Synthesis and properties of diarylsiloxane and (aryl/methyl)siloxane polymers:
1. Thermal properties

Michael K. Lee and Dale J. Meier*
Michigan Molecular Institute, 1910 West St. Andrews Road, Midland, MI 48640, USA
(Received 1 December 1992; revised 26 February 1993)

Poly(diarylsiloxane)s are highly crystalline, high-melting polymers with excellent high-temperature properties. As a consequence of the rigid polymer backbone, they show crystal–liquid-crystal transitions, and both nematic and smectic states have been observed by optical microscopy. The polymers of greatest interest in this investigation have been those containing phenyl and *p*-tolyl substituents on the siloxane backbone. We have prepared a series of polymers with various combinations of these substituents, as well as the end members of the series, poly(diphenylsiloxane) and poly(di(*p*-tolyl)siloxane). The polymers are prepared with controlled molecular weights and distribution by ring-opening anionic polymerization of the cyclic trimers in solution. The crystal–liquid-crystal transition temperatures, T_{lc}, for poly(diphenylsiloxane) and poly(di(*p*-tolyl)siloxane) are very high (265 and 300°C, respectively) and the polymers are only soluble in a few solvents at temperatures above 150°C. However, the T_{lc} values are reduced for the mixed poly((phenyl/*p*-tolyl)siloxane)s and the polymers become soluble at lower temperatures. The symmetric poly((phenyl/*p*-tolyl)siloxane) is of particular interest since T_{lc} is reduced to 150–160°C, and the polymer is soluble at room temperature in common solvents such as toluene, tetrahydrofuran and chloroform. In contrast to the retention of the crystalline and liquid-crystalline character in the mixed diarylsiloxanes, the replacement of a single phenyl group by a methyl group in the repeat hexaphenyl triad sequence of poly(diphenylsiloxane) is sufficient to destroy both the crystalline and liquid crystalline character of the polymer.

(Keywords: diarylsiloxanes; synthesis; thermal properties)

INTRODUCTION

To date, it is only poly(dimethylsiloxane), poly((methyl/trifluoropropyl)siloxane) and poly((methyl/phenyl)siloxane), out of the many possible types of siloxane polymers, that have become widely used. These polymers have excellent thermal, chemical and environmental stability, as well as excellent biocompatibility properties. As a result, they are widely used in numerous industrial and consumer applications[1,2]. Only limited attention has been paid to other siloxane polymers, although it is recognized that these too can have unique and perhaps desirable properties. For example, it has been established that the symmetrically substituted poly(dialkylsiloxane)s, such as poly(diethylsiloxane) or poly(dipropylsiloxane), are liquid-crystal-forming polymers[3–6], despite the absence of traditional mesogenic groups. The poly(diarylsiloxane)s, such as poly(diphenylsiloxane), also show liquid-crystalline properties[7]. Because of the relatively bulky phenyl groups and resulting steric interactions, the chains of poly(diphenylsiloxane) are rigid, in contrast to the highly flexible chains of siloxane polymers with the smaller methyl substituent group. As a consequence of chain rigidity, poly(diphenylsiloxane) is a highly crystalline polymer with a transition to the liquid crystalline state, T_{lc}, near 265°C, and a clearing temperature, T_m (to the isotropic melt), above 500°C[7–9].

Relatively few publications have dealt with the characterization and physical properties of poly(diarylsiloxane)s since the synthesis and the very high melting and solution temperatures have presented experimental difficulties[10–13]. The goal of this study has been to synthesize and characterize various poly(diarylsiloxane)s of controlled structure and molecular weight with a view to establishing structure/property relationships for this class of polymers. A further goal has been to obtain polymers with lower transition and solution temperatures than for poly(diphenylsiloxane), so that the liquid-crystalline states and the solution properties can be more easily characterized. Ring-opening anionic polymerization of the cyclic trimers is used to obtain polymers with well-defined compositions and molecular weights. This first paper in a series covers the synthesis and characterization of a number of cyclic trimer monomers and resulting polymers, with an emphasis on their thermal properties. Future papers will focus on solution and rheological properties.

EXPERIMENTAL

Materials

4-Bromotoluene (Aldrich), silicone tetrachloride (Aldrich), 1,3-dichlorotetramethyldisiloxane (Hüls), dimethyldichlorosilane (Aldrich), methylphenyldichlorosilane (Aldrich), phenyltrichlorosilane (Dow Corning), diphenyldichlorosilane (Dow Corning), hexaphenylcyclotrisiloxane

---

* To whom correspondence should be addressed

0032–3861/93/234882–11

(Dow Corning) and *sec*-butyllithium (Aldrich) were used without further purification. Diphenylether (Aldrich) was used as the solvent for the anionic polymerizations and was purified by vacuum distillation, passed through activated alumina and then distilled again over calcium hydride. Tetrahydrofuran (THF; Fisher) was refluxed with lithium aluminium hydride and distilled prior to use. Magnesium turnings (Aldrich) were dried at 100°C under vacuum to remove any trace of water.

Synthesis of the cyclic trimer monomers

The cyclotrisiloxanes of this investigation were prepared either by cyclization of the corresponding dichlorosilanes with ZnO[14] or by reaction of the dichlorosilanes with the pyridine complex of tetraphenyldisiloxanediol[15,16]. The diaryldichlorosilanes were prepared by the Grignard reaction between silicone tetrachloride and arylmagnesium bromide, or between phenyltrichlorosilane with arylmagnesium bromide[17,18]. The preparation procedures are outlined in *Figures 1–3*, and are described in the following sections.

*Di(*p*-tolyl)dichlorosilane and (phenyl/*p*-tolyl)dichlorosilane.* 4-Bromotoluene (1.05 mol) was dissolved in 300 ml of ethyl ether and slowly added to Mg turnings (1 mol) in 200 ml of ethyl ether. The Grignard reaction gradually initiated under refluxing conditions and after completion of the 4-bromotoluene addition (1 h), the reaction was allowed to continue for 1 to 2 h until the Mg was nearly completely consumed. $SiCl_4$ (0.48 mol) or $PhSiCl_3$ (0.90 mol) in 200 ml of ether was added dropwise at a rapid rate with vigorous stirring at room temperature. The desired di(*p*-tolyl)dichlorosilane or (phenyl/*p*-tolyl)dichlorosilane were obtained from the reaction mixture by fractional distillation under vacuum after the MgBrCl was filtered off. The yields were typically about 80%.

Pyridine complex of 1,1,3,3-tetraphenyldisiloxanediol-1,3. The pyridine complex of 1,1,3,3-tetraphenyldisiloxanediol-1,3 was prepared by the technique described in reference 15. Diphenyldichlorosilane (1.0 mol) in 200 ml acetone was slowly added over a 1 h period to a flask containing 800 ml of 1/1 acetone/water mixture at room temperature. After stirring for an additional 15 min, the acetone layer with the desired diol was separated from the water layer and the acetone was removed by evaporation. The crude diol product was dissolved in 400 ml of ether and the tetraphenyldiloxanediol–pyridine complex was precipitated by the addition of 150 ml of pyridine. This gave about an 80% yield of the complex, which was then purified by crystallization from methanol solution.

