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## RESEARCH ARTICLES

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### SYNTHESIS, CHARACTERIZATION, AND STRUCTURAL INVESTIGATION OF POLY(DIETHYLSILYLENE)

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(Received July 9, 1993)

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#### ABSTRACT

*Poly(diethylsilylene) was synthesized by dechlorination of diethyldi-chlorosilane with 40% sodium dispersed in mineral oil. Toluene was employed as a solvent. The polymer was characterized by FT-IR and NMR spectroscopies. Preliminary investigation of its structure was studied by GPC, DSC, X-Ray diffractions, and UV spectroscopy. The yield and molecular weights were found to depend on the reaction condition. The polymer was also found to be highly crystalline, and the higher molecular weight one gave the higher order-disorder transition temperature and the higher wavelength number of UV absorption maximum. The highest molecular weight one was insoluble in any kind of solvents.*

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#### INTRODUCTION

A new class of polymers with a backbone of silicon atoms bonded to various organic substituents, is undergoing rapidly. The reason is that they display many kinds of attractive properties, such as, the electronic conductivity, nonlinear optical property, etc. Especially, the symmetrically substituted ones have gained importance in the last few years due to their unusually interesting properties, such as  $\sigma$  - conjugation, thermochromic and piezochromic transitions, and a variety of potential applications, for examples, photoconductors and photoresists<sup>1-4</sup>. The earliest and most intensively studied member of this class has been the poly(dihexylsilylene) (PDHS), which has been investigated by UV, IR, NMR, and Raman spectroscopy<sup>5-10</sup>, by X-Ray and Electron diffraction<sup>5,11</sup>, thermal properties<sup>12</sup>, and emission properties<sup>13</sup>.

The structure of polysilylenes with shorter side chains has been found to be more complex. Under ambient conditions, the poly(dipentylsilylene) (PDPS) and poly(dibutylsilylene) (PDBS)<sup>14-15</sup> members were found to adopt a 7/3 helical rather than a trans conformation in the solid state. One study reported that a helical structure should be energetically preferred for the isolated molecule of poly(dialkylsilylenes) and that a critical

side-chain length of six carbon atoms or more was needed to force the Si backbone from such a helical conformation into the all trans<sup>16</sup>. However, Zeigler et.al<sup>17</sup> reported that the conformation of both poly(diethylsilylene) (PDES) and poly(dipropylsilylene) (PDPrS) was not helical, but all trans. They also found that only small, statistical deviations from exact trans planarity were also present. Recently, Welsh *et al.*<sup>18</sup> studied the molecular mechanics of PDES and found that an off-trans (160°) backbone structure was optimal in this polymer. Also a chair-like conformation for side-chain dihedral angles was preferred.

In this work, the synthesis and characterization of PDES were under taken, with particular emphasis on synthesizing a variety of different molecular weights. Preliminary investigation of their structures by use of GPC, UV, FT-IR, NMR, DSC, and X-Ray diffraction techniques were also studied.

