 2, and 3 respectively). "P" in these equations was described by Jacobson and Stockmayer as the probability that a chain would be in an appropriate configuration for ring formation (equation 19). Jacobson and Stockmayer actually set $<\vec{r}_x^{\,2}>$ equal

Equation 16: $$\Delta S_{(1)} = k \ln\left[\frac{V}{\sigma_A v_s}\right]$$

Equation 17: $$\Delta S_{(2)} = k \ln\left[P\,\frac{\sigma_A}{\sigma_{R_x}}\right]$$

Equation 18: $$\Delta S_{(3)} = k \ln\left[\frac{VP}{\sigma_{R_x} v_s}\right]$$

V = Volume of the system.
σ_A = Symmetry number for the chain species (σ_A = 2 for organosiloxanes).
σ_{R_x} = Symmetry number for the ring species of "x" repeating units ($\sigma_{R_x} = 2x$ for organosiloxanes).

Equation 19: $$P = \int_0^{v_s} W_x(\vec{r})\, d\vec{r} \simeq \left[\frac{\beta^3}{\pi^{3/2}}\right] v_s = \left[\frac{3}{2\pi\nu x}\right]^{3/2} \frac{v_s}{b^3}$$

$\nu x b^2 = \langle \vec{r}^{\,2}_x\rangle_o = \langle \vec{r}^{\,2}_x\rangle$
ν = Number of links per repeat unit.
b = Average "effective link length"
$\langle \vec{r}^{\,2}_x\rangle$ = The mean-square end-to-end length averaged over all configurations of chain size x.

to ($\nu x b^2$) which meant implicitly that $\langle \vec{r}^{\,2}_x\rangle$ was to be set equal to $\langle \vec{r}^{\,2}_x\rangle_o$, the mean-square end-to-end distance of the unperturbed chain. "$W_{x(\vec{r}=o)}(\vec{r})$" in equation 19 denotes the Gaussian distribution function expressing the density of end-to-end vectors, $\vec{r}$, in the vicinity of $\vec{r} = 0$. The existence of this function in the entropy term obviously implies a Gaussian distribution of end-to-end vectors. This point may, in fact, be a bad assumption for the cases of very short chains (which, in turn, form small rings). "v_s" was defined as the volume element within which two termini must meet in order to form a bond. It appears in the denominator of equation 16 due to the fact that the two atoms which formed the bond broken in process 1 were constrained to the volume element v_s prior to the occurrence of process 1. Since $\int_0^{v_s} W_x(\vec{r})$ is the probability of the termini of a molecule meeting in the volume range, v_s, this factor also appears in the entropy term describing process 2. The enthalpy terms for the first two processes presumably cancel each other with the assumption that the ring formed is not small enough to be sterically strained. This was rationalized by noting that the intramolecular bond formed in process 2 was similar in nature to the one severed in process 1. The equilibrium constant for process 3 (expressed in moles/liter) was derived from equation 18 (equations 20 and 21). The definition of "p" in this context (equation 21) differs slightly from its "normal" definition (i.e. extent of reaction). Here, "p" is defined as the extent of reaction of the functional endgroups in the chain portion of the system. "p" could also be identified as the ratio of the concentrations of acyclic species of

$$\text{Equation 20:}\quad K_x = \frac{\left(\frac{3}{2\pi\nu}\right)^{3/2}}{2b^3} N_A^{-1} x^{-5/2} = \frac{\left(\frac{3}{2\pi}\right)^{3/2}}{2\langle \vec{r}_x^{\,2}\rangle_o^{3/2} N_A} x^{-1}$$

$$\langle \vec{r}_x^{\,2}\rangle_o = \nu x b^2$$

$$\text{Equation 21:}\quad K_x = \frac{[C\text{-}M_x]\,[\text{-}M_{y-x}\text{-}]}{[\text{-}M_y\text{-}]} = \frac{[C\text{-}M_x]}{p^x}$$

sizes x to x-1 (100).

The combination of equations 20 and 21 predicted several interesting points:

1. The concentration of x-mer rings was shown not to be a function of dilution. The number of x-mer rings was predicted to increase linearly with dilution, thereby making the proportion of rings in the system greater as it is diluted. Upon incrementally adding solvent, this process eventually results in a "critical dilution point" above which only rings are present.
2. The rings formed are small species. As $p \rightarrow 1$, $K_x \rightarrow [C\text{-}M_x]$ and $[C\text{-}M_x]$ approaches proportionality to $x^{-5/2}$.

Jacobson and Stockmayer also reasoned that each subset of species (e.g. rings vs. chains) within the overall distributions must be in equilibrium with itself at thermodynamic equilibrium. Therefore, they predicted the normal distribution for the chain species whether or not ring species were formed. Figure 2 (reproduced from their 1950 paper) illustrates the predicted distribution for ring and chain species.

One large drawback of Jacobson and Stockmayer's interpretation was that in the cases of very small but unstrained rings, much higher concentrations were formed than were predicted. Flory and Semlyen (100) explained this deviation by saying that not only did two termini have to meet within a volume "v_s" in order to establish a bond, they also had to approach each other from a specified direction. This direction was specified by a solid angle fraction $\frac{\delta\omega}{4\pi}$. They explained that this term should appear in the entropy expression for process 1 in the

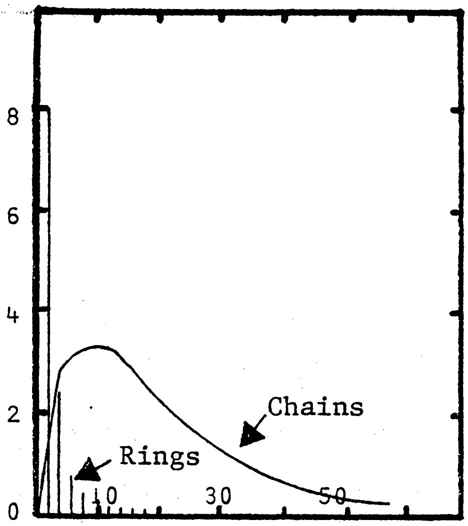


Figure 2: Typical Molecular Distribution for a Ring-Chain Equilibrium Polymer. Weight % is plotted against degree of polymerization (99)

inverse form, i.e. $\frac{4\pi}{\delta\omega}$. In process 2, if the chains were sufficiently long, there would be no correlation between the probability for two termini of a molecule to meet within v_s and to approach within the solid angle $\delta\omega$. In this case, the term $\frac{\delta\omega}{4\pi}$ would be valid for inclusion into the entropy term for process 2 and, hence, when the entropies for processes 1 and 2 were summed, these terms would cancel (and the equation for $\Delta S_{(3)}$ from Jacobson and Stockmayer's theory should be valid). However, for short chains, the probability of approach of two termini of one chain within v_s would depend on bond angles, steric factors, etc. particular to the specific system, and would deviate from $\frac{\delta\omega}{4\pi}$. In that case the probability "P" in Jacobson and Stockmayer's theory in the entropy term would be incorrect.

There have been several studies conducted investigating equilibrium distributions of polyorganosiloxanes experimentally. Theoretical and empirical weight fractions of cyclics and their distributions with variances in x are of particular interest to the synthetic chemist. Equation 20 can be rearranged to give the weight fraction, w_r, of cyclics (equation 22) for high extents of reaction (the empirical comparisons were all made at p → 1). Contributions from the weight

$$\text{Equation 22:} \quad w_r = \left(\frac{3}{\pi}\right)^{3/2} \frac{M_o}{2^4 \ell^3 N_A c} \sum_{x=4}^{\infty} (x\, C_x)^{-3/2}$$

c = Total siloxane concentration in g /ℓ

M_o = Molecular weight of a repeat unit.

ℓ = The length of a siloxane bond.

$\langle \vec{r}_x^{\,2} \rangle_o = C_x 2x\ell^2$

fraction of the strained cyclic trimer, not applicable to the theory, are neglected. Wright and Semlyen compared their own (102) values together with Brown and Slusarczuk's (103) calculated and experimental values of K_x for polydimethylsiloxane (PDMS). Calculated values were based on calculations of $\langle \vec{r}_x^{\,2} \rangle_o$ derived from Flory's rotational isomeric state model for PDMS (41). Empirical values came from measurements of the concentrations of x-meric rings according to Jacobson's and Stockmayer's relationship, $K_x = \frac{[C\text{-}M_x]}{p^x}$. Brown and Slusarczuk (103) equilibrated PDMS in toluene at 110 degrees centigrade and a concentration of 0.22 g /ml of siloxane. Values from that equilibration and Wright's and Semlyen's bulk equilibration (102) as a function of x are compared with theoretical values in Figure 3. As predicted, the K_x values in the range x = 11-40 were experimentally independent of dilution. In direct contrast, the cyclization constants for x = 4-10 increase with dilution (the increase becoming more pronounced with decreases in x). Siloxane chains for x greater than approximately 15 agreed well with theoretical values.

These same authors (101) also compared experimental K_x values as a function of x for a series of bulk equilibrates of the structure $\left[R(CH_3)Si\text{-}O \right]_x$ wherein R equalled H, CH_3, CH_3CH_2, $CH_3CH_2CH_2$, and $CF_3CH_2CH_2$ in order to assess the effect of the substituent size on the equilibrium distribution. The K_x values for the smallest unstrained rings (x = 4 or 5) were found to increase along the series R = H < CH_3 < CH_3CH_2 < $CH_3CH_2CH_2$ < $CF_3CH_2CH_2$. By contrast, the corresponding values for the larger cyclics decrease along the same series. The total weight fraction (experimental) of cyclics in these bulk

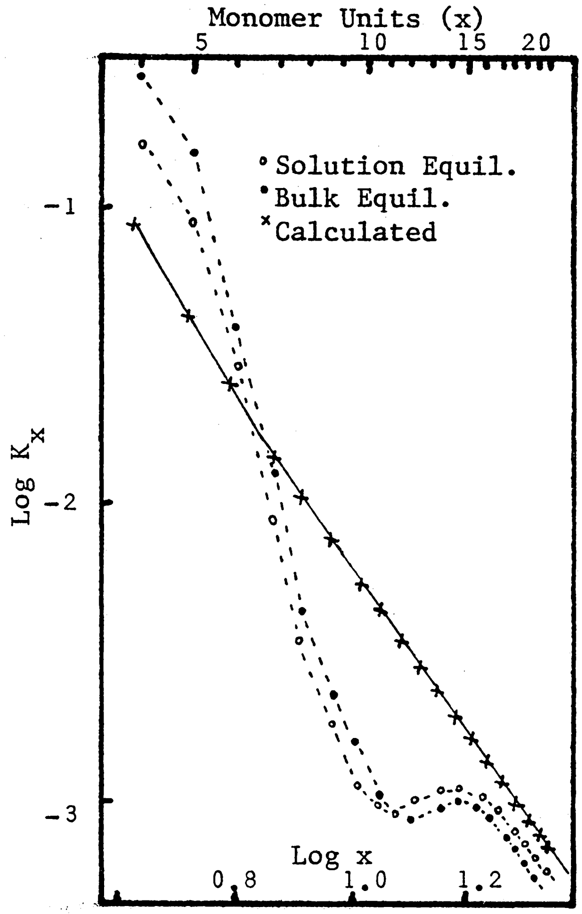


Figure 3: Molar Cyclization Equilibrium Constants of Dimethylsiloxanes at 110°C (102)

equilibrates are listed in Table 7. The effect of dilution with cyclohexanone in the syntheses of these same polymers is illustrated in Figure 4. In all cases, a critical dilution point was reached as predicted but it was reached at a lower diluent volume than the theoretical value. Molar cyclization equilibrium constants for undiluted poly(methylphenyl)siloxane were later measured (104) and found to be similar to those previously obtained in the case of poly(ethylmethyl)-siloxanes.

As predicted by theory, the position of the ring/chain equilibrium was found to be independent of the nature of the redistribution catalyst employed (acid or base) (32, 98, 108-109) and of the specific inert solvent used (110). Russian authors (32, 111) equilibrated mixtures of cyclosiloxanes comprised of dimethylsiloxane (75 mole %) and either trifluoropropylmethyl, cyanoethylmethyl, or cyanopropylmethyl siloxane (25 mole %) in acetone at a siloxane repeating unit concentration of 0.833 moles/ℓ. They measured the dipole moments of the respective cyclosiloxanes, $[(CH_3)_2\underbrace{SiO]_3[Si(CH_3)RO}]$, to be 2.76 for R = trifluoropropyl, 3.45 for R = cyanoethyl, and 3.58 in the case of R = cyanopropyl. The equilibrium weight fraction of rings, 54.7%, 96.2%, and $\sim$100% respectively, was found to increase with the dipole moment, and, hence, with the polarity of the substituent.

Carmichael et al. performed a series of bulk equilibrations of hexamethyldisiloxane and D_4 using sulfuric acid activated fuller's earth as the catalyst (112-113). These workers varied the molar ratio of endblocker to D_4 so as to obtain calculated molecular weights (on

Table 7 (101)

Cyclic Contents of Undiluted Polysiloxane Equilibrates

Substituent Group R of Monomeric Unit $[R(CH_3)SiO]$	Temperature T(K)	Weight Per Cent Cyclics in High Molecular Weight Equilibrates (p = 1)			
		x = 3-5	x = 6-18	x = 19-∞[+]	Total
H	273	4.5	3.4	4.6	12.5
CH_3	383	10.0	3.6	4.7	18.3
CH_3CH_2	383	17.0	4.9	3.9	25.8
$CH_3CH_3CH_2$	383	27.0	*	-	
$CF_3CH_2CH_2$	383	71.1	8.9	2.7	82.7

---

[*] 31.0% for $[CH_3CH_2CH_2(CH_2)SiO]_x$ with x = 3-8.

[+] These values have been computed by extrapolation of experimental K_{18} values assuming that K_x is proportional to $x^{-2.5}$.

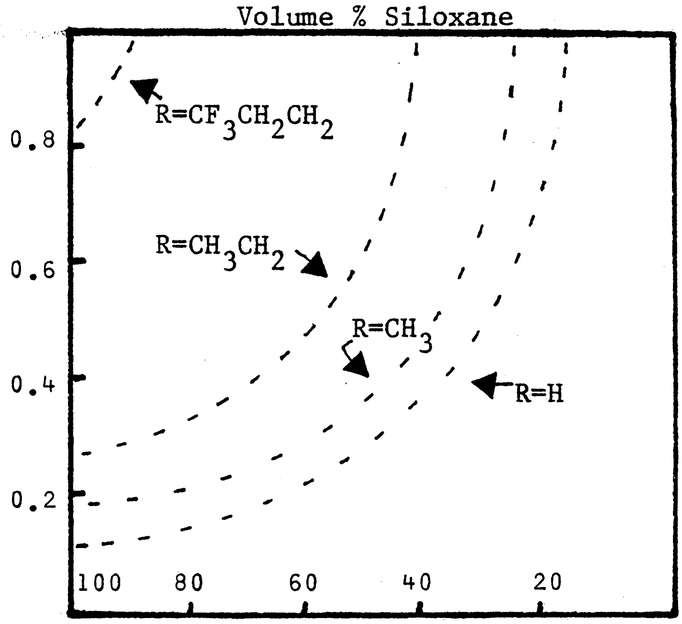


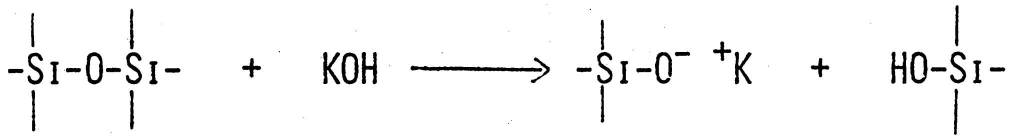
Figure 4: Weight Fractions of Cyclics $[R(CH_3)SiO]_x$ in High Molecular Weight ($p \simeq 1$) Polysiloxane Equilibrates at 383K ($R = CH_3$, CH_3CH_2, $CF_3CH_2CH_2$) and 273K ($R = H$) as a Function of the Volume % Siloxane in Cyclohexanone ($R = CF_3CH_2CH_2$) and Toluene ($R = H$, CH_3, CH_3CH_2) (101)

the basis of monomer ratio) of 459, 904, and 1348 g /mole. They found the total weight fractions of cyclics in these polymers to be 4.86%, 7.69%, and 8.92% respectively whereas they had obtained a corresponding value of 12.8% for an analogous polymer with <Mn> = 10^6 (108). They explained this molecular weight dependence by variances in "p" according to Jacobson's and Stockmayer's equation for cyclization equilibrium constants, $[C\text{-}M_x] = K_x p^x$, by assuming the equilibrium distribution of linear x-mers to be random (i.e. $[C_x] = Ap^x$ wherein $[C_x]$ = concentration of linear x-mer (moles/ℓ.), A = a normalization constant, and p = fraction of unreacted endgroups in the linear portion of the polymer). Carmichael et al. derived "p" for their polymers from the slopes of plots of ln $[C_x]$ vs. x. They used these values together with measured concentrations of cyclics as x was varied to calculate K_x values. In all cases their values of K_x derived as explained above agreed well with values of K_x calculated for a high molecular weight polymer.

The mechanism illustrated in equations 23-25 was proposed by Grubb and Osthoff (114) for the anionic ring opening polymerization. There is, however, considerable question as to whether the ion pair formed in equation 23 also participates as a propagating species (32).

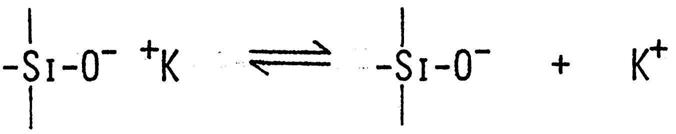
These anionic ring opening polymerizations are usually carried out either in bulk or in solution. A host of catalyst types are active. For synthetic references using specific catalysts, the reader is referred to several excellent sources (28, 32, 37, 115). Representative catalysts include hydroxides, alcoholates, phenolates, silanolates,

Equation 23



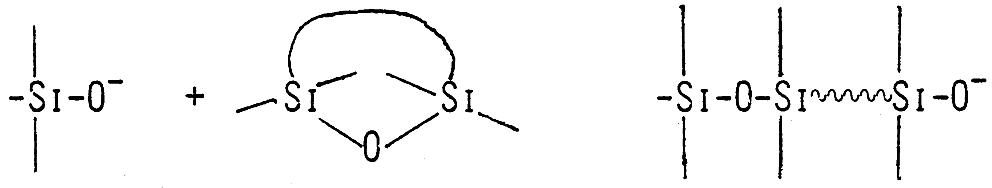
$$-\mathrm{Si{-}O{-}Si}- \;+\; \mathrm{KOH} \longrightarrow -\mathrm{Si{-}O^{-}}\;{}^{+}\mathrm{K} \;+\; \mathrm{HO{-}Si}-$$

Equation 24



$$-\mathrm{Si{-}O^{-}}\;{}^{+}\mathrm{K} \rightleftharpoons -\mathrm{Si{-}O^{-}} \;+\; \mathrm{K^{+}}$$

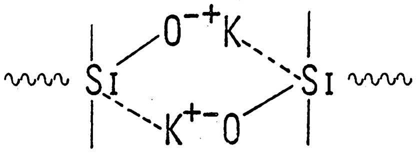
Equation 25



siloxanolates, mercaptides of the alkali metals, organolithium and potassium compounds, and quaternary ammonium and phosphonium bases and their silanolates and siloxanolates.

The activities of the often used hydroxides and siloxanolates decreases in the order Cs > Rb > K > Li (116). At equal molar concentrarions, the rates using the hydroxide or siloxanolate of the same metal have been found to be similar (114). Tetramethylammonium siloxanolates reportedly exhibit activities close to the cesium siloxanolates (116). Tetramethylammonium hydroxide, silanolate, and siloxanolate decompose above 130° yielding methanol, methoxy trimethylsilane, or methoxysiloxane respectively and trimethylamine (117-118). In the cases of the first two compounds listed above, the catalyst breakdown products are fugitive at the decomposition temperature. Thus, the usual need for catalyst neutralization and removal following polymerization is eliminated.

At low catalyst concentrations, the degree of polymerization is approximately inversely related to the catalyst concentration (119). Russian authors (32) have noted a deviation in the linearity of the $1/X_n$ vs. catalyst concentration function at high catalyst loadings. It was suggested that this deviation could be attributed to the presence of stable associated structures similar to **17** being formed.



17

Practically, polymerization temperatures are selected on the basis of the activities of the catalyst, cyclosiloxane, and endblocker used with the aim of arriving at thermodynamic equilibrium within an acceptable time period. In the bulk polymerization of D_4, temperature changes reportedly do not affect the final equilibrium number average molecular weight of the polymers (120).

Rates of anionic polymerization are influenced by the number of siloxane units present in the monomer rings. Due to ring strain in the three unit rings, all of the cyclotrisiloxanes polymerize faster than the cyclotetrasiloxanes. In the dimethylsiloxanes, D_3 reportedly polymerizes approximately 50 times faster than D_4 (32).

In equilibration reactions, hexaorganyl disiloxanes or low molecular weight siloxanes terminated with triorganylsiloxy groups in the reaction mixture can regulate molecular weight by acting as chain transfer agents. The efficiency of these agents depends on the relative amount of positive charge on their silicon atoms. Results of viscosity measurements as a function of time using hexamethyldisiloxane endblocker, D_4, and tetramethylammonium hydroxide catalyst (98) are shown in Figure 5. The initial large viscosity increase was found to be a result of the faster reaction of D_4 as compared to hexamethyldisiloxane under these conditions. Contrasted with the above results was the analogous reaction with the exception that a sulfuric acid catalyst instead of tetramethylammonium hydroxide (see Figure 6) was used (98). The shape of the curve in Figure 6 represents approximately equal reactivity of D_4 and hexamethyldisiloxane towards an acid catalyst.

Many compounds with an electron donor character are reported to have an accelerating effect on the anionic polymerizations. Representative "promoters" reported include tetrahydrofuran (121-123), dimethylformamide (124), and sulfoxides (125-126).

Cationic polymerization of cyclosiloxanes is well known but used much less frequently than anionic reactions. The most frequently used catalysts include sulfuric acid and its derivatives (32, 127-130). Trifluoroacetic acid has also been used to bulk polymerize D_4 at

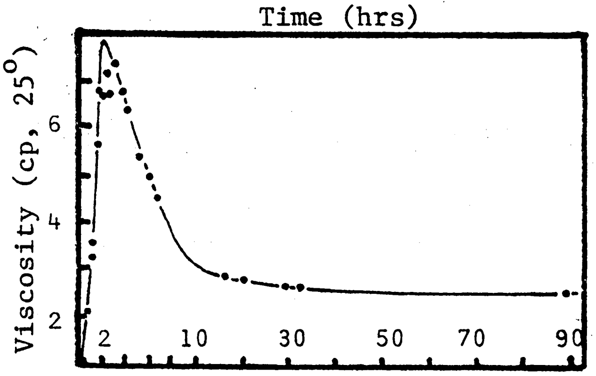


Figure 5: Viscosity vs. Time for Equilibration of One Mole of Hexamethyldisiloxane and One Mole D_4 with 0.1% $(CH_3)_4NOH$ at 80° (98)

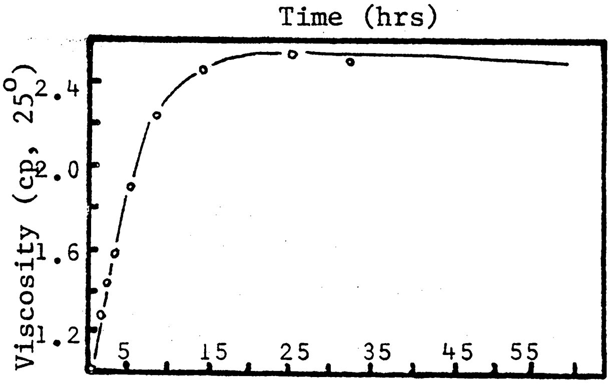


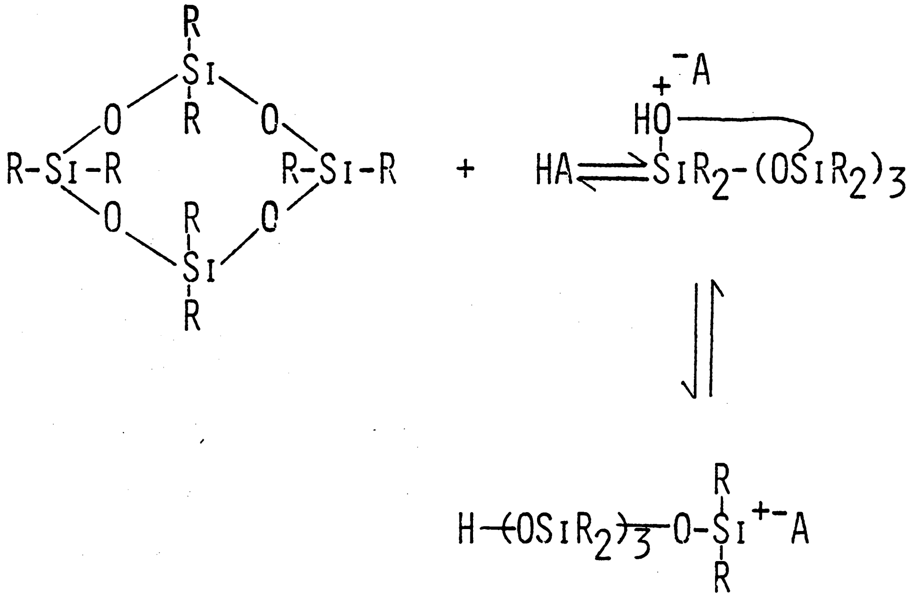
Figure 6: Viscosity vs. Time of Reaction for Equilibration of One Mole Hexamethyldisiloxane and One Mole of D_4 with 4% H_2SO_4 at Room Temperature (98)

reflux (131) temperature.

The mechanism of acid catalyzed polymerization is postulated to be that schematically illustrated in equations 26 and 27. According to Odian (132), there is no evidence for the rearrangement to the siliconium ion shown in these equations. It is possible that the tertiary oxonium ion is the propagating species.

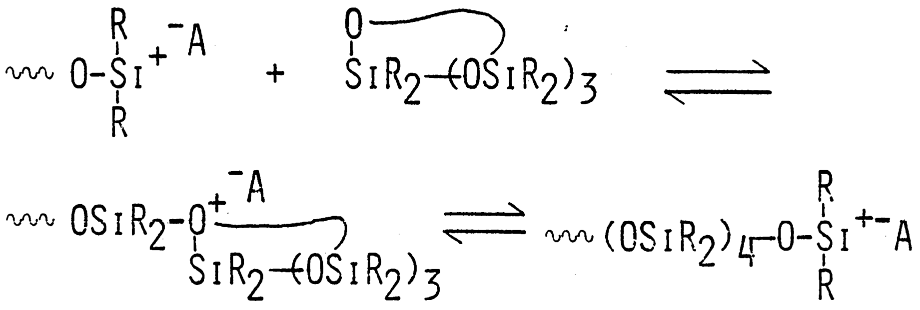
Equation 26 (132)

Initiation:



Equation 27 (132)

Propagation:



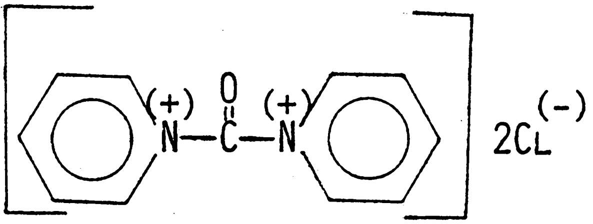
Bisphenol-A Polycarbonates: Synthesis

Polycarbonates derived from the bisphenol-A monomer have gained widespread industrial use since their commercial introduction in 1960. Chief in importance among the properties of these materials are high impact strength and a wide temperature use range, in conjunction with transparency and ease of processibility (133).

High molecular weight aromatic polycarbonates are synthesized via three basic processes:

1. Phosgenation of aromatic dihydroxy compounds in the presence of pyridine, i.e. "direct phosgenation."
2. The interfacial reaction of the alkali salts of the dihydroxy compounds with phosgene.
3. Transesterification of aromatic dihydroxy compounds with diaryl carbonates.

"Direct phosgenation" involves the reaction of bisphenol-A and its corresponding dichloroformate or phosgene in an anhydrous, inert chlorinated solvent (often methylene chloride). The presence of a tertiary amine (often pyridine) is necessary for two reasons. Aromatic dihydroxy compounds react with phosgene or chlorocarbonic esters quite slowly. It is well-known that pyridine or other tertiary amines form ionic adducts with phosgene, **18**, and chloroformates (134), **19**. Adducts of these types accelerate the reaction substantially as compared to the rate observed using the corresponding carbonic acid derivatives themselves. Since the polarity of the hydrochloric acid by-product renders it difficult to remove from anhydrous



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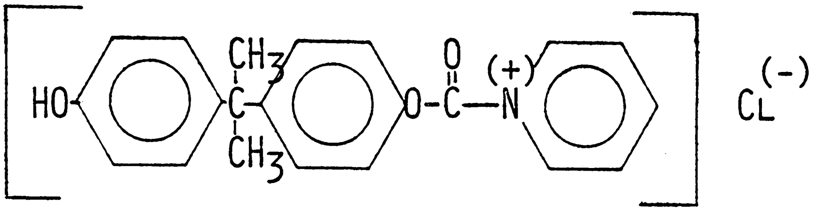

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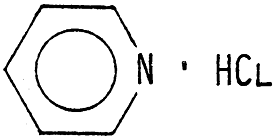
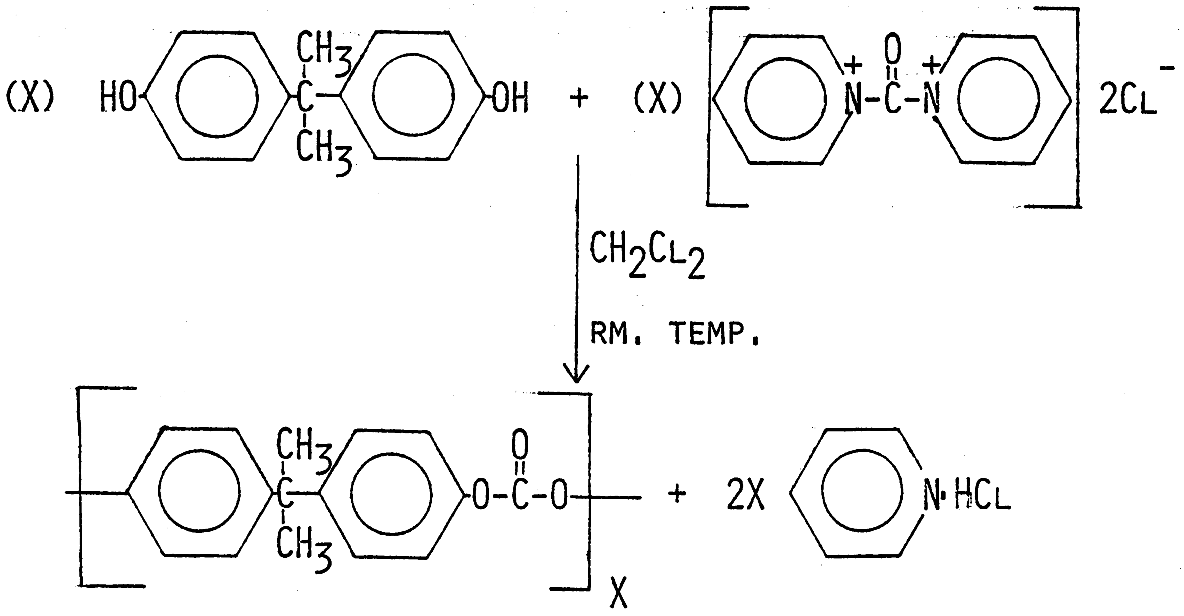
media as a gas, tertiary amines aid in its removal through formation of partially insoluble hydrochloride salts, **20**. The general reaction sequence using this method is shown (using phosgene) in equation 28. Although this "direct phosgenation" route is quite facile, it has the disadvantage of the requirement for quantitative removal of pyridine and its hydrochloride salt (135).



20

Equation 28



Substitution of the dichloroformate of bisphenol-A for the phosgene in a similar reaction is also effective. It is, in fact, necessary in cases wherein two different bisphenol structures are copolymerized and the perfectly alternating monomer sequence is desired. For a discussion of the syntheses and properties of various chloroformates, the reader is referred to an excellent review (136).

In the strictly bisphenol-A polycarbonate, the chloroformate reaction is useful for the production of controlled molecular weight hydroxy functional oligomers. These types of oligomers make interesting building blocks for the production of block copolymers (12, 15, 20, 137-140). Number average molecular weight is regulated according to basic step reaction theory by accurately varying the dichloroformate to bisphenol ratio according to equation 29 (132). This

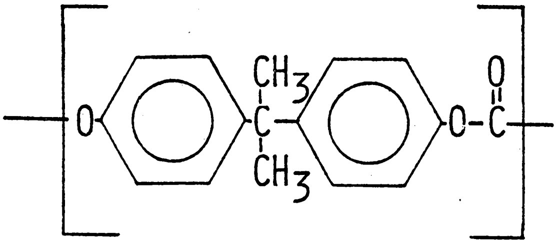
Equation 29

$$\bar{X}_n = \frac{1 + r}{1 + r - 2rp}$$

$$r = \frac{\text{Number of chloroformate functional groups}}{\text{Number of bisphenol-A functional groups}}$$

p = Extent of reaction (the fraction of chloroformate groups which have reacted at a particular time).

$\bar{X}_n$ = Degree of polymerization (the number of repeat units, 21, per polymer chain).



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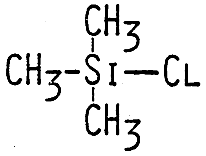
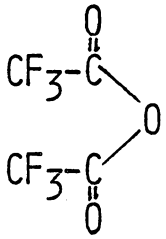
reaction, however, has a severe disadvantage in the requirement for the preparation of the chloroformate in an additional separate step. Molecular weights of these functional oligomeric precursors produced by the direct phosgenation route can also be monitored by a spectrophotometric technique (141). This method, however, is difficult to control.

The research presented in this thesis describes a novel, convenient technique for the attainment of reactive polycarbonates of well-controlled <Mn> using this simpler "direct phosgenation" method of synthesis. The approach involves blocking of a desired number of the phenolic endgroups with various protecting groups prior to phosgenation. These protecting groups are designed to produce bonds that are easily removed after the phosgenation is complete. The technique is demonstrated herein with polycarbonates derived from bisphenol-A and using trimethylchlorosilane (TMCS), **22**, trifluoroacetic anhydride (TFAA), **23**, and trifluoroacetic acid (TFA), **24**, as the blocking reagents.



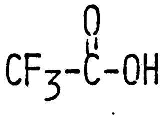
$$CH_3-\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{Si}}}}-Cl$$

22



$$CF_3-\overset{O}{\overset{\|}{C}}-O-\underset{\underset{O}{\|}}{C}-CF_3$$

23



$$CF_3-\overset{O}{\overset{\|}{C}}-OH$$

24

It is common practice to add small, controlled amounts of monofunctional reactants to these reactions (both to the direct phosgenation and the interfacial syntheses) for molecular weight control when hydroxyl functionality of the oligomers is not necessary. Compounds often used for this purpose include p-tert-butylphenol and p-phenylphenol (142). An additional benefit derived from this capping of the chain ends is an increase in the thermal stability of the products.

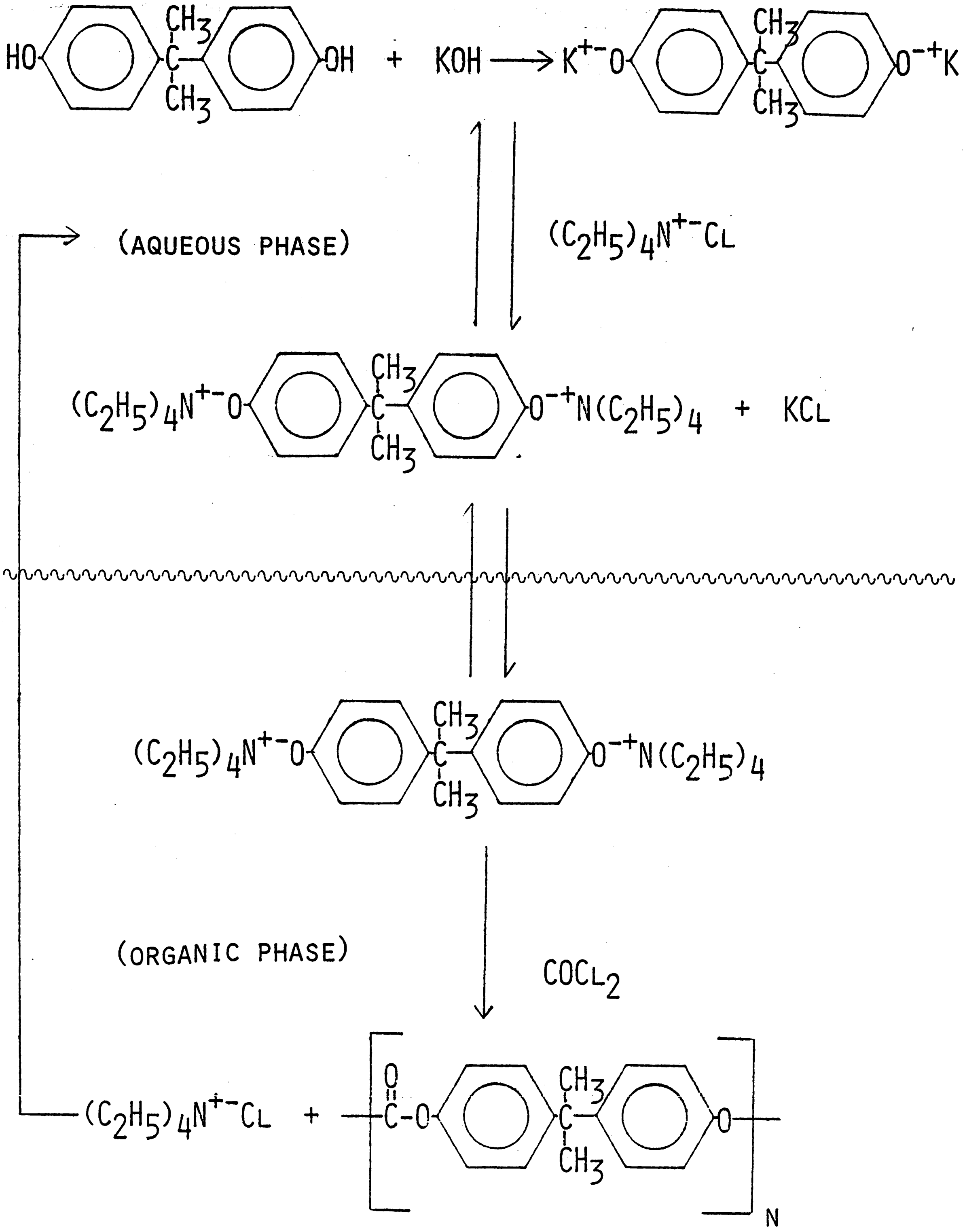
The interfacial synthesis of aromatic polycarbonates became a viable industrial reaction with the discovery that catalysis by tertiary amines and quaternary ammonium halides increased reaction rates dramatically (135). It is now the preferred method industrially.

The synthesis of polycarbonates derived from bisphenol-A in a two-phase medium via quaternary ammonium halide catalysis was one of the earliest applications of phase transfer catalysis (134, 143-148). Typically, bisphenol-A and the quaternary ammonium halide catalyst are dissolved in an aqueous caustic solution followed by addition of the quaternary ammonium halide. The aqueous phase is rapidly mixed with a (usually) water immiscible solvent such as dichloromethane. Phosgene is then introduced in stoichiometric quantities. The phase transfer catalysis cycle is reviewed in equation 30. The synthesis is well known to be both rapid, facile and insensitive to minor variations in reaction conditions.

The preparation of bisphenol-A polycarbonate homopolymer via such a mechanism, however, can be complicated by the fact that polymerization within the organic phase proceeds via a two-step reaction (equation 31). For the attainment of high molecular weight polymers, the rate of formation of chloroformate endgroups must be balanced against the rate of their further reaction with bisphenol-A or with the growing polycarbonate chain. Excessive build-up of aryl chloroformate endgroups which occurs if $k_1 >> k_2$, can be controlled via adjustment of a number of reaction parameters.

