Synthesis and characterization of perfectly alternating polyorganosiloxane– polyarylester and –poly(aryl formal) block copolymers

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Passive damping has been defined as a key element in vibration control. It is believed that the approach to passive damping could be addressed through the use of carefully designed viscoelastic polymeric materials. This article describes the synthesis and characterization of multiphase, transparent block copolymers that are potential candidates for passive damping applications in large space structures. Well defined, perfectly alternating polyorganosiloxane–polyarylester block copolymers of relatively high molecular weight were prepared via a silylamine–hydroxyl condensation reaction, as were polyorganosiloxane–polyaryl formal block copolymers. Due to the high degree of incompatibility between the 'soft' siloxane segments and the 'hard' ester or formal segments in the block copolymers, a multiphase microstructure developed at relatively low block molecular weights. To vary the miscibility of the siloxane and ester phases, and in turn the physical properties of the block copolymers, the block molecular weights and the siloxane block compositions (dimethyl, dimethyl-co-diphenyl, or dimethyl-co-trifluoropropylmethyl) were controlled. Structure analysis by nuclear magnetic resonance (proton and silicon) and Fourier transform infra-red (*FT*i.r.) verified that the desired difunctional oligomers and block copolymers were successfully prepared. The influence of copolymer composition on physical properties was studied by thermal, mechanical and surface characterization techniques.

INTRODUCTION

The use of large precision space structures (LPSS) for navigation, weather forecasting and communications is significantly increasing. Inherent in LPSS is the need to define vibration control carefully since dimensional tolerances are very small. Passive damping has been identified as a key element in vibration control. Though it is believed that the approach to passive damping could be addressed through the use of carefully designed viscoelastic materials, little work has been done in this area[1,2].

In general, there are several properties that must be addressed in a material to be used for vibration control in LPSS. These include low creep, relatively low density, low outgassing characteristics, adequate mechanical properties and the ability to survive long term exposure in the space environment. One material that is suggested by the above requirements is siloxane modified polyarylesters. The aromatic polyesters, I, are a relatively new class of engineering thermoplastic with good mechanical properties:
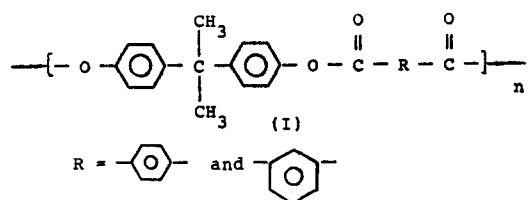

The Fries rearrangement of polyarylesters:
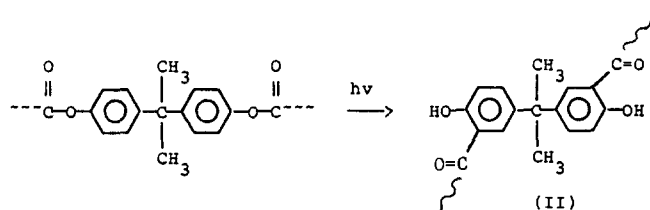
may possibly be used to dissipate absorbed ultraviolet energy from polymeric structures since it does not result in chain scission. Rather, it leads to the formation of an *ortho*-hydroxybenzophenone structure, II, that may further stabilize the polymer against photolytic degradation[3,4].

The incorporation of polyorganosiloxanes, III:
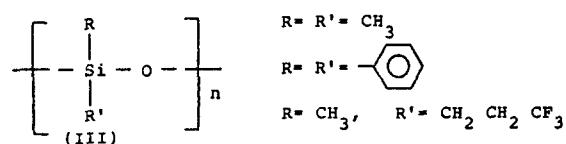
in these types of polyarylesters offers an opportunity for many improvements, such as lower temperatures for the ductile–brittle transitions and improved impact strength. The polysiloxanes display a unique combination of properties, which include low glass transition temperature, hydrophobicity, thermal stability, high gas permeability, a wide temperature use range and good ultraviolet and atomic oxygen resistance[6,7]. In addition, polysiloxanes

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have a lower surface energy than most other materials and, therefore, tend to predominate on the surface of materials, even if they are a component of a microphase separated copolymer system[8,9]. Thus siloxanes can be used for surface modification of engineering thermoplastics while retaining much of their bulk properties. Such surface modification may lead to improved lubricity and better resistance to atomic oxygen[10-12].

The synthesis and characterization of perfectly alternating block copolymers prepared from difunctional polysiloxane and polyarylester oligomers are discussed in this paper. Results are also presented on the synthesis and characterization of polyformals and polyformal-polysiloxane block copolymers.

EXPERIMENTAL

Materials and their purification

Octamethylcyclotetrasiloxane (D_4), octaphenylcyclotetrasiloxane (D_4'), and trifluoropropylmethylcyclotrisiloxane (F_3) were obtained from the Silicone Products Division of the General Electric Company. The low molecular weight bis(dimethylamino)polydimethylsiloxane oligomer was obtained from Petrarch Systems Inc. and used as a starting material for the synthesis of higher molecular weight, terminally reactive polyorganosiloxanes. The above silicon-containing starting materials were of high quality and used without further purification.

High purity polymer grade bisphenol-A and tetramethylbisphenol-A (TMBA) were obtained from the Dow Chemical Company and used without further purification. Reagent grade terephthaloyl chloride and isophthaloyl chloride were purchased from either Aldrich Chemical Company or Eastman Chemical Company. Purification of the acid chlorides was accomplished by recrystallization from hot hexanes.

General solvents and reagents were obtained from Fisher Scientific and typically distilled from calcium hydride and/or dried over molecular sieves.

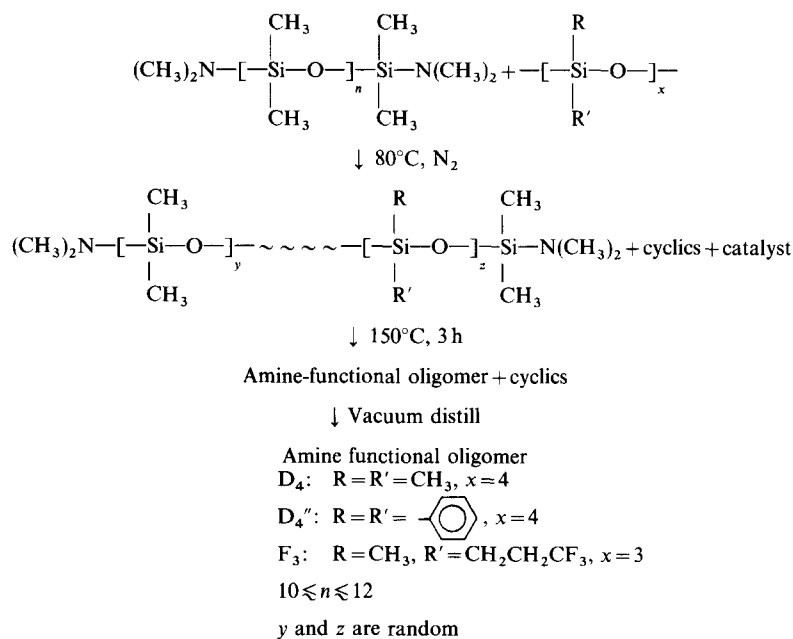### Synthesis of functional siloxane oligomers

The synthesis of difunctional, silylamine-terminated polyorganosiloxane oligomers is illustrated in *Scheme 1*. The reaction involves the bulk redistribution (or equilibration) of cyclic siloxane monomers with a silylamine endblocker in the presence of a base catalyst[9,13-15].

