

SYNTHESIS AND CHARACTERIZATION OF β -DIKETONE BASED SIDE CHAIN LIQUID CRYSTALLINE POLYSILOXANES

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ABSTRACT

A new type of β -diketone based side chain liquid crystalline polysiloxanes (DKLCP) with different length of flexible spacers and end groups have been synthesized by hydrosilation reaction. This is liquid crystal polymers (LCP) using coordinating β -diketone ligand as mesogens. The phase behaviour of DKLCP polymers was studied by differential scanning calorimetry and polarizing microscopy. X-ray diffraction investigations demonstrated that the polysiloxanes with sufficiently long flexible spacers were smectic liquid crystal polymers, while those with much shorter spacers were nematic ones.

Interest in thermotropic LCP is continuously increasing^[1,2,3,4]. The goal of melt spinning a fiber, with comparable high strength and high modulus properties to "Kevlar", is the initial incentive for research on thermotropic polyesters, which are closely related in structure to the "Kevlar" polyamide. Aromatic polyesters and copolyesters are the intensively studied main chain thermotropic LCP. On the other hand, side chain LCP, which are characterized by the combination of properties of liquid crystals and polymers, are becoming more and more important because of their potential uses as thermorecording materials, liquid crystalline photoelastomers, nonlinear optical materials and in display devices, etc.^[5,6,7]. Since Finkelmann and Ringsdorf pointed out that flexible spacers should be inserted between the main chain and the side chain mesogens. In order to decouple the motions of polymer main chains from that of side groups^[8], systematic investigations on side chain thermotropic LCP have been made during recent years^[2,9]. New side chain LCP without flexible spacers have also been reported by Zhou et al.^[10].

Polymer main chain and side chain mesogens play an important role in determining the properties of side chain LCP. Though many LCP using conventional rigid rod-like molecules (usually contain $-\text{COO}-$, $-\text{CH}=\text{N}-$, $-\text{N}=\text{N}-$, $-\text{CH}=\text{CH}-$ groups in their rigid part as linkage groups) as side chain mesogens, have been studied, continuous efforts are being made in searching for new kinds of side chain mesogens with new properties^[11,12,13].

β -Diketones are versatile coordinating ligands, they can form complexes with almost all kinds of metal ions^[14]. Recently, a series of publications have revealed that dibenzoyl methane derivatives carrying long alkyl or alkoxyl substituents at 4,4'-positions may exhibit either double melting behaviour or liquid crystallinity and their corresponding copper complexes were discotic liquid crystals^[15,16,17]. In spite

of this, the attachment of β -diketone mesogens or their copper complex discogens to polymer backbone as side chain mesogens has not been reported before. In view of metal-coordinated LCP possessing good conducting or semi-conducting or high paramagnetic properties^[18,19,20], the authors have prepared the LCP with low molecular β -diketone compounds attached to polysiloxanes via hydrosilation reaction. The liquid crystallinity combined with the complexibility of the mesogenic ligand polysiloxanes make themselves very attractive. They may form liquid crystalline photoelastomers by adequately crosslinking through complexation etc.. We have reported that suitable amount of europium complexed ligand polysiloxanes showed good fluorescent properties while still keeping the liquid crystallinity^[21] and have shown that the square planar copper complexes of DKLCP were still liquid crystal polymers^[22]. This paper only describes the synthesis and characterization of the mesogenic ligand polysiloxanes.

EXPERIMENTAL

Materials

Poly (hydrogenmethyl-co-dimethylsiloxane)s were obtained from Beijing Second Chemical Factory. p-Hydroxy methylbenzoate and allyl bromide were commercially available.

Synthesis

The following chemicals used in this work were all synthesized by the methods described in literature and are listed in Table 1.

Table 1 Chemical materials synthesized in this work

Chemicals	Reference
Poly (hydrogenmethylsiloxane)	23
p-Hydroxyacetophenone	24
Allyl 3-bromopropyl ether	25
Undecenyl bromide	26
Dicyclopentadienylplatinum (II) dichloride	27
p-Alkoxyacetophenones	
Methyl p-alkoxybenzoates	

p-Alkoxyacetophenones and Methyl p-alkoxybenzoates were synthesized following the standard Williamson reaction procedure using ethanol or methanol as solvent and potassium hydroxide as the base agent.

