

SYNTHESIS AND PROPERTIES OF LIQUID CRYSTAL POLYSILOXANES WITH MESOGENIC STILBENE SIDE GROUPS*

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Abstract A variety of mesomorphic side-chain polysiloxanes were synthesized by using hydrosilylation reaction with dicyclopentadienylplatinum(II) (DPPC) as the catalyst. The mesogenic groups are derivatives of stilbene with cyano or nitro tail groups. The products were characterized by DSC, X-ray diffraction and polarizing optical microscopy (POM). All the polymers were found to have relatively low T_g and can form a smectic liquid crystal phase.

Keywords Liquid crystal polymer, Polysiloxane

INTRODUCTION

Polysiloxane is often selected as backbone for side chain liquid crystal polymers because of its high chain flexibility and low glass transition temperature. When mesogenic groups are attached to the polysiloxane main chain, the flexible backbone will have less negative effect on the orientation of the mesogens, and the low T_g will permit the liquid crystal phase to form at a relatively low temperature^[1, 2]. We are interested in the synthesis of liquid crystalline polymers with high birefringence at relatively low temperature for certain potential applications. It is known that high anisotropy of molecular polarizability will lead to a high birefringence index^[3, 4]. In this study we select stilbene derivatives with a strong electron-withdrawing group at one end as the mesogenic group to constitute the side chain liquid crystal polymers because the stilbene structure is highly conjugated, and thus has high polarizability.

EXPERIMENTAL

Materials and Equipment

Poly(methylsiloxane), dicyclopentadiene and $H_2PtCl_6 \cdot 6H_2O$ were purchased from the Aldrich Chemical Co.. Dichlorodimethylsilane and chlorodimethylsilane were obtained from Acros. All other chemicals and reagents were from chemical companies of Beijing. Toluene was refluxed with CaH_2 and sodium before use.

^1H -NMR spectra were recorded with a Bruker ARX400 Spectrometer by using $CDCl_3$ as the solvent and TMS as the internal standard. DSC measurements were performed with a Perkin-Elmer series 7 instrument. IR data were recorded on a 5mx-S spectrometer. X-ray diffraction patterns were recorded with a Rigaku Dmax-2400, and the molecular weight was determined by GPC with a Waters 201 instrument. Mesophases were observed under a Leitz Laborlux polarizing optical microscope with a Leitz 350 hot stage.

Synthetic Procedure

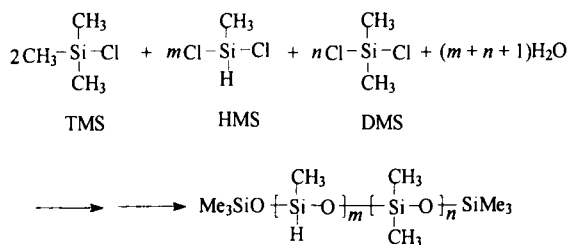
We selected two kinds of polysiloxanes as the main chain (see Scheme 1). That with $n = 0$ (see Scheme 1) was

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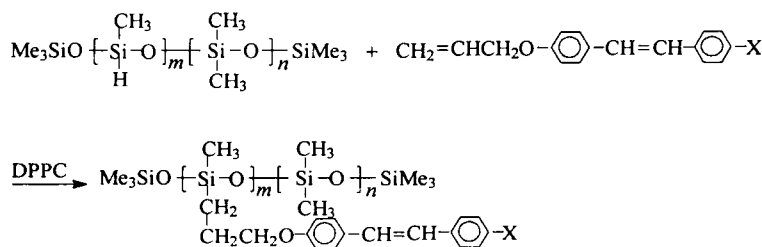
purchased from Aldrich Chemical Co. and the other with $m:n = 3:4$ was synthesized according to Scheme 1.