The equilibrations were carried out in a 250 ml, two-necked round bottom flask equipped with a condenser, drying tube, inert gas inlet, thermometer and magnetic stirrer. In a typical reaction to produce a 5000 $\bar{M}_n$ silylamine-terminated co-oligomer with 50 wt% dimethyl and 50 wt% diphenyl units, 0.40 g (0.0200 mol) of bis(dimethylamino)polydimethylsiloxane (titrated $\bar{M}_n = 720$) along with 35.60 g (0.1203 mol) of D_4 and 50.00 g (0.0631 mol) of D_4' were charged to the reaction flask. The mixture was heated, with stirring and inert gas flow, to 80°C and then 0.40 g (0.3 mol%) of a quaternary ammonium siloxanolate catalyst was added. The reaction was maintained at 80°C for 48 h to ensure complete equilibrations even though recent studies show that the linear/cyclic equilibrium is reached at shorter times[16]. The reaction temperature was then increased to 150°C for 3 h to decompose the transient catalyst. To remove equilibrium cyclics, the product was vacuum stripped at about 100°C and 0.5 torr (≈ 70 Pa). The number average molecular weight, $\bar{M}_n$, as determined by endgroup titration was 5400 g mol^{-1}.

The molecular weight of the various oligomers was controlled by the ratio of endblocker to cyclic monomer. At equilibrium, approximately 10–15% cyclics are present. This would give a lower molecular weight than desired. Therefore, it is necessary to add an additional 10–15% of the cyclic starting materials along with the initial charge of reactants to obtain the targeted molecular weight.

The composition of the oligomers was controlled by the cyclic monomer charge. Exclusive use of D_4 produces polydimethylsiloxane. A mixture of D_4 and D_4' or D_4 and F_3 produces poly(dimethyl-co-diphenyl)siloxane

Scheme 1 Synthesis of functional siloxane oligomers

D_4: $R = R' = CH_3$, $x = 4$

D_4'': $R = R' = $ phenyl, $x = 4$

F_3: $R = CH_3$, $R' = CH_2CH_2CF_3$, $x = 3$

$10 \leqslant n \leqslant 12$

y and z are random

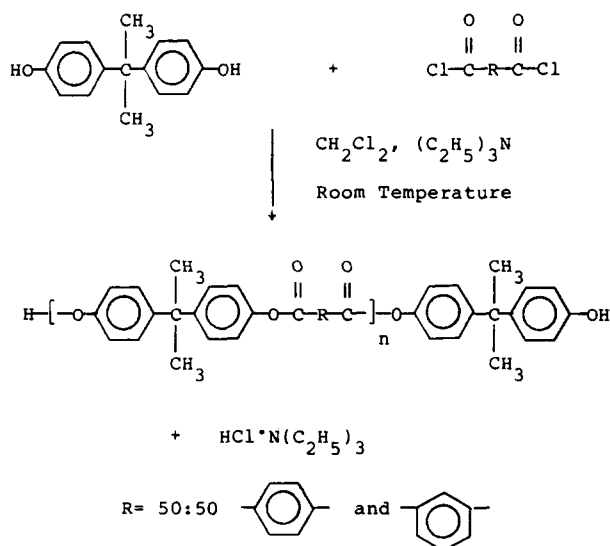and poly(dimethyl-co-trifluoropropylmethyl)siloxane, respectively.

The transient siloxanolate catalyst used in these equilibrations was prepared from the bulk reaction of 1 mol of tetramethylammonium hydroxide pentahydrate with 4.5 mol of D_4[17–19]. Alternative methods of preparing suitable catalysts have also been reported[16].

### Synthesis of functional polyarylester oligomers

Controlled molecular weight, amorphous polyarylesters were synthesized in solution by reacting bisphenol-A with a 50:50 mixture of terephthaloyl chloride and isophthaloyl chloride in the presence of an acid acceptor such as triethylamine, as shown in *Scheme 2*. The desired molecular weight was obtained through the use of a stoichiometric imbalance of the reactants according to the Carothers' equation[20].

The reactions were carried out in a 1 litre, four-necked round bottom flask equipped with a mechanical stirrer, condenser, drying tube, inert gas inlet, addition funnel and thermometer. In a typical reaction to produce a 5000 $\bar{M}_n$ hydroxyl-terminated polyarylester, 30.00 g (0.1316 mol) of bisphenol-A were charged to the reaction flask and dissolved in 550 ml of dry methylene chloride and 40.28 ml (0.2895 mol) of distilled triethylamine (acid acceptor). With stirring and inert gas flow, a solution of 12.43 g (0.0613 mol) of terephthaloyl chloride and 12.43 g (0.0613 mol) of isophthaloyl chloride in 50 ml of dry methylene chloride was placed in an addition funnel and added dropwise to the bisphenol-A solution over a period of 1 h, during which a slight exotherm above room temperature was noted. After 3 h at room temperature, the reaction mixture was filtered to remove the fine white precipitate of triethylamine-hydrochloride (salt complex) formed during the reaction. The filtrate was extracted with a 10% (w/v) aqueous solution of sodium bicarbonate until slightly basic or neutral. This extraction procedure removes the residual precipitate from the filtrate since it is slightly soluble in the reaction solvent, methylene chloride. The final product was precipitated in excess methanol, filtered, and dried under vacuum at 80°C overnight. The number average molecular weight, $\bar{M}_n$, determined by end-group titration[21] was 4900 g mol^{-1}, in good agreement with the stoichiometric value.

Scheme 2 Synthesis of functional polyarylester oligomers
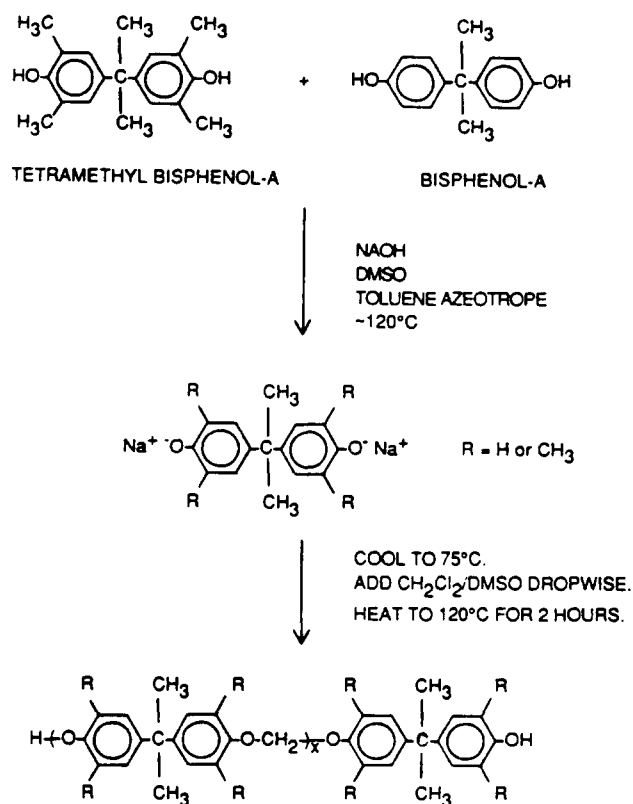
Synthesis of polyformals

Solution polymerization techniques were again used to prepare high molecular weight polyformals, as well as controlled molecular weight phenolic terminated poly-formals, based on tetramethylbisphenol-A and bisphenol-A. The synthetic route is illustrated in *Scheme 3*.

