ELSEVIER

Polymer 42 (2001) 1047–1053

polymer

www.elsevier.nl/locate/polymer

Phase structure and transitions in a poly(methyloctadecylsilane) oligomer

Zhimou Wu, Fengchao Xie, Zhijun Hu, Jieping Liu, Binyang Du, Tianbai He*

State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People's Republic of China

Received 28 June 1999; received in revised form 14 June 2000; accepted 14 June 2000

Abstract

A poly(methyloctadecylsilane) oligomer was synthesized by a typical Wurtz coupling reaction. Upon cooling, three transitions were observed at temperatures of 39.9, 37.5 and 33.9°C at a rate of 2.5°C/min in differential scanning calorimetry (DSC). The first transition, with enthalpy change of 0.47 kJ/mol and supercooling of 0.2°C, was characteristic of the conformational change in the Si–Si backbone into an all-*trans* conformation, which was detected by temperature-dependent Fourier transform infrared (FT-IR) spectroscopy. The second and the third transitions with large supercooling were identified as the formation of two-dimensional hexagonal crystal packing and three-dimensional two-chain orthorhombic crystal packing, respectively. The crystal structure was determined by the combination of WAXD and transmission electron microscopy (TEM) experiments. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Polysilane; Conformation; Crystallization

1. Introduction

Polysilanes have attracted much interest because they show unique electronic and optical properties due to the delocalization of σ-electrons along the silicon backbone [1]. They have been considered as photoresist [2], nonlinear optical [3], photoluminescent [4] and electroluminescent [5] materials. The function of polysilanes was correlated critically to the conformation of the polymer backbone similar to π-conjugated polymers [6,7]. Klemann et al. have found that the degree of asymmetry of the side chains influences the conformation of the silicon backbone and greatly affects the physical properties of polysilanes [8]. It has also been found that the crystallizable side chains forces the Si–Si backbone into an all-*trans* conformation with a more rigid structure [9]. This increase in rigidity of Si–Si backbone induced by the crystallization of side chains led to the formation of a mesophase even though there was no classical mesogen in those polysilanes with linear flexible chains [10,11]. The structure of those mesophases was identified as a hexagonal columnar phase based on WAXD [12,13]. However, detailed information on side chain crystallization, such as crystalline structure, crystal growth, and chain packing has not been studied.

In this work, a poly(methyloctadecylsilane) oligomer was synthesized. Because poly(methyloctadecylsilane) oligomer is stable under electron radiation, it is feasible to study crystal morphology and structure from transmission electron microscopy experiments. The easily crystallizable long side chains in the poly(methyloctadecylsilane) oligomer provide a pronounced hindrance to the conformational change of the Si–Si backbone. The influences of crystallization and asymmetry of the side chains of the poly(methyloctadecylsilane) oligomer on the conformation and rigidity of the Si–Si backbone are also discussed.

2. Instrumentation and experiments

2.1. Material

The poly(methyloctadecylsilane) (Si–C1C18) oligomer was prepared by a typical Wurtz coupling reaction of 6.73 g from dichloromethyloctadecylsilane with 0.86 g of highly dispersed molten Na in dry toluene under nitrogen. The reaction was kept at 110°C for 8 hr and then cooled to ambient temperature. 400 ml of 2-propanol was first added to eliminate any remaining Na, followed by precipitation using 300 ml methanol mixed with 30 ml warm toluene. After drying in a vacuum oven for a week at ambient temperature, a white powder solid oligomer with a monomodal molecular weight distribution of $M_w = 2489$ g/mol and $M_n = 1743$ g/mol and a polydispersity of 1.43 (M_w/M_n) from a gel permeation chromatography (GPC) was obtained

---

* Corresponding author. Tel.: +86-431-5682828; fax: +86-431-5685653.

E-mail address: tbhe@ns.ciac.jl.cn (T. He).

