Preparation and Cholesteric Behaviors of Novel PDMS-based Side-chain Liquid Crystalline Polymers

Chunlei Zhang [1, 2, a], Jinglan Liu [1], Junfeng Wei [1], Xiao Zhao [1], Tianjan Yang [1], Huaxin Rao [1, b, *] and Ziyong Zhang [1, c,*]

[1]Department of Materials Science and Engineering, Jinan University, Guangzhou 510632, China

[2]The First Affiliated Hospital of Jinan University, Guangzhou 510632, China

[a]zclsir@126.com, [b]traohx@jnu.edu.cn, [c]tzhangzy@jnu.edu.cn

Abstract

A series of cholesteryl as mesogenic groups containing unsaturated linkages were first synthesized using a super esterification method. Based on cross-linking reaction, a novel side-chain cholesteric liquid crystalline polymer (SCLCP) with alternating flexible and rigid segments was prepared by using Poly(dimethylsiloxane) (PDMS) containing vinyl groups as flexible back-chain, and the cholesteric liquid crystal (CLC) as rigid side-chain and HSO as a crosslinked agent. Their chemical structures and liquid crystalline behaviors were characterized by FTIR, EA, DSC and polarizing optical microscopy equipped with a hotstage and temperature regulator. The results showed that the preparation method exhibited higher yield and lower toxicity as well as simpler treatment than some traditional methods, in addition, the reaction could be carried out at room temperature and simple operation process. The spacer length of mesogenic groups markedly influenced liquid crystalline properties. The texture of the CLCs was the type of typical cholesteric liquid crystalline. It is predicted that the existence of rigid side-chain and flexible back-chain gives SCLCP wider ranges of properties and extends application fields of PDMS.

Keywords

Liquid crystalline polymer, PDMS, cholesteric liquid crystal, cross-linking, super esterification method.

1. Introduction

Liquid crystalline polymer combines mesogenic units and high molecular weight, and thus exhibits excellent anisotropic physical properties while possessing the advantage of easy processing and convenient molecular tailoring [1,2]. The liquid crystalline polymer not only possesses the individual properties of each of its parents, but also exhibits intrinsic features that its parents do not have. The liquid crystalline polymer can be classified into three broad groups: nematic, cholesteric and smectics liquid crystalline polymer. In recent years, growing attention was devoted to studies of cholesteric liquid crystals and side-chain cholesteric liquid crystalline polymers (SCLCP) [3,4]. The existence of rigid side-chain and flexible back-chain gives SCLCP wider ranges of properties and extends their application fields. SCLCPs play an important role in search for biocompatible materials as well as models for understanding complex Biosystems [5]. The synthesis of SCLCPs has been an active research area for the past three decades [6]. Majority of side-chain liquid crystal materials were made by two synthetic routes – free radical polymerization of acrylic type monomers, bearing mesogenic moieties and hydrosilylation of mesogenic terminal alkenes with linear poly[(methylhydro)siloxanes], copolymers bearing alkylhydrosiloxane monomeric units or polymer systems modified with reactive Si-H bonds [7-10]. Although, in the last century hundreds of structures of side chain LC polymers have been synthesized, there are still many new reports dealing with various novel architectures. Apart from SCLCPs in which the side groups are covalently bonded to the polymer chain, the other pathway involves formation of LC polymers via self-assembly of relevant moieties, exploiting

non-covalent interactions, such as ionic or hydrogen bonding [5,11,12]. In addition, the knowledge of structure-properties relationship is crucial for obtaining LC materials with optimum desired properties. It is worth pointing out that liquid crystal mesogen has been applied to improve physical properties and biocompatibility of polymers and biomaterials [13,14].