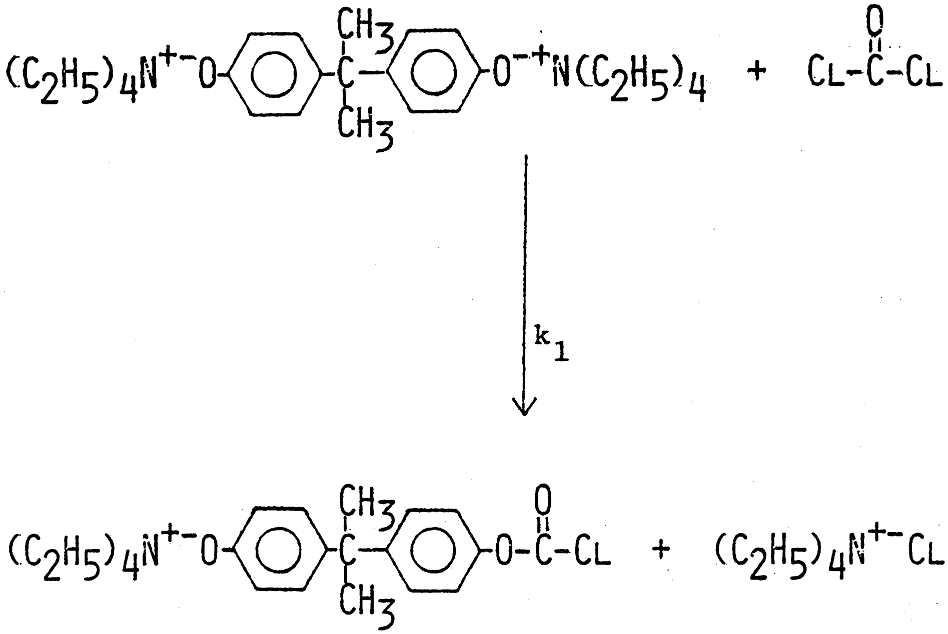
Transesterification of bisphenol-A with diphenyl carbonate in

Equation 30

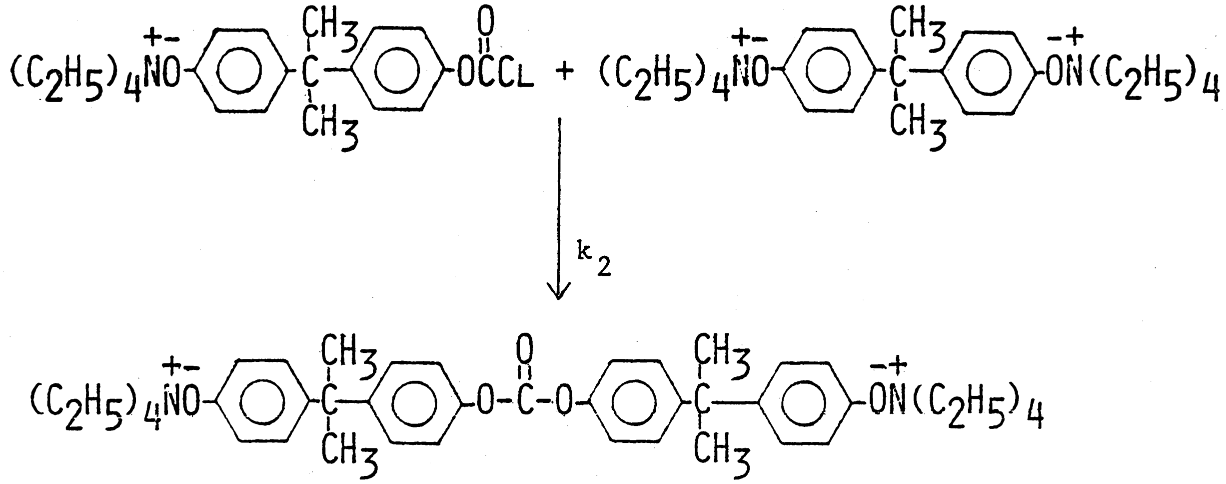

HO
CH3
CH3
OH
+ KOH
K+-O
O-+K
(AQUEOUS PHASE)
(C2H5)4N+-CL
(C2H5)4N+-O
O-+N(C2H5)4
+ KCL
(ORGANIC PHASE)
COCL2
(C2H5)4N+-CL
+
C-O
O
N

Equation 31

Step 1:

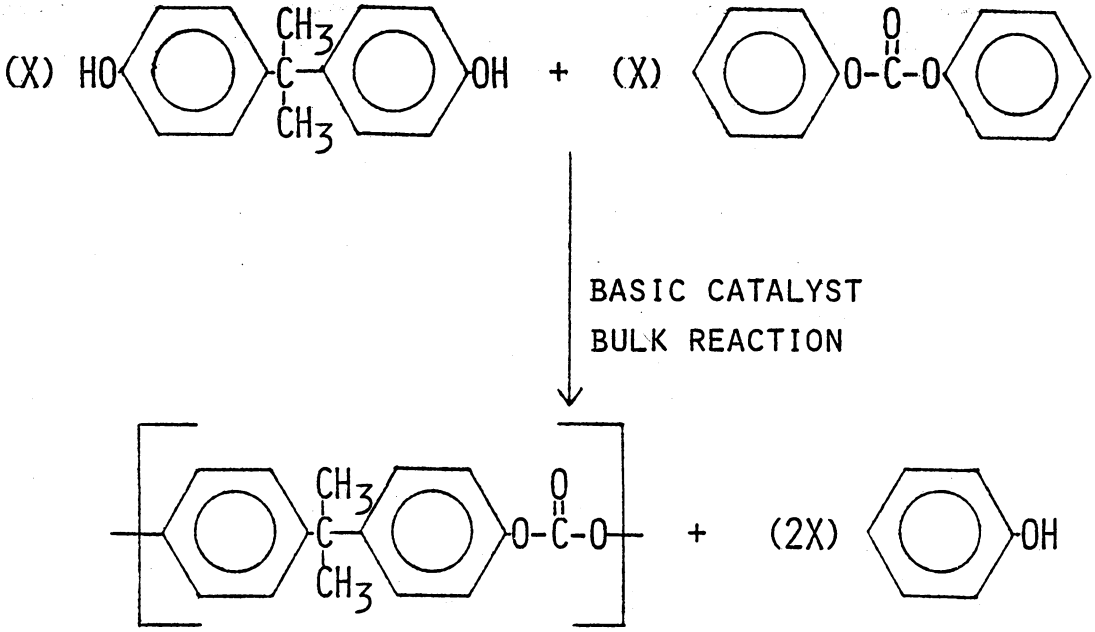


Step 2:



the presence of alkaline catalysts is depicted in equation 32. High temperatures and high vacuum are required due to the low volatility of the phenol by-product and the relatively high melt viscosity of the polycarbonate (134). Catalysts effective for the acceleration of the reaction include alkali metals and alkaline earth metals and their oxides, hydrides, or amides and basic metal oxides such as zinc oxide, lead oxide and antimony oxide (134).

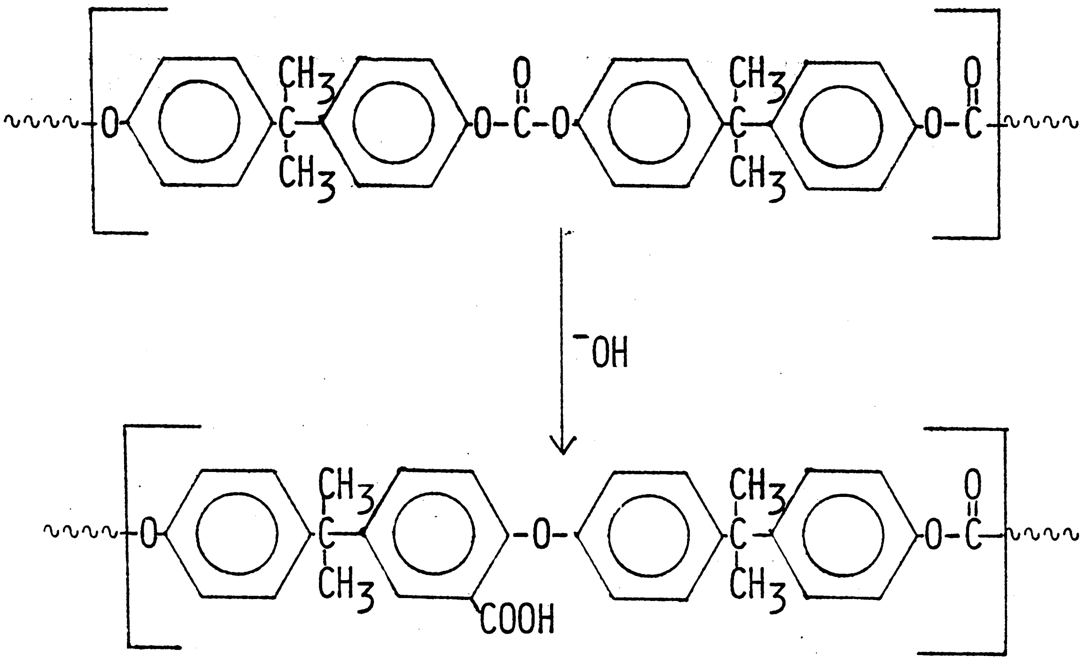
Equation 32



At the high reaction temperatures necessary using this method, the free hydroxyl groups of the bisphenol render these molecules thermally unstable (134, 149) whereas bis-ethers or bis-esters are substantially more stable. Therefore, it is necessary to carry out the transesterification using a slight excess of diphenyl carbonate rather than equimolar quantities.

Unfortunately, under the reaction conditions, the alkaline catalysts effect a side reaction (Kolbe-Schmidt type represented by equation 33) which leads to branching through esterification.

Equation 33



The rather extreme reaction conditions necessary together with limits on achievable molecular weights using this process preclude its use for the industrial production of polycarbonate films and fibers (135). Due to the bulk nature of the reaction, however, it is useful for the preparation of insoluble polycarbonate structures.

Bisphenol-A Polycarbonates: Properties

The mechanical properties of polycarbonates depend on the degree of orientation and possible development of crystallization (135, 150).

Crystallization from the melt, however, is greatly impeded kinetically and films obtained through rapid solvent evaporation or injection molded parts are at least principally amorphous (151). This amorphous nature results in optical transparency of products produced from the material. Polycarbonates with molecular weights less than 10,000 g/mole are generally brittle (151). Injection molded or extruded products are usually produced from these polymers in the molecular weight range of from 20,000 - 40,000 g/mole. Low strength materials result at molecular weights lower than these limits whereas the upper limit is set by the high melt viscosity encountered in these polymers.

Within this molecular weight range, amorphous polycarbonates can be described as extremely tough, resilient thermoplastics. Mechanical properties representative of injection-molded polycarbonates are given in Table 8. These materials have the ability to retain these properties along with excellent dimensional stability over an extremely wide temperature range (from $-150^{\circ}C$ to $+150^{\circ}C$) (135, 151).

Polycarbonates are probably even more highly esteemed due to their capacity for energy absorption under impact. This feature is still not well understood, but is often attributed simply to their amorphous character and to sub-chain motions as manifested by low temperature transitions occurring in the region of $-100^{\circ}C$ ($\sim$ 1 Hz) (152-154). Further understanding requires better knowledge of the non-equilibrium nature of the glassy state.

Due to their hydrophobic nature, polycarbonates are relatively stable to dilute aqueous acids and alkalies under mild conditions.

Table 8 (151)

Mechanical Properties of Injection-Molded Bisphenol A Polycarbonate

Property	DIN Method	Value	Property	ASTM Method	Value
density, g/ml	53 479	1.20			
yield strength in flexure, kp/cm^2	53 452	900	flexural strength, psi	D-790	11,000-13,000
			deformation under load, %	D-621	0.14
impact strength, (cm)(kp)/cm^2 notched	53 453	100% unbroken >20	impact strength (Izod), notched ft-lb/in.	D-256[a] D-256[b]	2-3 12-16
compressive strength, kp/cm^2	53 454	790-840	compressive strength at yield point, psi	D-695	12,000
ball indentation hardness of plastics, kp/cm^2	53 456[c]		Rockwell hardness	D-785	R-115
10 s		900-1050			
60 s		870-1000			
kp/mm^2	53 456[d]	Hc-10.6			
tensile yield strength, kp/cm^2	53 455	625	tensile yield strength, psi	D-638	8000-9000
elongation, %	53 455		elongation, %	D-638	
at yield		5-7	at yield		5-7
ultimate		>80-120	ultimate		>80-120
modulus of elasticity, kp/cm^2		22,000-25,000	modulus of elasticity tension, psi	D-638	2.8-3.2 X 10^5

NOTE: Kilopond, kp, means the same as kilogram force, kgf.

[a] For 1/2 in. x 1/4 in.

[b] For 1/2 in. x 1/3 in.

[c] DIN-Entwurf.

[d] DIN-Vornorm.

(Molecular weights range from 32,000-35,000 for these materials)

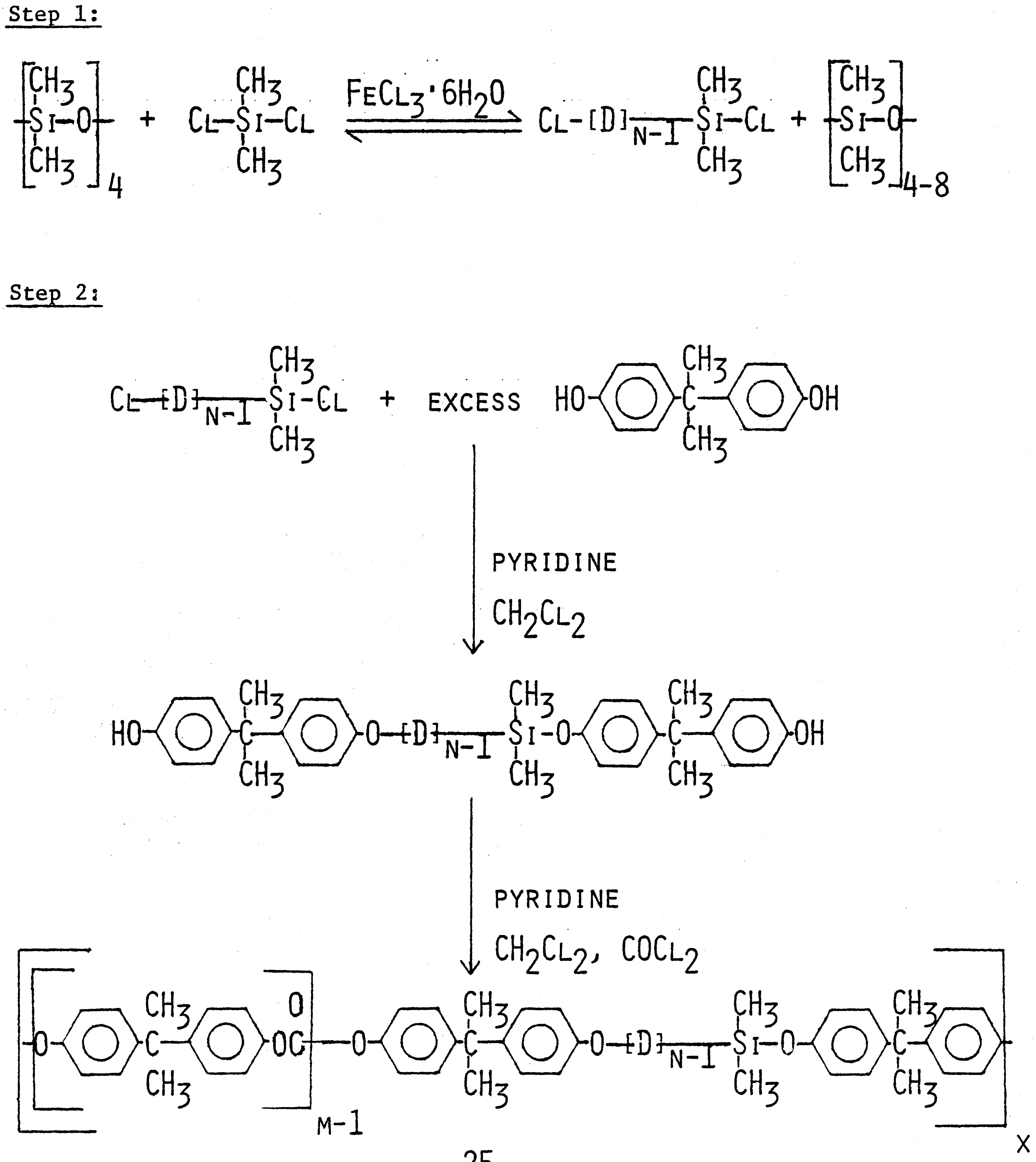
They are unstable towards the action of organic bases. As a consequence of their amorphous state, these polymers dissolve in a number of organic solvents. Therefore, processibility is relatively facile with solvent resistence being relatively poor. A distinct disadvantage of these materials is their tendency to undergo environmental stress cracking (155-156).

Polycarbonate-Polydimethylsiloxane Block Copolymers

Randomly coupled polycarbonate-polydimethylsiloxane block copolymers were first synthesized by Vaughn et al. for General Electric Co. (9, 17, 157-161). The synthetic scheme utilized is shown in equation 34. The method used provides no control over possible phosgene coupling of the bisphenol-A capped siloxane oligomers. Therefore, the copolymer structure, 25, shown is highly idealized. Although molecular weights of the chlorine terminated siloxane oligomeric precursors were known (determined by chlorine endgroup analysis), a statistical coupling in the polymerization step should have coupled some of these siloxane oligomers to each other. Since the polycarbonate blocks were produced in situ (a desirable feature since this eliminates the necessity for a separate synthesis of an oligomeric polycarbonate), these block lengths should have been statistically random in the copolymer. Molecular weights of the copolymers were reportedly all high as evidenced by intrinsic viscosities in chloroform being in the vicinity of 1.0 dl/g (16).

Several investigations in an effort to assess the "degree of randomness" of the monomer distributions in these polymers have been made.

Equation 34



25

First of all, it was established that the α,ω-dichlorosiloxane oligomers only approach a Gaussian distribution of molecular weights (162). Linear species comprised of 1-4 siloxy units had been suppressed, presumably due to electronic effects of the chlorine endgroups. Niznik and LeGrand (162) generated theoretical GPC curves for the bisphenol-A capped siloxane oligomers (based on the assumption of random chlorine substitution) as a function of the ratio of bisphenol-A to chlorine terminated oligomers in the capping step. A comparison of theoretical and empirical GPC curves revealed reasonably good correlations with the worst deviation being at the lowest endcapping ratio considered (1.2). Small angle X-ray scattering data and the sonic modulus suggested that the extent of microphase separation in the copolymers was influenced by the sequential distributions of the various species. Williams, Cargioli, and Hobbs (163) developed both ^{13}C and ^{29}Si nuclear magnetic resonance techniques whereby they could quantitatively assess the number of bisphenol-A units isolated between two siloxane blocks together with the number average molecular weight of both types of structures.

Mechanical properties of these copolymers were found to be dependent on composition. Elongation at break was found to decrease dramatically as polycarbonate composition was increased up to approximately 50%, then levelled off asymtotically with further increases in polycarbonate content (16). In examining polymers varying in composition but with siloxane block lengths of approximately 1500 and 3000 g/mole, the data suggests only a slight dependence of mechanical properties on siloxane block length (16). Not surprisingly, tensile strength increased from 1000 to 6000 psi as the composition of the polycarbonate was increased (16).

Narkis and Tobolsky studied the dynamic mechanical and swelling behavior of these copolymers (164). In solvents preferential for the siloxane, they observed that the average shear modulus between the glass transitions of the two components correlated well with the swelling ratio. The behavior demonstrated by these polymers was similar to that normally exhibited by crosslinked rubbers.

These same authors (164) found that two glass transitions occurred in all cases investigated (siloxane block length was approximately 1500 g/mole and bulk composition varied). The upper transition corresponding to the polycarbonate phase dropped as the siloxane composition was increased (see Table 9). The absolute value of the slope in the plateau region of the modulus-temperature plots (between the glass transitions) was found to increase with siloxane content. Although the existence of two Tg's shows that two microphases exist even at these low block molecular weights, the slopes of the modulus-temperature curves show phase separation to be systematically less defined as the polycarbonate block length becomes very low (12, 164).

In contrast, changes in composition affected the siloxane block Tg very little. Kambour (165) plotted upper copolymer Tg's in these same systems vs. the number average molecular weight of the polycarbonate blocks (calculated from the overall composition assuming alternating block copolymers). He suggested that the Tg's in the

Table 9 (164)

Glass Transitions as a Function of Polycarbonate Block Length

Polycarbonate Block Length[a]	Polysiloxane Block Length	Upper Tg
4500 g/mole	1500 g/mole	115°C
1500 g/mole	1500 g/mole	75°C
800 g/mole	1500 g/mole	55°C

---

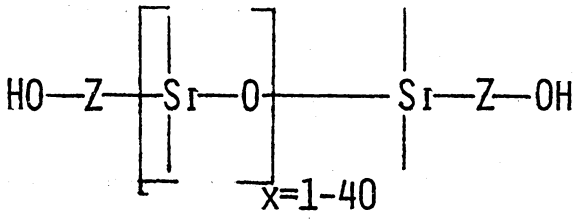
[a] Polycarbonate block length was determined assuming perfectly alternating blocks.

copolymers resulted from the homopolycarbonate oligomers' dependence of Tg on molecular weight. It was concluded that the flexible siloxane chains exert very little restraint on the polycarbonate in the copolymer architecture.

The mechanical properties as a function of oxygen and carbon dioxide permeability have been investigated for the purpose of assessing their potential for use in membranes for the membrane lung (166-167). The copolymers reportedly add "significant strength" (167) to thin films and capillaries. Overall gas permeabilities decreased from those observed in pure dimethylsiloxane but remained high. Relative rates of permeation among various gases remained approximately equal in the silicone homopolymer and copolymers.

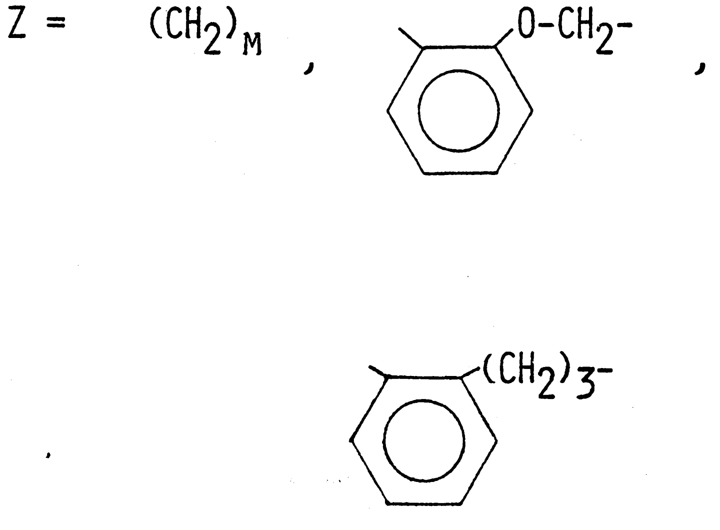
The morphology of these systems has been extensively studied. The reader is referred to the references cited herein for further discussion of these properties (16, 168-176).

Other workers (12, 177-179) have synthesized bisphenol-A polycarbonate-polydimethylsiloxane block copolymers by the reaction of preformed chlorine terminated polysiloxane oligomers with bisphenol-A terminated polycarbonate oligomers in the presence of a tertiary amine. Raigorodskii (180) et al. prepared similar structures via the interaction of preformed chloroformate terminated polysiloxanes with preformed polycarbonate oligomers. Sheludyakov (181) et al. reported copolymers produced from hydroxy terminated siloxane oligomers (26), bisphenol-A, and phosgene in the presence of a tertiary amine.



$$HO{-}Z{-}\left[Si{-}O\right]_{x=1\text{-}40}{-}Si{-}Z{-}OH$$

26



Synthetic details for a series of block copolymers of the same general structures will be presented in the experimental section of this thesis. These polymers were prepared from preformed polysiloxane and polycarbonate oligomers only capable of reacting to form the perfectly alternating block architecture. Therefore, the block molecular weights and monomer sequence distributions are much better characterized than in the more randomly coupled copolymers synthesized by Vaughn et al. Several authors (13, 19-21, 182-183) have already reported mechanical and morphological data pertaining to these polymers.

T. F. Davidson (182) studied essentially two series of block molecular weights along with investigating mechanical properties as a function of overall bulk composition. One series consisted of a constant polycarbonate block number average molecular weight of 16,000 g/mole combined with varying polydimethylsiloxane block sizes of 5,000, 10,000 and 15,000 g/mole. The complimentary group involved holding the polydimethylsiloxane block at 15,000 g/mole and varying the length of the polycarbonate section from 3,400 to 11,500 and 16,000 g/mole. Bulk composition ranged from 17% to 66% polycarbonate by weight. Kerner's analysis (184) was employed for determination of the phase inversion point (48% polycarbonate/52% polysiloxane). Microphase separation as evidenced by the existence of two glass transitions in both DSC and dynamic mechanical measurements occurred in all cases. Mechanical properties ranged from elastomeric behavior at low polycarbonate compositions to being ductile and "glassy-like" at high compositions.

S. H. Tang (19-20) investigated a series of structures wherein the polycarbonate block length remained relatively constant at 3000-4000 g/mole and the length of the siloxane segment was varied in the following sequence: 1800, 3000, 5000, 8000, 10,000, 15,000 g/mole. Stress-strain curves obtained in this study are reproduced in Figure 7. The curve of the block copolymer with the shortest polysiloxane block shows a yield point at low elongation ($\sim$5%) indicative of a polycarbonate

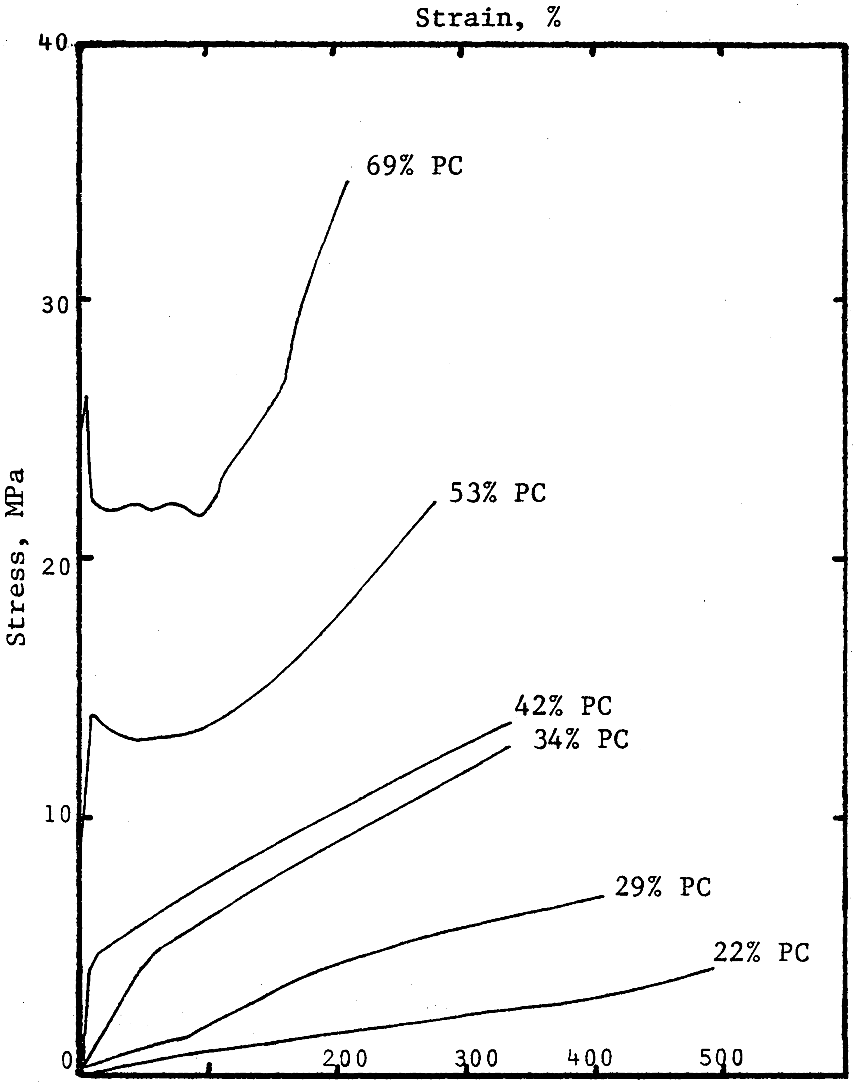


Figure 7: Stress-Strain Curves for Polycarbonate-Polydimethylsiloxane Block Copolymers (20)
<Mn> of polycarbonate block = 3000-4000 g/mole.
PC = polycarbonate

continuous phase. As the polysiloxane block length is increased, the copolymer becomes leathery (53% polycarbonate) and then more and more elastomeric. Again, two glass transitions were detected in all samples further demonstrating the extreme incompatibility of the block segments. Domain sizes estimated from transmission electron microscopy photographs reportedly (20) varied from 30-40 Å (PC/PDMS = 3400/1800) to ∿200 Å (PC/PDMS = 4200/15,000) throughout the series studied.

Sheehy and Ward (21, 183) have recently studied the morphology of these polymers utilizing inverse GC and SAXS. The copolymers involved had a siloxane block length maintained at 10,000 g/mole with the length of the polycarbonate block systematically varied (3400, 11,500, 16,000, and 19,000 g/mole). The polymer-polymer interaction parameter (χ) was found to be markedly higher for the case of the 10,000/3400 polysiloxane-polycarbonate polymer than for systems comprised of intermediate polycarbonate compositions. This suggests better interaction between the two components at more equal compositions. Polycarbonate domain surface areas and radii were determined from the specific retention volumes of n-decane at temperatures below the polycarbonate Tg. These domain sizes were compared to those obtained from SAXS. Correlation was good for the case where DSC results indicated efficient phase separation (for the 10,000/11,500 PDMS/PC sample) but poor where more mixing of the phases was indicated by DSC (for the 10,000/3400 PDMS/PC polymer). Analogous to the thermal data obtained by Davidson (182) and Tang (19-20), two glass transitions were observed in this series of copolymers in all cases investigated.

Surface Phenomena in Polyblends and Copolymers

It is now generally recognized that the physical blending of additives with low surface tensions will modify the surface properties of polymers. For example, a certain lubricity is imparted to polyethylene (185) and to polyvinylidene chloride-acrylonitrile copolymers (186) with the incorporation of low concentrations of long chain amides. Certain fluorocarbon additives reduce wettability and friction in poly(methylmethacrylate) and poly(vinyl chloride) (187).

It has become increasingly evident in the past few years that, in well phase separated block copolymer films, preferential (air) surface migration of the component of lower surface free energy occurs (23-27, 188-195). Moreover, when small amounts of some block copolymers possessing one low energy component are physically blended with a homopolymer of similar structure to the higher surface energy block, the lower energy structure also concentrates at the surfaces of the films (25, 27, 187, 191, 196). The block copolymers have been shown to be particularly suitable as additives because of their high resistance to removal from the surfaces by rinsing or solvent extraction (196). Copolymers used for these types of systems wherein one block structure is polydimethylsiloxane have a high potential for industrial use since this surface phenomena occurs at quite low concentrations of the additive (196).

Gaines and Bender (196) studied the surface tensions of blends containing an (A-B) polystyrene-polydimethylsiloxane block copolymer and polystyrene homopolymer (<Mn> = 9290). Copolymer concentrations were varied from 0.05-5 wt. percent. Results for the 5% and 0.2% copolymer blends at 185°C were within 1 dyne/cm of that for pure polydimethylsiloxane and 16 dynes/cm below the surface tension of polystyrene. In addition, surface tensions of the blends in the melt were all observed to decrease quite rapidly with time up to ∿ 25 minutes.

Owen and Kendrick (25) investigated the surfaces of a series of (A-B-A) triblock styrene-dimethylsiloxane-styrene copolymers at compositions of siloxane ranging from 20-77 wt. percent. Surface tensions of solutions of these polymers in styrene and critical surface tensions of blends (1.0 wt. % of the respective copolymers with polystyrene homopolymer) in film form were measured. Results of the blend study yielded critical surface tensions ranging from 28.3 dynes/cm for the lowest percentage of siloxane to 22 dynes/cm (identical to that of siloxane homopolymer) for the two highest percentages (59% and 77% siloxane in the copolymer). Films of all copolymers (neat) had critical surface tensions identical to that observed for the polydimethylsiloxane homopolymer.

Gaines and LeGrand (27) measured ethylene glycol contact angles of films made from blends of polycarbonate-polydimethylsiloxane copolymers (157) with Lexan polycarbonate. They observed all of the blends studied (lowest copolymer wt. % = 0.1%) to possess contact angles close to those observed on pure polydimethylsiloxane. This wettability was also found to be almost totally insensitive to silicone content or silicone block length over the range investigated (0.1-4.0 wt. % copolymer with silicone blocks of 1500 g/mole or higher).

O'Malley (191) performed a similar study of hexamethylene sebacate-polydimethylsiloxane perfectly alternating block copolymers and their blends with polyhexamethylene sebacate homopolymer. The number average molecular weight of the crystalline polyester block was held constant at 3160 g/mole while the siloxane block length was varied from 1400-10,600 g/mole. Critical surface tensions of 28 and 21 dynes/cm were determined for the homopolymers (hexamethylene sebacate and polysiloxane respectively) whereas all of the copolymers had γ_c's of 22 dynes/cm. Polyblends containing 1.0 - 10.0 wt. percent of the copolymer with the lowest siloxane content also all exhibited γ_c's of 22 dynes/cm. It should be noted that this is the only study which has been done of this type wherein one of the block structures was crystalline.

Sung and Hu (197-200) conducted several studies of a segmental polyurethane-polysiloxane system (Avcothane) known to be biocompatible. It is not clear whether this is a physical blend or a copolymer (or both). The patent literature suggests a very complicated structure. However, because of its blood compatibility, it is included herein. It is produced (201) by blending (in solution under high shear) a preformed, hydroxy terminated segmented polyether-urethane with 10% by weight of a diacetoxy terminated polydimethylsiloxane. To what extent the acetoxy terminated siloxane reacts with the hydroxy terminated oligomer is not defined. X-ray photoelectron spectroscopy (XPS or ESCA) yielded Si/C, O/C, and Si/O intensity ratios for the blood contact side of the films essentially equal to those obtained for pure polydimethylsiloxane. FTIR internal reflectance and Auger electron spectroscopy results supported the data obtained via ESCA.

Clark et al. (23-24) studied the surfaces of A-B diblock polystyrene-polydimethylsiloxane copolymers using ESCA coupled with contact angle measurements. Copolymers containing 23 and 59 wt.% polystyrene possessing number average molecular weights of approximately 120,000 g/mole both exhibited critical surface tensions of 22 dynes/cm (identical to that for polydimethylsiloxane homopolymer). In addition, the effect of varying the film casting solvent on surfaces of the copolymers was investigated. Normal angle ESCA results showed intensity ratios for the copolymer with 23% polystyrene (films cast from chloroform) to be closely matched to those of pure polydimethylsiloxane. Moreover, the data obtained for the copolymer containing 59% polystyrene revealed the same results when films were cast from solvents selective for the polystyrene phase (styrene and bromobenzene). The siloxane surface layers were estimated to be ∿ 40 Å deep based on ESCA depth profiling results. Analogous ESCA data on the copolymer (59% polystyrene) cast from solvents preferential for the siloxane suggested varying amounts of polystyrene to be in the surface area sampled.

X-ray spectroscopy for chemical analysis (ESCA) or X-ray photoelectron spectroscopy is a characterization technique capable of providing structural information of surface molecules in the solid state. Its applicability to the study of the surfaces of polymer films has been principally introduced by Clark and co-workers in England (23, 24, 189, 202-215).

Esca Applied to Polymers

For detailed information on the ESCA experiment, the reader is referred to one of the numerous texts or reviews on the subject (203, 216-

217). Basic principles will be briefly discussed herein along with detailed information on points specifically applicable towards the use of ESCA for analysis of the polycarbonate-polydimethylsiloxane systems presented in the research sections of this paper.

The ESCA experiment involves the measurement of binding energies of core electrons ejected through interactions with a narrow beam of soft X-rays (usually $Al_{K\alpha 1,2}$ or $Mg_{K\alpha 1,2}$). The principle is based on the photoelectric effect whereby all of the energy of the photon is expended in the ejections of the bound electron via a dipole interaction. Since core orbitals are essentially localized on atoms, electrons originating from those levels possess kinetic energies characteristic of a given element. Only small (but often quite useful) binding energy shifts are effected through altered electronic environments about a given atom.

Emitted electrons have kinetic energies given by equation 35.

Equation 35

$$KE = h\nu - BE - \phi_s$$

KE = The kinetic energy of the emitted electron.

$h\nu$ = The energy of the photon.

BE = The binding energy of the emitted electron.

ϕ = Principally the spectrometer work function.

Upon removal of a core electron, reorganization of valence electrons in response to an effective increase in nuclear charge occurs. This type of perturbation gives rise to a probability that a valence electron will be excited from an occupied to an unoccupied level (shake-up). This commonly results in shake-up satellites appearing on the low kinetic energy side of the main photoionization peak in unsaturated systems. Their origin is generally attributed to $\pi \longrightarrow \pi^*$ transitions. In saturated systems, these shake-up transitions occur but the satellites are normally masked by the tail on the primary peak resulting from inelastic scattering in the solid sample. Since the shake-up satellite peaks denote unsaturation, they can often be used as a valuable analytical tool.

Although ionization occurs to a depth of a few micrometers, only those electrons originating within tens of angstroms from the surface can leave that surface without energy loss. Electron mean free paths vary with kinetic energy from a minimum of a few angstroms at 80 eV with roughly a square root dependence on kinetic energy to the higher energy side and a steeply increasing function to the low energy side (213). The average values for mean free paths as a function of kinetic energy for the polymer systems studied by Clark and co-workers (213) are ∿ 14, ∿ 22, ∿ 23, and ∿ 29 Å for kinetic energies of ∿ 969, ∿ 1170, ∿ 1202, and ∿ 1403 eV respectively. For an escape depth of ∿ 10 Å , ∿ 50% of the intensity of the elastic peak is derived from the top ∿ 7 Å, 90% is derived from the top ∿ 27 Å (23, 207). Due to these extremely short electron ejection paths, it is only the top 50-100 Å of a sample that is analyzed via this technique.

Clark and co-workers have also established that quantitative ESCA measurements can be applied to polymer surfaces (213). For bulk homogeneous material of infinite thickness as compared to the mean free paths of the photoemitted electrons, the intensity of the elastic peak, I_∞, is represented by equation 36. The depth profiling capability of

Equation 36

$I_\infty = F\alpha NK\lambda.$

F = The X-ray flux.

α = The photoionization cross-section from a given shell in a given atom for a given X-ray energy.

N = The number of atoms per volume element.

K = A spectrometer factor.

λ = The electron mean free path.

the technique using normal angle measurements rests on the strong dependence of electron escape depths on kinetic energy. The intensity, I, of the signal from a given core level arising from a surface layer of thickness d is given by equation 37.

Equation 37

$I = I_\infty\ (1-e^{-d/\lambda}).$

I_∞= Intensity of an infinitely thick layer.

λ = Electron mean free path.

Depth profiling can also be accomplished by varying the effective sampling depth. This is done by rotating the sample relative to the analyzer by an angle θ (θ is designated as the angle between the normal to the sample and the energy analyzer (see Figure 8)).

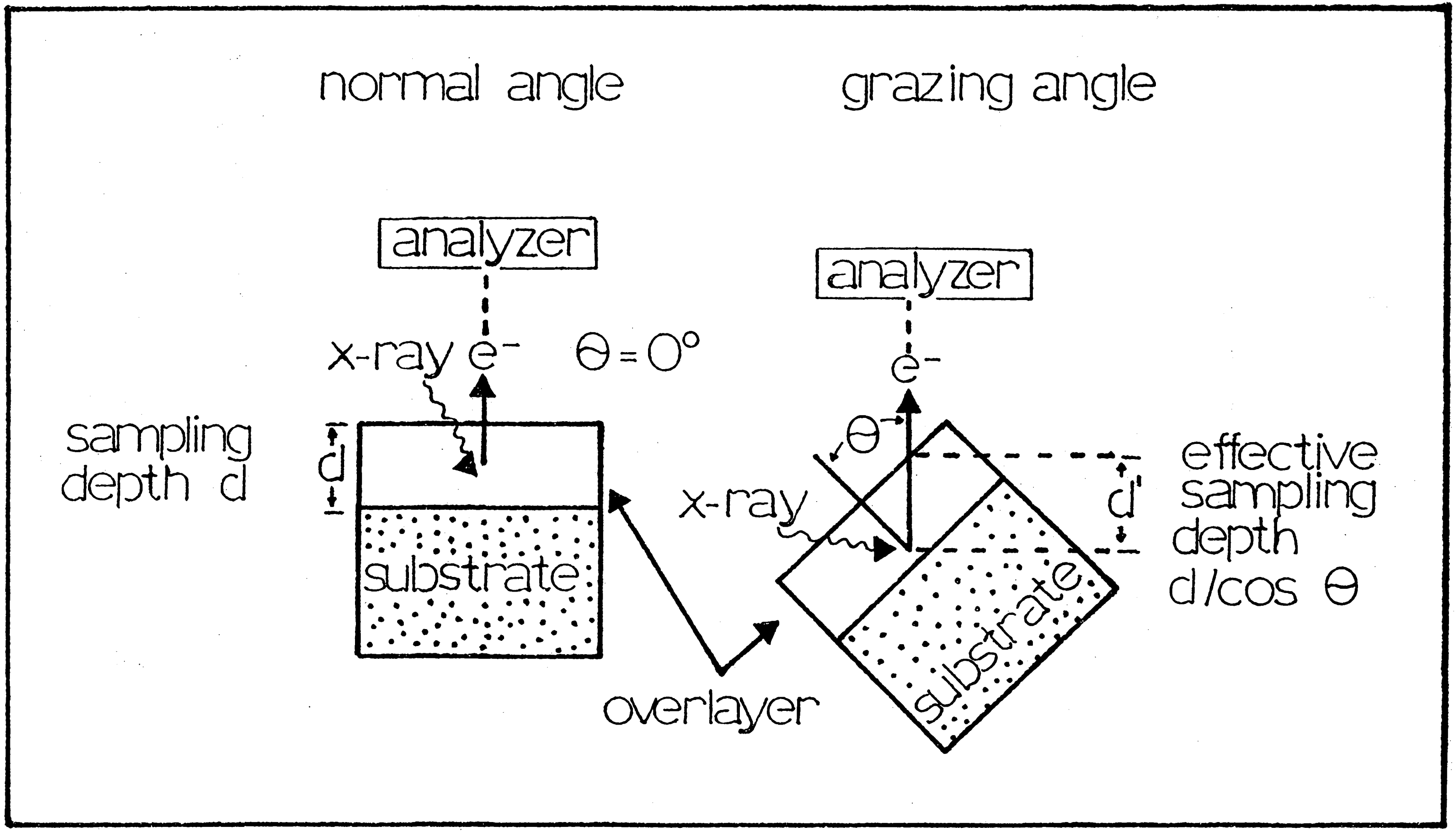


Figure 8: Effective Sampling Depths for the ESCA Experiment

Electrons collected at grazing exit angles relative to the surface will enhance the effects derived from the uppermost surface relative to electrons collected normal to the surface.