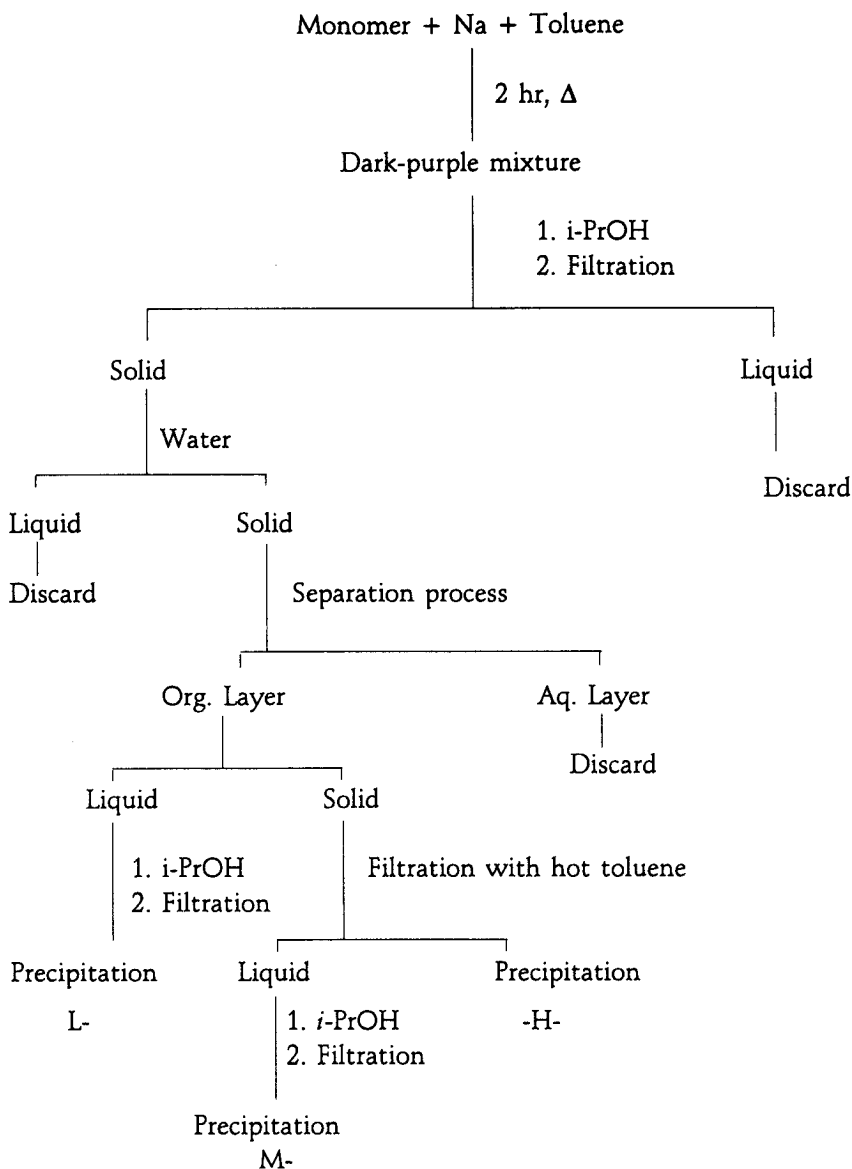
## EXPERIMENTAL

All reaction glasswares were dried in an oven at least for one day before running a reaction. All reactions including purifications of monomer and reaction solvent were performed under a dry nitrogen atmosphere throughout the reaction period.

**Chemicals:** Monomer, namely, diethyldichlorosilane (Petrarch System) was freshly distilled prior to use. 40% Sodium dispersed in mineral oil (Aldrich) and isopropanol were used as received. Toluene, as a reaction solvent, was distilled subsequently from calcium hydride (Aldrich) and stored over molecular sieve.

**Measurements:** FT-IR spectra of in KBr pellets were recorded on a PERKIN ELMER-1720-X spectrometer. All UV/VIS spectra, including variable temperature absorption spectra, were recorded on a JASCO-Ubest-55 spectrophotometer in cast films. The NMR spectra were recorded on a JEOL-270 NMR Spectrometer in deuterated benzene at the temperature of 40 C. DSC measurements of the polymers were performed on a PERKIN-ELMER-DSC-7 instrument at scanning rate of 10 C min<sup>-1</sup> under a N<sub>2</sub> atmosphere. The GPC results were obtained using a Waters 150-C ALC/GPC system at a toluene flow rate of 1 ml min<sup>-1</sup>. The system was equipped with an Ultrastyrigel-Linear 7 μm column with the length of 7.8x300 mm for determinations of polymers with wide range of molecular weights. Column and Injector temperatures were maximized at 70 C. Known polystyrene standards were used for calibration. X-Ray diffraction curves and photographs were examined on a PW-1700 X-Ray diffractometer and on a RIGAKU-Geigerflex X-Ray Diffractometer, respectively, by using Ni-filtered CuK<sub>α</sub> radiation. High temperature X-Ray diffraction curves were recorded by using the Position Sensitive Proportional Counter.

