

Synthesis and Structure of 1,5-Di-(Ethylphenyl)-1,5-Dimethyl-3,3,7,7-Tetraphenylcyclotetrasiloxane: a Novel Cyclotetramer

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Abstract Herein we report the first synthesis of 1,5-di-(ethylphenyl)-1,5-dimethyl-3,3,7,7-tetraphenylcyclotetrasiloxane using a new ‘One Pot’ procedure as recently reported for the preparation of strictly alternating 1,1,5,5-tetramethyl-3,3,7,7-tetraphenylcyclotetrasiloxane by the heterofunctional condensation of diphenylsilanediol with (phenylethyl)methylchlorosilane in the presence of the tertiary amine, triethylamine (Nguyen et al. *Silicon* 6:21–26, 2014). The prepared 1,5-di-(ethylphenyl)-1,5-dimethyl-3,3,7,7-tetraphenylcyclotetrasiloxane was fully characterized by single-crystal X-ray diffraction, ^1H , ^{13}C and ^{29}Si nuclear magnetic resonance spectroscopy, elemental analysis, mass spectroscopy, thermogravimetric analysis and differential scanning calorimetric studies.

Keywords Alternating · Co-polymers · Cyclics · Heterofunctional polycondensation

Abbreviations

Alt	Alternating
Co	Copolymerization
DPS	Diphenylsiloxane

PDMS	Polydimethylsiloxane
Poly	Polymer(ic)
ROP	Ring Opening Polymerization
T_g	Glass Transition Temperature

1 Introduction

The modification of siloxane polymers with various functionalities, such as amine, acrylate, polyesters, polyurethane, methylphenyl, diphenyl, and epoxy resin, etc., has become increasingly important for a wide range of applications [2–11]. There is an increasing demand for polymers exhibiting superior thermal stability, for which siloxane polymers are attractive materials having thermal stability at elevated temperature for many advanced applications in fields such as aerospace, computer chips [12], adhesives [13], packing for chromatographic columns [14], and lubricants [15]. Modern technologies demand high temperature-resistant materials able to exhibit and retain useful mechanical and/or specific surface properties over a wide range of operating temperatures from -30 to above 400 °C [12]. The temperature stability and usable properties of polysiloxanes may be further enhanced through structured alternating substitution of these materials.

The recently reported poly(dimethylsiloxane-*alt*-diphenylsiloxane) (poly(DMS-*alt*-DPS)) is one such polysiloxane derivative, with alternating methyl and phenyl functionalities [1]. This copolymer has the potential to offer improved thermal stability [8], mechanical strength [16], resistance to irradiation and oxidation [17] and optical properties [18]. The degree of improvement depends on the monomer sequence and the percentage of phenyl groups in the modified copolymers [8, 15, 19]. The reported structural architectures of the modified PDMS are either as

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random or block copolymers prepared most commonly by ring opening polymerization (ROP).

Cyclic siloxanes have many applications in their own right. They are widely used in, e.g., cosmetics [20], sun care formulas [20–22], antiperspirants [23], and can also be used for ring-opening syntheses of their polymer counterparts, leading to our interest in synthesizing these novel cyclic materials.

2 Results and Discussion

In this study, a ‘One Pot’ synthetic route for the preparation of 1,5-di-(ethylphenyl)-1,5-dimethyl-3,3,7,7-tetraphenylcyclotetrasiloxane was introduced (Scheme 1). The benefit of this synthetic route was the achievement of as high as 50 % of the ethylphenyl and methyl moieties on the silicon atom, with 50 % diphenyl moieties alternating on the tetrasiloxane cyclic molecule.

A ‘One Pot’ heterofunctionalpolycondensation reaction of diphenylsilanediol with (phenylethyl)methyldichlorosilane in the presence of triethylamine, resulted in a crystalline material, 1,5-di-(ethylphenyl)-1,5-dimethyl-3,3,7,7-tetraphenylcyclotetrasiloxane [24], with a melting temperature of 124 °C. When triethylamine is reacted with one mole of chlorosilane, a silylamine in the form of a quaternary salt is not formed. The triethylamine acts as a Bronsted base, forming a hydrogen bond complex with silanol which in turn reacts with chlorosilane in a rate-limiting step. Thus the reaction rate between the silanol group and the chlorosilane is slowed, promoting cyclization.