As briefly described earlier, Clark et al. (213) performed an extensive investigation of the mean free paths of electrons in polymeric materials. They first investigated samples of carbon overlayers of known thicknesses on a gold substrate. Conditions of this investigation included the use of a $Mg_{K\alpha 1,2}$ X-ray source and $\theta = 10^{o}$. The data showed electron mean free paths of 20.4 Å and 14.4 Å for kinetic energies of ∿ 1170 eV and ∿ 969 eV respectively (note that these kinetic energies are very close to those of Si_{2p} and C_{1s} electrons). These authors then looked at amorphous poly(p-xylylene) films of known thicknesses polymerized onto gold substrates. Experimental data was taken using both $Mg_{K\alpha 1,2}$ and $Al_{K\alpha 1,2}$ radiation with varied take-off angles ($\theta = 0^{o}, 10^{o}, 30^{o}, 50^{o}$). They reported excellent agreement between the measured mean free paths for electrons of similar kinetic energies measured using the two different X-ray sources.

In an earlier less extensive study, this group of workers (23, 207) found escape depths (using a $Mg_{K\alpha 1,2}$ source) of $\lambda_{C_{1s}} = 10$ Å, $\lambda_{O_{1s}} = 8$ Å, and $\lambda_{Si_{2p}} = 11.5$ Å. These values were determined on polyethylene-fluorinated polyethylene systems. Comparison of the results reveals the mean free path for silicon obtained in this earlier study to be quite low compared to the later investigation whereas the comparison of the mean free paths for the C_{1s} level is better.

Clark (212) et al. carried out non-empirical LCAO MO SCF computations in an effort to predict binding energies for an extensive series of oxygen-containing organic systems. Calculations were based on ground states and core hole states and binding energies were calculated directly as energy differences between the two. When compared to empirical data, it was evident that theoretical binding energies had been overestimated by ∿ 1%. However, in terms of relative values (close in energy), agreement was quite good.

C_{1s} level calculations indicated that the number of bonds to the oxygen atom was the important variable. Shifts relative to methane obeyed the trend:

∿ $\Delta + 1.5$ eV	Carbon singly bonded to oxygen.
∿ $\Delta + 3.0$ eV	Carbon singly bonded to two oxygens or doubly bonded to one oxygen.
∿ $\Delta + 4.5$ eV	Carboxylic acid and ester carbons.
∿ $\Delta + 6.0$ eV	Carbonate carbons.

Data pertaining to O_{1s} orbitals suggested carbonyl oxygens to be lower in binding energy than singly bonded oxygens in all cases. Based on unpublished results, Clark and Dilks (212) have suggested that oxygen peak positions are grouped in the following manner.

∿ 532.8 eV	Doubly bonded oxygen
∿ 533.7 eV	Singly bonded oxygen in alcohols, ethers, and peroxides.
∿ 534.3 eV	Singly bonded oxygen in acids, esters, and hydroperoxides.
∿ 535.2 eV	Singly bonded oxygen in carbonates, peroxyacids and peroxyesters.

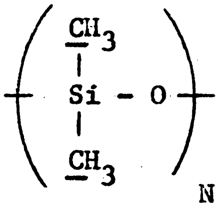
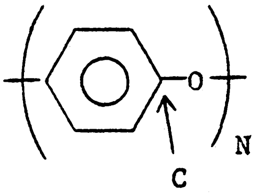
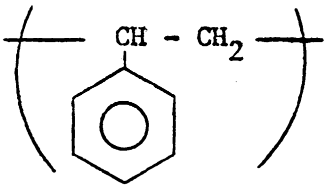
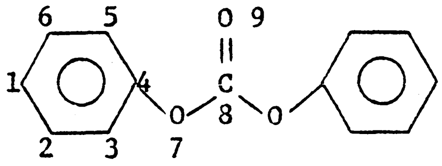
Clark and co-workers (215) also studied a series of 83 homopolymers empirically by ESCA. They observed that for carbon singly bonded to oxygen in alcohols, ethers, esters, and carbonates, C_{1s} shifts (from hydrocarbon) were consistent at 1.6 ± 0.2 eV. Moreover, in agreement with theoretical results (212), the effect was found to be additive. In going from a carbonyl to a carboxylate group, the binding energy shift associated with the additional oxygen singly bonded to the carbon was determined as ∿ 1.4 eV (giving a total shift of 4.0 eV). The additivity principle was also manifested in proceeding from a carboxylate to a carbonate group (∿ 1.4 eV making a total of 5.4 eV for the carbonate carbonyl carbon). For the particular case of the polycarbonate derived from bisphenol-A, the shift for the carbonate carbon overlapped the $\pi \longrightarrow \pi^*$ shake-up transition of the aromatic moiety. It was observed that the O_{1s} binding energies of polycarbonates spanned a range of ∿ 2 eV in going from singly to doubly bonded oxygen. In the polydimethylsiloxane, the C_{1s} binding energies coincided with the hydrocarbon C_{1s} peak. The O_{1s} binding energy was positioned at 533.6 ± 0.2 eV which was within experimental error of the corresponding values for the polyethylene oxides (533.8 ± 0.2 eV).

Additional literature values pertinent to the present study are given in Table 10.

ESCA data is often coupled with or compared to data derived from surface techniques such as contact angle or surface tension measurements, Auger electron spectroscopy data, FTIR internal reflection spectra or scanning electron microscopy photographs.

Table 10

Experimental Binding Energies: Reference Compounds

	Structure	Binding Energy	Reference
1.		285.0 eV	23-24
2.		~287 eV	215
3.	 all carbons	285.0 eV	190
4.		C_4 = 286.6 eV C_8 = 290.9 eV O_7 = 535.3 eV O_9 = 533.9 eV	215

Critical surface tensions of wetting can, in a relatively crude manner, provide information on the gross structure of the immediate outer layer of a polymer film. Unlike ESCA, it is not applicable to the identification of unknown surfaces. Provided the appropriate model compounds are available, its best use for a study comparable to that presented in this paper would be as supportive data for the ESCA measurements.

Auger electron spectroscopy is now often used in conjunction with ESCA simply because of its availability. It is often the case that the equipment necessary for both types of measurements is encompassed by one instrument. Both techniques supply at least qualitative identification of surface elements present and, in cases where both types of measurements are applicable, the two compliment each other well.

Photoionization differs from Auger spectroscopy in that it involves a single step process whereas the Auger technique involves two steps. This results in ESCA spectra being simpler to analyze and interpret than the corresponding Auger data (216). Unavoidable secondary electron emission, backscattered electrons, and relatively large amounts of inelastic scattering occurring in the Auger process make quantitative work more difficult than when using ESCA. A greater probability of charge build-up in nonconducting solids as a result of impinging electrons over that present when using an X-ray source also serves to decrease the signal to noise ratio in Auger spectroscopy. In addition to the data interpretation problems incurred when using the Auger process, difficulties associated with the electron beam source can render the technique undesirable for the analysis of many organic compounds (216, 216a). Radiation damage as a result of the high intensity, sharply focused electron beam is often encountered.

FTIR attenuated total reflectance spectroscopy provides the normal FTIR spectrum complete with detailed and quantitative structural information. It provides information corresponding to considerably more depth in the sample than ESCA (from approximately a few hundred angstroms to $\sim$ 1.5 μ). The combination of the FTIR-ATR and ESCA techniques can often be used for depth profiling.

Using the scanning electron microscope, the area examined is irradiated with a finely focused electron beam swept in a raster across the specimen surface. The primary signal of interest is the variation of secondary electron emission that takes place due to differences in surface topography. Maximum resolution on most of the instrumentation is approximately 100 Å. The technique provides an entirely different type of information from that derived from other methods discussed and, therefore, is difficult to compare. Composition can be obtained with the addition of an energy-dispersive X-ray detector (EDAX). EDAX, however, is not useful for obtaining structural composition with respect to carbon or oxygen and, hence, its use for organic compounds is limited (218).

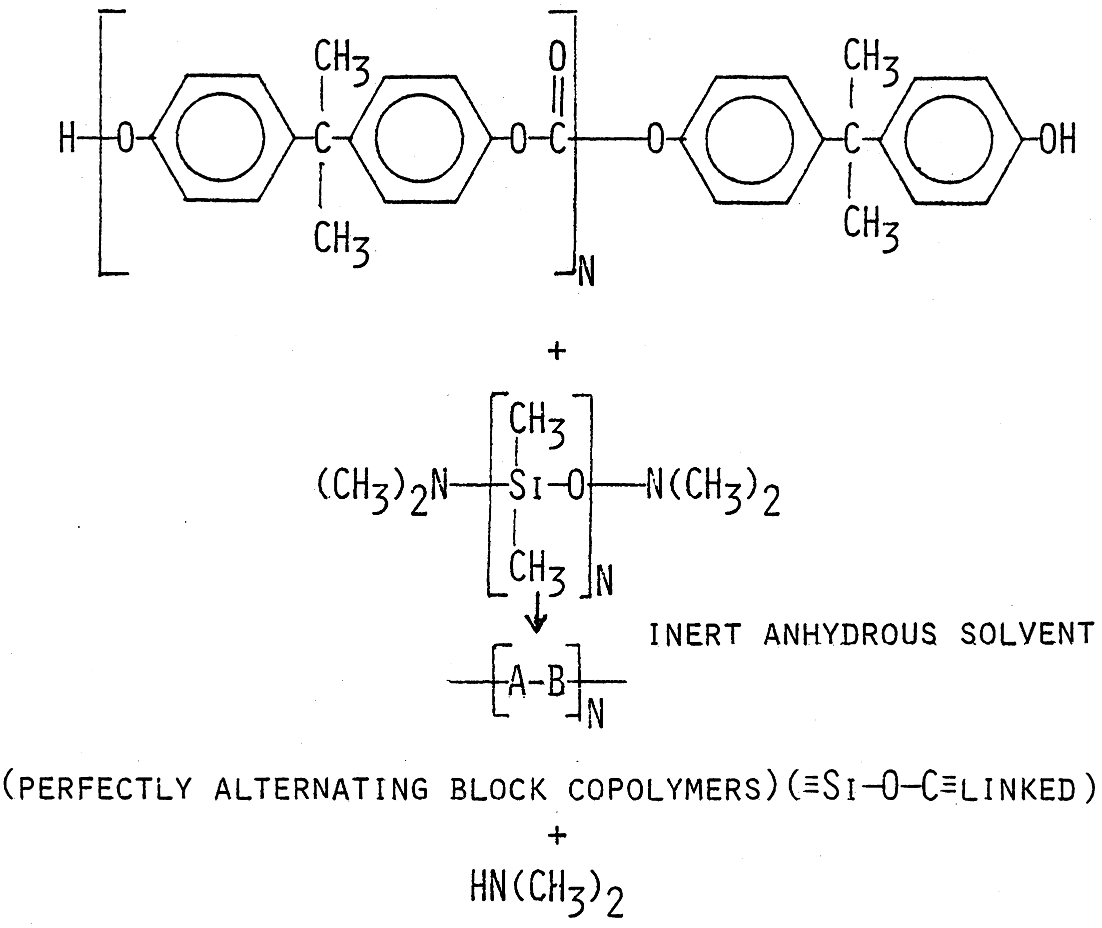
Chapter III

RESEARCH INTRODUCTION

Materials were prepared in this study which consisted of both perfectly alternating block copolymers containing the ≡Si-O-C and also, randomly coupled block copolymers containing the direct ≡Si-C bond between the blocks.

Perfectly alternating block copolymers were prepared essentially by Noshay and Matzner's procedure (12, 118) in refluxing chlorobenzene solution by reacting preformed dimethylamino terminated polydimethylsiloxane and hydroxyl terminated polycarbonate oligomers. The

Equation 38

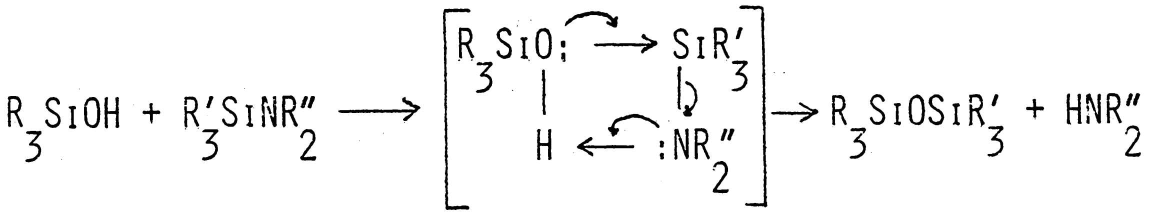


copolymer reaction proceeds by the general reaction shown in equation 38. Matzner et al. have previously synthesized several organosiloxane block copolymers via this type of silylamine reaction using the following organic oligomers as the "hard" blocks:

1. Polysulfone of bisphenol-A
2. Poly(bisphenol-A terephthalate)
3. Poly(bisphenol-A isophthalate)
4. Poly (2,2,4,4-tetramethyl-1,3-cyclobutylene carbonate)
5. Poly (α-methylstyrene)

Similar polymers have also been synthesized using poly(phenylene-oxide) as the rigid component (219). Noshay, Matzner, and Williams found copolymerization to be highly dependent upon the nature of the terminal hydroxyl groups of the rigid block (118). Phenolic endgroups reacted much more rapidly than the less acidic aliphatic hydroxyl endgroups. This is not surprising since catalysis by traces of acids and rate enhancement with increasing acidity of the alcohol have also been observed in the reactions of low molecular weight alcohols with silylamines (220). For the similar reaction of silanols with silylamines to form siloxanes, a cyclic transition state (equation 39) has been proposed (221).

Equation 39



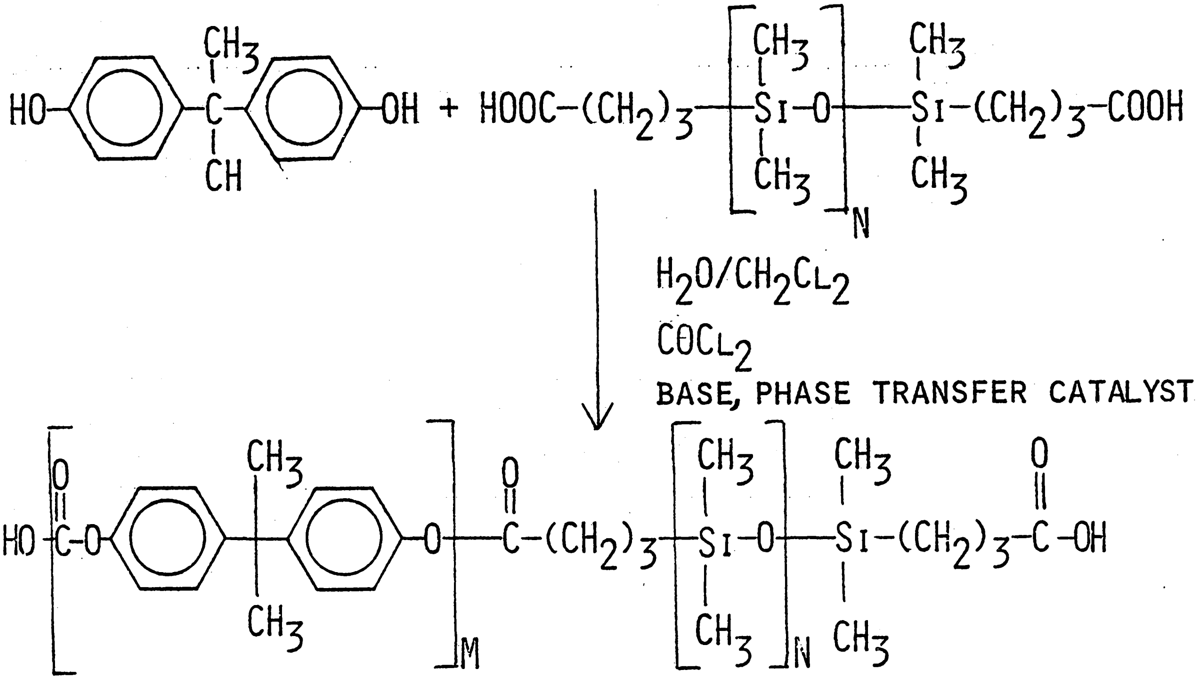
The rate of copolymerization was found to be considerably slower in tetrahydrofuran than in chlorobenzene with phenolic terminated oligomers (222). These workers postulated the effect to be due to hydrogen bonding effects. In tetrahydrofuran, the phenolic hydrogen might hydrogen bond with the solvent thereby reducing its availability to the silylamine nitrogen.

Mechanical properties of the perfectly alternating ($\{A\text{-}B\}_N$) polysulfone-polydimethylsiloxane block copolymers produced by the method discussed above were found to vary widely depending on the bulk composition (12). Materials ranged from being rigid with low extensibility at low siloxane contents to being quite elastomeric at high siloxane contents. Oxygen permeability reportedly also varied over a wide range ($1 \times 10^{-10}\ \frac{\mathrm{cm^3(STP)}}{\mathrm{cm^2\ sec.\ cm\ Hg}}$ at 24% siloxane to $4 \times 10^{-8}\ \frac{\mathrm{cm^3(STP)}}{\mathrm{cm^2\ sec.\ cm\ Hg}}$) (12, 184).

Two series of polycarbonate/polydimethylsiloxane copolymers produced via this method are discussed in the research sections of this paper. Both copolymer composition at constant block length and block lengths at given compositions were investigated.

The preparation of copolymers bearing the direct $\equiv$Si-C- bond between the blocks has proven to be quite challenging. The general synthetic route utilized a preformed carboxypropyl, hydroxypropyl, or hydroxybutyl terminated polydimethylsiloxane and in situ generated polycarbonate segments as schematically shown in equations 40 and 41. Note that the reaction of two moles bisphenol-A with one mole of phosgene, two moles of hydroxypropyl (or hydroxybutyl) terminated poly-

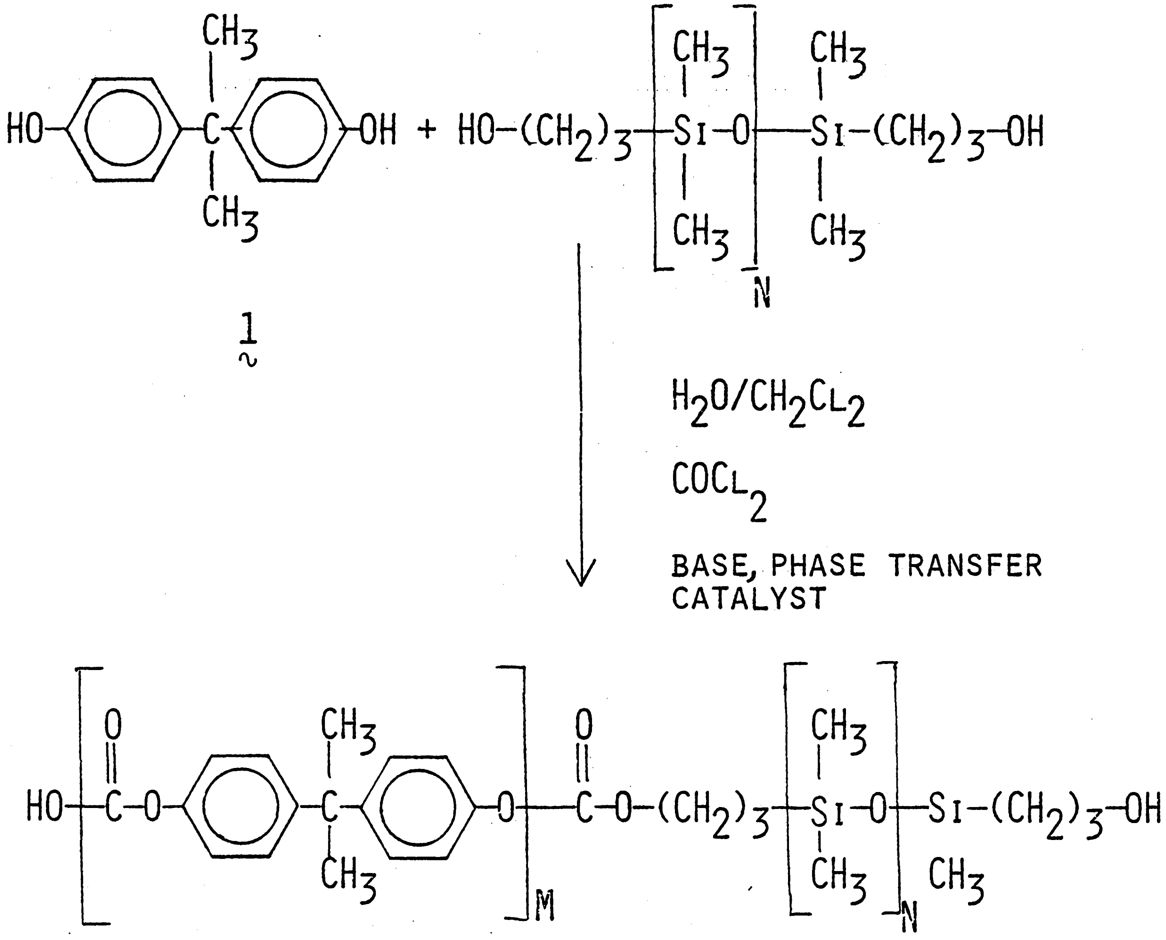
Equation 40



Randomly Coupled
Block copolymer, (Si—C) linked

siloxane oligomer with one mole of phosgene or one mole of bisphenol-A and one mole of hydroxypropyl (or hydroxybutyl) terminated siloxane oligomer with one mole of phosgene yields a carbonate $(-O-\overset{\overset{O}{\|}}{C}-O-)$ link. On the other hand, the corresponding reaction of one mole bisphenol-A, one mole of acid terminated polysiloxane oligomer, and one mole of phosgene is shown producing an ester $(-\overset{\overset{O}{\|}}{C}-O-)$ bond between the terminal carboxypropylsiloxane and the bisphenol. Interfacial (or rather, phase transfer catalyzed) methods have been investigated. It was reasoned that the interfacial route would insure a cleaner reaction product which in turn would be very important for biomedical applications. Solution processes might require pyridine which would be difficult to

Equation 41

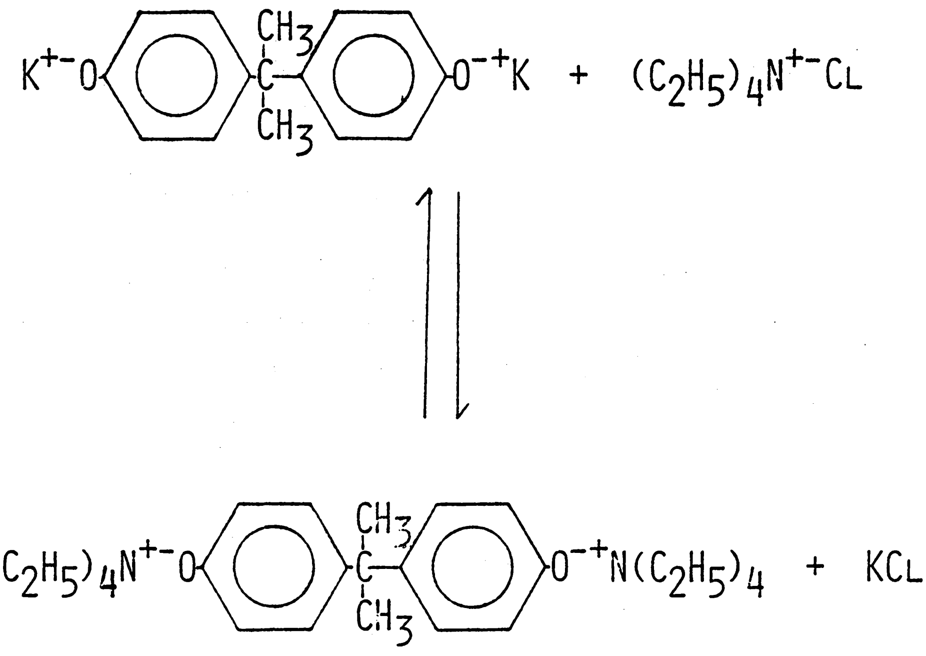


remove quantitatively after copolymer formation. Residual traces could degrade either segment. For example, the copolymer product from the solution reaction might result in rearrangements of the siloxane portions with time.

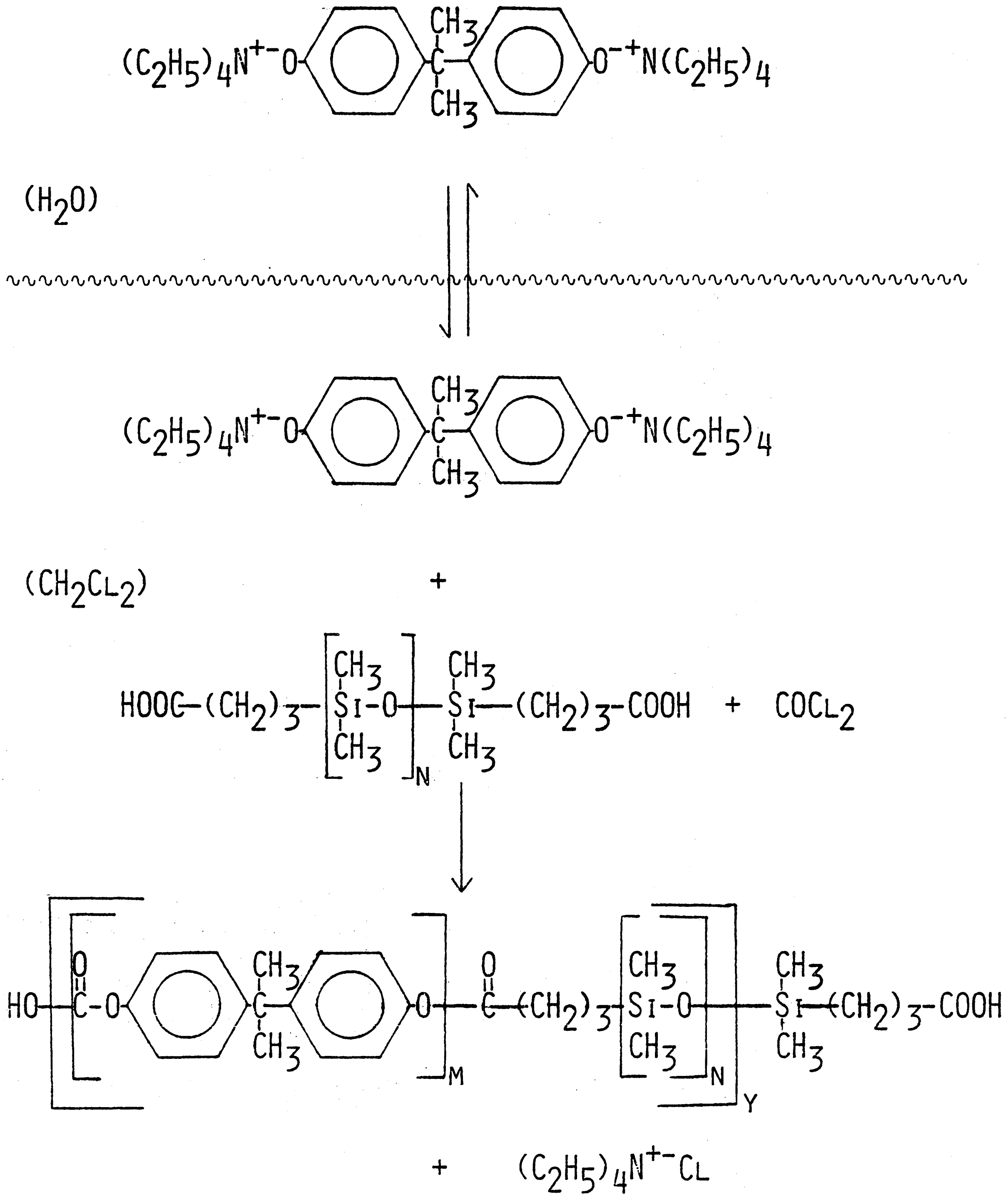
The phase transfer process envisioned as being operative in the formation of these polycarbonate/polysiloxane random block copolymers is an extension of the established sequence occurring in the production of the bisphenol-A polycarbonate homopolymers. It first involves dissolution of the bisphenol-A in an aqueous caustic solution. This is followed by reaction of a portion of the alkali metal salt of bisphenol-A with a phase transfer catalyst (P.T.C.) (equation 42). The latter usually possesses a relatively large organic cation.

The alkyl quaternary ammonium salt of bisphenol-A will then partition itself between the aqueous and an organic phase. As it moves into the organic phase, the highly reactive salt is brought into contact with both phosgene and the acid terminated or hydroxyl terminated polydimethylsiloxane oligomers and may react to form the copolymer (equation 43). The by-product of equation 43, which is the original phase transfer catalyst, is then transferred back to the aqueous phase which completes the catalytic cycle.

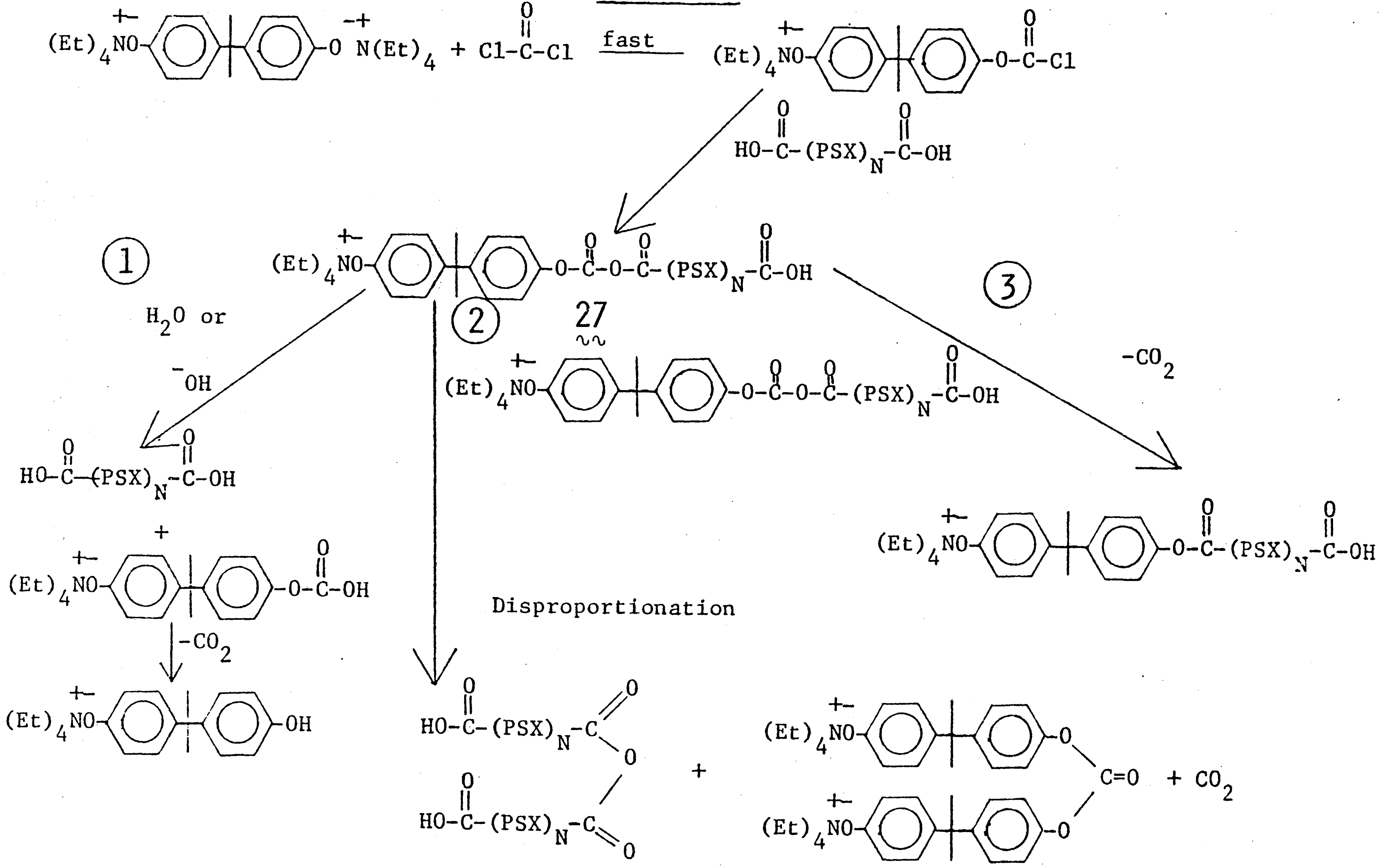
Equation 42



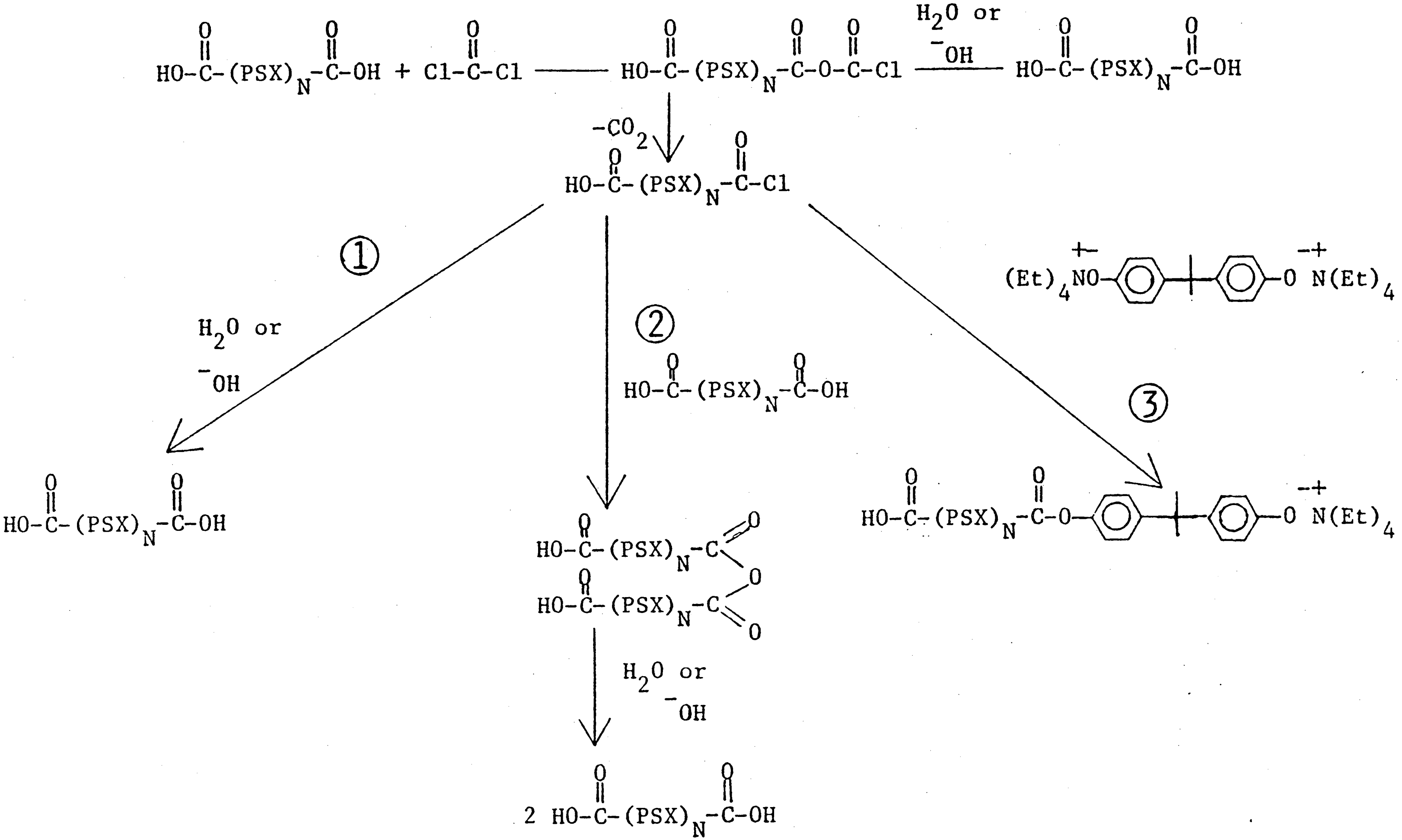
Equation 43



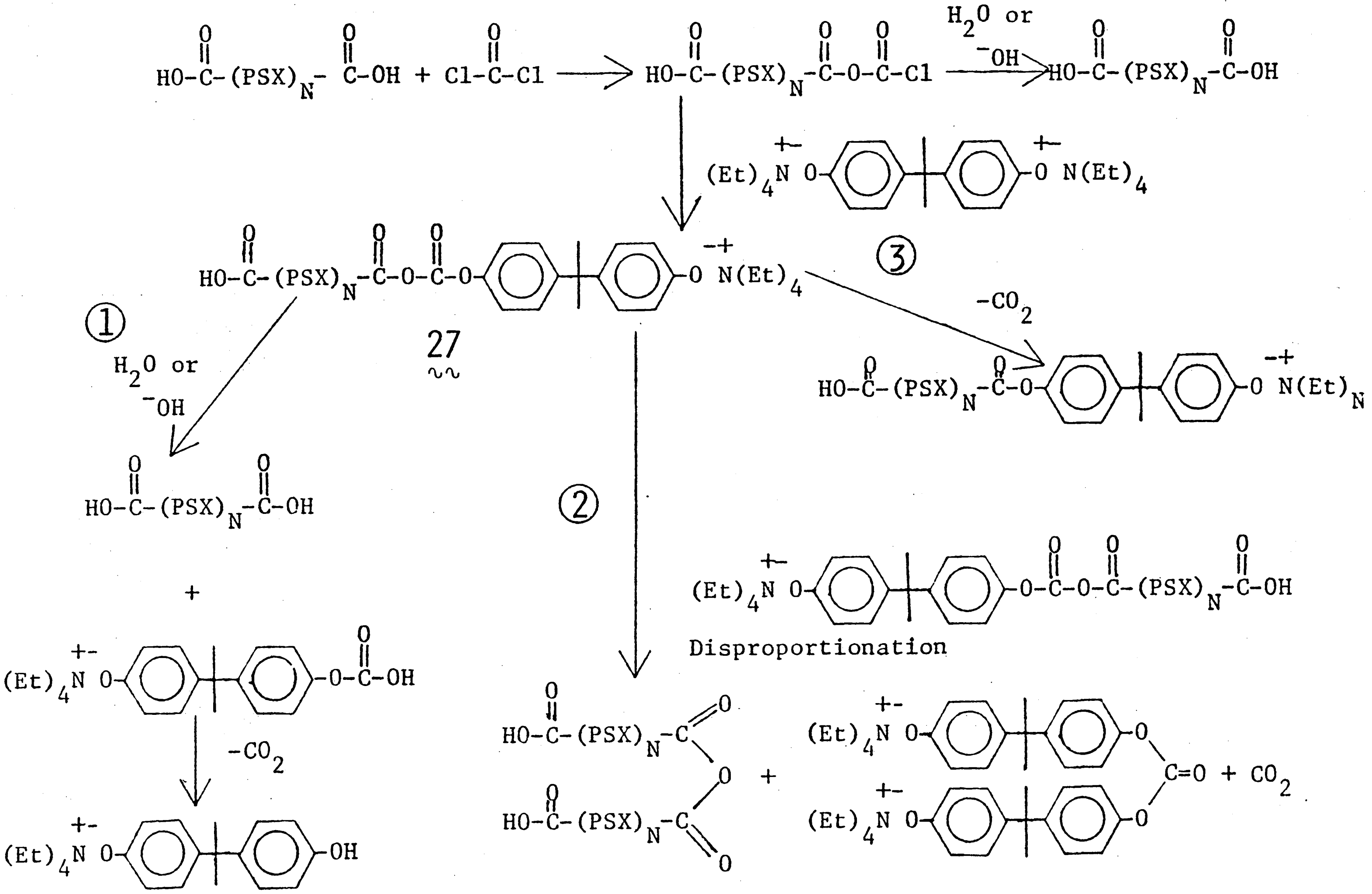
Equation 44



Equation 45a



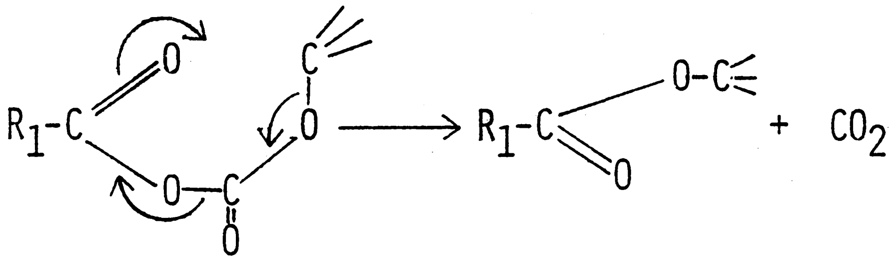
Equation 45b



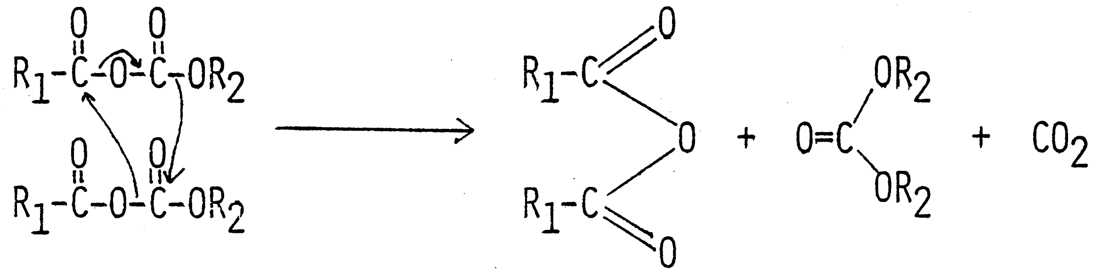
The reaction of the carboxylic acid terminated siloxane to form an ester bond in the reaction scheme adds at least one (and possibly more) series of steps to the overall reaction. Although the mechanistic pathways have not been clearly established, two plausible routes to ester formation are envisioned (equations 44, and 45a and 45b).