The low molecular β -diketone compounds were synthesized by the method described in literature^[28]. A typical example (compound 3c in Table 2) was as follows: A mixture of 12.0g (0.039 mol) of p-undecenyloxybenzoate and 12.2g (0.040 mol) of p-dodecyloxyacetophenone dissolved in 100ml of dimethoxyethane was refluxed for three hours in the presence of 3.5g of 80% sodium hydride (0.11 mol) and then stirred overnight. 10 ml of water was added carefully to the resulting yellow stew, and then 50 ml of 4N hydrochloric acid was added. The organic layer was separated and the water layer was extracted with dichloromethane, the combined organic solution was washed with water until neutral, evaporation gave

the crude product. By recrystallization from ethanol and subsequently from cyclohexane it gave a white solid powder of 3c in 80% yield. The purity of these β -diketone compounds were characterized by elemental analysis, thin layer chromatography and NMR spectroscopy. All these compounds gave enol — OH and enol =CH NMR signals at 17.05 and 6.68 ppm, respectively. Absorption peak at 784 cm^{-1} in the IR spectra was characteristic of =C — H vibration in β -diketone molecules. Their elemental analysis data were listed in Table 2.

Side chain DKLCP were synthesized by the following typical procedure: To a three neck, round bottom flask equipped with a refluxing condenser and a magnetic stirrer, 3.00g of compound 3c (0.005 mol) and 0.03g of poly (hydrogenmethylsiloxane) dissolved in toluene (freshly distilled after refluxing for several hours in the presence of sodium) was added. After the solution started refluxing, 1 ml of dicyclopentadienylplatinum(II) dichloride in dichloromethane (0.54mg/ml) was syringed into the reaction system. A nitrogen atmosphere was maintained throughout the whole reaction process. 48 hours later, the reaction solution was cooled down and the polymer precipitated out in methanol. To ensure complete removal of low molecular compounds, the precipitated polymer was dissolved in dichloromethane and precipitated in methanol again, and this process was repeated three times. The polymer was slightly yellowish powder. The completeness of this reaction was evidenced by the disappearance of strong IR absorption peak of Si-H group at around 2140 cm^{-1} and the disappearance of the NMR signals of $\text{CH}_2=\text{CH}-$ between $\delta = 5 - 6$ ppm. The characteristic NMR and IR spectroscopic data of DKLCP polymers were listed in Table 3.

Measurements

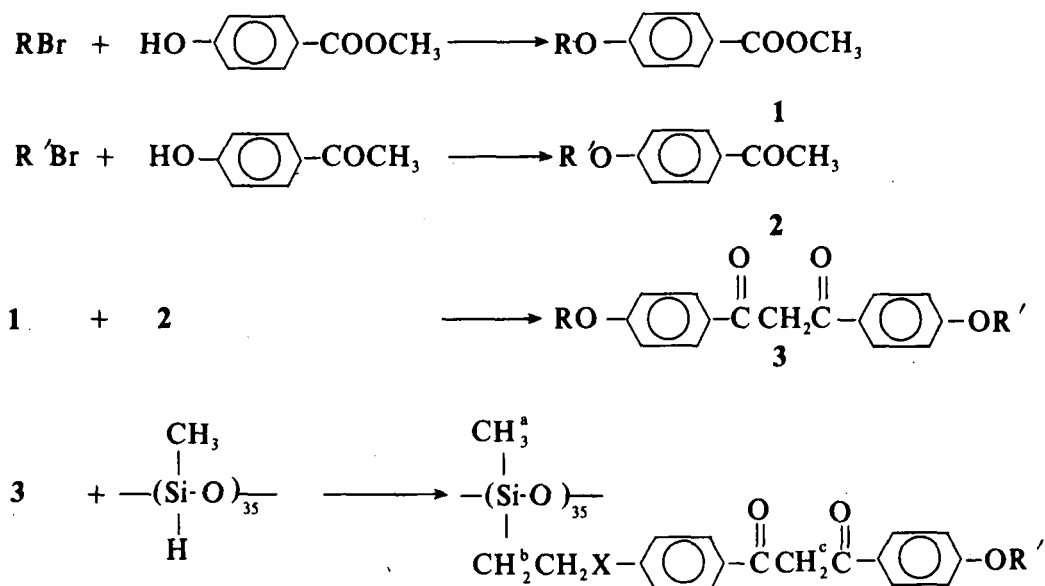
The elemental analysis was made by a ST-02 elemental analyzer. IR spectra were recorded on PE-983G IR spectrometer. NMR spectra were performed with a 100 MHz NMR spectrometer. The polarizing microphotographs were taken on an Olympus BH-2 optical polarizer at room temperature. DSC measurements were made on PE DSC-4. The X-ray diffraction patterns were obtained on Rigaku D/max-3B diffractometer, Cu-K α radiation with a wavelength of 0.154 nm was used.

