

Structural Regularity of Poly(phenylsilsesquioxane) Prepared from the Low Molecular Weight Hydrolysates of Trichlorophenylsilane

Eung-Chan LEE and Yoshiharu KIMURA

Department of Polymer Science and Engineering, Kyoto Institute of Technology,
Matsugasaki, Sakyo-ku, Kyoto 606, Japan

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ABSTRACT: Various hydrolysates of trichlorophenylsilane (TCP) and their polycondensates were reacted with trichlorosilane for capping the silanol groups formed in defect points of the ladder structure. The ^1H NMR spectra of the capping products obtained showed several signals due to the Me_3Si groups in different environment. Particularly, the polycondensate prepared from the TCP hydrolysate having higher molecular weight showed both sharp and broad Me_3Si signals, suggesting a core-shell type branched structure. No Me_3Si signal was shown in the polycondensate prepared from the hydrolysate with low molecular weight, supporting an almost perfect ladder structure with few bonding defects. The wide angle X-ray scattering (WAXS) of this polycondensate showed clear Debye-Scherrer rings due to the crystallization of the polymer chains having the regular ladder structure. The structural regularity of this polycondensate was also supported by the ^{29}Si NMR spectrum. This polymer, having a stable double-strand structure, was found to undergo no base-catalyzed depolymerization in solution. A stepwise polycondensation is proposed for the formation of the ladder polymer in which the trivalent (T_0 : $\text{PhSi}(\text{O}^-)_3$) or divalent (T_1 : $\text{PhSi}(\text{OSi})(\text{O}^-)_2$) siloxyl units should be involved in the reaction, leaving the monovalent siloxyl (T_2 : $\text{PhSi}(\text{OSi})_2(\text{O}^-)$) units unreacted.

KEY WORDS Hydrolysate of Trichlorophenylsilane / Poly(phenylsilsesquioxane) / Silanol Capping / Ladder Structure / Core-Shell Type Branched Structure / Depolymerization /

It was found in the 1870s that the alkaline treatment of the condensation products of phenylsilanetriol (PST) produces soluble oligomers having the empirical composition of $(\text{C}_6\text{H}_5\text{SiO}_{1.5})_x$.^{1,2} Around 1960 a crystalline polycyclic compound with identical composition was isolated from a solution of the hydrolysis product of trichlorophenylsilane (TCP) and KOH in diethyl ether/benzene mixture.^{3,4} In 1963 a soluble poly(phenylsilsesquioxane) (PPSQ) with very high molecular weight was prepared by the base-catalyzed bulk polycondensation of the hydrolysis product of TCP in bulk at high temperature.^{5,6} This double-chain ladder polymer may be formed in equilibrium with low molecular weight polycyclic species that could be isolated from a dilute solution system.⁷ The reaction mechanism of these interesting condensation systems, however, has been controversial, and the products with defined structure and properties could be hardly obtained in many experiments previously described in the literatures.⁵⁻¹¹ Recently,¹² we succeeded in isolating the low molecular weight hydrolysates from the aqueous layer by hydrolyzing TCP in a water/toluene solvent system and found that the base-catalyzed polycondensation of these hydrolysates affords a high molecular weight PPSQ under mild reaction conditions. Based on these facts we proposed a new mechanistic explanation for the formation of ladder structure in the dehydrative polycondensation of the TCP hydrolysates. This paper describes the further extension of our study on the structure and formation mechanism of PPSQ by focusing on the structure regularity of the crystalline PPSQ formed from the low-molecular weight hydrolysates. In the present study, the structure of PPSQ was analyzed by capping reactions of the silanol groups with chlorotrimethylsilane (TMC) (Scheme 1) as well as by spectroscopic and X-ray analyses. The PPSQ formed from PST and its early

condensates should have highly regular structure without bonding defects.

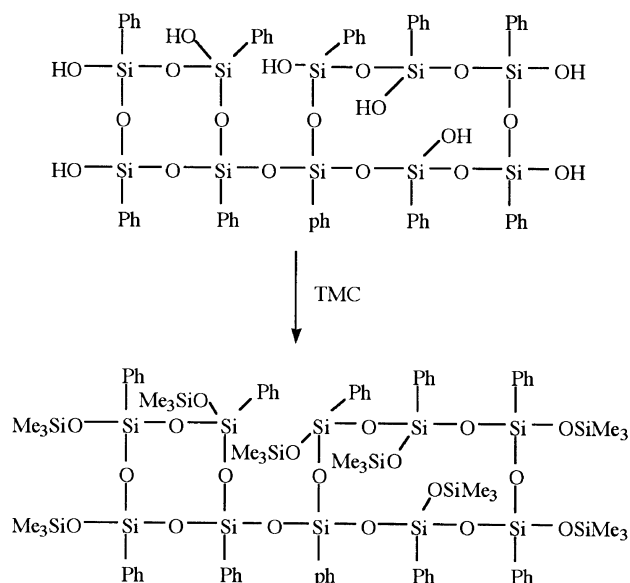
EXPERIMENTAL

Materials

TCP and TMC were supplied by Nacalai Tesque Inc. (Kyoto) and purified by distillation. Toluene and cyclohexane were distilled over sodium metal before use. Other solvents and reagents were commercially supplied and used without purification.

Measurements

^{29}Si NMR spectra were measured at 99.3 MHz on



Scheme 1.

a Bruker ARX-500 spectrometer in chloroform- d_1 (CDCl_3) and toluene- d_8 . A capillary glass tube containing pure tetramethylsilane (TMS) as the *in situ* external standard was put into an NMR sample tube made of glass (5 mm ϕ) together with a sample solution. Measurement was done at 21°C by spinning the sample tube at a revolution of 5000 s^{-1} . ^1H NMR spectra were measured at 200 MHz on a Varian XL-200 spectrometer in CDCl_3 with the solvent peak as the internal reference (δ 7.26). The number average molecular weight (M_n) and molecular weight distribution (M_w/M_n) were determined by gel permeation chromatography (GPC). The analyzer was composed of a Shimadzu LC-10A pump, a Shodex RI SE-31 RI detector, and a Shimadzu C-R7A Chromatopac data processor. A combination of two polystyrene gel columns of Tosoh TSK gel G4000 H_8 and G2500 H_8 was used with chloroform as the eluent at 35°C. The limited exclusion molecular weight was 7×10^5 dalton. The molecular weight was calibrated according to polystyrene standards. FT-IR spectra were recorded on a JASCO FT/IR-5300 spectrophotometer by the KBr pellet method. Wide angle X-ray scattering (WAXS) was measured on a JEOL DX-GE-E model diffractometer with Ni-filtered Cu-K_α radiation at a wavelength of 1.542 Å generated at 40 kV and 20 mA. Density was measured by the floating method using a heavy salt solution of KI/water.

