

# Synthesis and Phase Behavior of Chiral Side-Chain Liquid-Crystalline Polysiloxanes Containing Two Mesogenic Groups

Jian-She Hu,<sup>1</sup> Bao-Yan Zhang,<sup>1</sup> Zuo-Jun Liu,<sup>2</sup> Bao-Ling Zang<sup>1</sup>

<sup>1</sup> Department of Chemistry, Northeastern University, Shenyang 110004, People's Republic of China

<sup>2</sup> Resin Institute of Technique Center, Huajin Group, Panjin 124021, People's Republic of China

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**ABSTRACT:** The synthesis of chiral side-chain liquid-crystalline polysiloxanes containing both cholesteryl undecylenate ( $M_I$ ) and 4-allyloxy-benzoyl-4-(*S*-2-ethylhexanoyl) *p*-benzenediol bisate ( $M_{II}$ ) mesogenic side groups was examined. The chemical structures of the obtained monomers and polymers were confirmed with Fourier transform infrared spectroscopy or <sup>1</sup>H-NMR techniques. The mesomorphic properties and phase behavior of the synthesized monomers and polymers were investigated with polarizing optical microscopy, differential scanning calorimetry, and thermogravimetric analysis (TGA). Copolymers IIP-IVP revealed a smectic-A phase, and VP and VIP revealed a smectic-A

phase and a cholesteric phase. The experimental results demonstrated that the glass-transition temperature, the clearing-point temperature, and the mesomorphic temperature range of IIP-VIP increased with an increase in the concentration of mesogenic  $M_I$  units. TGA showed that the temperatures at which 5% mass losses occurred were greater than 300°C for all the polymers. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2670–2676, 2002

**Key words:** chiral; polysiloxanes; liquid-crystalline polymers (LCP)

## INTRODUCTION

In recent years, chiral side-chain liquid-crystalline polymers (SCLCPs) have attracted considerable attention and interest, mainly because of their unique properties, including the selective reflection of light and ferroelectricity, and their potential applications in numerous areas, especially in the fields of optics, electrooptics, thermoconducting materials, and fast switching.<sup>1–11</sup> For comblike polymers, the liquid-crystalline properties of SCLCPs depend on the nature of the polymer backbone, the type of mesogen, the flexible spacer and its length, and the nature of the terminal groups.<sup>12–15</sup> The polymer backbones of SCLCPs are primarily polyacrylates, polymethacrylates, and polysiloxanes; however, polyacrylates and polymethacrylates, because of their backbones, show higher glass-transition temperatures ( $T_g$ 's) and higher viscosities. For higher mobility of the liquid-crystalline phase at moderate temperatures and mesomorphic properties at room temperature, the polysiloxane

backbone and the flexible spacer are chosen and used. The mesogens are usually attached to the polymer backbone via a flexible spacer, which is generally an aliphatic hydrocarbon chain containing, normally, more than two methylene units. The flexible spacer decouples the mesogenic side groups from the backbone and makes the mesogens order anisotropically to a first approximation. Recently, some successful investigations into the synthesis and characterization of chiral side-chain liquid-crystalline polysiloxanes were reported.<sup>16–20</sup> Therefore, it would be both necessary and useful to synthesize various kinds of liquid-crystalline polysiloxanes to explore their potential applications.

In previous studies, we reported the synthesis and characterization of chiral side-chain liquid-crystalline polysiloxanes and ionomers.<sup>21</sup> In this study, the synthesis of chiral side-chain liquid-crystalline polysiloxanes containing both cholesteryl undecylenate ( $M_I$ ) and 4-allyloxy-benzoyl-4-(*S*-2-ethylhexanoyl) *p*-benzenediol bisate ( $M_{II}$ ) mesogenic side groups was examined. Their liquid-crystalline properties and phase behavior were characterized with polarizing optical microscopy (POM), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA).

