

Polysiloxane Side-chain Liquid Crystalline Polymers Prepared by Alkyne Hydrosilylation^{*}

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Abstract We describe in this work an alkyne-hydrosilylation approach to synthesize a series of novel polysiloxane side-chain LCPs attaching end-on or side-on mesogenic side groups. Their properties are characterized by NMR, FTIR, gel permeation chromatography, thermogravimetric analysis, differential scanning calorimetry, polarized optical microscopy and small-angle X-ray scattering. These obtained alkenylsilane linked novel LCPs exhibit higher glass transition temperatures and clearing points, and especially display the tendency of forming smectic phases, in strong contrast with the nematic phases of their comparative conventional alkylsilane linked analogues, which manifests more rigid features of the alkenylsilane linkages and their significant influence on the mesomorphic properties.

Keywords: Liquid crystalline polymer; Polysiloxane; Alkyne hydrosilylation.

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INTRODUCTION

Liquid crystal polysiloxanes are consisting of highly flexible polysiloxane backbone and pendant ordered mesomorphic groups, which render them many fascinating properties, such as superhydrophobicity, admirable thermal and mechanical stabilities, relatively low liquid crystalline phase transition temperatures, low glass transition temperatures (T_g), *etc*^[1,2]. As an important class of liquid crystalline polymers (LCP), liquid crystal polysiloxanes have received a lot of scientific attention ever since Finkelmann reported the first example of polysiloxane-based LCP in 1980^[3,4], and have been widely applied as electro-optic materials^[5], light emitting materials^[6], gas transportation^[7] and chromatography^[8] materials, and liquid crystalline elastomer (LCE) based devices^[9–11] thereafter.

Besides few examples of polysiloxane-based main-chain LCPs (MCLCP) containing mesogenic units and siloxane spacers in the backbones^[12–14], most of liquid crystal polysiloxanes are side-chain LCPs (SCLCP) and have been all prepared by a general synthetic method which grafts vinyl-terminated liquid crystalline monomers onto hydrogen-containing silicon oil (*i.e.* polymethylhydrosiloxane (PMHS)) backbones *via* platinum-catalyzed hydrosilylation reaction (Fig. 1). For example, Finkelmann took advantage of the moderate reaction rate of hydrosilylation, invented the famous 2-step-crosslinking process to prepare polysiloxane-based LCEs which lately became the predominant method in LCE field^[15]. Percec^[16–20], Hardouin^[21–25], Zhou^[26] and other scientists^[27–29] synthesized various polysiloxane-based end-on (with mesogens terminally attached) or side-on

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(with mesogens laterally attached) side-chain LCPs and mesogen-jacketed LCPs respectively by grafting well designed vinyl-terminated mesogens. Recently, our group has applied thiol-ene click chemistry instead of hydrosilylation, to synthesize liquid crystal polysiloxanes^[30].

In this work, we are very curious about the versatility of hydrosilylation between Si—H bond and unsaturated carbon-carbon bonds. As shown in Fig. 1, to the best of our knowledge, all the previously reported liquid crystal polysiloxanes were prepared *via* alkene hydrosilylation, which leaves us several interesting questions. Can liquid crystalline polysiloxanes be synthesized *via* alkyne hydrosilylation with acetylene-terminated monomers? Do these novel polymers possess liquid crystalline phases? How the mesomorphic properties of these novel LCPs behave in comparison with traditional alkylsilane-analogues? These concerns are the objectives of this work.

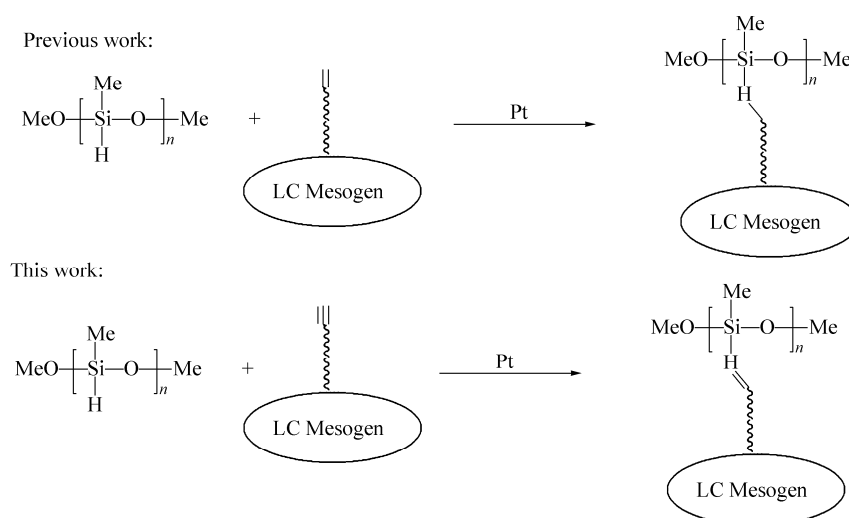


Fig. 1 Liquid crystalline polysiloxanes reported previously and designed in this work

EXPERIMENTAL

Materials and Instrumentation

Karstedt's catalyst (Pt(dvs), platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution in xylene, Pt ~2%) was purchased from Aldrich Inc. Polymethylhydrosiloxanes (HMS-993, M.W. 2200–2400) were purchased from Gelest Inc. Dicyclohexylcarbodiimide (DCC), and dimethylaminopyridine (DMAP) were purchased from Aladdin Inc. Liquid crystal cells were purchased from Instec Inc. THF was distilled from sodium benzophenone ketyl under nitrogen. Other chemical reagents were used without further purification. All non-aqueous reactions were conducted in oven-dried glasswares, under a dry nitrogen atmosphere. A Sigma 2K 15 centrifuge was used for isolation of polymers after precipitation. All flash chromatography were performed using Macherey-Nagel MN Kieselgel 60 (0.063–1.2 mm).