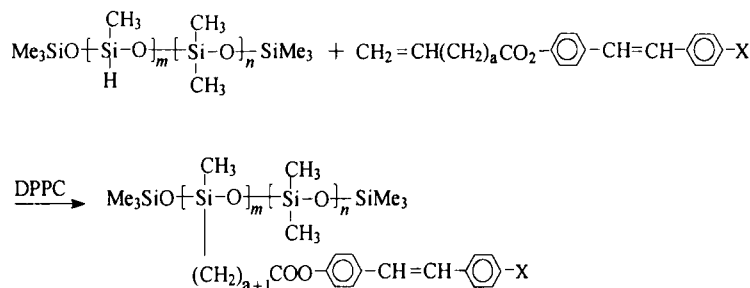
Scheme 1 Synthesis of poly(methylsiloxane) and copolymers

Synthesis of Poly(methylsiloxane)^[5]

Toluene (10 g) and water (18 mL) were vigorously stirred in a 3-necked flask. A mixture of TMS (3 g), DMS (6 g) and HMS (3 g) was gradually added to the flask while keeping the temperature below 25°C. Addition was stopped when half of the mixture had been added, stirring continued for 15 min, then the lower acid aqueous layer in the flask was removed. Another 18 g of water was added before the addition of the remaining half of the mixture. After that the aqueous solution was stirred for another 15 min and the lower aqueous layer removed. The upper layer was washed 3 times with water, then the solution was stirred for 10 min at room temperature with 5 wt% of sulfuric acid. The acid layer was removed, another 10 wt% of sulfuric acid was added and stirred for 6 h at 25–35°C. Then the upper layer was separated and 0.5 wt% charcoal was added. It was stirred for 30 min, washed with 70% of sulfuric acid. The washing with 5 wt% of sulfuric acid was repeated several times, until there was no charcoal in the waste acid. The resulting product was then washed with water to neutral. After the removal of toluene by a rotary evaporator, the final product was obtained with $m:n = 3:4$ which was determined by ¹H-NMR.



or:



Scheme 2 Synthesis of polysiloxane with mesogenic stilbene groups on the side chain

Synthesis of Dicyclopentadienylplatinum(II) Chloride (DPPC) Catalyst^[6]

Hydrated chloroplatinic acid (1 g) was dissolved in 2.5 mL of glacial acetic acid. The solution was diluted with 3.6 mL of water and then heated to 70°C. Dicyclopentadiene (1 mL) was added and the mixture was stirred for 24 h at room temperature. The crude product was filtered and recrystallized twice from THF. It yielded 0.4 g of white needles which melted at 217–218°C.

Synthesis of the Polymers

The title polymers were synthesized by hydrosilylation of the poly(methylsiloxane) and stilbene derivatives with a terminal vinyl group (Scheme 2). The details of the synthesis and properties of these stilbene derivatives will be reported in another paper.

In a 3-necked flask, polysiloxane and a 10% molar excess of stilbene derivatives were dissolved in dry toluene under the protection of nitrogen. DPPC in dichloromethane (the molar ratio of DPPC/monomer = 10^{-3} ~ 10^{-4}) was added to the mixture. Then the reaction mixture was heated to reflux until no Si-H can be detected by IR spectrometry. The mixture was added to methanol and the precipitate was collected by centrifugation. The polymer was purified by reprecipitation with methanol from its toluene solution followed by centrifugation. The wet gel-like product was dried in vacuum. The specific reaction conditions are listed in Table 1.

Table 1. Reaction conditions of hydrosilylation

Polymers	Main chain	Stilbene *		DPPC/monomer ($\times 10^3$)	Reaction time (h)	Yields (%)
		X	Y			
P1	$m : n = 3:4$	NO ₂	allyloxy	0.87	3.5	52
P2			$a = 2$	2.86	1.5	50
P3			$a = 8$	2.80	1.5	54
P4	$m : n = 3:4$	CN	allyloxy	1.15	1.5	45
P5			$a = 2$	5.51	36	36
P6			$a = 8$	7.24	36	54
P7	$n = 0$	NO ₂	allyloxy	1.31	1.5	61
P8			$a = 2$	3.38	24	50
P9			$a = 8$	4.56	24	62

* X and Y: types of the substituents of the stilbene derivatives (Scheme 2)

RESULTS AND DISCUSSION

The molecular weight and the polydispersity of the polymers were determined by GPC with polystyrene as the standard and THF as the eluent. The results are shown in Table 2.

