Crystalline structure of poly(diaryl siloxanes)

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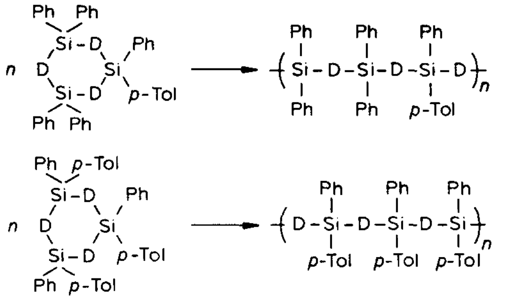
Transmission electron microscopy and X-ray diffraction were used to resolve the crystalline structure of linear poly(diphenyl siloxane) and also two polymers that contain *p*-tolyl substituents at the silicon atom along with phenyl substituents. It has been shown that an increase in the number of *p*-tolyl groups per macromolecule leads to an increase in the cross-sectional area of the unit cell per chain. The softening temperature is thereby lowered, and polymer solubility improved.

(Keywords: poly(diaryl siloxanes); transmission electron microscopy; X-ray diffraction)

INTRODUCTION

Poly(diphenyl siloxane) (PDPS) having the structure $(\text{-Ph}_2\text{SiO-})_n$[1] is a highly crystalline polymer with the highest melting point in the series of linear poly(diorganosiloxanes)[1,2]. At room temperature, it is a solid with extremely poor solubility. Its crystalline structure had not previously been determined.

We have succeeded in synthesizing poly(diaryl siloxanes) with diphenyl siloxy and phenyl(*p*-tolyl)siloxy units, with improved solubility and capacity for orientational crystallization[3]. The polymers were synthesized by anionic polymerization of the corresponding hexaaryl cyclotrisiloxanes according to the scheme:



2

3

The aim of the work presented here is to establish the crystalline structure and compare the properties of polymers **1**, **2**, **3**, which, as seen from above, differ only in number of *p*-tolyl groups per macromolecule chain. The formula of **1** is shown in *Table 1*.

EXPERIMENTAL

The synthesis of the polymers has previously been described[3]. The viscosities of polymers **2** and **3** were measured on a 1% solution in chloroform at 25°C after refluxing in toluene.

The softening temperatures of polymers **1**–**3** were determined from the thermomechanical curves.

The densities of polymers **1**–**3** were measured by hydrostatic weighing. *Table 1* shows the physical properties of polymers **1**–**3**.

The crystalline structure was studied using transmission electron microscopy and X-ray diffraction. For electron microscopy, films of polymers **2** and **3** were cast from a 0.25% solution in chloroform, extracted from the water with metal frames, dried in air and stretched uniaxially at 10°C below softening temperature with subsequent gradual cooling. Single crystals of polymer **1** were obtained by gradual cooling of 0.01% solution in *o*-dichlorobenzene. Micrographs and electron-beam selected area diffraction patterns were taken on a BS-540 TESLA microscope operated at 80 kV. Au-shadowing was used for calculating the polymer *d*-spacings from diffraction patterns as external standard. The d_{200} polymer value, determined from X-ray diffraction after indexing the lines, was used as an internal standard. The accuracy of the determination of the *d* spacings was ±0.1%.

Diffractograms of powders were obtained using a DRON-1 (USSR) with CuKα radiation.

The molecular weight of the R_1R_2SiO unit was taken to be one-third of the molecular weight of the corresponding monomer for calculating crystal density.

The cross-sectional area of the unit cell per chain was calculated according to the relationship:

$$S=\frac{V}{Cn}$$

where C is the value of the identity period along the chain axis; V is the volume of unit cell; and n is the number of macromolecules per unit cell.

RESULTS AND DISCUSSION

Diffractograms of powders have revealed that following synthesis, polymers **1**–**3** possess a crystalline structure with locations of the main reflections being very much alike for all three polymers. Prolonged refluxing in toluene led to complete dissolution of polymer **2**. After precipitation, this polymer had a crystallinity lower than initially and at room temperature it was soluble in toluene, chloroform and dichloroethane. The crystallinity was again increased when samples were heated at

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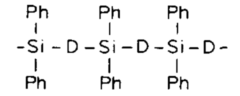
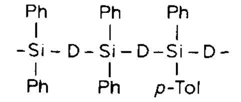
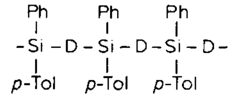
Table 1 Properties of poly(diaryl siloxane)s