Poly(dimethylsiloxane) (PDMS), as a linear silicone, has become one of the most important biomedical membrane materials among commercially available polymers due to its good membrane formation ability, low chemical reactivity, low temperature flexibility, high gas permeability and excellent mechanical properties as well as relatively good biocompatibility [15,16]. However, its membrane-forming ability and blood compatibility as a biomedical membrane material is so poor that direct applications are limited. In addition, many works had indicated that, when PDMS was on contact with blood, thrombus could be formed to some degree [17]. The thrombus formation is a severe limitation of silicone rubbers for biomedical applications. Therefore, attempts had been made to further improve the biocompatibility and membrane-forming ability of PDMS by modifying its backbone and side chain or by mixing it with other polymers [18-20]. Recently, Zhou prepared several mesogen-jacketed liquid crystalline polymers (MJLCPs) with polysiloxane backbones and discovered that the mesogen-jacketed effect could force polysiloxanes to self-assemble into supramolecular columnar nematic or smectic liquid crystalline phases [21]. Yang synthesized a series of side-chain liquid crystalline polymers (LCPs) with polysiloxane backbones by grafting mesogenic monomers to poly[3-mercaptopropylmethylsiloxane] (PMMS) via thiol−ene click chemistry [22]. However, those studies on cholesteric PDMS-based LCPs were really few.

Herein, in the work, a series of cholesteric liquid crystals containing unsaturated linkages and with low transition temperature for liquid crystal phase are first synthesized by a super esterification method. Based on addition reaction and via self-assembly method, SCLCP with alternating flexible and rigid segments was fabricated by using PDMS containing vinyl groups as flexible back-chain, and the cholesteric liquid crystal (CLC) as rigid side-chain and HSO as a crosslinked agent. Their chemical structures and liquid crystalline properties were characterized by FTIR, EA, DSC and polarizing optical microscopy (POM) equipped with a hotstage and temperature regulator. Effects of the spacer length of mesogenic groups on liquid crystalline properties were also investigated.

2. Experimental Procedure

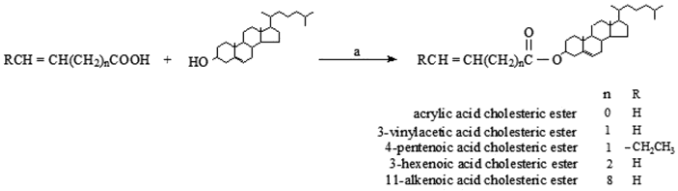
2.1 Materials

Acrylic acid cholesterol, 3-vinylacetic acid cholesterol, 4-pentenoic acid cholesterol, 3-hexenoic acid cholesterol and 11-alkenoic acid cholesterol were obtained from Alfa Aesar. 4-(dimethylamino) pyridine (DMAP), sulfur oxychloride ($SOCl_2$), pyridine, dichloromethane (CH_2Cl_2), ethyl acetate, chloroform, N,N-dicyclohexylcarbodiimide (DCC) were purchased from Guangzhou Chemical Reagent Co. Polydimethylsiloxane (PDMS), polymethylhydrosiloxane (HSO) and a chloroplatinic acid solution were purchased from the Research Center of Organic Silicone of Chengdu, China. The number-average molecular weight of PDMS was 500,000, and the vinyl content was 10% (molar percentage). The hydrogen content of HSO was 1.5% (mass percentage). Dichloromethane and chloroform were distilled from CaH_2 under nitrogen. THF was distilled from sodium benzophenone ketyl under nitrogen. All other solvents and chemical agents were analytical grade and used without further purification.

2.2 Synthesis of CLCs by the super esterification method

0.025 mol cholesterol was dissolved in 100 ml anhydrous CH_2Cl_2 to form a solution. 1.2 mmol DMAP, 0.03 mol acrylic acid (or 3-vinylacetic acid, 4-pentenoic acid, 3-hexenoic acid and 11-alkenoic acid) and 0.03 mol DCC were added to the solution under agitation. The resulting mixture was stirred at room temperature for 20 h. The reaction mixture was filtered to remove the by-produce. Subsequently, the filtrate was first washed with distilled water, then with 5% sodium hydroxide solution, 5% sodium bicarbonate solution and washed in distilled water, respectively. The resultant solution was dried over magnesium sulfate for 12 h and then filtered. A faint yellow produce

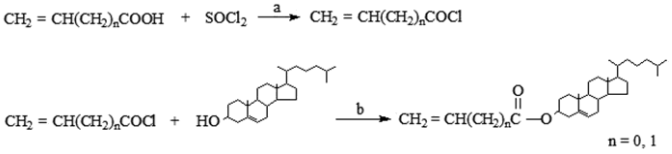
was obtained after removing CH_2Cl_2 by distillation at atmospheric pressure. The obtained solid was then purified by recrystallization from glacial acetic acid and ethanol to give the desired product. Yield: CLC1 prepared acrylic acid cholesteric ester 6.2 g (70.0%), CLC2 prepared 3-vinylacetic acid cholesteric ester 8.1 g (76.2%), CLC3 prepared 4-pentenoic acid cholesteric ester 7.1 g (67.1%), CLC4 prepared 3-hexenoic acid cholesteric ester 6.9 g (64.1%), CLC5 prepared 11-alkenoic acid cholesteric ester 5.9 g (59.4%). The synthetic route was shown in Scheme 1.



