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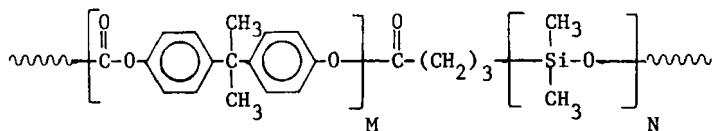
Interfacial Synthesis Part II: Phase-Transfer Catalyzed Synthesis of Polycarbonate/Polysiloxane Block Copolymers

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ABSTRACT

A phase transfer catalyzed (PTC) method for the preparation of bisphenol-A polycarbonate/polydimethylsiloxane multi-block or segmented copolymers of the structure shown below has been investigated.

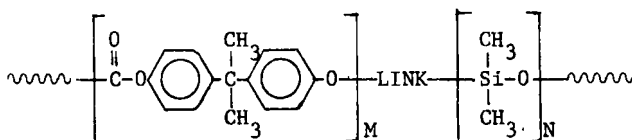


The synthesis route involves the reaction of a preformed carboxypropyl-terminated polydimethylsiloxane oligomer of various molecular weights with bisphenol-A, base, phosgene, and the PTC. The final copolymer contains a direct $\equiv\text{Si}-\text{C}-$ link between the block structures as compared to the relatively hydrolytically unstable $\equiv\text{Si}-\text{O}-\text{C}$ bond discussed previously by the authors and others. A phosgenation "pre-step" to the interfacial reaction was found to be desirable. This procedure involves bubbling phosgene through an anhydrous concentrated solution of the carboxypropyl-terminated polydimethylsiloxane in methylene chloride. Subsequently, a two-phase $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$ reaction medium with the phase transfer catalyst is employed in the interfacial step. The phosgenation pre-step

is believed to enhance the conversion of carboxyl to acid chloride, which then promotes the efficient incorporation of the polysiloxane into the copolymer. Moreover, anhydride linkages along the chain are reduced to undetectable levels. The copolymers could be of interest as thermoplastic elastomers, elastoplastics, or biomaterials.

INTRODUCTION

Thermoplastic elastomers based on polycarbonate-polysiloxane block copolymers display some intrinsic properties which may be of interest as biomaterials [1]. The generalized structure of these copolymers is shown below.



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 [2-4] and elsewhere [1,5-7] demonstrate that the subject block copolymers and related structures easily undergo a microphase separation above segment molecular weight 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 [7-10]. Quantification of this immiscibility has been probed by inverse gas chromatography [11,12]. Moreover, in polystyrene-polydimethylsiloxane block copolymer systems [13-15], in our preliminary work [2,16] and earlier work by Gaines and LeGrand [17] it was demonstrated that

the polydimethylsiloxane component migrates to the surface of films of these materials in preference to the other block.

This phenomenon was attributed [13-16] 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 [18]. The fact that surfaces of the films of these copolymers could be tailored to be composed predominantly of siloxane [2,3] suggested that the surface and, hence, the materials, could be tailored to be biologically "compatible" in the sense defined earlier.

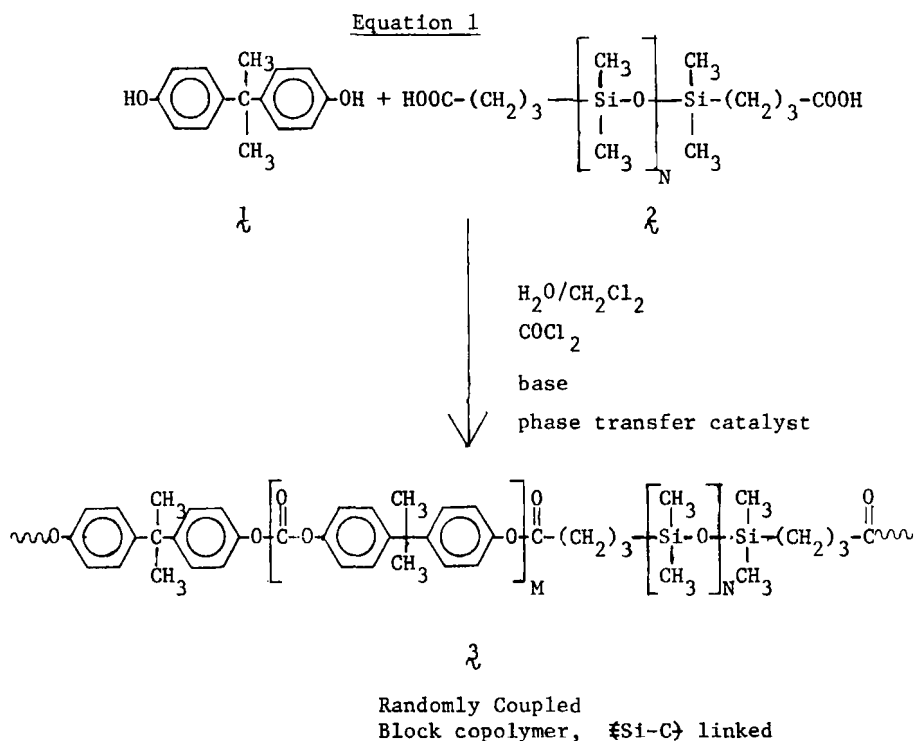
In view of the requirement for good hydrolytic stability, block copolymers with two different types of bonds between the block structures have been investigated.