Mixed carbonic-carboxylic anhydrides of the type illustrated in equations 44, 45a and 45b, 27, are known to decompose under anhydrous conditions via pathways analogous to 2 and 3 in both equations 44 and 45b (223-226). Proposed mechanisms for these decompositions (226) are given in equations 46 and 47. The relative proportions of the two

Equation 46



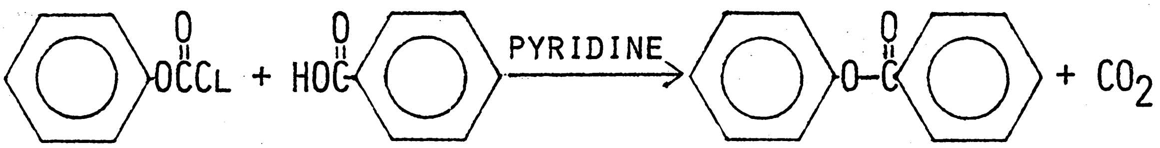
Equation 47



pathways occurring have been determined (226) for a variety of reactions which included systematic combinations of both aromatic and aliphatic acids and alcohols. For all cases investigated where the acid moiety was aliphatic (as it is in the copolymerization discussed in this thesis) decomposition proceeded *exclusively* to the ester even at room temperature. However, when the acid component was aromatic, *both* decomposition pathways were found operative at room temperature and, in some cases, decomposition occurred only at elevated temperatures.

Under anhydrous conditions, Goldberg et al. (227) supported the pathway to the ester shown in equation 44, route 3 as opposed to that given in equation 45a, route 3. From the model reaction of phenyl chloroformate with benzoic acid in pyridine at room temperature he was able to isolate phenyl benzoate in good yield (equation 48). Moreover, when phosgene was bubbled into a solution of phenol and benzoic acid in pyridine he obtained the same product. Goldberg et al. dismissed the possibility of the acid chloride intermediate from being plausible for two reasons: 1. acid chlorides are less reactive than chloroformates ($\sim\sim\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-Cl$), and 2. no evidence of carboxylic anhydrides was

Equation 48

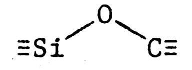


found in the infrared spectra of the products. While Goldberg's evidence does provide support for the feasibility of the pathway shown in equation 44, route 3, it would appear to not preclude the possibility of alternate routes. For example, some reactions not considered could be occurring simultaneously (i.e. equation 45b, route 3). Nevertheless, one must agree that good yields of the desired model compound were isolated. Of course, the analytical techniques employed were probably not sensitive enough to detect minor in chain anhydride imperfections. Quite recently, Prevorsek et al. (228) have reinvestigated the reaction of bisphenol-A, terephthalic acid, and phosgene under anhydrous conditions in pyridine/dichloromethane co-solvent. In contrast to Goldberg's work, they did observe carboxylic anhydrides in the infrared spectra of their products. Compared to the current work herein, both of these papers dealt with aromatic acid reactions which may indeed produce relatively more stable anhydride intermediates. It is clear that additional studies would be desirable.

Chapter IV

EXPERIMENTAL

Perfectly Alternating Block Copolymers: Synthesis of Reactive Polycarbonates:

The bisphenol-A polycarbonate oligomeric precursors used for preparation of the perfectly alternating block copolymers possessing the  $\equiv Si-O-C\equiv$ link between the block structures were synthesized in a manner closely resembling the facile "direct phosgenation" route. A convenient laboratory method was developed for the production of these reactive polycarbonates which utilizes either trimethylisilyl chloride (TMCS), **22**, trifluoroacetic anhydride (TFAA), **23**, or trifluoroacetic acid (TFA), **24**, capping of a portion of the bisphenol.

The suggested synthetic method differs slightly depending on the "functionality" of the blocking reagent used. However, the procedures using trifluoroacetic anhydride and trifluoroacetic acid are identical with the exception of the calculation for the required amounts of the blocking agents themselves. Hence, a typical procedure using trimethylchlorosilane is provided separately whereas the methods using the fluorinated reagents are combined.

Preparation of Polycarbonates Utilizing Trimethylchlorosilane (TMCS) For Control of <Mn>:

High purity bisphenol-A (usually Union Carbide high purity UCAR grade) was used as received. Fisher practical grade TMCS was distilled over P_2O_5 prior to use.

The apparatus consisted of a three-necked, round-bottomed flask equipped with a mechanical stirrer, combined argon and phosgene inlet (the gases must of course be bubbled through the reaction mixture, not into the air space above the solution), and condenser connected to a caustic trap. The argon purged reaction vessel is charged with the bisphenol-A together with an approximately equal amount of dry tetrahydrofuran. The required amount of TMCS (determined by $<X_n> = \frac{2}{X}$ where "X" is the molar ratio of blocking reagent to bisphenol-A) is added and the mixture is stirred at room temperature for 15-30 minutes. Pyridine (~2 moles per mole bisphenol-A) and enough methylene chloride to make up a ~10% solution are added and the phosgene gas is introduced. After formation of the polycarbonate, water is very slowly (care!) added to decompose excess phosgene. The solution is first washed with dilute hydrochloric acid. Hydrolysis of the trimethylsilyl ether endgroups is achieved by clarifying the organic phase with 10-15% of methanol, adding about 1 cm^3 of concentrated aqueous HCl/100 ml solution, reclarifying with methanol, and subsequently stirring the homogeneous mixture for one hour. After this, the solution is again washed twice with water. Finally, the polymer is isolated by coagulation in isopropanol followed by filtration and vacuum drying to a constant weight at ~80°C.

The procedure described below utilizing trifluoroacetic anhydride or trifluoroacetic acid shows THF as the solvent. It should be noted that dichloromethane can be substituted as the solvent and that several of the reactions listed in Table 11 were

TABLE 11

Synthesis of Bisphenol-A Polycarbonates of Controlled Molecular Weights

Blocking Reagent	$\frac{1}{X}$[b]	Solvent	<Mn> Theoretical	<Mn> Experimental
TMCS	10.73	CH_2Cl_2/Pyridine	5,450	5,300
TMCS	19.70	CH_2Cl_2/Pyridine	10,010	9,100
TMCS	19.70	THF/CH_2Cl_2/Pyridine	10,010	11,900
TMCS	40.87	THF/CH_2Cl_2/Pyridine	20,760	20,600
TMCS	9.84	THF/CH_2Cl_2/Pyridine	5,000	5,500
TFAA	11.34	THF/CH_2Cl_2/[a]TEA/Pyridine	2,880	3,000
TFAA	19.68	THF/CH_2Cl_2/[a]TEA/Pyridine	5,000	5,800
TFAA	59.0	THF/CH_2Cl_2/[a]TEA/Pyridine	15,000	16,000
TFAA	12.36	THF/Pyridine	3,140	2,268
TFAA	10.30	THF/Pyridine	2,617	2,679
TFA	5.0	THF/CH_2Cl_2/[a]TEA/Pyridine	2,540	2,700
TFA	19.33	CH_2Cl_2/Pyridine	9,820	9,100
TFA	5.92	THF/Pyridine	3,000	2,658

---

[a] TEA = TRIETHYLAMINE. These experiments were done using THF/TEA in a pre-step to polymerization analogous to that used with TMCS.

[b] $\frac{1}{X}$ = molar ratio of bisphenol-A to blocking reagent.

done in dichloromethane.

Preparation of Polycarbonates Utilizing Trifluoroacetic Anhydride (TFAA) or Trifluoroacetic Acid (TFA) for Control of <Mn>:

Trifluoroacetic anhydride obtained from Eastman was freshly distilled over P_2O_5 prior to use. Trifluoroacetic acid obtained from Aldrich Chemicals (purity 99%) and high purity bisphenol-A (Union Carbide, high purity UCAR grade) were used as received.

The required apparatus consists of a three-necked, round-bottomed flask equipped with a mechanical stirrer, combined argon and phosgene inlet and Dean Stark trap topped with a condenser connected to a caustic trap. A silicone oil bath is used for heating. The reaction vessel is charged with a ~10% solution of bisphenol-A dissolved in tetrahydrofuran and the pyridine (4 moles per mole bisphenol-A). Methylene chloride is added in the amount of approximately 30% (V/V) of the volume of tetrahydrofuran used, then is subsequently distilled off to dehydrate the system. The required amount of trifluoroacetic anhydride (determined by $\langle X_n \rangle = \frac{1}{X}$ where "X" is the molar ratio of blocking reagent to bisphenol-A) or trifluoroacetic acid (determined by $\langle X_n \rangle = 2/X$) is added. The justification of these expressions is presented in the discussion section of this thesis. Phosgene (three times the stoichiometric amount) is introduced over a 45 minute period, then the mixture is allowed to stir under argon for an additional hour. After polymerization has been completed, water is slowly added to decompose residual phosgene, the solution is washed several times with dilute

(~3%) hydrochloric acid, then with water several more times. Finally, the polymer is coagulated in methanol, isolated by filtration and dried to a constant weight under vacuum at approximately 80°C.

Analysis of Reactive Polycarbonates

Molecular weights (<Mn>) of the oligomers after hydrolysis of the protecting groups were assessed via a UV spectrophotometric technique (141) using either a Hitachi model 100-60 or a Perkin-Elmer 552 instrument. HPLC grade stabilizer free tetrahydrofuran from Fisher Chemicals was used as the spectroscopic solvent. Calculations were based on equation 49. It is not necessary that the

Equation 49 (141)

$$\langle Mn \rangle = \frac{3450}{\frac{(R)(4.29)}{1-0.17R} - 0.03}$$

$$R = \frac{\text{Absorbance due to the phenolic endgroups at 287 nm}}{\text{Absorbance due to the polycarbonate backbone at} \sim 264.6 \text{ nm}}$$

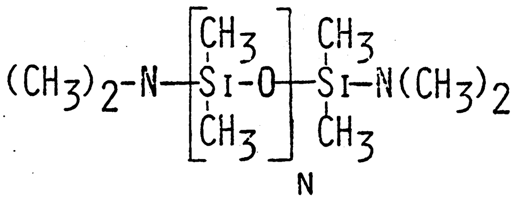
concentration of the analytical samples be known since molecular weights are derived from the ratio of two peaks.

High resolution proton NMR of the TMCS derivatized polymers and ^{19}F NMR of the trifluoroacetyl terminated compounds were performed using a Varian EM-390 spectrometer at 84.7 MHz and 30°C. 1,2-Difluorotetrachloroethane used for the ^{19}F lock signal and reference was obtained from Peninsular Chemical Research, Lancaster, Pennsylvania. Fisher certified grade (99 mole % pure) methylene chloride was used as the proton NMR lock and reference signal. Samples used for ^{19}F NMR spectra were taken directly from the reaction mixture. Therefore, solvent and base concentrations used for ^{19}F analysis were those utilized in the reaction procedure.

Molecular weight distributions were assessed by gel permeation chromatography (Waters 6000-A pump, Waters R-400 D.R.I. detector, Waters micro-styragel columns -500Å, 10^{3}Å, 10Å, 10^{5}Å, tetrahydrofuran solvent).

Synthesis of Dimethylamino Terminated Polydimethylsiloxanes

Dimethylamino-terminated polydimethylsiloxane oligomers, 28, used for copolymerization with the previously described polycarbonate precursors were either obtained from Union Carbide or were prepared in our laboratory via a redistribution reaction. An exemplary equilibration procedure follows.



$$(CH_3)_2\text{-}N\text{-}\left[\underset{CH_3}{\overset{CH_3}{Si}}\text{-}O\right]_N\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}N(CH_3)_2$$

28

Preparation of Dimethylamino Terminated Polydimethylsiloxane Oligomers 28:

Low molecular weight dimethylamino terminated polydimethylsiloxane oligomers which were the starting materials for the redistribution reaction leading to defined higher molecular weights and tetramethylammonium silanolate catalyst were obtained from Union

Carbide. Octamethylcyclotetrasiloxane (D_4) was obtained from either Union Carbide, Silar Laboratories, or Petrarch Chemicals, Levittown, Pennsylvania.

The method of preparation used for these oligomers has been previously described in the literature (118, 229). The apparatus consists of a three-necked, round-bottomed flask equipped with a mechanical stirrer, argon inlet, condenser with a drying tube, and heated with a silicone oil bath. The required proportions of the low molecular weight dimethylamine terminated siloxane oligomers and D_4 are charged to the reaction vessel and heated to 80°C. The cyclic monomer (D_4) is opened and becomes incorporated into the linear oligomer. Therefore, the necessary ratio of D_4 to linear oligomer is determined by the <Mn> of the beginning oligomer and by the final molecular weight desired. Tetramethylammonium silanolate catalyst is added in the amount of 0.3 grams per 100 grams polymer and the temperature is maintained with rapid agitation for three-hours. After the equilibration, the mixture is heated to 150°C and the temperature maintained for an additional three hours to decompose the "transient" catalyst and evolve the Hoffman degradation products of the tetramethylammonium silanolate catalyst.

Analysis of Dimethylamino Terminated Polydimethylsiloxanes

Endgroup analyses of these dimethylamino terminated oligomers were performed by potentiometric titration in isopropanol with an aqueous hydrochloric acid titrant. Fisher certified grade isopropanol was used as received. A blank titration of the solvent was run prior to each oligomer analysis. Standardized 0.1 N aqueous hydrochloric acid as the titrant (also from Fisher) was diluted with distilled water as necessary. In order to prevent precipitation of the oligomers during titration, titrant and solvent volumes were adjusted to require approximately 1 ml of titrant per 50 ml isopropanol. An Orion (Orion Research, Inc., Cambridge, Mass.) model 601A digital pH meter used on the millivolt scale in conjunction with glass and calomel electrodes (Fisher Chemicals) was used. The titrant was dispensed from a 2 ml Gilmont microburet (A. H. Thomas, Co., Philadelphia, Pa.) graduated in 0.002 ml increments. The apparatus used for the analysis is pictured in Figure 9.

Molecular weights below ~3000 g/mole were also determined by high resolution proton NMR (Varian EM-390 spectrometer operating at 84.7 MHz and 30°C) by means of a comparison of peak areas of the nitrogen bonded and silicon bonded methyls (see Figure 10). Fisher certified grade (99 mole % pure) methylene chloride was used as the NMR lock and reference signal (5.37 P.P.M. from TMS). Aldrich gold label $CDCl_3$ (99.9%) served as the analytical solvent.

Thermal gravimetric analysis (TGA) was found useful in assessing the level of non-reactive cyclic oligomers in both "as-received" and equilibrated siloxanes.

Synthesis of Perfectly Alternating Block Copolymers

Perfectly alternating block copolymers were prepared from a variety of preformed and characterized polycarbonate and polydimethylsiloxane oligomers by a method essentially paralleling that

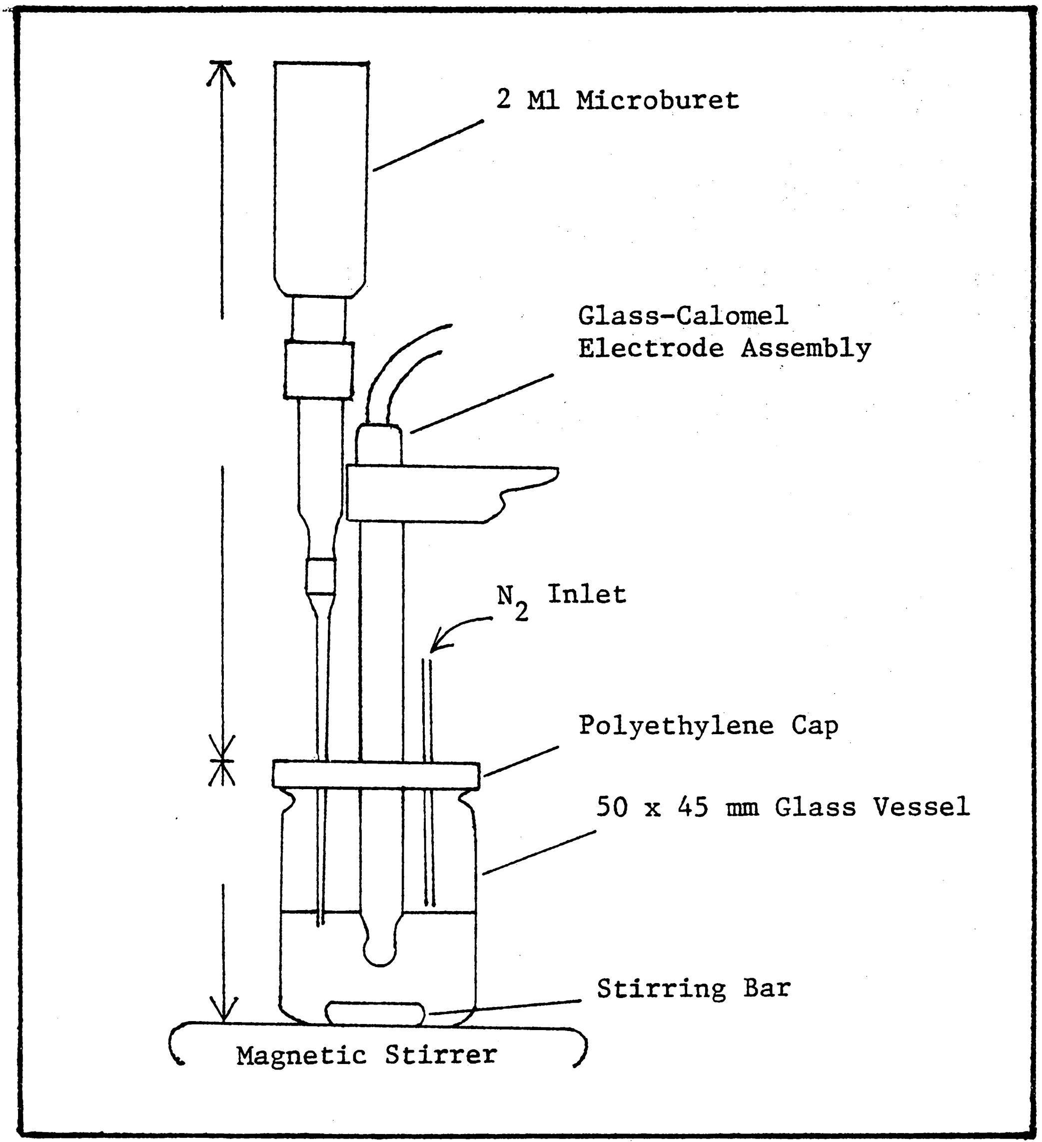


Figure 9: Apparatus for Potentiometric Titrations (230)

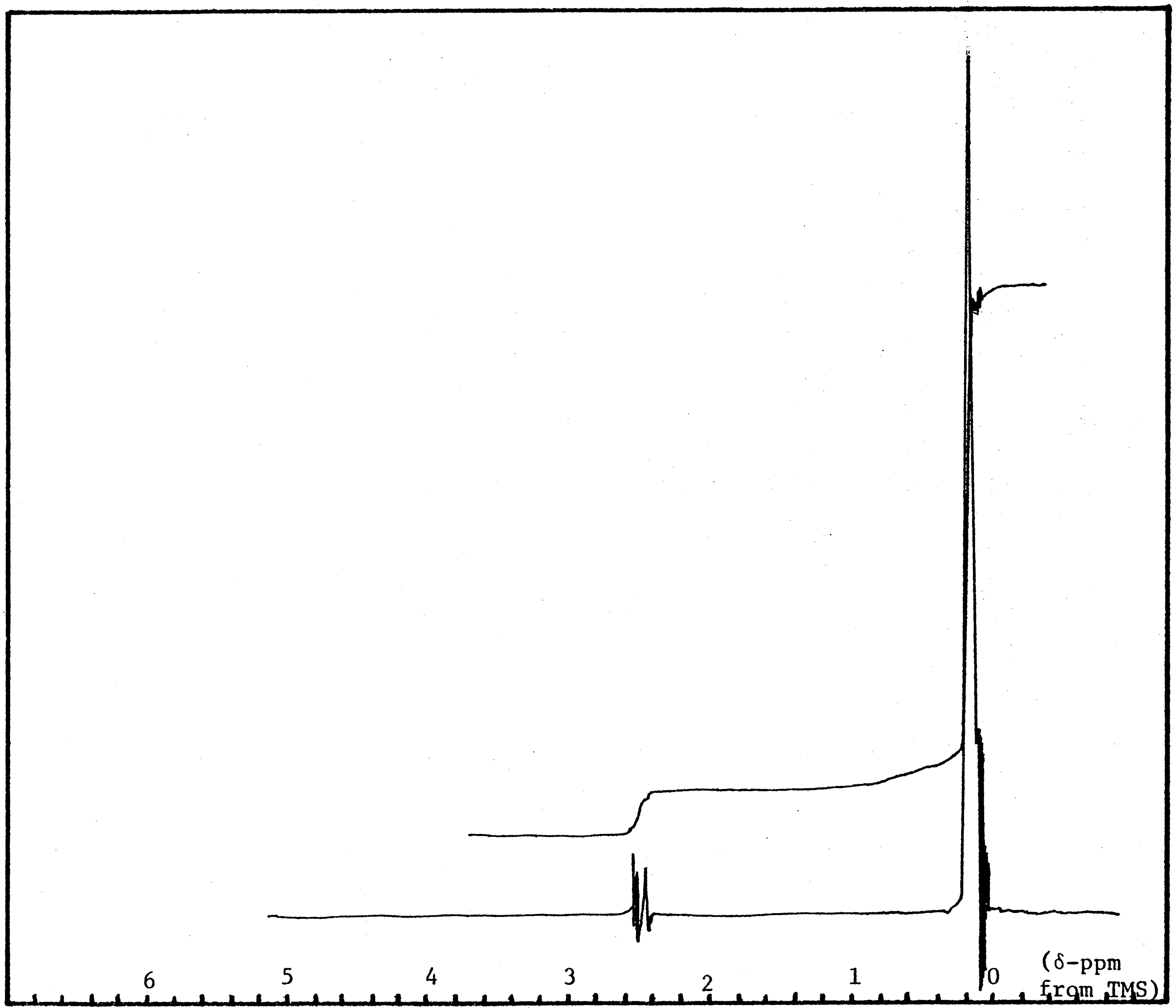


Figure 10: Proton NMR of Dimethylamino Terminated Polydimethylsiloxane Oligomer, (<Mn> ∿ 1500). Assignments: 0.16 ppm is silicon bonded methyls, 2.5-2.6 ppm is nitrogen bonded methyl endgroups.

used by Matzner and Noshay (118) for the synthesis of polysulfone-polydimethylsiloxane copolymers. The general procedure is described below.

Preparation of the Prefectly Alternating Block Copolymers

Materials needed consist of equimolar amounts of the dimethylamino terminated polydimethylsiloxane, **28**, and the phenolic terminated polycarbonate oligomers, together with enough chlorobenzene to make up approximately an 8% solution. The apparatus is pictured in Figure 11.

The apparatus is charged with the preformed polycarbonate oligomer, chlorobenzene and purged with argon. Approximately 10% of the chlorobenzene is distilled off to dehydrate the system, then copolymerization is carried out at reflux temperature. The siloxane is added in portions to insure that the necessary 1:1 stoichiometry between oligomers is reached. After all of the necessary siloxane has been added, refluxing is continued for approximately one hour. There should always be a slight (1-2 mole percent)excess of aromatic hydroxyl groups since the silylamine group per se is very hydrolytically unstable. After appropriate molecular weight is reached, one may cool the mixture, isolate by filtration, and coagulate in methanol. The copolymer should be carefully vacuum dried at ~100°C to constant weight.

Analysis of Perfectly Alternating Block Copolymers

Copolymers were analyzed for intrinsic viscosity in tetrahydrofuran at 25°C. Values given in the tables are reported in dl/g

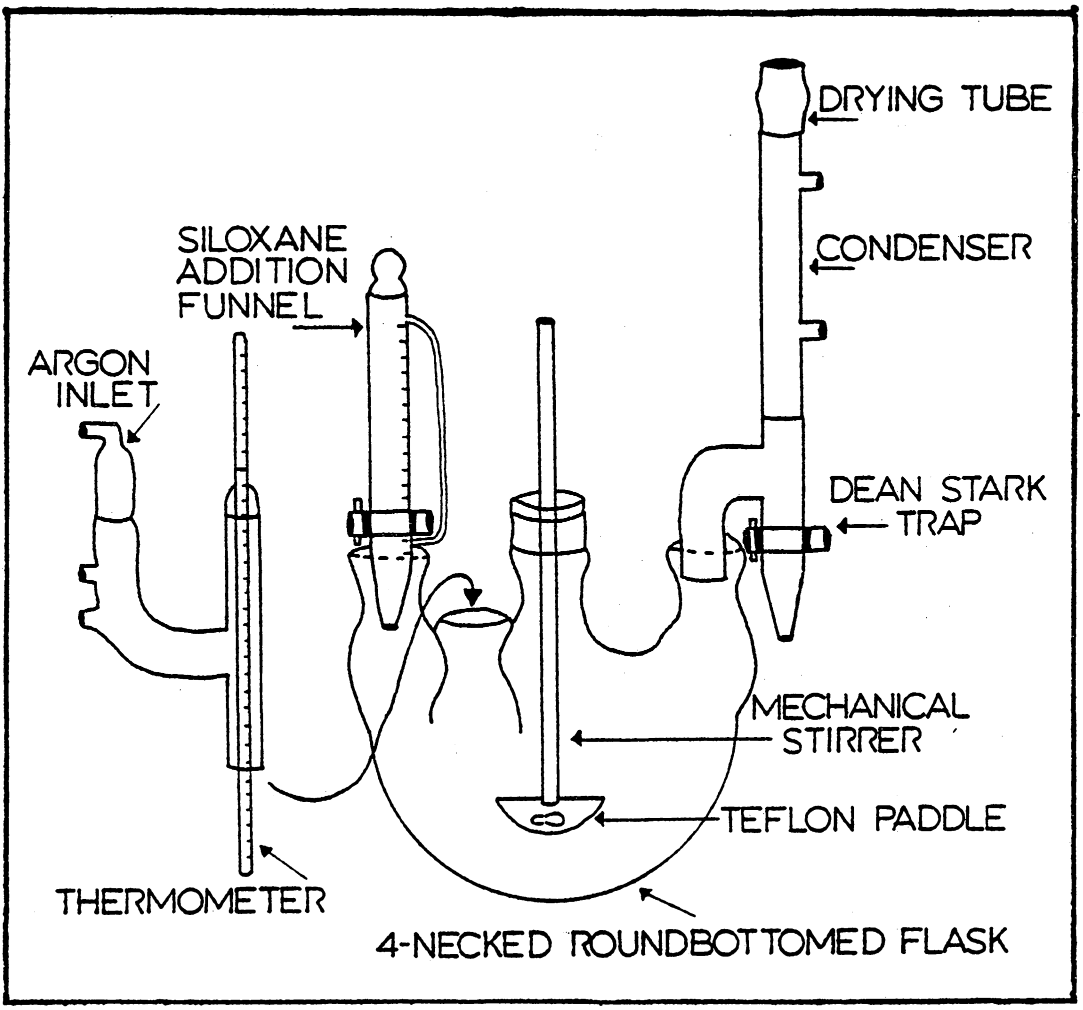


Figure 11: Apparatus for Preparation of Perfectly Alternating Block Copolymers

Copolymer compositional analyses were performed using high resolution proton NMR spectroscopy (Varian EM-390 spectrometer, $CDCl_3$ solvent) via comparison of the areas of the aromatic and silicon methyl peaks (see Fig. 12). The precision of the compositional analysis was estimated to be ± 1.0%.

Melting, crystallization, and glass transitions of selected copolymers and homopolycarbonates were determined by differential scanning calorimetry (Perkin-Elmer DSC-2 instrument). The instrument monitors temperatures in both the reference and sample cells and adjusts the temperature of the sample cell to match that of the reference by means of power changes (231). These power changes recorded on the abscissa of the DSC trace represent energy transferred to or from the sample in mcal./sec.

Subambient conditions were achieved by placing the "cold finger" attached to the bottom of the sample and reference holders in liquid nitrogen. The baseline was checked for flatness at each heating rate and millicalorie range used. Temperature was calibrated with transitions observed in cyclopentane (both 105 K and 206 K), chloroform, carbon tetrachloride, tetrahydrofuran, chlorobenzene, and ethylene glycol. Except in three cases (S-42, S-44, S-46), heating rates used in the experiments were 10K per minute. The remaining three samples were run at a slower rate (5K/min) in order to accurately define the weak glass transitions exhibited. Abscissa ranges used are specified in the tables.

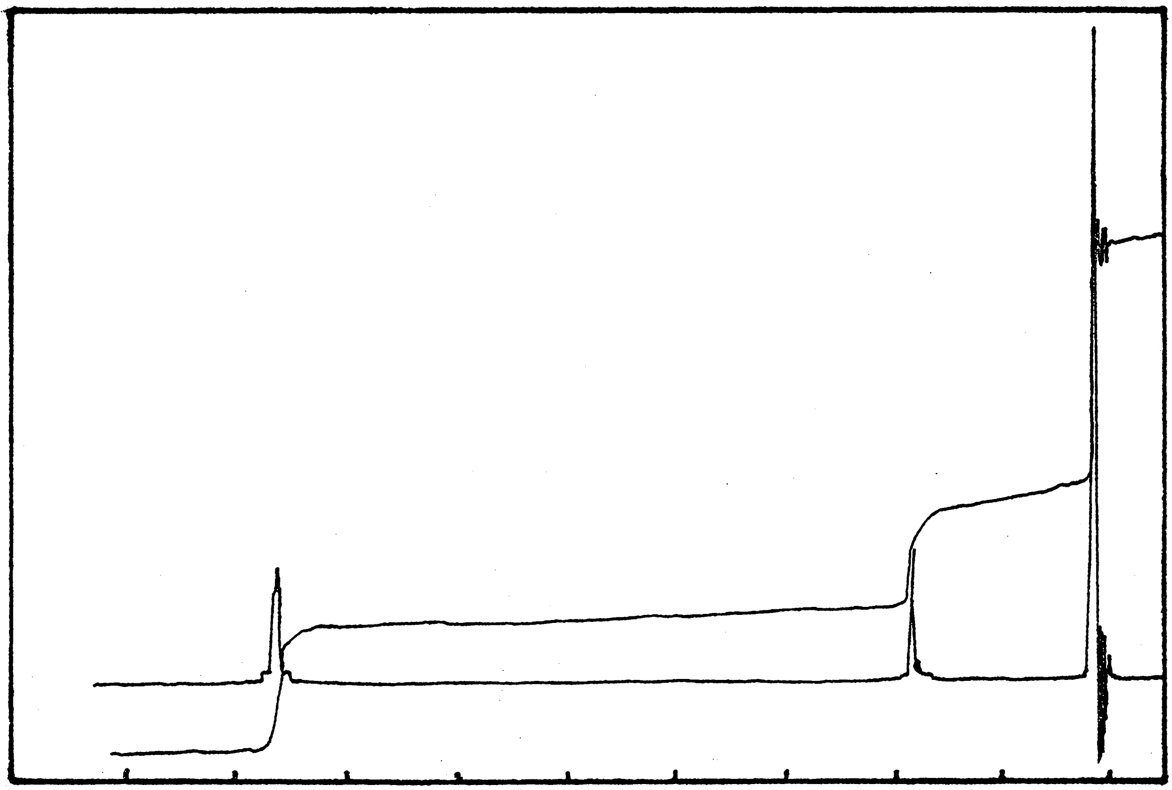


Figure 12: Proton NMR Spectrum of a Perfectly Alternating Polycarbonate-Polydimethylsiloxane Block Copolymer
Assignments: 0.16 ppm is silicon bonded methyls, 1.9 ppm is bisphenol-A methyls, 7.8-7.9 ppm is aromatic protons

Differential scanning calorimetry measurements at ambient temperatures were temperature calibrated using indium and tin melts and benzoic acid. All copolymers and polycarbonates were analyzed using a 10K/min heating rate. Values reported in the tables represent an average of several measurements.

ESCA spectra were collected with a duPont 650 X-ray photoelectron spectrometer in both the analog and MCA modes, with Mg anode operating at approximately 22 m-amps and 10kV. The hydrocarbon peak was set at 285.0 eV as a binding energy reference.

Spectra were taken of selected copolymers (perfectly alternating architecture) and of blends of the copolymers with a commercial polycarbonate homopolymer (Merlon M-50). Both copolymers and blend samples were analyzed with their surfaces normal to the path to the analyzer. In addition, copolymer surfaces were also investigated at a grazing exit angle of $\Theta \simeq 79°$. In the copolymer cases, all normal angle spectra were run a minimum of twice (each time using separately prepared samples). In an effort to assess the reproducibility of the experiment four separate samples of one copolymer (S-42) were analyzed. In addition, one sample of "S-42" was run in the analog mode (at three one-half hour intervals) as a function of time. Three separately prepared samples of "S-68" were analyzed at $\Theta \simeq 79°$. The remainder of the grazing angle experiments were only investigated once and are reported as "preliminary results" in the discussion section of this paper. The polycarbonate reference was analyzed at both the normal and grazing exit angles. Due to difficulties associated with sample preparation, the polydimethylsiloxane reference could only be run at the normal angle.

Peak assignments were based on spectra of polydimethylsiloxane and polycarbonate references together with literature values for related structures as presented in the literature review section of this thesis (215, 190, 23-24).

The ESCA spectra of the copolymers were deconvolved into Gaussian components using a nonlinear least squares fitting program. Parameters output by the program include binding energy, spectral line width, and the area for each component. Background was removed by a linear correction from the observed spectra before deconvolution.

Intensity measurements for the copolymers were derived from the deconvolution program and checked by manually determining the peak areas.

The blends comprised of homopolycarbonate and the copolymers were prepared by dissolution in chloroform, followed by methanol coagulation, filtration, and vacuum drying to a constant weight at 80°C.

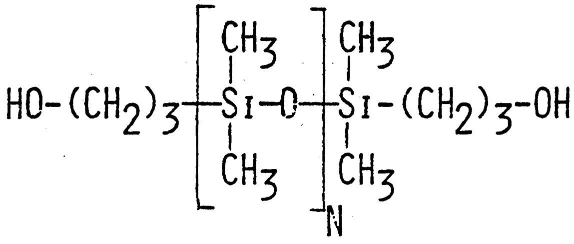
Both compression molded and solution cast films of the blends were studied by ESCA. Compression molding was done at 260°C (two minutes at low pressure, three minutes at high pressure, quench cooled by running water through the press coils). Thin films were cast from chloroform directly onto the probe.

Samples of copolymer films and of the homopolycarbonate reference were also prepared by casting directly onto the ESCA probes but these were derived from ~3% (wt/wt) solutions of the copolymers (and polycarbonate) in methylene chloride.

A solid linear polydimethylsiloxane reference sample was prepared by polymerizing a 10,000 <Mn> methacryloxy terminated polydimethylsiloxane with 1% (wt/wt) of cumyl peroxide overnight at 120°C (then the sample was kept under high vacuum for 48 hours). Interior slices of the rubber were carefully cut and wired onto the ESCA probe using ultrasonically cleaned gold wires.

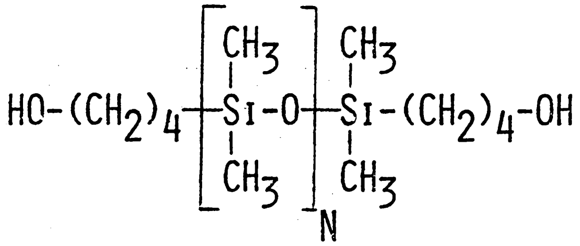
Randomly-Coupled Block Copolymers: Synthesis of Siloxane Oligomers

Hydroxypropyl terminated siloxane oligomers, 29, were obtained from Silar Labs and were presumably prepared via a platinum catalyzed addition of allyl alcohol to a hydride terminated siloxane. Hydrosilylation reactions of this type are used extensively in siloxane chemistry. Several recent reviews of it have been published and the reader is referred to these (232-234). By contrast, hydroxybutyl terminated oligomers, 30, and carboxypropyl terminated oligomers, 31, were prepared in our lab via the redistribution reaction.



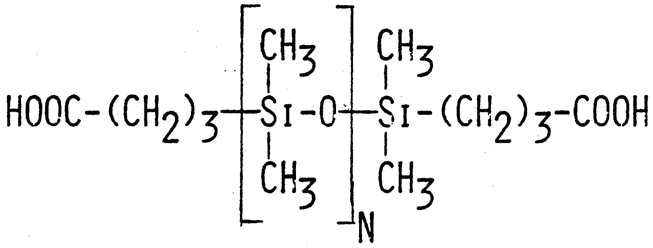
$$HO-(CH_2)_3-\left[\overset{CH_3}{\underset{CH_3}{Si}}-O\right]_N-\overset{CH_3}{\underset{CH_3}{Si}}-(CH_2)_3-OH$$

29



$$HO-(CH_2)_4-\left[\overset{CH_3}{\underset{CH_3}{Si}}-O\right]_N-\overset{CH_3}{\underset{CH_3}{Si}}-(CH_2)_4-OH$$

30



$$HOOC-(CH_2)_3-\left[\overset{CH_3}{\underset{CH_3}{Si}}-O\right]_N-\overset{CH_3}{\underset{CH_3}{Si}}-(CH_2)_3-COOH$$

31

Synthesis and Analysis of Hydroxyl Terminated Polydimethylsiloxane Oligomers

Preparation of Hydroxybutyl Terminated Polydimethylsiloxane Oligomers 30:

1,3-hydroxybutyltetramethyldisiloxane was obtained from Silar Laboratories, Scotia, New York. The octamethylcyclotetrasiloxane, D_4, can be obtained from Union Carbide, Silar Labs, Petrarch Chemicals, Levittown, Pennsylvania, or elsewhere. Trifluoroacetic acid used was reagent grade from Fisher.

The apparatus to be used is the same as described for the synthesis of the dimethylamine terminated siloxanes. The necessary amounts of 1,3-hydroxybutyltetramethyldisiloxane and D_4 are charged to the flask and heated to 60°C. Trifluoroacetic acid (~0.012 moles per 0.024 moles of starting material) is added and the 60°C temperature together with rapid agitation is maintained for 26 hours. After the equilibration, the mixture is washed three times with water to effect removal of the trifluoroacetic acid catalyst. Remaining traces of water can be azeotroped with tetrahydrofuran under vacuum.