The proton NMR spectrum of 1,5-di-(ethylphenyl)-1,5-dimethyl-3,3,7,7-tetraphenylcyclotetrasiloxane (Fig. 1)

shows a singlet at 0.122 ppm which corresponds to the methyl protons of the silicon - methyl unit with an integration of three. Two doublets of triplets were observed at 0.94 ppm and 2.54 ppm, both with the anticipated corrected peak area of 2. They indicate the presence of two methylene groups, adjacent to the silicon atom and phenyl ring, respectively. Also, a broad multiplet between 6.8 - 8 ppm is ascribed to the phenyl protons, with an integration of 17 which is slightly higher than the expected value of 15 due to the presence of a deuterated chloroform peak appearing in the same region as the phenyl protons.

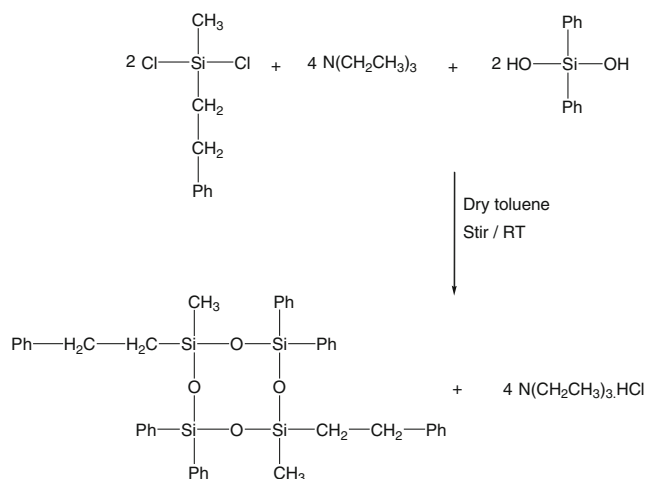
The carbon NMR spectrum (Fig. 2) shows the methyl carbon at -0.62 ppm, the methylene carbon next to the silicon atom at 19.3 ppm, the methylene carbon next to the phenyl ring at 28.8 ppm, and eight phenyl carbons at 125.5, 127.7, 127.8, 128.2, 130.1, 134.1, 135.4 and 144.6 ppm.

The silicon NMR spectrum (Fig. 3) shows two distinct peaks. The upfield peak at -17.3 ppm arises from the methyl(ethylphenyl)siloxane component, with a downfield peak at -45.6 ppm representative of the diphenylsiloxane. The silicon NMR results also support the formation of 1,5-di-(ethylphenyl)-1,5-dimethyl-3,3,7,7-tetraphenylcyclotetrasiloxane.

The elemental analysis verifies the percentage of hydrogen and carbon content which are as expected for the alternating cyclotetrasiloxane: Found (%) C: 69.41, H: 6.19 and calc. (%) C: 69.57, H: 6.12.

The mass spectrum also strongly supports the proposed structure. It shows a molecular ion peak (100 %) at 747.4 due to the [M + Na] which, minus a sodium atom, provides the accurate mass for the cyclic of 724.4, close to the calculated value of 725.1.

The results of the ‘low’-temperature single crystal X-ray diffraction study are consistent with the formulation 1,5-di-(ethylphenyl)-1,5-dimethyl-3,3,7,7-tetraphenylcyclotetrasiloxane as a neutral molecular compound, one-half of which comprises the asymmetric unit of the structure, the whole molecule being disposed about a crystallographic inversion centre. Projections of the molecule are shown in Fig. 4, with core dimensions presented in Table 1; the latter essentially conform to the expected norms developed through numerous studies of similar molecules, with the two Si-C(phenyl) distances essentially identical, and Si-C(methyl, ethylphenyl) respectively slightly shorter and longer. The Si-O distances are likewise similar, but there are significant differences in ‘equivalent’ Si...Si distances along and across the diagonals of the Si₄ ‘square’, associated with a considerable difference in the Si-O-Si angles at O(1) (138.93(11)) and O(2) (146.03(11)°), perhaps a consequence of a rather close approach to O(2) by an *ortho*-phenyl hydrogen atom (H(122')) (2.68 Å (est.)).