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

The relative hydrolytic stabilities of the $\equiv\text{Si-O-C}$ bond versus the $\equiv\text{Si-C}$ bond in some siloxane copolymers has been extensively studied and it is generally agreed that the $\equiv\text{Si-C}$ bond is much better, even though the $\equiv\text{Si-O-C}$ bond [18] is the link of choice when thermal stability is required. However, Noshay et al. [1,19] demonstrated that perfectly alternating block copolymers composed of poly(aryl ethers) or poly(aryl esters) and siloxanes were remarkably resistant to hydrolysis. This was thought [19] to be due to the hydrophobic siloxane nature and the relatively few links between blocks. Consequently, there is some reason to doubt whether the presence of $\equiv\text{Si-O-C}$ links between blocks in the strictly alternating $\langle\text{A-B}\rangle_N$ block copolymer architecture would detract from hydrolytic stability. In order to further assess these questions, materials were prepared in this study which consisted of both perfectly alternating block copolymers containing the $\equiv\text{Si-O-C}$ and also, randomly coupled block copolymers containing the direct $\equiv\text{Si-C}$ bond between the blocks.

Perfectly alternating block copolymers were prepared essentially by Noshay and Matzner's procedure [1] in refluxing chlorobenzene solution by reacting preformed dimethylamine-terminated polydimethylsiloxane and hydroxyl-terminated polycarbonate oligomers. Two series of copolymers produced via this method are briefly discussed herein. Both copolymer composition at constant block length and block lengths at given compositions were investigated.

The preparation of copolymers bearing the direct Si-C bond between the blocks has proven to be quite challenging. The general synthetic route utilized a preformed carboxypropyl-terminated polydimethylsiloxane and in situ generated polycarbonate segments as schematically shown in equation 1.



Note that the reaction of two moles bisphenol-A with one mole of phosgene yields a carbonate ($-\text{O}-\overset{\text{O}}{\text{C}}-\text{O}-$) link. On the other hand,

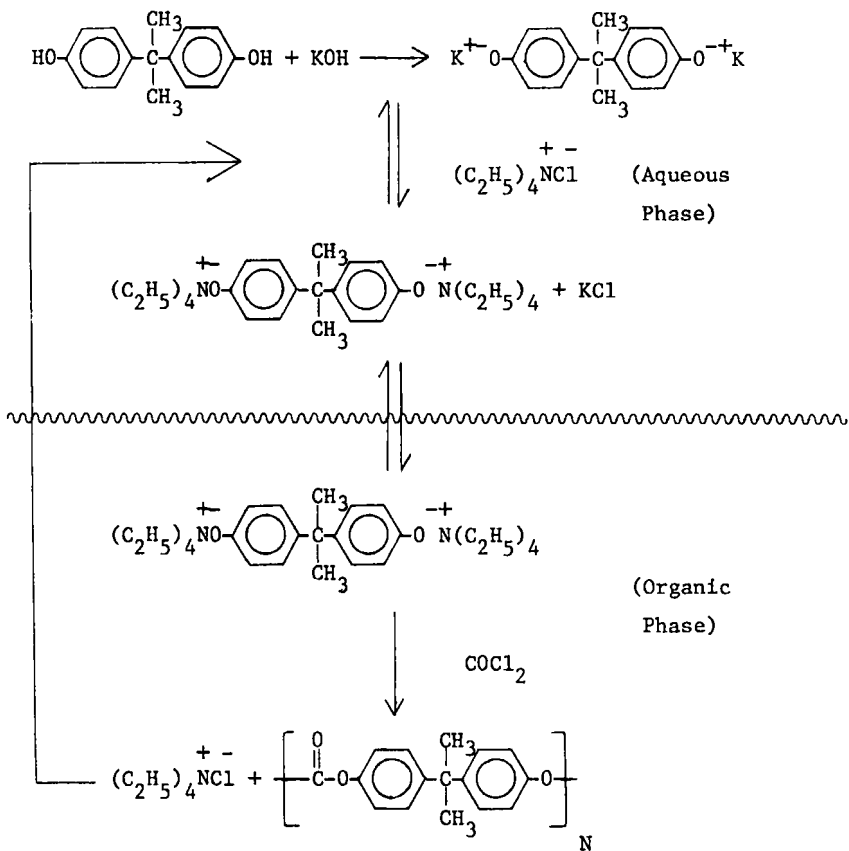
the corresponding reaction of one mole bisphenol-A, one mole of acid-terminated polysiloxane oligomer, and one mole of phosgene is shown producing an ester ($-\overset{\text{O}}{\text{C}}-\text{O}-$) bond between the terminal carboxypropylsiloxane and the bisphenol. Both solution and interfacial (or 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 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 main thrust of this paper is the development of procedures and the results obtained using the interfacial method for preparation of the randomly coupled block copolymers. The perfectly alternating copolymers are discussed in detail elsewhere [4].