0032-3861/01/$ - see front matter
PII: S0032-3861(00)00463-8

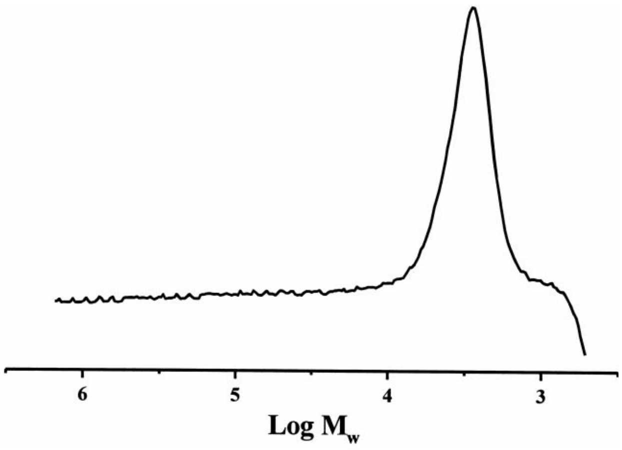

Fig. 1. GPC diagram of poly(methyloctadecylsilane) oligomer.

(Fig. 1). ^{1}H NMR($CDCl_3$, TMS): δ 0.5(3H, s, CH_3–Si–), 0.73(2H, s, –Si–CH_2–), 1.26(32H, s), 0.88(3H, s, –CH_2–CH_3) (Fig. 2).

Differential scanning calorimetry (DSC) experiments were carried out in a Perkin–Elmer DSC-7 at various cooling and heating rates from 2.5°C to 20°C/min under nitrogen atmosphere. The temperature range was from 0 to 80°C. The specimen size used were 7.840 mg. Consecutive heating was performed at the same scanning rate as the preceding cooling scan.

Wide angle X-ray diffraction (WAXD) experiments for the powder sample were performed on a Rigaku 50 kV/200 mA rotating anode generator (CuK_α radiation) equipped with a diffractometer. The scanning type was continuous scanning and the diffraction peak positions and widths were calibrated using standard silicon crystals.

Fourier transform infrared spectroscopy (FT-IR) was carried out on Bio-Rad FTS-135. The measurements were made on a film cast on KBr plate with 0.2% (w/w) chloroform solution. The measurement resolution was 4 cm^{-1}.

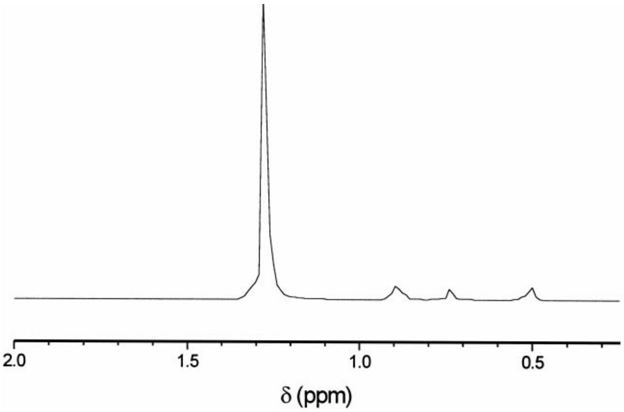

Fig. 2. ^{1}H NMR spectra of poly(methyloctadecylsilane) oligomer.

A thin film was made by casting a 0.1% (w/w) powder sample/chloroform solution. After the solvent evaporated at room temperature, the film was heated to 60°C and was then cooled to 35°C and held at this temperature for 2 h. The structure and morphology of the thin film was observed using a JEOL-2010 transmission electron microscopy (TEM) with an accelerating voltage of 200 kV. The thin film was coated by carbon and shadowed by Pt for morphology observations. Gold was used as calibration of the ED spacing.

The optical texture of the sample was observed on an Opton Feintechnik GmbH D-7082 Oberkochen polarized optical microscope (POM). The isothermal and non-isothermal observations with both cooling and heating rates of about 2.5°C/min were made.