Oligomer structure was characterized by high resolution proton NMR spectra in the low molecular weight range. The progress of the redistribution of the hydroxybutyl terminated siloxane was followed by gel permeation chromatography (Waters 6000-A pump, Waters R-400 DRI detector, Waters columns - 500Å, 10^3Å, 10^4Å, 10^5Å, toluene solvent).

Synthesis and Analysis of Carboxyl Terminated Polydimethylsiloxane Oligomers

Preparation of Carboxypropyl Terminated Polydimethylsiloxane Oligomers, **31**:

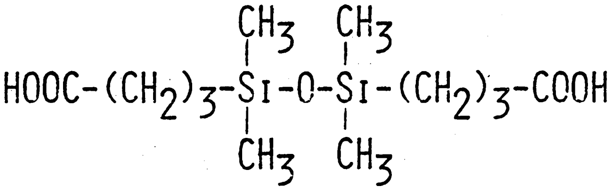
Carboxypropyltetramethyldisiloxane was obtained from Silar Laboratories, Scotia, N. Y. The octamethylcyclotetrasiloxane (D_4) was obtained from either Union Carbide, Silar Labs, or Petrarch (Levittown, PA). Trifluoroacetic acid was used as the redistribution catalyst and was reagent grade from Fisher Chemical.

The reaction apparatus consisted of a three-necked, round-bottomed flask equipped with a mechanical stirrer, argon inlet, condenser with a drying tube and heated with a silicone oil bath. The required proportions of the bis(1,3-carboxypropyl)tetramethyldisiloxane and D_4 were charged to the reaction vessel and heated to 60°C. In the reaction, the cyclic monomers (D_4) are opened and inserted into the 1,3-carboxypropyltetramethyldisiloxane. Therefore, the necessary ratio of D_4 to linear dimer is determined by the final <Mn> desired. Typically, trifluoroacetic acid (∿ 0.013 moles per 0.024 moles starting material) was added at 60°C for 26 hours. Rapid agitation was maintained throughout the reaction. After the equilibration, the reaction mixture was washed three times with water to remove the residual trifluoroacetic acid catalyst. Remaining traces of water were azeotroped with tetrahydrofuran under vacuum.

Oligomer structure was characterized by both high resolution proton NMR (Varian EM-390 spectrometer) and ^{13}C NMR (JEOL-PFT-100 spectrometer) to insure that the endgroup structure present in the dimer was retained in the final oligomers. Aldrich gold label (99.9%) $CDCl_3$ was used as the NMR (both ^{1}H and ^{13}C) solvent. As described previously for similar proton NMR spectra of siloxanes, Fisher certified grade (99 mole % pure) methylene chloride was used as the lock signal and reference (5.37 P.P.M. from TMS). ^{13}C NMR spectra were locked on and referenced with the $CDCl_3$ solvent.

Traces of residual cyclics can be assessed by means of liquid chromatography, GLC, or TGA. As with the hydroxybutyl terminated oligomers, **30**, the progress of the redistribution of these acid functional siloxanes was also followed by GPC (Waters 6000-A pump, Waters R-400 D.R.I. detector, micro-styragel columns - 500Å, 10^3Å, 10^4Å, 10^5Å, toluene solvent).

Molecular weights, <Mn>, of these oligomers were assessed via potentiometric titrations in isopropanol with an isopropanolic potassium hydroxide titrant. The apparatus used was the same as described for titration of the dimethylamine terminated siloxane oligomers and pictured in Figure 9. Fisher certified grade isopropanol was used as received. A blank solvent titration was run prior to each oligomer analysis. The potassium hydroxide titrant was standardized against carefully dried potassium hydrogen phthalate (obtained from Fisher) within 24 hours of the analytical titration for acidic groups. Based on titrations of known amounts of 1,3-carboxypropyltetramethyldisiloxane, 32, the error in this endgroup assessment was estimated to be ~± 3.0%.



$$HOOC-(CH_2)_3-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-(CH_2)_3-COOH$$

32

Synthesis of Randomly-Coupled Block Copolymers

Two quite different sets of interfacial reaction conditions were utilized throughout the study described herein. In the initial group of polymerizations, only the use of the hydroxypropyl terminated siloxanes were investigated. A typical reaction scheme used in this *earlier* part of the investigation was as follows: The polysiloxane oligomer (5.0 grams) was dissolved in methylene chloride (~350 ml).

The bisphenol (5.0 g), a stoichiometric amount of sodium hydroxide, and 2.0 g tetraethylammonium chloride (55 mole percent based on moles of bisphenol) were dissolved in distilled water. The organic and aqueous phases were mixed in a Waring blender fitted with a combination pH electrode (glass body, silver/silver chloride reference), a condenser, buret, and a phosgene inlet tube. The pH was constrained to the range of 9-9.5 throughout the reaction by the continuous addition of 20% aqueous sodium hydroxide to the solution. The latter neutralized the hydrochloric acid byproduct of the polycondensation. Phosgene was bubbled through the solution for a period of three hours at a rate of ~40 cc/min. Reactions performed under these conditions are summarized in Table 16, Part A. A somewhat better control of reaction conditions evolved from the early experiments and was utilized for the rest of the polymerizations. New reaction parameters were developed by systematically varying conditions (phosgene flow rates and catalyst concentrations) for the preparation of the bisphenol-A polycarbonate alone (no siloxane present). The apparatus for these reactions is identical to that used for the copolymerization (Figure 13). Typically, 7.5 g of bisphenol-A, a stoichiometric quantity of NaOH (2 moles per mole bisphenol-A), and the appropriate amount of the tetraethylammonium chloride catalyst were dissolved in 75 ml water. An equal volume of dichloromethane was then added. Approximately 18 N aqueous sodium hydroxide was added throughout the 30 minutes of phosgene addition. This allowed the pH to be maintained between 11-12.

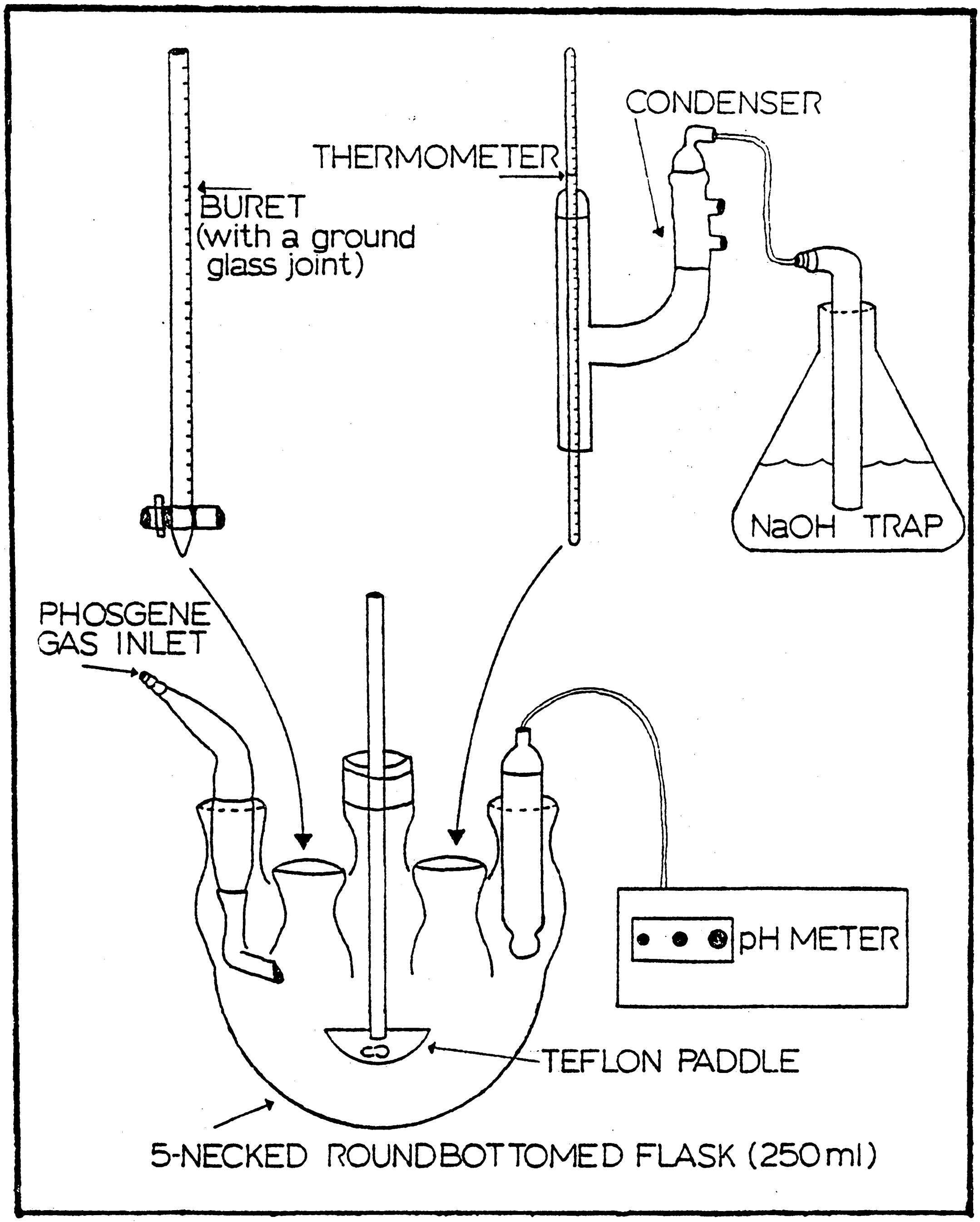


Figure 13: Apparatus for Preparation of the Randomly Coupled Block Copolymers via the Interfacial Method

The use of all three types of siloxane oligomers (hydroxypropyl terminated (29), hydroxybutyl terminated (30), and carboxypropyl-terminated (31)) were used in this latter half of the research. Different results were obtained depending on whether the siloxane was hydroxy or acid functional. Therefore, the suggested copolymer syntheses vary with this same parameter. For this reason, the reactions using the hydroxyl terminated siloxanes will be presented and discussed somewhat separately from the investigations using the siloxanes terminated with acid functional groups.

The suggested method of interfacial copolymerization using the hydroxyl terminated siloxanes based on our results to date is given below.

Copolymer Synthesis Using the Hydroxy Functional Siloxane Oligomers

The apparatus employed is shown in Figure 13. Bisphenol-A (7.5 g) and a stoichiometric amount of potassium hydroxide (2 moles KOH per mole bisphenol-A) were charged to the reaction vessel and dissolved in 75 ml water. Tetraethylammonium chloride catalyst (1.1 g, 20 mole percent based on moles of bisphenol-A) was added to the mixture. The appropriate hydroxyl terminated siloxane oligomer (either hydroxypropyl or hydroxybutyl) (7.5 g) was dissolved in 75 ml CH_2Cl_2 and then added to the aqueous mixture in the flask. The reaction was initiated by bubbling gaseous phosgene through the solution at a rate of 40-60 cc/min. for one hour. Throughout the hour, pH was monitored (using a combination pH electrode, glass body, silver/silver chloride reference) and constrained to a range of 11-12 by continuous addition of 12 N aqueous KOH solution (under these conditions, the reaction will require approximately 2 ml KOH solution every three minutes). Following the phosgene one hour reaction at pH 11-12, phosgene flow is continued at the same rate without any further addition of KOH for 10 more minutes or however long is required to bring the final pH to a value of about 6. Next, the organic phase was washed several times with water, coagulated in isopropanol, isolated by filtration, and vacuum dried at 100°C for 24 hours.

In addition to the methods already described, we also investigated two prereaction steps, aimed at first capping the siloxane hydroxyl. For the purposes of this report, we will call them "pre-step type 1" and "pre-step type 2". The suggested procedure for the type of "pre-step" which yielded the most promising results is outlined below.

Solution Capping of the Hydroxyl-Terminated Siloxane Ogliomer with the Dichloroformate of Bisphenol-A ("Pre-Step Type 1" to the Interfacial Copolymerization Method)

Bisphenol-A dichloroformate was prepared according to the method of Cotter (235).

Both the preformed hydroxypropyl and hydroxybutyl terminated siloxane oligomers are suitable for capping in this manner.

The apparatus consists of a three-necked, round-bottomed flask equipped with a mechanical stirrer, argon inlet, thermometer, and condenser with a drying tube. A typical reaction would be to first dissolve the bisphenol-A bis(chloroformate) (3.0 g, 0.0085 moles) in methylene chloride (~35 ml) and purge with argon. Pyridine (0.40 ml, ~0.005 moles) is then added dropwise (if it is added too rapidly, a yellow compound, probably a chloroformate/pyridine complex, will precipitate). The hydroxyl terminated siloxane oligomer (0.0025 moles) should be added in portions over approximately a 75 minute period. After addition of the total required amount of siloxane, the mixture was stirred at room temperature for an additional two hours. After the reaction, the solution was stirred first with dilute hydrochloric acid and then with water (several times). It is not necessary to isolate the capped oligomer prior to the interfacial procedure.

The overall reaction is shown in equation 50.

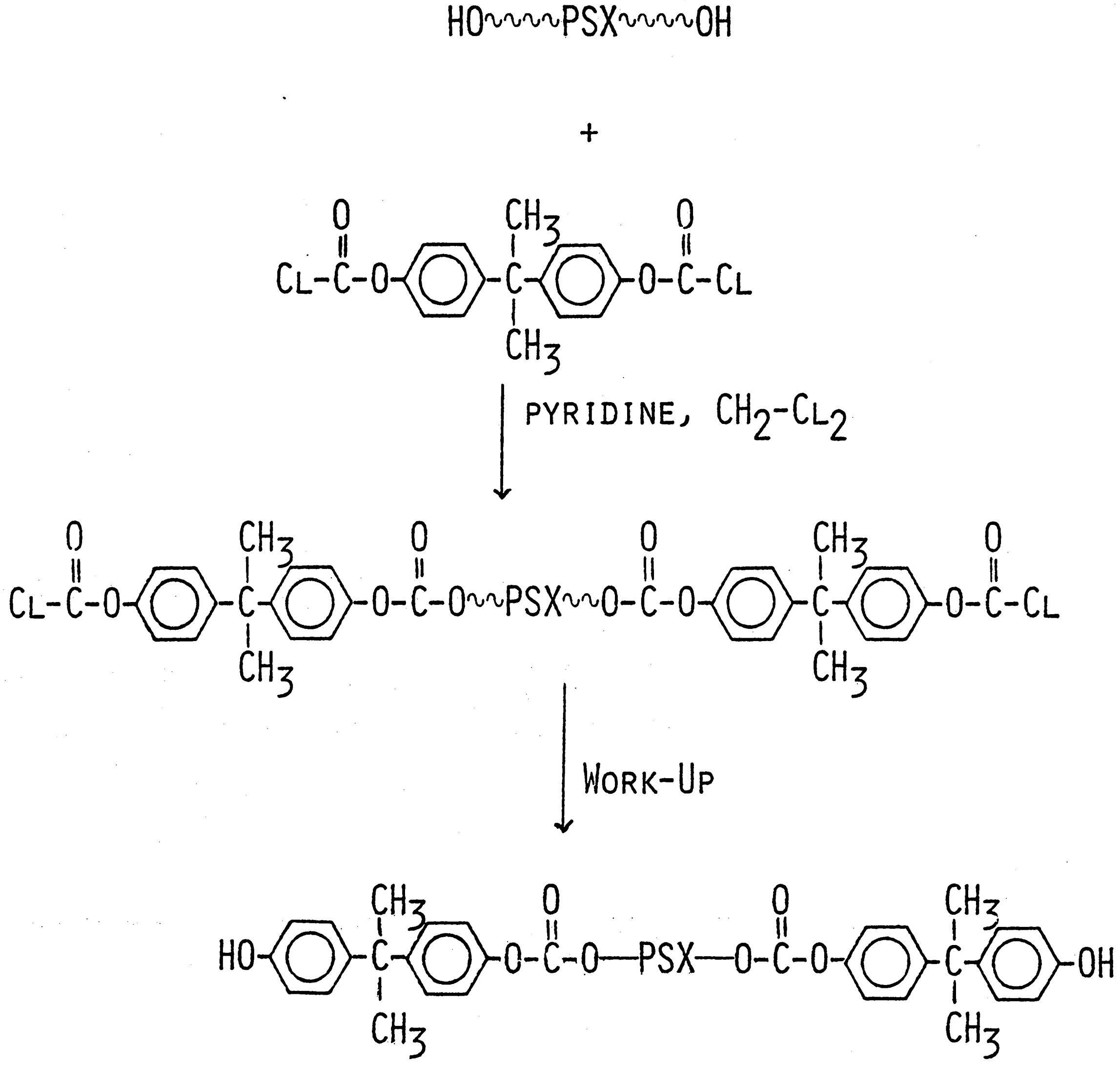
Preparation of Bisphenol-A Bis(chloroformate)

Bisphenol-A was high purity UCAR grade from Union Carbide and was used as received. Reagent grade toluene was dried over magnesium sulfate overnight prior to use. The dimethylaniline catalyst was certified grade obtained from Fisher.

The apparatus consisted of a 4-necked, round-bottomed flask equipped with a thermometer, mechanical stirrer, graduated dry-ice-isopropanol condenser, dropping funnel (for the amine catalyst), gas inlet tube and a water condenser connected to a caustic trap.

Typically, after argon evacuation of the apparatus, a mixture

EQUATION 50



of 2,2-bis(4-hydroxyphenyl) propane (57.0 g, 0.25 moles) and 400 ml toluene were charged and cooled to 0°C. Phosgene (61 g, 0.62 moles, 20% excess) liquified in the dry-ice-isopropanol bath, was added all at once, immediately followed by the dimethylaniline (64.7 g 0.53 moles) and 50 more ml of toluene. The mixture was slowly allowed to warm to room temperature and stirred under argon overnight. The solution was filtered, then stirred with 50 g silica gel for approximately 12 hours. Following subsequent filtration of the silica gel, the toluene was vacuum stripped on a rotavap yielding a light blue crystalline product. This was recrystallized twice from seven times its weight of hexane. 80 g (91%) of white, crystalline bisphenol-A bis(chloroformate) resulted (m.p. 93-95°C).

Copolymer Synthesis Using the Carboxy Functional Siloxane Ogliomers

Randomly placed block copolymerization was studied using principally a 2000 <Mn> carboxypropyl terminated polydimethylsiloxane oligomer. Results demonstrate that an anhydrous "pre-phosgenation" step (pre-step type 2) to the interfacial reaction is desirable. A typical 2-stage copolymer formulation using optimized experimental parameters is detailed below:

Preparation of Randomly Coupled Polycarbonate/Polydimethylsiloxane Block Copolymers

The preformed polydimethylsiloxane oligomer was prepared and characterized according to the methods previously described. High purity "UCAR grade" bisphenol-A obtained from Union Carbide was used as received. Tetraethylammonium chloride catalyst used was reagent grade from Fisher Chemical.

Step 1: "Pre-Phosgenation"

The apparatus, consisting of a two-necked, round-bottomed flask equipped with an argon inlet, Dean Stark trap, condenser with a drying tube, and a magnetic stirring bar, was heated with a silicone oil bath.

The carboxypropyl terminated polydimethylsiloxane oligomer (7.5 grams) and $\sim$ 40 ml dichloromethane were charged to the reaction vessel. The system was dehydrated via distillation of $\sim$ 20 ml of the dichloromethane, then was cooled to room temperature. Gaseous phosgene was then introduced into the anhydrous solution at a rate of 30 cc/min. for a fifteen minute period.

Step 2: Interfacial Copolymerization

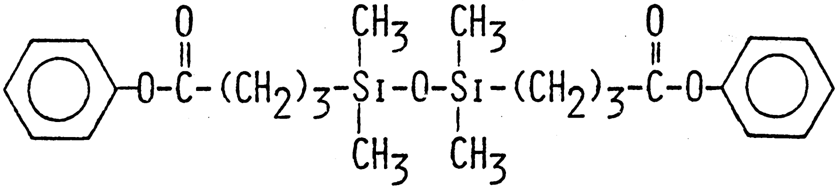
Bisphenol-A (7.5g) and a stoichiometric amount of potassium hydroxide (2 moles KOH per mole bisphenol-A) were charged to the reaction vessel (Figure 13) and dissolved in 75 ml water. Tetraethylammonium chloride catalyst (1.1g, 20 mole percent based on moles of bisphenol-A) was added to the mixture. The siloxane/dichloromethane solution from the "pre-phosgenation" step, followed by 55 ml additional dichloromethane were added. Phosgene was again introduced to the mixture at a rate of 40-58 cc/min. for one hour. Throughout the hour of phosgene addition, pH was monitored using a combination pH electrode (glass body, silver/silver chloride reference) and constrained to a range of 11-12 by the continuous additon of 12 N aqueous potassium hydroxide solution. For the concentrations employed, the reaction required approximately 2 ml KOH solution every 3 minutes. Following the hour of phosgene addition with the pH maintained between 11-12, phosgene flow was continued at the same rate without any further addition of KOH for an additional ten minutes. This generally desirably produced a neutral or slightly acidic pH. The organic phase was washed several times with water, coagulated in isopropanol, isolated by filtration and vacuum dried.

Analysis of Randomly Coupled Block Copolymers

All interfacially produced block copolymers and polycarbonate homopolymers were analyzed for intrinsic viscosity in tetrahydrofuran at 25°C. Values given in the tables are reported in deciliters per gram.

Copolymer compositions were assessed by means of proton NMR (see Figure 12) using the identical method previously described for compositional analysis of the perfectly alternating block copolymers.

Copolymer fine structure of the copolymers prepared with the acid terminated siloxane was also elucidated by comparison of both ^{13}C NMR (JEOL-FX60Q instrument) and IR (Perkin-Elmer model 283 instrument) spectra of the copolymers with that of model compounds and homopolymers. Aldrich gold label (99.9%) $CDCl_3$ was used as the NMR solvent, lock signal, and chemical shift reference. IR spectra were collected of the carbonyl region (1700-1800 wavenumbers) using the standard high resolution settings for the instrument and a 300 min. scan setting. Samples for the IR spectra of the copolymers were thin films produced by solution casting from dilute chloroform solutions. The diphenyl ester of 1,3-carboxypropyltetramethyldisiloxane 33 was prepared as a model compound in a manner closely paralleling that of Mulvaney and Marvel (236). The IR spectra of this compound and its



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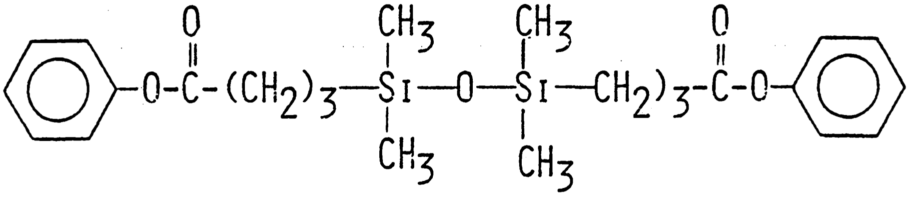
synthetic intermediates were collected of the neat liquids.

The preparation of this model ester is described below.

Preparation of



Thionyl chloride (Fisher reagent grade) and phenol (Fisher reagent ACS grade - 0.5% maximum water) were used as received.

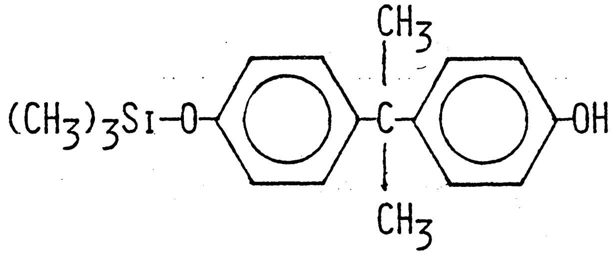
The apparatus consisted of a two-necked, round-bottom flask equipped with an argon inlet, condenser with a drying tube, magnetic stirring bar and a silicone oil heating bath. The 1,3- carboxypropyltetramethyldisiloxane (11 grams) and thionyl chloride (50 ml) were charged to the reaction vessel and refluxed for 2.5 hours to produce 1,3-propionyltetramethyldisiloxane. The excess thionyl chloride was stripped off under vacuum, and then a 20 mole percent excess of phenol was added. The mixture was heated at 85°C for three hours to produce the diphenyl ester. Following the reaction, the product mixture was dissolved in 60 ml of diethyl ether, washed with water, then with 100 ml 10% aqueous NaOH, and finally with water (two more times). Traces of water were removed via a tetrahydrofuran/water azeotrope under vacuum. Vacuum distillation of the product produced a small forecut, followed by a major fraction of the diester (B.P. 175°C, 0.2 mm).

Chapter V

RESULTS AND DISCUSSION

Perfectly Alternating Copolymers: Synthesis of Reactive Polycarbonates of Controlled Molecular Weights

The total reaction for formation of the reactive polycarbonates of controlled molecular weights can be envisioned as occurring in three steps (formulated in equations 52, 53, and 54, respectively using trimethylchlorisilane (TMCS) as blocking reagent): 1, Capping of the desired number of phenolic endgroups, 2, formation of the polymer, and 3, hydrolysis of the protecting groups. A basic assumption for calculating the theoretical degree of polymerization is of course that only one hydroxyl group on any bisphenol-A molecule is protected. The success of the method can be explained using step polymerization theory (132) where phosgene and bisphenol-A are considered to be in perfect stoichiometry and 34, for example, is considered the monofunctional



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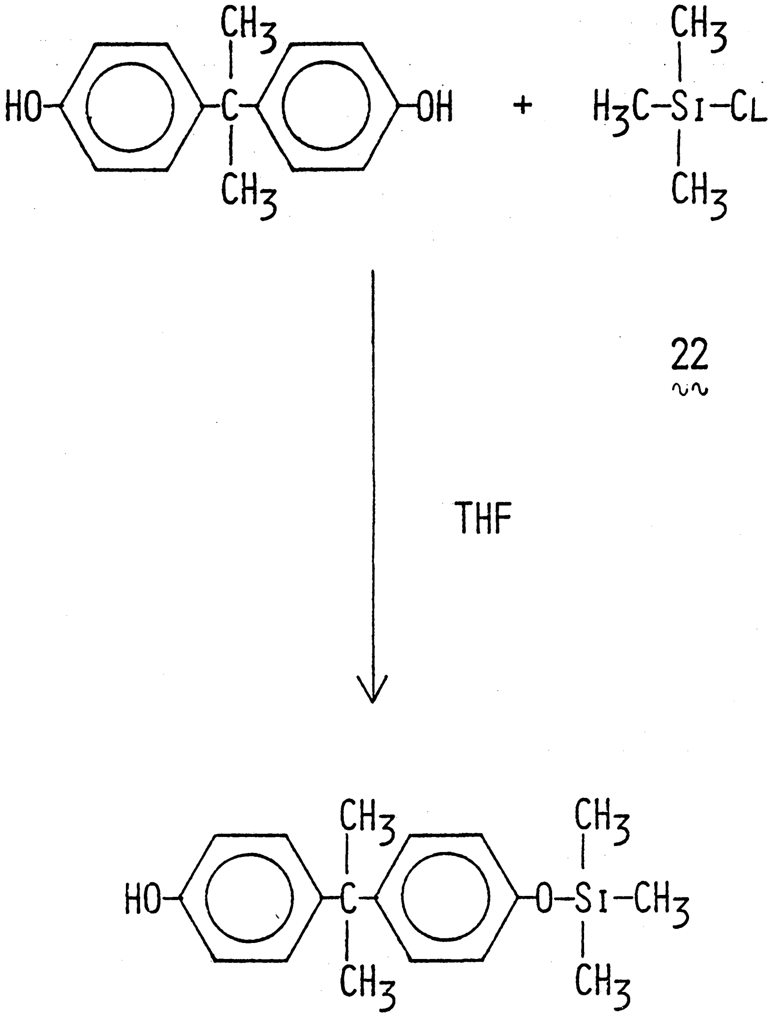
molecular weight regulator. For this case, r, the parameter describing stoichiometric imbalance can be written as in equation 55.

Equation 52



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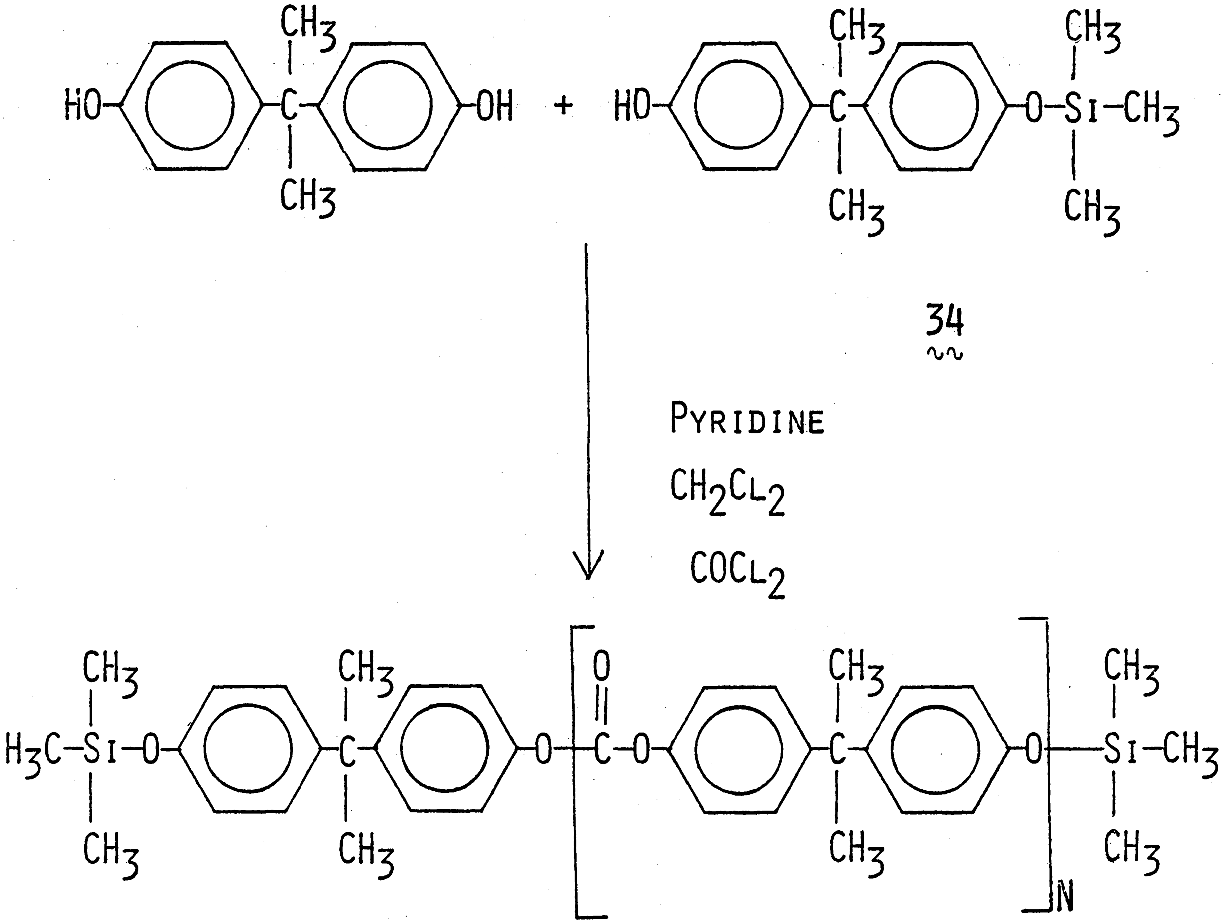
Equation 53



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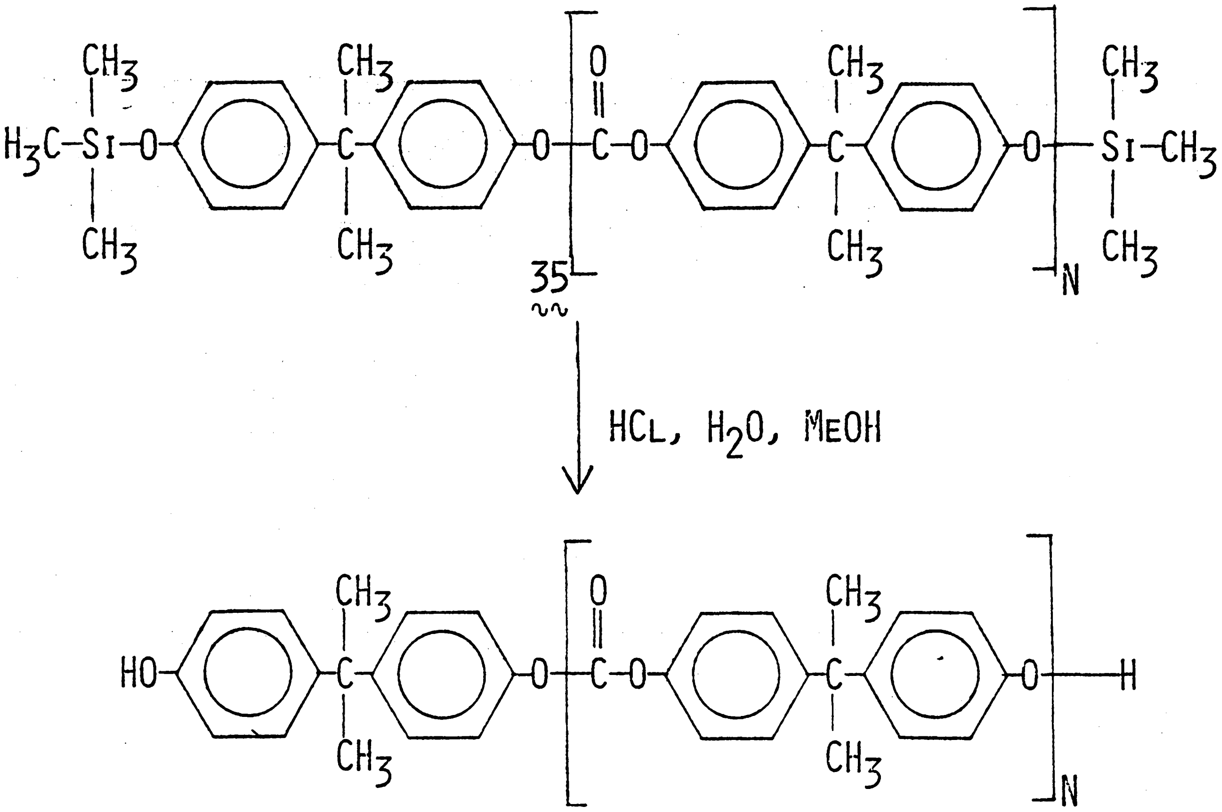
Equation 54



Equation 55: $r = \dfrac{N_A}{N_{B''} + 2N_{B'}}$

$N_{B'}$ = Number of moles trimethylsilyl capped bisphenol-A, 34, (note that this equals the number of moles endcapping reagent).

N_B = Number of phenolic endgroups before reaction of the endblocking reagent.

$N_{B''}$ = Number of phenolic endgroups on <u>uncapped</u> bisphenol-A after reaction of the endblocking reagent.

N_A = Number of moles chlorine on the theoretical amount of phosgene needed.

Equation 56: $\langle X_n \rangle = \dfrac{1 + r}{1 + r - 2rp}$

As $p \rightarrow 1$, i.e. "complete" phosgenation, equation 56 reduces to equation 57.

Equation 57: $\langle X_n \rangle = \dfrac{1 + r}{1 - r}$

Note, however, that in this case "r" is not the desired parameter. In order to react nearly all the phenolic groups present, phosgene is in fact introduced to the reaction in amounts far exceeding that theoretically called for (3 x the calculated amount). The above equation can be reduced to a more useful and simpler expression. It should be recognized that in equation 55 describing r, $N_A = N_{B''} = (N_B - 2N_{B'})$. Substituting these equalities into the expression for r, we obtain (equation 58):

$$\text{Equation 58:} \quad r = \frac{N_B - 2N_{B'}}{N_B}$$

Degree of polymerization, defined as the number of full repeat units per chain (i.e. not counting the final bisphenol-A unit which terminates the chain), then is

$$\text{Equation 59:} \quad \overline{X}_n = \frac{1 + r}{1 - r} = \frac{1 + \dfrac{N_B - 2N_{B'}}{N_B}}{1 - \dfrac{N_B - 2N_{B'}}{N_B}} = \frac{N_B}{N_{B'}} - 1.$$

If the final bisphenol-A unit in the polymer is also counted as a whole repeat unit, then

$$\text{Equation 60:} \quad \overline{X}_n = \frac{N_B}{N_{B'}} = \frac{\text{moles Bisphenol-A x 2}}{\text{moles monofunctional capping reagent}} = \frac{2}{x}$$

$$\text{where } x = \frac{\text{moles monofunctional capping reagent}}{\text{moles bisphenol-A}}$$

This final form of the calculation can be easily adapted to accommodate difunctional capping reagents, i.e.

$$\text{Equation 61:} \quad \overline{X}_n = \frac{\frac{2}{2}}{x} = \frac{1}{x}$$

In the case of using TMCS as the blocking reagent, three separate steps probably occur consecutively as formulated in equations 52-54. This is postulated even though the total reaction is performed in one pot and no intermediates need be isolated.

Number average molecular weights of the final hydroxy functional oligomers prepared using TMCS are in close agreement with the theoretical values in all cases (see Table 11). Quantitative efficiency of the hydrolysis procedure used is demonstrated by a comparison of endgroup analyses performed with proton NMR and ultraviolet spectroscopy (141). A ratio of proton NMR peak integrals $\left(\frac{\text{integral of silicon methyl peak}}{\text{integral of aromatic peaks}}\right)$ of a trimethylsilyl ether terminated oligomer which was coagulated in isopropanol prior to hydroylsis of the endgroups yielded an <Mn> of 2430 g/mole (see Figure 14). It is expected that the work-up procedure used for preparation of the trimethylsilyl ether terminated polymer sample would have extracted any excess TMCS or its by-products. Therefore, all silicon methyl groups in the NMR spectrum should have been in the form of polycarbonate endgoups. Following subsequent acid catalyzed hydrolysis of the endgroups, the silicon methyl peak was observed to disappear from the NMR spectrum and UV analysis of the hydroxyl groups yielded a quite similar <Mn> figure of 2328 g/mole (see Figure 15).

