



## Note

# Synthesis and characterization of a graft side-chain liquid crystalline polysiloxane



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## ABSTRACT

A graft side-chain crystalline polymer **PI** with polysiloxane as backbone and a liquid crystal polymer, poly [6-(4'-octyloxyphenyl-4''-benzoyl)hexyl acrylate], as side chain has been synthesized via atom transfer radical polymerization (ATRP) technique. Attaching mesogenic polymers to the polysiloxane main chain through ATRP technique brings about the high density of mesogenic units and avoids the subsequent crosslinking reaction by the residual Si–H in the traditional hydrosilylation. The properties of the graft liquid crystal polymer **PI** was studied in detail by TGA, DSC, POM and XRD. Thermal analysis shows that the polymer **PI** has wider mesophase temperature ranges with a high thermal stability in comparison to its mesogenic monomer.

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## Introduction

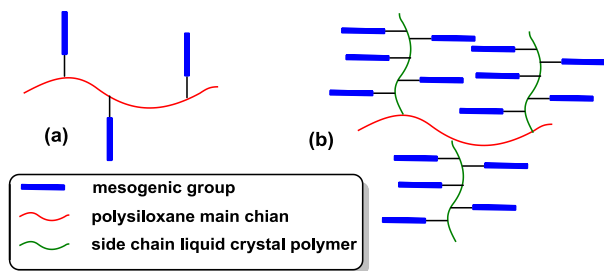
In recent years, the side chain liquid crystalline polymers (SCLCPs) have attracted significant interests due to the improved properties, such as higher thermal stability, wider phase transition temperature range, and relative higher viscosity, etc. [1–4], over their low molecular weight counterparts and their potential applications in many fields, such as nonlinear optic devices, optical data storage materials, and so on [5–9]. Among them, polysiloxane-based SCLCPs have received extensive attention because of the excellent physical properties of organosilicon, such as super flexibility, weatherability, low surface tension, water proof, etc. [10–13].

Generally, polysiloxane SCLCPs could be prepared by hydrosilylation of polymethylhydrosiloxane with alkenes-terminated mesogens using platinum complexes as catalysts [4,14]. The Si–H of polysiloxane is not always complete reaction because of the bulkiness of mesogens. Moreover, the residual Si–H generally brought about the unpleasant crosslinking reaction and the change in properties which would affect their application. One of the strategies to make the hydrosilylation completion is diluting the methyl(hydro)siloxyl unit in the polysiloxane backbone with dimethylsiloxyl units while this reduces the mesogens density. However, this definitely results in the lower mesogenic density

attached to the polysiloxane backbone since only one mesogenic group is attached to one silicon atom in the general side chain liquid crystal polysiloxane (Fig. 1a). Generally, the mesogen density seems to have a pronounced effect on the temperature window of the mesophase and the degree of order in the mesophase [15,16]. Moreover, high mesogenic density could stabilize the mesophase [17]. To attach a side chain liquid crystalline polymer to the macromolecular backbone will increase the mesogenic density without a doubt as shown in Fig. 1b. Atom transfer radical polymerization (ATRP) technique provides a convenient method to attach a polymer to macromolecular backbone [18–21]. Indeed, ATRP technique has been used in the preparation of functional polysiloxanes. For example, the comb-like graft copolymers with a polydimethylsiloxane (PDMS) backbone and polystyrene-*block*-poly(*tert*-butyl acrylate) (PS-*b*-PtBA) as side-chains were prepared via the sequential ATRP of styrene (St) and *tert*-butyl acrylate (tBA) [22]. PDMS macroinitiator with the initiating group at the end of the macromolecular chain was also successfully used to synthesize a series of hybrid liquid-crystalline rod-coil diblock copolymer by ATRP [23]. ATRP has also been used to prepare star-shaped LC polymer. For example, the star-shaped mesogen-jacketed LC polymers poly{2,5-bis[(4-methoxyphenyl)oxycarbonyl]styrene} (PMPCS) with polyhedral oligomeric silsesquioxane (POSS) core have been prepared by ATRP technique [24]. To our best knowledge, there is no report about the liquid crystalline polymer attached to the linear polysiloxane chain as the pendant (Fig. 1b). Herein, we introduced the ATRP technique to prepare a graft liquid crystal polysiloxane **PI** through the initiating of chloropropyl substituted

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**Fig. 1.** Structures of general side chain liquid crystal polysiloxane (a) and side chain liquid crystal polymer graft polysiloxane (b).

polysiloxane (Scheme 1). In comparison to the conventional polysiloxane liquid crystalline, the prepared graft liquid crystalline polysiloxane would contain no Si–H residues and higher mesogenic density.