Preparation of TCP Hydrolysates

The procedure was as reported previously.¹² A solution of 6.3 g of TCP in 163 ml of toluene was cooled to 0°C and added dropwise to 815 ml of water under vigorous agitation at 0°C for a period of 1 h. The mixture was kept stirred at the same temperature for 30 min, and the aqueous and toluene layers were separated at 0°C. The pH of the aqueous layer was adjusted to 4 by adding aqueous NaHCO_3 solution containing some ice to allow precipitation of the white crystalline product whose M_n was about 170 dalton. The white precipitates were filtered and dried thoroughly *in vacuo* at room temperature; yield: 0.50 g (9.3%). The filtrate was kept in a refrigerator at 0°C overnight for precipitation of the hydrolysate having $M_n=290$. The precipitated product was isolated by filtration, washed with an ice-water, and dried *in vacuo*; yield: 5.04 g (80%).

When the same hydrolysis reaction was carried out without cooling the toluene solution of TCP, no crystalline hydrolysate having $M_n=170$ was obtained from the aqueous solution whose pH had been adjusted at 4. The pH-adjusted solution was kept at 0°C overnight, the hydrolysate having $M_n=540$ precipitated out as a solid. Which was isolated and dried as above; yield: 5.04 g (80%).

In another experiment, the same TCP solution in toluene was added dropwise to the water layer at room temperature, and the toluene and aqueous layers were separated. In this case, the toluene layer was evaporated to dryness at reduced pressure to obtain the hydrolysate having $M_n=1560$ in a yield of 5.3 g (84%).

Polycondensation

5.0 g of the TCP hydrolysate and 5.0 mg of KOH (0.1 wt% relative to the hydrolysate) were mixed with

38 ml of toluene. The mixture was heated at the refluxing temperature of toluene for 16 h with the dehydrated water removed from the azeotropically distilled toluene/water mixture in a Dean–Stark tube. The viscous solution finally obtained was poured into excess methanol to precipitate the condensation product. The product was then filtered and dried *in vacuo* at 150°C for 10 h; yield: 4.4 g (88%). It was dissolved in toluene, cast on a glass plate, and air-dried to prepare a polymer film. The half-dried film was then taken off and thoroughly dried in a vacuum oven at 150°C. A fragment of this film was heat-treated at 350°C in solid state.

Silanol-Capping Reaction

A typical reaction was carried out as follows: 3.3 g of the TCP hydrolysate ($M_n=540$) obtained above were mixed with 4.4 g (43 mmol) of triethylamine in 100 ml of cyclohexane. With this solution stirred, 4.7 g (43 mmol) of TMC dissolved in 100 ml of cyclohexane were added dropwise below 20°C. Stirring was continued for 90 min. The white precipitates having formed during the reaction were removed by filtration, and the filtrate was evaporated to dryness to obtain yellowish powdery product, with a small portion of cyclohexane and thoroughly dried *in vacuo*. The yield of the product was 2.5 g. Capping reactions of the other TCP hydrolysates and their polycondensates were performed likewise by reacting excess amounts of triethylamine and TMC with the reactants. The IR spectra of the capping products showed absorption bands at 3080–2940 (C–H stretching), 1435 (Si–phenyl groups), 1050 (O–Si–phenyl), 1150 (O–Si), 750 and 700 (phenyl groups) cm^{-1} . These data were fundamentally similar to those of the corresponding TCP hydrolysate or its polycondensate except for the absorptions due to the trimethyl groups introduced.

Table I. Changes in molecular weight of polycondensates prepared from the TCP hydrolysates having different molecular weight^a

TCP hydrolysate		Polycondensate	
M_n /dalton	M_w/M_n	$M_n/10^4$ dalton	M_w/M_n
170	1.1	12.0	1.9
290	1.2	7.4	1.7
540	1.5	4.6	2.6
1560	3.1	1.4	3.2

^a Reported in the previous paper.¹²

Table II. Results of end-capping reaction of TCP hydrolysates (Hy) and polycondensates (Cn)

Run No.	Sample (M_n in dalton)	Yield %	M_n dalton	M_w/M_n	Unit ratio ^a $\text{Me}_3\text{Si}/\text{PhSi}$
1	Hy (170)	82	390	1.0	1.1/1.0
2	Hy (290)	82	730	2.1	0.56/1.0
3	Hy (540)	85	1,200	3.1	0.57/1.0
4	Hy (1,560)	88	1,900	3.2	1.27/1.0
5	Cn (14,000)	91	17,000	3.2	58/1000
6	Cn (46,000)	89	52,000	2.6	3.8/1000
7	Cn (74,000)	88	78,000	1.7	2.0/1000
8	Cn (120,000)	88	121,000	1.9	0.0/1000

^a By ^1H NMR.

