Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Synthesis and Anisotropic Behavior of New Ladderlike Polysilsesquioxanes with Side-on and End-on Fixed NLO Chromophores

Ping Xie [a], Jing-Sung Guo [a], Dao-Rong Dai [a], Sun-Zi Jin [a], Dong-Sheng Liu [a], Ze Li [a] & Rong-Ben Zhang [a]

[a] Polymer Physics Laboratory, Institute of Chemistry, Academia Sinica, Beijing, 100080

Version of record first published: 04 Oct 2006.

To cite this article: Ping Xie , Jing-Sung Guo , Dao-Rong Dai , Sun-Zi Jin , Dong-Sheng Liu , Ze Li & Rong-Ben Zhang (1996): Synthesis and Anisotropic Behavior of New Ladderlike Polysilsesquioxanes with Side-on and End-on Fixed NLO Chromophores, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 289:1, 45-57

To link to this article: http://dx.doi.org/10.1080/10587259608042311

Mol. Cryst. Liq. Cryst., 1996, Vol. 289, pp. 45–57
Reprints available directly from the publisher
Photocopying permitted by license only

Synthesis and Anisotropic Behavior of New Ladderlike Polysilsesquioxanes with Side-on and End-on Fixed NLO Chromophores†

PING XIE, JING-SUNG GUO, DAO-RONG DAI, SUN-ZI JIN, DONG-SHENG LIU, ZE LI and RONG-BEN ZHANG*

Polymer Physics Laboratory, Institute of Chemistry, Academia Sinica, Beijing 100080

(Received 31 May 1994; In final form 4 December 1995)

This report deals with a new kind of ladderlike polysilsesquioxanes with nonlinear optical (NLO) chromophores which are laterally (side-on) or terminally (end-on) fixed on the ladderlike macromolecular backbones. These new functionalized ladderlike polysiloxanes were synthesized via hydrosilylation reaction of a series of diphenyl acetylene (tolan) derivatives (for side-on fixed) or vinyl-terminated diphenylethylene (stilbene) derivatives (for end-on fixed) with ladderlike polyhydrosilsesquioxane [H-T] or its copolymers [PH-T]. The anisotropic behavior of the mesogenic polymers were studied by IR dichroism, temperature-variable X-ray diffraction and optical polarized microscopy. The "Rowboat model" for side-on fixed liquid crystalline polysilsesquioxane was confirmed by IR dichroism and X-ray diffraction observations.

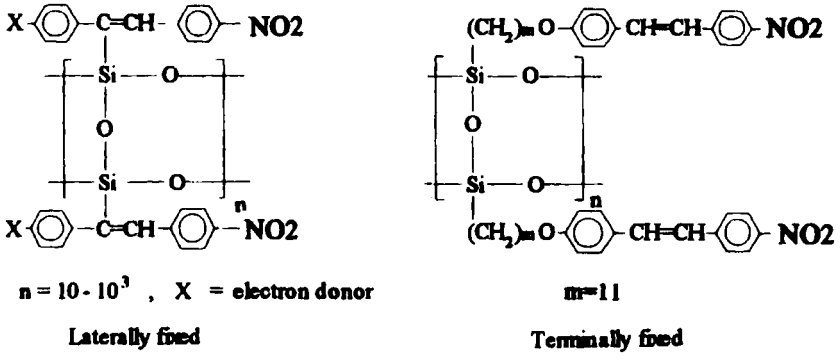
Keywords: Polysilsesquioxanes; NLO chromophores; anisotropic behavior; rowboat model

INTRODUCTION

As previously reported by Zhang *et al.*, a new kind of reactive polymers, [H-T] and [PH-T] with highly regular ladderlike structure have been synthesized by "stepwise coupling polymerization" [1]. Then a series of so-called "fishbone- like" liquid crystalline polymers(FBLCP's) [2, 3] have been

†The project was supported by NSFC.

synthesized by grafting a series of vinyl-terminal mesogenic side chains into the ladderlike backbone. This paper concerns a new kind of low-decay nonlinear optical polymer composed of ladderlike polysiloxane as backbone and stilbene-type NLO chromophores which are laterally or terminally fixed on it, respectively. Their structures are shown as follows.