All ¹H-NMR spectra were obtained using either a Bruker HW500 MHz spectrometer (AVANCE AV-500) or a Bruker HW300 MHz spectrometer (AVANCE AV-300) and recorded in CDCl₃ (internal reference δ = 7.26). All ²⁹Si-NMR measurements of the polymers in CDCl₃ solvent containing 0.1% TMS were completed on a Bruker AVANCE AV-600 instrument with the operating frequency of 119.2 MHz. Gel permeation chromatography (GPC) was performed on a Shimadzu LC20AD high pressure liquid chromatography (HPLC), equipped with an RID-20A refractive index detector and a Shodex KF-803 300–8 mm column (packed with 6 μ m particles). The column packing allowed the separation of polymers over a molecular weight range of 200–70000. THF was used as the eluent at a low flow rate of 1 mL/min at 40 °C. Polystyrene standards were used as the references. Differential scanning calorimetry (DSC) spectra were recorded on a TA Instruments Q20

instrument (New Castle, DE) under nitrogen purge at a heating rate of 10 K/min from $-50\text{ }^{\circ}\text{C}$ to $+150\text{ }^{\circ}\text{C}$. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGA7.

Polarized optical microscopy (POM) observations of the liquid crystalline textures of the monomers and polymers were performed on an Olympus BX53P microscope with a Mettler PF82HT hot stage. The images were captured using a Microvision MV-DC200 digital camera with Phenix Phmias2008 Cs Ver2.2 software.

X-ray scattering experiments were performed with a high-flux small angle X-ray scattering instrument (SAXSess, Anton Paar) equipped with a Kratky block-collimation system and a temperature control unit (Anton Paar TCS300). At each single steady temperature, both small angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS) were simultaneously recorded on an imaging-plate (IP) which extended to high-angle range (the q range covered by the IP was from 0.06 nm^{-1} to 29 nm^{-1} , $q = 4\pi(\sin\theta)/\lambda$, where the wavelength λ is 0.1542 nm of Cu $K\alpha$ radiation and 2θ is the scattering angle) at 40 kV and 40 mA for 30 min.

Synthesis of Monomer VLC1

Intermediate **5** was prepared following literature protocol^[31]. 3-Buten-1-ol (114 mg, 1.58 mmol), compound **5** (800 mg, 1.58 mmol), DMAP (38.4 mg, 0.32 mmol) and dry CH_2Cl_2 (20 mL) were added into a 50 mL Schlenk-type flask. Under a nitrogen atmosphere, DCC (359 mg, 1.74 mmol) was added into the above flask in one portion at r.t. The reaction mixture was stirred at r.t. for 12 h. After filtering off the solids, the reaction solution was then concentrated by rotary evaporation and the resulting crude solid was purified firstly by recrystallization from anhydrous ethanol and then by flash chromatography (5:1 = petroleum ether:ethyl acetate) to give the desired product (603 mg, Yield: 68%) as a white solid. $^1\text{H-NMR}$ (500 MHz, CDCl_3 , δ): 8.16 (4 H, m), 7.88 (1 H, s), 7.46 (1 H, d, $J = 8.7\text{ Hz}$), 7.27 (1 H, m), 6.98 (4 H, d, $J = 8.4\text{ Hz}$), 5.68 (1 H, m), 5.01 (2 H, m), 4.22 (2 H, t, $J = 6.8\text{ Hz}$), 4.06 (4 H, t, $J = 6.4\text{ Hz}$), 2.27 (2 H, m), 1.81 (4 H, m), 1.51 (4 H, m), 1.00 (6 H, t, $J = 7.3\text{ Hz}$).

Synthesis of Monomer ALC1

3-Butyne-1-ol (111 mg, 1.58 mmol), compound **5** (800 mg, 1.58 mmol), DMAP (38.4 mg, 0.32 mmol) and dry CH_2Cl_2 (20 mL) were added into a 50 mL Schlenk-type flask. Under a nitrogen atmosphere, DCC (359 mg, 1.74 mmol) was added into the above flask in one portion at r.t. The reaction mixture was stirred at r.t. for 12 h. After filtering off the solids, the reaction solution was then concentrated by rotary evaporation and the resulting crude solid was purified firstly by recrystallization from anhydrous ethanol and then by flash chromatography (5:1 = petroleum ether:ethyl acetate) to give the desired product (565 mg, Yield: 64%) as a white solid. $^1\text{H-NMR}$ (300 MHz, CDCl_3 , δ): 8.16 (4 H, m), 7.92 (1 H, s), 7.47 (1 H, m), 7.27 (1 H, m), 6.99 (4 H, d, $J = 8.7\text{ Hz}$), 4.28 (2 H, t, $J = 6.8\text{ Hz}$), 4.07 (4 H, t, $J = 6.4\text{ Hz}$), 2.42 (2 H, d, $J = 5.6\text{ Hz}$), 1.94 (1 H, s), 1.83 (4 H, m), 1.25 (4 H, m), 1.00 (6 H, t, $J = 7.4\text{ Hz}$).