**Synthesis:** Different molecular weight PDES were prepared by means of a Wurtz-type condensation with a modified purification developed in this work, as described as the following flow chart;



**RESULTS AND DISCUSSION**

**Synthesis:** In general, Wurtz method runs at elevated temperature in an inert solvent using molten sodium dispersed in mineral oil. This reaction is usually highly exothermic and can initiate suddenly. To prevent such an unforeseeable accident, the preparation of PDES was conducted at room temperature while the monomer was added into the molten sodium mixture. The reaction of the monomer with dispersed sodium was very slow at room temperature, but quickened abruptly at the refluxing temperature. As the reaction

progressed, polymers and by product, sodium chloride, separated as dark purple solids.

The total yield of PDES, as shown in Table 1, depended upon the reaction condition. The maximum yield was achieved after 2 hr of boiling under reflux and overnight of room temperature stirring. The average yield was 13%. However, if the reaction was allowed to undergo at refluxing temperature for 2 hr and worked-up right afterward, the total yield would be lower than the average, 6.6%, as can be seen at the entry No.3. The reported yields were also affected by purification process which would also extract the low molecular weight oligomers. As is well known, the Wurtz method always results in high yield of oligomers instead of the required high molecular weight polymers.

**Table 1.** Effect of Reaction Duration on Yields.

No.	Yield(%)			Rxn Condition	
	L	M	H	2 hr refluxing Temp.	Overnight room Temp.
1.	1.9	3.4	8.5	Yes	Yes
2.		4.5	8.3	Yes	Yes
3.	1.5	1.6	3.5	Yes	No
4.	1.4	3.2	8.3	Yes	Yes

**Solubility:** As can be seen in Table 1, there are three types of PDES, namely, L, M, and H-PDES. H is insoluble in any solvents, such as, toluene, xylene, THF, decane, tetradecane, etc. Whereas L and M are soluble in toluene at elevated temperatures, about 40° and 90° C, respectively. On the basis of DSC and UV spectroscopy results, to be described in later sections, L, M, and H are the PDES that have the lowest, middle, and highest molecular weights, respectively.

**GPC:** Because the high temperature was required to dissolve all soluble PDES, the molecular weight determination of M-PDES was not successful. However, the molecular weight result of L-PDES was approximately 14,000.

**NMR Spectra:** The assignments of <sup>1</sup>H- and <sup>13</sup>C-NMR spectra of L-PDES are listed in Table 2. These data were interpreted according to the data produced by both Miller *et al.*<sup>19</sup> and West *et al.*<sup>20</sup>.

**Table 2.**  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR Chemical Shifts of the L-PDES.

$^1\text{H}$ , ppm	$^{13}\text{C}$ , ppm	Assignment
1.35(b)*	11.29	$\text{CH}_3$
	6.74	$\text{CH}_2\text{-Si}$

\* (b) broad

**FT-IR-Spectra:** The structural assignments are given in Table 3, which shows characteristic absorptions in the regions corresponding to  $\text{Si-CH}_2\text{CH}_3$ , was consistent with those reported for the polymer named poly(ethyl-methylsilylene)<sup>21</sup>.

**Table 3.** Infrared Absorptions and Structural Assignments of PDES.

Absorption ( $\text{cm}^{-1}$ )	Assignments
(3468)	( $\text{H}_2\text{O}$ stretch)
2953	CH stretch
2873	
2726	
2077	Si-H stretch
(1630)	( $\text{H}_2\text{O}$ overtone)
1452	$\text{CH}_3\text{-(C)}$ deformation (a)*
1424	$\text{CH}_3\text{CH}_2\text{(Si)}$ deformation (a)*
1377	$\text{CH}_3\text{-(C)}$ deformation (s)*
1229	$\text{CH}_3\text{CH}_2\text{(Si)}$ deformation (s)*
1020	$\text{SiCH}_2\text{CH}_3$
1000	
945	
661	EtEtSi rocking
594	