*1,1,3,3,5-Penta(phenyl)-5-(*p*-tolyl)cyclotrisiloxane and 1,1,3,3-tetra(phenyl)-5,5-di(*p*-tolyl)cyclotrisiloxane.* (Phenyl/*p*-tolyl)dichlorosilane (0.1 mol) or di(*p*-tolyl)dichlorosilane (0.1 mol) in 100 g of benzene was slowly added to a flask containing 0.11 mol of tetraphenyl-

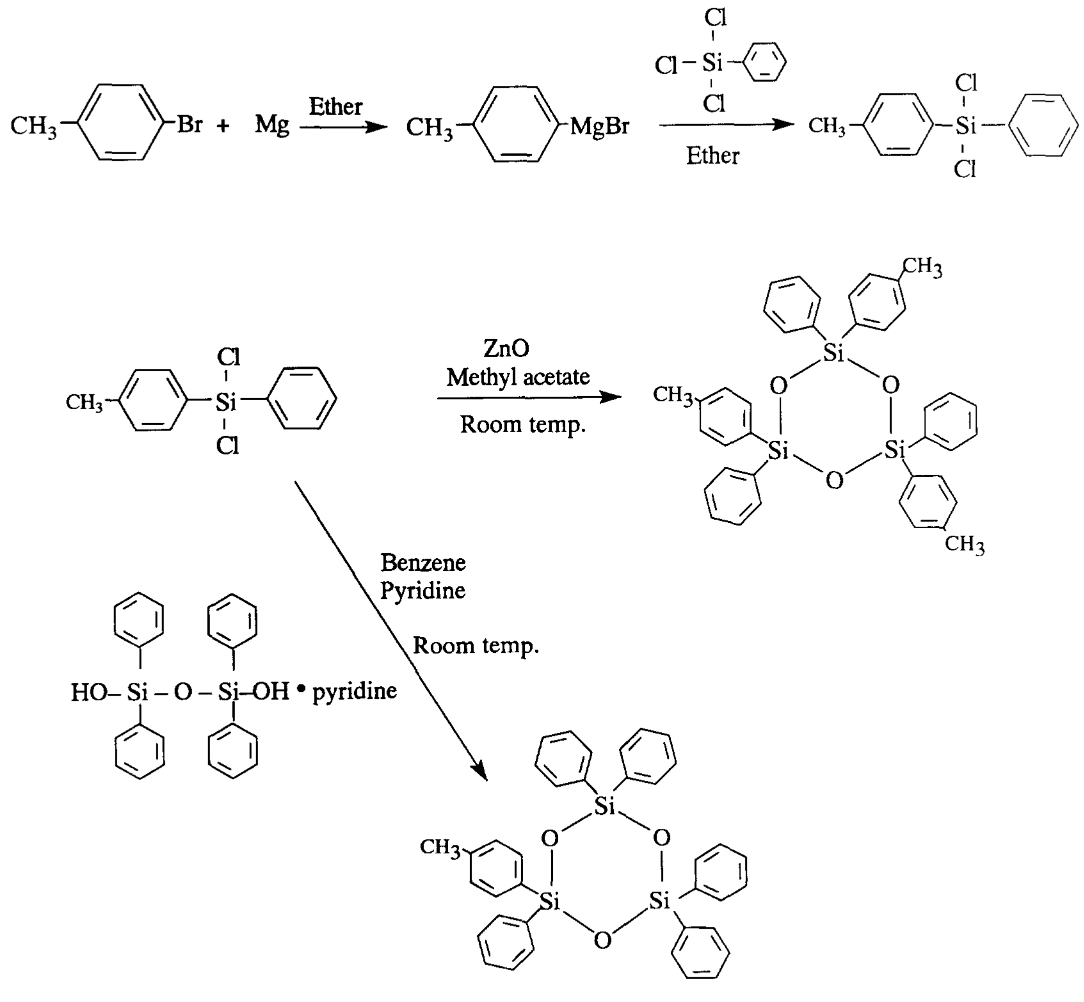


Figure 1 Synthesis of cyclotrisiloxanes containing diphenyl and phenyl/*p*-tolyl substituents

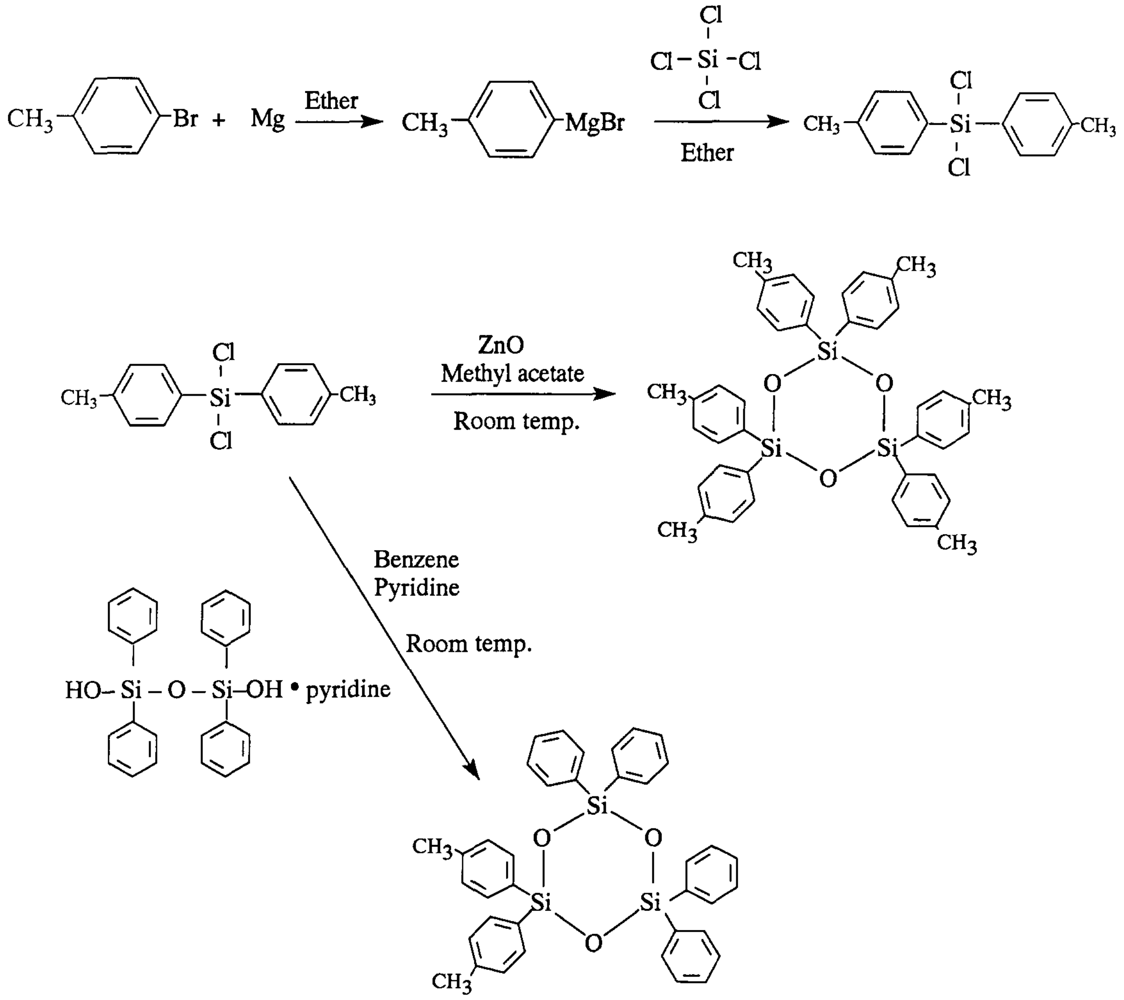


Figure 2 Synthesis of cyclotrisiloxanes containing diphenyl and di(p-tolyl) substituents

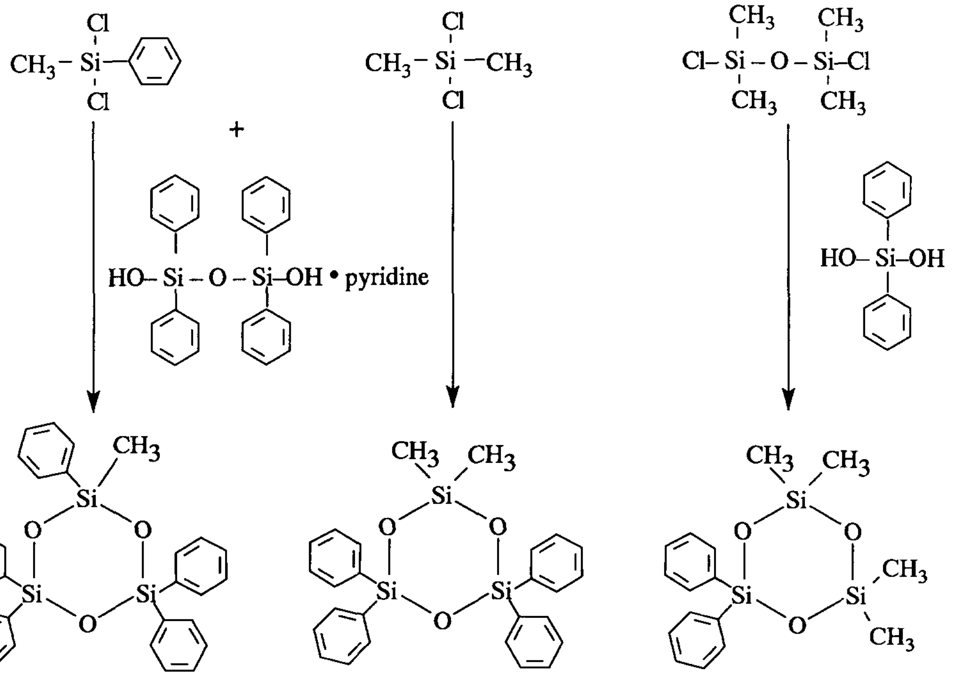


Figure 3 Synthesis of cyclotrisiloxanes containing diphenyl and dimethyl or phenyl/methyl substituents