Both trifluoroacetyl capping reagents provide a much simpler experimental procedure than that using trimethylsilyl chloride. Neither a capping step prior to polymerization nor a "post-hydrolysis step" is necessary using these reagents. ^{19}F NMR analysis of the reaction mixture before and after phosgene addition indicates that, under the re-

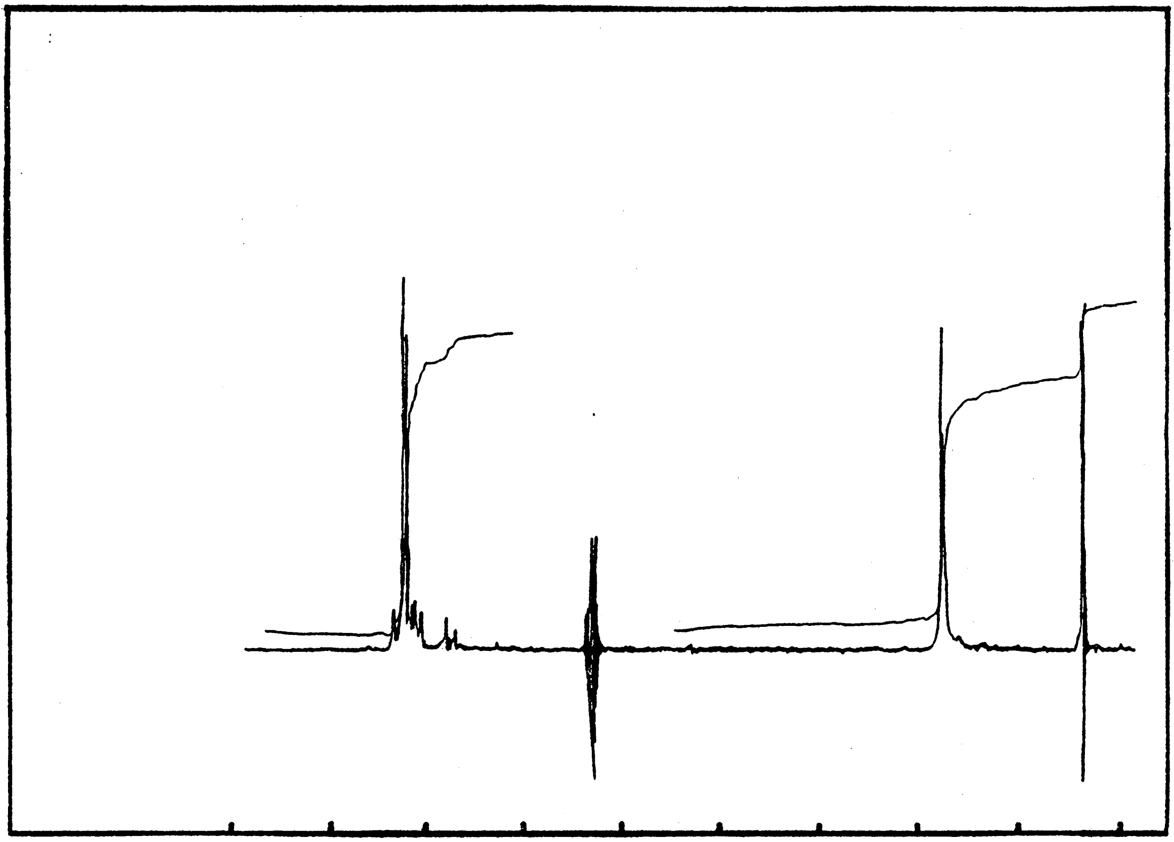


Figure 14: Proton NMR Spectrum of a Trimethylsilyl Ether Capped Bisphenol-A Polycarbonate Yielding <Mn> ∿ 2430 g/mole
Assignments: 0.16 ppm is silicon bonded methyls, 1.9 ppm is bisphenol-A methyls, 7.8-7.9 ppm is aromatic protons

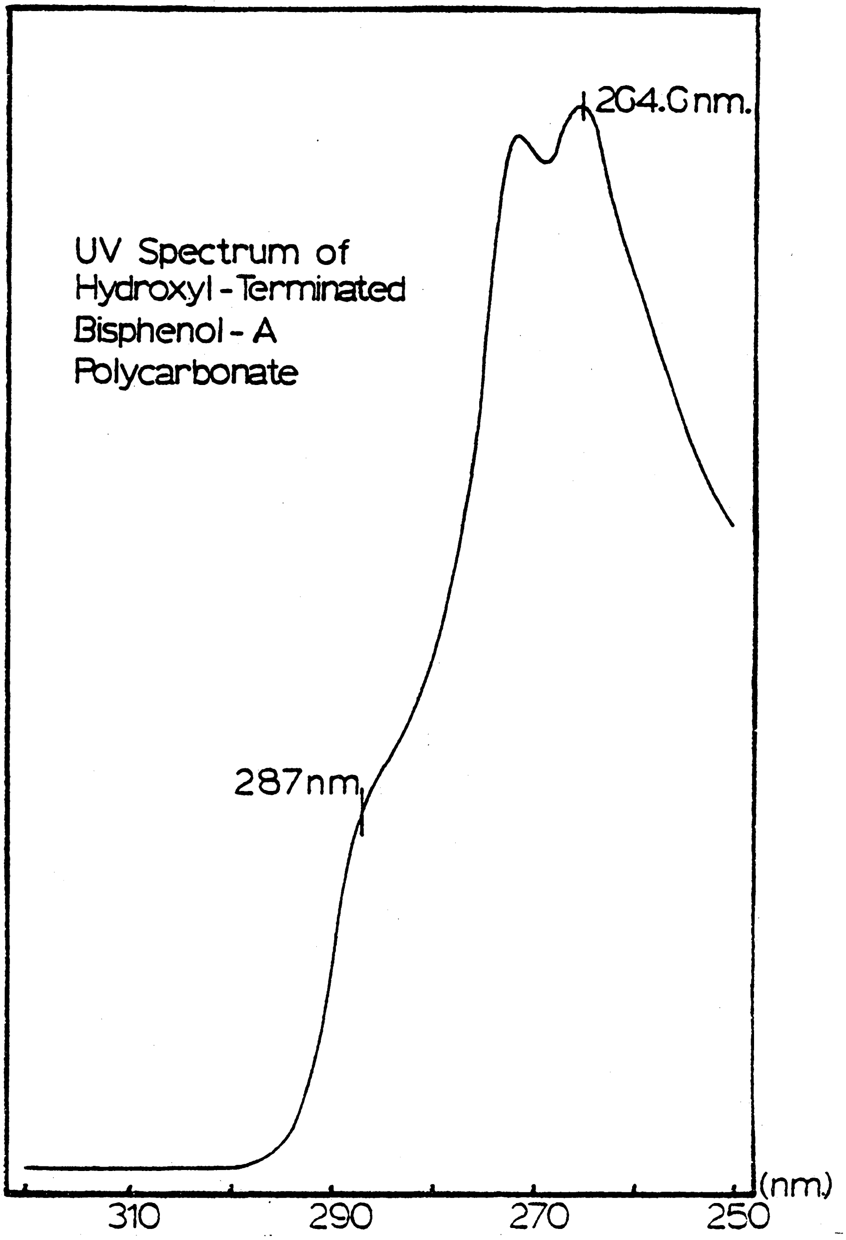


Figure 15: UV Spectrum of Hydroxyl Terminated Bisphenol-A Polycarbonate
Assignments: 287 nm is shoulder due to hydroxyl endgroups, 264.6 nm
is due to polymer backbone

action conditions, trifluoroacetyl esterification takes place during polymerization (i.e. only in the presence of phosgene and not in a "pre-capping step"). Therefore, a step analogous to that depicted in equation 52 is not required. Trifluoroacetyl "caps" are easily removed in the normal work-up procedure for the polymer, which includes the addition of water followed by coagulation in methanol. Hence, almost no additional procedures beyond those necessary for ordinary polycarbonate synthesis are necessary in order to produce accurate molecular weight control.

In order to show that esterification was indeed taking place <u>during</u> polymerization, ^{19}F NMR spectra were run on the reaction mixtures before, during, and after phosgene addition. In agreement with Dorn et al. (237) (spectra in the article cited were run in deuterochloroform), the trifluoroacetyl ester of bisphenol-A in dichloromethane appears at -7.42 P.P.M. from 1,2-difluorotetrachloroethane. It resonates at slightly higher field in tetrahydrofuran (-7.64 — -7.67 P.P.M) (see Figures 16 and 17). The direction and approximate magnitude of the solvent shift in tetrahydrofuran is also in agreement with literature values (238). ^{19}F NMR spectra of reaction mixtures using each of the two fluorine containing blocking reagents were run immediately after addition of the reagents. In both cases, only one fluorine peak appeared which resonates at -7.93 — -7.94 P.P.M. (presumably due to some type of pyridine complex with the blocking reagents). A spectrum of the sample taken from the trifluoroacetic anhydride reaction was checked again after a two day period and no changes were observed. Hence, it was evident that the desired ester was not forming at this stage in the

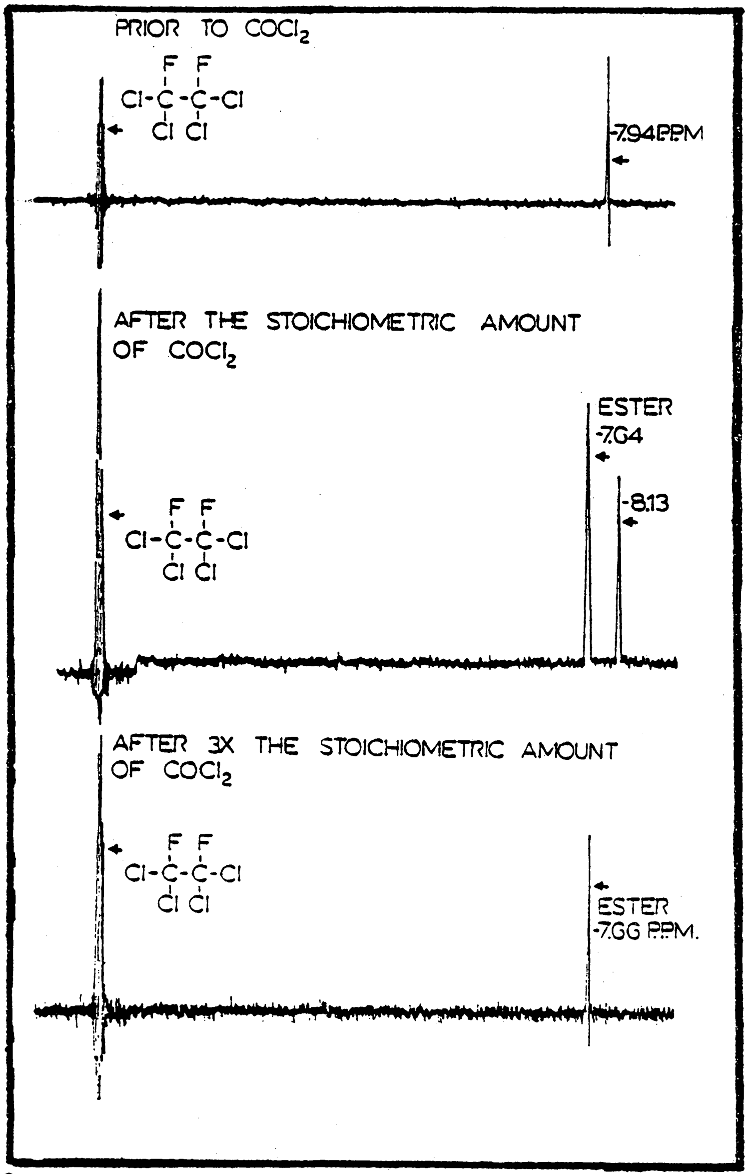


Figure 16: ^{19}F NMR Spectra Showing the Progression of the Polycarbonate Synthesis using Trifluoroacetic Anhydride Capping to Control <Mn>

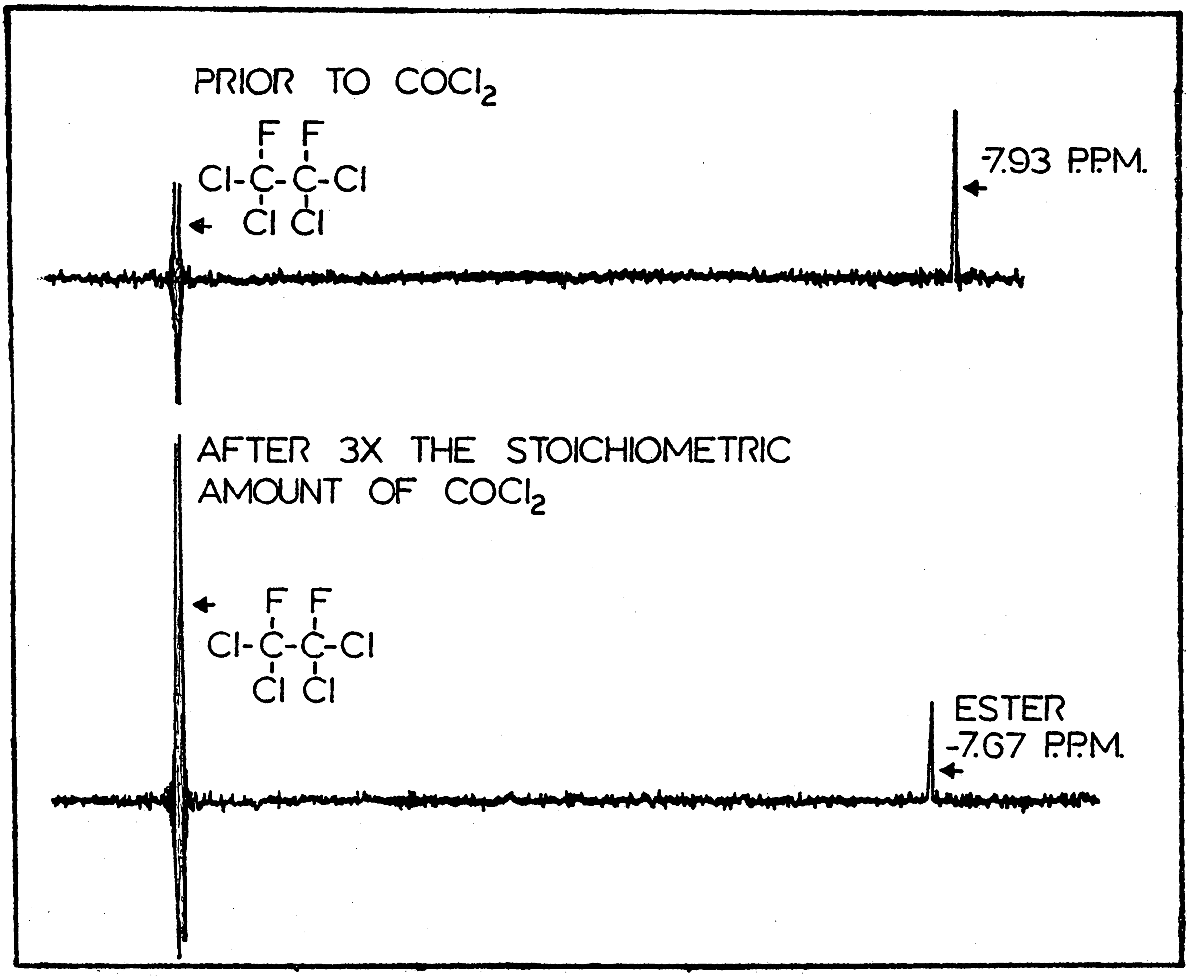


Figure 17: ^{19}F NMR Spectra Showing the Progression of the Polycarbonate Synthesis using Trifluoroacetic Acid Capping to Control <Mn>

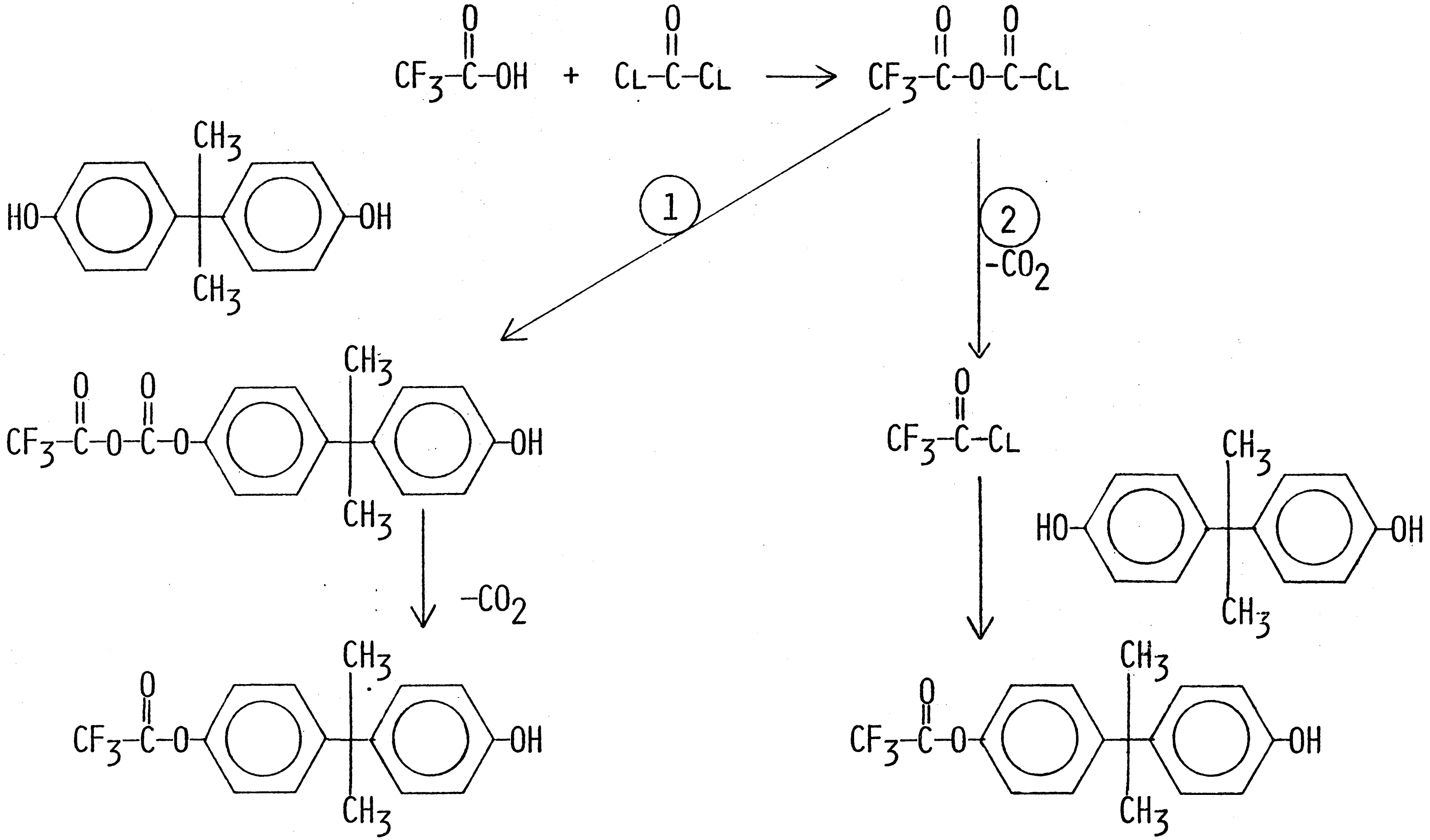
reaction. A second ^{19}F NMR spectrum of the reaction mixture using trifluoroacetic acid was run after the stoichiometric amount of phosgene had been introduced (see Figure 16). Both ester and a new fluorine-containing complex or reagent (resonating at -8.13 P.P.M.) were present whereas the original peak at -7.93 — -7.94 P.P.M. had disappeared. Finally, after three times the stoichiometric amount of phosgene had been bubbled through the reactions, the spectra showed only one peak, the ester, to be present in both cases (using either trifluoroacetic anhydride or trifluoroacetic acid as blocking agents) (see Figures 16 and 17).

Hydrolysis of these protecting groups in the work-up procedure was demonstrated by the disappearance of the ^{19}F NMR peak coupled with the growth of the shoulder due to the phenolic endgroups at 287 nm in the UV spectrum (141).

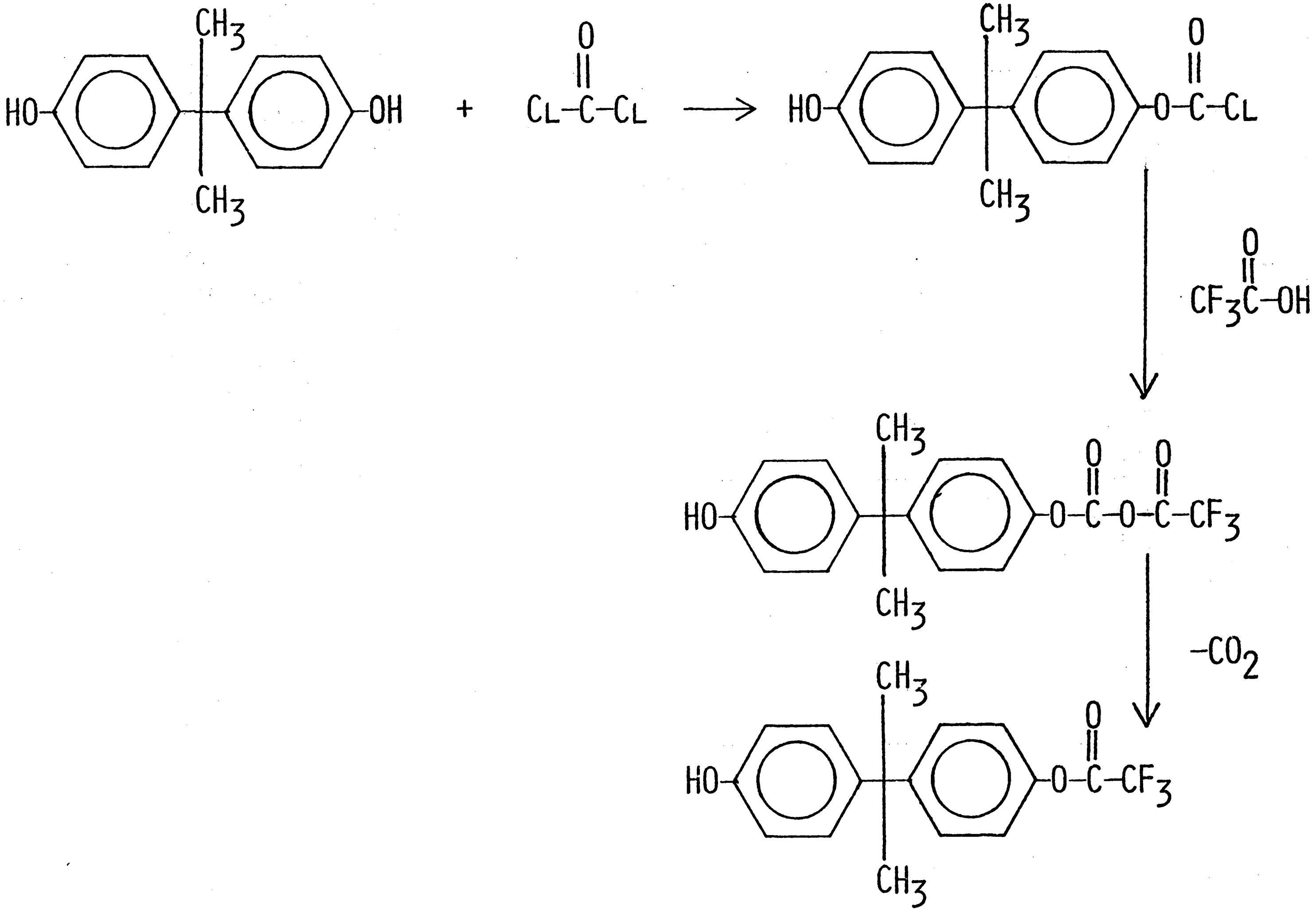
Although the mechanism of trifluoroacetylation is not understood, two plausible routes (schematically given in equations 62 and 63) using trifluoroacetic acid as the blocking reagent can be envisioned. Note that these equations are separated on the basis of the first step (i.e. whether it is the acid or the bisphenol which first reacts with phosgene). Similar routes to the ester utilizing trifluoroacetic anhydride are shown in equations 64 and 65.

For the case of the reaction of an acid with a phenol, recall that previous investigators have rejected (227) or accepted (228) the mechanism proceeding through the acid chloride intermediate (equation 62, route 2) mainly on the basis of whether or not carboxylic anhydrides appeared in the infrared spectra of their products. The assumption

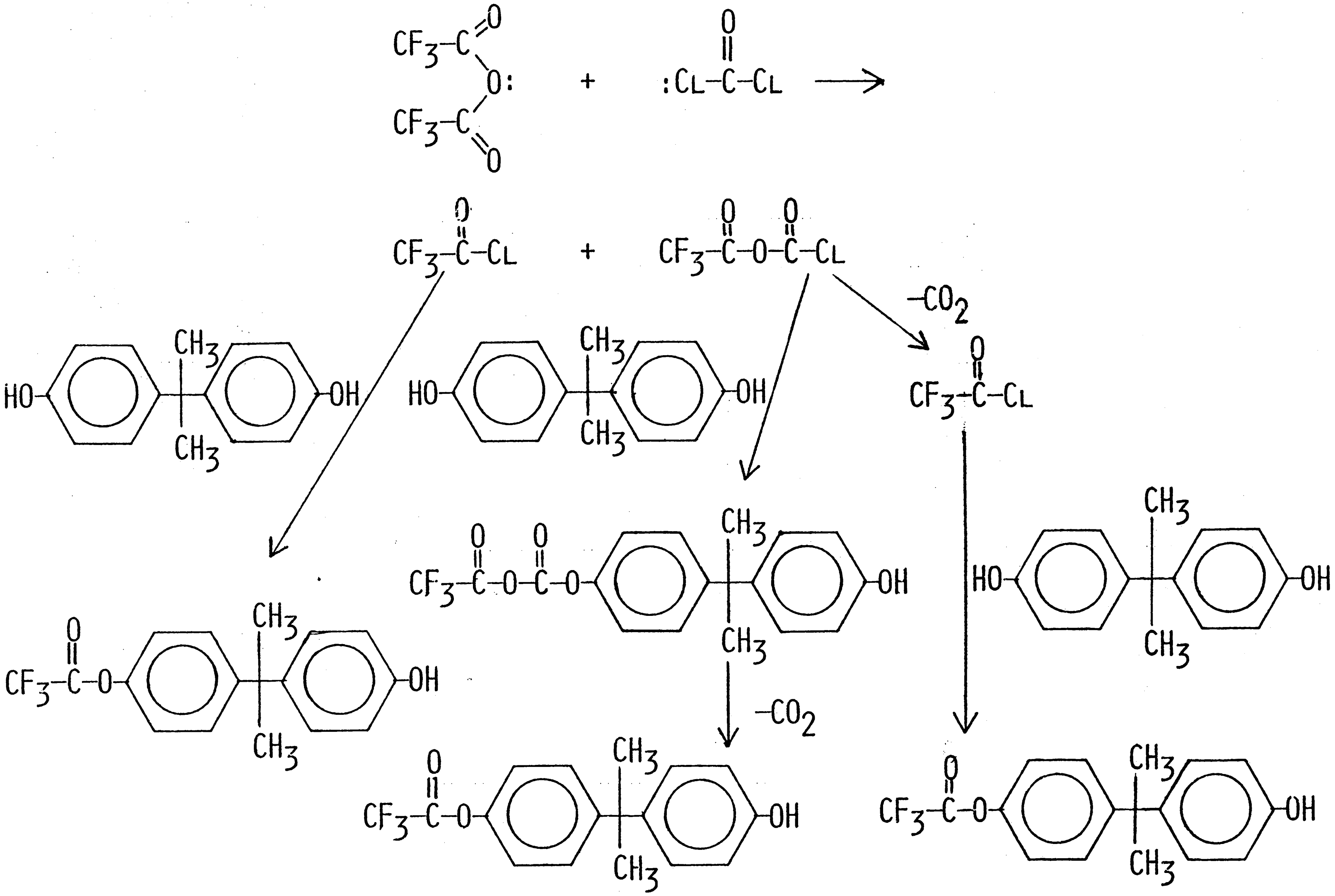
Equation 62



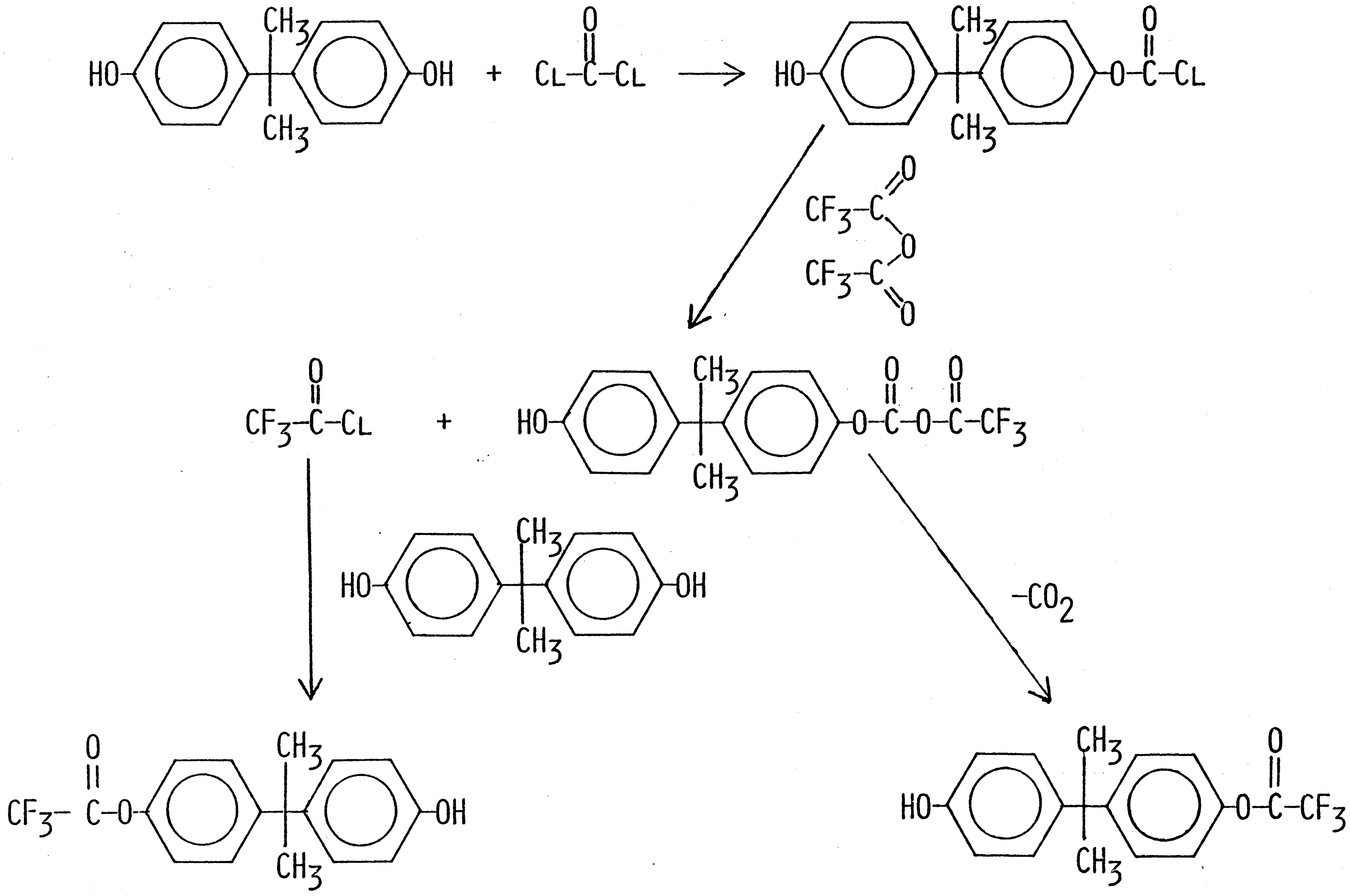
Equation 63


HO
OH
CH_3
CH_3
+
$Cl-\overset{O}{\overset{\|}{C}}-Cl$
$-O-\overset{O}{\overset{\|}{C}}-Cl$
$CF_3\overset{O}{\overset{\|}{C}}-OH$
$-O-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CF_3$
$-CO_2$
$-O-\overset{O}{\overset{\|}{C}}-CF_3$

Equation 64



Equation 65



made was that if acid chloride intermediates had been present, then carboxylic anhydrides should exist in the product. This reasoning, however, cannot be applied to the work described herein since it has been shown that even if trifluoroacetic anhydride was being formed, it would not survive the reaction.

Table 11 shows a comparison of theoretical and experimental number average molecular weights obtained using the three different blocking reagents and various solvent combinations. Calculated values are in reasonable agreement with experimentally obtained values in all cases. No advantage was observed in using either tetrahydrofuran or dichloromethane with any of the blocking groups. It was established, however, that a step prior to polymerization was not useful when using either fluorine containing reagent. For this reason, coupled with the fact that trifluoroacetyl groups are hydrolyzed in the normal polycarbonate work-up procedure, the method using the fluorinated reagents is easier and less time consuming than the procedure using TMCS. In the future, it would be of interest to evaluate the use of the methods described herein for the production of polycarbonates of differing structures.

Perfectly Alternating Copolymer Synthesis and Structural Characterization

Table 12 summarizes the information available on the solution synthesized perfectly alternating block copolymers prepared by the silylamine hydroxyl reaction. It is a very clean, efficient copolymerization reaction. With careful recovery procedures the yields are essentially quantitative. Most of the losses are mechanical in nature. Intrinsic viscosity values of 1.0 dl/g or higher are easily reached. A wide

TABLE 12

Perfectly Alternating Solution Synthesized Block Copolymers

Sample	Recovered Yield, %	25°C [η] CH_2Cl_2	Block $\overline{M}_n$		PSX Wt. % (Calculated)
			$\overline{M}_n$(PSX)	$\overline{M}_n$(PC)	
S-40	98%	1.51	1,800	12,800	12.3
S-42	92%	0.65	1,800	2,700	40.0
S-44	95%	1.6	1,800	6,300	22.2
S-46	98%	1.5	1,800	14,000	11.4
S-48	90%	1.1	5,000	6,300	44.2
S-50	96%	1.85	5,000	14,000	26.3
S-52	80%	0.48	5,000	2,660	65.3
S-54	94%	0.91	15,000	19,000	44.1
S-56	91%	0.91	15,000	16,000	48.4
S-58	94%	1.12	15,000	11,500	56.6
S-60	89%	1.12	15,000	3,400	82.5*
S-62	91%	0.80	10,000	19,000	34.5
S-64	93%		10,000	16,000	38.5
S-66	91%		10,000	11,500	46.5
S-68	86%		10,000	3,400	74.6
S-70	96%		5,000	19,000	20.8
S-72	97%		5,000	16,000	23.8
S-74	90%		5,000	11,50	30.3
S-76	87%		5,000	3,400	59.5

* 79.4% found by NMR

range of block sizes can be utilized. Cast or compression molded films are clear and tough and range from being very elastomeric to quite rigid depending on the copolymer composition. Theoretical siloxane contents are slightly lower than those obtained by means of the NMR compositional analysis. This is attributed to the exclusion of small amounts of cyclics which existed in the dimethylamino terminated siloxane oligomer.

The use of proton NMR to identify compositions in siloxane oligomers and in silicone-polycarbonate copolymers is illustrated in Figure 12. Clearly distinguished are the silicon bonded methyl groups and the aliphatic and aromatic portions of the polycarbonate segments. The silylamine-hydroxyl coupling reaction clearly results in a fairly symmetrical unimodel molecular weight distribution as shown in Figure 18.

Perfectly Alternating Copolymers: Thermal Analysis

Thermal transitions for a selected group of copolymers and polycarbonate homopolymers determined by differential scanning calorimetry are listed in Table 13. Microphase separation, as evidenced by the occurrence of two glass transitions, has occurred in all cases. As previously mentioned, this is attributed (12-18) to the rather extreme immiscibility of the two homopolymer structures involved and, hence, was not unexpected. It is well known that homopolymer glass transitions are dependent on molecular weight below a critical value (165,230,239). The expected trend in glass transitions of the polycarbonate phase as the PC block was lengthened is definitely observed. However, these transitions in the copolymers appear at consistently lower temperatures

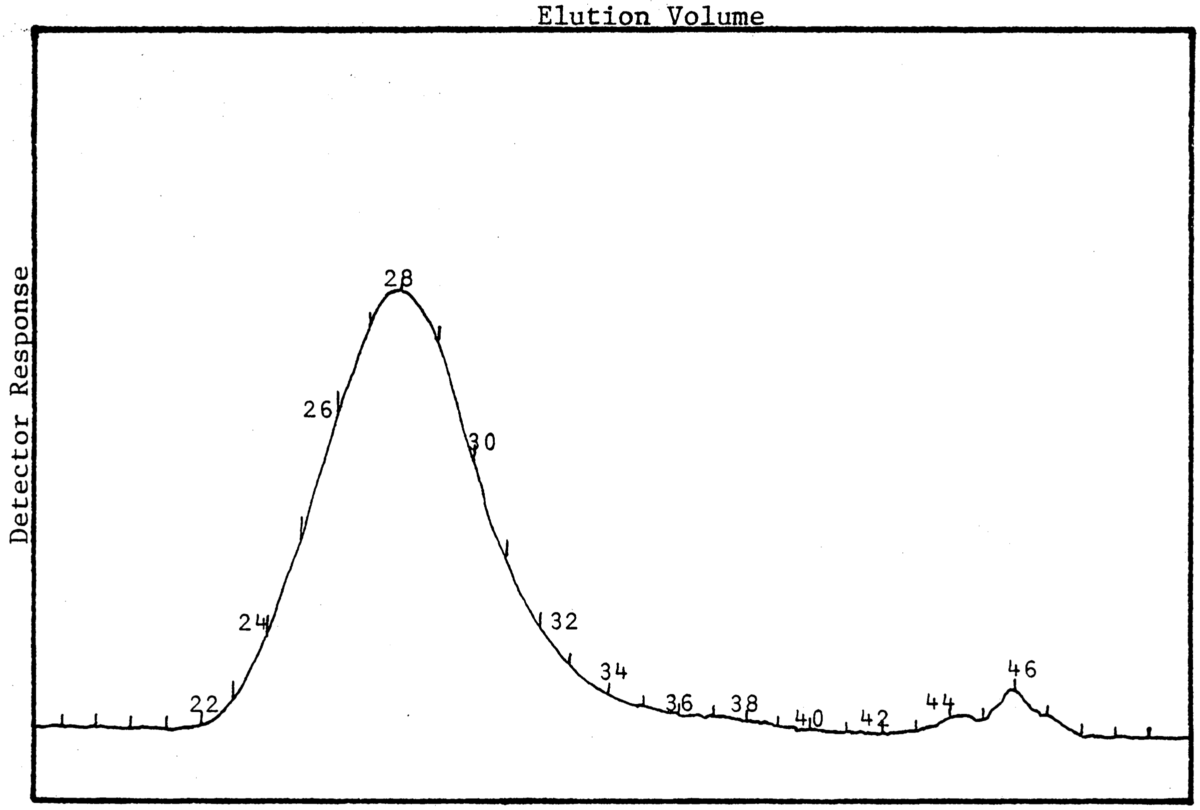


Figure 18: GPC Curve of a Perfectly Alternating Polycarbonate-Polydimethylsiloxane Block Copolymer
<Mn> of the polycarbonate block ≃ 14,000 g/mole, <Mn> of the polysiloxane block ≃ 4000 g/mole.

Table 13

Thermal Transitions[a] of Oligomers, Homopolymers and Block Copolymers of Various Compositions and Block Lengths

Sample	Block Length PC[b] / PSX[c]	Tg(PSX)	Tc(PSX)	Tm(PSX)	Tg(PC)
PC	2250/ --	--	--	--	111
PC	3410/ --	--	--	--	124
PC	4165/ --	--	--	--	132
PC	5863/ --	--	--	--	136
PC	Commercial "Merlon"[d]	--	--	--	147
S-42	2700/1800	-123[e]	--	--	85
S-52	2660/1800	-126	-96	-62	100
S-68	3400/10,000	-125	-100	-63	86
S-44	6300/1800	-123[e]	--	--	123
S-48	6300/5000	-127	-99	-56	127
S-66	11,500/10,000	-132	-105	-70	144
S-46	14,000/1800	-123[e]	--	--	142
S-56	16,000/15,000	-130	-109	-63	141

---

[a] Transitions were obtained by DSC at a heating rate of 10°K/min. with the exception of the subambient transitions for S-42, S-44, and S-46 which were observed at a heating rate of 5°K/min.

[b] PC = polycarbonate

[c] PSX = polydimethylsiloxane

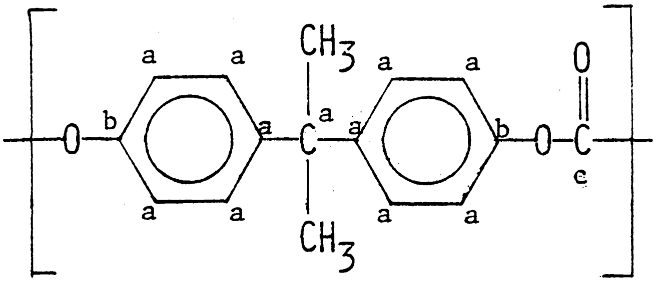
[d] Tradename for polycarbonates produced by Mobay.

[e] Very weak transitions. The range used to observe these transitions was 2 mcal./sec. whereas all others were observed at 5 mcal./sec.

than those for polycarbonate homopolymers of molecular weights similar to the copolymer block length. This occurs for polycarbonate block lengths of 6300 g/mole and lower and probably indicates partial phase mixing in these cases. The results of Sheehy and Ward, et al. (21,183) for S-66 (11,500 PC/10,000 PSX) as compared to S-68 (3400 PC/10,000 PSX) substantiates this conclusion.

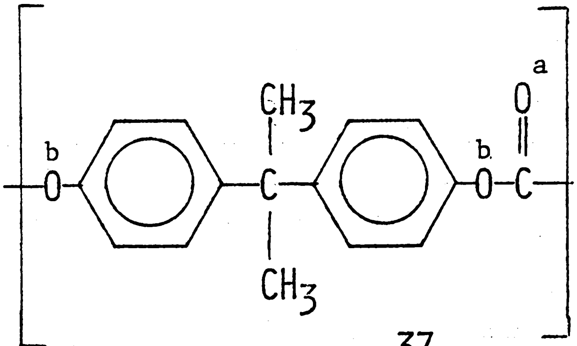
Perfectly Alternating Copolymers: ESCA Analysis of Films

ESCA spectra were run on the same group of copolymers which were investigated by DSC. The C_{1s} peaks for the polycarbonate homopolymer consist of a large peak at 285.0 eV with a shoulder on its high energy side (estimated placement is 286.6 eV) accompanied by a satellite at 291.15 eV. Based on literature data (23,24,190,215) discussed in the introductory section of this thesis (pp. 89-92), assignments to the respective peaks are given below (36). The satellite at 291.15 eV is attributed to both the carbonate carbons and the $\Pi \rightarrow \Pi^*$ transitions principally due to the benzene rings (215). With the polycarbonate hydrocarbon peak referenced at 285.0 eV, the corresponding oxygen peak appears at 534.3 eV. There is a large shoulder (approximately a 2:1 height ratio) on the low binding energy side peaking at 532.3 eV. Assignments were made as shown in 37 on the following page.



36

a = 285 eV
b = 286.6 eV
c = 291.15 eV



a = 532.5 eV
b = 534.3 eV

37

These oxygen assignments differ from those observed by Clark (215) for diphenyl carbonate by appearing approximately 1 eV lower in binding energy.