3. Results and discussion

3.1. Phase transition behavior

Three phase transitions have been observed in the DSC cooling process of poly(methyloctadecylsilane) at a scanning rate of 2.5°C/min (Fig. 3a). The first transition on cooling from the high temperature is observed clearly and the second and the third ones are overlapped. To obtain more distinct information on those transitions, a PeakFit software based on an asymmetric double sigmoidal function from Jandel Scientific was used for peak resolution. As shown in Fig. 3b, the peak temperatures of the three transitions are 39.9, 37.5, and 33.9°C, respectively. The phase transition behavior was studied by a series of DSC cooling and heating curves with different scanning rates (Fig. 4). It is found that the first transition, with as a minor enthalpy change of 0.47 J/g, has small supercooling of 0.2°C within the scanning rates from 2.5°C to 20°C/min. This indicates that the first transition is close to an equilibrium state upon cooling [14]. Such a transition with small supercooling and enthalpy change should not be considered as a traditional crystalline phase transition, which might be an entropy dominant term. A 5°C supercooling is found in the second and third transitions with the scanning rates from 2.5 to 20°C/min. On heating, the second and the third transition overlap, which leads to the formation of a sharp and large endothermic peak at 42°C, having an enthalpy of 31.8 kJ/mol. Therefore, it is deduced that that these two peaks could belong to more ordered crystalline transitions due to the kinetic dependence.

3.2. Conformational change of silicon backbone

It is of great interest to see that the small values of enthalpy change and supercooling, as of those in the first transition, are characteristic of a conformation change [15]. It is well known that the conformation change in polysilanes with long side chains is due to the steric hindrance of long side chains [9]. Temperature-dependent FT-IR spectroscopy