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 [20-26]. 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 illustrated for the specific case of the polycarbonate homopolymer is reviewed in equation 2. The synthesis is well known to be both rapid, facile and insensitive to minor variations in reaction conditions. However, the addition of a pre-formed, acid-terminated polydimethylsiloxane oligomer to the system produced numerous complications and necessitates a much more defined set of reaction parameters.

The phase transfer process envisioned as being operative in the formation of these polycarbonate/polysiloxane random block

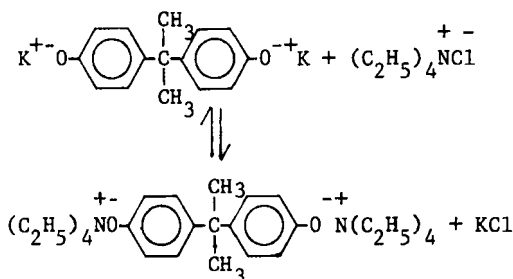
Equation 2



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 3). 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

Equation 3



moves into the organic phase, the highly reactive salt is brought into contact with both phosgene and the acid-terminated polydimethylsiloxane oligomers and may react to form the copolymer (equation 4). The by-product of equation 4, which is the original phase transfer catalyst, is then transferred back to the aqueous phase which completes the catalytic cycle.

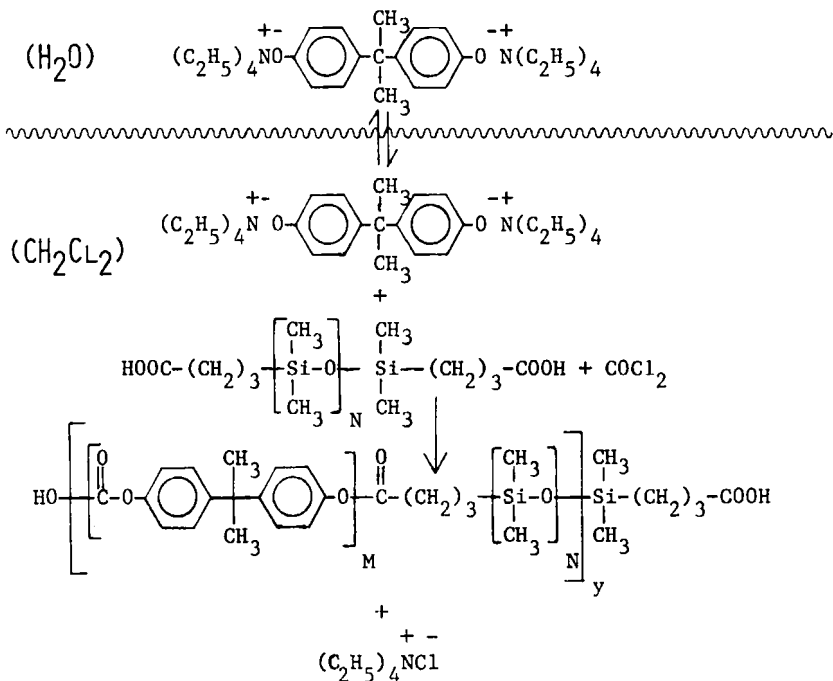
The preparation of bisphenol-A polycarbonate homopolymer via such a mechanism can be complicated by the fact that polymerization within the organic phase proceeds via a two-step reaction (equation 5).

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 $k_1 \gg k_2$, can be controlled via adjustment of a number of reaction parameters.