The binding energy positions for the polydimethylsiloxane components relative to the polycarbonates were established by adding small amounts of S-42 to a polycarbonate homopolymer and observing the oxygen peaks (see Figure 19). As evidenced by Figure 19, the addition of the siloxane oxygen caused the low binding energy shoulder of the polycarbonate oxygen peak to increase. Hence, the siloxane oxygen was also assigned to this position (532.5 eV). Using this as the binding energy reference for the siloxane, the siloxane carbon peak was found to be positioned at 285.0 eV and the $Si_{2p_{1/2}}$ and $Si_{2p_{3/2}}$ peaks at 102.65 eV.

The DSC data indicates reasonably good phase separation in all cases studied. In view of this, it appears that the siloxane may be preferentially oriented toward the surface to the extent that it could be treated as an overlayer. The depths of such overlayers can be computed according to equation 37, $I = I_\infty(1-e^{-d/\lambda})$, provided λ (mean free path of electrons) is known. Unfortunately, as previously discussed (23,207,213), dramatic deviations in the values of the appropriate "λ"

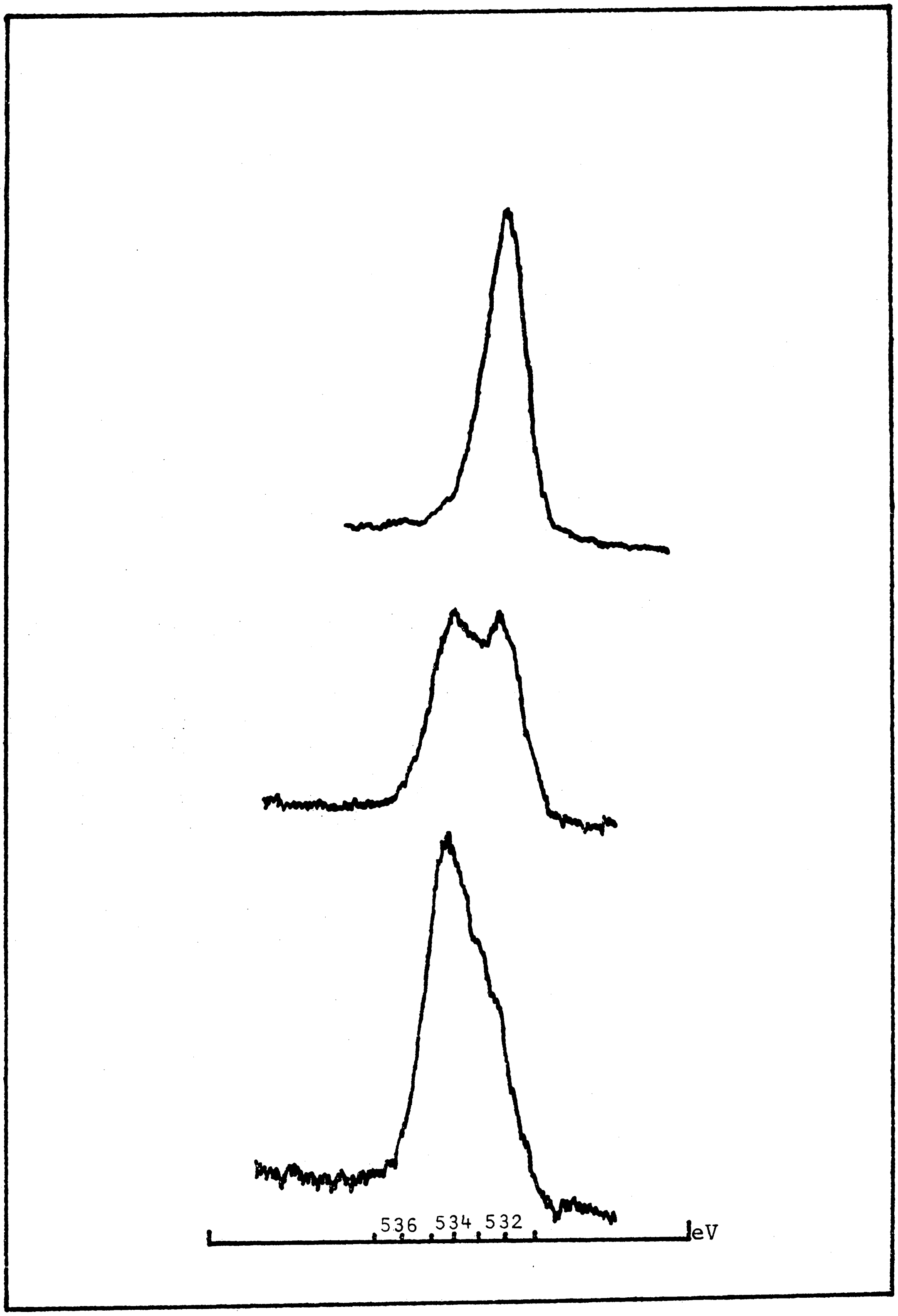


Figure 19: O_{1s} Peaks Used for ESCA Binding Energy Referencing. Top, pure polydimethylsiloxane; Middle, polycarbonate blended with S-42; Bottom, pure polycarbonate.

values (i.e. for Si_{2p} electrons) exist in the literature. Therefore, such a calculation would be meaningless in this case.

It is possible, however, to estimate the composition (polysiloxane vs. polycarbonate) of the area sampled by ESCA without knowledge of the electron mean free paths. A sample calculation based on S-42 follows. It can readily be seen that $\lambda_{C_{1s}}$ and $\lambda_{Si_{2p}}$ cancel in these equations.

It is worthwhile to recall equation 36 ($I = FK\ \alpha\ \lambda\ N$) describing the intensities (peak area multiplied by an attenuation factor) of ESCA peaks. For pure polydimethylsiloxane:

Equation 66: $$\frac{\dfrac{I_C}{\alpha_C}}{\dfrac{I_{Si}}{\alpha_{Si}}} = 2.0 = \frac{FK\ \lambda_C N_C}{FK\ \lambda_{Si} N_{Si}} = \frac{\lambda_C N_C}{\lambda_{Si} N_{Si}}$$

The corresponding values for S-42 are

$$\frac{I_{Si(S-42)}}{\alpha_{Si}} = 5919 = FK\ \lambda_{Si}\ N_{Si(S-42)}$$

and

$$\frac{I_{C(S-42)}}{\alpha_C} = 27136 = FK\ \lambda_C N_{C(S-42)}$$

"$N_{C(S-42)}$" must be separated into the number of carbons due to the carbonate component of S-42 ("$N_{C(S-42-PC)}$") and the number of carbons in the polydimethylsiloxane portion of S-42 ("$N_{C(S-42-PSX)}$") (Equation 67).

Equation 67: $$27136\ FK\ \lambda_C N_{C(S-42)} - \left(2.0\ \frac{\lambda_C N_C}{\lambda_{Si} N_{Si}}\right)\left(5919\ FK\ \lambda_{Si} N_{Si(S-42)}\right)$$

$$= 27136\ FK\ \lambda_C N_{C(S-42)} - 11838\ FK\ \lambda_C N_{C(S-42-PSX)}$$

$$= 15298\ FK\ \lambda_C N_{C(S-42-PSX)}$$

Having obtained the relative numbers of carbons in the carbonate and siloxane segments of S-42, these values can easily be converted to relative weight fractions (equations 68 and 68a).

Equation 68:
$$\left(15298\ \mathrm{FK}\ \lambda_C N_{C(S\text{-}42\text{-}PC)}\right) \frac{\left(254 \frac{g}{\text{Repeat unit}}\right)}{15 \frac{N_C}{\text{Repeat unit}}}$$

$$= (\mathrm{FK}\ \lambda_C)\ 259046\ g_{(PC)}$$

Equation 68a:
$$\left(11838\ \mathrm{FK}\ \lambda_C N_{C(S\text{-}42\text{-}PSX)}\right)\left(\frac{74 \frac{g}{\text{Repeat unit}}}{2 \frac{N_C}{\text{Repeat unit}}} \right)$$

$$= (\mathrm{FK}\ \lambda_C)\ 438006\ g_{(PSX)}$$

These relative weight fractions can be normalized and the percentage of sampled area comprised of polydimethylsiloxane can be obtained (equation 69).

Equation 69:
$$\frac{(\mathrm{FK}\ \lambda_C)\ 438006\ g_{(PSX)}}{(\mathrm{FK}\ \lambda_C)\ 25904\ g_{(PC)} + (\mathrm{FK}\ \lambda_C)\ 438006\ g_{(PSX)}} \times 100$$

= 63% Siloxane

The spectrometer factor (K), the X-ray flux (F), and the mean free path for the C_{1s} electrons (λ_C) become cancelled out in the final ratio.

Results of similar calculations are tabulated in Table 14. Due to the wide deviation in several of the percentages calculated for the same polymer, all of the data is listed in the table. Table 14 unequivocally demonstrates the preferential surface migration of the polydimethylsiloxane component in all of the copolymers studied. It also suggests that overall bulk composition is not the controlling factor in determining the percentage of the surface area sampled by ESCA which is composed of siloxane. Indeed, approximately 60% of this area is siloxane when the

Table 14

Percent of the Surface Area Sampled by ESCA Which is Composed of Siloxane

	Block Length $(\frac{g}{mole})$	% PSX in the bulk		% PSX on the	
Sample	PC / PSX	Theory,	NMR	Surface[a]	Ave.
S-46	14,000/1800	11	8	65% 59% 55%	60%
S-44	6300/1800	22	17	63% 60%	62%
S-42	2700/1800	40	33	63% 64% 61% 61% 66% 60%	63%
S-48	6300/5000	44	41	90% 73%	82%
S-66	11,500/10,000	47	41	94% 100^{+}% [b] 83%	92%
S-56	16,000/15,000	49	43	93% 83%	88%
S-52	2700/5000	65	62	88% 95%	92%
S-68	3400/10,000	75	70	95% 93%	94%

---

[a] This is weight percent of polydimethylsiloxane in the surface region sampled by ESCA at $\theta = 0^{\circ}$

[b] When the intensity due to the siloxane component was subtracted from the carbon peak, there were no carbons left in the carbonate component.

bulk percentage is 8, 17, and 33%. By contrast, the size of the siloxane block appears to play a predominant role in this respect. When the siloxane block is 1800 g /mole, approximately 60% of this surface area is siloxane. When the siloxane block is 5000 g /mole or higher, very high percentages of siloxane are obtained. This may be a result of more phase mixing at the low siloxane block molecular weight. The ill defined lower glass transitions observed by DSC for S-42, S-44, and S-46 suggest that some mixing does exist in the predominantly siloxane phases of these polymers. However, surface composition change could merely be a result of the covalently bonded polycarbonate segments being pulled into the sampled surface area by necessity due to the short lengths of the siloxane components.

The effect of siloxane block length almost disappears in the grazing angle experiments where the upper monolayers are investigated. Due to the unavailability of ESCA data on the polysiloxane homopolymer at $\theta = 79°$, numerical surface compositions could not be calculated for the grazing angle measurements. However, the trend toward surfaces composed of greater percentages of siloxane can easily be observed qualitatively through comparisons of peak shapes and positions as less film depth is sampled (see Figures 20 and 21). Figure 20 shows the C_{1s} peak at 291.15 eV due to the polycarbonate component prominently in the spectrum of S-42 collected at the normal angle ($\theta = 0°$) whereas it has almost completely disappeared in the grazing angle spectrum ($\theta = 79°$). The C_{1s} S-42 peak run at $\theta = 79°$ looks very much like the corresponding peak for pure polydimethylsiloxane. Likewise the O_{1s} peak for S-42

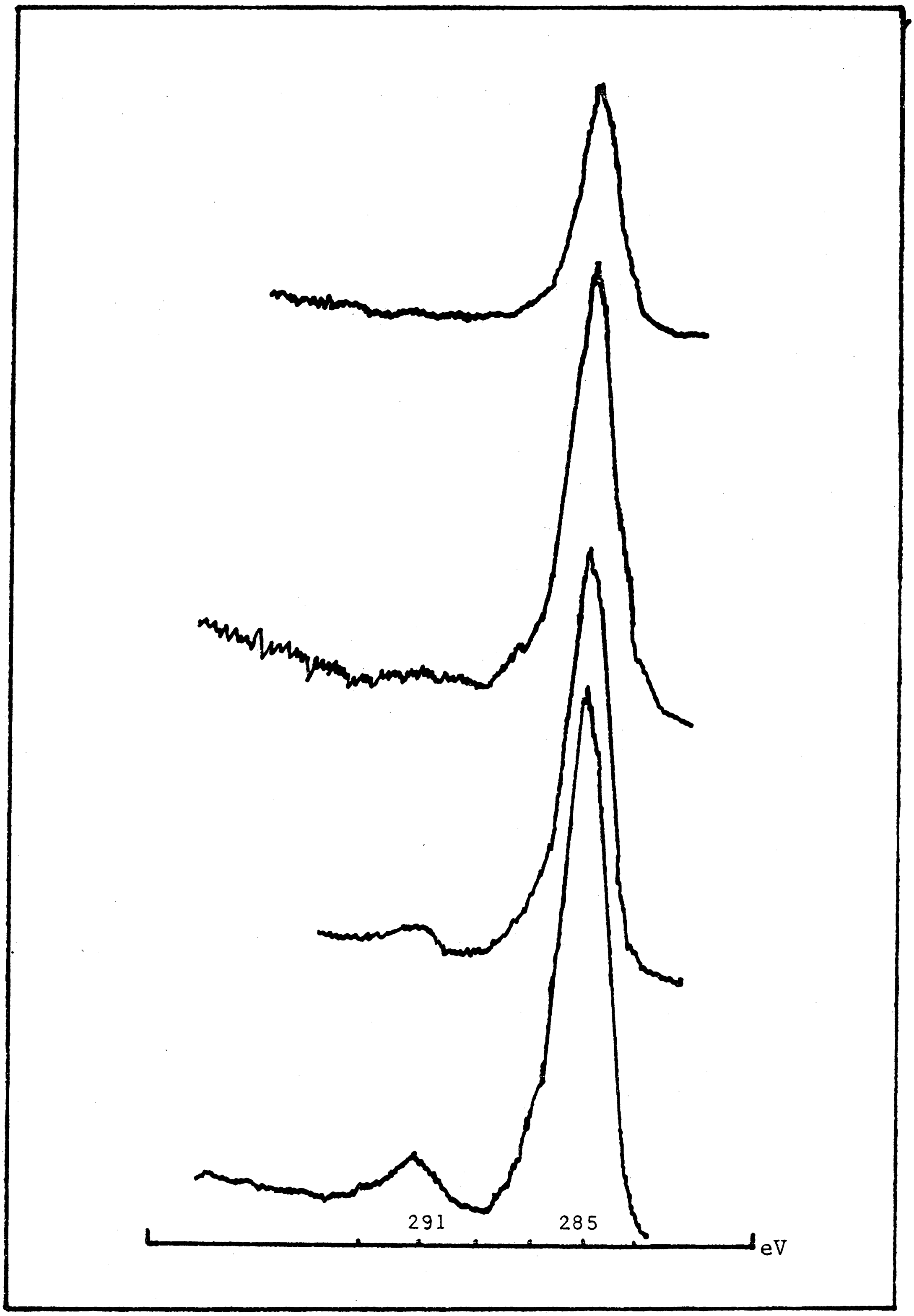


Figure 20: C_{1s} ESCA Peaks
Top to bottom: Pure polydimethylsiloxane, S-42 collected at $\theta=79^{\circ}$, S-42 collected at $\theta=0^{\circ}$, pure polycarbonate.

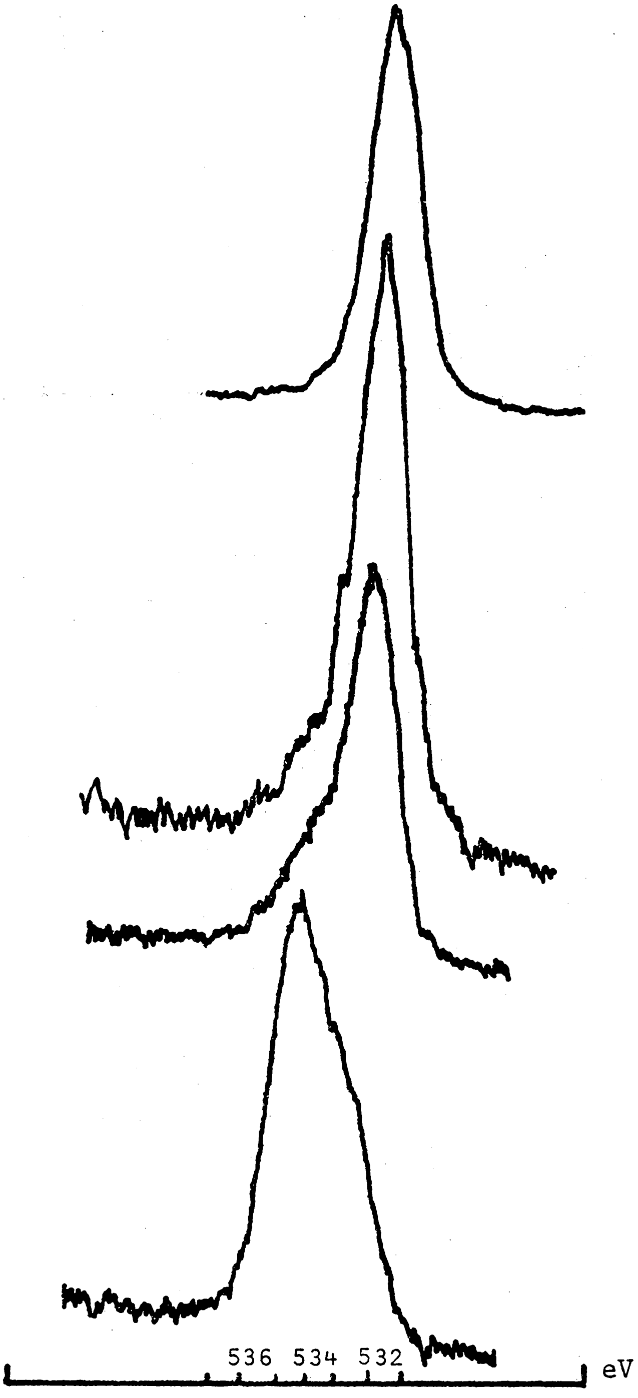


Figure 21: O_{1s} ESCA Peaks

Top to bottom: Pure polydimethylsiloxane, S-42 collected at $\theta=79^o$, S-42 collected at $\theta=0^o$, pure polycarbonate.

taken at normal angle (θ = 0°) exhibits the 534.3 eV shoulder corresponding to the polycarbonate component much more dramatically than the same data collected at the grazing angle (θ = 79°)(see Figure 21).

Polyblends of Perfectly Alternating Copolymers with Homopolycarbonate: ESCA Analysis of Films

ESCA spectra on the blends are summarized in Figure 22 and Table 15. These blends were all made from $(AB)_n$ copolymers in which the siloxane block length was 1800 g /mole. "Percent siloxane on the surface" was calculated in the same manner as for the copolymers (equations 66-69). Siloxane was seen on the surface even at the 0.05% siloxane level in molded films, films cast from $CHCl_3$, and in the powder form. When log "percent siloxane (in the bulk)" was plotted vs. "percent siloxane (on the surface)", Figure 22, a definite concentration break representing a critical siloxane concentration in the bulk for a large portion of the surface to be composed of siloxane became evident. This is true in the case of both molded and cast films.

Randomly Coupled Block Copolymers: Synthesis and Structural Characterization of Hydroxy and Carboxy Functional Siloxane Oligomers

The acid catalyzed equilibration of the hydroxybutyl and carboxypropyl terminated polydimethylsiloxane (disiloxane or oligomers) with the cyclic tetramer (D_4) provides a facile route to either of these functionalities with the capability of varying <Mn> between the respective disiloxane and ∿25,000 g /mole.

Although the preparation described for these polymers utilizes trifluoroacetic acid as the catalyst, it was found that a variety of strong acids (concentrated sulfuric acid, p-toluenesulfonic acid, methanesulfonic

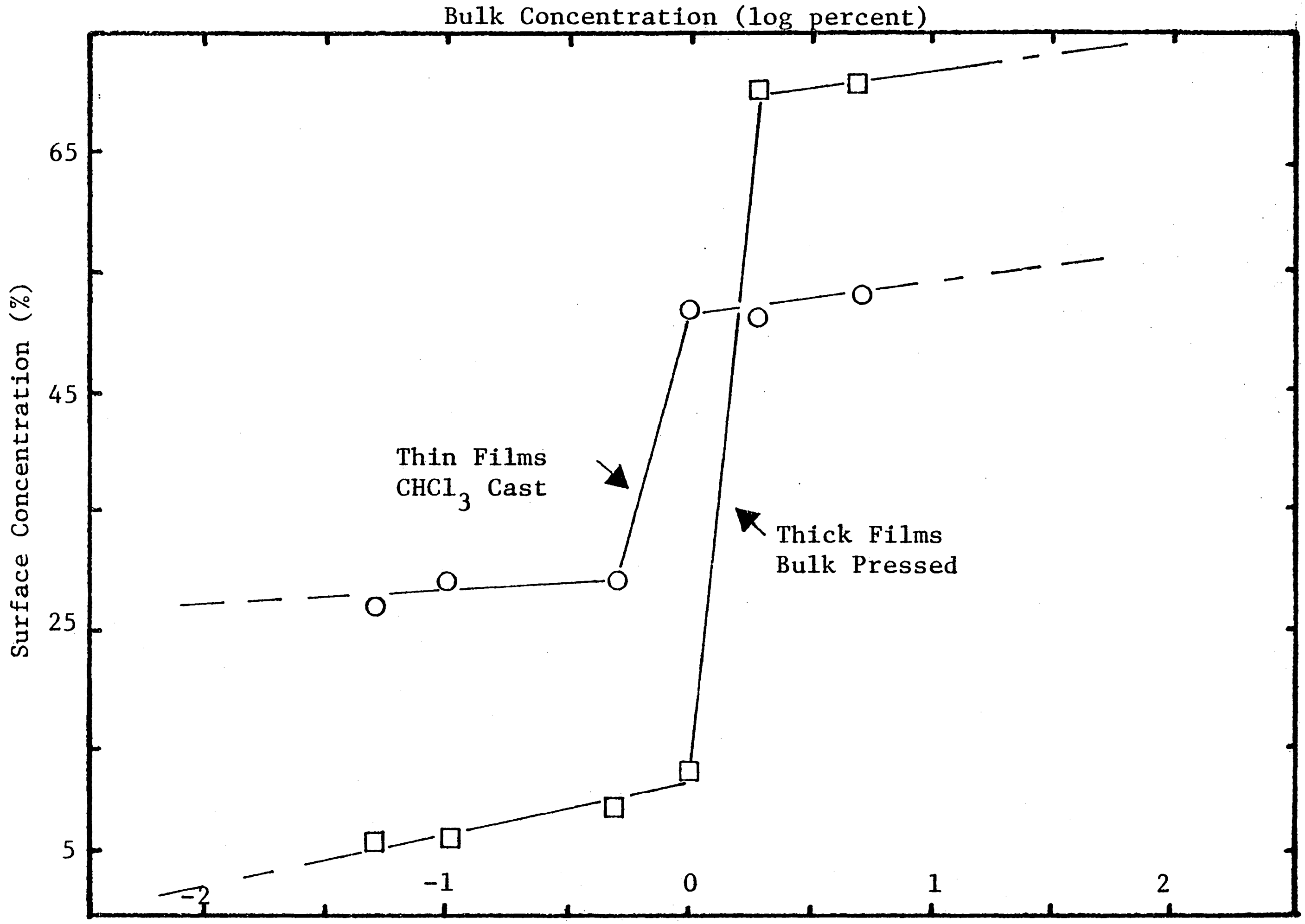


Figure 22: Surface Segregation in Polycarbonate-Polydimethylsiloxane Copolymer/Homopolycarbonate Blends

Table 15

ESCA Surface Analysis of Cast and Molded Polycarbonate/Polycarbonate-Polydimethylsiloxane Blends

Wt. % Siloxane in Bulk	Wt. % of the Surface Composed of Siloxane	
	Cast Film	Molded Film
0 (Control)	0	0
0.05	26.0	2.6
0.10	28.0	6.1
0.50	28.0	8.3
1.0	50.5	11.6
2.0	50.0	69.0
5.0	51.4	69.4

acid) were also effective. Trifluoroacetic acid (TFA) was chosen for two reasons; 1, it was found to be miscible with the siloxane oligomers and 2, it could easily be removed by means of washing the products with water. TFA is not ordinarily considered to be an equilibration catalyst. However, we found that relatively large quantities of this catalyst could induce the "equilibrations" to proceed within reasonable amounts of time. Almost one-half mole trifluoroacetic acid per mole siloxane starting material (e.g. the disiloxane plus the D_4) is suggested in the experimental section of this paper. If that amount is reduced by factors of even 2 or especially 10, no change in the viscosity of the reaction mixture can be observed after ∿48 hours. In contrast to the apparent general effectiveness of acids as catalysts for these reactions, bases (KOH, tetramethylammonium silanolate) appear to be totally ineffective. This could possibly be a result of interactions occurring between the bases and the acidic endgroups involved on the siloxanes.

Preliminary GPC data illustrates that both polymerization and equilibration occur in these reactions. Figure 23 shows the disappearance of D_4 (the cyclic tetramer starting material) with time accompanied by the growth of a reasonably symmetric peak in a higher molecular weight range for a carboxypropyl terminated oligomer (calculated <Mn> = 20,000 g/mole according to the procedure outlined in the experimental section. The GPC curves shown in Figure 24 correspond to an equilibration of a commercial ≃23,000 <Mn> hydroxypropyl terminated linear siloxane with α,ω-hydroxybutyldisiloxane. The shift of the 23,000 <Mn> material to a lower molecular weight range after equilibration

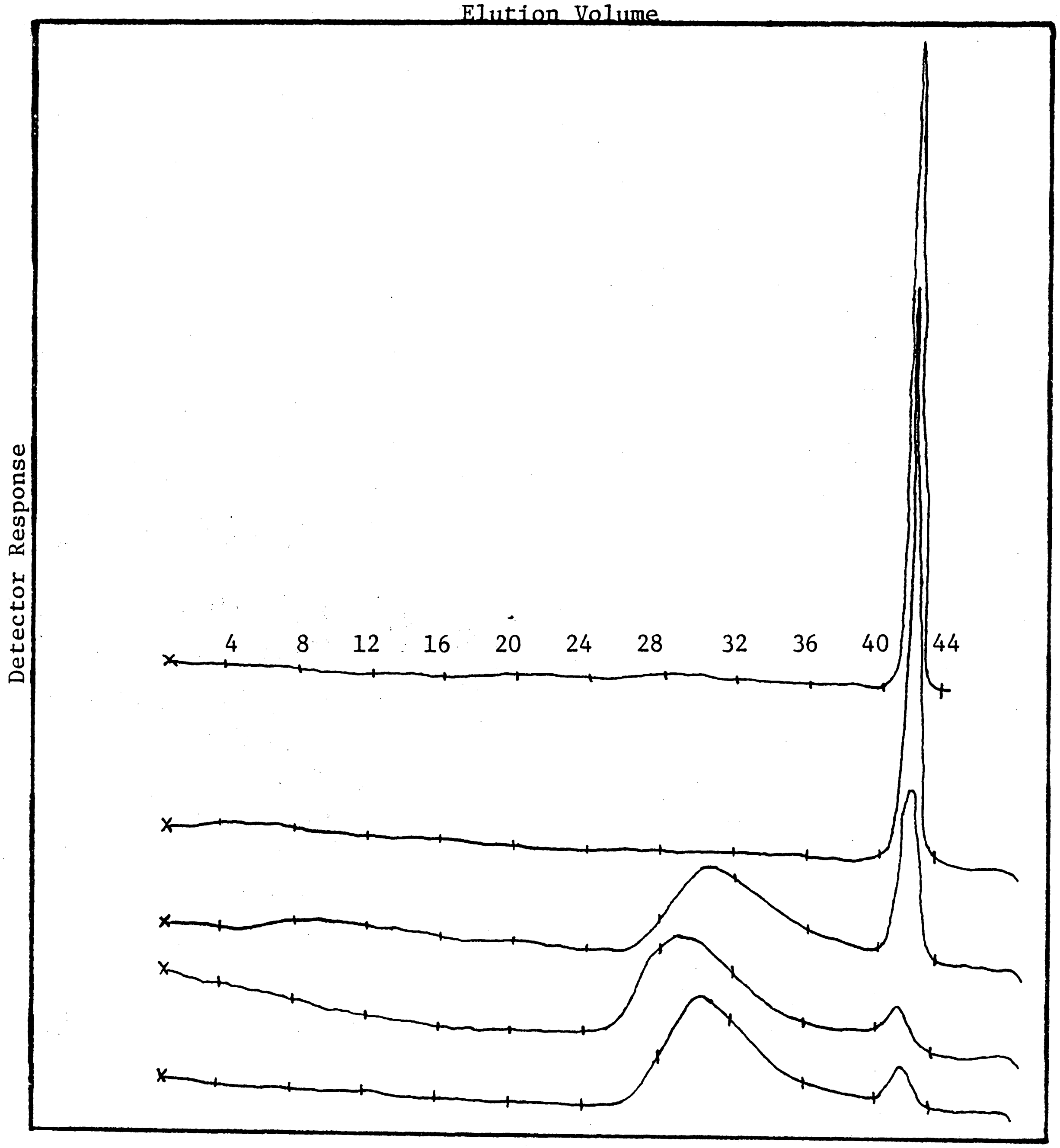


Figure 23: GPC Curves Showing the Disappearance of Tetramer and Formation of a 20,000 <Mn> Carboxypropyl Terminated Polydimethylsiloxane Top to bottom: 1. D_4, 2. After 20 min. reaction, 3. After 18.5 hrs. reaction, 4. After 24 hrs. reaction, 5. After 43.5 hrs. reaction

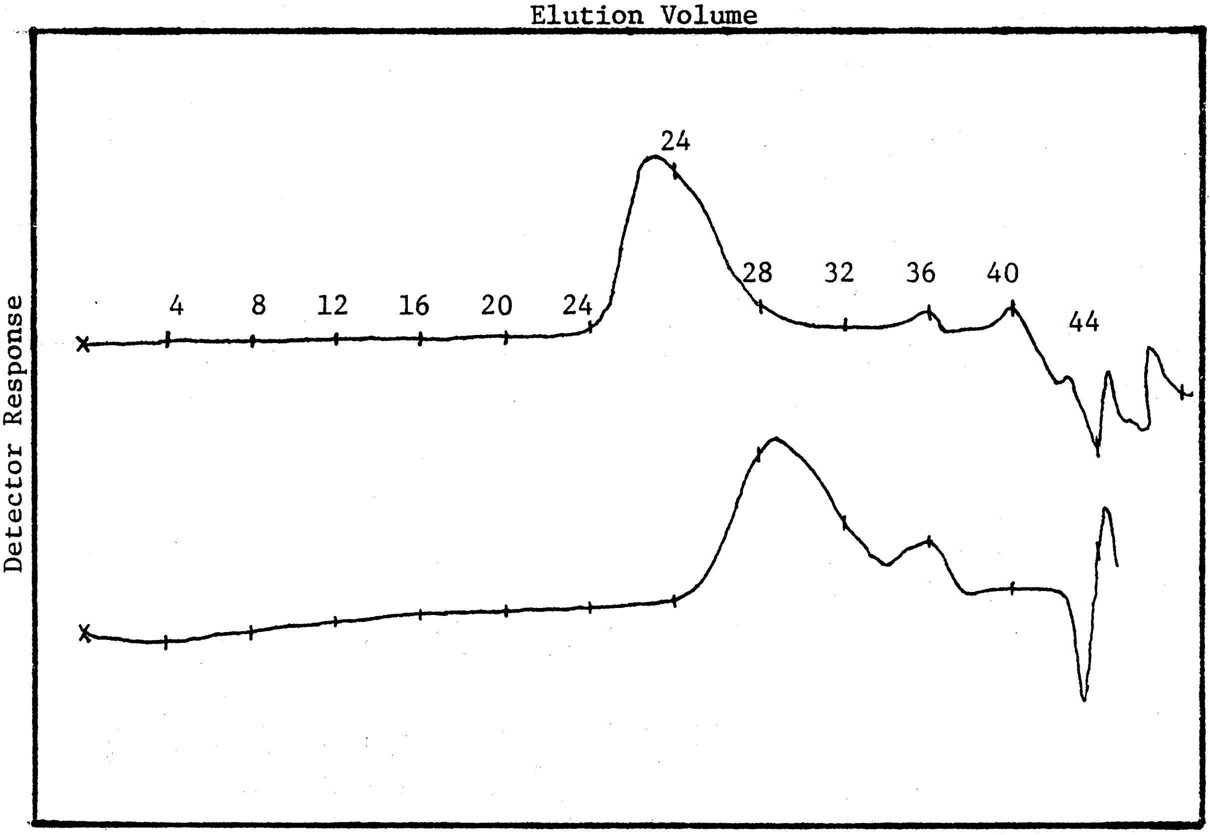


Figure 24: GPC curves
Top: 23,000 <Mn> hydroxypropyl terminated polydimethylsiloxane
Bottom: 23,000 <Mn> oligomer (top) after equilibration with
1,3-(bis)hydroxybutyltetramethyldisiloxane

clearly demonstrates that linear chains as well as cyclic structures can be redistributed. The exact rate to reach equilibrium and the level of cyclic structures at equilibrium remains unassessed as yet. As discussed in the literature review (pp. 38-58), considerable information has been derived by studying somewhat similar reactions. However, none of this prior work has incorporated the highly polar functional groups studied herein. It seems possible that associative effects due to these organofunctional groups may affect the ring-chain equilibrium normally encountered. There is some evidence suggesting that the level of cyclics in the carboxypropyl terminated siloxane equilibration (according to the procedure suggested in the experimental section of this paper) is remarkably low. D_4 is insoluble (in the absence of trifluoroacetic acid) in low molecular weight carboxy functional siloxanes. However, when low molecular weight oligomers of this type are produced, no D_4 precipitates out after removal of the catalyst. Conversely, in a related reaction where the same type of solubility phenomena applies (capping of epoxide terminated polysiloxanes with methacrylic acid), two phases (one containing cyclics, the other containing linear products) always result (240). Clearly, additional information pertaining to cyclics concentration would be desirable and is being pursued by LC and GC techniques.

Interfacial Copolymerization of Randomly Coupled Block Copolymers: Introduction

The interfacial copolymerization using the hydroxyl or carboxyl terminated siloxane oligomers is not as efficient as the silylamine reaction previously discussed. Only the hydroxyl terminated siloxanes were used in the initial investigations. The data were not reproducible and suggested that an extremely tight control of reaction parameters was of utmost importance. This was the reason for the change in apparatus from the blender to a flask. The present set-up enables one to better control both temperature and concentration (particularly of the methylene chloride phase), even though stirring rates are more limited. Table 16-Part A summarizes these early copolymerizations which used the hydroxybutyl and hydroxypropyl terminated oligomers. Both the use of carboxyl and hydroxy functional siloxanes was investigated in the latter, better controlled stage of this research. Results of these reactions using the hydroxyl terminated oligomers will be discussed first. This will be followed by the experiments utilizing the carboxypropyl terminated siloxanes. The new reaction parameters for the copolymers were based on results of a series of homopolycarbonate polymerizations. These will be discussed along with the copolymers involving the carboxyl terminated siloxanes, since numerous referrals to and from the copolymer and homopolymer results must be made in those cases.

Interfacial Copolymerization Using Hydroxy Functional Siloxane Oligomers

The problem in the interfacial reaction using the hydroxyl terminated siloxane appears to be a difficulty in incorporating the aliphatic hydroxyl group itself. This conclusion is substantiated with several pieces of evidence. It is known that the reaction of both phosgene and aliphatic chloroformate groups with water is faster than the reaction of either with aliphatic hydroxyl groups (134). Under anhydrous conditions (see reaction #S-37, Table 16, Part A), the amount of siloxane

TABLE 16 (PART A)

BIS-HYDROXY PROPYL TERMINATED POLYDIMETHYLSILOXANE/BISPHENOL-A POLYCARBONATE BLOCK COPOLYMERS

Type of Polymer	Type of Reaction$^{(a)}$	pH	Reaction Time Minutes$^{(b)}$	Solvent	Phase Transfer Catalyst$^{(c)}$ (PTC)	[η]	Ideal % Siloxane	% Siloxane Obtained (NMR)
S-23	IF	6-7	95 + 60 Stabilization	CH_2Cl_2	$(C_2H_5)_4\overset{+}{N}\,\overset{-}{Cl}$ unless otherwise specified - 2 g.	low	47%	31%
S-20	IF	7.5-8.5	60 + 60 Stabilization	CH_2Cl_2	2 g.	0.3	47%	23%
S-25	IF	9-10	60 + 60 Stabilization	CH_2Cl_2	2 g.	0.58	47%	39%
S-27	IF	9-9.5	120 + 80 Stabilization	CH_2Cl_2	2 g.	0.37	47%	40%
S-31	IF	9-9.1	120 + 60 Stabilization	CH_2Cl_2	low	53%	46-49%	
S-33	IF	10	120 + 60 Stabilization	CH_2Cl_2	2 g.	low	47%	50%

TABLE 16 (PART A - CONTINUED)

Type of Polymer	Type of Reaction$^{(a)}$	pH	Reaction Time Minutes$^{(b)}$	Solvent	Phase Transfer Catalyst (c) (PTC)	$[\eta]$	Ideal % Siloxane	% Siloxane Obtained (NMR)
S-35	Solution starting with A carbonate oligomer (~2,000<Mn>) instead of from Bis-A	----	120 + 40	CH_2Cl_2/pyridine	----	low	47%	-42%
S-37	Solution starting with Bis-A	----	120	CH_2Cl_2/Pyridine (more concentrated and less pyridine than with S-35)	----	0.48	54%	52%
S-39	IF	11	90 with CO-Cl_2 Flow very slow (Relatively)	CH_2Cl_2	0.175 g	low	47%	31%
S-41	IF	9	60 stabilization with 60, 120, 180 samples	CH_2Cl_2	2 g	60 min-.18 120 min-.22 180 min-.26	47%	180 min-44.5%
S-43	IF	9	120 + 60 Stabilization	CH_2Cl_2	(2 g) + $(C_2H_5)_3N$	low	47%	39%

TABLE 16 (PART A - CONTINUED)

Type of Polymer	Type of Reaction[(a)]	pH	Reaction Time Minutes[(b)]	Solvent	Phase Transfer Catalyst[(c)] (PTC)	[η]	Ideal % Siloxane	% Siloxane Obtained (NMR)
S-47	IF	9	120 + 60 Stabilization	CH_2Cl_2	4 g	0.39	47%	
S-49	IF	9	120 + 60 Stabilization	CH_2Cl_2	$(C_4H_9)_4\overset{+}{N}\ \overset{-}{Br}$ 7.78 g (Molar Equivalent of 4g of $(C_2H_5)_4\overset{+}{N}\ \bar{Cl}$	0.28	47%	
S-53	IF	9	80 + 40 Stabilization	Chlorobenzene	(2 g)	0.48	47%	
S-55	IF	9	180 with 60, 120, and 180 samples	Chlorobenzene	2 g	60 min-low 160 min-.41 180 min-.20	47%	
S-57	IF	9	80 + 40 Stabilization	Chlorobenzene	Benzyl Triethyl ammonium chloride 2.7 g (Molar Equivalent of 2 g of $(C_2H_5)_4\overset{+}{N}\ \bar{Cl}$)	----	47%	

TABLE 16 (PART A - CONTINUED)

Type of Polymer	Reaction[a]	pH	Reaction Time Minutes[b]	Solvent	Phase Transfer Catalyst[c] (PTC)	$[\eta]$	Ideal % Siloxane	% Siloxane Obtained (NMR)
S-59	IF	9 + varied	150	CH_2Cl_2	Benzyl Triethyl ammonium chloride - 2.7 g	0.22	47%	
S-61	Solution capping of Siloxane oligomer with the chloroformate of Bis-A, (pre-step type 1) then interfacial. "Pre-Step" done according to the method described in the experiment	9 for the IF	190 for solution step, then 70 for the interfacial step	CH_2Cl_2	2 g	0.76	47%	40%
S-63	IF with the first part of the reaction done at 12°C to try to generate the chloroformate of Bis-A *insitu*	9	180	CH_2Cl_2	2 g	47%	38%	

TABLE 16 (PART A - CONTINUED)

Type of Polymer	Type of Reaction[(a)]	pH	Reaction Time Minutes[(b)]	Solvent	Phase Transfer Catalyst[(c)] (PTC)	$[\eta]$	Ideal % Siloxane	% Siloxane Obtained (NMR)
S-67	Sol'n capping of the PSX with dichloroformate of Bis-A prior to interfacial reaction. (Pre-step type 1) Pyridine was added all at once in the "pre-step" An insoluble PPT forms immediately.	9 for the IF part	190 for Sol'n step, then 70 for the interfacial step.	CH_2Cl_2	2 g	0.11	47%	39%
S-69	Sol'n capping of the PSX with dichlorofcrmate of Bis-A prior to interfacial reaction. (Pre-step type 1) Pyridine was added dropwise but PSX was added all at once	9 for the IF part	190 for Sol'n step then 70 for the interfacial step.	CH_2Cl_2	2 g	0.40	47%	39%

FOOTNOTES FOR TABLE 16 (PART A)

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a. "IF" means "interfacial", Polysiloxane oligomer always nominally 2000 $\langle M_n \rangle$.

b. "Stabilization" refers to the time required for the reaction mixture to drop from the pH maintained up to that point to neutrality (No NaOH is added to maintain a certain pH during the stabilization period).

c. The amount of phase transfer catalyst added is "The amount per 5g Bisphenol-A".

d. "PTC" means "Phase Transfer Catalyst."

e. "Bis-A" means "Bisphenol-A".