## Experimental

### General considerations

All the reagents were purchased from Shanghai Chemical Reagents except for the special statement. Cu(I)Cl was washed with acetic acid to remove any soluble oxidized species, filtered, washed with ethanol and dried under vacuum.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were obtained using a Bruker HW300 MHz spectrometer (AVANCE AV-300) and recorded in  $\text{CDCl}_3$ . FT-IR spectra were recorded on a Nicolet IS10 in the region of  $4000\text{--}400\text{ cm}^{-1}$  using KBr pellets or film. The average molecular weights of polymer were estimated by a Waters Associates gel permeation chromatography (GPC) system in THF calibrated by monodisperse polystyrene standards. Differential scanning calorimetry (DSC) was performed using a Mettler Toledo DSC822e at a scan rate of  $10\text{ }^\circ\text{C}/\text{min}$  under a nitrogen atmosphere. Thermogravimetric analysis (TGA) was carried out by Aetaram Setsys16 at a scan rate of  $10\text{ }^\circ\text{C}/\text{min}$  under a nitrogen atmosphere. Polarized optical microscopy (POM) observations of the liquid crystalline textures of the monomer, LC polymer 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 diffraction (XRD) experiments were carried out on a Philips X'Pert Pro diffractometer with a 3 kW ceramic tube as the X-ray source ( $\text{Cu K}\alpha$ )

and an X'cletator detector. The polymer samples for the XRD measurements were prepared by quick freezing the molecular arrangements in the liquid crystalline state with liquid nitrogen.

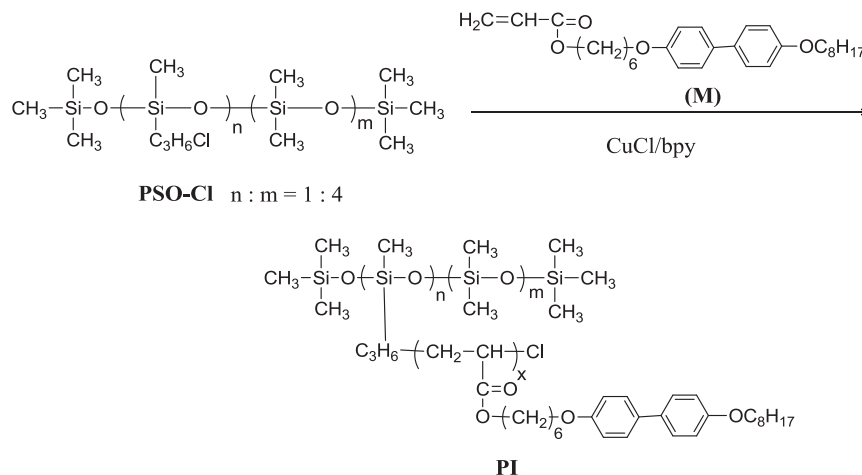
### Synthesis of graft liquid crystal polymer PI

A Schlenk flask was charged with **PSO-Cl** (0.08 g, containing 0.2 mmol C–Cl), copper (I) chloride (0.04 g, 0.4 mmol), 2, 2-dipyridyl (0.18 g, 1.2 mmol), **M** (1.50 g, 3.3 mmol) and 2.0 mL of toluene. The flask was degassed with three freeze-evacuate-thaw cycles, and the solution was stirred at  $120\text{ }^\circ\text{C}$  for 24 h. The crude product was diluted with THF and passed through a short silica gel column to remove the copper catalysts. The solution was concentrated to ca. 10 mL and added dropwise to 200 mL of methanol, the white precipitates was recovered. Purified polymer (0.77 g, 49%) was obtained by additional twice reprecipitation in THF/methanol and dried in a vacuum. FT-IR (KBr,  $\text{cm}^{-1}$ ): 2957, 2934, 2856, 1731, 1607, 1568, 1500, 1473, 1393, 1328, 1273, 1247, 1178, 1034, 995, 824, 809, 728, 598, 516.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  [ppm]: 7.36 (br, Ar–H), 6.85 (br, Ar–H), 4.05 (br,  $-\text{OCH}_2-$ ), 3.88 (br,  $-\text{OCH}_2-$ ), 2.31 (m,  $-\text{CH}-$ ), 1.75 (br,  $-\text{CH}_2-$ ), 1.43 (m,  $-\text{CH}_2-$ ), 1.29 (br,  $-\text{CH}_2-$ ), 0.89 (m,  $-\text{CH}_3$ ), 0.63 (br,  $-\text{SiCH}_2-$ ), 0.09 (s, Si– $\text{CH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  [ppm]: 174.4, 158.0, 133.0, 127.5, 114.6, 67.9, 67.7, 64.6, 41.4, 31.8, 29.2, 28.5, 26.0, 25.8, 22.6, 14.1, 1.4, 0.9, 0.1,  $-0.6$ .

## Results and discussion

### Synthesis and characterization of compounds

The macroinitiator containing chloropropyl was chosen as initiator since it has been used to initiate ATRP procedure for preparing star-shaped poly(methyl methacrylate) with the POSS as a core [25]. Therefore, **PSO-Cl** was designed for macroinitiator. 3-Chloropropylmethyltrimethoxysilane was firstly hydrolyzed with water to form 3-chloropropylmethylsiloxyl oligomer. Then the linear polysiloxane **PSO-Cl** bearing 3-chloropropyl pendant was prepared by the polymerization of 3-chloropropylmethylsiloxyl oligomer, DMC and MM as the end-capped reagent catalyzed by 732 cation exchange resins (for details, see the Supporting information). The ratio of 3-chloropropylmethylsiloxyl unit with dimethylsiloxyl unit in the prepared **PSO-Cl** had been determined to be 1/4 by  $^1\text{H}$  NMR through the integral area ratio of  $-\text{CH}_2\text{Cl}$  and  $-\text{SiCH}_3$ . This value is comparable to the feed ratio of two kinds of monomers. The average molecular weight was estimated by GPC



**Scheme 1.** Synthesis of PI.

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