No.	Chemical formula	Viscosity η	T^*_{soft}	Solvents	Density after synthesis (g cm^{-3})	Crystalline structure Unit cell	 Crystal. density (g cm^{-3})	 S† (nm^2)
1	 $-\underset{Ph}{\overset{Ph}{Si}}-D-\underset{Ph}{\overset{Ph}{Si}}-D-\underset{Ph}{\overset{Ph}{Si}}-D-$	–	220	diphenyl oxide, *o*-dichlorobenzene + refluxing	1.16	rhombic $a = 2.010$ nm $b = 1.051$ nm $c = 1.024$ nm $n = 2$‡	1.22	1.056
2	 $-\underset{Ph}{\overset{Ph}{Si}}-D-\underset{Ph}{\overset{Ph}{Si}}-D-\underset{p\text{-}Tol}{\overset{Ph}{Si}}-D-$	1.86‖	180	toluene + refluxing	1.12	rhombic $a = 2.106$ nm $b = 1.053$ nm $c = 1.036$ nm $n = 2$‡	1.17	1.109
3	 $-\underset{p\text{-}Tol}{\overset{Ph}{Si}}-D-\underset{p\text{-}Tol}{\overset{Ph}{Si}}-D-\underset{p\text{-}Tol}{\overset{Ph}{Si}}-D-$	1.66‖	170	toluene, chloroform, dichloroethane, etc. at 20°	1.13	rhombic $a = 2.104$ nm $b = 1.086$ nm $c = 0.997$ nm $n = 2$‡	1.24	1.142

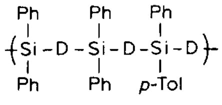
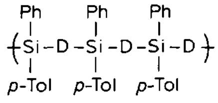
* from thermomechanical curve[8]; load: 100 g; ϕ: 4 mm; 1.5°C min^{-1}

† cross-sectional area of the unit cell per chain

‡ number of macromolecules per cell

‖ in 1% chloroform at 25°C after precipitation with ethanol from solution in toluene

Table 2 Poly(diaryl siloxane) *d*-spacings

Chemical formula	Experimental electron beam diffraction data layer line no.	 *d* (nm)	Calculated data *d* (nm)	 *hkl*	Experimental X-ray diffraction data *d* (nm)
 $\left[\underset{Ph}{\overset{Ph}{Si}}-D-\underset{Ph}{\overset{Ph}{Si}}-D-\underset{p\text{-}Tol}{\overset{Ph}{Si}}-D\right]$	0	1.053	1.052	200	1.052
		0.940	0.941	110	0.940
		0.526	0.526	400	–
		0.476	0.470	220	0.467
		–	0.470	410	
		0.421	0.422	320	0.429
		0.391	0.391	510	0.395
	1	–	0.737	011	0.737
		–	0.738	201	
	2	0.492	0.503	102	0.498
		0.464	0.464	202	0.467
		0.450	0.453	112	0.448
		0.425	0.425	212	–
		0.367	0.369	402	0.365
	3	0.326	0.328	203	–
		0.324	0.324	113	0.325
	4	0.259	0.259	004	–
 $\left[\underset{p\text{-}Tol}{\overset{Ph}{Si}}-D-\underset{p\text{-}Tol}{\overset{Ph}{Si}}-D-\underset{p\text{-}Tol}{\overset{Ph}{Si}}-D\right]$	0	1.052	1.052	200	1.053
		0.960	0.965	110	0.960
		0.520	0.526	400	–
		–	0.525	120	0.526
		0.455	0.473	410	0.468
	1	–	0.738	011	0.757
		–	0.465	401	0.468
	2	0.483	0.485	102	–
		0.455	0.458	202	–
		0.445	0.442	112	0.443
		0.420	0.416	212	0.423
	3	0.335	0.3284	103	–
		0.317	0.3169	203	–
	4	0.249	0.249	004	–

temperatures close to softening. *Figure 1* shows the changes in the diffractograms due to the above treatment. Polymer **3** has the best solubility of the polymer **1**–**3** series (see *Table 1*).

Electron microscopy of thin films of polymers **2** and **3** reveals crystalline formations (*Figure 2a*). Stretched films have an oriented crystalline structure (*Figure 2b*).

Analysis of the electron beam diffraction patterns yielded the parameters of unit cells of polymers **2** and **3**, which enabled us to index the lines of the X-ray diffractograms of corresponding powders. It should be mentioned that conditions of polymer treatment introduce some change in the diffractogram. It is for this reason that comparative analysis of X-ray and electron beam diffrac-