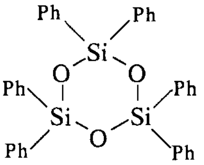
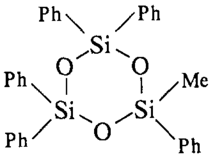
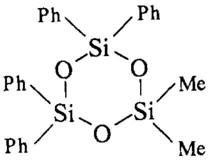
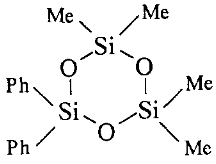
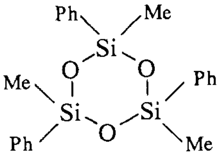
disiloxanediol–pyridine complex, 0.15 mol of pyridine and 100 ml of benzene at room temperature. After the last addition of the dichlorosilane (45 min), the solution mixture was stirred for 15 min, then 100 ml more benzene was added and the system was stirred for a further 10 min. The solution was then washed three times with 200 ml of water, followed by removal of the benzene by evaporation. The resulting white powder was washed twice with 200 ml of methanol. The yield of the cyclic trimers was between 60 and 80%.

*1,3,5-Tri(phenyl)-1,3,5-tri(*p*-tolyl)cyclotrisiloxane and hexa(*p*-tolyl)cyclotrisiloxane.* (Phenyl/*p*-tolyl)dichlorosilane (0.7 mol) or di(*p*-tolyl)dichlorosilane (0.7 mol) in 350 ml ethyl acetate (or methyl acetate) was slowly added with vigorous stirring to a suspension of ZnO (1.06 mol) in 500 ml of ethyl acetate at room temperature. After the last addition of the dichlorosilane (1 h), the solution mixture was stirred for a further 16 h at room temperature. The resulting $ZnCl_2$ and the excess ZnO were filtered off and the solution was washed four times with 200 ml of water. Solvent was removed by evaporation to yield a mixture consisting mainly of cyclic trimers and other cyclic oligomers. The cyclic trimers were separated by recrystallization from a toluene solution, with about a 40% yield.

1,1,3,3,5-Penta(phenyl)-5-(methyl)cyclotrisiloxane and 1,1,3,3-tetra(phenyl)-5,5-di(methyl)cyclotrisiloxane. (Methyl/phenyl)dichlorosilane (0.09 mol) or dimethyldichlorosilane (0.09 mol) in 100 ml of benzene was slowly added (90 min) to a flask containing 0.1 mol of pyridine–tetraphenydisiloxanediol complex, 0.2 mol of pyridine and 200 ml of benzene at room temperature. The reaction was allowed to continue for an additional 60 min. After washing three times with 200 ml of water, the benzene was removed by evaporation. The resulting white powder was washed twice with 100 ml of methanol and dried, with a resulting yield of trimers of between 50 and 70%.

1,1-Di(phenyl)-3,3,5,5-tetra(methyl)cyclosiloxane. 1,3-Dichlorotetramethyldisiloxane (0.17 mol) in 200 ml of benzene was slowly added over 1 h to a reaction flask containing 0.2 mol of diphenylsilanediol, 0.4 mol of pyridine and 200 ml of benzene at room temperature. After the last addition of the dichlorosilane, the solution mixture was stirred for a further 16 h at room temperature. After washing the mixture three times with 200 ml of water, the benzene was removed by evaporation. The cyclic trimers were separated from the mixture by recrystallization from a hexane solution, with an overall yield of about 65%.

Table 1 Thermal behaviour and ^{29}Si n.m.r. chemical shifts of cyclotrisiloxanes containing phenyl and methyl substituents

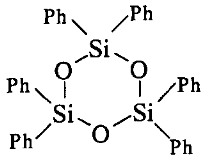
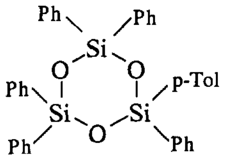
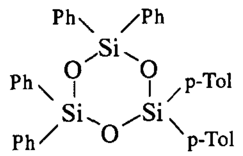
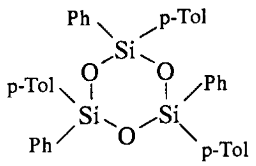
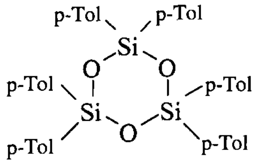
Cyclic trimer	T_m (°C)	ΔH_m (J g^{-1})	^{29}Si n.m.r. chemical shift (ppm)
	190	64	−33.84
	117	60	−19.28 −34.38
	87	62	−5.00 −35.23
	62	38	−6.65 −36.77
	105 (*cis* isomer)	69	−30.62

The properties of the cyclic trimers having phenyl and methyl groups and those having phenyl and *p*-tolyl groups are shown in *Tables 1* and *2*, respectively. The data in *Table 1* illustrate that the replacement of phenyl groups by methyl groups in hexaphenylcyclotrisiloxane dramatically reduces the melting temperature T_m. In contrast, the data in *Table 2* show that the substitution of phenyl by *p*-tolyl groups has only a minor effect on the melting points until all of the phenyl groups are completely replaced by *p*-tolyl groups. Then the melting temperature is substantially increased, from 190°C for hexaphenylcyclotrisiloxane to 260°C for hexa(*p*-tolyl)cyclotrisiloxane. The different effects produced by substituting methyl or *p*-tolyl groups is, of course, related to their substantially different molecular volumes and the concomitant steric effects.

Polymer synthesis

The polymerization of cyclic siloxanes with bulky substituents by conventional basic catalysts is difficult, yields are low and the sequential distribution of a copolymer is randomized. However, Bostick[19], Lee and Marko[20] and our earlier work[7] showed that ring-opening polymerization of the cyclic trimers could be initiated by lithium alkyls and silanolates, and copolymers could be prepared in high yield without appreciable randomization of copolymer sequence distributions. We also showed[21] that lithium initiators could be used to prepare poly(diphenylsiloxane)s with controlled molecular weights and narrow distributions by polymerization of the cyclic trimer in a solution in diphenyl ether at high temperatures (150–190°C). By polymerization in a homogeneous solution, we avoided the problems associated with the earlier bulk polymerizations, where

Table 2 Thermal behaviour and ^{29}Si n.m.r. chemical shifts of cyclotrisiloxanes containing phenyl and *p*-tolyl substituents

Cyclic trimer	T_m (°C)	ΔH_m (J g^{-1})	^{29}Si n.m.r. chemical shift (ppm)
	190	64	−33.84
	162	62	−33.87 −33.28
	180	59	−34.05 −32.85
	202	71	−33.61
	260	60	−33.44

major problems occurred in the control and the product uniformity because of very high viscosities and attendant inability to properly mix components[7]. The polymers for this investigation have been prepared by the lithium-initiated, ring-opening polymerization of the cyclic trimers in solution.

sec-Butyl lithium was used as the polymerization initiator with THF (3.5–7.0 vol%) as the promoter. The polymerization reactions were conducted in a purified nitrogen atmosphere to exclude air and moisture, and at temperatures of 170 or 190°C for a 90 min period. The polymerizations require control of a number of variables, e.g. polymerization time, temperature, promoter concentration, etc. *Table 3* shows the effect of the polymerization variables on the yield of poly(di(*p*-tolyl)siloxane). The polymerization reactions were terminated with a stoichiometric excess of diphenylmethylchlorosilane. Poly(diphenylsiloxane) and poly(di(*p*-tolyl)siloxane) were recovered by precipitation in toluene, followed by filtration and repeated washing with toluene to remove the remaining cyclic and initiator impurities. The other polymers were recovered by precipitation with methanol and purified by fractional precipitation with a toluene/methanol mixture. The necessity to exhaustively purify the polymers from initiator residues will be discussed in a later section. Polymers were dried in a vacuum oven at 100°C for 16 h.