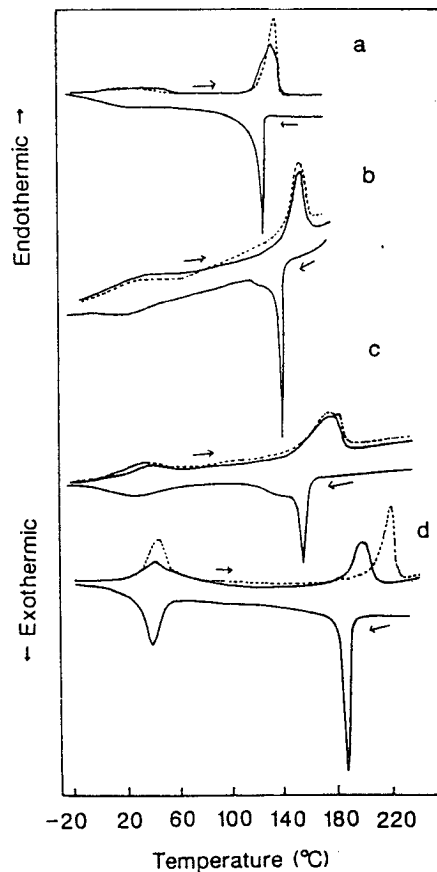
\* (a) : asymmetry

(s) : symmetry

**DSC Thermograms:** Thermal analyses of PDES were made by the DSC method in the temperature range of  $-20^{\circ}$  to  $250^{\circ}$  C. The DSC thermograms of L, M, and H-PDES, as illustrated in Figure 1 (The corresponding temperatures and heat capacities are listed in Table 4), showed one major (peak 1) and one minor (peak 2) endotherms. The peak temperature of the major one, which is the order-disorder transition, increased as the solubility decreased, and the heats of the transition were in between  $27\sim 35$  J/g for the second run, which was a little larger for H. It can reasonably be said that the transition temperature increased as the molecular weight increased. As mentioned previously, L, M, and H-PDES are in fact the lowest, middle, and highest molecular weights of PDES, respectively.

It is interesting that the peak 2 was observed at almost the same temperature for all types of PDES, although it was a little lowered in the second runs. The difference is only their heat. The endotherm results gave higher values as the molecular weight increased, especially for the second run of H, in which the temperature and the height of peak 1 also increased. This result indicates that the crystallinity was considerably improved after the first runs, and the heat of peak 2 increased with increasing crystallinity, as well. This can be implied to the heat-pressed film of H, since the result was similar to that of the second run for H powder in Fig. 1.

**Fig.1.** DSC Thermograms of PDES Powder;  
(a) L, (b) M-1, (c) M-2, (d) H ( ..... were first runs, - - - - were second runs after quickly cooling to  $-20^{\circ}$ C)



**Table 4.** Endotherms of PDES.

Sample	Peak 2		Peak 1	
	Temp.(°C)	Heat (J/g)	Temp.(°C)	Heat (J/g)
L Powder	-36	-7.3	133.2	27.5
M-1 Powder	-38	-8.2	155.2	28.9
M-2 Powder	41.0	10.0	177.6	31.3
M-2 Powder	44.2	14.9	200.8	25.7
H Pressed Film	42.7	18.7	221.4	35.3

The cooling curves measured after the second runs also had correspondingly two exothermic peaks. The temperature differences between the endothermic and exothermic peaks for peak 1 increased as the molecular weight increased, but were very small for peak 2. The main effect of molecular weight on the order-disorder and the reverse transitions should be considered that superheating and supercooling increased as the molecular weight increased.

**X-Ray Diffraction Curves:** The diffraction curves (reflection mode) of PDES are seen in Figure 2. They strongly indicated that the polymers were highly crystalline. The curves of PDES are almost exactly the same as reported in ref.17. However, it should be noted that there is somewhat difference at the diffraction angle of around  $26^\circ$  ( $2\theta$ ) region. The peaks in ref.17 showed broader, amorphous-like background. The fact that the polymer in this work has higher crystallinity, since the reflection at the mentioned region increased significantly in intensity, as the molecular weight increased. According to the paper 17, the crystalline structure of PDES is a rectangular lattice containing two chains ( $a=1.108$  nm,  $b=1.210$ ).

