Synthesis and properties of diarylsiloxane and (aryl/methyl)siloxane polymers: 2. Solution and rheological properties

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Polydiarylsiloxanes and polydialkylsiloxanes, with alkyl groups larger than methyl, have liquid-crystalline states, presumably as the result of a chain-rigidifying effect from steric interactions of the bulky aryl or alkyl groups along the chain. In the first paper of this series, we reported on the thermal behaviour of a number of diarylsiloxane polymers with phenyl and/or *p*-tolyl substituents, all of which showed liquid-crystalline behaviour at high temperatures. The solution properties of several of the 'mixed' poly(phenyl/*p*-tolyl)siloxane polymers have now been investigated in order to characterize their chain stiffness properties and to relate these to the tendency to form a liquid-crystalline state in bulk. The 'mixed' poly(phenyl/*p*-tolyl)siloxanes were chosen for investigation since they have a major advantage in experimental convenience over the 'unmixed parent' polymers, polydiphenylsiloxane and polydi(*p*-tolyl)siloxane. The former are soluble at room temperature in common solvents, whereas the latter polymers are only soluble at temperatures above 150°C. The various diarylsiloxane polymers were prepared by anionic polymerization of the cyclic trimers, and the preservation of the triad sequences (absence of 'scrambling') was confirmed by ^{29}Si n.m.r. Values of the Mark–Houwink–Sakurada exponent, a, for three different types of poly(phenyl/*p*-tolyl)siloxanes are essentially equal, at ~ 0.83. This value of the exponent is below the value expected for a rigid chain ($a > 1.0$) but is above the maximum value expected for a flexible random-coil polymer in a good solvent ($a \leqslant 0.8$). The shear viscosity of solutions of the mixed poly(phenyl/*p*-tolyl)siloxane polymers increases monotonically with increasing polymer concentration up to 60 wt%, and does not show an abrupt drop in viscosity above a critical concentration, as is often observed with rigid-rod polymers. This observation, together with the value of the Mark–Houwink–Sakurada exponent, $a < 1$, indicates that these polymers do not behave in solution as rigid-rod polymers, but most likely as worm-like chains with a relatively large persistence length.

(Keywords: polysiloxanes; rheology; solution properties)

INTRODUCTION

Liquid-crystalline polymers of the polyarylester[1] and polyaramid[2] types are currently receiving a great deal of attention as a result of their excellent strength and high-temperature properties. The solution and rheological properties of these main-chain liquid-crystalline polymers have been the subject of a number of investigations[3–9], but there are many questions yet unanswered about their solution behaviour. Most main-chain polymers which form liquid crystals are produced by condensation reactions, which limit the molecular weight range available and also give a broad molecular weight distribution. Even more important, such liquid-crystalline polymers dissolve in only a few (usually corrosive) solvents such as concentrated sulfuric or phosphoric acids, which makes the characterization of their molecular and solution properties difficult. Additional complications arise from polyelectrolyte effects from protonation of the polymers when dissolved in strong acids[5,7].

Another class of polymers that has been shown to have liquid-crystalline states includes certain polydialkylsiloxanes, e.g. polydiethylsiloxane[9] and polydiarylsiloxanes such as polydiphenylsiloxane[10]. These siloxane polymers have a great advantage over the conventional liquid-crystalline polymers produced by condensation reactions in that they can be obtained with any desired molecular weight and with a narrow molecular weight distribution by use of anionic polymerization techniques. The published work to date on the properties of the polydialkylsiloxanes and polydiarylsiloxanes has focused on their various thermal transitions and thermal stabilities. Solution properties, and their relation to chain stiffness properties, have been reported only for polydipropylsiloxane[11]. In this paper, we report on the solution properties (inherent viscosity, $[\eta]$/molecular weight, M, and viscosity, η/concentration relationships) of various diarylsiloxanes which have a liquid-crystalline state in bulk.

In a previous paper[10], we described some of the thermal properties of various polydiarylsiloxanes with phenyl and *p*-tolyl substituents. These polymers are highly crystalline and, depending on composition, melt to a liquid-crystalline state at temperatures from 150 to 300°C. Melting to the isotropic liquid state occurs at temperatures near or above 500°C. The polymers that have been of greatest interest for this investigation have been those containing both phenyl and *p*-tolyl substituents on the

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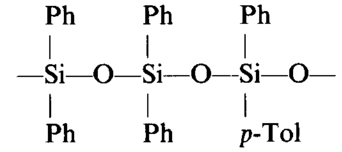
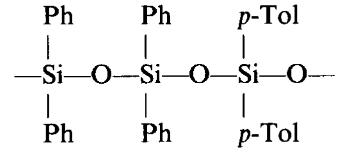
siloxane backbone. By combining these substituents, the liquid-crystalline transition temperatures are reduced and, more importantly, the polymers become soluble in common solvents at room temperature. In contrast, the 'parent' polymers, polydiphenylsiloxane and polydi(*p*-tolyl)siloxane, are only soluble in a few solvents and then only at temperatures above 150°C, which obviously makes characterization of their solution properties more difficult. The mixed phenyl/*p*-tolyl polydiarylsiloxanes investigated are:



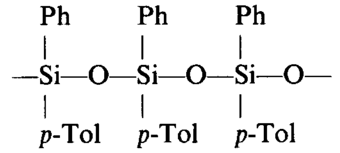
$$-\underset{Ph}{\overset{Ph}{Si}}-O-\underset{Ph}{\overset{Ph}{Si}}-O-\underset{p\text{-Tol}}{\overset{Ph}{Si}}-O-$$

designated as PPP′



$$-\underset{Ph}{\overset{Ph}{Si}}-O-\underset{Ph}{\overset{Ph}{Si}}-O-\underset{p\text{-Tol}}{\overset{p\text{-Tol}}{Si}}-O-$$

PPP″



$$-\underset{p\text{-Tol}}{\overset{Ph}{Si}}-O-\underset{p\text{-Tol}}{\overset{Ph}{Si}}-O-\underset{p\text{-Tol}}{\overset{Ph}{Si}}-O-$$

P′P′P′

where *P* represents a diphenylsiloxane group, P′ represents a phenyl/(*p*-tolyl)siloxane group and P″ represents a di(*p*-tolyl)siloxane group in the repeat triads of these polymers. Note that these triad sequences repeat exactly along the polymer chains, since head-to-head polymerization or randomization ('scrambling') of the individual siloxane units occurs to a negligible degree with the polymerization method used[10].

EXPERIMENTAL

Polymer synthesis

The mixed poly(phenyl/*p*-tolyl)siloxanes with different molecular weights have been prepared by the lithium-initiated, ring-opening polymerization of the cyclic trimers in diphenyl ether solution. The detailed procedure was described in a previous paper[10]. The polymerization reactions were done near 160°C under a purified nitrogen atmosphere, using *s*-butyl lithium as the polymerization initiator and dimethylsulfoxide (DMSO) or tetrahydrofuran (THF) as the promoter. The polymers were recovered by precipitation with methanol and purified from residual cyclics by fractional precipitation using a toluene/methanol mixture.

Molecular weights

The molecular weights of the polymers were obtained by gel permeation chromatography (g.p.c.) in toluene or chloroform solution at 40°C using polystyrene standards. The results were corrected to 'absolute' molecular weights using the Universal Calibration relationship[12], i.e. by the relationship

$$[MW]_{\mathrm{Si}}[\eta]_{\mathrm{Si}} = [MW]_{\mathrm{PS}}[\eta]_{\mathrm{PS}}$$

at equal elution (hydrodynamic) volumes.

Intrinsic viscosities

Ubbelohde viscometers (Cannon Instruments Co.) were used for viscosity measurements. They had drop times sufficiently long (>100 s) that kinetic energy corrections were not necessary. Intrinsic viscosities were obtained by extrapolating $(\eta_r - 1)/c$ and $(1/c)\ln\eta_r$ to a common intercept at zero concentration (η_r is the relative viscosity, $\eta_{\mathrm{solvent}}/\eta_{\mathrm{solvent}}$, and c is the polymer concentration).

Viscosities of concentrated solutions

Solution viscosities as a function of concentration of the P′P′P′ polymer in toluene at 25°C were obtained with a Carri Med CLS-100 Controlled-Stress Rheometer, using cone-and-plate geometry with a 60 mm cone and 1° cone angle.

RESULTS AND DISCUSSION

Log–log plots of intrinsic viscosities as a function of molecular weight of the polymers PPP′, PPP″ and P′P′P′ are shown in *Figure 1*. Within experimental error, the slopes (the exponents, *a*, of the Mark–Houwink–Sakurada equation $[\eta]=KM^a$) are the same ($a \cong 0.83$) for these polymers. The intrinsic viscosities (in units of dl g^{-1}) as a function of molecular weight are:

PPP′ $[\eta]=2.1\times10^{-5}M^{0.83}$ in chloroform at 40°C
PPP″ $[\eta]=2.6\times10^{-5}M^{0.83}$ in toluene at 40°C
P′P′P′ $[\eta]=2.4\times10^{-5}M^{0.83}$ in toluene at 40°C

It is of interest to note that the exponents, *a*, reported for polydimethylsiloxane (a very flexible chain) in toluene at 25°C have covered the surprisingly large range of values, from 0.5 to 0.84 (refs 13 and 14), with intermediate values of 0.59, 0.62, 0.66 and 0.72 (refs 15–18) also reported. Values reported for other siloxane polymers are 0.58 for polydipropylsiloxane[11] and 0.78 for poly(methyl/phenyl)siloxane[19], both in toluene at 25°C. It is obvious that the values of the exponents do not correlate with the tendency to form a liquid-crystalline state in bulk, since polydipropylsiloxane ($a=0.58$) does have a liquid-crystalline state[20], while poly(methyl/phenyl)siloxane ($a=0.78$) does not[10]. Of course, the values of the exponents are also a function of the solvent 'quality', so a comparison of *a* and the tendency to form a liquid-crystalline state is completely valid only for solutions of similar thermodynamic quality, e.g. theta solutions.