Previously, Hessel and Finkelmann [4] and Zhou *et al.* [5] have studied on the polyacrylates with laterally fixed mesogenic group; Keller' [6] and Gray [7] *et al.*, have also studied polysiloxanes having laterally or terminally fixed mesogenic side chains involving a long flexible spacer. In most cases their mesomorphic behaviour was similar to that of common comblike LCP, but in general the directly connected mesogenic groups (without flexible spacer) would result in regidization of the polyethylene main chain, and to some extent their liquid crystalline behaviour was similar to that of main chain liquid crystalline polymer. Several molecular models have been proposed to describe the anisotropic configuration of these LCP molecules in different fixing types [7].

Several well-ordered polysilsesquioxanes and its copolymers containing different side groups (such as H, Me, Ph) synthesized previously [1, 9, 10] are soluble polymers, from which a transparent solid film with good mechanical properties and high laser damage-thereshold can be formed. Chromophore laterally or terminally fixed on the ladderlike macromolecular backbone result in a novel kind of NLO polymer with peculiar anisotropic behaviour which was characterized using optical polarised microscopy, infrared dichroism, variable-temperature X-ray diffraction and DSC techniques.

EXPERIMENTAL

A. Synthesis and Characterization of Parent Polymers–[H-T] and [PH-T]

The more detailed synthesis procedure of [H-T] can be refereed to the privious report [1].

A-1. [H-T]

A solution of 25 ml of dried acetone containing 2.7 g (0.025 mol) of 1,4-phenylenediamine (PDA) was added dropwise into a solution of 15 ml of toluene dissolved containing 3.4 g (0.025 mol) of trichlorosilane (TCS) on vigorously stirring at $-15 \sim -5°C$ and then the system was kept stirring for 30 minutes. A solution of 10 ml of acetone and 0.9 ml of water was dropwise introduced into the system and stirred for 30 minutes and the system gradually turned from pink to slightly brown. Then an additional solution of 0.45 ml of water and 5 ml of acetone was added and stirred for one hour at 5°C. After that the mixture was filtered in vacuum to remove the solid amine salt and the filtrate solution was evaporated in vacuum to distil out acetone and then dried with anhydrous sodium sulphate overnight at below 0°C. Next, agitation was kept at 30°C for one day in the presence of 0.041 mg (0.00025 mmol) of hexamethyldisiloxane used as molecular weight-controlling agent and three drops of concentrated sulphuric acid as the catalyst of polycondensation and equilibration reaction. Finally, the solution was washed at least five times with a saturated aqua solution of sodium chloride to be neutral. The solution was dried with sodium sulphate again and became transparent and colourless after filtration. Its concentration was 15 mg/ml and the yield was 57%.

A-2. [PH-T] (molar ratio of $PhSiO_{3/2}$:$HSiO_{3/2}$ = 1)

A Solution of 20 ml of acetone containing 0.6 g (0.010 mol) of EDA was added dropwise into a solution of 20 ml of dried toluene dissolved with 2.12 g (0.010 mol) of phenyltrichlorosilane (PTCS) at $0 \sim 5°C$ and stirred for 30 minutes. Then another solution of 30 ml of tolune dissolved with 2.05 g (0.015 mol) of trichlorosilane (TCS) was added into the above-mentioned solution and stirred together, to which a solution of 30 ml of acetone containing 1.62 g of PDA was added at $-15 \sim -5°C$. After being stirred for 30 minutes at $-5°C$. The preaminolyzed chlorosilane solution was

hydrolysed with 1.35 ml of water dissolved in 50 ml of acetone upon stirring for 3 hours from $-10°C$ to room temperature. Same procedures adopted in A – 1 were taken to obtain a clear solution, which was subjected to condensation and equilibration reaction in the presence of 0.004 mg (0.00025 mmol) of hexamethyldisiloxane and three drops of sulphuric acid upon stirring for one day at 40°C. After being washed to neutral and dried overnight, a clear colourless solution of [PH-T] was obtained with a yield of 63% and a concentration of 30 mg/ml.