Synthesis of Monomer VLC2

4-Cyano-4'-hydroxybiphenyl (1.95 g, 10.0 mmol) and 4-bromo-1-butene (1.02 mL, 10.0 mmol) were dissolved in 30 mL dry dimethylformamide. Potassium iodide (0.08 g, 0.75 mmol) and 5.5 g (39.0 mmol) fine powdered potassium carbonate were then added. The reaction mixture was stirred for 2 h at r.t. Water ($\sim 15\text{ mL}$) was added and the mixture was extracted with ethyl acetate ($4 \times 20\text{ mL}$). The combined organic phases were washed with 10% HCl (15 mL) and with 10% aqueous K_2CO_3 solution (15 mL), then dried over anhydrous MgSO_4 , filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (5:1 = petroleum ether:ethyl acetate) to give the desired product (2.07 g, Yield: 83%) as a white needle-like solid. $^1\text{H-NMR}$ (300 MHz, CDCl_3 , δ): 7.60 (4 H, m), 7.52 (2 H, d, $J = 8.7\text{ Hz}$), 6.99 (2 H, d, $J = 8.7\text{ Hz}$), 5.92 (1 H, m), 5.15 (2 H, m), 4.07 (2 H, t, $J = 6.7\text{ Hz}$), 2.57 (2 H, m).

Synthesis of Monomer ALC2

4-Cyano-4'-hydroxybiphenyl (3.90 g, 20.0 mmol) and 4-bromo-1-butyne (1.84 mL, 20.0 mmol) were dissolved in 60 mL dry dimethylformamide. Potassium iodide (0.16 g, 1.50 mmol) and 11.0 g (78.0 mmol) fine powdered potassium carbonate were then added. The reaction mixture was stirred for 2 h at r.t. Water ($\sim 30\text{ mL}$) was added and the mixture was extracted with ethyl acetate ($4 \times 40\text{ mL}$). The combined organic phases were washed with

10% HCl (30 mL) and with 10% aqueous K_2CO_3 solution (30 mL), then dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (5:1 = petroleum ether:ethyl acetate) to give the desired product (1.14 g, Yield: 23%) as a white solid. ^1H -NMR (500 MHz, $CDCl_3$, δ): 7.69 (2 H, d, $J = 8.1$ Hz), 7.64 (2 H, d, $J = 8.1$ Hz), 7.54 (2 H, d, $J = 8.5$ Hz), 7.01 (2 H, d, $J = 8.5$ Hz), 4.15 (2 H, t, $J = 7.0$ Hz), 2.73 (2 H, d, $J = 6.7$ Hz), 2.06 (1 H, s).

