Synthesis and properties of diarylsiloxane and (aryl/methyl)siloxane polymers: 3. New aryl substituents

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In this paper we describe the synthesis and characterization of a new series of diarylsiloxane polymers, in which the aryl substituents are either *m*-tolyl, 4-methoxyphenyl or 4-propylphenyl. The polymers were prepared by the ring-opening anionic polymerization of cyclic trimers in solution at high temperatures. The structure and compositions of the cyclic trimers were confirmed by ^{1}H and ^{29}Si n.m.r. The new diaryl polymers are all highly crystalline, and each melts to a liquid crystalline state. The crystal–liquid crystal transition temperatures depend on the nature of substituents and follow the order: di(4-methoxyphenyl) $\cong$ di(*p*-tolyl) > di(phenyl) > di(4-propylphenyl) > di(*m*-tolyl). The transition temperatures of polydi(4-methoxyphenyl)siloxane and polydi(*p*-tolyl)siloxane are both very high (300°C). The solubility of the diarylsiloxane polymers is strongly affected by the nature of the aryl substituents. Polymers having di(4-methoxyphenyl), di(*p*-tolyl) or di(phenyl) substituents are only soluble at temperatures above 150°C in solvents such as dimethylsulfoxide and diphenyl ether. Polydi(*m*-tolyl)siloxane and the mixed poly(*p*-tolyl/phenyl)siloxanes are soluble in toluene and chloroform at room temperature. Polydi(4-propylphenyl)siloxane crystallizes slowly, and if recovered and tested before becoming fully crystalline it will dissolve in common solvents such as toluene and chloroform at room temperature. However, after annealing it becomes soluble only at high temperatures. The cyclic trimer of di(*o*-tolyl)siloxane could only be prepared in trace quantities, and we were unsuccessful in preparing polydi(*o*-tolyl)siloxane, probably because of the steric interactions of the *o*-tolyl groups.

(Keywords: synthesis; characterization; poly(diarylsiloxane)s)

INTRODUCTION

In previous papers[1,2], we described the thermal and solution properties of a number of diarylsiloxane polymers in which the aryl substituents were either phenyl and/or *p*-tolyl. We showed that polydiphenylsiloxane and poly(*p*-tolyl)siloxane are highly crystalline and melt at high temperatures (265 and 300°C, respectively) to liquid crystalline states. The liquid crystalline character is still observed in the 'mixed' poly(phenyl/*p*-tolyl)siloxanes, although the transition temperatures are lower and the solubility properties are quite different from the 'unmixed parents', polydiphenylsiloxane and poly(*p*-tolyl)siloxane. In contrast to the ubiquitous liquid crystalline behaviour of the diarylsiloxane polymers, we also showed[1] that the replacement of even one aryl group in the repeat triad of a polydiarylsiloxane chain by a methyl group (e.g. changing the repeat triad from hexaphenyl to pentaphenyl/monomethyl) was sufficient to completely eliminate the crystalline and liquid crystalline character of the polymer.

In this paper, we report on the synthesis and properties of several new diarylsiloxane polymers, with the objective of providing additional information concerning the relationship between structure and properties for this class of polymers. In particular, the thermal properties of these polymers are emphasized.

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EXPERIMENTAL

Materials

1-Bromo-4-methoxybenzene (Aldrich), 1-bromo-4-propylbenzene (Aldrich), 2-chlorotoluene, 3-chlorotoluene, silicone tetrachloride (Aldrich) and *s*-butyl lithium (Aldrich) were used without further purification. Diphenyl ether (DPE, Aldrich) was used as the solvent for the anionic polymerization; it was purified by vacuum distillation, passed through activated alumina and then distilled again over calcium hydride. Dimethylsulfoxide (DMSO, Aldrich) and hexane (Fisher) were distilled over calcium hydride before use. Magnesium turnings (Aldrich) were dried at 100°C under vacuum to remove any trace of water.