## EXPERIMENTAL

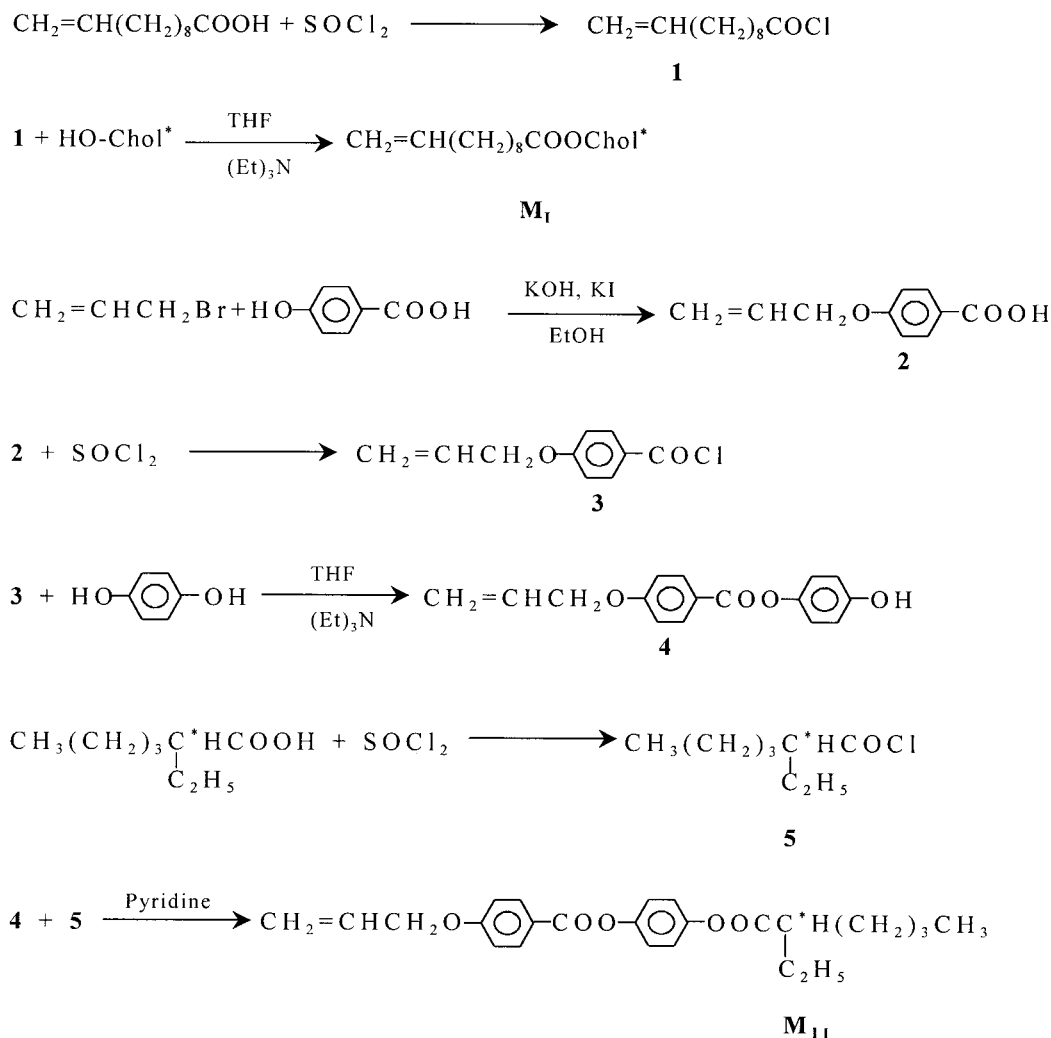
### Materials

Poly(methyl hydrosiloxane) (PMHS; number-average molecular weight = 700–800) was purchased from

Correspondence to: B.-Y. Zhang (baoyanzhang@hotmail.com).

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Scheme 1 Synthetic routes for the monomers.

Jilin Chemical Industry Co. (Jilin City, China). 2-Ethyl hexanoic acid was obtained from Xinxi Reagent Co. (Shenyang, China). Undecylenic acid was purchased from Beijing Jinlong Chemical Reagent Co., Ltd. (Beijing, China). Cholesterol was purchased from Henan Xiayi Medical Co. (Xiayi, China). Toluene used in the hydroxylation reaction was first refluxed over sodium and then distilled. All other solvents and reagents were purified by standard methods.