Scheme 1 Synthesis of CLCs by the super esterification method. Reagents and conditions: (a) CH2Cl2, DMAP, DCC, 25 °C, 57.0% (acrylic acid cholesteric ester), 76.2% (3-vinylacetic acid cholesteric ester), 67.1% (4-pentenoic acid cholesteric ester), 64.1% (3-hexenoic acid cholesteric ester), 59.4% (11-alkenoic acid cholesteric ester)

2.3 Synthesis of CLCs by the acylation method

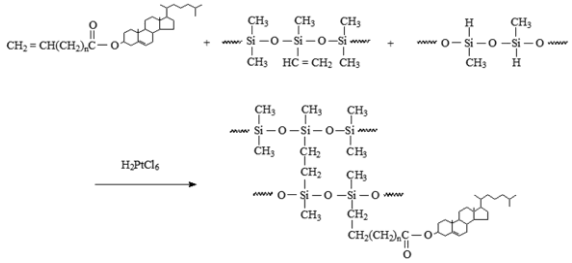
The mixture solution of 0.01 mol acrylic acid cholesterol (or 3-vinylacetic acid cholesterol) and excess $SOCl_2$ was refluxed and then refluxed again for 0.5 h after forming a solution. A light yellow solution was obtained after removing excess $SOCl_2$ by distillation at vacuum pressure and then cooled in an ice bath. The mixture solution of 6.2 g (0.016 mol) cholesterol, 15 ml pyridine and 20 ml benzene was added drop wise to the above solution with a constant pressure dropping funnel and a large amount of white gases were produced. The resulting mixture was stirred at room temperature for 16 h, and then refluxed at atmospheric pressure for 5 h to remove benzene. After cooling, the resulting solution mixed with 20 ml THF was added into large amounts of 1 mol/L HCl solution and stirred quickly. A yellow and viscous product was obtained after separating the organic level. A white product was obtained after filtration, washing, drying, recrystallization with ethyl acetate for several times and decolorization with activated carbon. Yield: CLC1 (28.2%), CLC2 8.1 g (25.3%). The synthetic route was shown in Scheme 2.



Scheme 2 Synthesis of CLCs by the acylation method. Reagents and conditions: (a) reflux, 75-77 °C; (b) pyridine, THF, 28.2% (acrylic acid cholesteric ester), 25.3% (3-vinylacetic acid cholesteric ester)

2.4 Preparation of SCLCPs

CLC (0.25 g) and PDMS containing vinyl groups (1.0 g) were dissolved in 25 ml THF to form a solution. Subsequently, polymethylhydrosiloxane (0.012 g) and proper chloroplatinic acid solutions were added slowly into the solution. The cross-linking reaction was continued for 10 min at room temperature. Finally, the SCLP film samples were obtained by casting the sol onto a polyethylene terephthalate (PET) sheet at room temperature were dried in an oven for 1 h at 60 °C in the presence of air. The preparation process was shown in Scheme 3.



Scheme 3 Preparation process of PDMS-based SCLCPs

2.5 Characterization

Elemental analyzer was measured with Elementar Vario EL of German.

The FTIR spectra of the CLCs and SCLCPs were obtained with a Bruker EQUINX 55 of German measuring in the range of 4000–500 cm^{-1}.

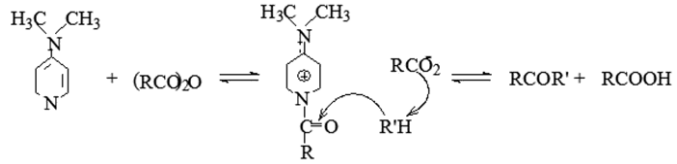
LC phase behaviors and optical properties of the cholesteric liquid crystals were characterized using thermal polarized optical microscopy equipped with a hotstage and temperature regulator (XPT-7, produced by Nanjing Optical Instrument Co.).