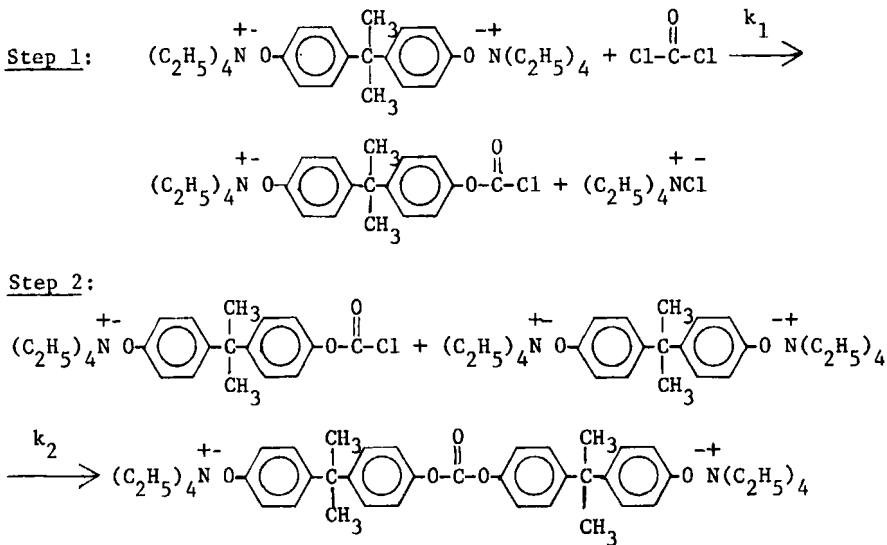
The reaction of the carboxylic acid-terminated siloxane to form an ester bond in the reaction scheme adds at least one (and possibly more) series of steps to the overall reaction. Although the mechanistic pathways have not been clearly established, two plausible routes to ester formation are envisioned (equations 6, and 7a and 7b).

Mixed carbonic-carboxylic anhydrides of the type illustrated in equations 6, 7a and 7b (A) are known to decompose under anhy-