### Experimental techniques

$^1\text{H-NMR}$  spectra (400 MHz) were recorded on a Varian VXR-300 spectrometer (Palo Alto, CA) in a  $\text{CDCl}_3$  solution with tetramethylsilane as an internal reference. Fourier transform infrared (FTIR) spectra were measured on a Nicolet 510 FTIR spectrometer (Madison, WI). Polymer sample films used for measurements were obtained via casting on a KBr table. Phase transitions and thermodynamic parameters were determined with a PerkinElmer DSC-7 (Foster City, CA)

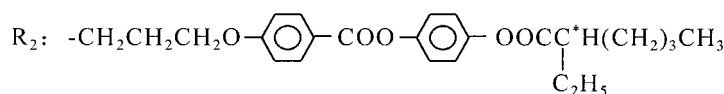
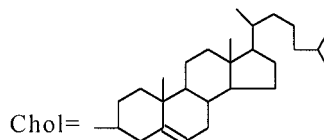
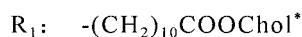
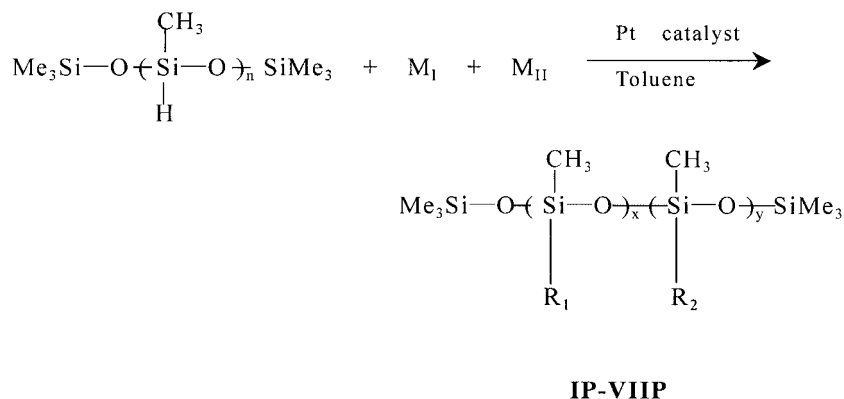
equipped with a liquid nitrogen cooling system. The heating and cooling rates were  $10^\circ\text{C}/\text{min}$ . The reported phase transitions were collected during the second heating and cooling scans. A Leitz Microphot-FX polarizing optical microscope (Wetzlar, Germany) equipped with a Mettler FP 82 hot stage and a Mettler FP 80 central processor (Leitz, Germany) was used to observe the phase transitions and to analyze the mesophase for the liquid-crystalline pure compounds and polymers through observations of the optical textures.

### Synthesis of the monomers

The synthesis of the vinyl monomers was performed as shown in Scheme 1.

### $\text{M}_{II}$

$\text{M}_{II}$  was synthesized according to literature procedures.<sup>21</sup>



**Scheme 2** Synthetic routes for the polysiloxanes.

$\text{M}_I$

Undecylenic acid (40 mL, 0.2 mol) was reacted at room temperature with excess thionyl chloride (22 mL) containing a few drops of dimethylformamide for 3 h, and then the excess thionyl chloride was removed under reduced pressure to give the corresponding acid chloride. The product was dissolved in 25 mL of dry tetrahydrofuran and added dropwise to a cold solu-

tion of cholesterol (38.7 g, 0.1 mol) and triethylamine (14 mL) in 100 mL of tetrahydrofuran. The solution was stirred for 2 h at room temperature and then refluxed for 2 h. The solvent was distilled, diluted with a threefold-to-fourfold excess of ether, neutralized with dilute HCl, and washed several times with distilled water, and the organic layer was dried with anhydrous magnesium sulfate. After evaporation of

**TABLE I**  
Polymerization and Optical Texture of the Polymers

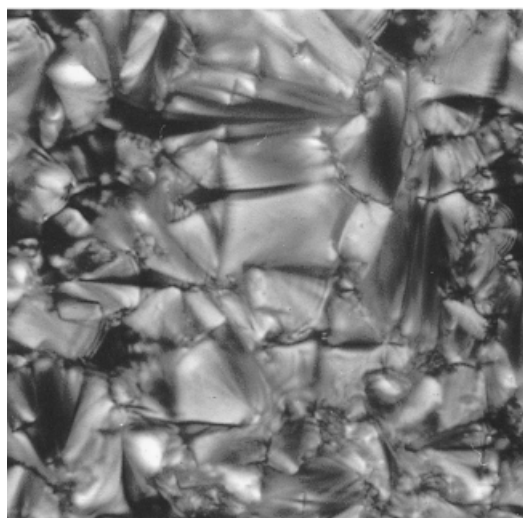
Polymer	Feed		Yield (%)	POM		
	$\text{M}_I$ (mmol)	$\text{M}_{II}$ (mmol)		$T_{cl}^a$ (°C)	$T_{lc}^b$ (°C)	Texture
IP	0	100	89	110	106	Fan-shaped
IIP	30	70	85	132	130	Fan-shaped
IIIP	50	50	84	140	132	Fan-shaped
IVP	70	30	86	148	143	Fan-shaped
VP	80	20	82	152	151	Oily streak
VIP	90	10	85	158	154	Fan-shaped
VIIP	100	0	90	161	155	Oily streak

<sup>a</sup> Temperature at which the birefringence disappeared completely.