Scheme 1 Synthesis of 1,5-di-(ethylphenyl)-1,5-dimethyl-3,3,7,7-tetraphenylcyclotetrasiloxane

Fig. 1 ^1H NMR of 1,5-di-(ethylphenyl)-1,5-dimethyl-3,3,7,7-tetraphenylcyclotetrasiloxane

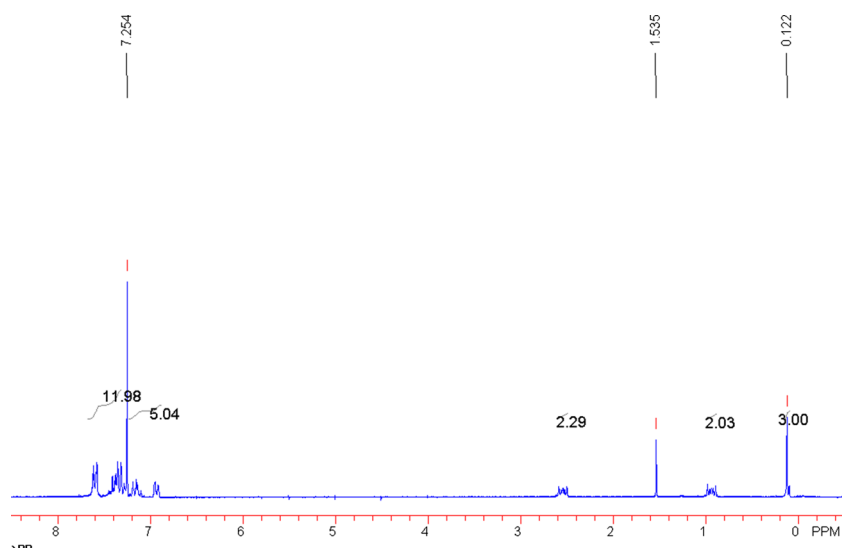


Fig. 2 ^{13}C NMR of cyclic 1,5-di-(ethylphenyl)-1,5-dimethyl-3,3,7,7-tetraphenylcyclotetrasiloxane

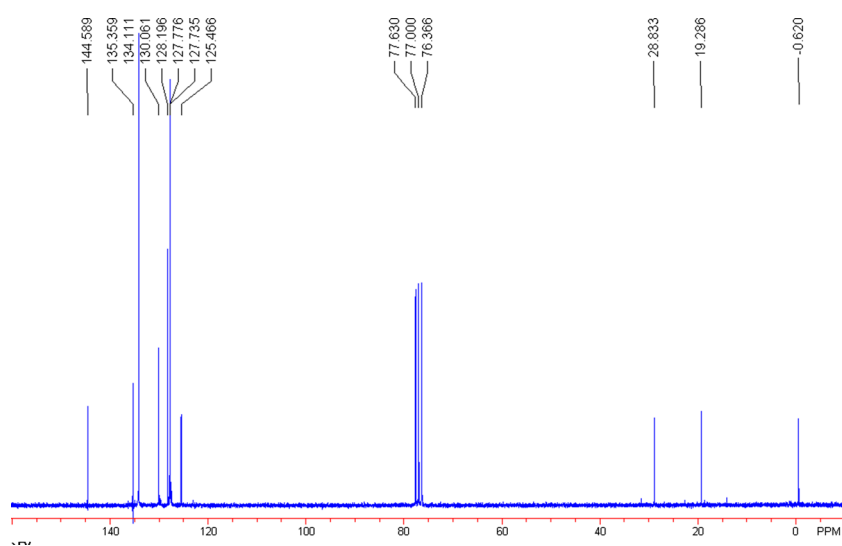
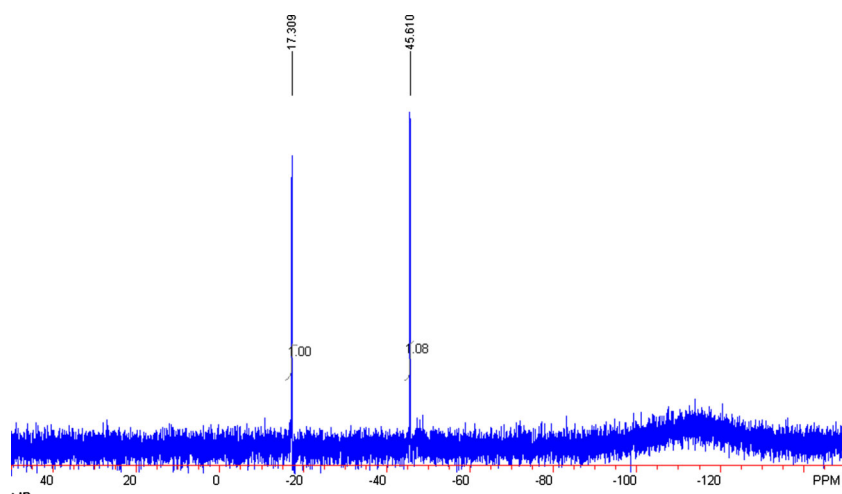