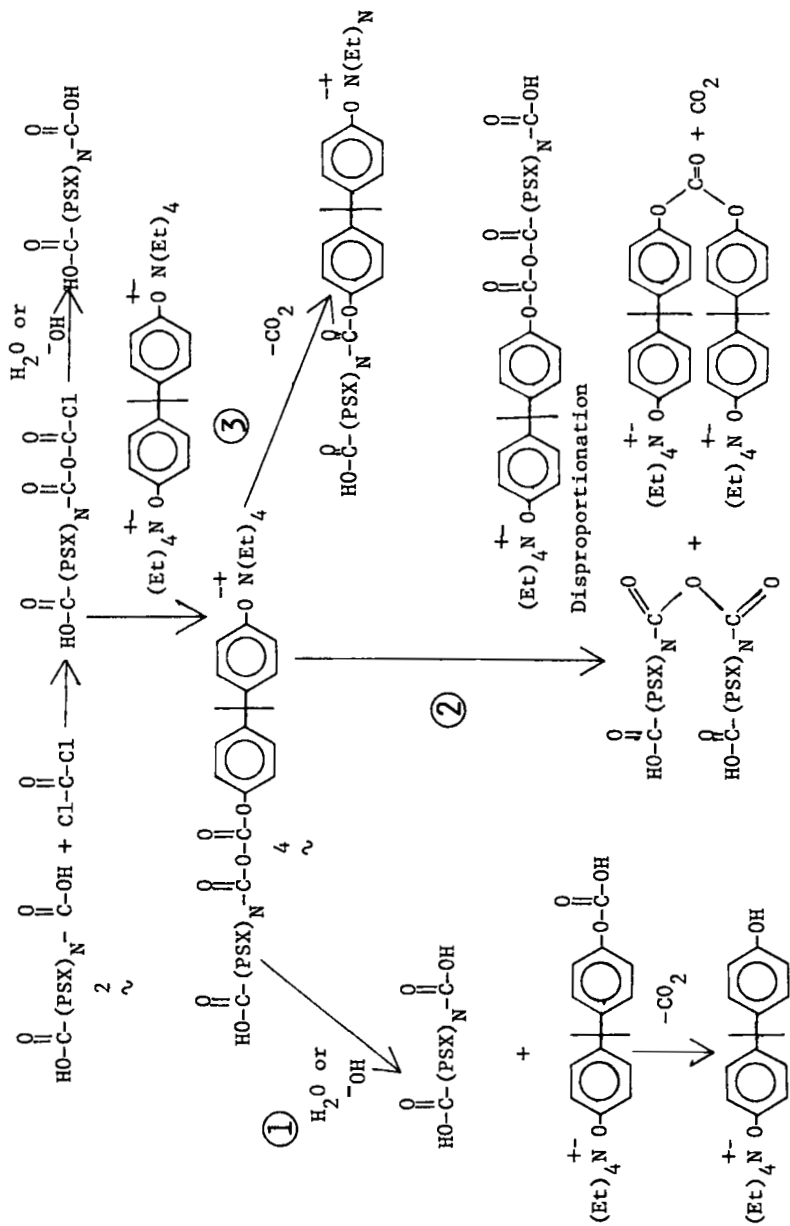
Equation 4



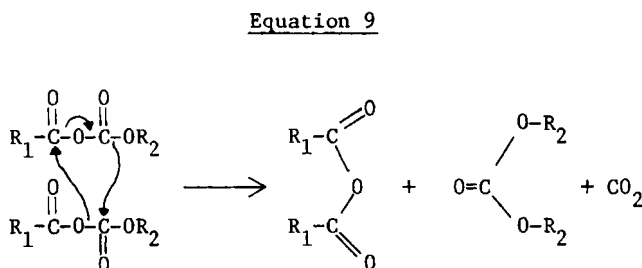
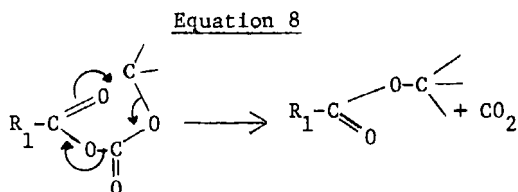
Equation 5



Equation 7b



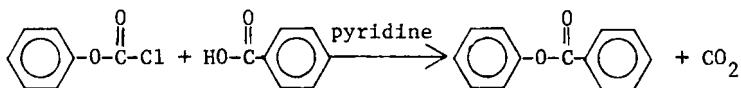
drous conditions via pathways analogous to 2 and 3 in both equations 6 and 7b [27-30]. Proposed mechanisms for these decompositions[30] are given in equations 8 and 9.



The relative proportions of the two pathways occurring have been determined[30] 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 paper) 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. [31] supported the pathway to the ester shown in equation 6, route 3 as opposed to that given in equation 7a, 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 10).

Equation 10



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 ($\text{R}-\text{C}(=\text{O})-\text{O}-\text{C}(=\text{O})-\text{Cl}$), and 2) no evidence of carboxylic anhydrides was found in the infrared spectra of the products. While Goldberg's evidence does provide support for the feasibility of the pathway shown in equation 6, route 3, it would appear to not preclude the possibility of alternate routes. For example, some reactions not considered could be occurring simultaneously (ie. equation 7b, 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. [32] 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.

EXPERIMENTAL

α,ω - carboxypropyl-terminated polydimethylsiloxane oligomers (2) of controlled number average molecular weights were produced in our laboratory via a siloxane redistribution reaction. Details of the synthetic procedure and analytical aspects will be provided

separately [33]. However, a typical synthesis is briefly described below.

Preparation of Carboxypropyl-Terminated Polydimethylsiloxane Oligomers:

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 $\langle Mn \rangle$ desired. Typically, trifluoroacetic acid (~ 0.013 moles per 0.024 moles starting material) was added at 60°C for 24 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. Traces of residual cyclics can be assessed by liquid chromatography, GLC, or TGA. The progress of the redistribution of the carboxypropyl-terminated siloxane was followed by gel permeation chromatography (Waters 6000-A pump, Waters R-400 D.R.I. detector, micro-styragel columns - 500 Å, 10^3 Å, 10^4 Å, 10^5 Å, toluene solvent). Molecular weights, $\langle Mn \rangle$, of these oligomers were assessed via potentiometric

titration in isopropanol with an isopropanolic potassium hydroxide titrant [33].

The development of the synthetic procedures for the randomly placed block copolymers required that a number of bisphenol-A polycarbonate homopolymers be produced under different phosgene flow rates and catalyst concentrations. The apparatus for these reactions is identical to that used for the copolymerization (Figure 1). Typically, 7.5 gm 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