Characterization

Molecular weights were obtained by gel permeation chromatography (g.p.c.) using chloroform solutions at 40°C, and the reported molecular weights are based on polystyrene standards. Differential scanning calorimetry (d.s.c.) data were obtained using a DuPont 910 thermal analyzer at a heating rate of 10°C min^{-1} and with a nitrogen flow rate of 40 ml min^{-1}. The glass transition temperatures (T_gs) are reported as the onset temperatures of the transition, while the T_{lc}s are reported as peak temperatures. Thermogravimetric analysis (t.g.a.) was performed on a DuPont 951 TGA at a heating rate of 10°C min^{-1} with a nitrogen flow rate of 50 ml min^{-1}. ^{13}C and ^{29}Si n.m.r. spectra were obtained using a Bruker 360 MHz spectrometer. A Leitz optical microscope (Dialux-Pol SB) with a Mettler FP2 hot stage was used for optical microscopy. The hot stage allowed examination of samples to 300°C.

RESULTS AND DISCUSSION

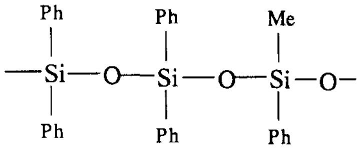
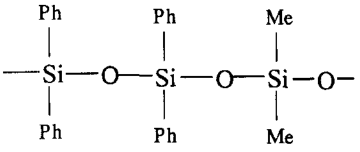
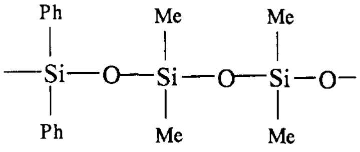
The structure of each cyclic trimer was confirmed by ^{29}Si n.m.r. The cyclic trimer 1,3,5-tri(phenyl)/1,3,5-tri(*p*-tolyl)cyclotrisiloxane is probably a mixture of *cis* and *trans* isomers, but the differences between them are so small that we were unable to distinguish the separate species by n.m.r. or d.s.c. techniques. Both ^{29}Si and ^{13}C n.m.r. spectra show the presence of only one species and only one sharp melting point is observed by d.s.c. The fact that the separate species cannot be resolved is not too surprising. Similar results are found for the *cis* and *trans* isomers of 1,3,5-trimethyl-1,3,5-triphenylcyclotrisiloxane, for which only minor differences in melting points and n.m.r. spectra were found, in spite of a very large difference in the size of phenyl and methyl groups[22].

The data in *Table 4* show that the polymers prepared here were of reasonably high molecular weight (g.p.c. data also indicated narrow molecular weight distributions) and had yields between 50 and 80%. In contrast, Zhadanov *et al.*[11] reported a maximum yield of only 39% in the synthesis of some similar polymers using a basic

Table 3 Polymerization yield and the liquid crystal transition temperature, T_{lc}, of poly(di(*p*-tolyl)siloxane) as a function of polymerization variables. THF promoter levels: high ≈ 7 vol%; low ≈ 3.5 vol%

Polymerization temperature (°C)	THF promoter level	Polymerization time (min)	Yield (%)	T_{lc} (°C)
230	Medium	60	0	–
210	High	90	0	–
190	High	60	9	275
190	Low	300	27	280
190	Low	180	42	285
190	High	90	52	300

Table 4 Polymerization yields, molecular weights, solubility and ^{29}Si n.m.r. chemical shifts of siloxane polymers having phenyl and methyl substituents: w = weak; vw = very weak

Polymer repeat unit	Molecular weight	Yield (%)	Soluble in CHCl$_3$ at r.t.?	^{29}Si n.m.r. chemical shift (ppm)
 $-\underset{Ph}{\overset{Ph}{Si}}-O-\underset{Ph}{\overset{Ph}{Si}}-O-\underset{Ph}{\overset{Me}{Si}}-O-$	48 000	50	Yes	−32.68 −33.28 (vw) −46.42 (vw) −46.91 −47.24 (vw)
 $-\underset{Ph}{\overset{Ph}{Si}}-O-\underset{Ph}{\overset{Ph}{Si}}-O-\underset{Me}{\overset{Me}{Si}}-O-$	20 000	83	Yes	−19.02 −20.39 (w) −46.41 (vw) −47.43 −48.03 (vw)
 $-\underset{Ph}{\overset{Ph}{Si}}-O-\underset{Me}{\overset{Me}{Si}}-O-\underset{Me}{\overset{Me}{Si}}-O-$	15 000	30	Yes	−19.27 (vw) −20.47 −21.67 (w) −47.60 (vw) −48.37

potassium initiator and an extremely strong promoter (18-crown-6-crown ether). In addition, it is likely that the strongly basic initiator that they used 'scrambled' or randomized the sequence distribution of the resulting polymers, in contrast to the retention of the triad sequence distributions of the cyclic trimers when lithium initiators are used[19].

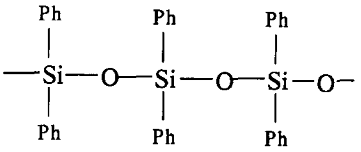
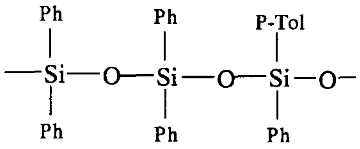
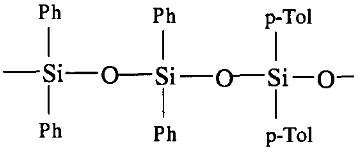
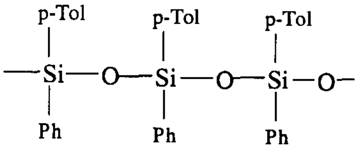
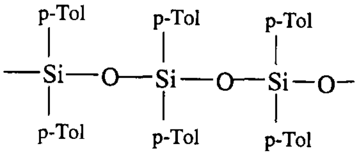
The sequence distributions of the polymers prepared here were determined by ^{29}Si n.m.r.[23]. Such data show that the polymerization of the cyclic trimers was predominantly head-to-tail, e.g. the polymer prepared from the cyclic trimer |-P-P-P*-|, with P representing a diphenylsiloxane group and P* a phenyl/*p*-tolylsiloxane or di(*p*-tolyl)siloxane group, retained the same -P-P-P*-P-P-P*- sequence distribution in the polymer with only a minor amount of the head-to-head sequence -P-P-P*-P*-P-P- present. These data also indicate that a negligible degree of randomization ('scrambling') of the individual siloxane units occurred in the *p*-tolyl-substituted series, but occurred to a somewhat larger degree in the methyl-substituted series, as indicated by noticeable (but weak) secondary peaks in the n.m.r. spectra (not shown). The chemical shifts of the n.m.r. spectra are listed in *Tables 4* and *5* and spectra of the *p*-tolyl-substituted series are shown in *Figure 4*.

Poly(diphenylsiloxane) is soluble in few solvents and then only at high temperatures. The replacement of the phenyl group in the molecule of poly(diphenylsiloxane) by *p*-tolyl or methyl groups improves the solubility, except when all the phenyl groups are substituted by *p*-tolyl, when again the polymer becomes soluble only at very high temperatures. The mixed phenyl/*p*-tolyl polymers are soluble in common solvents such as chloroform, toluene and THF at room temperature or upon slight heating[13], even though the polymers are highly crystalline and have T_{lc} values above 150°C.

In contrast to the crystalline and liquid-crystalline character of the mixed phenyl/*p*-tolyl polymers, the substitution of even one of the six phenyl groups of the repeat triad in poly(diphenylsiloxane) by a methyl group destroys the crystalline and liquid-crystalline character. The polymers having either one, two or four phenyl group(s) (P) in the repeat diphenyl triad substituted by a methyl group(s) (M), -P$_2$-P$_2$-(P/M)-, -P$_2$-P$_2$-M$_2$- or -P$_2$-M$_2$-M$_2$-, are totally amorphous materials with T_gs at 14, −1 and −48°C, respectively. This series of methyl-substituted polymers (together with the properties of the end members of the series, poly(dimethylsiloxane) and poly(diphenylsiloxane)) shows that the effect of methyl substitution on T_g is a monotonic function of the degree of methyl substitution, as shown in *Figure 5*. It should be noted that the literature value[24] for T_g of poly(phenyl/methyl)siloxane with 50 mol% symmetric substitution is −86°C (187 K) and does not fall on this curve. However, a sample of this polymer prepared by Y. Tarshiani at MMI (unpublished work) shows a T_g of −22°C (251 K) which does fall nicely on the curve. We suspect that the low literature value was the result of using a low-molecular-weight oligomeric sample.