<sup>b</sup> Temperature at which the mesophase occurred.



(a)



(b)

**Figure 1** POM micrographs of monomer  $M_I$  (320 $\times$ ): (a) cooling to 75 $^{\circ}\text{C}$  and (b) cooling to 60 $^{\circ}\text{C}$ .

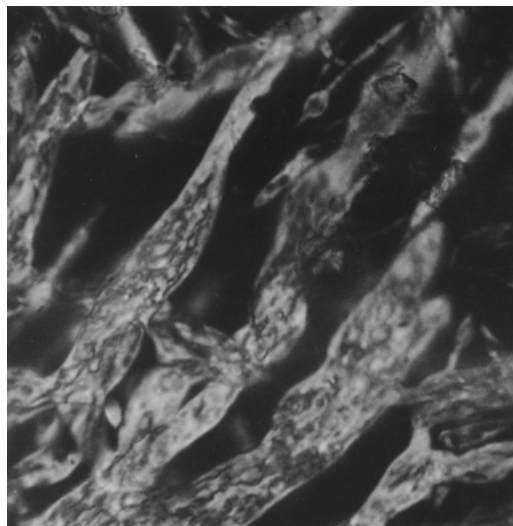
the solvent, the crude product was recrystallized from ethanol. White crystals were obtained (mp = 80 $^{\circ}\text{C}$ , yield = 75%).

IR (KBr,  $\text{cm}^{-1}$ ): 3078 ( $=\text{C}-\text{H}$ ), 2928, 2868 ( $\text{CH}_3-$ ,  $-\text{CH}_2-$ ), 1734 ( $\text{C}=\text{O}$ ), 1642 ( $\text{C}=\text{C}$ ).

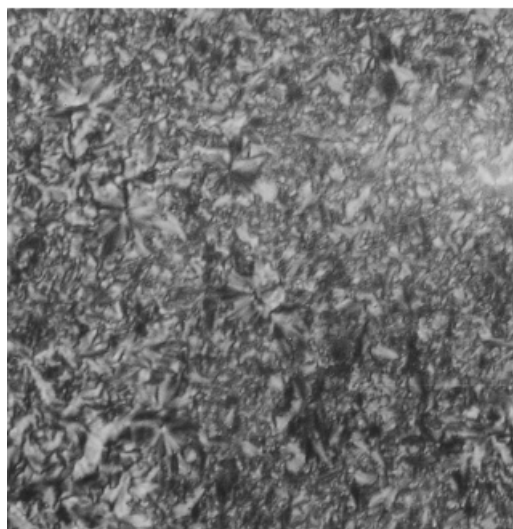
### Synthesis of the polymers

The synthetic routes of the polymers are outlined in Scheme 2. All synthesized polymers are listed in Table I. For the synthesis of polymers IP-VIIP, the same method was used. The synthesis of polymer IIIIP is given as an example.

The monomers  $M_I$  and  $M_{II}$  and PMHS were dissolved in dry, freshly distilled toluene. The reaction



(a)



(b)

**Figure 2** POM micrographs of VP (320 $\times$ ): (a) cooling to 135 $^{\circ}\text{C}$  and (b) cooling to 110 $^{\circ}\text{C}$  (annealing for 3 h).

TABLE II  
DSC and TGA Data for the Polymers

Polymer	Phase transitions (°C; corresponding enthalpy changes in J/g):		$\Delta T^a$ (°C)	TGA $T_{5\text{ wt}\%}^b$ (°C)
	Heating	Cooling		
IP	$G-3.6S_A100.3(8.7)I$	$I95.2(3.1)S_A$	103.9	310.4
IIP	$G8.9S_A118.8(4.5)I$	$I112.4(2.2)S_A$	109.9	315.8
IIIP	$G11.2S_A126.5(3.4)I$	$I120.1(2.5)S_A$	115.3	324.6
IVP	$G18.3S_A139.2(3.5)I$	$I133.6(1.6)S_A$	120.9	323.8
VP	$G21.5S_A142.7(2.7)Ch148.8(-)I$	$I144.3(-)Ch134.6(1.2)S_A$	127.3	305.3
VIP	$G22.8S_A138.2(2.3)Ch150.4(-)I$	$I144.7(-)Ch135.4(1.3)S_A$	127.6	306.4
VIIP	$G23.7S_A153.6(2.6)I$	$I147.3(1.4)S_A$	129.9	322.8

G-glassy; S-smectic; Ch-cholesteric; I-isotropic.