The reactor was a 500 ml, four-necked round bottom flask equipped with a mechanical stirrer, Dean Stark trap with condenser, thermometer, inert gas inlet and addition funnel. In a typical reaction to produce a 10 000 g mol^{-1} phenolic terminated polyformal, 19.901 g (0.0700 mol) TMBA and 6.845 g (0.0300 mol) bisphenol-A were charged to the flask and dissolved in 100 ml of freshly distilled dimethylsulphoxide (DMSO). This corresponds to approximately 30% solids for the reaction. The bisphenate of the monomers was formed by the slow addition of 17.20 g of a 46.5 wt% aqueous sodium hydroxide solution. Formation of the phenate resulted in a slight exotherm, as well as a noticeable colour change in the reaction mixture. The phenate species produced a clear dark amber solution, which turned to a clear olive green upon the addition of 80 ml of toluene. The temperature was raised to ≈120°C to allow dehydration of the system via a toluene/water azeotrope. Once the system had been dehydrated, the reaction was cooled to 80°C for dropwise addition of 8.26 g (0.097 mol) of methylene chloride in 10 ml of DMSO. An exotherm was again observed (generally 10–15°C) and the solution became turbid due to the formation of sodium chloride salt as the reaction proceeded. After 3 h, the whitish-green reaction mixture was cooled and the polymer could be observed as a viscous gel on the bottom of the reactor due to its limited solubility in DMSO. The mixture was diluted with methylene chloride, which slowly dissolved the polymer. The solution was neutralized with oxalic

Scheme 3 Synthesis of polyformals

acid in DMSO, resulting in more salt formation and a colour change (to white) at the equivalence point. The solution was filtered through a Buchner funnel, producing an amber–gold solution which was not perfectly clear due to residual salt contamination. The polymer was coagulated in methanol and isolated by filtration to produce a fine tanish powder.

Perfectly alternating block copolymer synthesis

The silylamine-hydroxyl condensation reaction, shown in *Scheme 4*, was used to synthesize perfectly alternating block copolymers in solution[22,23]. The reactions were carried out in a 1 litre, four-necked round bottom flask equipped with a mechanical stirrer, inverse Dean Stark trap, condenser, drying tube, thermometer, inert gas inlet and addition funnel. In a typical reaction to produce a polyarylester–polyorganosiloxane block copolymer, 6.00 g (0.0012 mol) of a 5000 $\bar{M}_n$ hydroxyl-terminated polyarylester was placed in the reaction flask with 200 ml of chlorobenzene and the temperature was raised to 132°C (chlorobenzene reflux). Approximately 80 ml of solvent was removed through the trap to dehydrate the system. Then 6.48 g (0.0012 mol) of a 5400 $\bar{M}_n$ silylamine-terminated polyorganosiloxane was placed in an addition funnel and added dropwise to the polyarylester solution over a period of 1–2 h. As the stoichiometric point was approached, a noticeable increase in the viscosity of the reaction mixture was observed, and the evolution of dimethylamine was detected by using pH paper. Generally, the reaction was allowed to run overnight even though the evolution of dimethylamine was no

longer observed after a few hours of reflux. The reaction mixture was cooled and the product was precipitated in excess methanol/isopropanol. The white, fibrous product was isolated by filtration, then dried under vacuum at 80°C overnight. The recovered yield was 92%. A similar procedure was followed to prepare polyorganosiloxane-polyformal block copolymers.

Characterization techniques

The chemical structures of the monomers, oligomers and block copolymers were confirmed by Fourier transform infra-red (*F*Ti.r.) and nuclear magnetic resonance (n.m.r.). A Nicolet MX-1 spectrophotometer was used to record *F*Ti.r. spectra. Proton n.m.r. spectra were obtained using a Varian EM-390 90 MHz spectrometer on 10% (w/v) solutions of sample in deuterated chloroform. Tetramethylsilane (TMS) was used as the lock reference for the polyarylester oligomers; methylene chloride (5.37 ppm from TMS) was used as a lock reference for the siloxane-containing samples.

High resolution silicon-29 *F*T-n.m.r. proved to be a powerful tool in the structural elucidation of the siloxane oligomers[24-26]. The spectra were obtained at 53.67 MHz using a Brucker WP-270SY spectrometer. The samples were dissolved in deuterated chloroform (20% w/v) and TMS was used as the internal reference. A small amount (0.02 M) of a shiftless relaxation agent such as chromium acetylacetonate was added to reduce the long T_1 times associated with silicon-29. Typically, about 500 free induction decays (FIDs) were recorded with a flip angle of 40°. The spectra were also broadband decoupled at

Scheme 4 Synthesis of perfectly alternating block copolymers
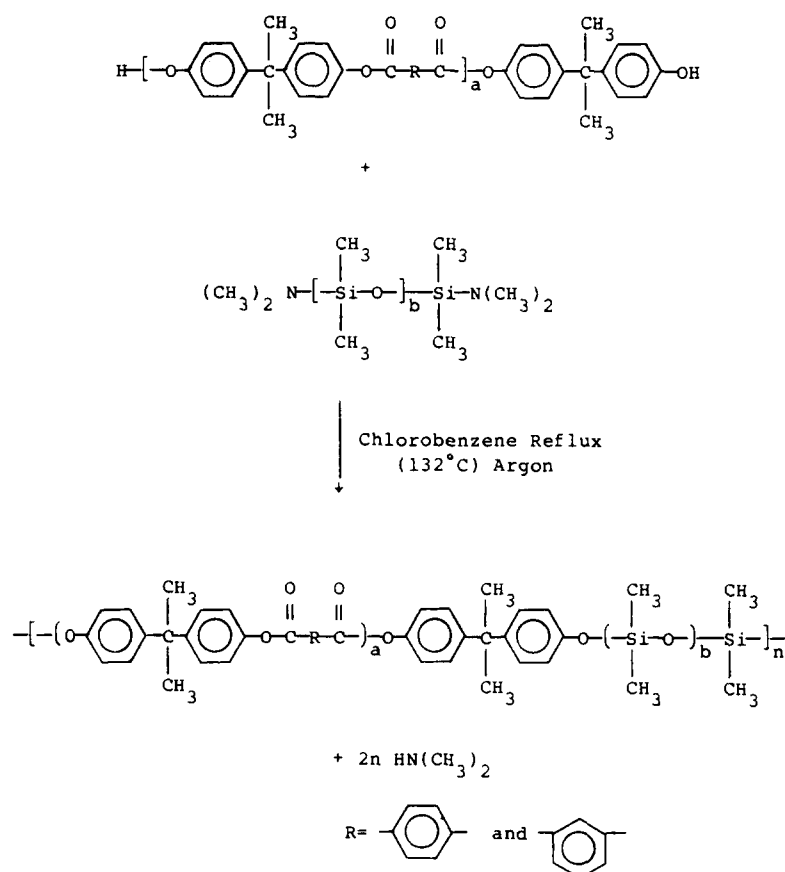
the proton frequency; the nuclear Overhauser effect (NOE) was not measured. Both proton and silicon n.m.r. were useful in calculating molecular weight and composition of siloxane oligomers and co-oligomers.