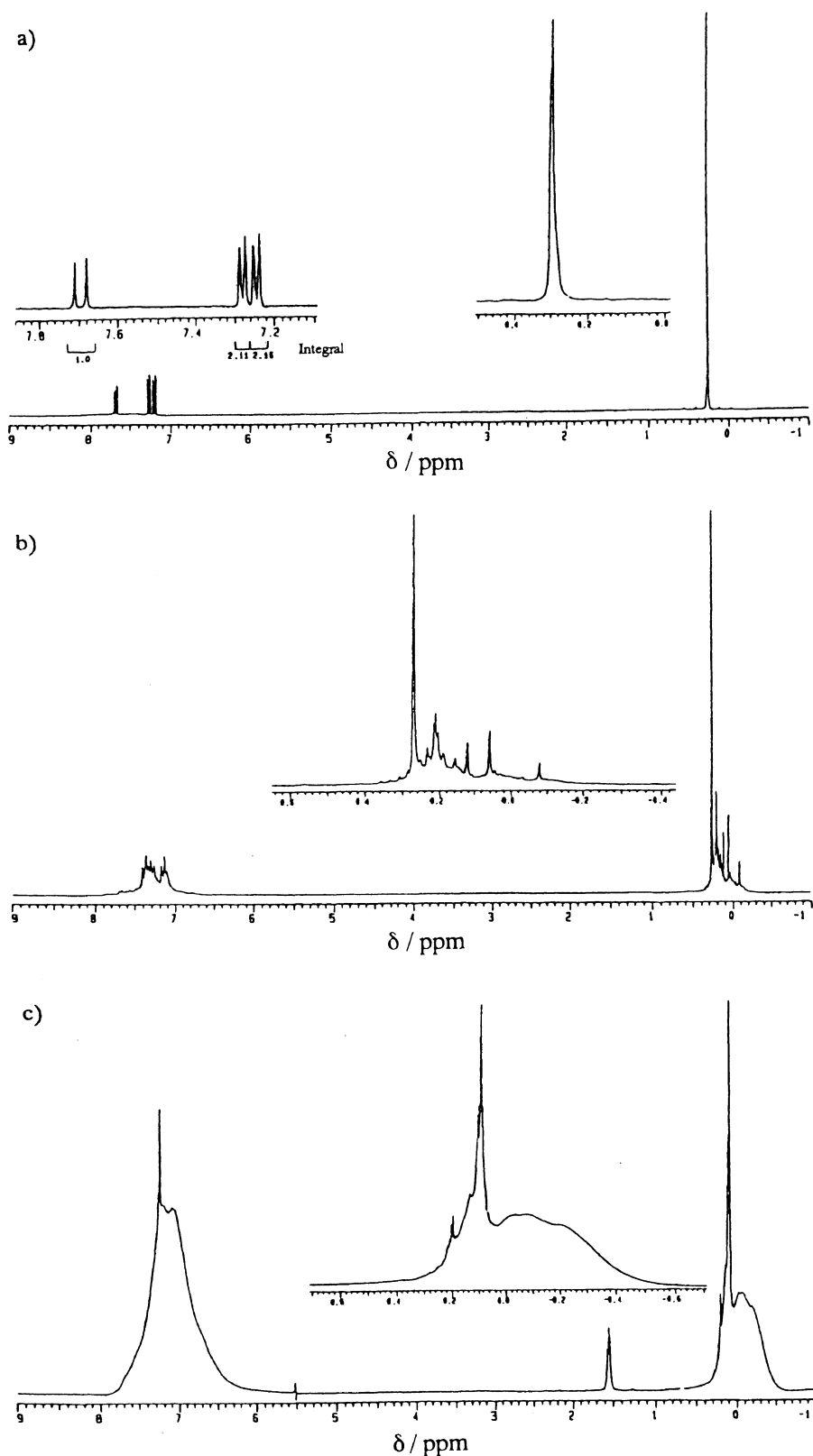


Figure 1. ^1H NMR spectra of the capping products obtained from the hydrolysates having M_n =(a) 170, (b) 290, and (c) 1560.

Depolymerization

2.5 g of PPSQ prepared from the hydrolysate having $M_n=170$ were dissolved in 76 ml of toluene. Into this solution 2.5 mg of KOH were added, and the mixture was refluxed for 20 h. The solution was poured into excess methanol to precipitate the product. The white resinous product was filtered and dried *in vacuo*. Recovery of the

product was 2.32 g (94%).

RESULTS AND DISCUSSION

Detection of Structural Defects by Silanol Capping

The structure and molecular weight of PPSQ are greatly affected by the type of TCP hydrolysate used in

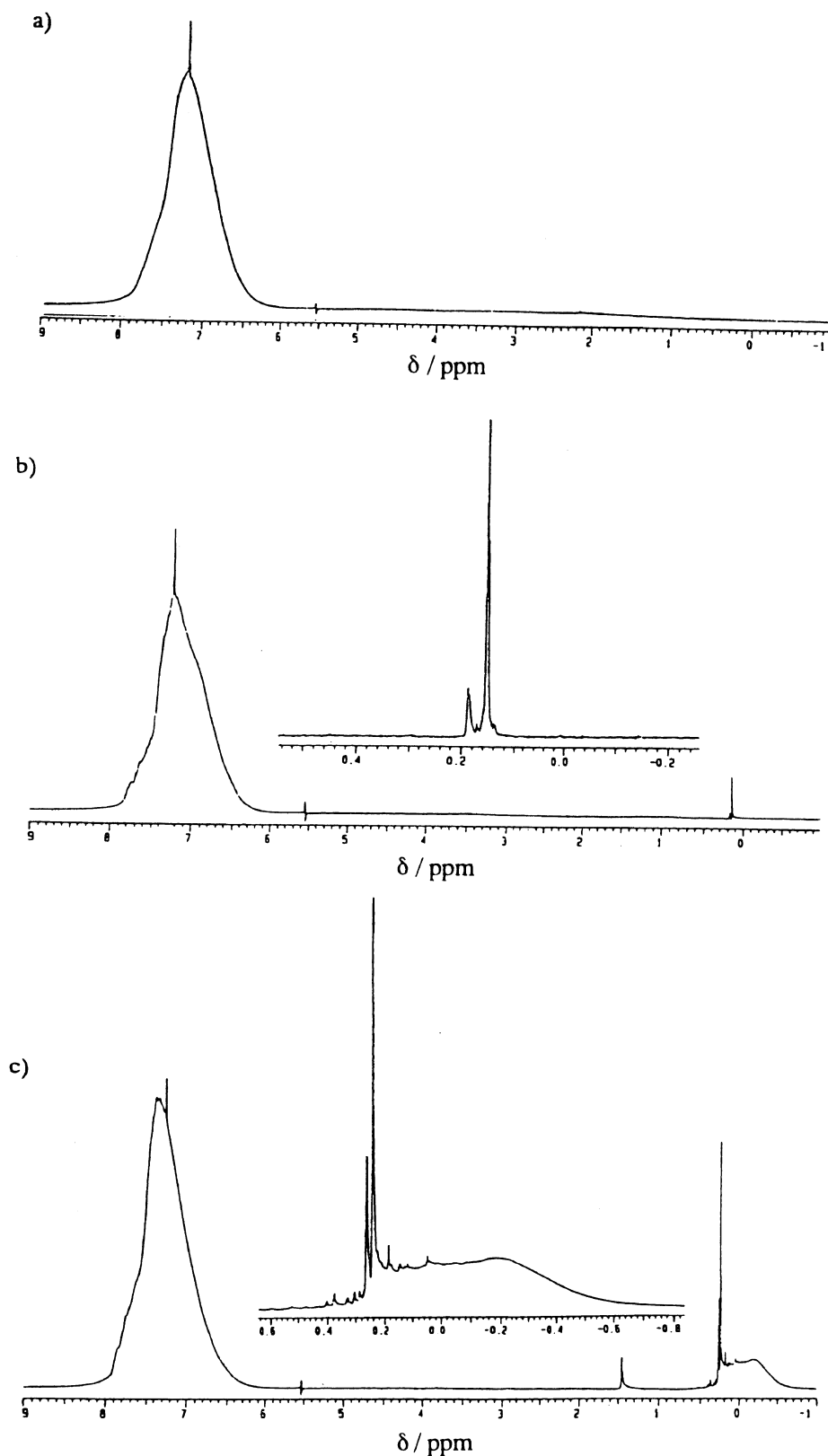


Figure 2. ¹H NMR spectra of the capping products obtained from the polycondensates having M_n =(a) 120000, (b) 74000, and (c) 14000.