The characterization data of the [H-T] and [PH-T] are listed in Table I.

TABLE I Characterization data of parent ladderlike polysiloxanes

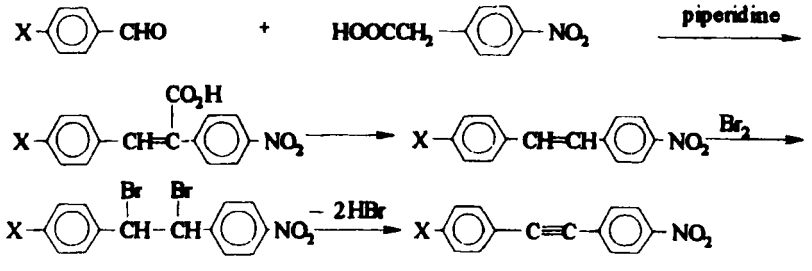
Items	*[H-T]*	*[PH-T]*
Solubility (in toluene)	soluble	soluble
Content of Si—H (%) cal./found	1.88/1.46	0.83/0.82
DSC curve from $-50 \sim 300°C$	almost horizontal	almost horizontal
Regularity by ^{29}Si-NMR*	~ 100%	90–95%
Distance (Å) / Intensity by X-ray diffraction	d_1 8.733/190 d_2 4.040/210 d_3 3.843/210	

B. Synthesis and Characterization of the Side Chain Precursors Containing NLO Chromophores and the Titled Polymers

The chromophore-containing precursors used for hydrosilylation reaction with [H-T] and [PH-T] includes two types: tolan derivatives used for laterally fixed on the backbone and vinyl terminated stilbene derivative used for teminally fixed on the backbone. The reaction scheme for synthesis of tolan precursor is shown as follows, it is referred to literature [8].

Synthetic scheme for tolane derivative:

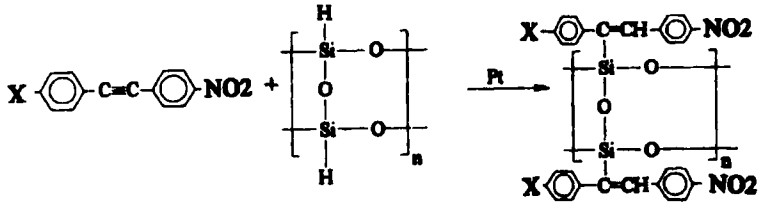
$X = Me_2N$, MeO, $C_8H_{17}O$, NH_2, H.



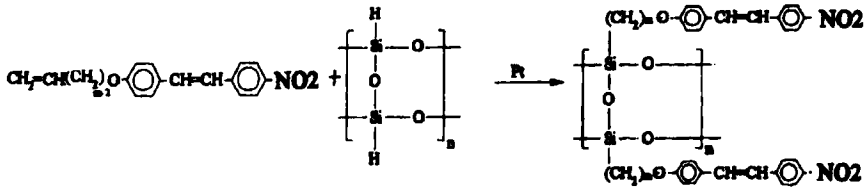
The properties of these precursors are listed in Table II.

The above mentioned NLO chromophore-containing precursors were fixed on the ladderlike main chain by well-known hydrosilylation using $H_2PtCl_6 \cdot 6H_2O$/isopropanol or Cp_2PtCl_2 as catalyst, the reaction scheme is illustrated as follows:

Side-on fixed:



End-on fixed:



The hydrosilylation reaction can be monitered by thin-layer chromatography (TLC), IR, NMR and film-forming ability. The chromophore content in the products was determined by elemental analysis.