**Fig. 2.** X-Ray Diffraction Curves of PDES. (A) M, (B) H, and (C) PDES reported in ref. 17.

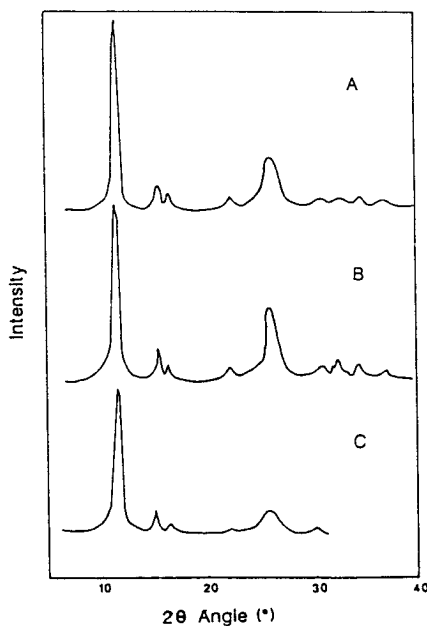
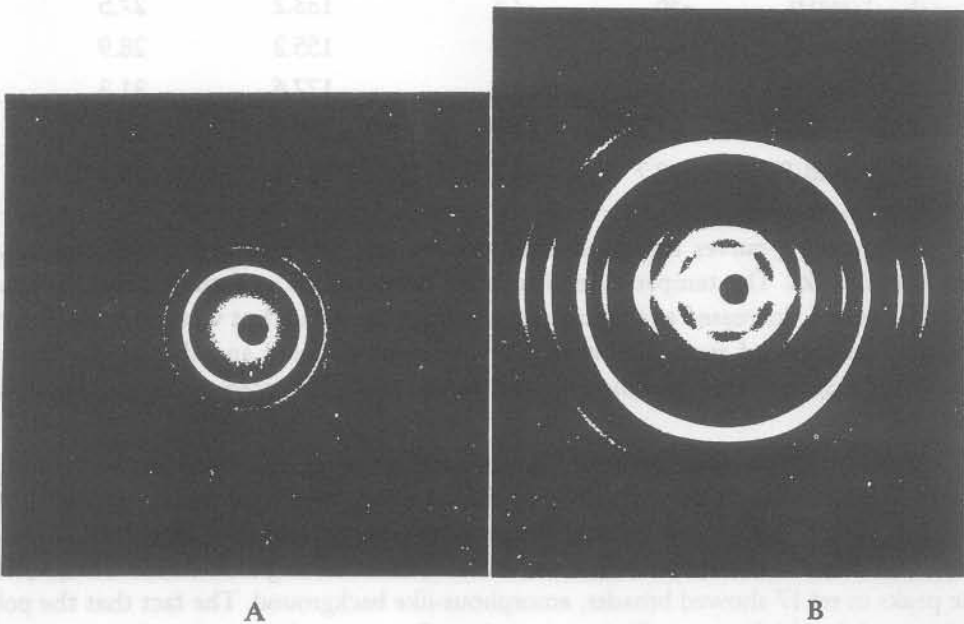


Figure 3 shows the diffraction patterns of M- and H-PDES. The patterns also provided consistent results. The cast film for M-PDES was very crumbly and had no orientation, whereas the heat-pressed film of H showed a high uniaxial orientation. The molecular chains for H were easily oriented by the heat press because of its high molecular weight. The X-ray diffraction pattern was not affected by the heat treatment.



**Fig. 3.** X-Ray Diffraction Patterns taken with perpendicular beam to the film surface. (A) film of M, casted from a hot toluene solution on a hot substrate, (B) film of H, heat-pressed at 230°C under 200 kg.cm<sup>2</sup> for 5 min. The orientation of polymer chains was almost in the direction of vertical axis of the photograph.

The photograph was calibrated by dusting the specimens with aluminium powder, which gives a diffraction ring at a d-spacing of 2.3379 Å. The relative distances (d-spacings), and diffraction angles are listed in Table 5.

Figure 4 shows the high temperature X-Ray diffraction curves of the highest molecular weight PDES. The peak around 11° (2θ) gradually shifted to lower angle, with intensity, becoming sharp at 220°C. The peak around 26° (2θ) slowly became broader (and probably splitted) as the temperature got higher, and finally was disappeared at the temperature of 220°C. This indicated that the ordered phase changed to disordered phase at 220°C for H. It was estimated from these results that a crystal-crystal transition occurred in the temperature region of peak 2 in the DSC curves.