The high-temperature thermal behaviour (d.s.c.) of poly(diphenylsiloxane) is shown in *Figure 6*, which shows the d.s.c. behaviour of a polymer as prepared (lower trace) and a polymer that has been exhaustively purified to remove residual (lithium) impurities (upper trace). Both d.s.c. traces show the T_{lc} near 265°C, but the thermal behaviour at high temperatures is quite different. The sample as recovered from the polymerization medium and purified in the normal manner by washing several times with toluene shows a complex group of endothermic transitions in the 450–480°C range, which we attribute to decomposition reactions. In contrast, the upper trace of *Figure 6* shows that decomposition in that temperature range is completely eliminated when the polymer is purified (by repeated solution and precipitation) to reduce the residual lithium content to below 1 ppm. The polymer now shows a reproducible sharp transition at approximately 540°C, which we attribute to the clearing temperature T_m (melting to the isotropic liquid). Because of the importance of the residual lithium content on the high temperature properties, all of the polymer samples

Table 5 Polymerization yields, molecular weights, solubility and ^{29}Si n.m.r. chemical shifts of siloxane polymers having phenyl and *p*-tolyl substituents

Polymer repeat unit	Molecular weight	Yield (%)	Soluble in $CHCl_3$ at r.t.	^{29}Si n.m.r. chemical shift (ppm)
 $-Si(Ph)_2-O-Si(Ph)_2-O-Si(Ph)_2-O-$	30 000	67	No	–
 $-Si(Ph)_2-O-Si(Ph)_2-O-Si(P\text{-}Tol)(Ph)-O-$	23 000	62	Yes	−46.16 −46.83
 $-Si(Ph)_2-O-Si(Ph)_2-O-Si(p\text{-}Tol)_2-O-$	17 000	50	Yes	−45.66 −46.99
 $-Si(p\text{-}Tol)(Ph)-O-Si(p\text{-}Tol)(Ph)-O-Si(p\text{-}Tol)(Ph)-O-$	27 000	58	Yes	−46.49
 $-Si(p\text{-}Tol)_2-O-Si(p\text{-}Tol)_2-O-Si(p\text{-}Tol)_2-O-$	100 000	52	No	–

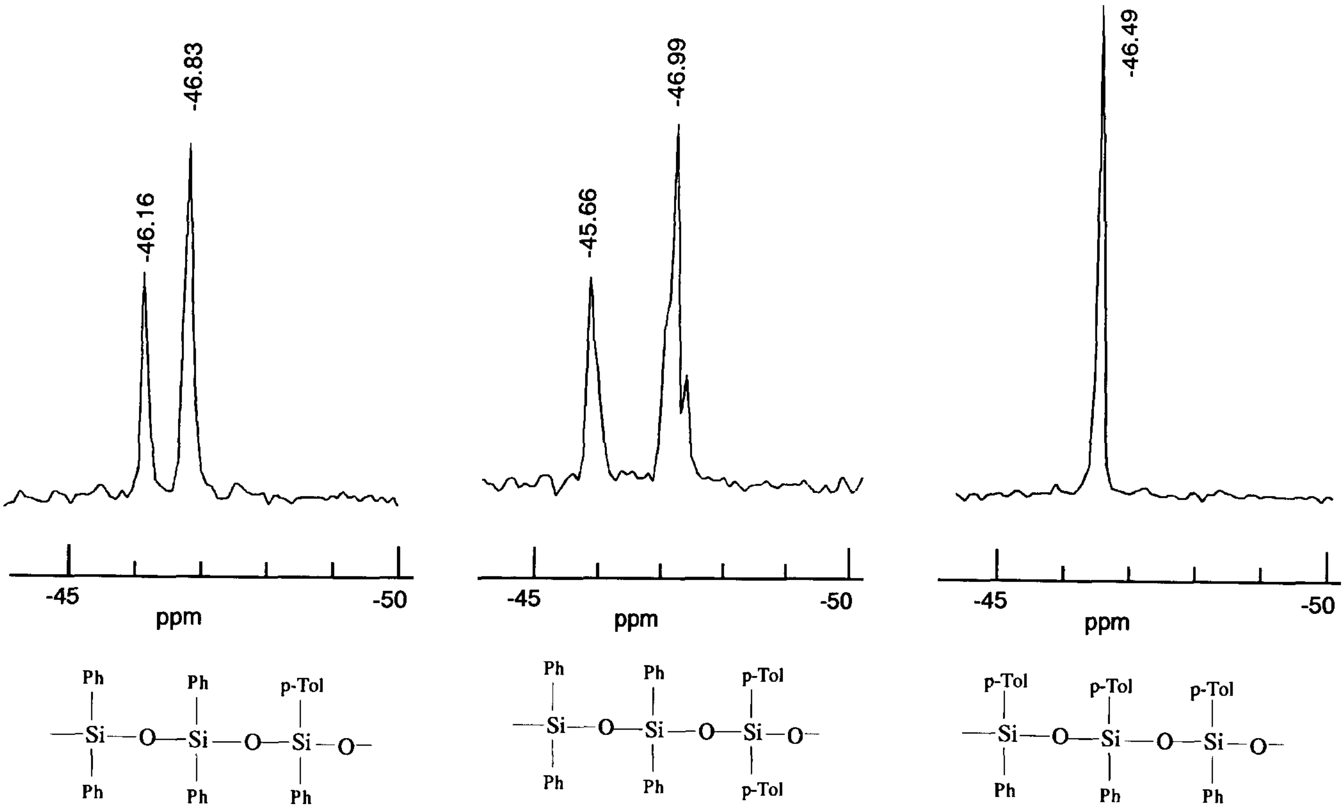


Figure 4 ^{29}Si n.m.r. spectra of diarylsiloxane polymers

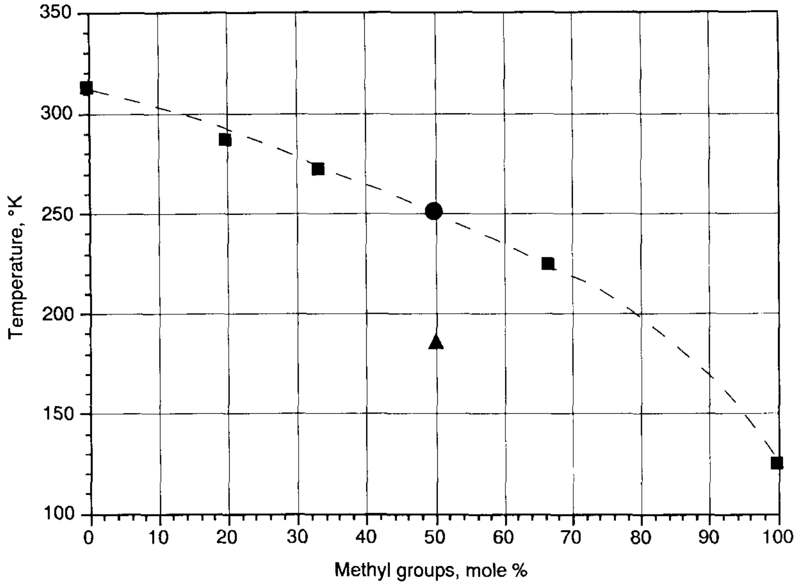


Figure 5 Glass transition temperature *versus* methyl substitution: ■, samples prepared in this investigation; ●, sample prepared at MMI by Y. Tarshiani; ▲, literature value[24]. (The line is only a guide for the eye)