Example Preparation of DMANT-based Rowboat-like Polymer:
Equivalent DMANT and [PH-T] (mole ratio of chromophore and Si—H on the macromolecules is 1:1) were reacted in methylthiophene-free toluene solution and argon atmosphere for more than 48 hrs at 80°C in the presence of Pt-catalyst, after that, excess cooled methanol was added in cooled solution for precipitation of product. The crude product was then redissolved in toluene and precipitated in methanol again. This process was repeated for at least three times. Purified product pre-detected by thin-layer

TABLE II Characterization data of precursors

	Sample	*MNT*	*DMANT*	*ONT*
Element	C(Cald/Fund.)	71.15/69.89	72.18/70.58	73.39/74.72
analysis	H(Cald/Fund.)	4.34/5.09	5.26/5.33	7.74/7.37
	N(Cald/Fund.)	5.53/5.33	10.53/9.89	4.28/4.03
tm(°C)		123	214	108
UVλ (nm)		350.8	402.3	354.6
solvent		benzen	Ethanol	ethanol
IR		2200(acetylene)	2214(acetylene)	2214(acetylene)
cm^{-1}		1500, 1330(NO_2)	1500,1330(NO_2)	1500,1340(NO_2)
NMR(δ)			6.7–8.3	6.9–8.2
			2.9–3.1	4, 0.9–1.8

MNT:*P*, *P*-methoxy-, nitrogen-diphenyl acetylene.
DMNAT: *P*, *P*-dimethylimine-, nitrogen-diphenyl acetylene.
ONT: *P*, *P*-Octyloxy, nitrogen-diphenyl acetylene.

chromatography was used for elemantal analysis. The results indicated that chromophore-grafted units are about 60% of total ladderlike structure units ($SiO_{3/2}$) in which the H-substituted units are about 65% based on the H-content determination by released H-gas volume measurement. Element analysis results: cald. (detd.) C: 59.26 (59.28), H: 4.53 (4.55, N: 6.91 (6.75). Almost the same value was also obtained for hydrosilylation of non-substitued tolan with [PH-T], Element analysis results: cald (detd) C: 61.00 (60.55), H: 6.10 (6.05, N: 0.00(0.00). In order to avoid hydrolysiscrosslinking of remained Si—H bonds on the macromolecules, after the hydrosilylation was finished (detected by TLC and IR), heptene used as Si—H blocking agent was added to the system to remove the residual Si—H group.

CHARACTERIZATION

Polarizing Microscopy

The sample between two glass slides was heated to exceed melting point, birefringent bright bands or spots can be observed with the crossed polarizers, and then it was subsequently quenched to room temperature. Photomicrographs were taken using Olympus polarizing microscope (type BHS-730)

Infrared Dichroism

To prepare oriented specimens for ℝ measurement, NaCl single crystal slide was used instead of glass slide, the polymer melt on the hot slide was

quickly sheared and subsequently quenched, the film thickness was about 10 μm. The absorbance of the polarized ℝ light in the shearing direction ($A_{\parallel}$) and the perpendicular direction ($A_{\perp}$) for some special bands was determined using ℙS-113V FTℝ of Bruke Company, the dichroism ratio was calculated by $R = A_{\parallel}/A_{\perp}$ [11].

Temperature-Variable X-ray Diffraction

The polymer sample was pressed into a boron-glass capillary with *d* 1.5 mm, it was tempered at above the melting point, the X-ray diffraction was made by Rigaku D/Max-RA diffractometer.

DSC measurement was performed using SR-1 DSC made by Beijing Optical Instrument Factory.