Synthesis of the cyclic trimers

The general procedure for preparing the cyclotrisiloxanes was by cyclization of the corresponding dichlorosilanes with ZnO[3]. The diaryldichlorosilanes were prepared by the Grignard reaction between silicone tetrachloride and the arylmagnesium bromides[4–7]. The detailed procedures are described below and an example is shown in *Figure 1*.

Di(4-propylphenyl)dichlorosilane. 1-Bromo-4-propylbenzene (1 mol) was dissolved in 200 ml of ethyl ether and slowly added to Mg turnings (0.95 mol) in 400 ml of ether. The Grignard reaction gradually initiated under reflux

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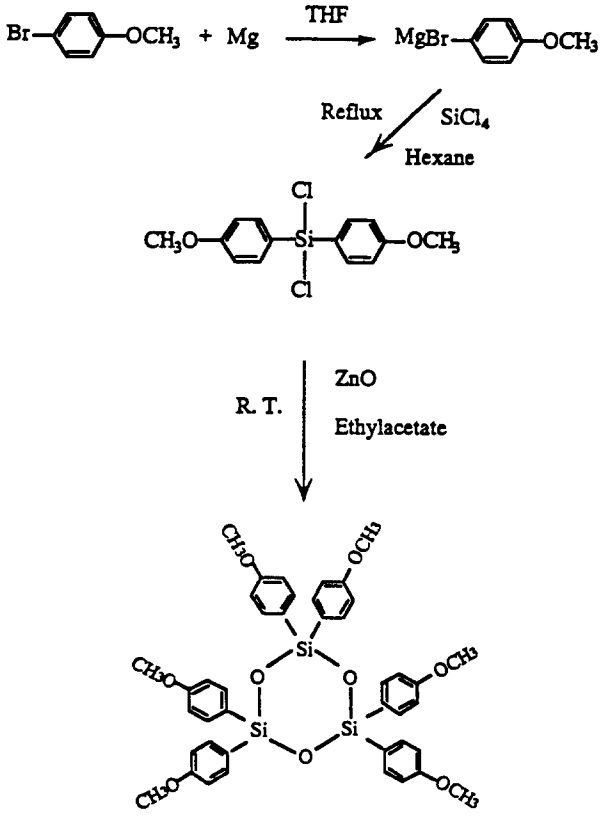


Figure 1 Synthesis of hexa(4-methoxyphenyl)cyclotrisiloxane

conditions, and after completion of the 1-bromo-4-propylbenzene addition (1 h) the reaction was allowed to continue for 1–2 h until the Mg was almost completely consumed. $SiCl_4$ (0.45 mol) in 150 ml of ether was added at a rapid dropwise rate with vigorous stirring at room temperature. The addition time was 1 h and the reaction was continued for 2 h under reflux conditions. The desired di(4-propylphenyl)dichlorosilane was obtained from the reaction mixture by fractional distillation under vacuum (~170°C/200 Pa) after the MgBrCl was filtered off. The yield was about 56%.

Di(4-methoxyphenyl)dichlorosilane. 1-Bromo-4-methoxybenzene (1 mol) was dissolved in 150 ml of tetrahydrofuran (THF) and slowly added to Mg turnings (0.95 mol) in 100 ml of THF. The Grignard reaction gradually initiated at room temperature and after completion of the 1-bromo-4-methoxybenzene addition (1.5 h), the reaction was allowed to continue for 2 h until the Mg was almost completely consumed. $SiCl_4$ (0.45 mol) in 250 ml of hexane was added at a rapid dropwise rate with vigorous stirring at room temperature. The addition time was 1 h and the reaction was continued for 2 h at 60°C. The desired di(4-methoxyphenyl)dichlorosilane was obtained from the reaction mixture by fractional distillation under vacuum (~200°C/266 Pa) after the MgBrCl was filtered off. The yield was about 40%.