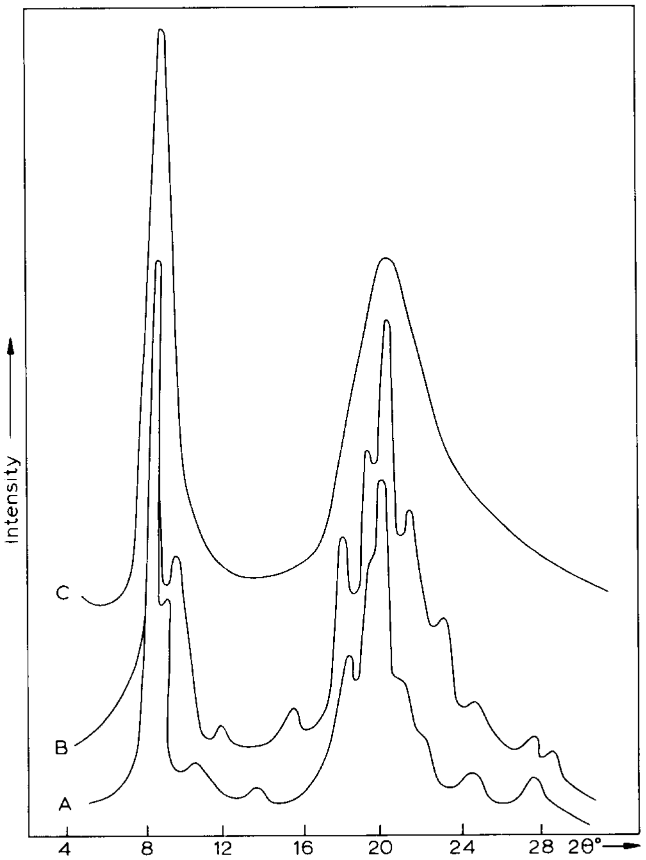


Figure 1 Diffractograms of poly(diaryl siloxane) **2**: curve A, following synthesis; curve B, following precipitation; curve C, heating at 170°C after precipitation

tion patterns was conducted for identical samples that were treated under exactly corresponding conditions.

Table 2 shows the *d*-spacings in polymer **2** and **3** crystals, and *Table 1* lists calculated crystallographic data.

Since PDPS could not be prepared as an oriented crystalline film, we considered it possible to calculate the parameters *a*, *b*, *c* using X-ray diffractograms indexed similarly to diffractograms of polymers **2** and **3**, as both the chemical structure and the diffractograms of all three compounds are alike. Confirmation of parameters *a* and *b* for PDPS, as well as the angle formed by vector H_{200} and H_{110} was made possible by analysis of electron beam diffraction patterns of single crystals (*Figure 2c*). Six point reflections that correspond to the cross-section of the reciprocal lattice through the *hk*0 plane were found. The reflections form a rectangular net with *a* and *b parameters corresponding to those found with the indexed diffractogram; d*-spacings in PDPS crystals are presented in *Table 3*, calculated crystallographic data in *Table 1*.

Electron microscopy studies of uniaxially stretched films of polymers **2** and **3** (*Figure 2*) revealed exact meridional reflexes at the 4 and 8 layer lines, i.e. for a number of 00*l*, only reflections with indexes $l=4n$ were observed. This led to the conclusion that the polymer chain had a helical conformation 4_l, with 4 –R_1R_2SiO– units per coil. From identity period values (*Table 1*) it is possible to calculate the values of repeat unit projections on the chain axis, which, for polymers **1**–**3**, are: 0.256, 0.259, 0.249 nm, respectively.

We have assumed the existence of a helical conformation in the studied poly(diaryl siloxanes) corresponding

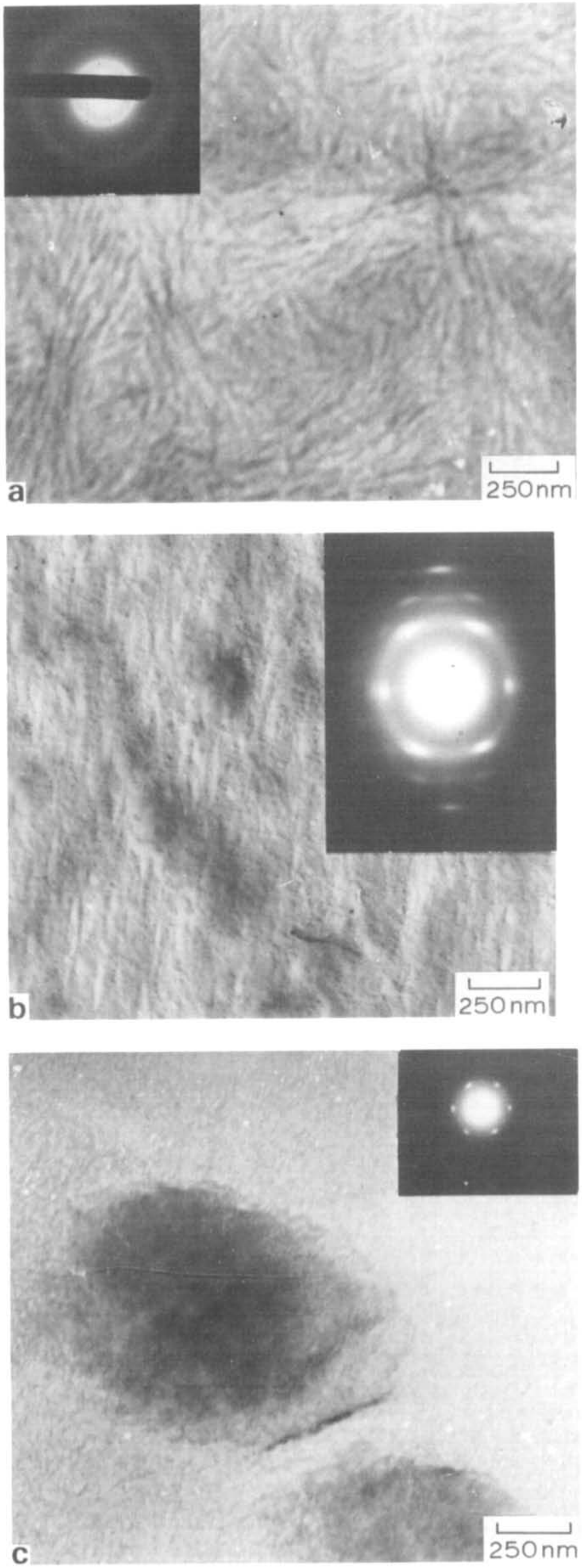
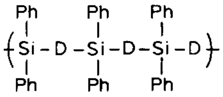