RESULTS AND DISCUSSION

The ladderlike parent polymers, H-T and PH-T, can be soluble in organic solvent, such as tolune, xylene, acetone..., but are infusible. As same as previously reported "fishbonelike" lcp's, the new class of ladderlike polysiloxanes with side-on fixed stilbene units are also thermotropic mesomorphic polymers. Another one of titled polymer with end-on fixed chromophore which has been linked with main chain by a longer spacer is also "fishbonelike" LCP. As DSC curves shown (Fig. 1), there is no any evidence of glass transition for the "fishbone-like" LCP with a long flexible spacer, and its ΔH of the mesomorphic transition is much higher, that means the solid state of the fishbonelike LCP's behaves semicrystalline; but the DSC curves of new kind of NLO polymer in which the stilbene units are directely side-on fixed on the ladderlike backbone, show a obvious glass transition and lower ΔH value of the mesomorphic transition, that suggests the solid state behaves like glassy rather than crystalline. The mesophase is stable until its decomposition. In contrast, the DSC curve of the usually single chain polysiloxane with directely side-on fixed stilbene units does not demonstrate any anisotropic transition in a wide temperature range. That indicates it is not LCP.

The mesomorphic texture of the new ladderlike polymers bearing stilbene units was similar to that of "fishbonelike" lcp's containing same ladderlike macromolecular backbone, some birefringent bright bands or spots on the dark background were observed under crossed polarizers (Fig. 2). In the

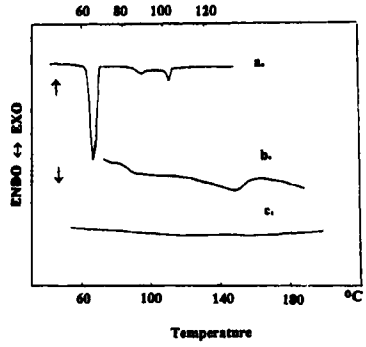


FIGURE 1 DSC curves of three kinds of polysiloxanes: a. $S-C_{11}$: b. D; C.Tolan fixed on sinle chain polysiloxane.

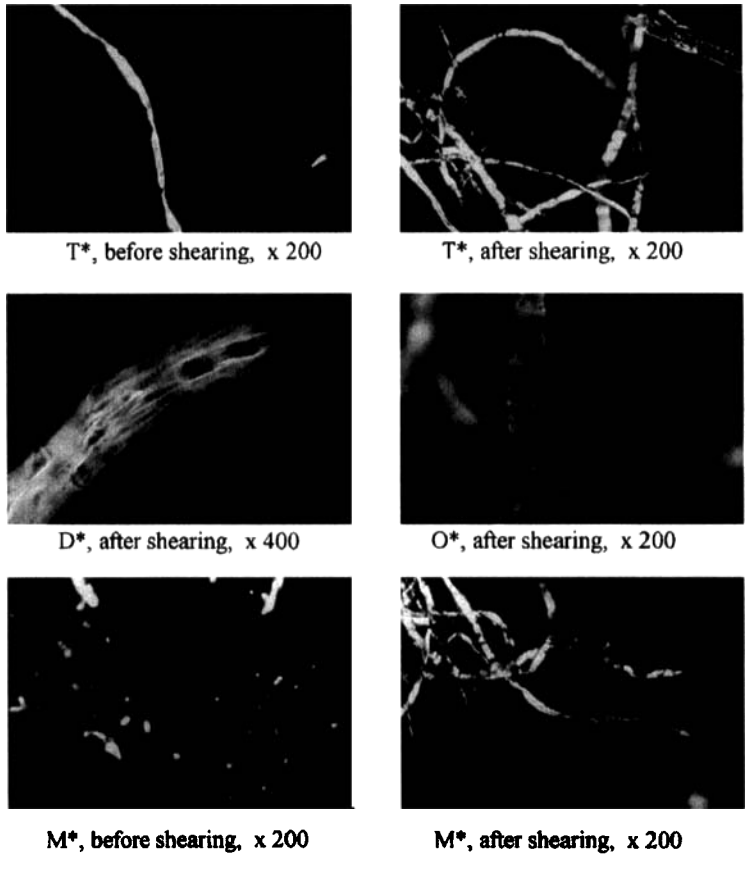


FIGURE 2 Polarized microscopic photographs.