the KOH-catalyzed polycondensation. A typical relationship between the molecular weight of the hydrolysate and that of the polycondensate is illustrated in Table I whose data were reported in the previous paper.¹² It is clearly shown that the degree of polymerization of PPSQ increases with decreasing molecular weight of the starting hydrolysate. IR spectroscopy suggested that a

double-stranded structure of PPSQ should become more regular with decreasing molecular weight of the hydrolysate. Particularly, the high-molecular weight PPSQ prepared from the hydrolysate consisting mainly of PST (monomeric hydrolysate) seemed to consist of a completely regular ladder sequence. The regularity of the double-stranded structure of PPSQ has not been well

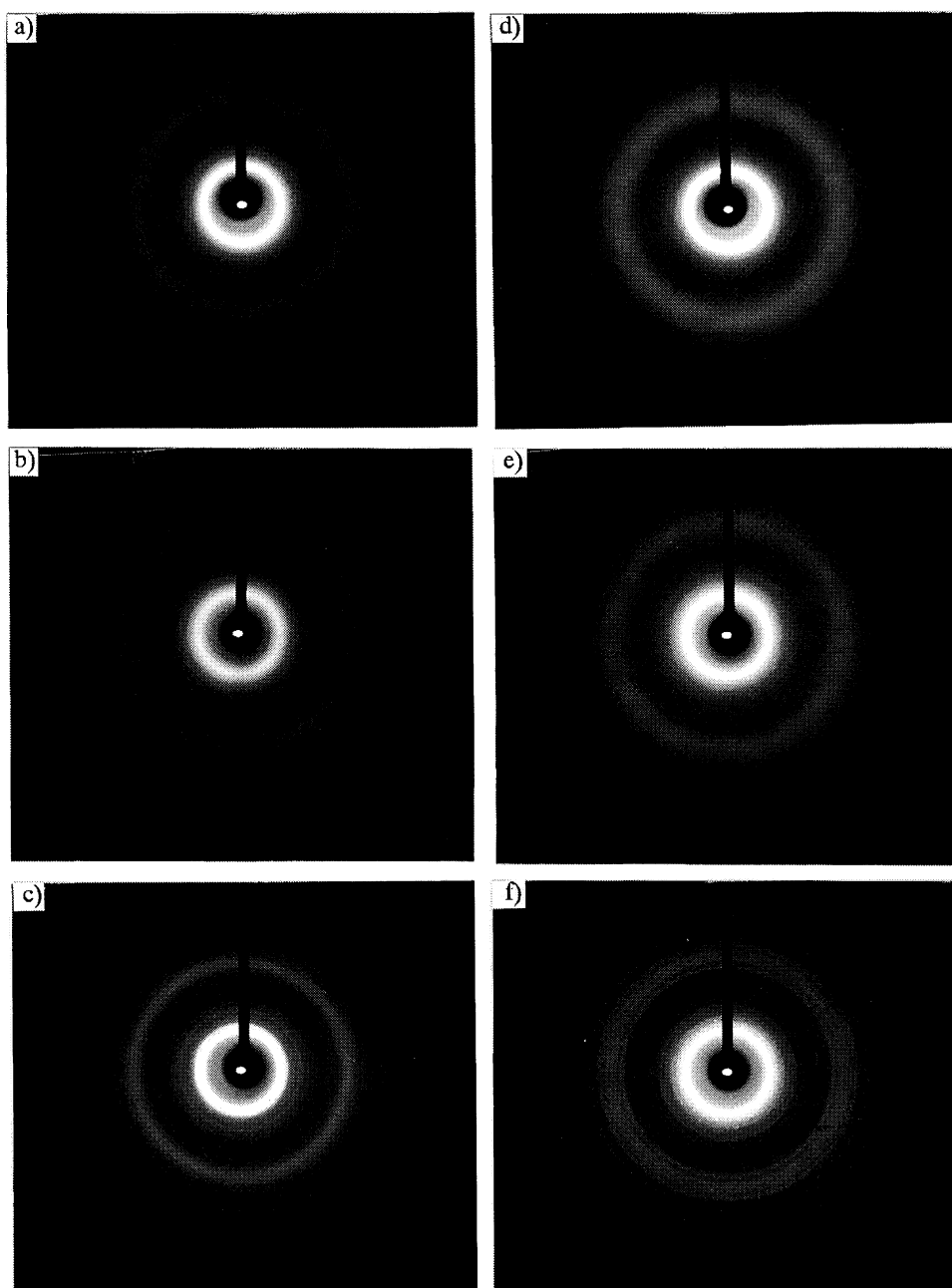


Figure 3. WAXS of the as-prepared (AP) and heat-treated (HT) PPSQ films; (a) $M_n=14000$, AP; (b) $M_n=74000$, AP; (c) $M_n=120000$, AP; (d) $M_n=14000$, HT; (e) $M_n=74,000$, HT; (f) $M_n=120000$, HT.

identified by other analytical methods, and it is controversial how many structural defects would be contained in the ladder sequence^{13,14} or at what stage of the polycondensation the ladder structure would be formed.^{15,16}