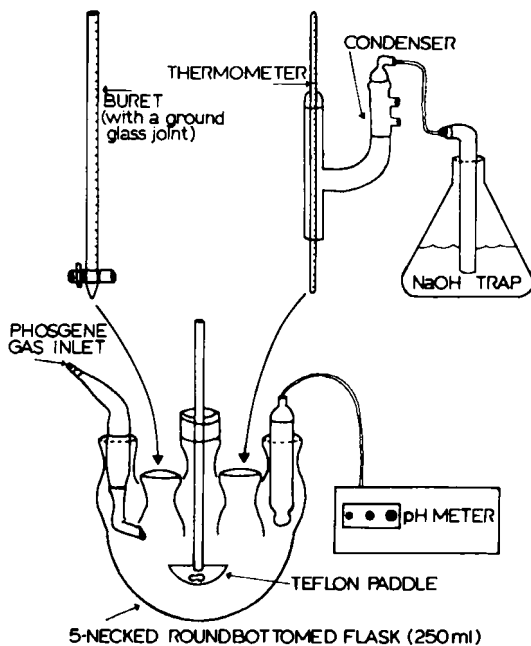


FIG. 1. Copolymerization apparatus

added throughout the 30 minutes of phosgene addition. This allowed the pH to be maintained between 11-12.

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

Preparation of Randomly Placed 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 ~ 40 ml dichloromethane were charged to the reaction vessel. The system was dehydrated via distillation of ~ 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

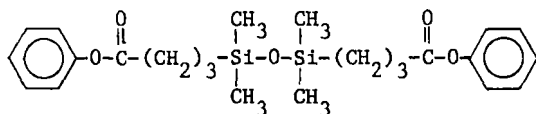
Bisphenol-A (7.5g) and a stoichiometric amount of potassium hydroxide (2 moles KOH per mole bisphenol-A) were charged to the reaction vessel and dissolved in 75 ml water. Tetraethylammonium chloride catalyst (1.1g, 20 mole percent based on moles of bisphenol-A) was added to the mixture. The siloxane/dichloromethane

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 addition 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.

Copolymers and bisphenol-A polycarbonate homopolymers were analyzed for intrinsic viscosity at 25°C in tetrahydrofuran. Values given in the tables are reported in deciliters per gram.

Copolymer compositional analyses were performed using high resolution proton NMR spectroscopy (Varian EM-390 spectrometer) via comparison of the areas of the aromatic and silicon methyl peaks (see Fig. 2). The precision of the compositional analysis was estimated to be $\pm 1.0\%$.

Copolymer fine structure 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. The diphenyl ester of 1,3-carboxypropyltetramethyldisiloxane (ζ) was prepared as a model compound in a manner closely paralleling that of Mulvaney and Marvel. [34]



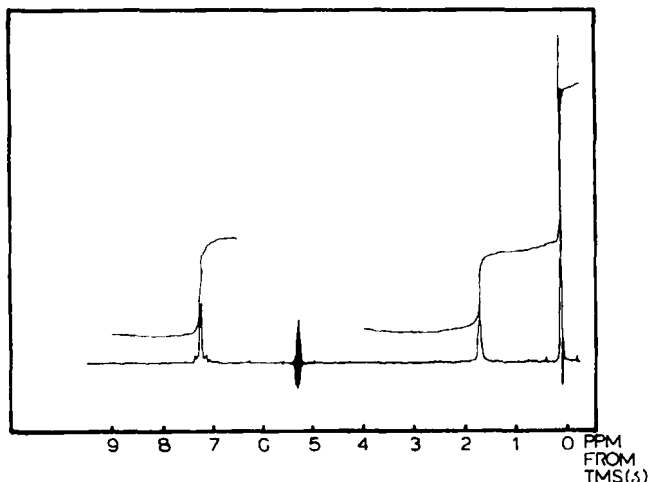
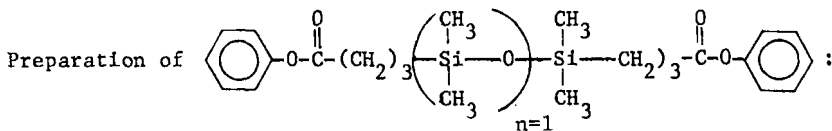


FIG. 2. Proton NMR spectrum of a randomly coupled polycarbonate/polydimethylsiloxane copolymer

Assignments: ~ 0.17 P.P.M. - Silicon Bonded Methyls
 ~ 1.75 P.P.M. - Bisphenol-A Methyls
 $\sim 7.1 - 7.4$ P.P.M. - Aromatic Protons
 ~ 5.30 P.P.M. Methylene Chloride
 (Lock Signal and Reference)



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-carboxypropyltetramethylsiloxane (11 grams) and thionyl chloride (50 ml) were charged to the reaction vessel and refluxed for 2.5 hours to produce 1,3-propionyltetramethylsiloxane. 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).