Differential scanning calorimetry (DSC) was conducted with a Perkin Elmer DSC-2C thermal analyzer at a heating rate of 10 °C/min under a nitrogen atmosphere.

3. Results and discussion

3.1 Synthesis of CLC and preparation of SCLCPs

DMAP have been widely used as an efficient esterification catalyzer. The catalytic mechanism was shown in Scheme 4 [23,24]. According to the structure of DMAP, the conjugation between dimethyl amino and pyridine ring of the structure can strongly activate the nitrogen atom in the ring carrying on the nucleophilic substitution reaction. DMAP as a super nucleophile reagent and matrix substrate can react and form a large and stable "target substrate" which is benefit for the attack of alcohol types, resulting in increasing the reaction rate and yield. Now, DMAP is known as a super catalyst of esterification reaction due to its good catalyst efficiency. Compared to alkaline catalyst (such as pyridine, triethylamine), DMAP catalytic reaction has the following advantages: (1) a smaller amount of catalyst. For example, only 0.05~0.20 mmol DMAP is used for 1 mol of reactants; (2) a milder reaction condition. The reaction is easy to control and operate because many reactions can be carried out at room temperature; (3) shorter catalytic reaction time. The reaction times used pyridine as catalyst need several hours but those of DMAP only need several minutes; (4) higher reaction yield and product purity, fewer by-product and simpler post-processing; (5) wider solvent selectivity. Many solvents (such as chloroform, dichloromethane, ethyl acetate, hexane, THF, pyridine, triethylamine, dimethylformamide) can be used as a solvent for DMAP catalytic reaction [25]. In the paper, DMAP with low toxicity and high efficiency is used as a catalyzer for the synthesis of cholesteric liquid crystals containing unsaturated linkages. The yields of the super esterification method were increased by 50% as compared to the acylation method and up to 76.0%. In addition, the reaction by the super esterification method can carry out at room temperature for 16 h and the post-processing was simple.



Scheme 4 The catalytic mechanism of DMAP as a catalyzer

Cross-linking, including covalent bonds and metal ion bonds, is very effective in reinforcing performance of polymeric materials [26,27]. In our previous study, properties of modified PDMS membranes using cross-linking method were obviously enhanced [28]. In the paper, we selected PDMS containing vinyl groups as flexible back-chain, the above cholesteric liquid crystal containing vinyl groups as rigid side-chain, HSO containing active Si-H groups as a crosslinked agent, and chloroplatinic acid solution as a catalyst. By controlling the molar ratio of PDMS, CLC and HSO, in theory each cross-linked agent molecular containing two hydrogen atoms could crosslink with PDMS containing vinyl groups and CLC containing vinyl groups. The SCLCPs with alternating flexible and rigid segments was fabricated through addition reaction at room temperature. The preparation process and vulcanization reactions of the SCLCPs were completed simultaneously. This modification method was simple and the preparation process could be carried out at room temperature to retain the liquid crystalline properties of the side-chain.

3.2 Structural characterization

The carbon and hydrogen contents of the CLC samples measured by elemental analyzer were determined and list in Table 1. As shown in the table, the found values of the carbon and hydrogen contents were near to calculated value.

Table 1 Elemental Analysis of Different CLCs

Samples	Found (wt%)		Calculated (wt%)	
	C	H	C	H
CLC1	81.72	11.46	81.75	10.98
CLC2	81.64	11.10	81.94	11.01
CLC3	82.07	11.06	82.05	11.11
CLC4	82.13	11.17	82.16	11.20
CLC5	82.48	11.68	82.54	11.67

The chemical structures of the CLC1 and CLC5 samples were characterized with FTIR analysis and the spectra are shown in Fig. 1. As shown in the Figure, the characteristic stretching peaks of carbonyl have appeared. Compared to the characteristic peaks of carbonyl at 1740 cm^{-1}, the stretching peaks of carbonyl in the CLC1 at 1716 cm^{-1} were shifted to a low-frequency due to the conjugated function between C = O and C =C bonds. The stretching vibration peak of the double bond (-C = C-) was 1633 cm^{-1}. As shown in Fig. 1(b), the stretching peaks of carbonyl in the CLC5 is 1729 cm^{-1} because the conjugated function between C = O and C =C bonds is not exhibit. Two strong and wide absorption peaks in 1300 ~ 1000 cm^{-1} are the characteristic peaks of the ester bonds (-C-O-C-). The stretching vibration peaks of the double bond (-C = C-) was 1660 cm^{-1}. These results indicated that the olefine acid could react with the cholesterol by the super esterification based on DMAP as a catalyzer.