Figure 2 Micrographs and electron beam diffraction patterns of poly(diaryl siloxanes): (a), polymer **2** isotropic film; (b), polymer **2** uniaxially stretched film; (c), single crystal of polymer **1** (PDPS)

Table 3 Poly(diphenyl siloxane) *d*-spacings (heated at 210°)

Chemical formula	Experimental X-ray diffraction data, *d* (nm)	Calculated data		Experimental electron beam diffraction data single crystals, *d* (nm)
		d (nm)	*hkl*	
 $\left(\overset{Ph}{\underset{Ph}{Si}}-D-\overset{Ph}{\underset{Ph}{Si}}-D-\overset{Ph}{\underset{Ph}{Si}}-D\right)$	1.005	1.004	200	1.005
	0.931	0.930	110	0.933
	0.762	0.733	011	
	0.679	0.669	300	
	0.496	0.495	102	
	0.467	0.465	220	
	0.452	0.455	121	
	0.440	0.448	112	
	0.408	0.401	500	
	0.480	0.375	510	
	0.352	0.358	402	

to that in other linear poly(organosiloxanes)[4,5].

It is a characteristic feature of the organosilixane chain structure that the valency angles OSiO and SiOSi are radically different. Thus, while OSiO angles in mono- and poly(organosiloxanes) are approximately constant and differ from the tetrahedral (109.5°) by 2–3°, the SiOSi valency angles in siloxanes with large numbers of units vary from 140° to 160°[6].

In this respect, one $-R_1R_2SiO-$ unit in poly(organosiloxanes) cannot be a structurally repeated group, and the unit cell thould therefore comprise at least two repeat units. In this case, the macromolecule could have the flat zig-zag conformation with the identity period value being 0.53 nm (calculated Si–O bond length: 1.64 Å; OSiO angle: 110°; SiOSi angle: 160°).

Nevertheless, if the silicon atom is surrounded by bulky phenyl groups, a flat zig-zag conformation is impossible because of steric hindrance from neighbouring phenyl groups. Therefore, to attain a stable conformation, a helical chain arrangement is required.

A helical conformation 4_l governs macromolecule packing in the equatorial plane. The equatorial cell is rectangular for all three polymers, with parameter *a* being approximately double the parameter *b*. The number of polymer chains per unit cell equals 2.

The lack of sufficient number of reflections makes it impossible to establish the space group accurately. But the absence of the odd *h*00 and 0*k*0 reflections points to the orthorhombic $P2_l2_l2$ space group, where two neighbouring polymer chains are located at the origin of the coordinates and at centre *ab* plane are superimposed by way of a second order screw axis. This is rectangular to the chain axis and located at by a translation 1/4 of the length of the axis *a*. This means that the most densely packed layer has a succession of right and left spirals 4_l and 4_3.

Determination of the crystalline structure of polymers **1**–**3** made it possible to calculate the cross-sectional area of the unit cell per chain (*S*). As seen from *Table 1*, an increase in the number of *p*-tolyl groups leads to an increase in the value of *S*, i.e. to greater distance between adjacent macromolecules, which should in turn be accompanied by weaker intermolecular interaction. This factor obviously influences the physico-chemical properties of polymers; it becomes apparent with a fall in the softening temperature and an improved solubility of the **1**–**3** polymer series. Such a trend in *S* parameter influence on the properties of crystalline polymers of various chemical structure has already been reported[7]. Nevertheless, this is the first time that we have examined compounds of largely similar chemical structure.

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