Fig. 3 ^{29}Si NMR of cyclic 1,5-di-(ethylphenyl)-1,5-dimethyl-3,3,7,7-tetraphenylcyclotetrasiloxane



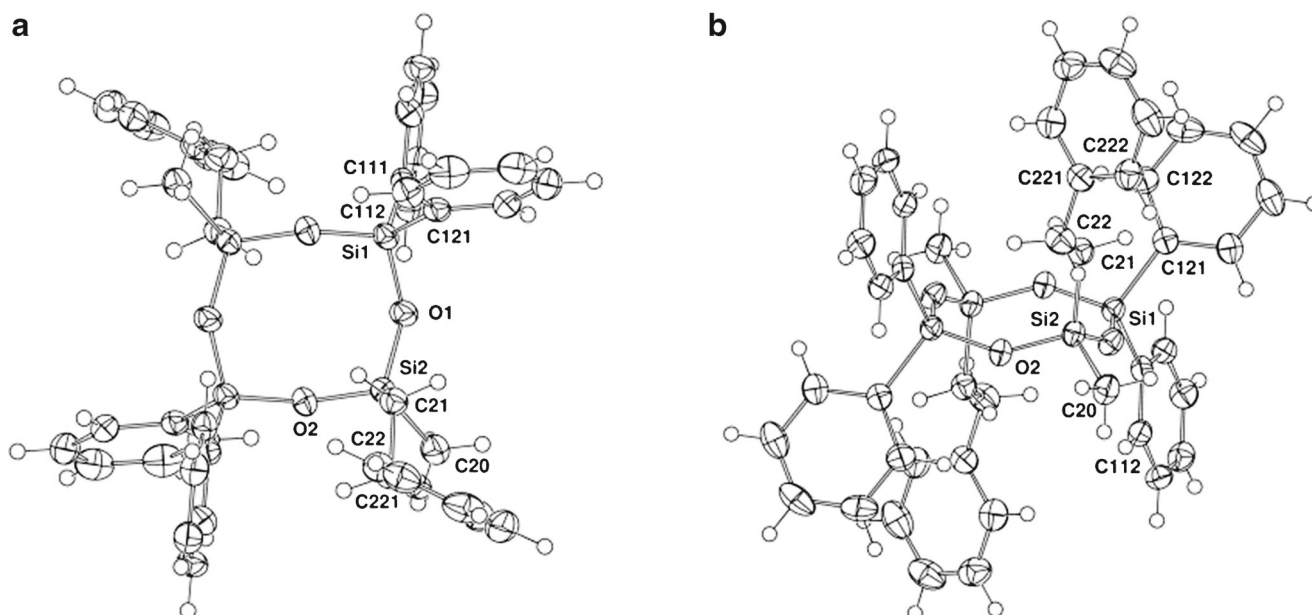


Fig. 4 Molecular structure of centrosymmetric 1,5-di-(ethylphenyl)-1,5-dimethyl-3,3,7,7-tetraphenyl cyclotetrasiloxane projected **a** normal and **b** oblique to the Si_4 plane

The thermal stability of the alternating cyclotetrasiloxane was evaluated by TGA. It exhibited a one-step mass loss. The onset of mass loss occurs at 322 °C, *via* a steady state loss profile suggesting that this occurred by volatilization of a single compound, rather than from decomposition

Table 1 Selected bond lengths and angles for 1,5-di-(ethylphenyl)-1,5-dimethyl-3,3,7,7-tetraphenylcyclotetrasiloxane