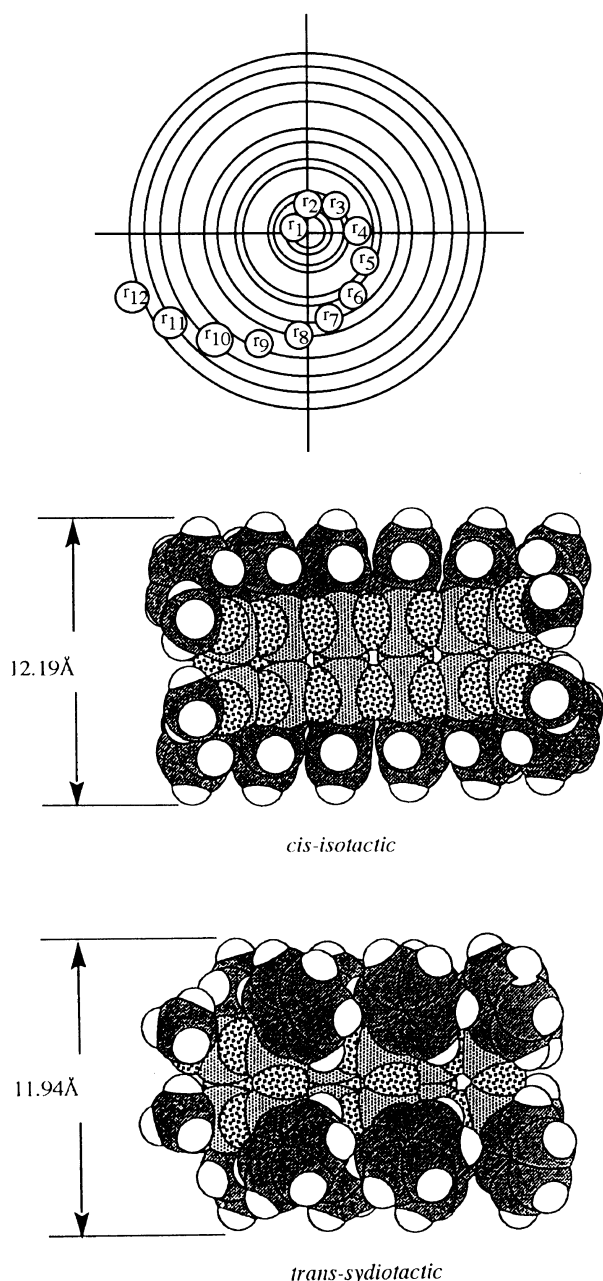
Here, the silanol groups of the TCP hydrolysates and their polycondensates were trimethylsilylated to cap and detect them by ¹H NMR spectroscopy. Analysis of the introduced silanol groups should give insight into the structures of the polymer tails and the defect points of the ladder structure. Table II summarizes the results of the silanol capping reactions for various TCP hydrolysates and their polycondensates. In each case, recovery of the capping product was higher than 80%. The molecular weights of the capping products became significantly higher than the original compounds probably

because some of the labile silanol groups had incurred intermolecular coupling during the capping reaction. Therefore, this method could not provide the quantitative analysis of the silanol groups in spite of much important structural information.

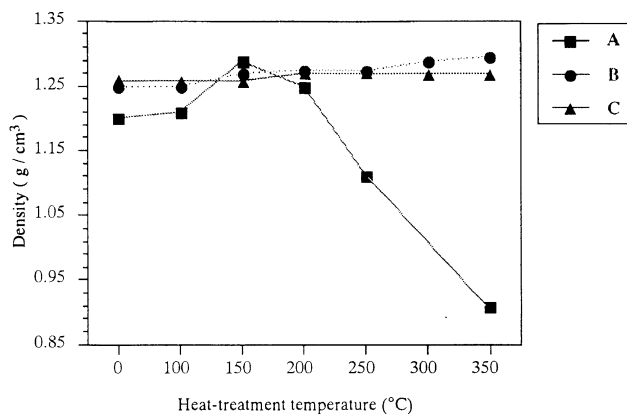
The typical ¹H NMR spectra of the capping products of the TCP hydrolysates and their polycondensates are shown in Figures 1 and 2, respectively. It is known that most capping products show ¹H signals around 7–8 ppm and –0.5–0.3 ppm which are attributed to the PhSi and Me₃Si groups, respectively. From the integral ratio of these signals, the unit ratio of Me₃Si/PhSi in each capping product was calculated. The results are summarized in the last column of Table II. For the capping product from the hydrolysate having $M_n=170$ (Figure 1a), which showed only one GPC peak, the unit ratio of Me₃Si/PhSi

Table III. Results of X-ray diffraction of the PPSQ ($M_n = 120000$) film heat-treated at 350°C

Debye-Scherrer ring	2θ °	d -Spacing Å	Debye-Scherrer ring	2θ °	d -Spacing Å
r_1	8.18	12.01	r_7	22.90	4.31
r_2	10.41	9.43	r_8	23.92	4.13
r_3	12.12	8.11	r_9	25.92	3.81
r_4	13.24	7.43	r_{10}	27.86	3.55
r_5	19.78	4.93	r_{11}	29.75	3.33
r_6	21.87	4.51	r_{12}	31.58	3.14

**Scheme 2.**

was 1.1/1.0 and much lower than the ratios of 3/1 and 2/1 for the ideal capping products of PST (monomeric) and dimeric hydrolysate of $[\text{PhSi}(\text{OH})_2]_2\text{O}$, respectively. Observation of the sole Me_3Si signal, indicated that this product should have a simple cyclic structure which probably might have been produced both through

**Figure 4.** Temperature-dependent changes in density of the PPSQ films having $M_n = 120000$ (▲), (b) 74000 (●), and (c) 14000 (■).

intermolecular coupling and intramolecular cyclization during the capping reaction. Therefore, the original hydrolysate itself should have such a simpler structure as PST monomer or dimer.^{17,18} The capping product from the hydrolysate having $M_n = 290$ showed several small signals due to the Me_3Si groups around -0.1 – 0.3 ppm in addition to the large singlet signal (Figure 1b). These high-field signals were mainly separated into five peaks and became larger in the capping product from the hydrolysate having $M_n = 540$. Therefore, these capping products would have a complex branched structure in which the Me_3Si groups exist in different environment. The capping product of the hydrolysate having $M_n = 1560$, isolated from the toluene layer, showed sharp and broad signals around 0 ppm together with a broad phenyl signal (Figure 1c). The former sharp and broad signals should probably be attributed to the Me_3Si groups with high and restricted mobilities, respectively.¹³ This strongly suggests that tri-dimensionally branched structure of a core-shell type is formed in this hydrolysate and that the Me_3Si groups in the core should have low mobility resulting in the broad line shape of the NMR signal while those in the shell should have an ordinary mobility and sharp line shape. The signal due to the unreacted silanol groups was detected at 1.6 ppm, indicating that some silanol groups in the core may not have reacted. These data strongly indicate that the original hydrolysate having higher molecular weight should have a complex branched structure whose complexity decreases with the molecular weight of the hydrolysate being smaller.