Compositional information on the polyformals was obtained through the use of ^{13}C n.m.r. The ^{13}C spectra were collected using a Bruker NR-80 spectrometer operating at 20 MHz and employing an inverse-gated proton decoupling program. The polymer solutions were approximately 10% solids (w/v) in deuterated chloroform.

The $\bar{M}_n$ of the amine functional siloxane oligomers and hydroxyl-terminated polyarylester oligomers were determined by endgroup titration using a Fisher Titrimeter II automatic titration system. A standard column electrode was used with a double junction reference. The siloxane oligomers were dissolved in isopropanol and titrated with a 0.1 N solution of hydrochloric acid in isopropanol. The polyarylester oligomers were dissolved in freshly distilled tetrahydrofuran and titrated with a 0.2 N solution of tetramethylammonium hydroxide in methanol. Hydroxyl-terminated polyformal oligomers were dissolved in freshly distilled dimethylacetamide for titration with 0.2 N tetramethylammonium hydroxide.

Intrinsic viscosity values, $[\eta]$, of the oligomers and polymers were determined by a Cannon–Ubbelohde dilution viscometer. All measurements were made at 25°C with methylene chloride as the solvent. Four concentrations of each sample solution were used for the measurements.

Size exclusion chromatography (SEC) was used as a qualitative check on the nature of the molecular weight distribution of the functional oligomers and block copolymers. SEC data was obtained with tetrahydrofuran solutions using a Waters instrument with 50, 10^2, 10^3 and 10^5 nm microstyrogel columns. Both differential refractive index and u.v. detectors were employed. The flow rate was 1.0 ml min^{-1}.

A Perkin–Elmer Model DSC-2 was used to determine the glass transition temperature (T_g), crystallization temperature (T_c) and melting temperature (T_m) of the oligomers and block copolymers. The scans were run at 10°C min^{-1} with a sensitivity of 5 mcal s^{-1}. A Perkin–Elmer TMA-2, in the penetration mode, was used along with a System 4 Microprocessor temperature controller to generate pseudo modulus *versus* temperature curves of the oligomers and block copolymers.

Tensile property determinations were made using an Instron table model tensile tester. Dog-bone shaped samples were cut from polymer films using a die. The sample (0.11 in × 0.28 in (2.8 mm × 7.1 mm)) was held by pneumatic clamps and elongated at a rate of 10 mm min^{-1}.

Dynamic-mechanical spectra of polymer films were obtained using a Polymer Laboratories Dynamic Mechanical Thermal Analyzer operating at 1 and/or 30 Hz. Samples were run in single cantilever mode with a 1 mm free length. The heating rate was 5°C min^{-1}.

X-ray photoelectron spectroscopy (X.p.s.) was used to study the surface properties of solution cast polymer films. Spectra were obtained on a Kratos XSAM-800 X-ray spectrometer equipped with a dual anode X-ray source (Mg) and a hemispherical electron energy analyser. Angle-dependent depth profiling was accomplished by the variation in the electron take-off angle between the analyser and the sample surface.

RESULTS AND DISCUSSION

Siloxane–ester block copolymers

To produce perfectly alternating siloxane–ester block copolymers potentially suitable for passive damping applications in the space environment, the silylamine–hydroxyl condensation reaction was used[22,23,27]. This quantitative step reaction is now known to produce hydrolytically stable materials in spite of the potentially labile≡Si–OC bond. Apparently, water cannot easily reach this isolated bond through the hydrophobic macromolecular matrix[6,7]. *Tables 1* and *2* list the characteristics of silylamine-terminated polyorganosiloxane oligomers and hydroxyl-terminated polyarylester oligomers, respectively. Actual $\bar{M}_n$ values for the difunctional oligomers were obtained from endgroup titration and correspond very well with theoretical values. Characteristics of the siloxane–ester block copolymers prepared from these oligomers are presented in *Table 3* and are discussed below.

Analytical characterization. Structure analysis of both oligomers and the block copolymers was accomplished by *F*Ti.r. and proton n.m.r. Typical spectra of siloxane-ester block copolymers are shown in *Figures 1* and *2*. Corresponding *F*Ti.r. band assignments and n.m.r. peak assignments are listed in *Tables 4* and *5*, respectively. The proton n.m.r. integration was used to calculate the percentage siloxane incorporated into the block copolymer. This was done by calculating the ratio of the silicon-methyl peak at 0.3 ppm to the isopropylidene peak of the polyarylester at 1.7 ppm.

Size exclusion chromatography (SEC) was used as a qualitative check on the nature of molecular weight and molecular weight distribution. Representative SEC curves are shown in *Figure 3*. The two siloxane–ester block copolymer SEC traces are observed at low elution

Table 1 Silylamine-terminated polyorganosiloxane oligomer characteristics

| Sample number | Composition^a (wt%) | $\bar{M}_n$ | | D.s.c. T_g (°C) |
		Theory	Titrated^b	
1	100CH$_3$	5000	6000	−123^c
2	100CH$_3$	10000	10500	−124^c
3	50CH$_3$/50F	5000	5700	−105
4	50CH$_3$/50F	10000	11500	−101
5	50CH$_3$/50Φ	5000	5400	−74
6	50CH$_3$/50Φ	10000	11800	−71

^{a} CH$_3$, dimethyl siloxane units; Φ, diphenyl siloxane units; F, trifluoropropylmethyl siloxane units
^{b} Titrated with 0.1 N alcoholic HCl
^{c} Polydimethylsiloxanes also displayed $T_m \approx -36$°C and $T_c \approx -89$°C

Table 2 Hydroxyl-terminated polyarylester oligomer characteristics

| Sample number | $\bar{M}_n$ | | $[\eta]$ CH$_2$Cl$_2$ (25°C) | Yield^b (%) | D.s.c. T_g (°C) |
	Theory	Titrated^a			
1	5000	5100	0.27	75	171
2	5000	5100	0.27	75	171
3	10000	9900	0.39	77	174
4	10000	10000	0.37	75	178

^{a} Titrated with 0.2 N alcoholic tetramethylammonium hydroxide
^{b} Recovered yield after work-up

Table 3 Characteristics of polyorganosiloxane–polyarylester block copolymers

Sample number	Siloxane block			Ester block		Copolymer
	Comp.[a] (wt%)	$\bar{M}_n$	T_g (°C)	$\bar{M}_n$	T_g (°C)	T_g (°C)
1	100CH₃	6000	−123	5000	171	−123[b], 135
2	100CH₃	10000	−123	5000	171	−126[b], 158
3	100CH₃	6000	−123	9900	174	−123[b], 168
4	100CH₃	10500	−123	10500	175	−125[b], 173
5	50CH₃/50F	5700	−105	5100	171	−102, 138
6	50CH₃/50F	11500	−101	5100	171	−96, 144
7	50CH₃/50F	5700	−105	10900	180	−104, 174
8	50CH₃/50F	11500	−101	10900	180	−95, 175
9	50CH₃/50Φ	5400	−74	5100	171	−61, 156
10	50CH₃/50Φ	11800	−71	5100	171	−64, 156
11	50CH₃/50Φ	5400	−74	9900	174	−72, 175
12	50CH₃/50Φ	11800	−71	9900	174	−69, 176