Atoms	Parameter	Atoms	Parameter
Distances (Å)			
Si(1)-O(1)	1.624(2)	Si(2)-O(1)	1.641(2)
Si(1)-O(2')	1.623(2)	Si(2)-O(2)	1.634(2)
Si(1)-C(111)	1.854(2)	Si(2)-C(20)	1.836(3)
Si(1)-C(121)	1.848(2)	Si(2)-C(21)	1.859(2)
Si(1)...Si(2)	3.0579(10)	Si(1)...Si(2')	3.1148(10)
Si(1)...Si(1')	4.4858(13)	Si(2)...Si(2')	4.2407(12)
Angles (°)			
O(1)-Si(1)-O(2')	110.24(9)	O(1)-Si(2)-O(2)	107.43(9)
O(1)-Si(1)-C(121)	110.62(10)	O(1)-Si(2)-C(20)	108.43(11)
O(2')-Si(1)-C(121)	106.92(10)	O(2)-Si(2)-C(20)	107.84(11)
O(1)-Si(1)-C(111)	107.84(10)	O(1)-Si(2)-C(21)	109.37(10)
O(2')-Si(1)-C(111)	110.70(10)	O(2)-Si(2)-C(21)	111.45(10)
C(111)-Si(1)-C(121)	110.54(11)	C(20)-Si(2)-C(21)	112.17(12)
Si(1)-O(1)-Si(2)	138.93(11)	Si(1')-O(2)-Si(2)	146.03(11)

Primed atoms are generated by the inversion centre at the centre of the molecule

under the nitrogen atmosphere at a heating rate of 10 °C/min (Fig. 5).

DSC analysis (Fig. 6) shows that the material melts at T_m 124 °C with an enthalpy of 74 J/g. The crystallization transition was not observed during the cooling cycles of the DSC runs, suggesting that the bulky pendant groups of the cyclic siloxane with four Si-O units may impose a more dominant conformation and some associated degree of ring tension that tends to control the arrangement of the pendant groups, with associated difficulty in the molecular arrangement process during crystallization, so that no crystallization transition was observed. This is reflected in a glass transition at 29 °C, due to the amorphous nature of this material.

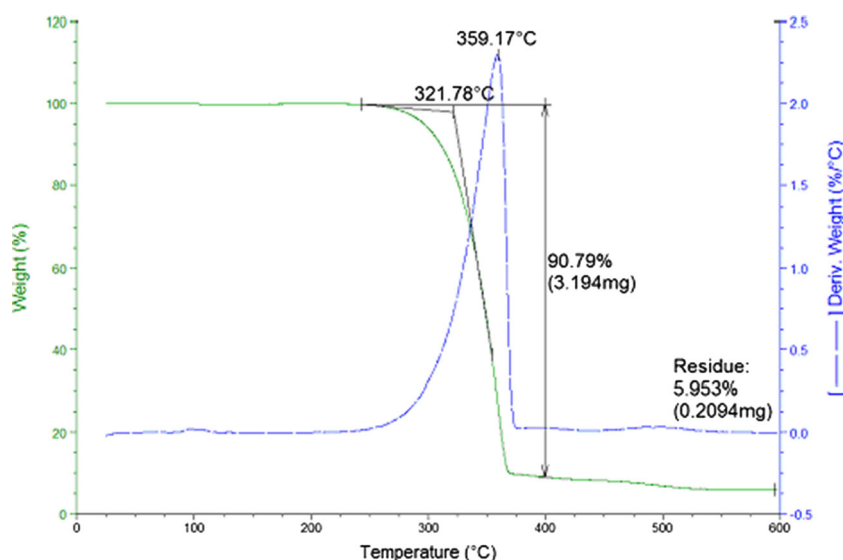
3 Materials

Triethylamine, diethylamine (99.5 %) and diphenylsilanediol (95 %) were purchased from Sigma Aldrich, and (phenylethyl)methyldichlorosilane (also known as 2,2-dichloro-4-phenyl-2-silabutane) (99.5 %) from Academic Laboratory.

4 Instrumentation and Characterization Techniques

Nuclear magnetic resonance spectroscopy (NMR) The spectra were recorded using a Varian Gemini FT-NMR, liquid-nitrogen-cooled 300 MHz spectrometer. The VNMR 6.1 analysis software with a Sun Workstation based on a Unix system was used to analyze the spectra.

Fig. 5 TGA of 1,5-di-(ethylphenyl)-1,5-dimethyl-3,3,7,7-tetraphenylcyclotetrasiloxane