Di(o-tolyl)dichlorosilane and di(m-tolyl)dichlorosilane. 2-Chlorotoluene or 3-chlorotoluene (1.5 mol) was dissolved in 300 ml of THF and slowly added to Mg turnings (1.35 mol) in 100 ml of THF. The Grignard reaction was initiated by adding 5 ml of 1,2-dibromoethane or the corresponding bromotoluene at 100°C. After completion of the chlorotoluene addition (90 min), the reaction was allowed to continue for 2 h until the Mg was almost completely consumed. $SiCl_4$ (0.65 mol) in 100 ml of THF was added at a rapid dropwise rate with vigorous stirring at room temperature. The desired di(*o*-tolyl) or di(*m*-tolyl)dichlorosilane was obtained from the reaction mixture by fractional distillation under vacuum (~140°C/133 Pa) after the $MgCl_2$ was filtered off. The yields were typically about 50%.

Hexa(4-propylphenyl)cyclotrisiloxane, hexa(4-methoxyphenyl)cyclotrisiloxane, hexa(o-tolyl)cyclotrisiloxane and hexa(m-tolyl)cyclotrisiloxane. The diaryldichlorosilanes (0.25 mol) in 200 ml ethyl acetate were slowly added with vigorous stirring to a suspension of ZnO (0.375 mol) in 250 ml of ethyl acetate at room temperature or at 50°C. After the last addition of the dichlorosilane (1 h), the solution mixture was stirred for a few hours up to 24 h at room temperature. The resulting $ZnCl_2$ and excess ZnO were filtered off and 300 ml of benzene was added, followed by washing four times with 200 ml of water. Solvents were removed by evaporation to yield a mixture consisting mainly of cyclic trimers and other cyclic oligomers. The cyclic trimers (other than hexa(*m*-tolyl)cyclotrisiloxane) were separated by recrystallization from a toluene/methanol solution, with a yield of about 10–30%. The yield for hexa(*o*-tolyl)cyclotrisiloxane was only about 2–3%. Hexa(*m*-tolyl)cyclotrisiloxane was recovered by precipitation in toluene/methanol solution, but significant amounts of the cyclic tetramer could not be removed, and remained in this sample.

Polymer synthesis

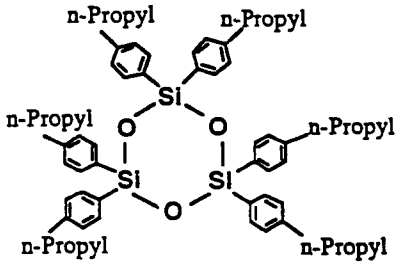
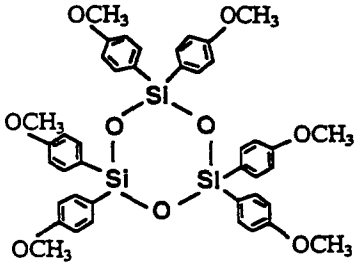
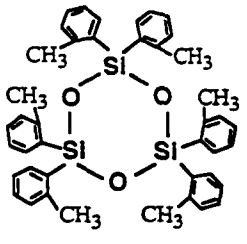
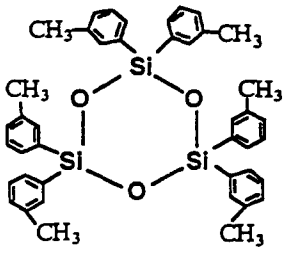
The detailed polymerization procedures have been described in a previous paper[1], and will be only briefly described here. In general, the polymers were prepared by the ring-opening anionic polymerization of corresponding cyclic trimers in diphenyl ether solution at 150 or 190°C. *s*-Butyl lithium was used as the polymerization initiator with DMSO as the promoter[1,8,9]. Polymerization occurred over a 1 h period. Polydi(4-methoxyphenyl)siloxane was recovered by precipitation in toluene, followed by filtration and repeated washing with toluene to remove the remaining cyclic and initiator impurities. Polydi(*n*-propylphenyl)siloxane and polydi(*m*-tolyl)siloxane were recovered by precipitation with methanol and purified by fractional precipitation with a toluene/methanol mixture. The polymers were dried in a vacuum oven at 80–100°C for 16 h.