RESULTS AND DISCUSSION

Polysiloxanes, polyacrylates and polymethacrylates have been widely used as the main chain component in side chain LCP. Side chain liquid crystalline polysiloxanes, which are of great interest due to their lower T_g and higher thermal stabilities, are usually prepared via hydrosilation reaction between Si-H group and terminal double bond using $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ as the catalyst. In some cases, however, it is very difficult to repeat the preparation by the same procedure, product are sometimes even crosslinked. This was ascribed to the nature of the catalyst used^[29]. It should be pointed out the conventional hydrosilation catalyst H_2PtCl_6 is not applicable in this system because of the oxidative properties of Pt^{4+} ion and the reductive properties of β -diketone molecules. When $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in isopropanol was used as the catalyst, dark grey polymers were usually obtained in our experiments, partially hydrosilated polysiloxanes and partially oxidized

products (acids) were the main products. In the hydrosilation reaction of β -diketone compound 4b, cleavage of the allyl ether was observed. When $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in isopropanol was put together with poly(hydrogenmethylsiloxane), evolving of gas bubbles from the solution was often observed, this may be that some of the Si-H bonds were destroyed in this condition. Hence, dicyclopentadienylplatinum (II) dichloride, which has been used in the hydrosilation of compounds with terminal cyano groups and 2,5-disubstituted 1,3-dioxane mesogens^[13,30], was selected as the reaction catalyst and has been proved to be successful. In the preparation of the side chain DKLCP, the synthetic route illustrated in Scheme 1 was employed.

Scheme 1: Synthetic route for DKLCP



X, R, R': see Table 2 and Table 4

Despite that many of the β -diketone compounds having the same alkoxy substituents ($\text{R}=\text{R}'$ in compound 3 as illustrated in Scheme 1) were reported to be smectic liquid crystals when the number of carbon atoms in R was equal to or greater than 8^[15,16], all these asymmetrical β -diketone compounds synthesized in this work showed no liquid crystallinity. It is interesting that the newly prepared compound 3b (Table 2) has a melting point of 69 °C, and its melting point gradually increased to a constant of 83–85 °C after storing for enough time. NMR, IR and mass spectroscopic studies showed that the spontaneous cleavage of the allyl ether in compound 3b was responsible for this phenomenon. Table 2 presented the elemental analysis data and the melting points of the low molecular β -diketone compounds.

The phase transition temperatures of the side chain liquid crystalline polysiloxanes and co-polysiloxanes with different length of flexible spacers and end groups were listed in Table 4. It can be seen from Table 4 that all the polysiloxanes except polymer 4a, which has a much shorter flexible spacer, have

Table 2 Elemental analysis data and the melting points of the low molecular β -diketone compounds