magnifying feature of inside of light band, some parallel bands which nearly perpendicular to the axis of the light band could be observed, this phenomenon was similar to that of main chain LCP, but it was only observed in small local region even with big defect. The polysilsesquioxane main chain could be imagined as a bendable rope ladder, the alignment of the mesogens or chromophores fixed on it was constrained by the macromolecular conformation and the ladderlike polymeric main chain shows a strong tendency to aggregate together to form stable birefringent light band. However, it is very difficult dynamically to be aligned in a broad region or to take fully extended conformation. So it is hard to get favourable alignment as in normal mesophase.

Infrared dichroism was used to investigate the orientation state of the chromophores and double chain backbone, the preliminary result was illustrated in Table III and Figure 3. The ratio of the absorbance of radiation polarized in the shearing direction ($A_{\parallel}$) and in the lateral direction ($A_{\perp}$)–dichroism ratio $R(A_{\parallel}/A_{\perp})$ can be detected in the spectrum figure. The ℝ bands, 1093 or 1096 cm^{-1} were used to represent the orientation of the main chain axis. It can be assigned to the Si-O-Si stretching of the main chain as π(parallel) bands, since R is more than unity. It implies that in the oriented specimen the main chain of the macromolecules tends to orient in the shearing direction. the ℝ bands, 1598 or 1594 cm^{-1} can be assigned to the phenylring stretching as σ (vertical) bands to the specimen of ladderlike polymer with directely side-on fixed chromophores, since R is less then unity. This result indicated that the axis of side-on fixed chromophore tended to be perpendicular to the macromolecular back-

TABLE III Band assignments and dichroism mode of shearing samples

Sample	*Band(cm^{-1})*	*Dichroism mode*	*Tentative assignment*
T	1598	σ	Pheny ring stretching
	1096	π	Si—O—Si stretching
	1030	σ	phenyl in-plane bending
	773	σ	phenyl out-of plane bending
	700	σ	phenyl out-of plane bending
D	1594	σ	Phenyl ring stretching
	1093	π	Si—O—Si stretching
	755	σ	phenyl out-of plane bending
	700	σ	phenyl out-of plane bending
S—C_{11}	1603	π	Phenyl ring stretching
	1580	π	Pheny ring stretching
	1150	π	Si—O—Si stretching
	730	π	phenyl out-of plane bending

T: Tolen-side-on fixed on [H-T].
D: DMANT-side-on-fixed on [H-T].
S-C_{11}: p-Nitrogen-stilbene-end on fixed on [H-T] by longer spacer (hendecane).

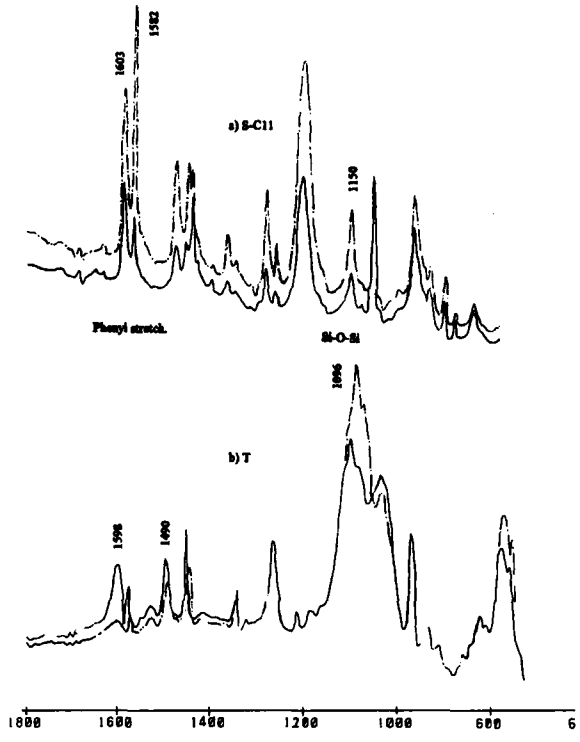


FIGURE 3 ℝ dichroism spectra of melting-sheared polymers.