[a] CH₃, dimethyl siloxane units; F, trifluoropropylmethyl siloxane units; Φ, diphenyl siloxane units
[b] Also displayed $T_c \approx -96°C$ and $T_m \approx -62°C$
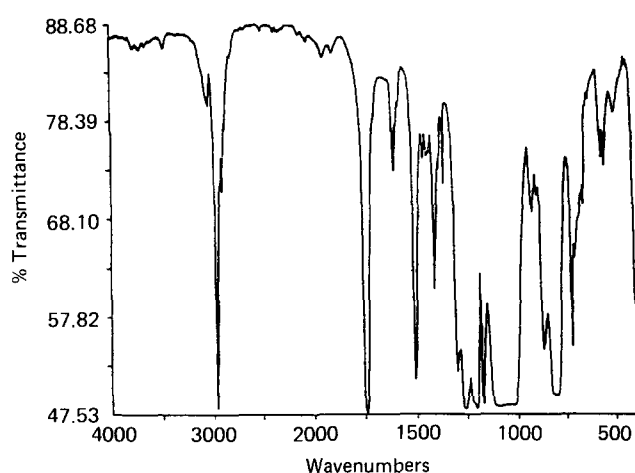
Figure 1 The *FT*i.r. spectrum of a perfectly alternating polydimethyl-siloxane–ester block copolymer
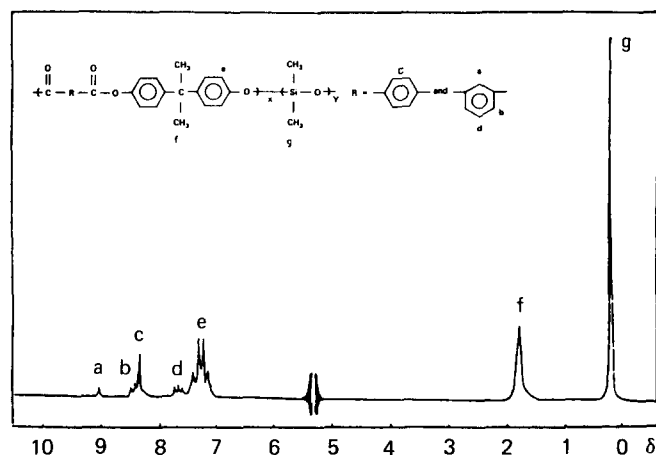
Figure 2 The proton n.m.r. spectrum of a perfectly alternating polydimethylsiloxane–ester block copolymer. Block lengths: 5000 $\bar{M}_n$

Table 4 Siloxane–ester block copolymer *FT*i.r. band assignments

Frequency (cm⁻¹)	Assignment
3050	C–H stretch, aromatic
2950	C–H stretch, aliphatic
1750	Ester carbonyl stretch
1600, 1500	C–C stretch, aromatic
1410	CH₃ asymmetric deformation
1275	CH₃ symmetric deformation
1270–1170	Strong ester bands
1100–1000	Si–O–Si stretch vibration
800	Si(CH₃)₂O stretch; CH₃ rock
715	Si(CH₃)₂O stretch
510	Si–O–Si bend vibration

Table 5 Siloxane–ester block copolymer proton n.m.r. results

Peak (ppm)	Assignment
0.3, singlet	Dimethylsiloxane hydrogens
1.7, singlet	Isopropylidene hydrogens derived from bisphenol-A
5.3, lock	CH₂Cl₂ reference and lock
7.3, AA′BB′ multiplet	Aromatic hydrogens derived from bisphenol-A
7.5, triplet	Aromatic hydrogens derived from isophthaloyl chloride
8.2, singlet	Aromatic hydrogens derived from terephthaloyl chloride
8.3, doublet	Aromatic hydrogens derived from isophthaloyl chloride
8.8, singlet	Aromatic hydrogens derived from isophthaloyl chloride

volumes, indicating higher molecular weights than the polyarylester oligomer, which is observed at a higher elution volume. Both the polyarylester oligomers and the block copolymers displayed broad, unimodal molecular weight distributions, typical of step-growth or condensation polymers.

Thermal analysis. The influence of diphenyl and trifluoropropylmethyl siloxane content on the glass transition temperature of the siloxane co-oligomers is apparent from the d.s.c. results listed in *Table 1*. The increase in the glass transition temperature with incorporation of diphenyl or trifluoropropylmethyl content was expected since these more polar and bulky units restrict molecular motions.

Thermal characteristics of the siloxane–ester block copolymers are included in *Table 3*. Microphase
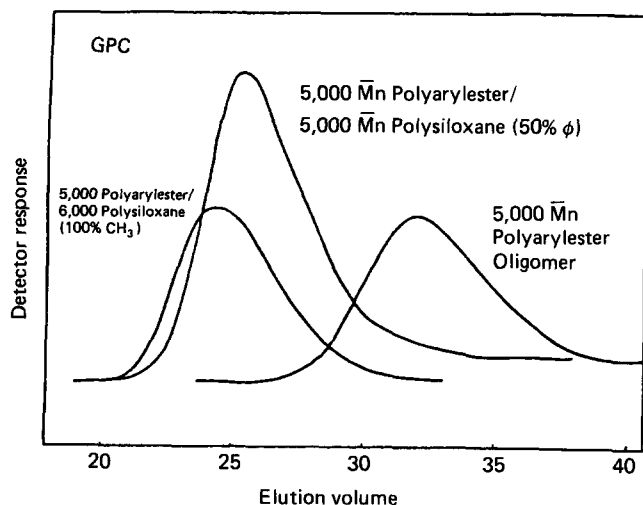
Figure 3 SEC curves of a polyarylester oligomer and two siloxane–ester block copolymers

separation of the component blocks is indicated by the fact that two glass transition temperatures are observed for each sample. The low temperature transitions are attributed to the 'soft' siloxane phases and in most cases they agree with the T_g values of the siloxane oligomers, suggesting a low or negligible degree of mixing of the ester phase into the siloxane phase. In addition to a glass transition, crystallization and melting transitions are displayed by copolymers containing a siloxane phase composed of dimethylsiloxane units only. This type of thermal behaviour is expected since long dimethylsiloxane sequences are symmetrical and, therefore, crystallizable. This observation was also noted for the previously discussed functional polydimethylsiloxane oligomers. No crystallization or melting transitions were displayed by siloxane phases containing diphenyl or trifluoropropylmethyl units which disrupt the symmetry of the dimethyl sequences.

The high temperature transition of each block copolymer is attributed to the 'hard' polyarylester phase. From the data presented in *Table 3* it is readily apparent that the block copolymer high temperature transitions are generally lower than those of the polyarylester homopolymers. It is probable that there is some degree of mixing of the siloxane phase into the ester phase. This would plasticize the ester phase, thereby lowering its glass transition temperature. However, this would not necessarily be accompanied by an increase of the siloxane phase glass transition temperature if the only mixing taking place was of the siloxane into the ester phase.

The degree of phase mixing between components of the block copolymers appears to be dependent upon block molecular weight, as one would expect. Block copolymers consisting of low molecular weight blocks phase mix more readily than block copolymers containing higher molecular weight blocks. In contrast to 5000 $\overline{M}_n$ ester blocks, the T_g values of the 10 000 $\overline{M}_n$ blocks are not observed to change significantly after copolymerization. Thus, block copolymers with 10 000 $\overline{M}_n$ segments do not phase mix as readily as block copolymers with 5000 $\overline{M}_n$ segments.