RESULTS AND DISCUSSION

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. 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 1, #1-3). These values are seemingly high, but were based on some earlier work by Morgan, et al.[35,36]. 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

TABLE 1. Interfacial Polycarbonates: Investigation of the Effect of Catalyst Concentration and Phosgene Flow Rate

Phosgene Flow Rate (cc/min.)	pH	Reaction Time	(a) $(Et)_4NCl$ + -	25°C [η] (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 $(Et)_4NCl$ per mole bisphenol.

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 of a large excess of phosgene should also enhance the effect. Results of reactions run with a high phosgene gas flow rate (see Table 1) 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 homo-

polymers (cf. No. 2 and No. 4, Table 1). After one hour of reaction, a moderate portion of the theoretical amount of siloxane (90% and 85%, respectively - see Table 2) had been incorporated into both copolymers, but only relatively low molecular weights were obtained. These results suggested a difficulty in the incorporation of the acid-terminated siloxane oligomer.

If the mechanism shown in equation 6 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 7 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 1 were postulated to have produced a nearly exclusive aryl chloroformate endgroup. It appears reasonable that if the above is true, then parameters used for reaction 5, Table 1 (same as for reaction 3, Table 1 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 1 were encouraging (see Table 2, 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 7 might be favored. In this case, an anhydrous "pre-phosgenation" step was used. This consisted of bubbling an excess of phosgene through a dichloromethane solution

Table 2. 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) $(Et)_4NCl$ Conc.		25°C [η] THF		(b) % of Theoretical PSX Incorporated into the Copolymer		
	1 hr.	3 hrs.	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.

of the siloxane oligomer prior to the interfacial reaction. It was anticipated and then confirmed that one or more of the possible intermediates, $\text{HO}-\overset{\text{O}}{\parallel}{\text{C}}-(\text{PSX})_N-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{Cl}$ and/or $\text{HO}-\overset{\text{O}}{\parallel}{\text{C}}-(\text{PSX})_N-\overset{\text{O}}{\parallel}{\text{C}}-\text{Cl}$, 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 3). 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 3, with reaction 3, Table 3). 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 3).

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,

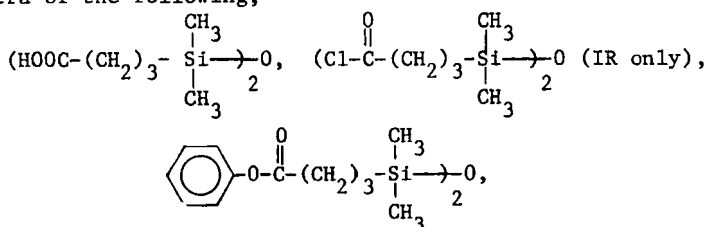


Table 3. Interfacial Polycarbonate/Polydimethylsiloxane Copolymers: Investigation of the Effect of Using a "Pre-phosgenation" Step.

"Pre-phosgenation Step"	Phosgene Flow Rate (cc/min.)	pH	(b)		[η] ^{25°C} THF	(e) % of Theoretical PSX Incorporated into the Polymer
			PSX	(Et) ₄ NCl Conc.		
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 = polydimethylsiloxane

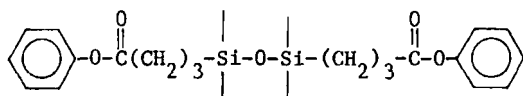
(b) Mole percent based on moles bisphenol-A

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

(d) $\langle Mn \rangle$ of all oligomers = 2000g/mole

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

and of a polycarbonate homopolymer. The carbonyl region of the infrared spectra of the model compounds shows a progression of an absorption at $\sim 1713 \text{ cm}^{-1}$ for the carboxylic acid group to $\sim 1803 \text{ cm}^{-1}$ for the acid chloride (this compound was not isolated, its IR spectrum also contains acid starting material) to $\sim 1767 \text{ cm}^{-1}$ for the phenyl ester (see Fig. 3). Unfortunately, the polycarbonate carbonyl absorption occurs at $\sim 1771 \text{ cm}^{-1}$ (see Fig. 4), so close to the ester absorption that resolution of the two peaks in the copolymer (see Fig. 4) 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 [17]) did however confirm the ester structure below,



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 Fig. 5) ester carbonyl resonance at 171.8 ppm from TMS. The carbonyl resonances due to the polycarbonate and to the acid-terminated polysiloxane (see Fig. 5) 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 Fig. 6) 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