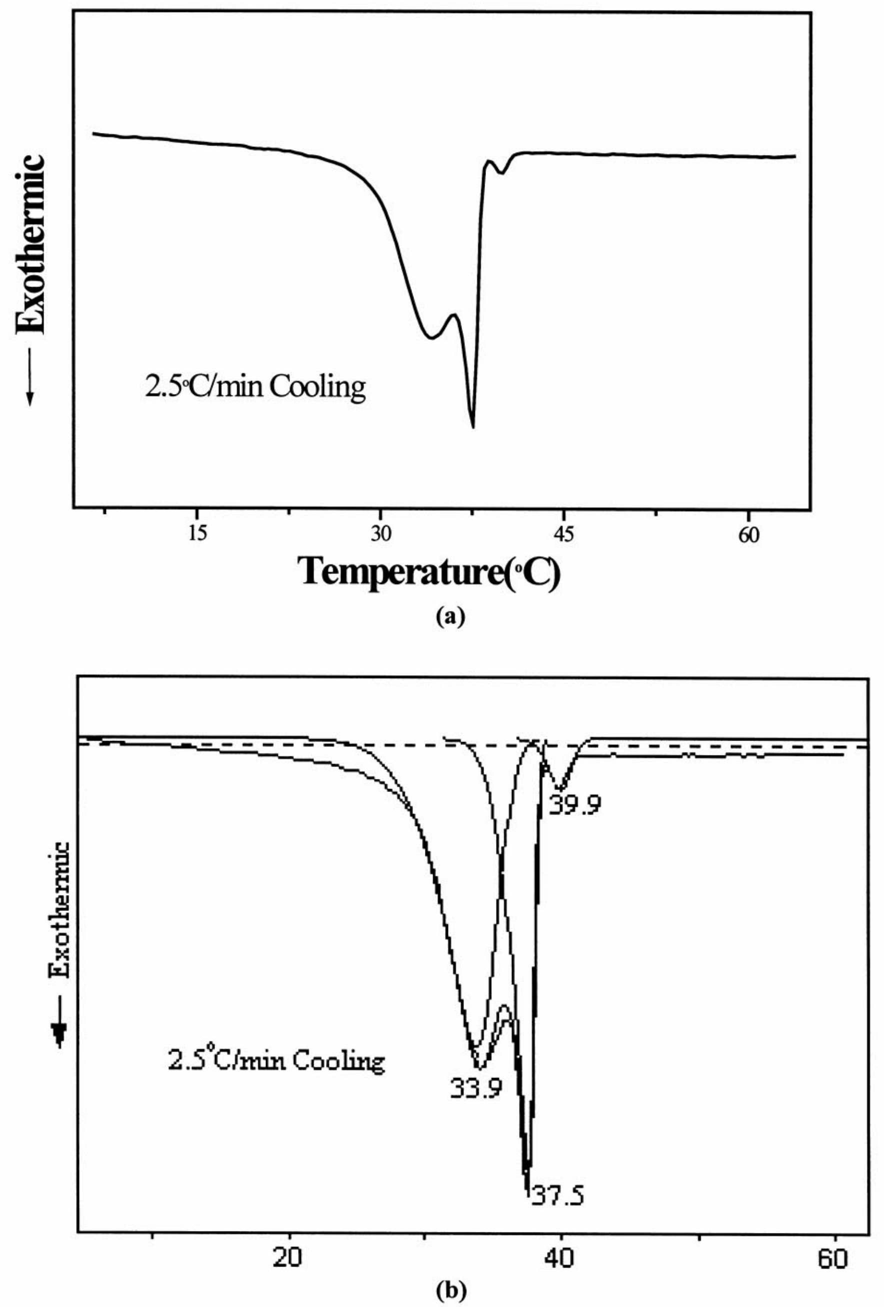

Fig. 3. The original DSC cooling curve of poly(methyloctadecylsilane) oligomer at: (a) scanning rate 2.5°C/min; (b) after the peak resolution.

in Fig. 5 provides evidence for such conformational change in the sample. At 25°C, a series of peaks in the region of 400–500 cm^{-1} attributed to the stretching vibration of the Si–Si bones are observed. When the sample is heated to 50°C, which arrives in the first transition of the sample upon heating, the peaks become weak and disappear soon. During cooling, a similar phenomenon is observed. When the temperature is lowered to the first transition temperature, the peaks in the region of 400–500 cm^{-1} appear again. The sharp vibration appearing at 418 cm^{-1} may be attributed to the all-*trans* conformation of the backbone [16].

When the temperature is below the first transition, the intensity of peaks in the region of 400–500 cm^{-1} remains constant. This result indicates that the conformational change of the Si–Si backbone takes place at the first transition. Also, the intensity of the peak at 721 cm^{-1}, which represents the CH_2 rocking vibration of the side chains, does not change at the first transition. This result also demonstrates that the first transition arises from the

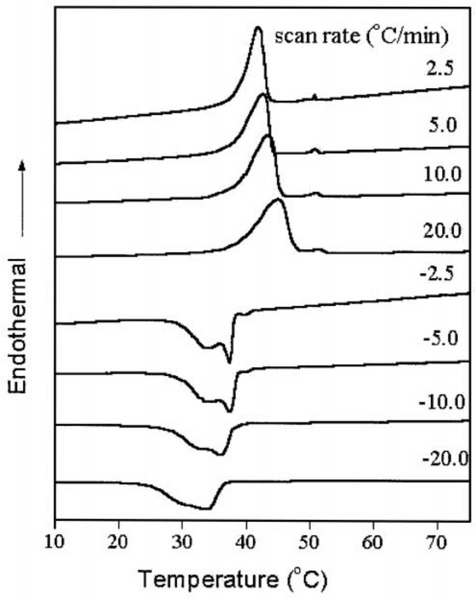

Fig. 4. DSC cooling and heating curves of poly(methyloctadecylsilane) oligomer at different scanning rates.

conformational change of the Si–Si backbone rather than the side chains.

3.3. Crystal structure

In DSC experiments, because the second and the third transitions overlap on cooling, a careful thermal treatment should be performed to investigate the crystal structure. First, the sample is isothermally annealed at 37.5°C for 24 h, at which temperature the third transition just begins. The WAXD pattern of the isothermally treated sample is