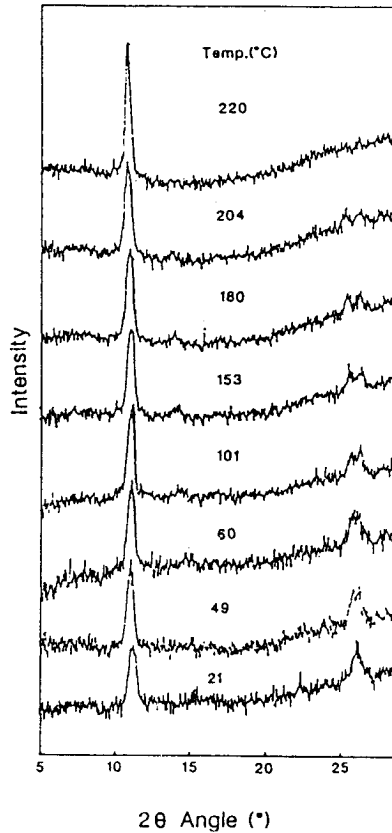


**Table 5.** X-Ray Diffraction Values for PDES.

M		H*	
2θ (°)	d(A)	2θ (°)	d(A)
10.8	8.15	10.8	8.15
14.8	5.97	14.9	5.94
16.0	5.53	15.9	5.56
21.5	4.07	21.5	4.14
25.7	3.46	25.3	3.52
30.1	2.96	30.2	2.95
-	-	31.7	2.82
33.9	2.64	33.8	2.65
36.7	2.44	36.3	2.47

\* Heat Pressed

**Fig. 4.** X-Ray Diffraction Curves of the second run for the H - PDES powder recorded at the indicated temperatures during heating from 20-220°C.



**UV/VIS Spectra:** As far as the UV/VIS absorbance concerns, polysilanes display an intense UV absorption bands and its absorptivity per Si-Si bond increases regularly with increasing chain length. As can be seen in Table 6, at ambient temperature, the H-PDES appeared at the highest wavelengths (nm). This may be because of their disorderly conformational structures. The higher molecular weight one resulted in the less disorderly conformational structure.

**Table 6.** Solid State UV Absorption Values of PDES.

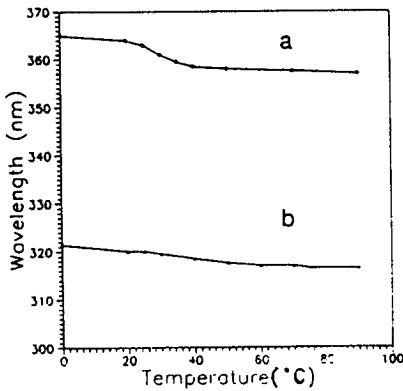
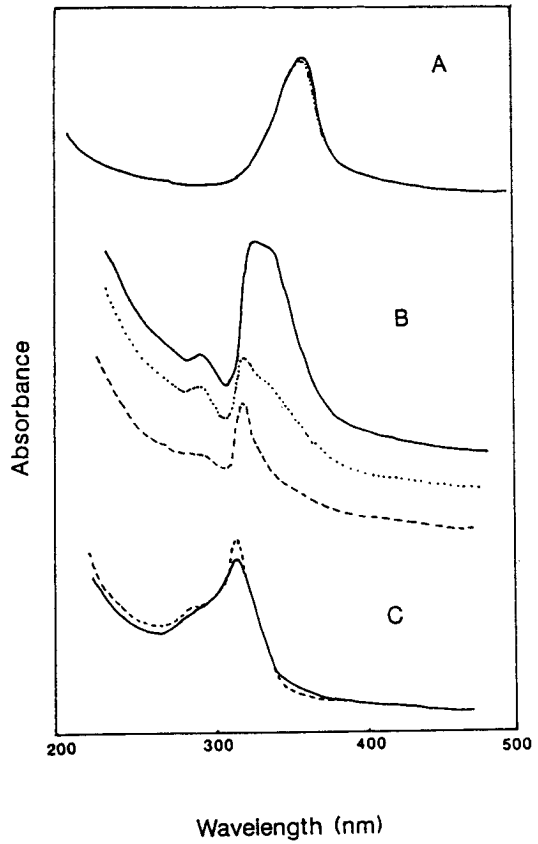
Polymer	Wavelength (nm)
PDES	
L	315
M-1	320-340
M-2	346
H	363

The solid state UV spectra of PDES films subjected to heat treatment at various temperatures are summarized in Figure 5. The UV absorption peaks of PDES remained at almost the same wavelengths after heat treatment at the order-disorder transition region for H and L. However, the broad peak of M became sharp at the lower wavelength of the peak.