Table 2. The molecular weight and polydispersity of the polymers

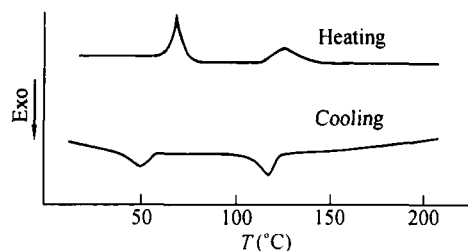
Polymers	$M_n (\times 10^{-3})$	$M_w (\times 10^{-4})$	M_n/M_w
P1	7.4	2.2	3.0
P2	7.5	1.7	2.3
P3	9.7	2.1	2.2
P4	10.9	2.4	2.2
P5	5.3	1.6	3.1
P6	9.0	1.8	2.0
P7	7.2	1.4	2.0
P8	4.6	1.0	2.2
P9	5.5	1.4	2.6

Table 3 lists the transition temperatures of the monomers and the polymers, which were determined according to the DSC heating curves. For example, Figure 1 is the DSC curves for the polymer P1, from which we see two endothermic peaks in the heating process and two exothermic peaks in the cooling process. The observation of P1 under a polarizing microscope revealed that the first endothermic peak was due to melting and the second corresponded to the transition from liquid crystal phase to isotropic state. The focal conic texture of the polymer under a polarizing microscope (see Fig. 2) shows that the polymer forms a smectic liquid crystal phase at temperatures between these two peaks. The same phenomena were observed for other polymers. As revealed by the formation of focal-conic textures of all the polymers, we could assign the mesophases of these polymers as smectic, even though no X-ray studies have been made to identify to which subclass of the smectic phase they belong.

Table 3. DSC data of the polymers and monomers

Polymers	Monomer (°C)			Polymer (°C)	
	T_m	T_{sn}	T_i	T_m	T_i
P1	117	—	—	69	126
P2	112	—	122	*	138
P3	89	98	111	48	125
P4	128	—	150	97	123
P5	102	—	153	103	158
P6	81	115	126	45	151
P7	117	—	—	90	212
P8	112	—	122	51	180
P9	89	98	111	72	146

*The sample is in liquid crystalline state at room temperature; no T_m was detected when DSC measurement was run from 0°C

**Fig. 1** The DSC curves of the polymer P1**Fig. 2** The focal conic texture of P1 upon cooling from isotropic state to 119°C

The data in Table 3 also demonstrate that the attachment of stilbene moiety to a polysiloxane main chain via a flexible spacer does not destroy the liquid crystalline nature of the stilbene compounds. Most polymers have a liquid crystal phase in a wider temperature range than the low molar mass stilbene compounds. In particular, while the low molar mass 4-allyloxy-4'-nitrostilbene is not liquid crystalline, the two polymers (P1 and P7) made from it both form a liquid crystalline phase of broad temperature range. However, the polymers and the low molar mass stilbenes may have different mesophases. For example, most of the stilbenes used in this study have a nematic phase while all the polymers only have a smectic phase. This trend was also discovered by other researchers^[7]. They found that the nematic monomers will usually lead to smectic polymers. When the end group of the mesogenic group was cyano and the main chain was polysiloxane, the polymers showed great ability in the formation of smectic liquid crystals^[8].

Furthermore, from Table 3 it can be seen that the phase transition temperatures of the homo-poly(methylsiloxane) ($n = 0$) are higher than those for poly(methylsiloxane-co-dimethylsiloxane) ($m:n = 3:4$) when the same mesogenic group is used. T_m and T_i of P7, P8 and P9 are much higher than those of P1, P2 and P3, respectively. This should be incurred by the different population of mesogenic units attached to the polymer backbone. Polymers with more mesogenic groups as side chains have higher chain stiffness and higher transition temperature. Therefore, the proper choice of the ratio $m:n$ will be a good way to control the phase transition of the polymers.

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