The preparation of polydi(*o*-tolyl)siloxane by these procedures was unsuccessful. An attempt was also made to obtain this polymer by polymerization of the cyclic trimer in bulk using KOH as the initiator, but again without success.

Characterization

The molecular weights of polydi(*n*-propylphenyl)-siloxane and polydi(*m*-tolyl)siloxane (which are soluble in chloroform at 40°C) were obtained by gel permeation chromatography (g.p.c.), with reported molecular weights being based on polystyrene standards using elution peak values. The molecular weight of polydi(4-methoxyphenyl)siloxane was obtained from intrinsic viscosity measurements in DPE at 200°C, using an Ubbelohde viscometer (Cannon Instruments Co.). The reported value is based on the intrinsic viscosities of polystyrene standards, also obtained at 200°C in DPE. No evidence

Table 1 Thermal behaviour and ^{29}Si n.m.r. chemical shifts of cyclotrisiloxanes containing 4-(*n*-propyl)phenyl, 4-methoxyphenyl, *o*-tolyl or *m*-tolyl substituents

Cyclic trimer	T_m (°C)	ΔH_m[a] ($J g^{-1}$)	^{29}Si n.m.r. chemical shift (ppm)
	118	54	−33.28
	212	35	−33.10
	201	60	−33.61
	–[b]	–	−33.61

[a]Heat of fusion
[b]Contains 55% of cyclic tetramers and oligomers

of degradation of either polydi(4-methoxyphenyl)siloxane or polystyrene was observed during the time required for the measurements.

Differential scanning calorimetry (d.s.c.) data were obtained using a DuPont 910 thermal analyser 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_g, are reported as the mid-point of the temperature range of the transition, while the crystal–liquid crystal transition temperatures, T_{lc}, are reported as peak temperatures.

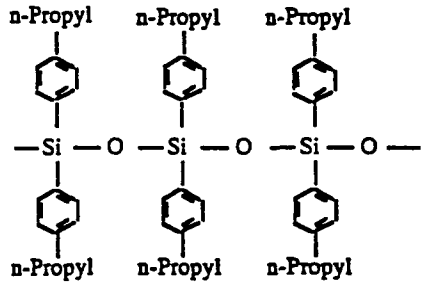
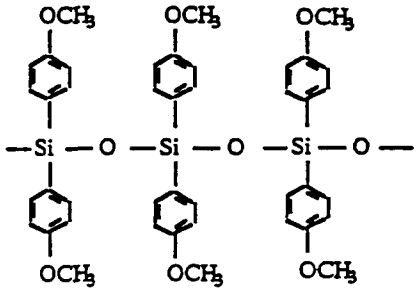
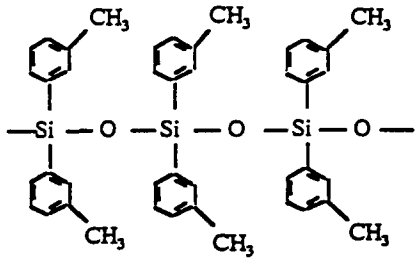
Thermogravimetric analysis (t.g.a.) was performed on a DuPont 951 TGA at a heating rate of 10°C min^{-1} with a nitrogen flow rate of 50 ml min^{-1}.

^1H and ^{29}Si n.m.r. spectra were obtained using a Bruker 360 MHz spectrometer.