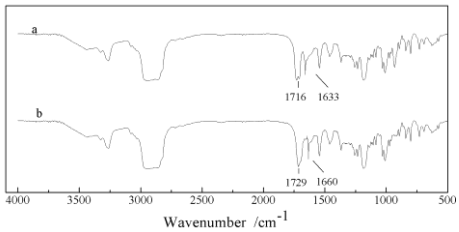


Fig. 1 FTIR spectrum of CLC1 (a) and CLC5 (b)

The chemical structure changes for pure PDMS, the CLC and the SCLCPs during the crosslinked process were monitored by FTIR and shown Fig. 2. The characteristic peaks of vinyl groups (-CH=CH_2) at 1603 cm^{-1} and 2980 cm^{-1} for PDMS completely disappeared in the FTIR spectra of the cross-linked membrane, indicating that the vinyl groups of PDMS reacted with the Si-H groups of HSO. Compared to that of the SCLCP, the intensities of the characteristic peaks for the CLC at 1600 cm^{-1} (-CH=CH_2) almost disappeared, which suggesting that the vinyl groups of CLC nearly reacted with Si-H groups of HSO by addition reaction. In addition, Si-C-C-Si bonds (characteristic peak at 1374 cm^{-1} and 787 cm^{-1}) were formed in the SCLCPs.

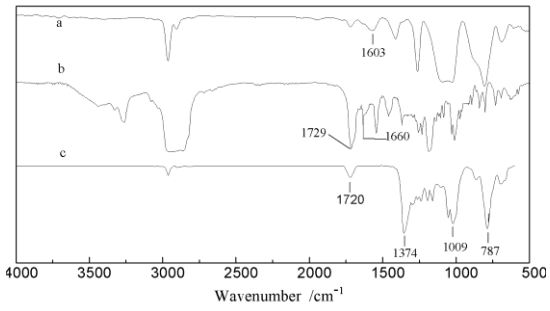


Fig. 2 FTIR spectrum of PDMS (a), CLC (b) and SCLCPs (C)

3.3 Liquid crystalline behaviors

CLCs have beautiful and interesting optical properties, e.g., the selective reflection of circularly polarized light, significant optical rotation, circular dichroism, etc. Under the polarized optical microscope, the liquid crystal films show colorful patterns, i.e., the optical textures. Each liquid crystal phase shows its typical texture which provides the means to identify the phase of the liquid crystals. The typical textures are the schlieren, threadlike, homeotropic, homogeneous, marble, finger-print, focal-conic, Dupin cyclide, fan-shape, sanded, mosaic, and so on [29]. In the paper, the liquid crystal textures and phase behavior of the title compounds were observed under a polarizing optical microscope equipped with a hotstage and temperature regulator which could be used to identify liquid crystal phases, characterize molecular order, and quantify the distribution of defects. Transition temperatures and corresponding enthalpy changes were determined using a differential scanning calorimeter.

Liquid Crystalline Behaviors of CLC1

The two endothermic peaks for the CLC1 present at 117 °C and 121.8 °C in the first heating cycle (shown in Fig. 3). However, the peaks does not present in the first cooling cycle and the second heating. In addition, the liquid crystal texture was not observed with the polarizing optical microscope in the first heating cycle and the sample become very thick after melting process. And the exothermic phenomenon did not appear in the first cooling cycle. The reason for the behavior might be that the CLC1 appeared a heating polymerization in the heating process. Acrylic ester is a monomer prone to free radical polymerization and polyacrylate types are mostly amorphous compounds. At the same time, the DSC curve in the second heating cycle does not appear the ladder change of glass transition temperature. The reason might be that the conjugated function between C = O and C = C bonds in the chemical structure of the CLC1 is not benefit for the formation of cholesteric liquid crystal phase and the spacer configuration of the CLC1 is not also benefit for order arrangement of the CLC layer.