bone (b). Compared with this, the mesogenic side chains which were end-on fixed on the backbone via longer flexible spacer tended to be parallel to the macromolecular backbone, since the ℝ bands, 1582 and 1603 cm^{-1} asssigned to the phenyl ring stretching are π bands (a).

Different molecular models as shown in Figure 4 have been proposed for the polymers containing laterally or terminally fixed mesogenic side chains, they were related to the fixing types and the length of flexible spacer. Zou proposed a mesogen-jacketed model for the SCLCP with mesogens laterally fixed to the polyacrylate main chain, and Xu proved that the mesogens tended to be perpendicular to the backbone [12]. Wang and Warner proposed oblate NI, prolate NIII for the SCLCP with end-on fixing mesognes [13, 14]. Prolate NII and NIII represented oriented molecular conformation induced by an external field, they were related to the length of flexible spacers. Based on our results of characterization, it is reasonable to propose a "Rowboat" model for the ladderlike polysiloxane with laterally fixed chromo-

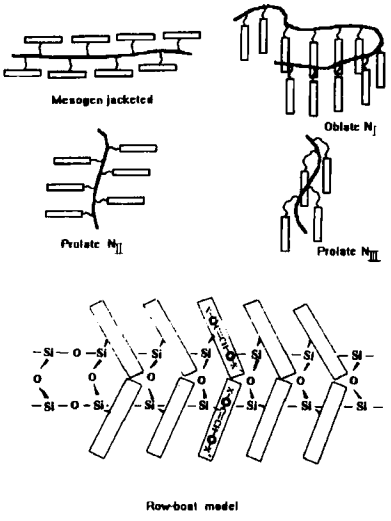


FIGURE 4 Several possible models for SCLCP's conformation of different fixing types.

phores. The Si—O double chains of the backbone could be taken as the boat sides, and the side-on fixed chromophores could be imagined as the oars, they tended to be perpendicular with the body of boat, especially when the length of the oar was much longer than the distance between "sailors". When mesogenic side chains were connected with the double chain backbone with longer spacer, the situation would be similar to prolate NIII. Infrared dichroism measurements supported above-mentioned model representation.

Temperature-variable X-ray diffraction, which was performed above the mesomorphic transition temperature of the samples, has shown a wide peak presented at $2\theta \sim 22°$ and one or two sharp peaks in small angle region ($2\theta \sim 3$–$7°$) (Fig. 5), which proved the existence of the layer structure with long range order. The distance between the layers: d_1, d_2 was calculated from 2θ to compare with the chromophore length L as shown in Table IV. It was found that in most cases d_1 was between L and $2L$, and d_2 was near to or smallar than L.

The determination of orientation parameter ϕ by UV absorbance measurement demonstrated that the poled film prepared form ladderlike polysiloxanes with directly side-on fixed chromophores by "in situ poling/crosslinking (in sol-gel process)" exhibited low decay SHG nonlinear optical property [15].