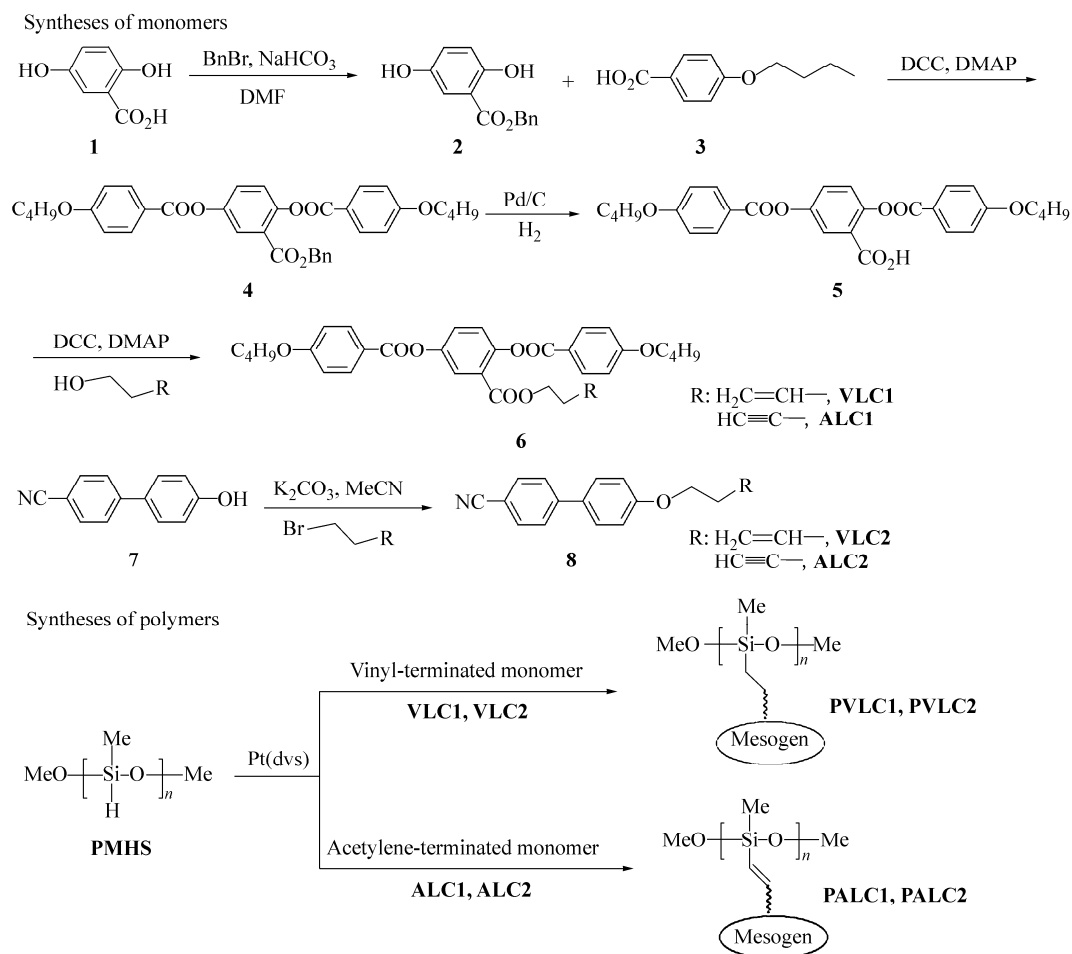
Typical Synthetic Procedure of LCPs

4-(3-Butyn-1-yloxy)-4'-cyano-1,1'-biphenyl (**ALC2**) (800 mg, 3.20 mmol) and PMHS (38 mg, 0.63 mmol Si—H groups) were dissolved in 15 mL freshly distilled THF under N_2 atmosphere. Pt(dvs) dissolved in xylenes (50 μ L) was added to the stirred solution, then the mixture was kept refluxing for 2 days. The mixture was then cooled to r.t., filtered, concentrated, and poured into 300 mL methanol. The mixture was stirred and filtered off. The solid was collected and redissolved in chloroform, then precipitated in methanol (three times), and finally dried at 40 °C under vacuum for 24 h, to give the desired product (135 mg, Yield: 72%) as a yellow solid.

RESULTS AND DISCUSSION

For comparison purposes, we designed and synthesized a side-on acetylene-terminated monomer **ALC1** and an end-on acetylene-terminated monomer **ALC2**, as well as their vinyl-analogues **VLC1** and **VLC2**. As shown in Scheme 1, the starting material, 2,5-dihydroxybenzoic acid (**1**) was first transformed into a benzyl ester (**2**), which was then DCC-coupled with 4-butyloxybenzoic acid (**3**)^[32, 33] to give a mesogenic benzyl ester (**4**). Through a Pd/C-catalyzed hydrogenation-deprotection step, the key intermediate **5** was synthesized, and then modified with vinyl-terminated or acetylene-terminated alcohols to prepare the desired side-on mesogenic monomers **VLC1** and **ALC1** respectively. The synthetic protocols of end-on mesogenic monomers **VLC2** and **ALC2** are much more straightforward, by using one step etherification reaction between 4-cyano-4'-hydroxybiphenyl (**7**) and bromo-terminated alkene or alkyne.

With mesogenic monomers in hand, we first used the traditional alkene-hydrosilylation procedure to synthesize a side-chain side-on LCP, **PVLC1**, and a side-chain end-on LCP, **PVLC2**. As shown in Fig. 2(A), after hydrosilylation reaction, the terminal vinyl protons of monomer **VLC1** originally locating at $\delta = \sim 5.0$ and ~ 5.7 , disappear completely, while the resonance signals of the aromatic protons still remain at $\delta = 7.0$ – 8.0 on the ^1H -NMR spectrum of polymer **PVLC1**, which indicates that the vinyl-terminated mesogenic monomers have been successfully grafted onto PMHS backbones. Furthermore, the spectrum showed broad peaks instead of sharp ones, typical for polymers due to the slower motion of the protons. However, we can not accurately measure the graft density of mesogenic monomers by calculating the integral ratio of aromatic protons and CH_3 —Si protons, since the resonance signals of CH_3 —Si groups presenting at $\delta = \sim 0$ are interfered with the peak of tetramethylsilane (TMS) reference contained in $CDCl_3$ solvent. Alternatively, Fourier transform infrared spectroscopy (FTIR) was applied to examine these novel LCPs. As shown in Fig. 3(a), the starting polymer PMHS possesses a broad absorption band around 2170 cm^{-1} which is attributed to the stretching vibration of Si—H bond. After the hydrosilylation-grafting experiment, the full extinction of 2170 cm^{-1} peak in **PVLC1** sample (Fig. 3c) reveals that the Si—H functional groups of PMHS are fully saturated with mesogenic units and the graft density is roughly 100%. As to **PVLC2** sample, a new sharp band assigned as the —CN group appears at 2220 cm^{-1} instead of 2170 cm^{-1} region, which also verifies a complete hydrosilylation reaction with an almost 100% grafting ratio. These quantitative grafting yields are further confirmed by ^{29}Si -NMR experiments. As shown in ^{29}Si -NMR spectra listed in the supporting information, a single peak at $\delta = -21 \sim -22$ ascribed to $\underline{Si}$ —C groups appears while the $\underline{Si}$ —H groups located at $\delta = \sim -38$ ^[34] are absent.