The capping products of the polycondensates also showed signals due to the Me_3Si groups introduced, although their strength was much weaker than that of the corresponding hydrolysates. The product from the polycondensate having $M_n = 14000$ (prepared from the hydrolysate having $M_n = 1560$) showed sharp and broad Me_3Si signals (Figure 2c) as the capping product of the corresponding hydrolysate did. This suggests that the product should have the core-shell type branched structure. The capping product from the polycondensate having higher molecular weight showed only sharp Me_3Si signals (Figure 2b) which correspond to the silanol groups at the defect points of the ladder as well as the polymer tails. The assignment of the two signals has not been made, but they may possibly be due to the Me_3Si groups

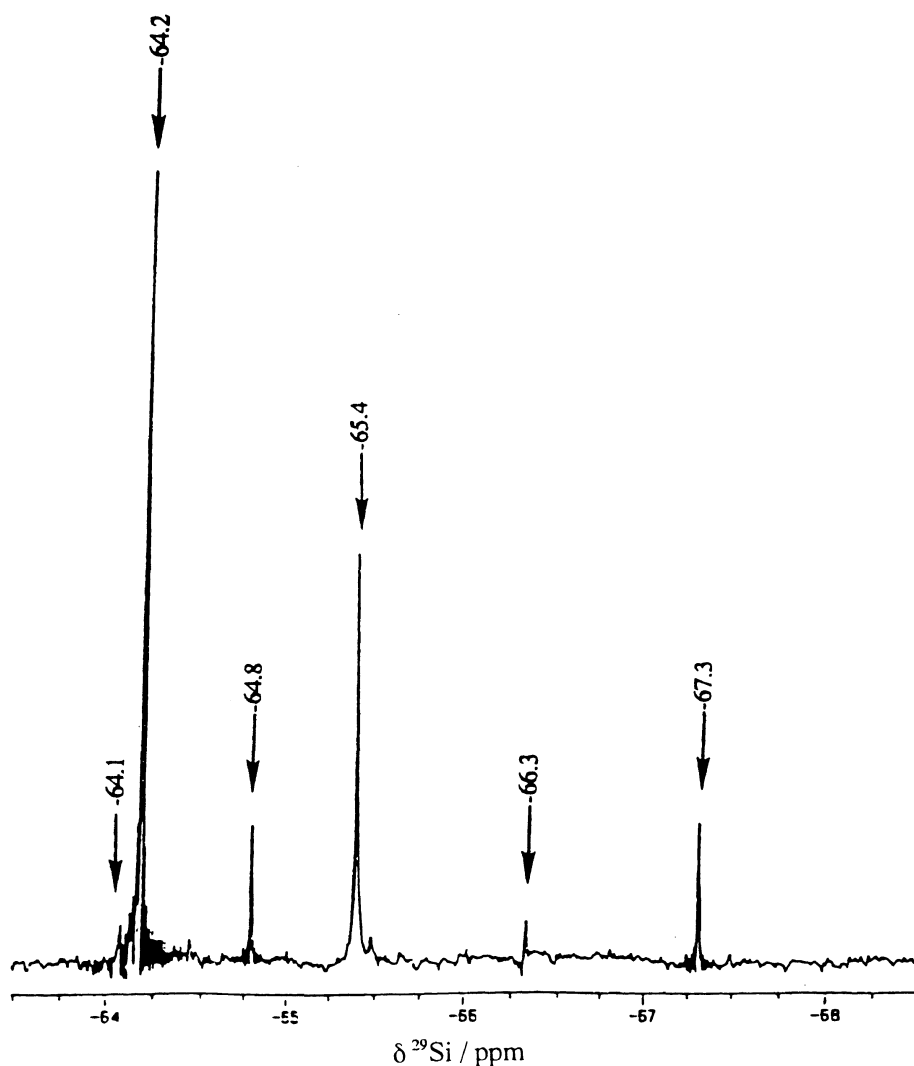


Figure 5. A typical 99.3 MHz ^{29}Si NMR spectrum of the hydrolysate having $M_n = 540$ in chloroform- d_1 .

in different environment which should be related to the difference in shielding effect. No Me_3Si signal was detected (Figure 2a) for the product from the polycondensate having $M_n = 120000$ (prepared from the hydrolysate having $M_n = 170$), probably because it contained few structural defects in the ladder and too few end groups to be detected by NMR spectroscopy. These findings support that the PPSQ prepared from the hydrolysate consisting mainly of PST should have an almost perfect ladder structure while those from oligomeric hydrolysates should involve a significant numbers of structural defects.

Solid-State Structure of PPSQ

Figure 3 shows the WAXS of the as-prepared and heat-treated polycondensates having different molecular weight. The polycondensate having $M_n = 14000$ showed two halos at $2\theta = 7.77^\circ$ and 19.08° due to the partial arrangement of the repeating units. These results are almost identical with those reported by Andrianov *et al.*,¹⁹ suggesting that PPSQ is originally crystalline. This pattern was preserved even in the heat-treated polymer whose M_n increased to 500000 during the heat treatment in solid state. The polycondensate having $M_n = 46000$ showed identical halos (at $2\theta = 7.98, 19.52^\circ$) even after

heat-treatment. The polycondensate having $M_n = 120000$, showed many clear Debye-Scherrer rings at $2\theta = 7.96, 20.90^\circ$, and 28.57° which were further separated into fine ones at $2\theta = 8.18, 21.87^\circ$, and 31.58° in the heat-treated sample. The polycondensate prepared from the hydrolysate having $M_n = 170$ is thus highly crystalline, probably because the chain structure is stereo regular. This is the first example of crystalline PPSQ whose Debye-Scherrer rings can be distinguished accurately. Evidently, the crystal structure should be complex because of the many reflections.

The planar spacings calculated from the observed Debye-Scherrer rings are summarized in Table III. The middle d -spacing around 12.01 \AA is considered to correspond to the side lengths (e.g., $\text{H}_{\text{Ph}}-\text{H}_{\text{Ph}}$) of the eight-membered ring of the cyclic tetramer which is the repeating segment of the ladder chain (see Scheme 2).¹⁹ The sharpness of this reflection indicates that the polymer chains consist of cyclic tetramers as repeating segments. The short d -spacings around 4.51 \AA suggest that the chain packing should be as that of ordinary crystalline polymers. Since the double-strand chains would crystallize only when their micro structure is also regular, the polymer chains of the crystalline PPSQ should have a stereoregular structure which may be either *cis*-isotactic