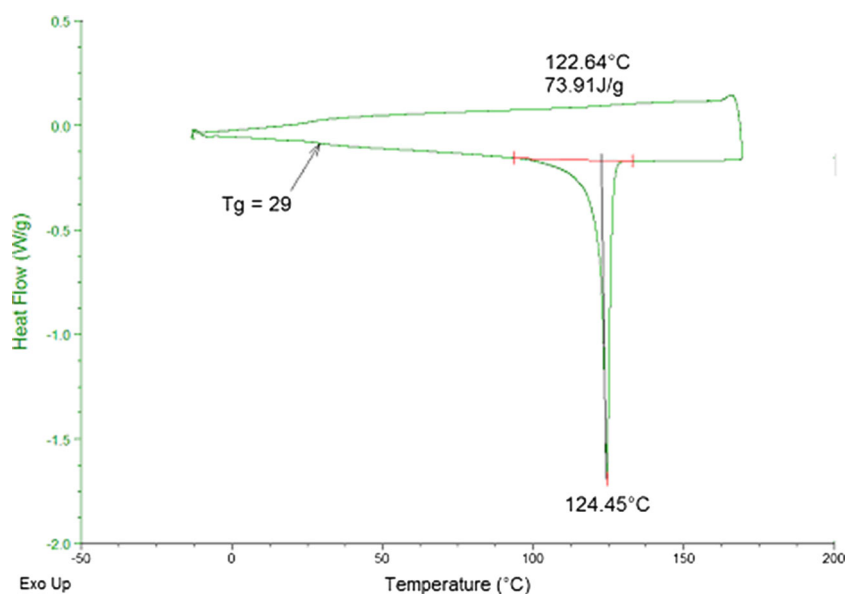
Microchemical analyses These were performed by the Microanalytical Service, Department of Chemistry, University of Queensland, Australia and Campbell Microanalytical Laboratory, University of Otago, New Zealand, using Carlo Erba Elemental Analyser EA 1108 instruments.

Mass spectrometry measurements These were performed at the School of Chemistry, Faculty of Science, Monash University, Australia, on a BrukerBioApex II 47e Fourier Transform Mass Spectrometer (FT-MS) instrument, using Xmass Version 5.0 software, Electrospray Ionisation (ESI) being used to determine the molecular weight of the samples. A capillary voltage of 80 volts was used with a Shimadzu QP5050A GC-MS system, fitted with a solid

probe. The probe was heated from 60 to 280 °C, at a heating rate of 15 °C/min.

Thermogravimetric analysis (TGA) Data were collected using a TGA 2950 ThermoGravimetric Analyzer from TA Instruments. Platinum pans were used. Samples were accurately weighed at zero time by the instrument, then the mass was continuously measured during the heating process. Sample was heated from room temperature to 600 °C at a rate of 10 °C/min under 50mL/min high purity N₂. The instrumental temperature calibration was performed using the Curie temperatures of nickel and alumel standard reference materials. The percent weight loss was measured as a function of temperature.

Fig. 6 DSC of 1,5-di-(ethylphenyl)-1,5-dimethyl-3,3,7,7-tetraphenylcyclotetrasiloxane



Differential scanning calorimetry (DSC) Differential Scanning Calorimetry analysis was carried out using a TA Instruments 2920 DSC (with TMDSC capability), fitted with liquid nitrogen cooling. Approximately 5 milligram samples were weighed into an empty, pre-weighed aluminium, hermetic DSC pan and lid. The lid was crimped tightly on the pan and accurately reweighed. The sample weight was found by difference. The sample was subjected to a heating cycle at a rate of 5 °C / minute under nitrogen atmosphere. Analysis was carried out using Windows NT based Universal Analysis software, available from TA Instruments.

Structure determination A full sphere of ‘low’-temperature CCD area-detector diffractometer data was measured (Bruker AXS instrument, ω -scans, monochromatic Mo K α radiation, $\lambda = 0.71073$ Å; T ca 153 K), yielding 39320 total reflections, these merging to 4455 unique ($R_{\text{int}} 0.077$) after ‘empirical’/multiscan absorption correction (proprietary software) (2752 with $I > 2\sigma(I)$ considered ‘observed’). These were used in the full matrix least square refinements on F^2 , refining anisotropic displacement parameters for C, O, Si, hydrogen atom treatment following a riding model (reflection weights: $(\sigma^2(F)^2 + (0.091 P)^2)^{-1}$ ($P = (F_o^2 + 2F_c^2)/3$)); neutral atom complex scattering factors were employed within the SHELXL97 program [25]. Pertinent results are given below and in Table 1 and Fig. 4, the latter showing 50 % probability amplitude displacement envelopes for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å. A full .cif deposition (excluding structure factors) has been lodged with the Cambridge Crystallographic Data Centre, CCDC 987108.