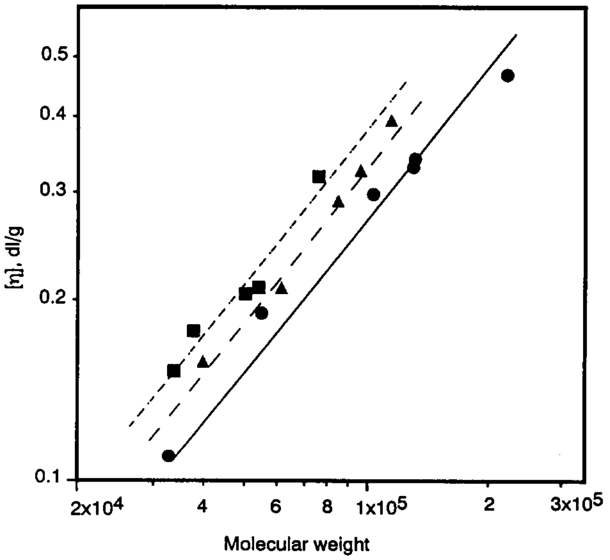


Figure 1 Log[η] *versus* log(MW) for poly(phenyl/*p*-tolyl)siloxanes: ■, PPP″; ●, PPP′; ▲, P′P′P′. See text for sample designations

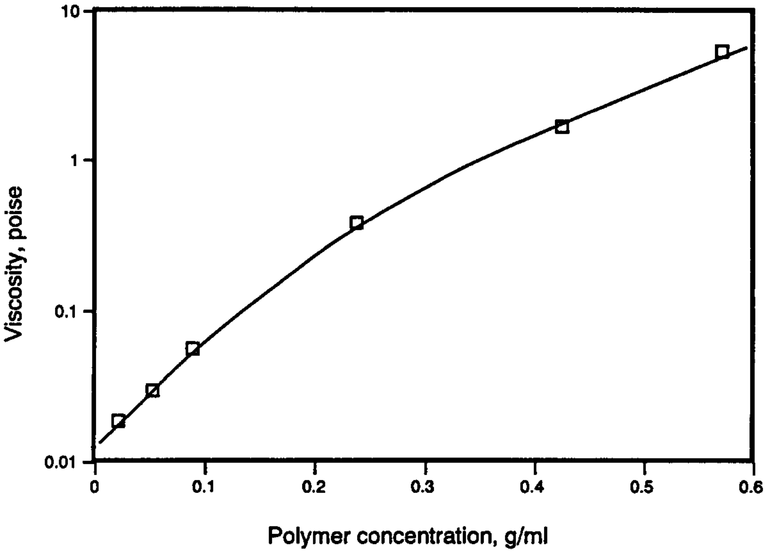


Figure 2 Viscosity of solutions of poly(phenyl/*p*-tolyl)siloxane(P′P′P′) in toluene as a function of concentration

The Mark–Houwink–Sakurada exponents found here for the polydiarylsiloxanes ($a \cong 0.83$) are lower than those expected for a rigid-rod polymer ($a > 1.0$), but are above the maximum value ($a \leqslant 0.8$) expected for a flexible-chain polymer in a 'good' solvent environment. The relatively high values for the diarylsiloxanes are most likely a consequence of the bulkiness and resulting steric interactions of the diaryl substituents along the chain, which force the chains to become extended worm-like chains with a relatively large persistence length, i.e. to show some degree of chain rigidity.

The shear viscosity of the P′P′P′ polymer increases in a monotonic fashion with increasing polymer concentration, as shown in *Figure 2*. There is no indication of an abrupt drop in viscosity above a critical concentration, as has been observed with many rigid-chain polymers, e.g. the aramides in sulfuric acid solution[7,8,21]. This fact, together with the Mark–Houwink–Sakurada exponent being lower than expected for a rigid-rod polymer, again indicates that the poly(phenyl/*p*-tolyl)siloxanes do not behave as typical rigid-rod polymers in solution.

CONCLUSIONS

The solution properties of three types of polydiarylsiloxanes with mixed phenyl and *p*-tolyl substituents on the siloxane backbone have been investigated in order to characterize their chain stiffness properties. The mixed phenyl/*p*-tolyl diarylsiloxanes were chosen for experimental convenience, since polymers with mixed phenyl/*p*-tolyl substituents are soluble at room temperature in common solvents such as toluene and chloroform, in contrast to polydiphenylsiloxane and polydi(*p*-tolyl)siloxane which are soluble only above 150°C. The values of Mark–Houwink–Sakurada exponent, *a*, for the various polymers are the same ($a \cong 0.83$) within experimental error. This value is below that expected for a rigid-rod polymer ($a > 1.0$), but is above the maximum value ($a \leqslant 0.8$) expected for a flexible polymer in a good solvent. The relatively high value indicates that the polymers in solution are most likely 'worm-like' with a relatively large persistence length. An additional indication that these polymers do not behave as very rigid rods in solution is the absence of an abrupt drop in solution viscosity above a critical concentration, as is observed with many rigid-rod polymers. In spite of the evidence that the polymers do not behave as very rigid rods in solution, these polymers do have a liquid-crystalline state in bulk, which is a characteristic of rigid-rod polymers.

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