Scheme 1 The synthetic routes of mesogenic monomers and the corresponding liquid crystalline polysiloxanes

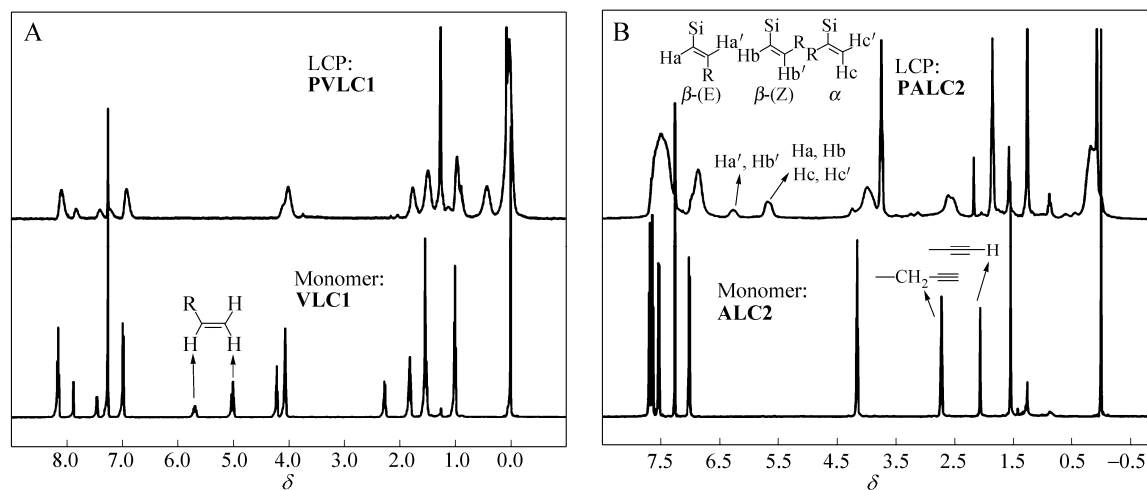


Fig. 2 ^1H -NMR spectra of (A) monomer VLC1 and the corresponding polymer PVLC1, (B) monomer ALC2 and the corresponding polymer PALC2

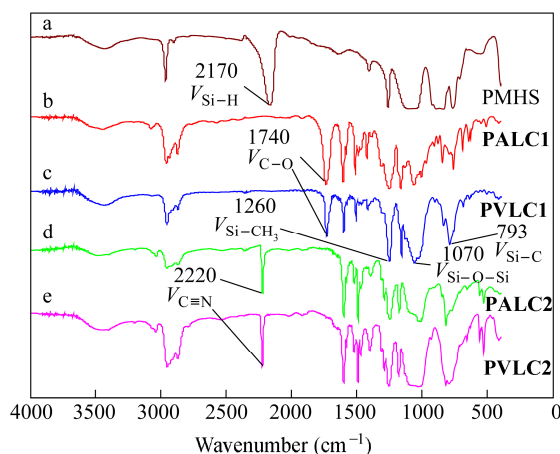


Fig. 3 FTIR spectra of (a) PMHS, and liquid crystalline polysiloxanes: (b) **PALC1**, (c) **PVLC1**, (d) **PALC2**, (e) **PVLC2**

Alkyne-hydrosilylation is the most atom-economical approach to prepare alkenylsilanes which has attracted considerable attention in recent years^[34, 35]. Compared with alkene-hydrosilylation, the regioselectivity and stereoselectivity of alkyne-hydrosilylation are much more complicated since hydrosilylation of terminal alkynes can form not only Markovnikov product α -alkenylsilane but also two anti-Markovnikov products, β -(E)-alkenylsilane and β -(Z)-alkenylsilane^[36]. Although many transition metal catalysts as well as radical and Lewis acid induced procedures^[37–40] have been developed to perform alkyne hydrosilylations, we herein choose the conventional platinum catalyst, Karstedt's catalyst, due to its high catalytic activity (turnover number > 10000)^[41]. In order to inhibit the possibility of two Si–H groups reacting with one terminal alkyne, we set the initial concentration of alkyne-terminated monomers as five times of available Si–H bonds' concentration. As demonstrated in Figs. 3(b) and 3(d), the Si–H vibrational stretching bands originally at 2170 cm^{−1} on FTIR spectra of **PALC1** and **PALC2** fully extinguish which verifies almost quantitative alkyne hydrosilylation conversions.

In **PALC2**'s ¹H-NMR spectrum (Fig. 2B), there are two newly emerging peaks at $\delta = \sim 6.3$ and ~ 5.6 , which are attributed to the resonance signals of Si–C=CH–C and Si–CH=C, Si–C=CH₂ vinyl protons respectively. Thus, we can roughly determine the molar ratio of β -alkenylsilane form and α -alkenylsilane form by solving the following equation: $[\beta\text{-alkenylsilane}]/[\alpha\text{-alkenylsilane}] = I_{6.3}/[I_{5.6}-I_{6.3}]$, where $I_{6.3}$ and $I_{5.6}$ represent the integral values of the $\delta = \sim 6.3$ and ~ 5.6 resonance peaks. Through this equation, we recognize that the distributions of β -alkenylsilane forms and α -alkenylsilane forms in **PALC1** and **PALC2** are 58/42 and 59/41 respectively. However, β -(E)-alkenylsilane and β -(Z)-alkenylsilane can not be distinguished based on our currently obtained information.