Phase mixing was also influenced by siloxane composition. As the dimethyl content of a siloxane oligomer is decreased by incorporation of diphenyl or trifluoropropylmethyl siloxane units, the ability of the

siloxane phase to mix with the organic phase is increased. Phase mixing is observed by an increase in the low temperature transition of the block copolymer relative to the siloxane co-oligomer T_g before copolymerization. No such change in T_g was noted for a dimethylsiloxane oligomer copolymerized with a polyarylester oligomer.

Figure 4 illustrates typical thermomechanical analysis (TMA) curves for two siloxane co-oligomers and two siloxane–ester block copolymers. Unfortunately, the polyarylester oligomers used to synthesize the block copolymers were of too low molecular weight for preparation of films suitable for TMA. As in the d.s.c. studies, each block copolymer displayed two transitions, one for each component of the microphase separated block copolymer system. Above the low temperature transition of the siloxane phase, material integrity is maintained (broad plateau) until the high temperature transition of the ester phase is surpassed.

Mechanical properties. As one would expect, the mechanical properties of the siloxane–ester block copolymers were also dependent upon block molecular weight and siloxane block composition. The effect of ester block length is illustrated in *Figure 5*. In general, samples with high aromatic ester content display higher modulus values and lower elongations at break than samples with high siloxane content.

The effect of siloxane block composition is shown in *Figure 6*. The block copolymer containing dimethylsiloxane units displays lower modulus, lower tensile stress and higher elongation at break than the block copolymers containing the more rigid diphenyl or trifluoropropylmethyl siloxane units.

Dynamic mechanical thermal analysis (DMTA) was used to study the modulus–temperature behaviour and the damping characteristics (tan δ) of the siloxane–ester block copolymers. As seen in tensile testing and thermal analysis, the DMTA results were dependent upon block molecular weight and siloxane block composition. A representative DMTA curve is shown in *Figure 7*. As expected, two transitions were observed, one for each component of the copolymer system. Both samples are
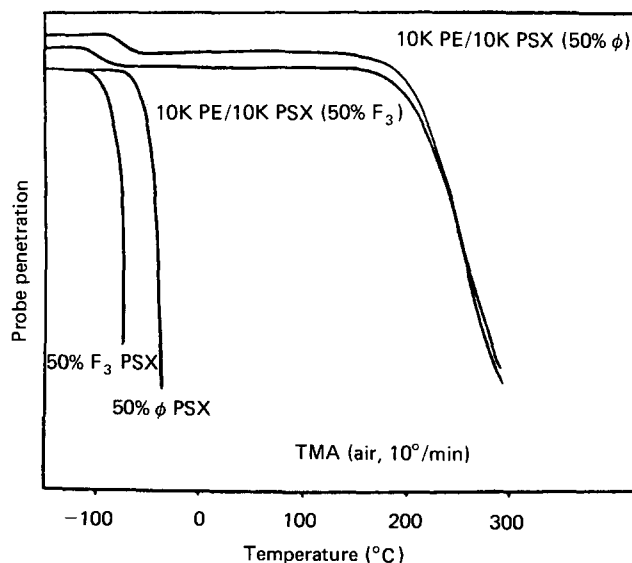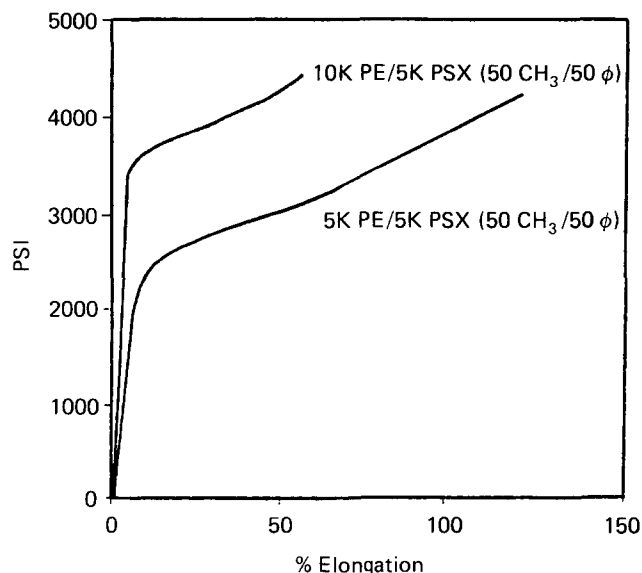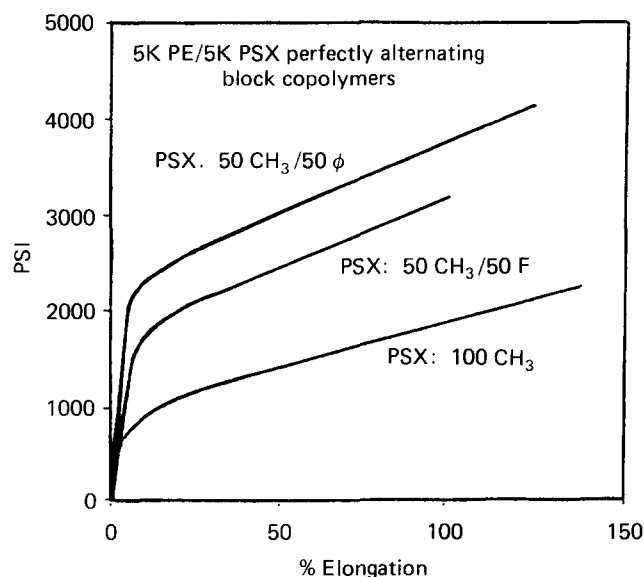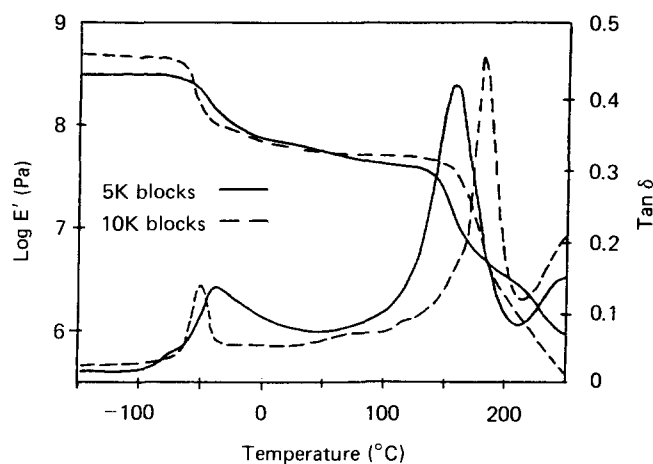

Figure 4 TMA curves for siloxane–ester block copolymers and corresponding siloxane oligomers

Figure 5 The effect of block molecular weight on tensile properties of siloxane–ester block copolymers

Figure 6 The effect of siloxane composition on tensile properties of siloxane–ester block copolymers


Figure 7 The effect of block molecular weight on tan δ for two siloxane (50CH$_3$/50Φ)–ester block copolymers

(dimethyl–diphenyl) siloxane–ester block copolymers, where the siloxane segments contain 50 wt% of each type of unit. One sample has 5000 $\bar{M}_n$ blocks and displays broad tan δ peaks. The second sample has 10 000 $\bar{M}_n$ blocks and exhibits much sharper tan δ peaks, which are also further apart from each other, indicating better phase separation than the copolymer with lower block molecular weights.