Other crystal/refinement details C₄₂H₄₄O₄Si₄, $M = 725.1$. Orthorhombic, space group $Pbca$ (D_{2h}^{15} , No. 61), $a = 18.766(5)$, $b = 10.428(3)$, $c = 19.818(5)$ Å, $V = 3878(2)$ Å³. D_c ($Z = 4$) = 1.24₂ g cm⁻³. μ_{Mo} = 0.19 mm⁻¹; specimen: 0.16 × 0.10 × 0.10 mm; $T'_{\text{min/max}}$ = 0.73. $2\theta_{\text{max}}$ = 55°; $R1 = 0.057$, $wR2 = 0.149$; $S = 0.93$. $|\Delta\rho_{\text{max}}| = 0.72$ e Å⁻³.

5 Synthetic Procedure

Anhydrous toluene (100ml), diphenylsilanediol (0.0046 mol), (phenylethyl)methyldichlorosilane (0.0046 mol) and triethylamine (0.0092 mol) were charged into a dry, three neck-flask containing a magnetic stirrer. The flask was sealed with a glass stopper to minimize toluene evaporation. The mixture thickened considerably during the chlorosilane addition. The suspension became less viscous and stirred

more easily. These observations occurred together with some heat evolution and the formation of a white powder. The reaction mixture was gently stirred at room temperature for two days under a nitrogen atmosphere to give a white solid which was vacuum filtered then washed with toluene. The filtrate was transferred to a separation funnel and washed with water (3 × 100 ml). The organic phase was dried over anhydrous sodium or magnesium sulphate, filtered and concentrated on the rotary evaporator. A combination of crystalline and oily material was obtained. The crystalline product was separated from the crude material by sublimation. The crystalline material was washed with methanol/hexane (10:3 by volume) and then recrystallised from hexane (32 % yield).

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References

1. Nguyen K-AT, Clarke S, Matison J, Skelton BW, White AH, Markovic E (2014) Silicon 6:21–26
2. Sobhani S, Jannesari A, Bastani S (2012) J Appl Polym Sci 123:162–178
3. Pergal MV, Antić VV, Govedarica MN, Goëvac D, Ostojić S, Djonlagić J (2011) J Appl Polym Sci 122:2715–2730
4. Xie K, Hou A, Zhang Y (2006) J Appl Polym Sci 100:720–725
5. Zong J, Zhang Q, Sun H, Yu Y, Wang S, Lui Y (2010) Polym Bull 65:477–493
6. Antić VV, Pergal MV, Antić MP, Djonlagić J (2010) Hem Ind 6:537–545
7. Poojari Y, Clarson SJ (2009) Chem Commun 44:6834–6835
8. Deshpande G, Rezac ME (2002) Polym Degrad Stab 76:17–24
9. Xie K-L, Xu L, Shi Y-Q (2008) J Fiber Bioeng Inform 1:151–156
10. Xie K, Hou A, Shi Y (2008) J Appl Polym Sci 108:1778–1782
11. Mazurek M, Kinning DJ, Kinoshita T (2001) J Appl Polym Sci 80:159–180
12. Dvornic PR, Lenz RW (1992) Macromolecules 25:3769–3778
13. Hofer DC (1986) ACS Proc Polym Mat Sci Chem 55:85–90
14. Haaglund I, Janak K, Blomberg L, Bemgaard A, Claude SG, Lymann M, Tabacchi R (1991) J Chromatogr Sci 29:396–402
15. Umanskaya OI, Ishchuk YuL, Abadzheva RN, Smerechinskii VB (1990) Chem Technol Fuel Oils 26:151–153
16. Wang S, Mark JE (1990) J Mater Sci 25:65–68
17. Liu L, Yang S, Zhang Z, Wang Q, Xie Z (2003) J Polym Sci Part A: Polym Chem 41:2722–2730
18. Yang MH, Li HT, Lin CC (2003) J Chin Chem Soc 50:51–57
19. Chou C, Yang MH (1993) J Thermal Anal 40:657–667
20. De Backer G, Ghirardi D (1993) Parfums, Cosmétiques. Aromes 114:61–64
21. Lanwet M (1986) Cosmetics & Toiletries 101(2):63–72
22. DiSapio A (1987) Cosmetics & Toiletries 102(3):102–6
23. Abrutyn E, Bahr B (1993) Cosmetics & Toiletries 108(6):51–54
24. Nguyen K-AT, Schamshurin A, Clarke SR, Matison JG (2004) Polym Prepr 45:706–707
25. Sheldrick GM (2008) Acta Crystallogr. Sect A 64:112–122