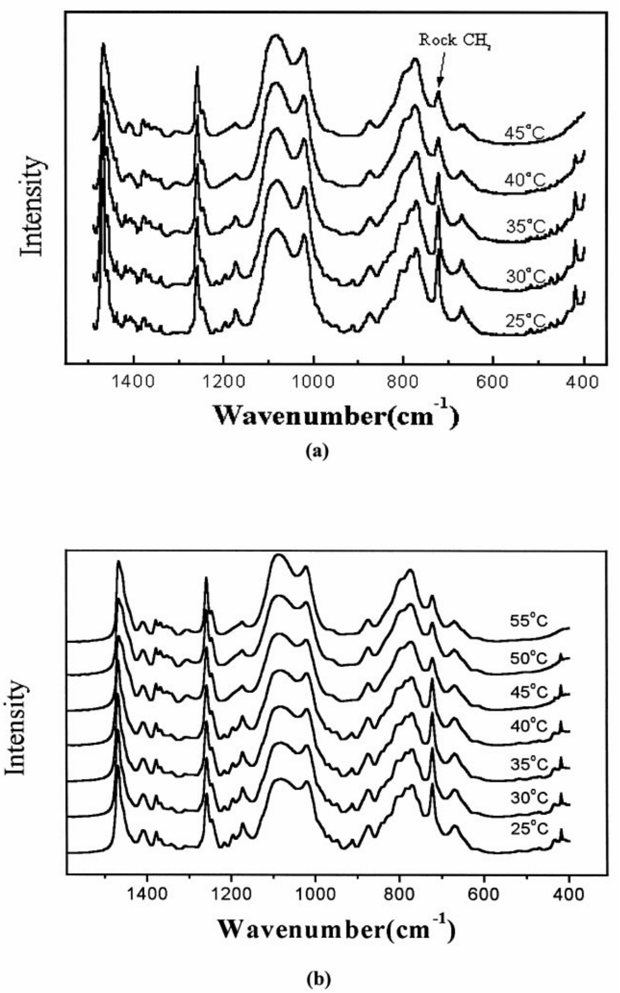

Fig. 5. Temperature-dependent FT-IR spectrum of poly(methyloctadecylsilane) oligomer during: (a) cooling; (b) heating.

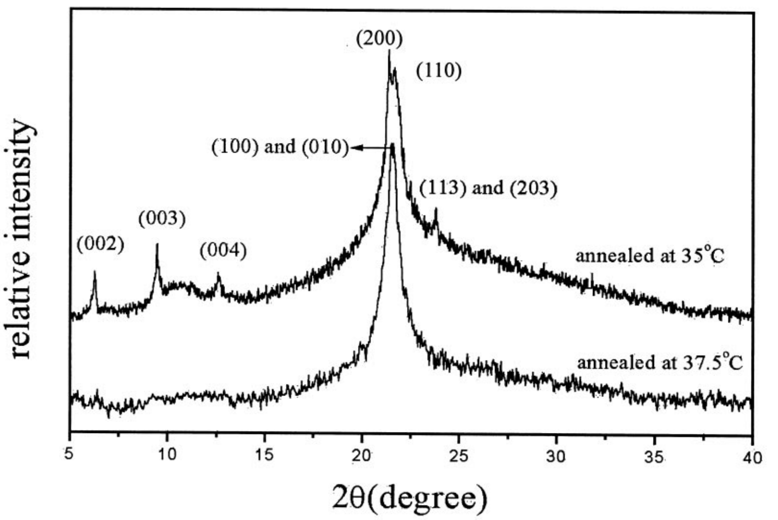

Fig. 6. WAXD power diffraction patterns of poly(methyloctadecylsilane) oligomer annealed at 37.5 and 35°C.

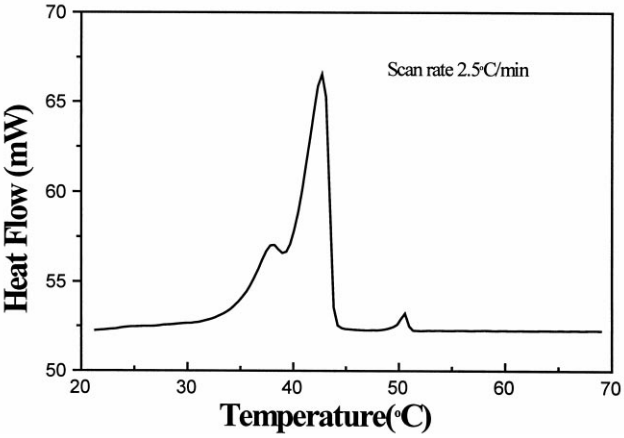

Fig. 7. DSC heating curve with rate of 2.5°C/min of poly(methyloctadecylsilane) oligomer annealed at 30°C for 2 h.