<sup>a</sup> Liquid crystalline range ( $T_i - T_g$ ).

<sup>b</sup> Temperature at which 5% mass loss occurred.

mixture was heated to 60°C under nitrogen and anhydrous conditions, and then the proper amount of a tetrahydrofuran solution of a hydrogen hexchloroplatinate(IV) hydrate catalyst was injected with a syringe. The reaction was continued for 72 h. The solvent was removed under reduced pressure, and the crude polymers were purified by repeated precipitation in toluene with excess methanol and then dried in vacuo. The yield and FTIR spectra were obtained.

IR (KBr,  $\text{cm}^{-1}$ ): 2800–3000 ( $-\text{CH}_3$ ,  $-\text{CH}_2-$ ), 1740, 1735 (C=O), 1610, 1509 (Ar—), 1260 (C—O—C, Si—CH<sub>3</sub>), 1000–1140 (Si—O—Si).

## RESULTS AND DISCUSSION

### Optical micrograph analysis

The optical textures of the polymers observed by POM with a hot stage under a nitrogen atmosphere are given in Table I.

The mesomorphism and textures of monomer  $M_{II}$  and homopolymer IP are described in detail in a previous article.<sup>21</sup> The visual observations under POM revealed that monomer  $M_I$  exhibited an enantiotropic oily streak texture and a monotropic fan-shaped texture during its heating and cooling cycles. When  $M_I$  was heated to about 80°C, the oily streak texture of the cholesteric phase appeared, and the birefringence totally disappeared at 89°C. When the isotropic state

was cooled to 83°C, the spiral oily streak texture appeared again; when cooling continued to 68°C, a fan-shaped texture of the smectic phase appeared, and with continued cooling to 54°C, the liquid-crystalline phase began to crystallize. Photomicrographs of  $M_I$  are shown in Figure 1(a,b). During cooling from the

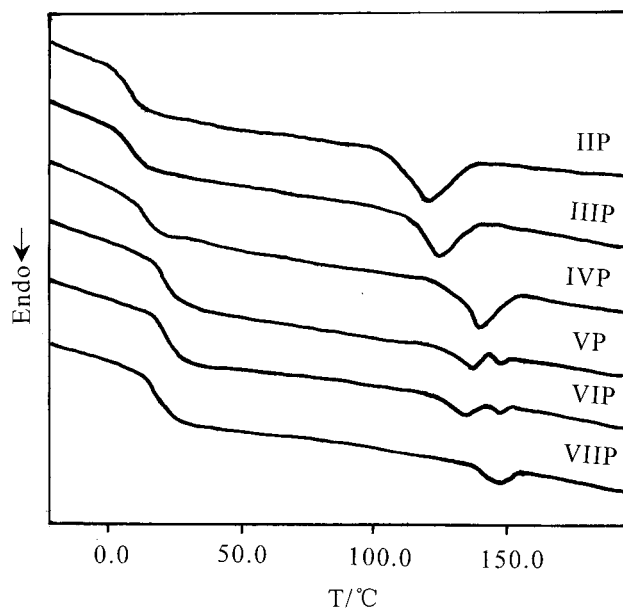


Figure 3 DSC thermographs of IIP–VIIP (second heating).