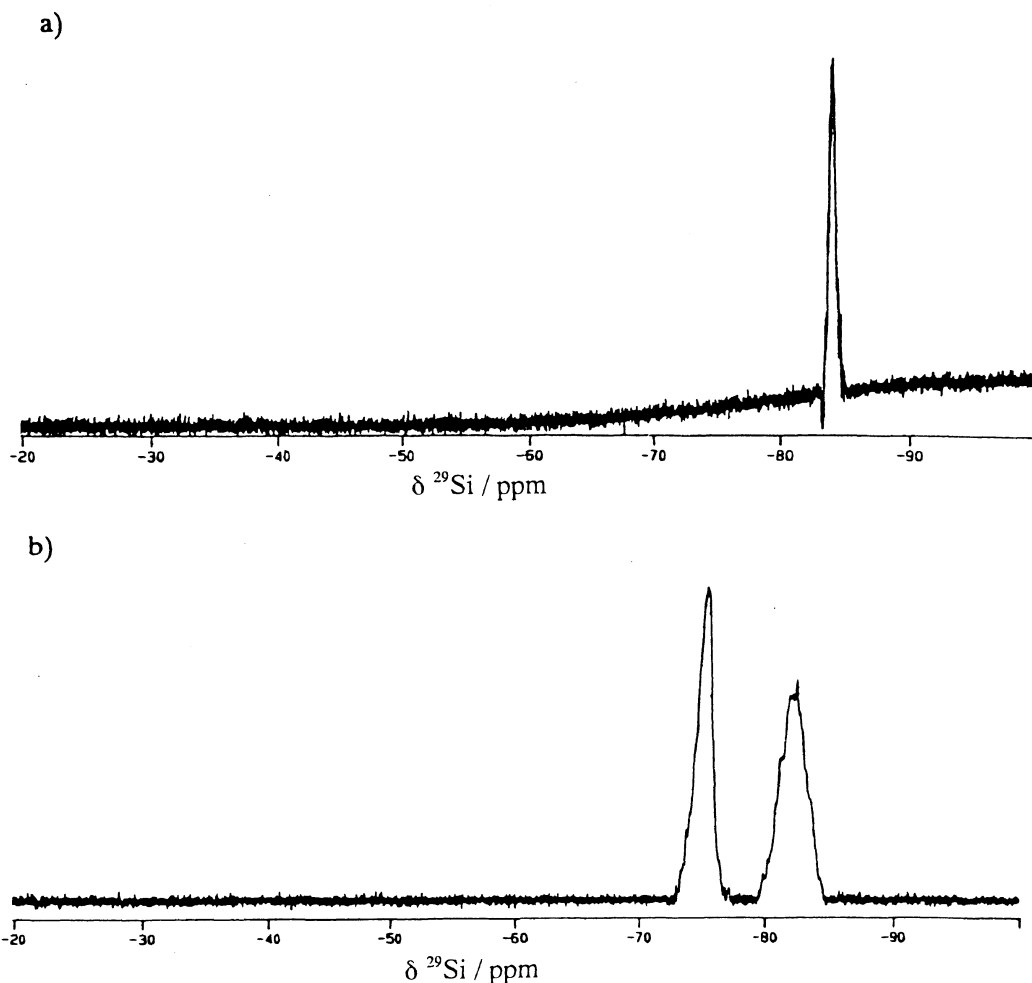


Figure 6. Typical 99.3 MHz ^{29}Si NMR spectra of the polycondensates having M_n =(a) 120000 and (b) 14000 in toluene- d_8 .

or *trans*-syndiotactic with respect to the repeating segments of the cyclic tetramer (scheme 2).⁵ At present the real micro structure could not be determined from the WAXS data. The preliminary molecular mechanical calculation, indicated that the *trans*-syndiotactic is more stable and gives a good correspondence between calculated distances and observed *d*-spacings.²⁰ Further study will be necessary for analyzing the stereoregularity of the chain.

Figure 4 shows temperature-dependent changes in density of the polycondensates having different molecular weight. The polycondensates prepared from the hydrolysates having low M_n showed very small changes in density, while that prepared from the hydrolysate having higher M_n showed a large decrease above 150°C. In the latter case the molecular weight increased with rise of temperature, and the density change should be attributed to the chain rearrangement necessary for further polycondensation in the solid state. In the former case, little increase in molecular weight was observed with temperature. These data also support that the PPSQ prepared from the hydrolysate isolated from the aqueous layer should have regular structure that is different from the one prepared by the conventional way.

Polycondensation of TCP Hydrolysate

Figure 5 shows the 99.3 MHz ^{29}Si NMR spectrum of the hydrolysate having $M_n=540$.²¹ To designate the

structural units of the species present in the solution, the symbol T for the $\text{PhSi}(\text{O}^-)_3$ unit is used throughout this paper. The number of siloxane bridges is indicated with a numerical subscript; T_0 : $\text{PhSi}(\text{O}^-)_3$, T_1 : $\text{PhSi}(\text{OSi}(\text{O}^-)_2)$, T_2 : $\text{PhSi}(\text{OSi})_2(\text{O}^-)$, and T_3 : $\text{PhSi}(\text{OSi})_3$. In the spectrum, signals due to the monomeric PST (whose unit is depicted as T_0) and the dimer can be detected at $\delta -64.1$ and -64.2 ppm, respectively. The former signal was much larger in the hydrolysate having $M_n=170$. The signals of the trimer and tetramer are also detected as two sets of peaks with different ratios. The smaller set at -64.8 and -66.3 ppm should be attributed to the trimer, while the larger set at -65.4 and -67.3 ppm to the tetramer. In both sets the weaker signal appearing at the higher magnetic field should be attributed to the divalently connected PhSi unit, *i.e.*, T_2 unit, while the stronger one, to the singly connected one, *i.e.*, T_1 unit. These data support a stepwise condensation of the TCP hydrolysates in which the dimer is formed from the monomeric PST and the tetramer is formed from the dimers, although there is an additional course that the monomer and the dimer can react to produce the trimer. The hydrolysates formed in this way should be linear oligomers if the degree of condensation is low enough, and they precipitate from the aqueous layer when TCP is hydrolyzed in water/toluene bilayer system, as we reported before.¹²

In the KOH-catalyzed polycondensation the trivalent

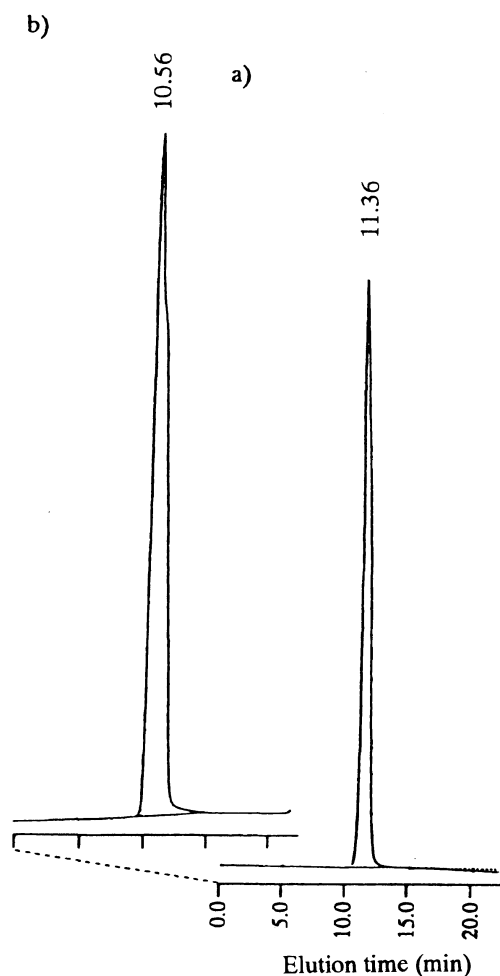


Figure 7. GPC of the PPSQ (a) before and (b) after the heat-treatment in the presence of 0.1 wt% of KOH at 110°C for 20 h.