No.	R	R'	C% Found (calcd)	H% Found (calcd)	m. p. *($^{\circ}$ C)
3a	$\text{CH}_2=\text{CHCH}_2$	$\text{C}_{12}\text{H}_{25}$	77.70 (77.53)	8.88 (8.90)	82
3b	$\text{CH}_2=\text{CHCH}_2\text{OCH}_2\text{CH}_2$	$\text{C}_{12}\text{H}_{25}$	75.40 (75.53)	8.90 (8.70)	69
3c	$\text{CH}_2=\text{CH}(\text{CH}_2)_9$	$\text{C}_{12}\text{H}_{25}$	79.33 (79.10)	9.86 (9.79)	83
3d	$\text{CH}_2=\text{CH}(\text{CH}_2)_9$	C_6H_{13}	79.66 (79.41)	9.94 (10.00)	68
3e	$\text{CH}_2=\text{CH}(\text{CH}_2)_9$	$\text{C}_{14}\text{H}_{29}$	78.07 (77.99)	8.95 (9.01)	84

* The melting points were measured on a microscope with a hot plate and were not corrected

Table 3 Characteristic NMR and IR data of DKLCP polymers

No.	$\delta(\text{H}^a)$	$^1\text{H-NMR}$ (H^b)	$\delta(\text{H}^c)$	IR $\gamma(\text{C}=\text{O})$	IR $\gamma(\text{C}-\text{H}^c)$
4a	0.17	0.63	6.68	1602	784
4b	0.11	0.63	6.68	1604	784
4c	0.09	0.63	6.68	1603	784

δ in ppm, γ in cm^{-1}

Table 4 Phase transition temperatures of side chain DKLCP

No.	X	R'	Phase transition temperatures in $^{\circ}\text{C}$ (by DSC)			
4a	CH_2O	$\text{C}_{12}\text{H}_{25}$	K 52.7	LC 68.3	I	
4b	$\text{CH}_2\text{OCH}_2\text{CH}_2\text{O}$	$\text{C}_{12}\text{H}_{25}$	K 53.7	S 83.3	I	
4c	$(\text{CH}_2)_9\text{O}$	$\text{C}_{12}\text{H}_{25}$	K 43.2	S 90.0	I	
4d	$(\text{CH}_2)_9\text{O}$	C_6H_{13}	K 61.0	S 83.0	I	
4e	$(\text{CH}_2)_9\text{O}$	$\text{C}_{14}\text{H}_{29}$	K 74.0	S 90.0	I	
4b*	$\text{CH}_2\text{OCH}_2\text{CH}_2\text{O}$	$\text{C}_{12}\text{H}_{25}$	K 44.0	S 77.4	I	
4b**	$\text{CH}_2\text{OCH}_2\text{CH}_2\text{O}$	$\text{C}_{12}\text{H}_{25}$	K 55.6	S 77.6	I	

* prepared from poly (hydrogenmethyl-co-dimethylsiloxanes), Si-H content was determined by $^1\text{H-NMR}$ to be 82%

** prepared from poly (hydrogenmethyl-co-dimethylsiloxane), Si-H content was determined to be 64%

K: crystalline, S: smectic liquid, LC: liquid crystalline phase, I: isotropic mesophase.

higher clearing temperatures than the melting points of their low molecular counterparts, and that the attachment of potentially mesogenic β -diketone compounds to polysiloxane backbone gave rise to the formation of side chain LCP.

Typical DSC heating curves of the polysiloxane samples were shown in Fig.1. It was confirmed by the polarizing microscopic observations that the first small endothermic transitions in the first heating runs were the transitions from crystalline to liquid crystalline state and the last endothermic transitions were the transitions from crystalline state to isotropic liquids (curve a, b, and c in Fig. 1).

Polymer 4a gave an additional endothermic peak at 61.8 °C, this transition needs to be further investigated. One of the most important peculiarities of side chain liquid crystal polymers is that liquid crystalline structures of these polymers can be preserved in their solid state on cooling. In the cooling run and in the second heating scan, polymers 4a, 4b and 4c gave just one thermal transition, which meant that the polymers did not crystallize on cooling from their isotropic phases and supercooled mesophase structures were thus formed. This is the basis for carrying out X-ray diffraction measurements of these supercooled polysiloxane samples at room temperature.