PART 16 (PART B)

— Reaction	PSX Oligomer	"Pre-Step"	Reaction Time	Solvent	Catalyst	$[\eta]^{25°}_{THF}$	Ideal % PSX	% Siloxane Obtained
S-71 (G 1130)	20,000 <Mn> Hydroxybutyl terminated siloxane	Yes-Type 2	15 min. "pre-60 min. IF, 10 min. acidification	(b) CH_2Cl_2-75 ml H_2O-75 ml	1.1g/7.5 g	0.89	50%	24%
S-73 (G 1132)	20,000 <Mn> Hydrobutyl Terminated Siloxane	NO	60 min. IF, 10 min acidification	CH_2Cl_5-75 ml H_2O-75 ml	1.1g/7.5 g	1.43	50%	18%
S-75 (J 5142)	23,000 <Mn> Hydrobutyl terminated siloxane	NO	60 min. IF, 10 min. Acidification	CH_2Cl_2 75 ml H_2O-75 ml	1.1g/7.5 g	0.90	50%	32%
S-77 (J 5144)	23,000 <Mn>	Yes-Type 2	15 min. "pre-step", 60 min IF 10 min acidification	CH_2Cl_2-75 ml H_2O-75 ml	1.1g/7.5 g Bis-A	1.20	50%	23%
S-79	2000 <MN> Hydroxylpropyl terminated PSX	NO	60 min. IF, 10 min acidification	CH_2Cl_2-75 ml	1.1g/7.5 g Bis-A	0.35	50%	43%
S-81	200 <Mn> Hydroxylpropyl terminated Siloxane	Yes-Type 2	15 min. "pre-step" 60 min. IF 10 min. acidification	CH_2Cl_2-75 ml H_2O-75 ml	1.1g/7.5 g Bis-A	0.26	50%	44%

a. pH was maintained between 11-12 in all of the reactions listed in Part B.

b. 15 g polymer was the theoretical yield in all reactions listed in Part B.

incorporated is the total theoretical amount; yield is nearly quantitative, molecular weight is higher than under interfacial conditions and good film properties are observed. Also, using conditions under which the polycarbonate of bisphenol-A goes to a very higher molecular weight in 1/2 hour (those of reaction #2, Table 17, $[\eta] = 1.20$) an intrinsic viscosity of only 0.35 (see reaction #S-79, Table 16, Part B) is reached in 1 hour for the copolymers. It was thought originally that the problem with this copolymerization reaction might have been in nonfunctional and/or monofunctional species in the commercial siloxane oligomer. However, copolymers prepared from similar molecular weight siloxane oligomers, but where the oligomers were made via different methods, yield very similar results (cf. reactions #S-71 with S-77 and reactions #S-73 with #S-75, Table 16, Part B). This suggests that the problem is probably not due to the oligomer functionality, but as discussed above, in the incorporation of the aliphatic hydroxyl group.

Several approaches were examined to circumvent the problems of incorporation of the aliphatic hydroxyl. Esentially two procedures were explored in some depth: (1) The siloxane oligomer was capped in an anhydrous "pre-step" with the dichloroformate of bisphenol-A prior to the interfacial reactions (pre-step type #1), (2) Alternatively the siloxane oligomer was subjected to an excess of phosgene in another type of anhydrous pre-step (type #2). It was envisioned that "pre-step" type #1 mentioned above would eliminate the necessity of ever having to form the hydrolytically unstable aliphatic chloroformate group. The intention in the use of "pre-step type #2" listed was to quantitatively convert the aliphatic hydroxyl to an aliphatic chloroformate endgroup in hopes that a high percentage of it would then react with bisphenol-A prior to hydrolysis.

Results obtained via capping the siloxane with the dichloroformate of bisphenol-A prior to the interfacial reaction were quite promising. Reaction S-61 produced by this method (as discussed in the experimental section) yielded a very satisfactory intrinsic viscosity of 0.76 dℓ/g using the 2000 <Mn> siloxane oligomer.

The second type of "pre-step" described (pre-step type #2) did not produce noticeably improved results (c.f. reactions S-71 with S-73, S-75 with S-77, and S-79 with S-81). The method used was to rapidly introduce excess phosgene gas into an ∿50% solution of the siloxane oligomer in dry methylene chloride (no basic catalyst) at room temperature (a detailed description of this is found in the experimental section as the "suggested pre-step" to the copolymerization using the carboxyl terminated siloxane oligomer). It has been previously noted that bischloroformates of aliphatic dihydroxy compounds (but not high molecular weight polycarbonates) could be obtained in good yields by this type of method (134). This was attributed to the fact that step 1 of the reaction to form a carbonate link is overwhelmingly faster than step 2 under non-catalyzed conditions. If, indeed, quantitatively capped aliphatic chloroformate groups do form in this case, the fact that no improved results are observed in the copolymers produced by this method further substantiates our belief that the hydrolytic instability of the aliphatic chloroformate group is the overriding difficulty in these syntheses.

Using the "suggested method of synthesis" for these random copolymers (detailed in the experimental section), a series of reactions were run using different molecular weight siloxane oligomers (2000, 5000, 23,000). It was anticipated that if hydrolysis of the aliphatic chloroformate group was the overriding difficulty, then higher molecular weight siloxane oligomers might be incorporated more easily than their lower molecular weight counterparts. Results show that molecular weight (as evidenced by intrinsic viscosities) of the copolymer does increase as the molecular weight of the siloxane oligomer used in increased (c.f. reactions S-79, S-83, and S-75, Table 16, Part B). Indeed, use of a 5000 <Mn> siloxane (S-83) produced an intrinsic viscosity of 0.55 with 90% of the theoretical amount of siloxane incorporated. However, using high molecular weight siloxane oligomers (see reactions S-75 and S-73), a large percentage of the siloxane does not become incorporated at all.

In conclusion, two synthetic routes show promise for the preparation of the random block copolymers using the aliphatic hydroxyl terminated siloxane via interfacial methods: (1) Capping of the hydroxyl terminated siloxane oligomer with the dichloroformate of bisphenol-A prior to the interfacial procedure, and (2) The use of intermediate molecular weight (between 5000 and 20,000) siloxane oligomers in the reaction.

Interfacial Copolymerization Using Carboxy Functional Siloxane Oligomers

The investigation described in this paper is perhaps the first simultaneous reaction of a carboxylic acid, a phenol, and phosgene to be studied in an aqueous PTC type medium. As mentioned previously, the approach taken for development of the synthesis of these block copolymers was to first investigate the formation of the homopolycarbonate. Copolymerizations including the siloxane oligomers were then conducted under analogous conditions. This method allowed a systematic study of the major differences between homopolycarbonates and copolymer formation. Consequently, results and interpretations pertinent to the homopolymer study will first be discussed, followed by aspects related to copolymerization.

A series of homo-polycarbonates were produced where the amount of phase transfer catalyst was systematically varied from 4-40 mole percent tetraethylammonium chloride based on number of moles of bisphenol-A (cf. Table 17, #1-3). These values are seemingly high, but were based on some earlier work by Morgan, et al. (142,241). A maximum in intrinsic viscosity was observed at the middle catalyst concentration (20%) initially studied. This suggested that a 4% catalyst concentration might be too low to promote migration of bisphenol-A to the organic phase. Hence, a slower reaction ensues which results in a lower molecular weight. Alternatively, the 40% catalyst concentration probably causes a relatively rapid transfer of the bisphenol to the dichloromethane phase. Such a rate of phase transfer might allow formation of nearly complete chloroformate endgroup functionality. The result would be that the correct stoichiometry needed to produce high molecular weight polymers would never be achieved.

It was reasoned that if chloroformate endgroups could be built up through the use of a large concentration of catalyst, then the presence

Table 17

Interfacial Polycarbonates:
Investigation of the Effect of Catalyst
Concentration and Phosgene Flow Rate

	Phosgene Flow Rate (cc/min.)	pH	Reaction Time	$^{(a)}$ $(Et)_4\overset{+}{N}\overset{-}{Cl}$	25°C $[\eta]$(dℓ/g.) THF
1.	40-58	11-12	1/2 hr.	4%	0.34
2.	40-58	11-12	1/2 hr.	20%	1.20
3.	40-58	11-12	1/2 hr.	40%	0.22
4.	120-140	11-12	1/2 hr.	4%	1.50
5.	120-140	11-12	1/2 hr.	40%	0.23

(a) Expressed in mole % of $(Et)_4\overset{+}{N}\overset{-}{Cl}$ per mole bisphenol.

of a large excess of phosgene should also enhance the effect. Results of reactions run with a high phosgene gas flow rate (see Table 17) support this hypothesis. Indeed, high molecular weights are achieved at lower catalyst concentration as phosgene flow rate is increased.

Copolymerizations were normally performed under basically the identical conditions which were used for the homopolycarbonates.

The polydimethylsiloxane oligomer was added to the reaction to yield a theoretical copolymer composition of approximately 50% polysiloxane and 50% polycarbonate by weight. The reactions also were continued for longer periods of time than the 30 minutes used for the homopolymers.

Block copolymers were first prepared utilizing reaction parameters which had been shown to produce high molecular weight homopolymers (cf. No. 2 and No. 4, Table 17). After one hour of reaction, a moderate portion of the theoretical amount of siloxane (90% and 85%, respectively - see Table 18) had been incorporated into both copolymers, but only relatively low molecular weights were obtained. These results suggested a difficulty in the incorporation of the <u>acid</u> terminated siloxane oligomer.

If the mechanism shown in equation 44 was operative, then formation of the ester would be enhanced by first producing a high concentration of aryl chloroformate endgroups. By contrast, the routes shown in equation 45 would be promoted by a large excess of phosgene in the organic phase. It was conceived that copolymerization might be assisted if either or both of the abovementioned conditions could be achieved. Recall that the conditions of reaction 3, Table 17 were postulated to

Table 18: Interfacial Polycarbonate/Polydimethylsiloxane Copolymers: Investigation of the Effect of Catalyst Concentration and of Phosgene Flow Rate on Intrinsic Viscosity and Polysiloxane Incorporation.

Phosgene Flow[c] Rate (cc/min.)	[a] $(Et)_4\overset{+}{N}\overset{-}{Cl}$ Conc.	$[\eta]^{25°C}_{THF}$			[b] % of Theoretical PSX Incorporated into the Copolymer		
		1 hr.	2 hrs.	3 hrs.	1 hr.	2 hrs.	3 hrs.
1. 40-58	20%	0.56	0.50	0.41	90%	93%	92%
2. 120-140	4%	0.44	---	---	85%		
3. 40-58	40%	0.42	0.53	0.79	98%	92%	90%
4. 120-140	40%	0.48	---	---	87%		

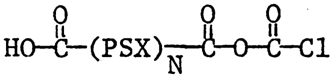
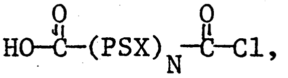
(a) Figures are expressed in mole percent based on bisphenol.

(b) 100% would result in 50% of polysiloxane by weight in the copolymer.

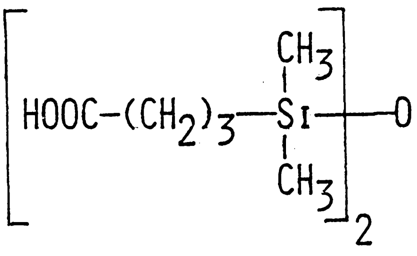
(c) pH was held in the range of 11-12.

have produced a nearly exclusive aryl chloroformate endgroup. It appears reasonable that if the above is true, then parameters used for reaction 5, Table 17 (same as for reaction 3, Table 17 except with a much faster phosgene flow rate) should produce both of the desired situations.

Results obtained in the copolymerization under the conditions of reaction 3, Table 17 were encouraging (see Table 18, reaction 3). After three hours of reaction, a relatively high intrinsic viscosity of 0.79 dl/g was obtained. Moreover, the stoichiometric amount of siloxane was essentially incorporated. Copolymerization under the analogous conditions at a higher phosgene flow rate was much less successful. Unfortunately, the use of a large excess of phosgene results in excessive phosgene hydrolysis and hence renders the technique impractical. For example, neutralization of the HCl by-product with base produces very large quantities of salt.

A second attempt was made to define conditions where the mechanism shown in equation 45 might be favored. In this case, an anhydrous "pre-phosgenation" step (pre-step type #2) was used. This consisted of bubbling an excess of phosgene through a dichloromethane solution of the siloxane oligomer prior to the interfacial reaction. It was anticipated and then confirmed that one or more of the possible intermediates,  $HO-\overset{\overset{O}{\|}}{C}-(PSX)_N-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-Cl$ and/or  $HO-\overset{\overset{O}{\|}}{C}-(PSX)_N-\overset{\overset{O}{\|}}{C}-Cl$, would be formed via this approach. The carboxypropyl terminated disiloxane or rather, an anionic form of it, is soluble in the aqueous medium used for the interfacial reaction. Experiments were conducted using the precursor siloxane dimer for the copolymerization. In the absence of the anhydrous pre-step, almost no disiloxane could be incorporated into the copolymers (see reactions 1 and 2, Table 19). By contrast, when the pre-step was used, the theoretical and actual copolymer compositions were extremely close. Differences are believed to reflect analytical errors and possibly some non-functional siloxane (cf. reactions 1 and 2, Table 19, with reaction 3, Table 19). It is hypothesized that when the dimer is used in the interfacial reaction (no pre-step), it does not react because it is easily extracted into the basic aqueous phase. If this is indeed the case, then the fact that it does react when the pre-step is utilized suggests that the "dimer" was not in an extractable form when the aqueous phase was added, and must have been in the form of one of the intermediates proposed earlier. Reactions performed with the siloxane oligomer using the "pre-phosgenation" step showed definite improvements in both molecular weights and copolymer compositions (ideal copolymer composition is 100% of the theoretical amount of siloxane incorporated into the copolymer) in all cases investigated (see Table 19).

To insure that the ester bond was indeed forming in the interfacial copolymerizations, both ^{13}C NMR and infrared spectra were run on the copolymers and compared with the analogous spectra of the following,



$$\left[HOOC-(CH_2)_3-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{Si}}}}-\right]_2 O$$

32

Table 19: Interfacial Polycarbonate/Polydimethylsiloxane Copolymers: Investigation of the Effect of Using a "Pre-phosgenation" Step.

	"Pre-phosgenation Step"	(a) PSX	Phosgene Flow Rate (cc/min.)	pH	(b) $(Et)_4\overset{+}{N}\overset{-}{Cl}$ Conc.	$[\eta]^{25°C}_{THF}$	(e) % of Theoretical PSX Incorporated into the Polymer
1.	No	Dimer	120-140	9-10	40%	0.68	15%
2.	No	Dimer	40-48	11-12	40%	----	33%
3.	Yes	Dimer	40-58	11-12	40%	----	95%
4.	No	(d) Oligomer	40-58	9-10	40%	0.29	76%
5.	No	Oligomer	40-58	9-10	40%	0.28	92%
6.	Yes	Oligomer	40-58	9-10	40%	0.50	94%
7.	No	Oligomer	40-58	11-12	20%	0.56	90%
8.	Yes	Oligomer	40-58	11-12	20%	0.67	93%
9. (c)	No	Oligomer	40-58	11-12	20%	0.28	85%
10. (c)	Yes	Oligomer	40-58	11-12	20%	0.67	93%

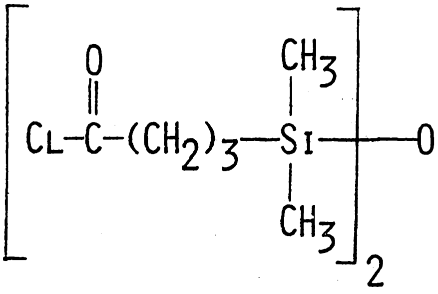
(a) PSX = polydimthylsiloxane

(b) Mole percent based on moles bisphenol-A

(c) KOH was used as the base, NaOH was used in all other cases

(d) <Mn> of all oligomers ≈ 2000g/mole

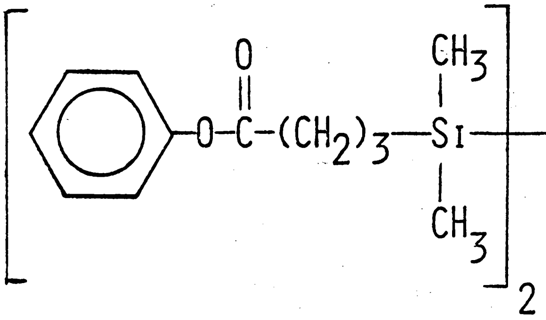
(e) 100 % would result in 50% of polysiloxane by weight in the copolymer



$$\left[\mathrm{Cl{-}\overset{O}{\overset{\|}{C}}{-}(CH_2)_3{-}\underset{CH_3}{\overset{CH_3}{Si}}}\right]_2{-}\mathrm{O}$$

(IR ONLY)

38



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and of a polycarbonate homopolymer. The carbonyl region of the infrared spectra of the model compounds shows a progression of an absorption at ∿1803 cm^{-1} for the acid chloride (this compound was not isolated, its IR spectrum also contains acid starting material) to ∿1767 cm^{-1} for the phenyl ester (see Figure 25). Unfortunately, the polycarbonate carbonyl absorption occurs at ∿1771 cm^{-1} (see Figure 26), so close to the ester absorption that resolution of the two peaks in the copolymer (see Figure 26) is difficult. The progression of the absorptions shown in the model compounds together with the fact that the boiling point of the diester very closely matched the previous literature value (175°C at 0.2 mm as compared to 190°C at 0.3 mm (236) did however confirm the ester

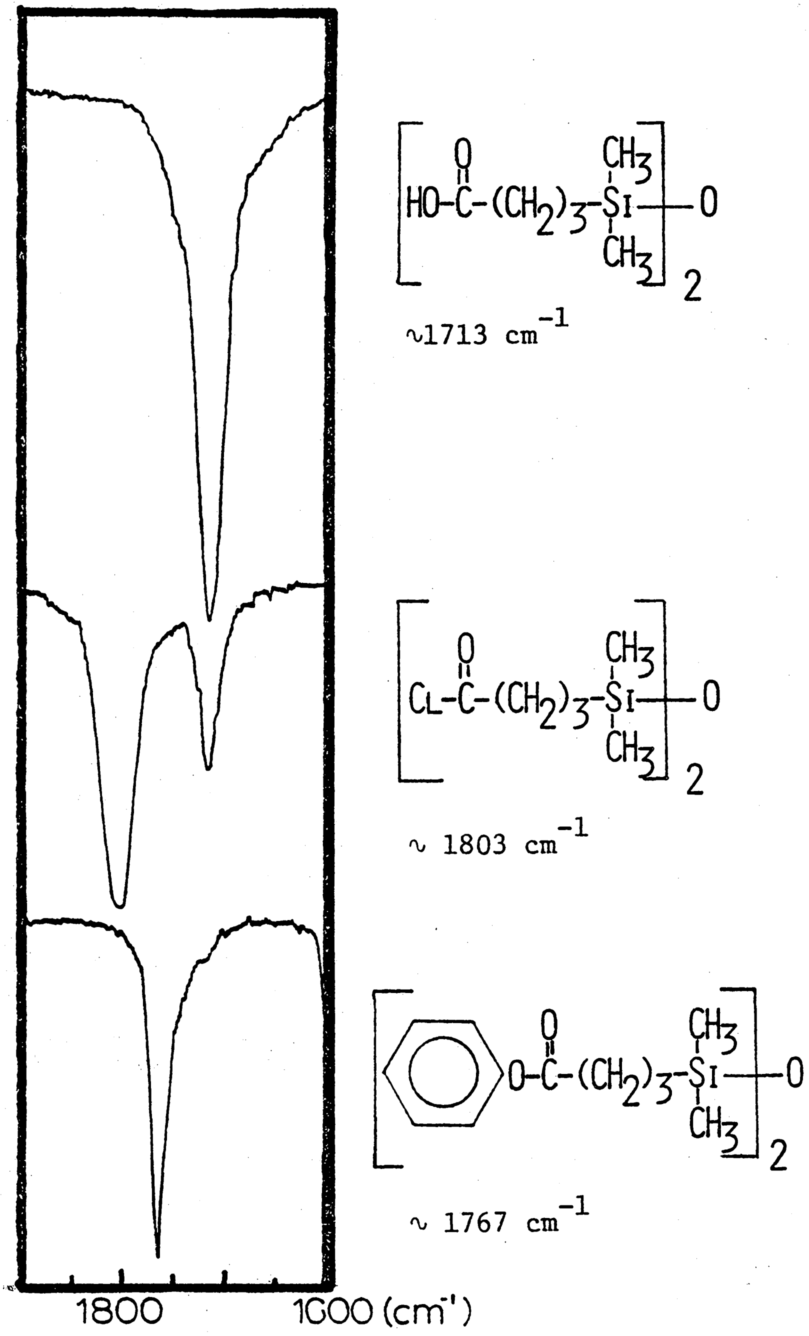


Figure 25: Model Compound Infrared Spectra Showing the Progression of the Carbonyl Absorbance Band as the Diphenyl Ester of 1,3-Carboxypropyltetramethyldisiloxane is Produced

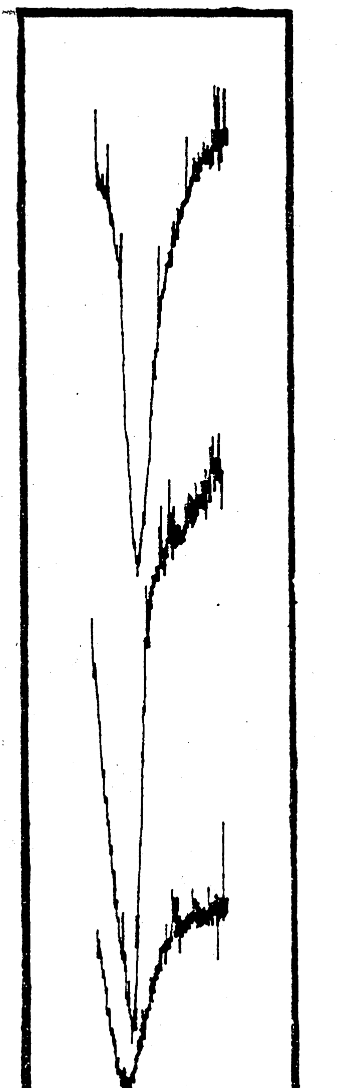
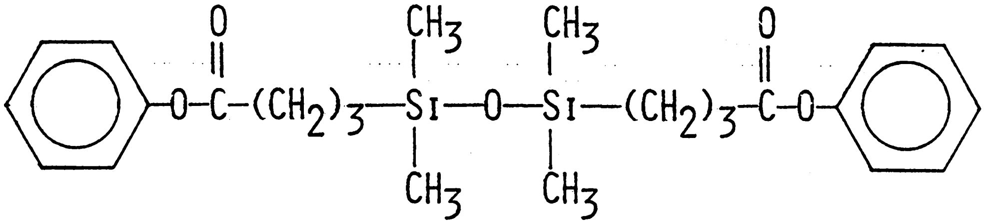


Figure 26: Comparison of the Carbonyl Region of the Infrared Spectra of Model Compounds with a Polycarbonate/Polydimethylsiloxane Copolymer Top: The diphenyl ester of 1,3-Carboxypropyltetramethyldisiloxane, ∿1767 cm^{-1}. Middle: Homopolycarbonate, ∿1771 cm^{-1}. Bottom: Polycarbonate/Polysiloxane Copolymer Containing Both the Carbonate and the Ester Bond.

structure below,



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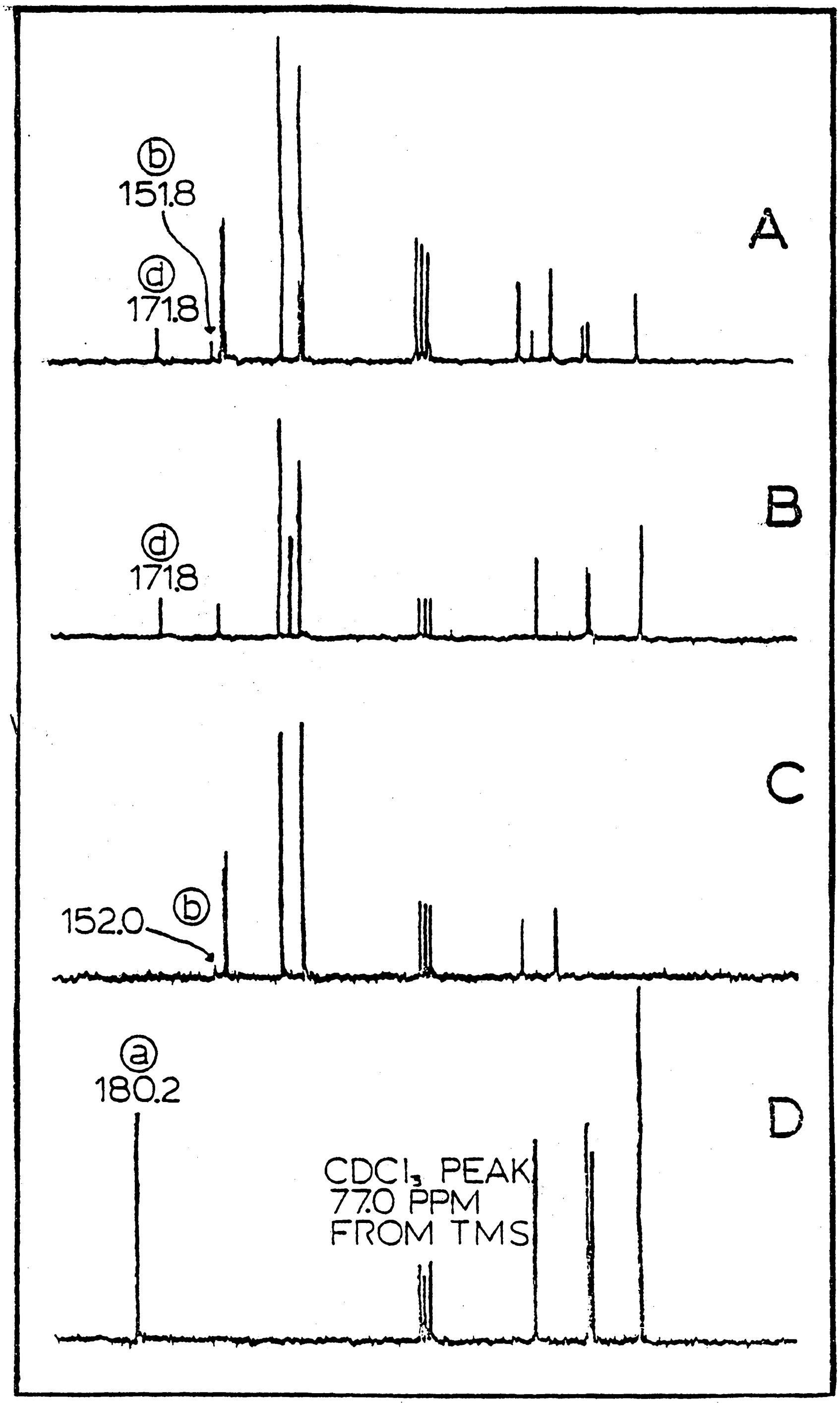
and, hence, provided a model ester for ^{13}C NMR analysis.

The diphenyl ester, a copolymer structurally analogous to the interfacial copolymer discussed herein but produced in an anhydrous medium (dichloromethane/pyridine) and a copolymer produced in the interfacial reaction all exhibit ^{13}C NMR (see Figure 27) ester carbonyl resonances at 171.8 ppm from TMS. The carbonyl resonances due to the polycarbonate and to the acid terminated polysiloxane (see Figure 27) are all well resolved from the ester region.

Upon expansion of the abscissa scale of the ∿140-180 ppm (from TMS) region of the copolymer, several small unidentified peaks in the ∿147-149 ppm (from TMS) region (see Figure 28) became apparent. This is the region in which the aromatic carbon next to the carbonate group and the aromatic carbon adjacent to the isopropylidene group in the bisphenol-A polycarbonate homopolymer resonate. It seems probable that the unidentified peaks are due to random copolymer sequence distributions but the proximity of this area in the spectrum to the carbonate carbonyl region means that the possibility of residual mixed carbonic-carboxylic anhydrides (not visible in the infrared spectra) cannot yet be ruled out.

Figure 27: Comparison of ^{13}C NMR Spectra of Model Compounds With a Polycarbonate/Polydimethylsiloxane Copolymer
Carbonyl Carbon Assignments:
A: Copolymer Spectrum, b = carbonate carbon, d = ester carbon
B: Diphenyl ester of 1,3-carboxypropyltetramethyldisiloxane, d = ester carbon
C: Homopolycarbonate, b = carbonate carbon
D: 1,3-carboxypropyltetramethyldisiloxane, a = carboxylic acid carbon


ⓑ
151.8
ⓓ
171.8
A
ⓓ
171.8
B
152.0
ⓑ
C
ⓐ
180.2
D
CDCl$_3$ PEAK
77.0 PPM
FROM TMS

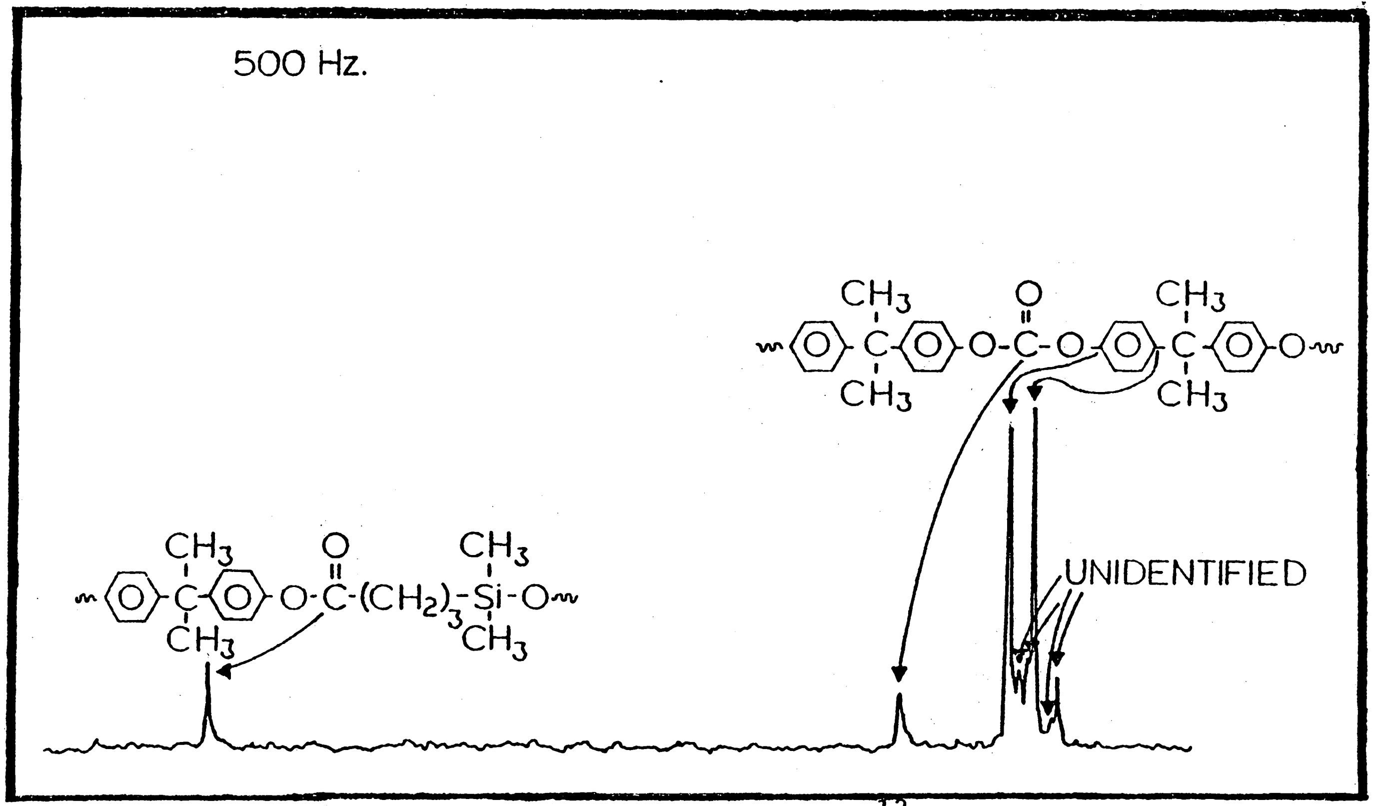


Figure 28: Expansion of the Carbonyl Region of the ^{13}C NMR Spectrum of Polycarbonate/Polysiloxane Copolymer Containing Both Carbonate and Ester Links

Carboxylic anhydrides normally appear ∿10 ppm upfield from the resonance of their parent acid (242). The fact that the unidentified peaks all appear ∿30 ppm from the acid peak suggests that, although carboxylic anhydrides may form via several pathways (see equations 44, route 2, 45a, route 2, and 45b, route 2), they apparently cannot survive the conditions of the reaction.

In conclusion, if copolymerization is indeed benefited by an excess of aryl chloroformate groups as our results imply, then this suggests that the reaction pathway proceeding through the mixed carbonic-carboxylic anhydride **27** to the ester (equation 44, route 3) is operative to some extent. Likewise, the fact that higher molecular weight copolymers (and with improved incorporation of the siloxane component) are formed when the "pre-phosgenation" step is added, implies that one or more of the pathways to the ester shown in equation 45 (equation 45a, route 3, and/or 45b, route 3) are also viable. The potential extent to which the interfacial copolymerization can be guided through a particular mechanism is not yet clearly understood. Copolymers with reasonably high molecular weights ($[\eta]$ = 0.6-0.7), good incorporation of the siloxane, and with good film properties can however, be produced via utilization of the "pre-phosgenation" step and the reaction conditions suggested in the experimental sections herein. Infrared and ^{13}C NMR specra confirm the copolymer structure with the presence of the desired ester link between the block types. The hydrolytic stability and surface composition of films of these block copolymers relative to those of the solution-synthesized perfectly alternating block copolymers containing the Si-O-C link between blocks will be the subject of future papers.

Chapter VI

SUMMARY

Basically, two methods for the preparation of bisphenol-A polycarbonate/polydimethylsiloxane multi-block or segmented copolymers have been investigated. One involves the "silylamine reaction" of a preformed dimethylamine terminated siloxane with a preformed polycarbonate oligomer to form well defined, perfectly alternating block copolymers. This is a clean, extremely efficient reaction which can be utilized to produce polymers of a variety of block sizes ranging from dimeric to approximately 25,000-30,000 g /mole. It does, however, incorporate the relatively hydrolytically unstable $\mathrm{Si}\overset{\diagup \mathrm{O} \diagdown}{\quad}\mathrm{C}$ moiety as the link between the block structures. A facile, novel method for preparation of the polycarbonate, oligomeric precursors of controlled molecular weights for the silylamine reaction was also developed.

Thermal analysis of these perfectly alternating copolymers reveals their two-phase nature even at block molecular weights of as low as $\sim$2000 g/mole. Surface analysis of films of these polymers performed by X-ray photoelectron spectroscopy indicates preferential surface migration of the siloxane component in all cases studied. A method for estimating the percentage of the surface area sampled by ESCA which was comprised of siloxane was derived. The results indicated the particular importance of the siloxane block size in determining surface composition. Moreover, the siloxane surface rich features of these block copolymers were defined. The results are important to various areas such as biomaterials, composites, and possibly "drag reduction" phenomena.

The second synthetic method utilized a phase transfer catalyzed preparation of randomly coupled block copolymers. Preformed hydroxypropyl, hydroxybutyl, or carboxypropyl terminated siloxane oligomers were used whereas the polycarbonate blocks were produced in situ. These reactions, in general, were found to be less efficient than the silylamine reaction. However, promising results were obtained using the hydroxyl terminated oligomers in two types of cases: 1, when siloxanes of <Mn> ≃ 5000 g/mole were used, and 2, when the siloxane oligomers were capped with the dichloroformate of bisphenol-A prior to the interfacial step. When these phase transfer catalyzed reactions were conducted in the presence of the carboxyfunctional siloxanes, high molecular weight well defined copolymers could be obtained when an anhydrous pre-phosgenation step was utilized. By contrast to the perfectly alternating copolymer systems, these randomly coupled block copolymers do not contain $\mathrm{Si}\overset{\mathrm{O}}{\diagup\,\diagdown}\mathrm{C}$ bonds, but rather are linked by Si-C bonds.

A new approach to the synthesis of the hydroxy and carboxy terminated siloxanes used for the interfacial reactions was developed. It used trifluoroacetic acid in high concentration to effect the polymerization. However, further characterization of the ring-chain equilibria involved in these systems is warranted.

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SYNTHESIS AND CHARACTERIZATION OF
POLYCARBONATE-POLYDIMETHYLSILOXANE
BLOCK COPOLYMERS

by

Judy S. Riffle

(ABSTRACT)

Two methods for the preparation of bisphenol-A polycarbonate-polydimethylsiloxane multi-block or segmented copolymers have been investigated.

The first is a solution reaction which utilized the interaction of a preformed, α,ω-dimethylamino terminated polydimethylsiloxane with a preformed, α,ω-hydroxyl terminated polycarbonate. This synthesis produces perfectly alternating block copolymers wherein the block molecular weights are equal to the number average molecular weights of the respective well characterized oligomeric precursors. This silylamine-hydroxyl reaction is clean, efficient and can be utilized to produce copolymers which consist of a variety of block sizes ranging from approximately dimeric to 25,000-30,000 g/mole. Intrinsic viscosities of 1.0 dℓ/g are easily attained and mechanical properties range from being elastomeric to rigid depending on the overall bulk composition. However, these copolymers do incorporate the relatively hydrolytically unstable $\mathrm{Si}^{\diagup \mathrm{O} \diagdown}\mathrm{C}$ moiety as the link between the block structures.

Thermal analysis of these perfectly alternating block copolymers

reveals their two-phase nature even at block molecular weights as low as ∿ 2000 g/mole. Surface analysis of the copolymer films performed by X-ray photoelectron spectroscopy (known as ESCA) indicates preferential surface migration of the siloxane component in all cases studied. In addition, preliminary ESCA studies of blends of these materials with a commercial polycarbonate homopolymer show siloxane on the surface even when bulk percentage of siloxane is as low as 0.05 wt.%. A method for estimating the percentage of the surface area sampled by ESCA which is comprised of siloxane was developed. Results derived from this procedure indicate the particular importance of the siloxane block size in determining surface composition.

The second synthetic method investigated was a phase transfer catalyzed reaction which produced a more randomly coupled block copolymer. Preformed hydroxypropyl, hydroxybutyl, or carboxypropyl terminated siloxane oligomers were used whereas the polycarbonate blocks were produced in situ. These reactions, in general, were found to be less efficient than the "silylamine reaction." However, promising results were obtained using the hydroxyl terminated siloxanes in two cases: 1, when siloxanes of $\langle M_n \rangle \simeq 5000$ g/mole were used and, 2, when the siloxane oligomers were capped with the dichloroformate of bisphenol-A prior to the interfacial step. When these phase transfer catalyzed reactions were carried out utilizing the carboxyfunctional oligomeric siloxanes, reasonably high molecular weight copolymers could be obtained. The best results were achieved when an anhydrous "prephosgenation" step was utilized. In contrast to the perfectly alternating copolymer systems previously described, these randomly coupled block copolymers contain the ≡Si-C≡ bond which may be preferable in some applications (e.g. biomaterials).

One problem which must be addressed for the synthesis of block copolymers derived from preformed oligomers is the separate synthesis of those oligomers. The techniques for the preparation of hydroxybutyl and carboxypropyl terminated siloxane oligomers were developed in this research. Moreover, a novel, facile method for the production of polycarbonate oligomers of well controlled number average molecular weights was also devised. This procedure involves monofunctional capping of a calculated fraction of the phenolic endgroups prior to oligomerization by the direct phosgenation route. The hydroxyl endgroups can then be regenerated by selective hydrolysis of the protecting groups. Trimethylsilyl chloride, trifluoroacetic acid and trifluoroacetic anhydride were shown to be suitable capping reagents.

Additional information pertaining to the physical characteristics of these novel copolymers was derived from collaborative studies with other colleagues at this university and at the University of Akron.