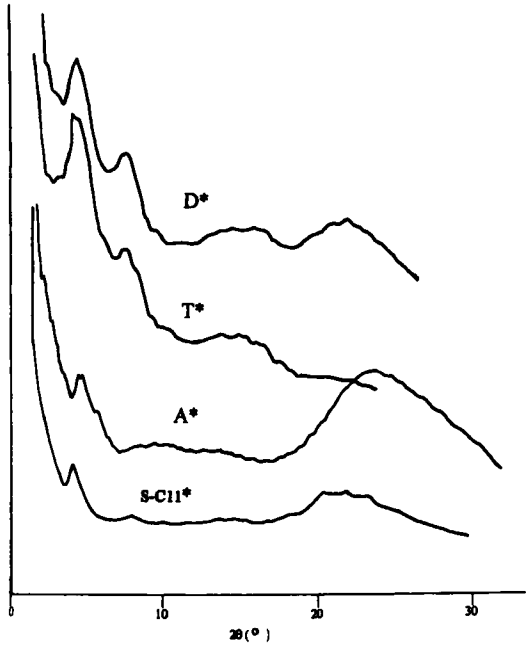


FIGURE 5 X-ray diffraction figures of the melted mesomorphic ladderlike polymers.

TABLE IV Comparison of layer distance d and mesogen length L*

Sample	*Meas. temp. (°C)*	d_1(Å)	d_2(Å)	L(Å)
T	120	20.3	11.6	9.61
D	210	22.1	12.6	14.73
S—C_{11}	150	21.03		

*Layer distance is calculated based on 2θ Value of X-ray diffraction peaks in small angle region, mesogen length is calculated from bond length and angle.

CONCLUSION

A novel ladderlike polysiloxanes with laterally or terminally fixed NLO chromophores–stilbene derivatives have shown peculiar anisotropic behavior. Infrared dichroism and temperature-variable X-ray diffraction measurements supported the "rowboat" model.

Acknowledgements

The authors express thanks to Prof. Dy. Shen & Beijing Zhong Guan Cun Associated Center for analysis and measurement.

References

[1] Zs. Xie, Sz. Jin, Yz. Wan and Rb. Zhang, *Chinese J. Polym. Sci.*, **10**(4), 361 (1992).
[2] Rb. Zhang, Zs. Xie, Yz. Wan, Sz. Jin and Ja. Hou, *Chinese J. Polym. Sci.*, **11**(3), 210 (1993).
[3] P. Xie, Rb. Zhang, Yz. Wan, Bs. Zhou, Dr. Dai, Z. Li and Ds. Liu, *Chem. & Phys.*, **197**, 745 (1996).
[4] V. Hessel and H. Finkelmann, *Polym.Bull.*, **14**, 3751 (1985).
[5] Q. Zhou, Hm. Li and Xd. Feng, *Macromolecules*, **20**(1), 233 (1987).
[6] P. Keller, F. Hardouin, M. Mauzac and M. F. Achard, *Mol. Cryst. Liq. Cryst.*, **155** (Pt.B) 171 (1988).
[7] G. W. Gray, Js. Hill and D. Lacey, *Mol. Cryst. Liq. Cryst.*, **197**, 43 (1991).
[8] T. M. Leslie, *US Pat.* 4,801,659; 4,807, 968.
[9] Zs. Xie, Zq. He, Dr. Dai and Rb. Zhang, *Chinese J. Polym. Sci.*, **7**(2), 183 (1989).
[10] Zs. Xie, Zq. He, Dr. Dai and Rb. Zhang, *Chinese J. Polym. Sci.*, **9**(3), 266 (1991).
[11] H. W. Siesler, "*Infrared and Raman Spectroscopy of Polymer*", (Marcel Dekker Inc., N.Y., 1980).
[12] Gz. Xu, W. Wu, Dy. Shen, Ja. Hou, Sf. Zhang, M. Xu and Qf. Zhou, *Polymer*, **34**(9), 1818 (1993).
[13] X. J. Wang and M. Warner, *J. Phys.*, **A20**, 713 (1987).
[14] M. Warner, "*Side Chain Liquid Crystal Polymers*", C. B. McArdle. Blackie, Ed., (Glasgow and London, 1989), Ch. 2.
[15] P. Xie, Js. Guo, Dr. Dai, Sz. Jin, Ds. Liu, Z. Li and Rb. Zhang, *Polym. Adv. Tech.*, **7**, 98 (1996).