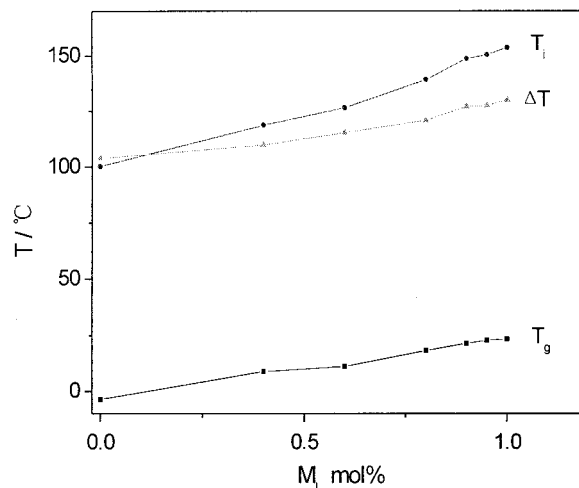
isotropic melt, if a mechanical field was superimposed on  $M_I$ , for example, a slight shearing of the melt caused macroscopic orientation of the domains and exhibited the property of selective reflection of light, which is typical of low molecular weight, cholesteric liquid-crystalline monomers. The homopolymer VIII was enantiotropic and liquid-crystalline, but the expected cholesteric phase did not appear, and it exhibited mesomorphism of smectic-A textures, a possible reason for which is that the polymeric chains hindered the formation of the characteristic helical supermolecular structure of the mesogens. Copolymers IIP-IVP displayed smectic-A mesomorphism, whereas VP and VIP also exhibited a cholesteric-phase oily streak texture in addition to a smectic-A fan-shaped texture. Photomicrographs of VP are shown in Figure 2(a,b) as examples. In copolymers VP and VIP, the formation of the cholesteric phase was influenced not only by the structure of the mesogenic groups but also by the copolymer composition.

### Thermal analysis

The phase transitions and corresponding enthalpy changes of polymers IP-VIII are summarized in Table II. Representative DSC curves of the polymers, obtained on the second heating scan, are presented in Figure 3.

During the second heating scan of IIP-IVP (Fig. 3), we can observe a  $T_g$  and a transition from the smectic-A phase to the isotropic phase, whereas during the second heating scan of VP and VIP, we see a  $T_g$  and transitions of the smectic-A phase to the cholesteric phase and of the cholesteric phase to the isotropic phase. All transitions were reversible and did not change with repeated heating and cooling cycles; the phase-transition temperatures noted in DSC thermograms were consistent with the mesomorphic transition temperatures observed by POM.

$T_g$  is an important parameter in connection with the structures and properties of polymers. In general, the  $T_g$  value of SCLCPs is strongly influenced by the polymeric chain flexibility, molecular weight, mesogenic group, and length of the spacer group. Figure 4 shows that the  $T_g$  value of IIP-VIP increased with an increase in the concentration of mesogenic  $M_I$  units in the copolymers. As we know,  $T_g$  involves the mobility of chain segments, and the  $T_g$  value increases with a decrease in the mobility of chain segments. In copolymers IIP-VIP, with an increase in the concentration of  $M_I$  units, the space steric hindrance increased, making the chain flexibility decrease; therefore, the mobility of chain segments decreased, and the  $T_g$  value increased. From Table II and the DSC curves (Fig. 3), we can see that the  $T_g$  values of IIP-VIP were 8.9–22.8°C. The reason for the lower  $T_g$  values is the better flexibility of the polysiloxane backbone and the flexi-



**Figure 4** Phase-transition temperature versus the  $M_I$  content of IP-VIII.

ble spacer group of mesogenic units. Therefore, copolymers IIP-VIP existed in a rubbery state and displayed mesomorphism at room temperature. Compared with the  $T_g$  value of IIP-VIP, the clearing-point temperature ( $T_i$ ) and the mesomorphic temperature range ( $\Delta T$ ) of IIP-VIP also increased with an increase in the concentration of  $M_I$  units (Fig. 4):  $T_i$  increased from 118.8 to 150.4°C and  $\Delta T$  widened from 109.9 to 127.6°C.

TGA showed that the temperatures at which 5% mass losses occurred were greater than 300°C for all the polymers; this shows that the synthesized chiral side-chain liquid-crystalline polysiloxanes had higher thermal stability.

In a comparison of the phase transitions and corresponding enthalpy changes of IIP-VIP, a flexible polymer backbone can be seen here to have a tendency toward having a lower  $T_g$  value, a wider mesomorphic range, and enthalpy changes. The most important tendency is that the flexible polymer backbone leads to a wide temperature range for the mesomorphic phases.

### CONCLUSIONS

In this study, a series of chiral side-chain liquid-crystalline polysiloxanes containing both  $M_I$  and  $M_{II}$  mesogenic side groups were prepared successfully. The synthesized copolymers IIP-IVP exhibited a smectic-A fan-shaped texture, whereas VP and VIP exhibited smectic-A fan-shaped and cholesteric-phase oily streak textures; all optical textures and phase transitions were reversible and did not change with repeated heating and cooling cycles. Flexible polymer backbones enhanced the coupling of the motions of the side chains and the main chains; therefore, they tended to give rise to a higher thermal stability of the mesomorphic phases.

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