Siloxane block composition, in addition to block molecular weight, influences phase separation and, in turn, damping characteristics. The DMTA curves confirmed the d.s.c. results: as the dimethyl content of the siloxane segment is decreased by incorporation of diphenyl or trifluoropropylmethyl siloxane units, the ability of the siloxane phase to mix with the organic phase is increased. Therefore, the tan δ peaks for dimethyl siloxane–ester block copolymers were observed to be sharper and more separated than copolymer systems where the siloxane segments contained diphenyl or trifluoropropylmethyl units.

Surface analysis. Angle dependent x.p.s. proved to be an excellent spectroscopic technique for studying the surface structure of these copolymer systems[31]. *Figure 8* depicts the angular dependence of the O$_{15}$ peak from a representative dimethylsiloxane–ester block copolymer. Dimethylsiloxane homopolymer and homopolyarylester O$_{15}$ peaks are also shown as controls. The homopolyaryl-ester O$_{15}$ peak is made up of two component peaks of equal size, one at 532.2 eV due to C–O–C and the other at 533.9 eV due to C=O. In contrast, the siloxane homopolymer displays a single O$_{15}$ peak at 532.4 eV due to the Si–O–Si backbone. The O$_{15}$ peak of the siloxane–ester block copolymer at three different take-off angles is similar to the single peak observed for the siloxane homopolymer. This suggests that the surface of the solution cast copolymer film is dominated by siloxane, the low surface free energy component of the copolymer system. These findings were quickly confirmed by contact angle measurements, where a 20 μl drop of water was placed on the surface of a 1 in (25 mm) square of polymer film. The polyarylester homopolymer had a contact angle of 77°, whereas the various siloxane–ester
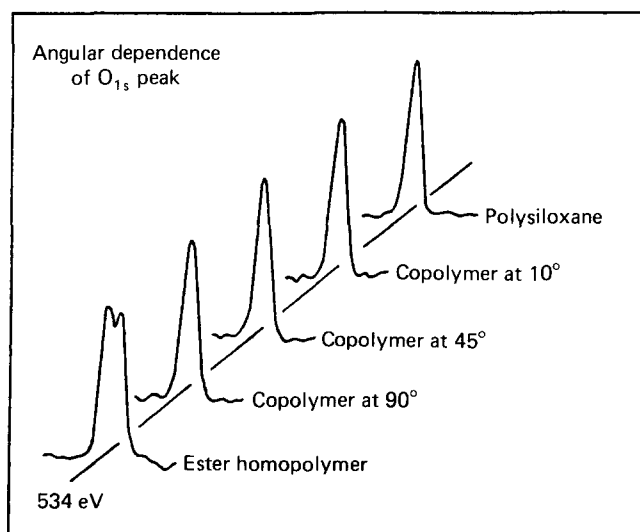
Figure 8 The X.p.s. angular-dependent behaviour of a dimethylsiloxane (6700 $\bar{M}_n$)–ester (5000 $\bar{M}_n$) block copolymer

block copolymers had contact angles which ranged from 96 to 105°.

Polyformals and siloxane–formal block copolymers

Initial efforts to prepare a polyformal based solely on tetramethylbisphenol-A and methylene chloride as monomers were unsuccessful due to the tendency towards crystallization, which prevented the reaction from going to completion. Polyformals based on bisphenol-A monomer had been reported earlier[29], and were repeated here as a control. Since the bisphenol-A control experiments proceeded readily and remained soluble throughout the reaction, experiments were then conducted using increased amounts of this monomer along with the tetramethylbisphenol-A (TMBA), until at a molar ratio of 70:30 TMBA:bisphenol-A a successful polymerization was achieved. Incorporation of 30 mol% of bisphenol-A was sufficient to break up the symmetry and keep the polymer from crystallizing out of solution.

Structure analysis of the polyformals was determined by FTi.r. and ^{13}C n.m.r. The FTi.r. spectrum for a 70:30 TMBA:bisphenol-A polyformal is shown in *Figure 9*. The large band at $1050\,cm^{-1}$ confirms the presence of the $-O-CH_2-O-$ linkage in the polyformal.

The presence of both the TMBA and bisphenol-A monomers in the polyformal backbone was readily detected by n.m.r. Three peaks were observed for the polyformal linkage by proton n.m.r., indicating that the formal linkage had formed readily between the TMBA monomers, between two bisphenol-A monomers, and between one TMBA monomer and one bisphenol-A monomer. The ^{13}C n.m.r. spectra of a polyformal based on 100% bisphenol-A is shown in *Figure 10*. This spectrum was useful for identifying the peaks in the ^{13}C spectrum of a 70:30 TMBA:bisphenol-A polyformal, as shown in *Figure 11*. The number average molecular weights of the phenolic terminated polyformals (as determined by titration with 0.2 N tetramethylammonium hydroxide) agreed well with the targeted values.

Proton n.m.r. was used for structure analysis, as well as for the determination of the percentage siloxane incorporated into the block copolymer. This was done using the integration ratio of the peaks due to the silicon methyl groups relative to any of the peaks due to the repeating unit of the polyformal block. A comparison of
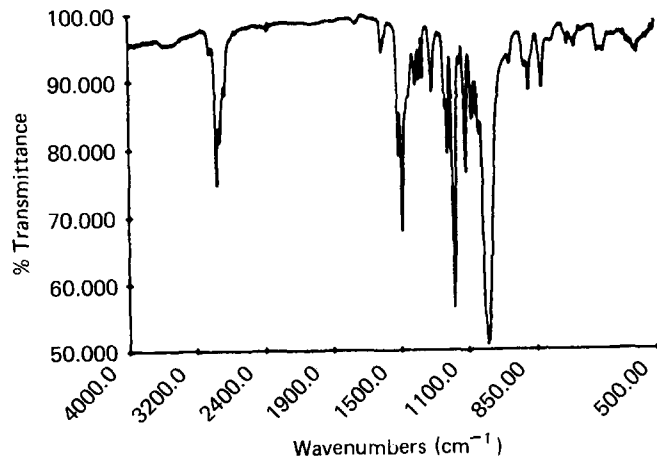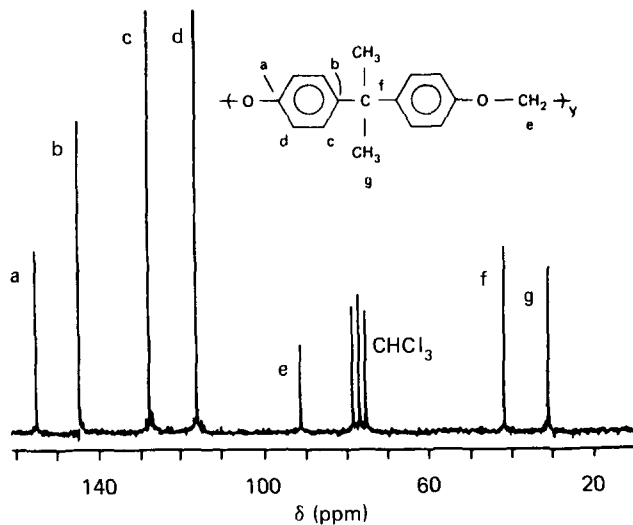