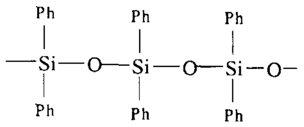
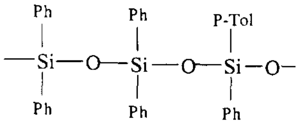
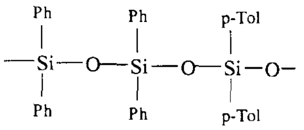
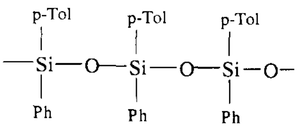
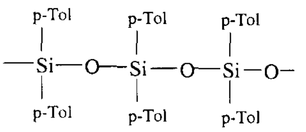
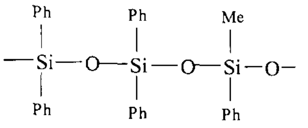
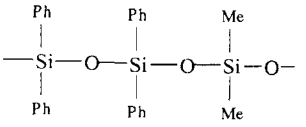
used to obtain d.s.c. and t.g.a. data had residual lithium concentrations below 1.5 ppm. As shown in *Table 6*, the various diarylsiloxane polymers examined here are thermally stable polymers, with t.g.a. 10% weight loss temperatures ranging from 455 to 515°C. It should be noted that the d.s.c. data for poly(diphenylsiloxane) show that the polymer is apparently stable to at least 540°C (with a sharp (melting) transition at this temperature), while t.g.a. shows a 10% weight loss at a lower temperature (511°C). The differences are probably related to the different test conditions, i.e. in the d.s.c. test the sample was in a sealed pan, whereas in the t.g.a. test the sample was exposed to a flowing stream of nitrogen.

The poly(diarylsiloxane)s examined in this study show T_gs between 40 and 50°C, but these transitions can only be observed by d.s.c. on the first heating cycle. If the polymers are recovered from the polymerization procedures without heating above their T_{lc} value, they remain partially amorphous and a T_g can be detected. However, when heated above T_{lc}, further crystallization occurs and the amorphous content becomes so low that the transition cannot be observed by d.s.c. *Figure 7* shows this effect for poly(diphenylsiloxane), in which the T_g is apparent near 50°C on the first heating cycle, but not on the second heating.

The T_{lc} values of this series of polymers pass through a minimum as phenyl groups are replaced by *p*-tolyl groups, with the end member of the series, poly(diphenylsiloxane) and poly(di(*p*-tolyl)siloxane), having the highest values (approximately 265 and 300°C, respectively). The clearing temperatures, T_m, also follow the same pattern, decreasing at first with increasing numbers of *p*-tolyl groups, and then rising with additional units. The T_{lc} values also increase with increasing molecular weight up to a molecular weight of about 55 000 (degree of polymerization, DP ≈ 250), as shown in *Figure 8* for poly((phenyl/*p*-tolyl)siloxane). The T_{lc} values of the poly(diarylsiloxane)s appears much more sensitive to molecular weight than for other liquid-crystal-forming polymers[25], where the liquid crystal and clearing temperatures generally level off at DPs above 100.

The average difference between T_{lc} and T_m for these

Table 6 Thermal gravimetric behaviour of siloxane polymers having phenyl and *p*-tolyl or methyl substituents

Polymer repeat unit	T.g.a. 10% weight loss temp. (°C)	Residual lithium content (ppm)
 $-\underset{\mathrm{Ph}}{\overset{\mathrm{Ph}}{\mathrm{Si}}}-\mathrm{O}-\underset{\mathrm{Ph}}{\overset{\mathrm{Ph}}{\mathrm{Si}}}-\mathrm{O}-\underset{\mathrm{Ph}}{\overset{\mathrm{Ph}}{\mathrm{Si}}}-\mathrm{O}-$	511	<1
 $-\underset{\mathrm{Ph}}{\overset{\mathrm{Ph}}{\mathrm{Si}}}-\mathrm{O}-\underset{\mathrm{Ph}}{\overset{\mathrm{Ph}}{\mathrm{Si}}}-\mathrm{O}-\underset{\mathrm{Ph}}{\overset{\mathrm{P\text{-}Tol}}{\mathrm{Si}}}-\mathrm{O}-$	483	<1.1
 $-\underset{\mathrm{Ph}}{\overset{\mathrm{Ph}}{\mathrm{Si}}}-\mathrm{O}-\underset{\mathrm{Ph}}{\overset{\mathrm{Ph}}{\mathrm{Si}}}-\mathrm{O}-\underset{\mathrm{p\text{-}Tol}}{\overset{\mathrm{p\text{-}Tol}}{\mathrm{Si}}}-\mathrm{O}-$	454	<1.5
 $-\underset{\mathrm{Ph}}{\overset{\mathrm{p\text{-}Tol}}{\mathrm{Si}}}-\mathrm{O}-\underset{\mathrm{Ph}}{\overset{\mathrm{p\text{-}Tol}}{\mathrm{Si}}}-\mathrm{O}-\underset{\mathrm{Ph}}{\overset{\mathrm{p\text{-}Tol}}{\mathrm{Si}}}-\mathrm{O}-$	469	–
 $-\underset{\mathrm{p\text{-}Tol}}{\overset{\mathrm{p\text{-}Tol}}{\mathrm{Si}}}-\mathrm{O}-\underset{\mathrm{p\text{-}Tol}}{\overset{\mathrm{p\text{-}Tol}}{\mathrm{Si}}}-\mathrm{O}-\underset{\mathrm{p\text{-}Tol}}{\overset{\mathrm{p\text{-}Tol}}{\mathrm{Si}}}-\mathrm{O}-$	516	<1
 $-\underset{\mathrm{Ph}}{\overset{\mathrm{Ph}}{\mathrm{Si}}}-\mathrm{O}-\underset{\mathrm{Ph}}{\overset{\mathrm{Ph}}{\mathrm{Si}}}-\mathrm{O}-\underset{\mathrm{Ph}}{\overset{\mathrm{Me}}{\mathrm{Si}}}-\mathrm{O}-$	–	–
 $-\underset{\mathrm{Ph}}{\overset{\mathrm{Ph}}{\mathrm{Si}}}-\mathrm{O}-\underset{\mathrm{Ph}}{\overset{\mathrm{Ph}}{\mathrm{Si}}}-\mathrm{O}-\underset{\mathrm{Me}}{\overset{\mathrm{Me}}{\mathrm{Si}}}-\mathrm{O}-$	489	–

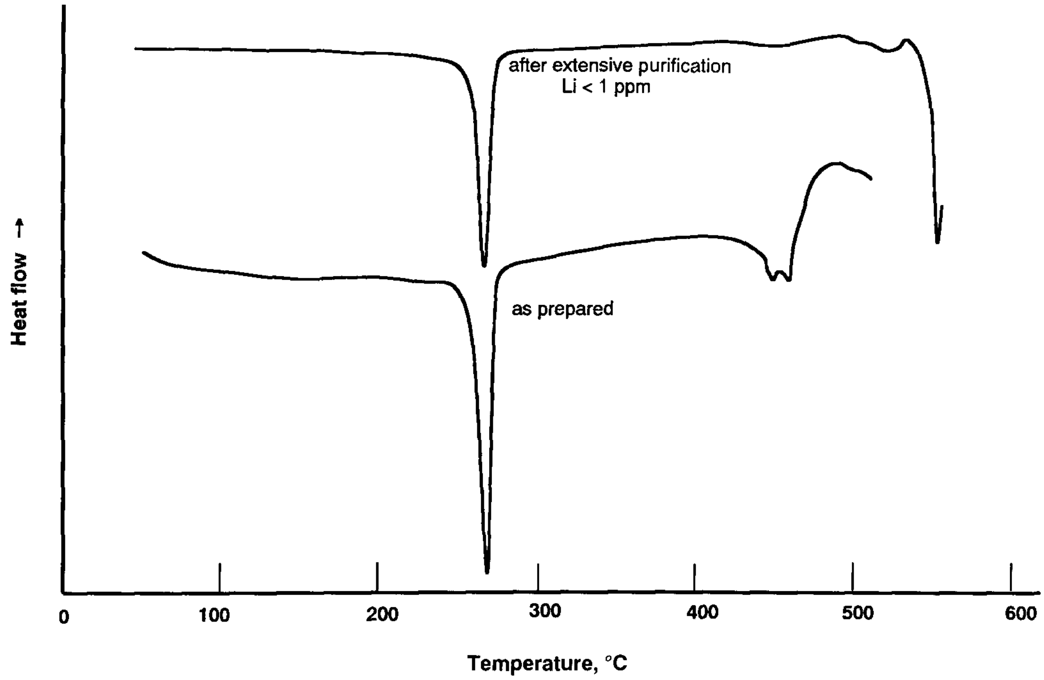


Figure 6 High-temperature d.s.c. behaviour of as-prepared and purified poly(diphenylsiloxane)