(T_0) or divalent (T_1) siloxyl units should be first elected to form chains, and the T_2 siloxyl units, if any, should remain somewhere in the chains. If the starting hydrolysates contain only T_1 and T_2 units, the chain extension would progress with few defects formed. If many T_2 units are involved, their silanol groups would be expelled from the formation of the ladder chain and finally form the defects and chain branching. Figure 6 shows the 99.3 MHz ^{29}Si NMR spectra of the polycondensates prepared from the hydrolysates with different molecular weights. The product prepared from the low molecular weight hydrolysate ($M_n=170$) showed only one signal due to the T_3 units ($\delta -83$ ppm), while that one from the high-molecular weight hydrolysate ($M_n=1560$) showed T_2 ($\delta -75$ ppm) and T_3 ($\delta -82.1$ ppm) units which became broad owing to different environment in the irregular polymer sequences.

PPSQ may depolymerise into such cage compounds as octaphenylcyclotetrasiloxane (T8) when refluxed.²² Our polymer prepared from the hydrolysate having $M_n=170$ was dissolved in toluene and subjected to refluxing in the presence of a catalytic amount of KOH for 20 h. Figure 7 shows the GPC curves of the PPSQ before and after refluxing. The molecular weight even increased after refluxing with slight increase in molecular weight distribution. This indicated that the ladder sequence is stable if the chains consist of regular double-strands. The bond

cleavage and rearrangement reported before may be allowed only when the chains contain single strands.

CONCLUSION

Various TCP hydrolysates and their polycondensates were reacted with TMS for capping the silanol groups. The ^1H NMR spectra of the produced capping products showed several signals due to the Me_3Si groups introduced. Observation of sharp and broad signals for the polycondensate prepared from the hydrolysate having $M_n=1560$ (isolated from the toluene layer) suggests that this polymer may have a core-shell type branched structure with many bonding defects. No Me_3Si signal was detected for the polycondensate prepared from the hydrolysate having $M_n=170$ (isolated from the aqueous layer), supporting an almost perfect ladder structure with few structural defects. WAXS analysis revealed that the latter polycondensate was highly crystalline, having a stereo regular chain structure. Its ^{29}Si NMR spectrum also supported structural regularity. This polymer having the double-strand structure was found so stable as not to undergo depolymerization in solution. The present isolation of the crystalline polycondensate contributes to the understanding of the structure-property relationship of PPSQ.

REFERENCES

1. A. Ladenburg, *Ber.*, **6**, 379 (1873).
2. J. Meads and F. S. Kipping, *J. Chem. Soc.*, **105**, (1914).
3. K. Larsson, *Arkiv Kemi*, **16**, 209 (1960).
4. K. Larsson and C. Grunwall, *Arkiv Kemi.*, **17**, 529 (1961).
5. J. F. Brown, Jr., L. H. Vogt, Jr., and P. I. Prescott, *J. Am. Chem. Soc.*, **86**, 1120 (1963).
6. J. F. Brown, *J. Polym. Sci. Part C.*, **1**, 83 (1963).
7. J. F. Brown, Jr. and L. H. Vogt, *J. Am. Chem. Soc.*, **87**, 4313 (1965).
8. M. M. Sprung and F. O. Guenther, *J. Polym. Sci.*, **28**, 17 (1958).
9. J. S. Hrkach and K. Matyjaszewski, *J. Polym. Sci., A, Polym. Chem.*, **33**, 285 (1995).
10. K. J. Mcneil, J. A. Dicaprio, D. A. Walsh, and R. F. Pratt, *J. Am. Chem. Soc.*, **102**, 1859 (1980).
11. T. Takiguchi, R. Fujikawa, Y. Yamamoto, and M. Ueda, *Nippon Kagaku Kaishi*, 108 (1974).
12. E. C. Lee and Y. Kimura, *Polym. J.*, **29**, 678 (1997).
13. H. Nishida, H. Yamane, Y. Kimura, and T. Kitao, *Kobunshi Ronbunshu*, **53**, 193 (1996).
14. H. Ban, A. Tanaka, Y. Kawai, and S. Imamura, *Polymer*, **31**, 564 (1990).
15. M. Smaih, T. Jermoumi, and J. Marignan, *Chem. Mater.*, **7**, 2298 (1995).
16. P. Xie, Y. Wan, B. Zhou, J. Hou, D. Dai, Z. Li, D. Liu, and R. Zhang, *Macromol. Chem. Phys.*, **197**, 745 (1996).
17. T. Takiguchi, *J. Am. Chem. Soc.*, **81**, 2359 (1959).
18. B. L. Tyler, *J. Am. Chem. Soc.*, **77**, 770 (1955).
19. K. A. Andrianov, G. L. Slonimsky, A. A. Zhdanov, D. Ya. Tsvankin, V. Yu. Levin, V. S. Papkov, Yu. P. Kvachev, and E. M. Belavtseva, *J. Polym. Sci.*, **14**, 1205 (1976).
20. M. Konda, E. C. Lee, and Y. Kimura, unpublished data.
21. We have reported 59.6 MHz ^{29}Si NMR spectra of the TCP hydrolysates having different molecular weight. Here we re-investigated the same spectra at a higher frequency of 99.3 MHz by using a pure TMS in a capillary tube as the *in situ* external reference. The chemical shift of the signals was found to be significantly different from the former value by $\delta -7.5$ ppm which had been measured with the signal of a sample of TMS in chloroform- d_4 , as the machinery 0 ppm (see ref 12).
22. J. Chojnowski, *Spec. Publ. R. Soc. Chem.*, **166**, 59 (1995).