Figure 6 shows the changes in the wavelengths of UV absorption with temperatures during heating and cooling. The wavelength decreased a little with increasing temperatures in the range of 20-50° C for H. This change, however, was very small for M, whose film was previously heat-treated at 170° C. The small change in the UV absorption at 20°-50° C suggested a very small conformational change in the backbone, which was caused by the structural change in the side chains. The effect of the molecular weight on UV spectra might be related to the structural properties that PDES has, the trans conformation with a small, statistical deviations from exact trans planarity, as mentioned in ref.17.

**Fig. 5.** Effect of Heat Treatment on Solid State UV Absorption Spectra of PDES; (A) H\*, (B) M, and (C) L (— is for ambient temp., --- is for 150 C, ... is for 140 C, and -.-.- is for 220 C)

\* measured at the indicated temp., whereas others were measured at ambient temp. after being treatment.



**Fig.6.** Effect of Temperatures on the UV Absorption, (a) H, (b) M, (heat- treated at 170°C)

## CONCLUSION

Poly(diethylsilylene) has been synthesized and characterized. According to the results of DSC and UV spectra, the syntheses resulted in different types of polymers in term of molecular weights, depending upon the reaction conditions. It was found that the UV absorption and the transition behavior greatly depended upon the molecular weight. The higher molecular weight polymer absorbed the higher wavelength in its UV spectra, gave higher order-disorder transition temperature in DSC, and showed higher crystalline in X-Ray diffraction. There was also a small structural change around 20-50° C, which was related to the crystallinity of films, and could be crystal-crystal transition. Effect of the heat treatment on the structure was not observed by X-Ray diffraction, but a little complicated in the UV absorption.

## ACKNOWLEDGEMENTS

This work was supported by the Japan International Corporation Agency (JICA). The authors would like to express their sincere thanks to the National Institute of Material and Chemicals Research (NIMC), especially Dr. K. Ueno's group for making this project come true. The authors are also thankful to Dr. N. Tanigaki for helping in running GPC and NMR.

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### บทคัดย่อ

การสังเคราะห์สารโพลิเมอร์โพลีไดเอทิลไซลิซีน สามารถทำได้ด้วยปฏิกิริยาของการดึงอะตอมคลอรีน ออกจากสารโมโนเมอร์ไดเอทิลไดคลอโรไซเลน ด้วยโลหะโซเดียม ในตัวทำละลายโทลูอีน โครงสร้างของผลิตภัณฑ์ที่สังเคราะห์ได้ ตรวจสอบโดยใช้วิธีสเปกโตรสโคปีชนิด FT-IR และ NMR คุณสมบัติอื่นๆ ของผลิตภัณฑ์ ได้แก่ น้ำหนักโมเลกุล ปริมาณความร้อนที่ใช้ในการหลอมละลาย และลักษณะการเรียงตัวของอะตอมในโมเลกุล ได้ทำการศึกษาโดยใช้ GPC DSC และ X-Ray Diffraction ตามลำดับ ผลการทดลองและการศึกษาพบว่า ปริมาณและน้ำหนักโมเลกุลของผลิตภัณฑ์ที่สังเคราะห์ได้ ขึ้นอยู่กับสภาวะของปฏิกิริยาที่ใช้ในการทำการทดลอง และผลิตภัณฑ์ที่มีน้ำหนักโมเลกุลสูงมากขึ้น คุณสมบัติของความเป็นผลึก อุณหภูมิที่ใช้ในการเปลี่ยนแปลงการเรียงตัวของอะตอมในโมเลกุล และการดูดแสง UV ของผลิตภัณฑ์ก็มีมากขึ้น นอกจากนี้ โพลิเมอร์ที่มีน้ำหนักโมเลกุลสูงสุด จะไม่มีคุณสมบัติในการละลายในตัวทำละลายต่างๆ ที่ดี