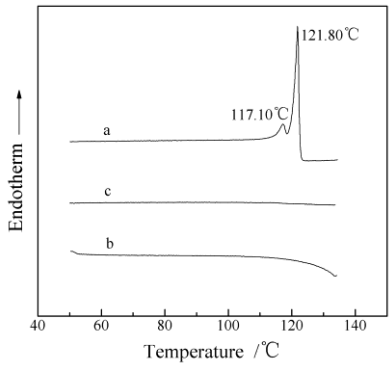


Fig. 3 DSC heating and cooling curves of CLC1 (a) the first heating; (b) the first cooling; (c) the second heating

Liquid Crystalline Behaviors of the Other CLCs

The molecules in the CLCs are arranged as thin layers. The molecules lie in the layers and are parallel to each other, but the director rotates along the helical axis continuously and uniformly. The helical pitch is much greater than the spacing of successive molecular layers. On the basis of the analytical methods, the results indicated that the other CLCs exhibited CLC behavior. For example, the liquid crystal behavior of CLC2 in polarized microscopy was dependent upon the temperature (shown in Fig. 4). At room temperature, the sample showed crystal double refraction. When the sample was heated to 65.7 °C, it began to flow and present chain texture, indicative of the presence of typical CLC texture [30]. When the sample was heated to 73.1 °C, the viewing field of the sample, which transited into an isotropy liquid state, became dark. When the sample was gradually cooled to 68.2 °C, it formed liquid crystal state (showed in Fig. 4a). As the temperature of the sample decreased slowly, the liquid crystal flow appeared to have a finger-print texture, and the sample developed a helical texture with finger-print at 69.5 °C (showed in Fig. 4b); this texture is also typical CLC. When the

sample was further cooled to 64.5 °C, it displayed a fan-shaped texture with smectic LCs, and slowly crystallized between 55 °C and 30 °C.

Fig. 4 Optical textures of CLC2 (a. heating to 73°C; b. cooling to 65°C)

The thermal properties of CLC2 were showed in Fig. 5 and listed in Table 2. As shown in Fig. 5b (cooling curve), the endotherm peak at 64.5 °C was a transition peak from the cholesteric phase to the smectic phase, resulting in a lower enthalpy value. Because the cholesteric ester crystallized slowly between 55 °C and 30 °C, the crystal peak did not appear in the cooling curve. In addition, the enthalpy value associated with the melting point in the second heating cycle (Fig. 5c) was smaller than that of the first heating cycle (Fig. 5a). The enthalpy value of the clearing point changed some, affirming that the sample did not completely crystallize when cooling to 50 °C. Compared to the heating curve of the sample, the cooling curve had a transition peak related to the changes from the cholesteric phase to the smectic phase. The other CLCs also exhibited the liquid crystal textures similar to CLC2.

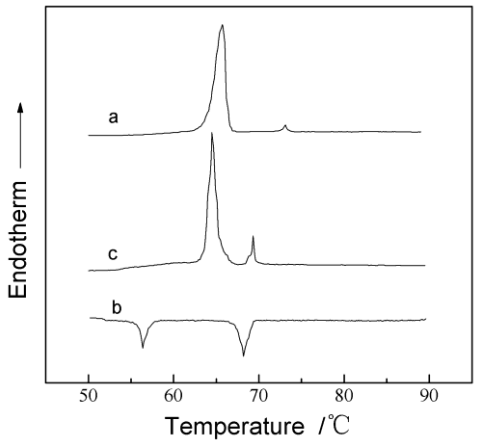


Fig. 5 DSC curves of CLC2: (a) the first heating; (b) the first cooling; (c) the second heating

Table 2 Phase Transition Temperatures and Enthalpy Values of Different CLC Samples

Samples	Heating and cooling process	Phase transition temperature (°C)			ΔH_m ($J \cdot g^{-1}$)	ΔHs ($J \cdot g^{-1}$)	ΔHi ($J \cdot g^{-1}$)
		Cr—S	S—Ch	Ch—I			
CLC2	a	65.7		73.1	42.46		1.02
	b		56.4	68.2		−0.35	−1.4
	c	64.5		69.5	11.3		1.01
CLC3	a	69.7		75.4	48.36		1.19
	b		58.8	71.0		−0.61	−1.47
	c	67.9		74.9	15.48		1.33
CLC4	a	71.3		77.0	52.38		1.26
	b		60.5	72.1		−0.74	−1.55
	c	70.3		75.3	17.49		1.43
CLC5	a	78.6		84.9	56.95		1.30

	b		64.9	81.4	−0.83	−1.70
	c	77.9		84.8	18.16	1.51

a: the first heating cycle; b: the first cooling cycle; c: the second heating cycle;