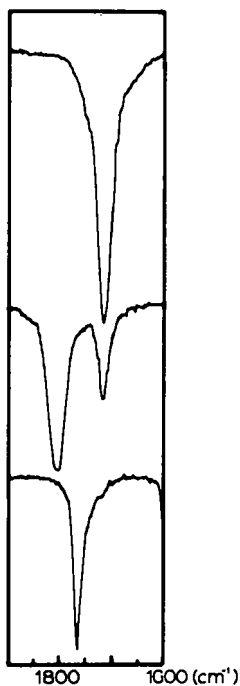
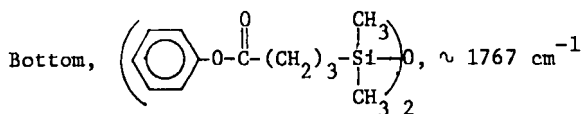
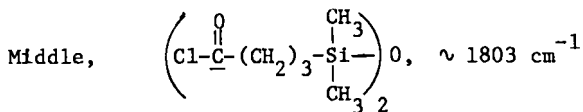
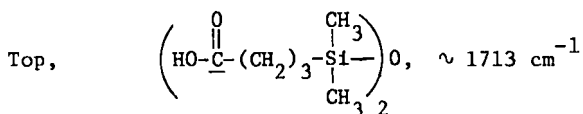


FIG. 3. Model compound infrared spectra showing the progression of the carbonyl absorbance band as the diphenyl ester of 1,3-carboxypropyltetramethyldisiloxane is produced

Assignments:



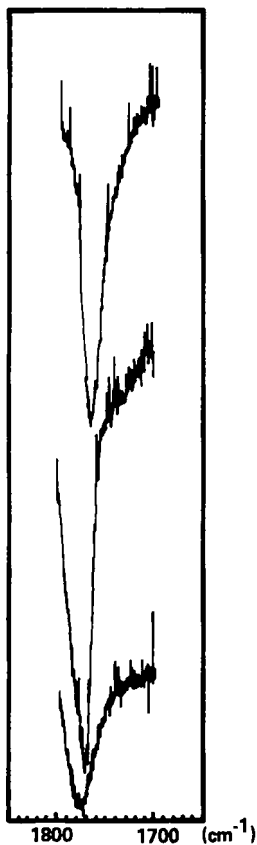


FIG. 4. Comparison of the carbonyl region of the infrared spectra of:

- Top: The diphenyl ester of 1,3-carboxypropyltetramethylsiloxane, $\sim 1767 \text{ cm}^{-1}$
- Middle: Homo-polycarbonate, $\sim 1771 \text{ cm}^{-1}$
- Bottom: Polycarbonate/polysiloxane copolymer containing both the carbonate and the ester bond

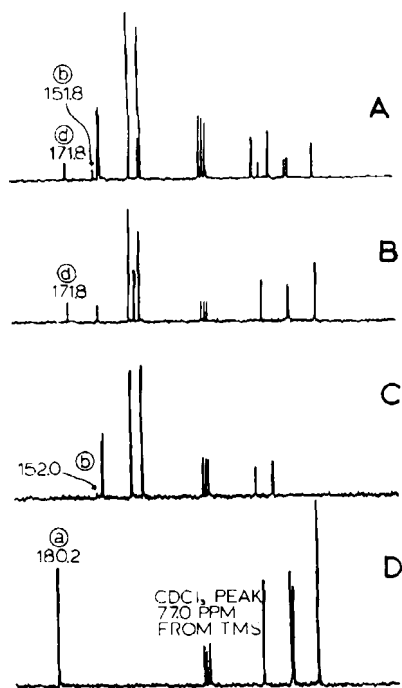


FIG. 5. Comparison of ^{13}C NMR spectra: (top to bottom)

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

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. Carboxylic anhydrides normally appear ~ 10 ppm upfield

500 Hz.

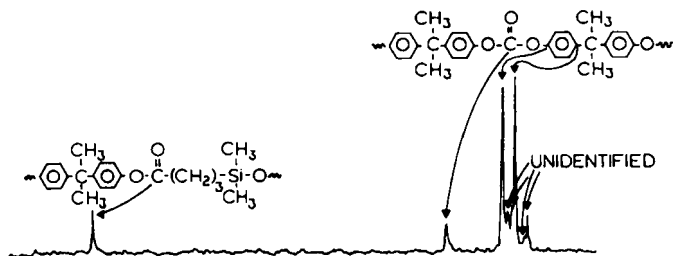


FIG. 6. Expansion of the carbonyl region of the ^{13}C NMR spectrum of polycarbonate/polysiloxane copolymer containing both carbonate and ester links

from the resonance of their parent acid [37]. 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 6, route 2, 7a, route 2, and 7b, 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 (4) to the ester (equation 6, 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 7 (equation 7a, route 3, and/or 7b, 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 spectra 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.

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