RESULTS AND DISCUSSION

Thermal data for the diaryl cyclic trimers are shown in *Table 1*. The melting point, T_m, of trimers decreases as the length of the alkyl group on the benzene ring increases, as shown by comparing the melting points of hexa(*p*-tolyl)cyclotrisiloxane[1] (260°C) with that of hexa(*n*-propylphenyl)cyclotrisiloxane (118°C). The melting point of the *o*-tolyl trimer is also significantly lower than that of the *p*-tolyl trimer. Vasilenko *et al.*[10] have reported the melting point of hexa(*m*-tolyl)cyclotrisiloxane as 80°C, but we did not observe a melting transition, perhaps because our sample contained a significant amount of the cyclic tetramer. A mixture of the cyclic trimer of dimethylsiloxane (hexamethylcyclotrisiloxane, D_3) and

Table 2 Molecular weights, polymerization yields and solubility of siloxane polymers having 4-(*n*-propyl)phenyl, 4-methoxyphenyl or *m*-tolyl substituents

Polymer structure	MW	Yield (%)	Soluble in $CHCl_3$ at r.t.
	21 000	32	No (after annealing)
	44 000	66	No
	16 000	10	Yes

the cyclic tetramer (octamethylcyclotetrasiloxane, D_4) is a liquid although D_3 is a crystalline solid with a melting point of 65°C. It would therefore not be surprising to find that a mixture of trimers and tetramers of di(*m*-tolyl)cyclotrisiloxane is also a liquid at room temperature.

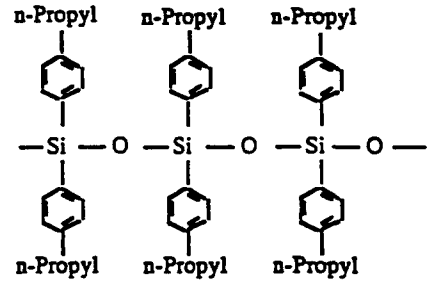
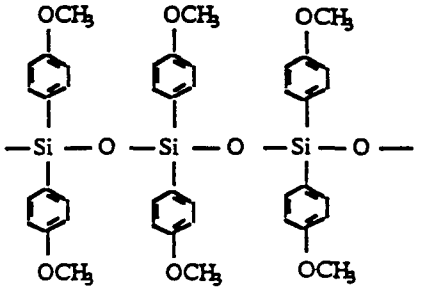
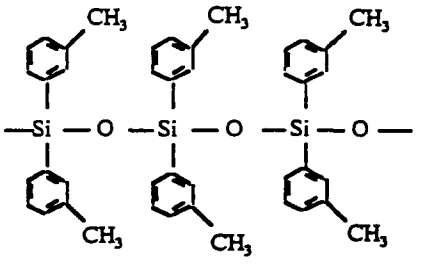
The cyclization of di(*o*-tolyl)dichlorosilane was very difficult, and only a trace amount of the cyclic trimer was obtained. The limited yield could arise from either steric hindrance of *o*-tolyl groups preventing the cyclization reaction, or from the limited solubility of di(*o*-tolyl)-dichlorosilane in the methylacetate or ethylacetate used as the cyclization medium.

The composition and structure of these trimers were confirmed by ^1H and ^{29}Si n.m.r. The chemical shifts of ^{29}Si n.m.r. are shown in *Table 1* and confirm that the materials are the cyclic trimers. The ^{29}Si peaks are located between -33 and -34 ppm, a region which has been identified as that for the cyclic trimers[1]. The cyclic tetramers have chemical shift peaks between -42 and -43 ppm[11].

The yields and molecular weights of the polymers are shown in *Table 2*. All molecular weights are based on polystyrene standards, either g.p.c. standards in $CHCl_3$ at 40°C or intrinsic viscosity standards in DPE at 200°C. Polydi(4-propylphenyl)siloxane is a highly crystalline solid and is not soluble at or near room temperature in chloroform. However, it can be recovered from the hot polymerization medium by precipitation with cold methanol in a form which is soluble in chloroform at 40°C. This allows the molecular weight to be determined by g.p.c. techniques at modest temperatures. However, if the polymer is annealed for 1 day at 120°C, the crystallinity increases to the extent that it is no longer soluble except at very high temperatures. Polydi(*m*-tolyl)siloxane is soluble in common solvents such as chloroform and toluene at room temperature. The solubility of polydi(4-methoxyphenyl)siloxane is similar to that of polydi(*p*-tolyl)siloxane and polydiphenylsiloxane in that it is only soluble in DPE or DMSO at temperatures above 150°C.