shown in Fig. 6. Only a sharp and intense Bragg reflection peak at $2\theta = 21.3°$ is observed. Generally speaking, in a WAXD powder pattern the presense of a single intense peak at about $2\theta = 21.3°$ reflected by the (100) and (010) planes and the absence of other reflections at the vicinity of $2\theta = 21.3°$ is characteristic of two-dimensional (2D) hexagonal packing [11,17–19]. So, one can conclude that the second transition in the DSC for the poly(methyloctadecylsilane) oligomer is the formation of 2D hexagonal packing with dimensions of $a = b = 4.80$ Å, $\gamma = 120°$.

When the sample is annealed at 30°C, a different WAXD pattern is obtained, as shown in Fig. 6. There are six Bragg diffraction peaks. The molecular *c*-axis is calculated from this WAXD powder pattern. The diffraction peaks at $2\theta =$ 6.29, 9.44, and 12.67 are assigned as (002), (003) and (004) with *d*-spacing values of 14.05, 9.36 and 6.98 Å, respectively. The two major diffraction peaks with d-spacing values of 4.05 and 4.10 Å reflect superimposed (110) and (200) crystal planes, which can be further observed in the following electron diffraction pattern. The diffraction peak at $2\theta = 23.76$ is assigned as (113) or/and (203) with d-spacing values of 3.72 and 3.75 Å. Therefore, it is deduced that this three-dimensional (3D) crystal structure could be assigned as two-chain orthorhombic packing with size of $a = 8.20$ Å, $b = 4.66$ Å, $c = 28.10$ Å. Although the *c*-axis is larger than the extended conformation of aliphatic side chains (22.86 Å), an interdigitated model of side chains could be considered in this case. The calculated density of this crystal packing is 0.92 g/cm^3, which is quite consistent with the measured density of 0.90 g/cm^3. Thus, the third transition can be identified as the transition from the 2D hexagonal packing to 3D orthorhombic packing.

During heating, it seems that there are only two transitions in DSC curves, as shown in Fig. 4. In fact, it is not that only two transitions exist, but that the second and third transitions overlap. The DSC curve of the sample annealed at 35°C confirms this statement. A DSC scan of this sample with a heating rate of 2.5°C/min is shown in Fig. 7. Three separable transitions are observed as expected, which are reproducible from three scanning operations.

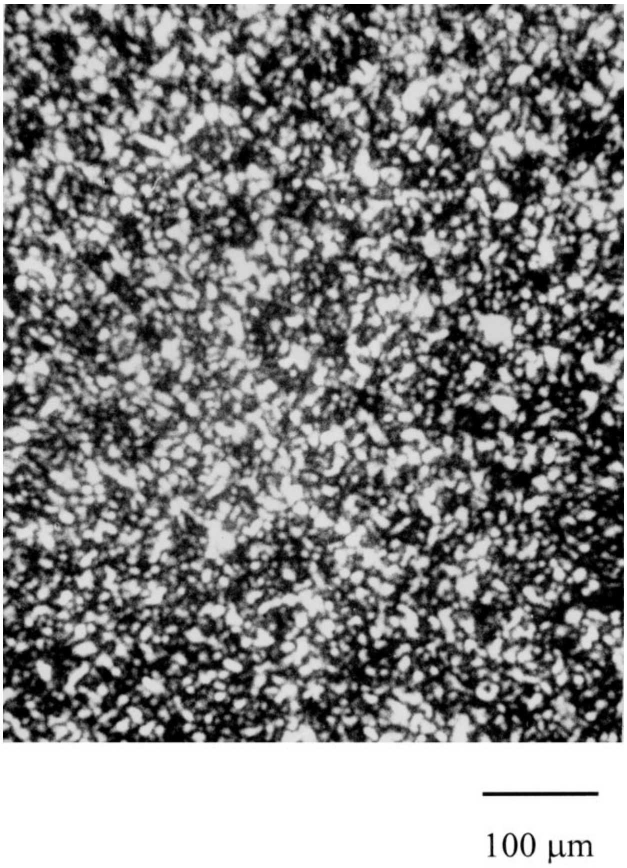

Fig. 8. POM micrograph of poly(methyloctadecylsilane) oligomer cooled to 35°C from the melt.