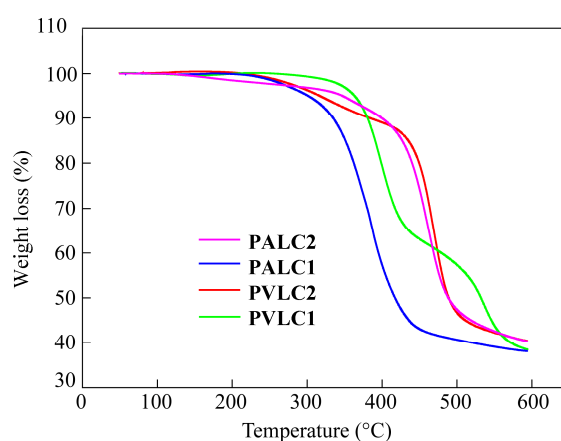
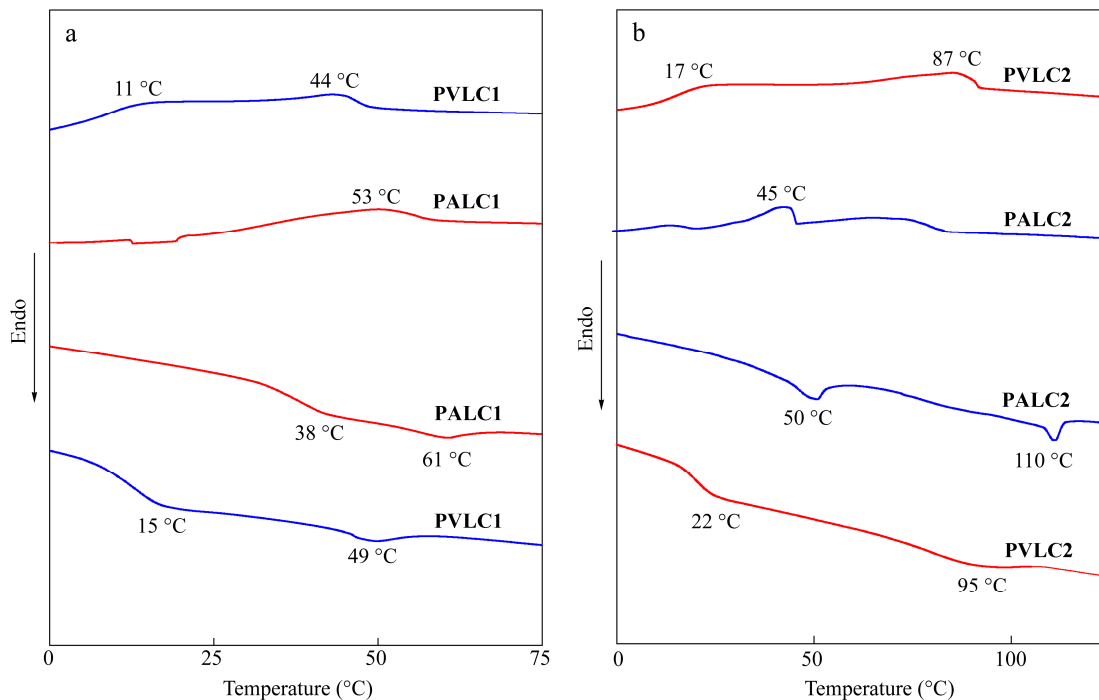
These successful grafting results were further confirmed by gel permeation chromatography (GPC). As shown in Table 1, all the M_n values of the prepared liquid crystalline polysiloxanes increase dramatically, compared with the starting material PMHS. However, the polydispersity index (PDI) value of each polymer varies from each other, which might derive from one possible reason that since these LCPs are short polymers, some low molecular weight oligomers soluble in chloroform/methanol solvents might be excluded.

The thermal properties of the four LCPs were investigated by TGA and DSC. As illustrated in Fig. 4, the temperatures at 5% weight loss (T_d) of these LCP samples under N₂ are all over 300 °C, implying that the thermal stabilities of all the polymers are good enough for regular application scenarios. The DSC experiments of four polysiloxane-based LCPs all show one apparent glass transition and another first-order phase transition during the first cooling and subsequent heating scans. As shown in Fig. 5 and Table 1, the glass transition temperatures of two polysiloxane-based LCPs **PVLC1** and **PVLC2** prepared by alkene-hydrosilylation are respectively lower than those of their alkenylsilane-analogues **PALC1** and **PALC2**.