The thermal properties of these three new polymers are shown in *Table 3*. The thermal behaviour of polydi(4-methoxyphenyl)siloxane and polydi(*p*-tolyl)siloxane are similar, with $T_g \approx 35$°C and $T_{lc} \approx 300$°C. However, the clearing or melting temperature, T_m, of polydi(4-methoxyphenyl)siloxane was not observed, because the polymer began to degrade at about 425°C before the clearing temperature was reached. Both polydi(4-propylphenyl)-siloxane and polydi(*m*-tolyl)siloxane have T_g values below 0°C, and their T_{lc} values are much lower than that for

Table 3 Thermal transitions and t.g.a. behaviour of siloxane polymers having 4-(*n*-propyl)phenyl, 4-methoxyphenyl or *m*-tolyl substituents

Polymer structure	T_g (°C)	T_{1c} (°C)	T_m (°C)	T.g.a. 10% wt loss temp. (°C)
	−7	149	500	509
	35	300	(decomp. at 425°C)	450
	−5	131	530	458

polydi(*p*-tolyl)siloxane or polydiphenylsiloxane. However, their T_m values are only slightly lower than that for polydiphenylsiloxane (500°C for polydi(4-propylphenyl)-siloxane, 530°C for polydi(*m*-tolyl)siloxane, *versus* 541°C for polydiphenylsiloxane).

The t.g.a. data in *Table 3* show that these polymers are thermally stable, with 10% weight loss temperatures between 450 and 509°C. For comparison, the 10% weight loss temperature for polydimethylsiloxane is reported[12] as 400–440°C, for poly(methyl/phenyl)siloxane[13] as 450–470°C and 511°C for polydiphenylsiloxane[1]. Polydi(4-methoxyphenyl)siloxane seems to have a lower decomposition temperature than any of the other diarylsiloxane polymers that we have examined.

SUMMARY AND CONCLUSIONS

Three new polydiarylsiloxanes with 4-methoxyphenyl, 4-propylphenyl or *m*-tolyl substituents have been synthesized and characterized. The polymers were prepared by the lithium-initiated, ring-opening anionic polymerization of the cyclic trimers in solution. The structure and compositions of these cyclic trimers were confirmed by ^1H and ^{29}Si n.m.r. The polymers are all highly crystalline and all show a transition to a liquid crystalline state at high temperatures. Polydi(*m*-tolyl)siloxane is soluble in common solvents such as chloroform and toluene at room temperature, while polydi(4-methoxyphenyl)siloxane is only soluble in DPE or DMSO at temperatures greater than 150°C. Poly(4-propylphenyl)siloxane can be obtained in a soluble form by precipitation in cold methanol, but after annealing it also becomes soluble only at high temperatures. The crystal–liquid crystalline transition temperature for polydi(4-methoxyphenyl)siloxane is much higher than for polydi(4-propylphenyl)siloxane or polydi(*m*-tolyl)siloxane, and is similar to that for polydi(*p*-tolyl)siloxane, i.e. ~300°C. The effect of various diaryl substituents on the crystal–liquid crystal transition temperatures for the polydiarylsiloxanes, reported here and in a previous publication[1], follow the order di(4-methoxyphenyl) ≅ di(*p*-tolyl) > diphenyl > di(4-propylphenyl) and > di(*m*-tolyl). The t.g.a. 10% weight loss temperatures of the various diarylsiloxane polymers are generally between 450 and 510°C, but polydi(4-methoxyphenyl)siloxane has a somewhat lower value, with d.s.c. measurements showing degradation beginning at about 425°C.

The preparation of hexa(*o*-tolyl)cyclotrisiloxane by reacting the corresponding dichlorosilane with ZnO yielded only trace amounts of the trimer, and subsequent attempts to prepare the polymer in solution with *s*-butyl lithium as initiator or in bulk with KOH as initiator were

not successful. The problem is probably due to the extreme steric interaction of the *o*-tolyl substituents.

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