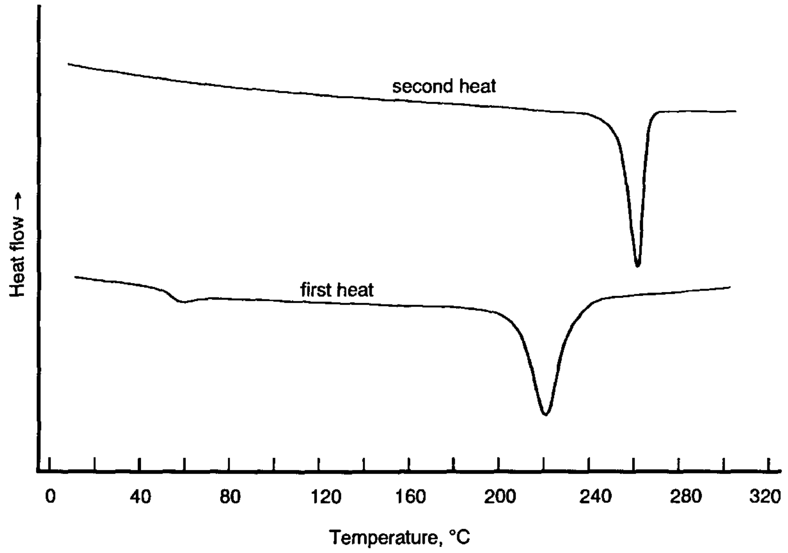


Figure 7 First and second d.s.c. heats of poly(diphenylsiloxane) showing T_g only on first heat

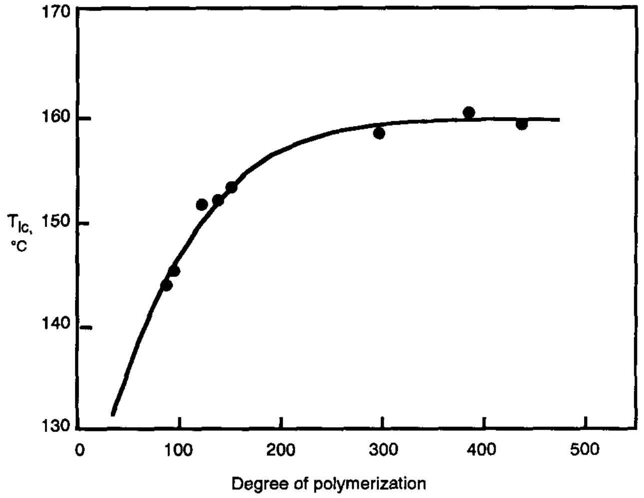


Figure 8 Liquid crystal transition temperature, T_{lc}, of poly((phenyl/*p*-tolyl)siloxane) *versus* degree of polymerization

polymers is about 285°C, which is much larger than the difference found for other types of liquid-crystalline polymers[26]. Thermal transition data are summarized in *Tables 7* and *8*.

The liquid-crystalline state of these polymers was observed visually by cross-polarized optical microscopy at 10 to 40°C above their T_{lc}. However, in order to allow high-magnification photography, the samples were quenched to room temperature, as has been described in other work[27]. By visual observation, the liquid-crystalline character was not changed by quenching. *Figure 9* shows the threaded Schlieren pattern typical[27] of the nematic state, which was found for all of the diarylsiloxane polymers except poly(di(*p*-tolyl)siloxane). *Figure 10* shows the smectic pattern[28] observed with poly(di(*p*-tolyl)siloxane) (the differences in the nematic and smectic textures are much more obvious when observed in colour).

Table 7 Thermal transitions of siloxane polymers having phenyl and *p*-tolyl substituents

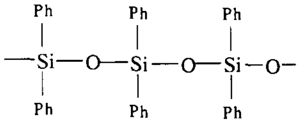
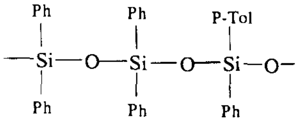
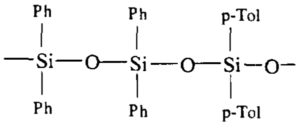
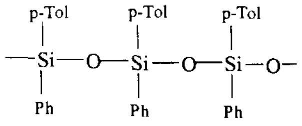
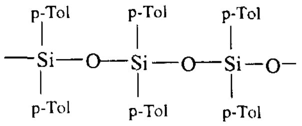
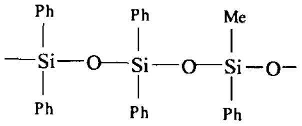
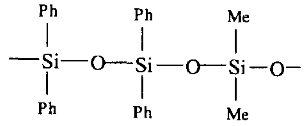
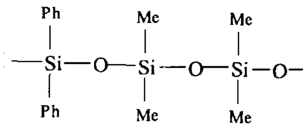
Polymer repeat unit	T_g (°C)	T_{lc} (°C)	T_m (°C)	$T_m - T_{lc}$ (°C)
 $-\underset{\text{Ph}}{\overset{\text{Ph}}{\text{Si}}}-\text{O}-\underset{\text{Ph}}{\overset{\text{Ph}}{\text{Si}}}-\text{O}-\underset{\text{Ph}}{\overset{\text{Ph}}{\text{Si}}}-\text{O}-$	40	265	540	275
 $-\underset{\text{Ph}}{\overset{\text{Ph}}{\text{Si}}}-\text{O}-\underset{\text{Ph}}{\overset{\text{Ph}}{\text{Si}}}-\text{O}-\underset{\text{Ph}}{\overset{\text{P-Tol}}{\text{Si}}}-\text{O}-$	40	185	460	275
 $-\underset{\text{Ph}}{\overset{\text{Ph}}{\text{Si}}}-\text{O}-\underset{\text{Ph}}{\overset{\text{Ph}}{\text{Si}}}-\text{O}-\underset{\text{p-Tol}}{\overset{\text{p-Tol}}{\text{Si}}}-\text{O}-$	40	140	430	290
 $-\underset{\text{Ph}}{\overset{\text{p-Tol}}{\text{Si}}}-\text{O}-\underset{\text{Ph}}{\overset{\text{p-Tol}}{\text{Si}}}-\text{O}-\underset{\text{Ph}}{\overset{\text{p-Tol}}{\text{Si}}}-\text{O}-$	50	160	450	300
 $-\underset{\text{p-Tol}}{\overset{\text{p-Tol}}{\text{Si}}}-\text{O}-\underset{\text{p-Tol}}{\overset{\text{p-Tol}}{\text{Si}}}-\text{O}-\underset{\text{p-Tol}}{\overset{\text{p-Tol}}{\text{Si}}}-\text{O}-$	50	300	480 (decomposition)	>180

Table 8 Thermal transitions of siloxane polymers having phenyl and methyl substituents

Polymer repeat unit	T_g (°C)	T_{lc} (°C)	T_m (°C)
 $-\underset{\text{Ph}}{\overset{\text{Ph}}{\text{Si}}}-\text{O}-\underset{\text{Ph}}{\overset{\text{Ph}}{\text{Si}}}-\text{O}-\underset{\text{Ph}}{\overset{\text{Me}}{\text{Si}}}-\text{O}-$	14	None	None
 $-\underset{\text{Ph}}{\overset{\text{Ph}}{\text{Si}}}-\text{O}-\underset{\text{Ph}}{\overset{\text{Ph}}{\text{Si}}}-\text{O}-\underset{\text{Me}}{\overset{\text{Me}}{\text{Si}}}-\text{O}-$	-1	None	None
 $-\underset{\text{Ph}}{\overset{\text{Ph}}{\text{Si}}}-\text{O}-\underset{\text{Me}}{\overset{\text{Me}}{\text{Si}}}-\text{O}-\underset{\text{Me}}{\overset{\text{Me}}{\text{Si}}}-\text{O}-$	-48	None	None

SUMMARY AND CONCLUSIONS

We have shown that a variety of poly(diarylsiloxane) and poly((aryl/alkyl)siloxane) polymers with controlled sequential distribution, molecular weight and distribution can be prepared by the lithium-initiated, ring-opening anionic polymerization of the cyclic trimers in solution. The polymers having phenyl and *p*-tolyl substituents are of great interest since they have a liquid-crystalline state as a consequence of steric interactions, which leads to chain rigidity. The liquid-crystalline state of the polymers is nematic except for poly(di(*p*-tolyl)siloxane), which shows a smectic texture by optical microscopy. In contrast to poly(diphenylsiloxane) and poly((*p*-tolyl)siloxane), which become soluble (in solvents such as diphenyl ether) only at very high temperatures, the mixed poly((phenyl/*p*-tolyl)siloxane)s are soluble in common solvents such as THF and chloroform at room temperature. We find this somewhat surprising since these polymers are highly crystalline and have T_{lc} values above 140°C.