The process of crystallization in polysilane is also observed through POM, as shown in Fig. 8, when the temperature is decreased to 35°C. The micrograph of POM shows the polymer birefringence is relatively weak and the optical structure is small. Above 42°C, the high-temperature phase only exhibits very weak birefringence without any clear observation of low-ordered liquid crystalline phases.

To understand more details of the side chain crystallization, a single crystal of poly(methyloctadecylsilane) sample formed from the melt was obtained (Fig. 9). The electron diffraction on the single crystal is from a (001) zone. According to the electron diffraction spots along the *(hk0)* plane, the lateral packing symmetry of the single crystal is 2D orthorhombic with diffraction spots of (110) and (200) planes. This phase look like a pseudohexagonal phase with $\gamma = 60°$ between the (110) and (200) planes, in which the dimensions of (110) and (200) diffraction spots are quite close. The morphology of this single crystal implies that the asymmetric shape has the feature of orthorhombic packing crystal with

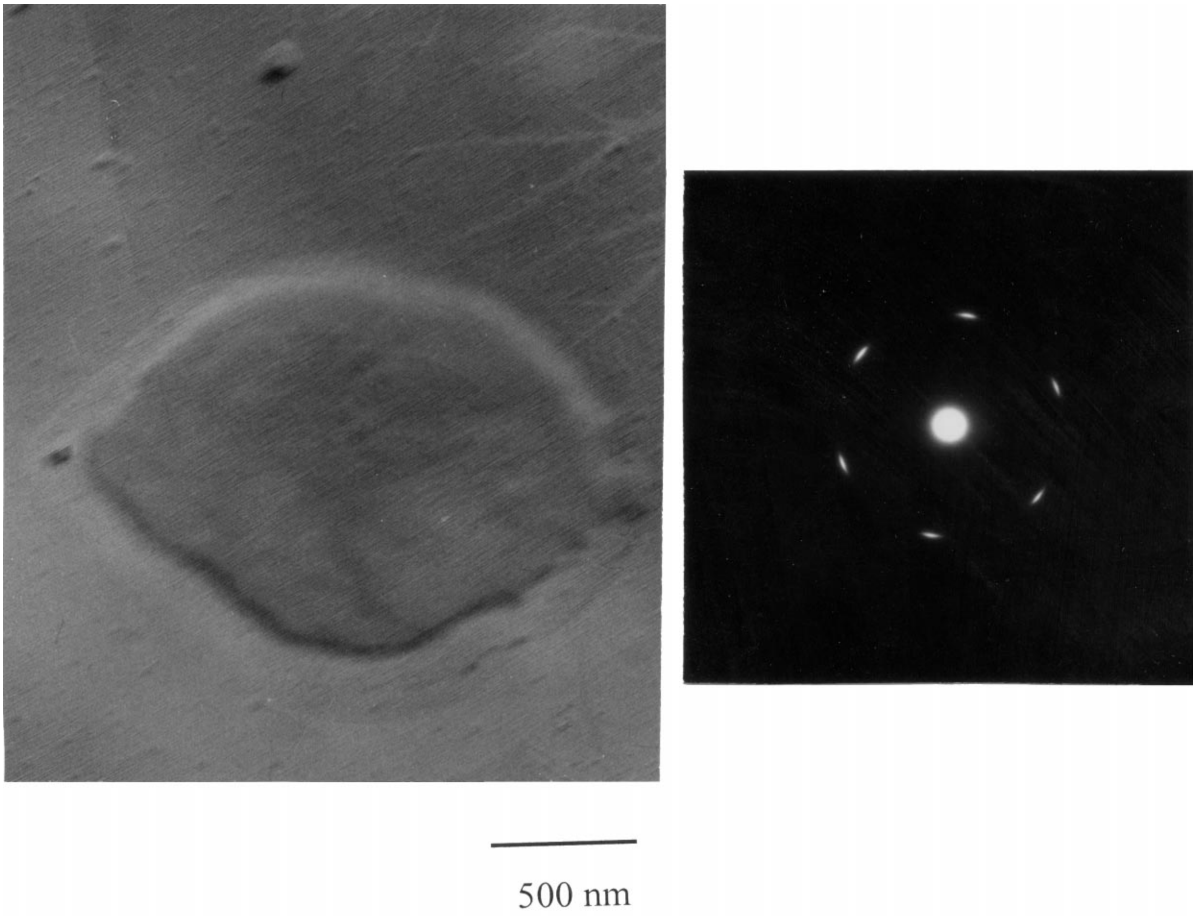

Fig. 9. TEM observation and ED pattern of the single crystal of poly-(methyloctadecylsilane) oligomer obtained at 35°C from the melt.

dimensions of $a = 8.20$ Å, $b = 4.66$ Å, $c = 28.10$ Å, which are consistent with the WAXD at 30°C (Fig. 6).

4. Conclusions

Upon cooling, three phase transitions with transition temperatures of 39.9, 37.5, and 33.9°C were found in poly(methyloctadecylsilane) oligomer. Those transitions were identified as a conformational change of the Si–Si backbone, a 2D hexagonal phase, and a 3D orthorhombic phase, respectively. The all-*trans* conformation is only observed in ordered structures in the Si–Si backbone. Then, the second transition that appears in DSC is a 2D hexagonal packing with $a = b = 4.80$ Å, $\gamma = 120°$. The low-temperature phase could be assigned as the two-chain orthorhombic lattice with parameters of $a = 8.20$ Å, $b = 4.66$ Å, $c = 28.10$ Å.