Table 1. Molecular weights and thermal properties of the polymers

Polymer	M_n^a (g/mol)	M_n^c (g/mol)	M_w^c (g/mol)	M_w/M_n	T_g^d (°C)	T_d^e (°C)
PMHS	2200–2400 ^b	976	1760	1.81	–	–
PALC1	23480	15620	17650	1.13	38	300
PALC2	11660	9950	13040	1.31	50	347
PVLC1	23560	13620	19200	1.41	15	363
PVLC2	11740	10790	15320	1.42	22	316

^a Calculated according to a polymerization degree of 38; ^b Merchant label; ^c Measured by GPC based on calibration using polystyrene standards; ^d Evaluated by DSC at a rate of 10 K/min; ^e The temperature at which 5% weight loss of the sample from TGA under nitrogen atmosphere at a heating rate of 10 K/min

**Fig. 4** Thermogravimetric analysis of the four novel liquid crystalline polysiloxanes**Fig. 5** DSC curves of (a) PVLC1, PALC1 and (b) PVLC2, PALC2 during the first cooling scan and the second heating scan at a rate of 10 K/min under nitrogen atmosphere

Polarized optical microscopy was used to investigate the mesomorphic behaviors of these four liquid crystalline polysiloxanes (Table 2). As shown in Fig. 6, **PALC1**, **PVLC1** and **PVLC2** show ambiguous birefringent textures which are actually typical for polymers due to their high viscosities, while **PALC2** appears fan-shaped textures (Fig. 6c) which are characteristics of smectic phases^[42]. Similar to the glass phase transition comparison result, the LC-isotropic transition temperatures of two polysiloxane-based LCPs **PVLC1** and **PVLC2** prepared by alkene-hydrosilylation are also lower than those of their alkenylsilane-analogues **PALC1** and **PALC2** respectively. This scenario might derive from the alkenylsilane linkers, which compared with traditional alkylsilane linkers, are much more rigid and thus raise the phase transition temperatures of LCPs.

Table 2. Mesomorphic Properties of the Monomers and Polymers ^a

Monomer	Phase transitions (°C)	Polymer	Phase transitions (°C)
VLC1	K 101 N 115 I I 113 N 79 K	PVLC1	G 15 N 49 I I 44 N 11 G
ALC1	K 95 N 104 I I 103 N 82 K	PALC1	G 38 N 61 I I 53 N
VLC2	K 58 N 98 I I 95 N 52 K	PVLC2	G 22 N 95 I I 87 N 17 G
ALC2	K 51 N 85 I I 84 N 45 K	PALC2	G 50 SmX 110 I I 108 SmX 45 G

^a Detected by polarized optical microscopy; Glass phases determined by DSC; K = crystalline, G = glass phase, N = nematic, SmX = unknown smectic phase, I = isotropic; First line obtained on heating, second line obtained on cooling

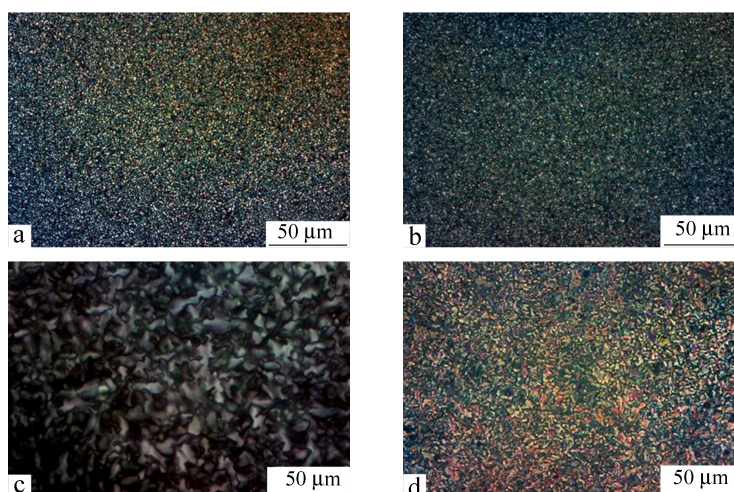


Fig. 6 POM images of (a) **PALC1** recorded at 45 °C, (b) **PVLC1** recorded at 30 °C, (c) **PALC2** recorded at 70 °C and (d) **PVLC2** recorded at 50 °C

To elucidate these four LCPs' mesomorphic properties, one dimensional temperature-varied wide-angle X-ray scattering experiments were performed. As shown in Fig. 7(a), the WAXS patterns of **PALC1** powder sample present two diffuse peaks in low- and wide-angle regions. Compared with the fully extended 1,4-di(4'-butyloxybenzoyloxy)benzene mesogen length ($l = 2.75$ nm) estimated by Dreiding models, the observed d -spacing of ~ 2.41 nm attributed to the diffuse peak at low angles ($q = 2.61$ nm⁻¹) is relatively shorter, which indicates a nematic phase with smectic C fluctuation^[43–45] existing in **PALC1** system. As illustrated in Fig. 7(b), the WAXS profiles of **PALC2** powder sample present one much sharper scattering peak at low angles. The corresponding lamellar thickness of **PALC2** is 2.38 nm which is much higher than the fully extended 4'-but-3-ynyloxy-biphenyl-4-carbonitrile mesogen length ($l = 1.62$ nm) estimated by Dreiding models, and however is less than twice the mesogen length. Taking into account the fan-shaped texture shown in Fig. 6(c), we thus consider that **PALC2** possesses an interdigitated smectic phase (SmA_d or SmC_d). Meanwhile, it is noticed that

compared with traditional smectic molecules' XRD spectra, this low-angle scattering peak is slightly broader which might derive from the coexistence of β -alkenylsilane forms and α -alkenylsilane forms in **PALC2**. Since β -alkenylsilane forms and α -alkenylsilane forms have different mesogen lengths, the corresponding smectic layer has a non-uniform molecular arrangement which results in a broad peak width. As to the alkylsilane analogues **PVLC1** and **PVLC2**, they have either one diffuse peak or none in low-angle regions, which are characteristics of nematic phase.