The T_gs of the diarylsiloxane polymers are near 40°C, but the transitions are only detectable if the polymers have not been heated above T_{lc}. If heated above T_{lc} and then cooled, the polymers become so highly crystalline that T_g is no longer detectable by d.s.c. The T_{lc} span for these polymers is very large, i.e. the difference between T_c and T_m is about 285°C.

In contrast to the crystalline and liquid-crystalline character of polymers with phenyl and *p*-tolyl substituents, the replacement of a single phenyl group by a methyl group in the repeat triad of diphenyl units is sufficient to destroy both the crystalline and liquid-crystalline character of the polymer. This difference in the behaviour of the phenyl/*p*-tolyl systems and the phenyl/methyl systems is attributed to the different molecular volumes of the methyl and *p*-tolyl substituents and the concomitant differences in the steric interactions on the polymer chain.

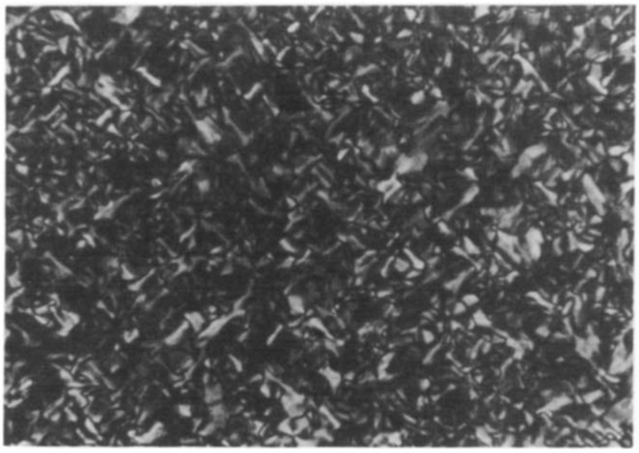


Figure 9 Optical micrograph (450×) of 'nematic' texture of poly((phenyl/*p*-tolyl)siloxane). Sample quenched from 200°C to room temperature

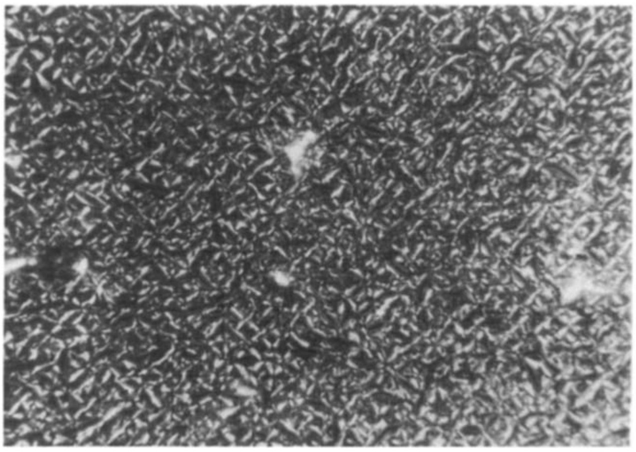


Figure 10 Optical micrograph (450×) of 'smectic' texture of poly(di(*p*-tolyl)siloxane). Sample quenched from 300°C to room temperature

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support provided by the Dow Corning Corporation, and thank Drs Gary Burns of the Dow Corning Corporation and Ned Gvozdic and John Saam of the Michigan Molecular Institute for their helpful advice and Anne Jurek for the n.m.r. data.

REFERENCES

1 Warrick, E. L., Pierce, O. R., Polmanteer, K. E. and Saam, J. C. *Rubber Chem. Technol.* 1979, **52**, 437

2 Lewis, F. M. *Rubber Chem. Technol.* 1962, **35**, 1222

3 Beatty, C. L., Pochan, J. M., Froix, M. F. and Hinman, D. D. *Macromolecules* 1975, **8**, 547

4 Godovsky, Y. K. and Papkov, V. S. *Makromol. Chem., Macromol. Symp.* 1986, **4**, 71

5 Lee, C. L., Johannson, O. K., Flaningam, O. L. and Hahn, P. *ACS Polym. Prepr.* 1969, **10**, 1319

6 Moller, M., Siffrin, S., Out, R. and Boileau, S. *ACS Polym. Prepr.* 1992, **33**, 176

7 Ibemesi, J., Gvozdic, N. V., Keumin, M., Lynch, M. J. and Meier, D. J. *ACS Polym. Prepr.* 1985, **26**, 18

8 Mark, J. E. and Chiu, D. S. *ACS Polym. Prepr.* 1977, **18**, 481

9 Falender, J. R., Yeh, G. S. Y., Chiu, D. S. and Mark, J. E. *J. Polym. Sci., Polym. Chem. Edn* 1980, **18**, 389

10 Vasilenko, N. G., Tartakovskaya, L. M., Lavrukhin, B. D. and Zhdanov, A. A. *Polym. Sci. USSR* 1989, **31**, 2225

11 Zhdanov, A. A., Tartakovskaya, L. M., Kopylov, V. M. and Vasilenko, N. G. *Polym. Sci. USSR* 1985, **27**, 2346

12 Vasilenko, N. G., Tartakovskaya, L. M., Babchinitser, T. M., Yermilova, N. V. and Zhdanov, A. A. *Polym. Sci. USSR* 1989, **31**, 1737

13 Babchinitser, T. M., Kazaryan, L. G., Tartakovskaya, L. M., Vasilenko, N. G., Zhdanov, A. A. and Korshak, V. V. *Polymer* 1985, **26**, 1527

14 Takiguchi, T., Sakurai, M. and Kishi, T. *J. Org. Chem.* 1960, **25**, 310

15 Prescott, P. I., Hills, B. and Selin, T. G. US patent no. 3,325,525 (to General Electric Co.), 1967

16 Prescott, P. I. and Selin, T. G. US patent no. 3,317,578 (to General Electric Co.), 1967

17 Ramsden, H. E., Balint, A. E., Whitford, W. R., Walburn, J. J. and Cserr, R. *J. Org. Chem.* 1957, **22**, 1202

18 Rosenberg, D., Walburn, J. J. and Ramsden, H. E. *J. Org. Chem.* 1957, **22**, 1606

19 Bostick, E. E. *ACS Polym. Prepr.* 1969, **10**, 877

20 Lee, C. L. and Marko, O. W. *ACS Polym. Prepr.* 1978, **19**, 250

21 Ibemesi, J., Gvozdic, N. V., Kuemin, M., Tarshiani, Y. and Meier, D. J. in 'Polymer Based Molecular Composites' (Eds J. E. Mark and D. W. Schaefer), Material Research Society, Pittsburgh, 1990

22 Momper, B., Wagner, Th., Maschke, U., Ballauff, M. and Fischer, E. W. *Polym. Commun.* 1990, **31**, 186

23 Engelhardt, G. and Jancke, H. *Polym. Bull.* 1981, **5**, 577

24 Polmanteer, K. E. and Hunter, M. J. *J. Appl. Polym. Sci.* 1959, **1**, 3

25 Sirgu, A. in 'Liquid Crystallinity in Polymers' (Ed. A. Ciferri), VCH Publishers, New York, 1991

26 Donald, A. M. and Windle, A. H. 'Liquid Crystalline Polymers', Cambridge University Press, Cambridge, 1992

27 Economy, J., Volksen, A. H., Viney, C., Geiss, R., Siemens, R. and Karis, T. *Macromolecules* 1988, **21**, 2777

28 Chung, T. S. *Polym. Eng. Sci.* 1986, **26**, 901