Acknowledgements

This work was supported by National Science Foundation of China. We would like to thank Prof. Stephen Z.D. Cheng and Dr Jason J. Ge at the University of Akron for the WAXD assistance and structural analysis.

References

[1] Miller RD, Michl J. Chem Rev 1989;89:1359.
[2] Yamaguchi A, Ogawa T, Tachibana H, Oizumi H, Soga T, Matsumoto M, Matsuzaka T, Takeda E. J Electrochem Soc 1996;143(2):657.
[3] Kishida H, Tachibana H, Sakurai K, Matsumoto M, Tokura Y. Phys Rev B 1996;54(20):R14254.
[4] Majima Y, Kawata Y, Nakano Y, Hayase S. J Polym Sci, Part A: Polym Chem 1997;35:427.
[5] Hoshino S, Suzuki H, Fujiki M, Morrita M, Matsumoto N. Synth Metals 1997;89:221.
[6] Lim KC, Heeger AJ. J Chem Phys 1985;82:522.
[7] Roux C, Leclere M. Macromolecules 1992;25:2141.
[8] Klemann B, West R, Koutsky JA. Macromolecules 1993;26:1042.
[9] Rabolt JF, Hofer D, Miller RD, Fickes GN. Macromolecules 1986;19:611.
[10] Weber P, Guillon D, Skoulios A, Miller RD. J Phys France 1989;50:793.
[11] Ungar G. Prog Colloid Polym Sci 1992;87:53.
[12] Asuke T, West R. Macromolecules 1991;24:343.
[13] Asuke T, West R. J Inorg Organomet Polym 1994;4(1):45.

[14] Yoon Y, Zhang A, Ho R-M, Cheng SZD, Percec V, Chu P. Macromolecules 1995;29:294.
[15] Wunderlich B, Moller M, Grebowicz J, Baur H. Adv Polym Sci 1988;87:1.
[16] Menescal R, Eveland J, West R, Leites LL, Bukalov SS, Yadritseva TD, Blazso M. Macromolecules 1994;27:5885.
[17] Yoon Y, Ho RM, Moon B, Cheng SZD, et al. Macromolecules 1996;29:3421.
[18] Ungar G, Zhou J-P, Percec V, Chu P. Macromol Symp 1995;98:951.
[19] Ungar G, Feijoo JL, Percec V, Yourd R. Macromolecules 1991;24:953.