Cr: crystalline; S: smectic; Ch: cholesteric; I: isotropic

3.4 Effect of spacer length of mesogenic groups on LC behaviors

In addition, according to Table 2, we have already seen that the transitional behavior of CLCs depends strongly on the length and the spacer of methylene groups in the chemical structure. The results revealed that the spacer length of mesogenic groups markedly influenced liquid crystalline properties. Compared to CLC2, CLC5 exhibits the spacer length of mesogenic groups and contains more methylene groups which can weaker the function between the molecules in cholesteric liquid crystals and contribute to the molecular anisotropy. The transition temperatures and the enthalpy changes of the CLC5 (crystal-smectic transition, smectic-cholesteric transition, cholesteric-isotropic transition) are considerably higher than those of the CLC2. Therefore, the transition temperatures and the enthalpy changes from CLC1 to CLC5 can rapidly strengthen with increasing spacer length containing more methylene atoms.

4. Conclusion

In summary, we first developed and synthesized a series of CLCs containing unsaturated linkages by the super esterification method. Compared to acylation method, the super esterification method exhibited higher yield, lower toxicity and simpler operation process and the yield of CLC could be up to 76%. In addition, the SCLCPs with alternating flexible and rigid segments was fabricated by addition reaction. On the basis of DSC and POM results, the CLCs apart from CLC1 prepared by the method showed typical cholesteric textures. In comparison, the spacer length plays a role in determining the optical and liquid crystal properties of CLCs through controlling the shape of the molecules. It can be predicted that the fabrication of the self-assembled SCLCPs will exhibit some advantage as follows. First, the introduction of side-chain CLC mesogenic groups is benefit of increasing blood compatibility for PDMS. Second, the side-chain rigid structure is benefit of developing usage temperature for PDMS. Finally, the flexible back-chain of PDMS is benefit of formation of cholesteric liquid crystal.

Acknowledgements

This work was supported by the National Nature Science Fund of China (No. 31000446), and the Fundamental Research Funds for the Central Universities (No. 21612440).

References

[1] X.J. Wang, Q.F. Zhou: *Liquid Crystalline Polymers* (World Scientific Publishing, Singapore 2004), p.1-3.

[2] A.M. Donald, A.H. Windle and S. Hanna: *Liquid Crystalline Polymers*. (Cambridge university press, Section edition 2006), p.4.

[3] T. Itahara, S. Furukawa, K. Kubota, et al. Cholesteryl benzoate derivatives: synthesis, transition property and cholesteric liquid crystal glass, Liquid Crystals, Vol.40 (2013), 589-598.

[4] J.B. Guo, F. Liu, L.P. Zhang, et al. Preparation and reflectance properties of new cholesteric liquid crystalline copolymers containing cholesteryl group, Polymer Engineering & Science, Vol.49 (2009), 937-944.

[5] P. Masson and D. Guillon: Molecular design of thermotropic ionic side-chain liquid crystalline polymers, Molecular Crystals and Liquid Crystals Science and Technology, Vol.362 (2001), 313-346.

[6] G. Tomasz and S. Włodzimierz: Side-chain liquid crystal polymers (SCLCP): methods and materials. An overview, Materials, Vol.2 (2009), 95-128.