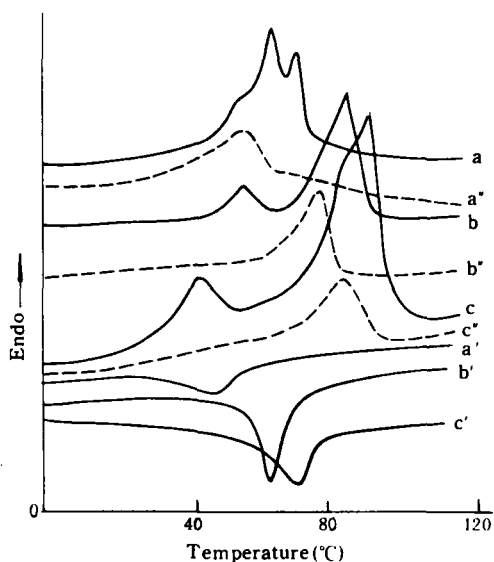


Fig. 1 DSC curves of DKLCP polymers

a, b, and c: first heating scan of polymer 4a, 4b, and 4c respectively

a', b', and c': cooling run of polymer 4a, 4b, and 4c respectively

a'', b'', and c'': second heating scan of polymer 4a, 4b, and 4c respectively

heating rate: 20 °C/min

cooling rate: 10 °C/min

Fig. 2 presented the polarizing microphotographs of polymers 4a, 4b and 4c. These optical textures were not very typical, it was very difficult to judge from these microphotographs whether these polymers were of the smectic or nematic liquid crystal type. When compared with the DSC measurements and the X-ray diffraction results of polymer 4a, 4b, and 4c, it could be concluded that polymer 4b and 4c were smectic polymer liquid crystals, while polymer 4a was nematic polymer liquid crystal.

Fig. 3 and Fig. 4 display the X-ray diffraction patterns of polymer 4a, 4b and 4c, which were measured on samples of the supercooled mesophase, obtained by cooling from their isotropic melts to room temperature. All polymers exhibited broad diffraction peaks in the wide angle region, approximately 21°, the corresponding d value of about 4.1 Å represented the distance between two adjacent side chain mesogens. The sharp reflections in the small angle region were

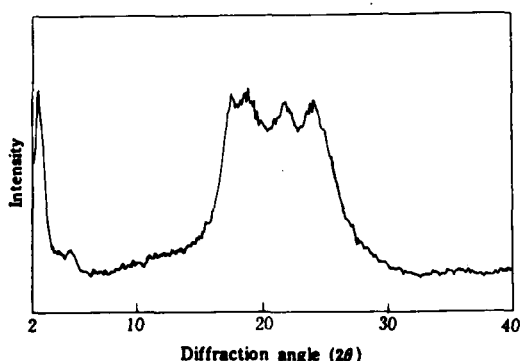


Fig. 5 X-ray diffraction patterns of polymer 4c annealed at 65 °C for 12 hours after cooling from its isotropic phase

peak in this small angle region, indicating the presence of a nematic mesophase. Fig. 5 gave the X-ray diffraction pattern of polymer 4c after cooling from its isotropic phase and annealed at 65 °C for 12 hours. As can be seen from Fig. 5, annealing greatly sharpened the diffraction peak at $2\theta = 2.480^\circ$, indicating the formation of a much more ordered smectic mesophase after the annealing treatment. These results demonstrated that long flexible spacers favor the formation of smectic mesophases. The small angle X-ray diffraction data of polymers 4a, 4b and 4c were given in Table 5.

Table 5 X-ray diffraction data of DKLCP at lower diffraction angles

No.	2θ	$d(\text{\AA})$	I/I_0
4a	—	—	—
4b	2.080	42.440	100
	2.320	38.050	95
	2.620	33.694	96
4c	2.260	39.060	100
	2.360	37.405	99
4c*	2.480	35.595	99
	4.660	18.947	29
	4.880	18.094	29

*: Annealed for 12 hours at 65 °C after cooling from its isotropic phase.

Keywords :

β -Diketone based side chain liquid crystal polysiloxanes.

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