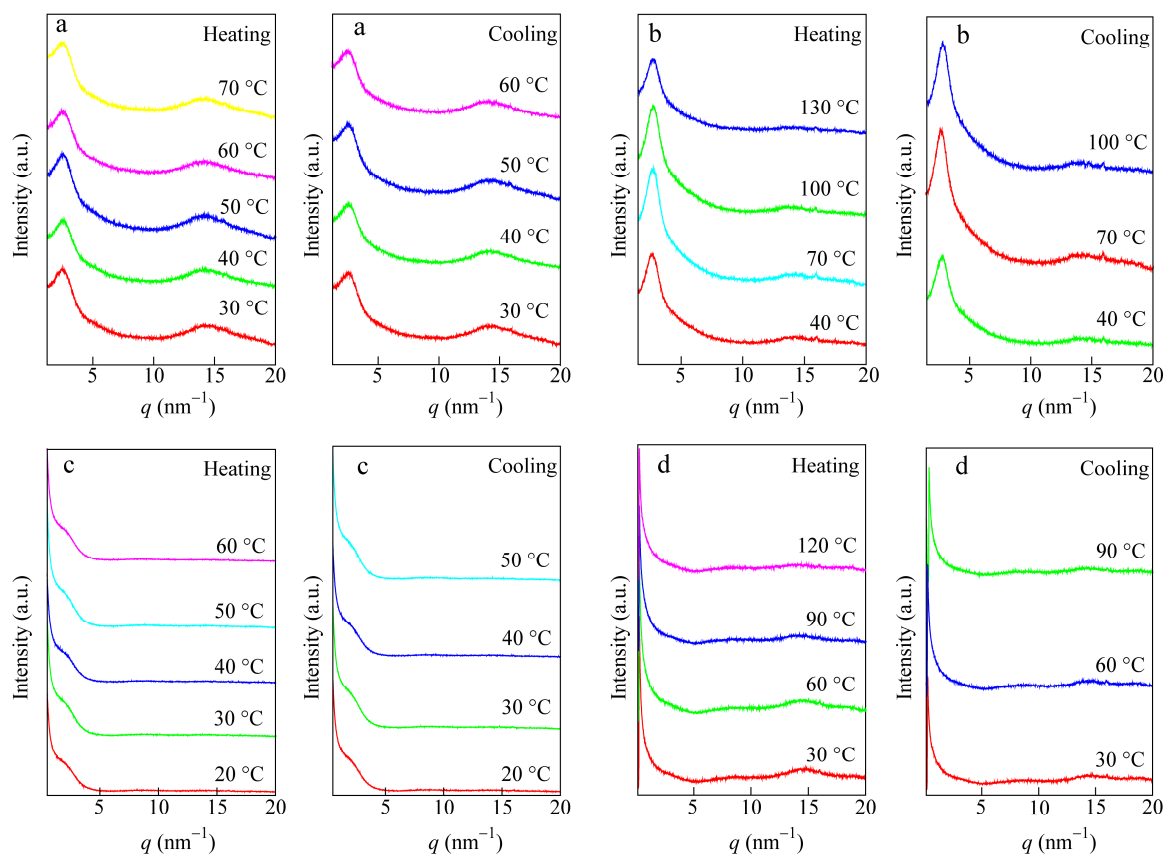


Fig. 7 One-dimensional WAXS patterns of (a) **PALC1**, (b) **PALC2**, (c) **PVLC1**, and (d) **PVLC2**

Obviously, compared with traditional LC polysiloxanes bearing alkylsilane linkers, our newly developed LCPs grafted with acetylene-terminated mesogens are prone to form lamellar phases. This phenomenon should be also associated with the more rigid alkenylsilane linkers which compared with flexible alkylsilane junctions, tend to force the attached mesogens to pack in relatively more ordered anisotropic structures and thus bring in additional positional orders. This hypothesis might explain why **PALC2** presents interdigitated smectic phase while **PVLC2** shows nematic phase.

CONCLUSIONS

In conclusion, this paper reports an alkyne-hydrosilylation approach to synthesize a series of novel side-chain liquid crystalline polymers bearing alkenylsilane linkers between the polysiloxane backbones and mesogenic units. NMR, FTIR and GPC experiments of these polysiloxane-based LCPs show that the alkyne hydrosilylation conversions are almost quantitative although the complicated regioselectivity and stereoselectivity bring up three addition forms including α -alkenylsilane, β -(E)-alkenylsilane and β -(Z)-alkenylsilane. The mesomorphic properties of LCPs are characterized by TGA, DSC, POM and SAXS. These novel polymers, in comparison with

their traditional alkylsilane-analogues, possess higher glass phase and LC-to-isotropic phase transition temperatures, meanwhile become more prone to form smectic phases. This scenario indicates that alkenylsilane linkers, compared with traditional alkylsilane linkers, are much more rigid and markedly influence the mesomorphic properties of LCPs.

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