[7] P.J. Collings and M. Hird: *Introduction to Liquid Crystals* (Taylor & Francis: London 1997), p.174.
[8] G. H. Mehl, F. Valvo, D. Lacey, et al. Properties of side chain liquid crystal polyesters containing chiral groups in the main chain, Polymer Engineering & Science, Vol.36 (1996), 2921-.
[9] G.H. Hsiue, Y.A. Sha, S.J. Hsieh, et al. Synthesis and characterization of halogen-containing ferroelectric liquid crystals and side chain liquid crystalline polymers, Liquid Crystals, Vol.28 (2000), 365-374.
[10] T. Ganicz, W.A. Stanczyk, N.K. Gladkova, et al. Vinylsilanes as Monomers for Side Chain Polymer Liquid Crystals, Macromolecules, Vol.33 (2000), 289-293.
[11] J.M. Pollino and M. Weck: Non-covalent side-chain polymers: design principles, functionalization strategies, and perspectives, Chemical Society Reviews, Vol.34 (2005), 193 -207.
[12] W. Huang and C.D. Han: Synthesis of combined main-chain/side-chain liquid-crystalline polymers via self-assembly, Macromolecules, Vol.39 (2006), 4735-4745.
[13] D Hartono, Hody, and K.L. Yang: The effect of cholesterol on protein-coated gold nanoparticle binding to liquid crystal-supported models of cell membranes, Biomaterials, Vol.31 (2010), 3008-3015.
[14] N. Canilho, E. Kase1mi, A. Dieter Schlu1ter, et al. Comblike liquid-crystalline polymers from ionic complexation of dendronized polymers and lipids, Macromolecules, Vol.40 (2007), 2822-2830.
[15] P.R. Pandey and S. Chauhan: Membranes for gas separation, Progress in Polymer Science, Vol.26 (2001), 853-893.
[16] A. Simmons, A.D. Padsalgikar, L.M. Ferris, et al. Biostability and biological performance of a PDMS-based polyurethane for controlled drug release, Biomaterials, Vol.29 (2008), 2987-2995.
[17] L.H. Li, M. Tu, S.S. Mou, et al. Preparation and blood compatibility of polysiloxane /liquid-crystal composite membranes, Biomaterials, Vol.22 (2001), 2595-2599.
[18] G.J. Dahe, R.S. Teotia, S.S. Kadam, et al. The biocompatibility and separation performance of antioxidative polysulfone/vitamin E TPGS composite hollow fiber membranes, Biomaterials, Vol.32 (2011), 352-365.
[19] S.L. Peterson, A. McDonald and P.L. Gourley: Poly (dimethylsiloxane) thin films as biocompatible coatings for microfluidic devices: cell culture and flow studies with glial cells, Journal of Biomedical Materials Research. Part A, Vol.72 (2004), 10-18.
[20] B.R. Winton, M. Ionescu, C. Lukey, et al. Micro-patterned surface modification of poly (dimethylsiloxane) (PDMS) substrates for tissue engineering, Advanced Science Letters, Vol.4 (2011), 431-436.
[21] L.Y. Zhang, S. Chen, Z.H. Shen, et al. Synthesis and properties of a series of mesogen-jacketed liquid crystalline polymers with polysiloxane backbones, Macromolecules, Vol.43 (2010), 6024-6032.
[22] H. Yang, M.X. Liu, Y.W. Yao, et al. Polysiloxane-based liquid crystalline polymers and elastomers prepared by thiol–ene chemistry, Macromolecules, Vol.46 (2013), 3406-3416.
[23] C. Grondal: 4-Dimethylamino-pyridine (DMAP), Synlett, Vol.10 (2003), 1568-1569.
[24] C. Gilon, Y. Klausner and A. Hassner: A novel method for the facile synthesis of depsipeptides, Tetrahedron Letter, Vol.40 (1979), 3811-3815.
[25] T.D. Bailey and K. Charles: Process for substituting and dequaternizing pyridylethyl quaternary salts of pyridine and by pyridine bases. US Patent 4158093. (1979).
[26] B.T. Low, Y.C. Xiao, T.S. Chung, et al. Simultaneous occurrence of chemical grafting, cross-linking, and etching on the surface of polyimide membranes and their impact on H_2/CO_2 separation, Macromolecules, Vol.41 (2008), 1297-1309.
[27] W.J. Koros and R.J. Mahajan: Pushing the limits on possibilities for large scale gas separation: which strategies? Journal of Membrane Science, Vol.175 (2000), 181-196.
[28] H.X. Rao, Z.Y. Zhang, C. Song, et al. Polydimethylsiloxane/liquid crystal cross-linked

membranes: Preparation, characterization and oxygen transport properties, Reactive and Functional Polymers, Vol.71 (2011), 537-543.
[29] I.C. Khoo and S.T. Wu: *Optics and Nonlinear Optics of Liquid Crystals* (World Scientific, Singapore 1993).
[30] I. Dierking: *Textures of Liquid Crystals* (WILEY-VCH 2003).