Figure 10 ^{13}C n.m.r. spectrum of a bisphenol-A polyformal

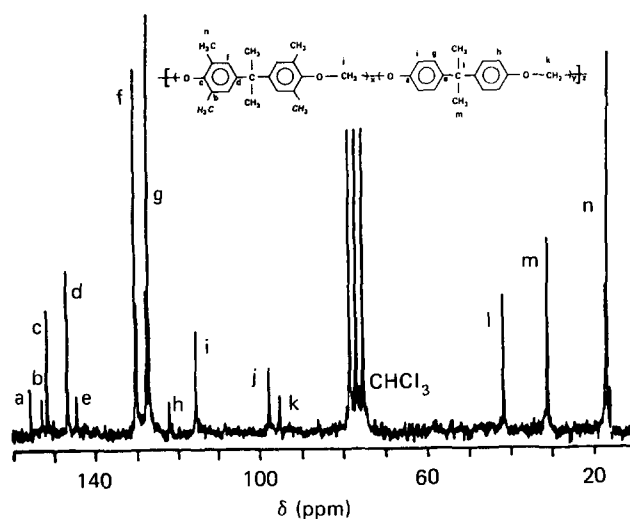**Figure 11** ^{13}C n.m.r. spectrum of a 70:30 tetramethylbisphenol-A: bisphenol-A polyformal

Table 6 Characterization results on aromatic polyformals and perfectly alternating polyformal–polysiloxane block copolymers

Sample	[η] CHCl$_3$ (25°C)	T_g (°C)	G.p.c. results $\bar{M}_n$	G.p.c. results $\bar{M}_w/\bar{M}_n$
100% bisphenol-A polyformal	1.28	88	210 000	1.78
70:30 TMBA:bisphenol -A polyformal	1.10	113	190 000	2.21
8000 M_n polyformal 70:30 TMBA: bisphenol-A	0.12	108	14 500	1.76
Polyformal–polysiloxane block copolymer (6.5 wt% polysiloxane)	1.38	Upper: 97 Lower: weak	151 000	1.8

[a] Polystyrene standards

Figure 9 FTi.r. spectrum of a 70:30 tetramethylbisphenol-A: bisphenol-A polyformal

the results obtained using the separate ratios generally gave approximately the same siloxane content.

Characterization results on the polyformals and a polyformal–polysiloxane block copolymer are shown in *Table 6*. Intrinsic viscosity values for the high molecular weight polyformals based on 100% bisphenol-A and

70:30 TMBA:bisphenol-A are indicative of high molecular weight materials. The intrinsic viscosity value for the 8000 g mol^{-1} is quite low, but increases dramatically upon incorporation of this functional oligomer into a perfectly alternating block copolymer.

The glass transition temperature of the polyformal based mostly on TMBA is higher than the T_g of the material based on bisphenol-A, due to the lower mobility which results from the presence of the bulky methyl groups on the aromatic rings. As expected, the T_g of the 8000 $\bar{M}_n$ oligomer which contains 70 mol% TMBA is slightly lower than the T_g of the 70:30 TMBA:bisphenol-A high molecular weight polyformal. The glass transition temperature is depressed even further in the siloxane-containing block copolymer, indicating that some of the siloxane phase had mixed into the polyformal phase. Again this was expected based on the low molecular weight of the individual blocks in this copolymer. The low temperature transition was too weak to be observed in this sample.

Gel permeation chromatography (g.p.c.) was used as a qualitative check on the nature of the molecular weight and molecular weight distribution. The polymers were characterized with respect to polystyrene standards. In general, the polymers displayed broad, unimodal distributions of molecular weight typical of step-growth polymers. The functional oligomers eluted at higher elution volumes than the siloxane-containing copolymers, indicating they were of lower molecular weight than the corresponding block copolymers. Another important observation made from the g.p.c. traces was the presence of significant amounts of low molecular weight material eluting with the polyformal homopolymer based on bisphenol-A. The oligomer had been precipitated twice in methanol to remove unreacted starting materials, and the peaks were not due to monomer. It had been reported in the literature[29] that the polyformals based on

bisphenol-A form significant amounts of low molecular weight linear and cyclic species. Indeed, the presence of these impurities was readily observed by g.p.c.. It was immediately noted, however, that the polyformals based mostly on tetramethylbisphenol-A did not show the presence of similar impurities by g.p.c. analysis. The oligomers were subsequently analysed by high performance liquid chromatography (h.p.l.c.) for improved sensitivity in characterizing these low molecular weight materials. The results of the HPLC analyses are shown in *Figure 12*. The h.p.l.c. conditions used were those which had been reported[30] for analysis of bisphenol-A based polyformals. The HPLC results again showed the presence of the low molecular weight cyclics and linear species in the bisphenol-A based system, but the low molecular weight materials were not observed in the polyformal based mostly on tetramethylbisphenol-A. It is feasible that the presence of the methyl groups on the phenyl rings in TMBA is effectively hindering the formation of significant amounts of cyclics in this system. Certainly this would be advantageous since the presence of low molecular weight species can greatly affect the properties of polymeric materials.
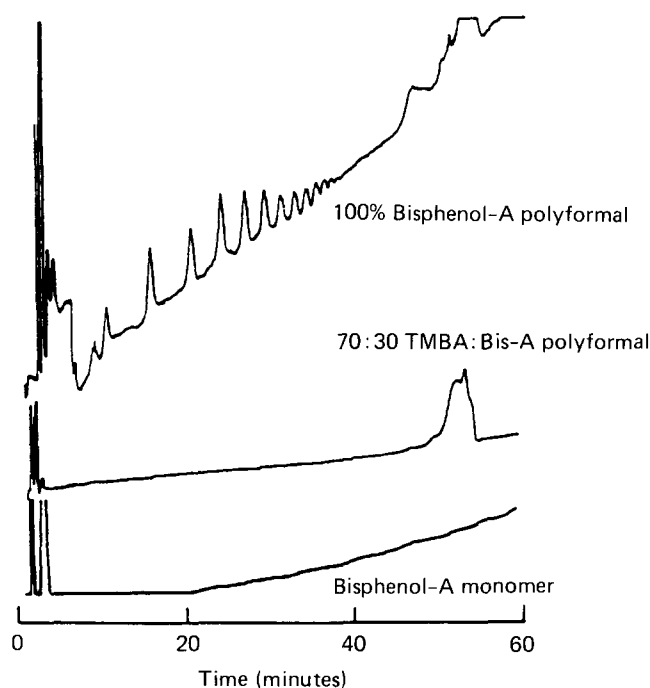
CONCLUSIONS

The preparation and characteristics of perfectly alternating polyorganosiloxane–polyarylester and polyorganosiloxane–polyaryl formal block copolymers have been presented. Structure analysis shows that the block copolymers were indeed prepared. Due to the high degree of incompatibility of the 'soft' siloxane phase and 'hard' organic phase in the block copolymers, a two-phase microstructure developed at relatively low block molecular weights. The thermal and mechanical properties of these materials were shown to be dependent upon block molecular weight and siloxane block composition, both of which influence the degree of phase mixing. Surface analysis indicated that the surfaces of the copolymer films were dominated by siloxane. The damping characteristics, along with the silicone-rich surface of films, make these materials candidates for passive damping applications. Future work will include stability studies of these materials in a simulated space environment.

Figure 12 H.p.l.c. analysis of low molecular weight cyclic and linear species in polyformals. (Reverse phase C$_{18}$ column. U.v. detector, 254 nm; 20 μl sample loop; 1% solutions; 1 h solvent gradient: THF, 60–100%; H$_2$O, 40–0%)

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