Preparation and Characterization of Organosiloxanes with A Liquid Crystalline Trans-4-Pentylcyclohexanoate Moiety

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ABSTRACT

In the course of this research, we successfully created three series of liquid crystalline compounds featuring the trans-cyclohexane structure. One series of compounds featured a double bond at the terminal position of the molecules, whereas the remaining two series incorporated disiloxane and trisiloxane groups. Each series comprised five spacers of different lengths, specifically 3, 4, 5, 6, and 11 methylene units. We identified the structures of the synthesized compounds using Nuclear Magnetic Resonance spectroscopy and characterized their liquid crystalline behavior through thermal analysis and polarized optical microscopy. The results revealed that both the length of the spacer and the presence of siloxane groups significantly influenced the liquid crystal phase transitions, transition temperatures, and temperature ranges. These findings provide valuable insights for designing and developing new liquid crystal materials with tailored properties for various applications.

Keywords: Siloxane, Spacer, Liquid crystalline.

INTRODUCTION

When comparing small molecule liquid crystals with side-chain polymer liquid crystals[1,2,5,10,15,16], small molecules have the advantages of low viscosity and faster photoelectric response rates. Conversely, side-chain polymers exhibit increased viscosity and slower response rates; however, their polymer backbone plays a crucial role in enhancing the stability of the liquid crystal phase and extending its temperature range. Among the primary backbones, including polyacrylate, polymethacrylate, and polysiloxane, it is polysiloxane that demonstrates the highest degree of flexibility in its siloxane molecular chains, thus enabling the expansion of the liquid crystal phase's temperature range.

Professor Coles synthesized disiloxane compounds containing a liquid crystal base with a 4-cyanobiphenyl group, all of which exhibited a smectic A (SA) phase. Additionally, compounds with a liquid crystal base containing a chiral group were synthesized, and these compounds displayed chiral

smectic C (Sc*) liquid crystal phases. These liquid crystal disiloxane compounds not only demonstrated the fast response speed of small molecule liquid crystals but also exhibited arrangement properties similar to those of high molecular weight liquid crystals, making them highly promising for various applications[11,14].

In this study, a liquid crystal base containing trans-cyclohexane will be designed. Trans-cyclohexane offers numerous conformational isomers, which can prevent the occurrence of side-chain crystallization phenomena. Moreover, trans-cyclohexane liquid crystals exhibit low viscosity, high thermal stability, and easily form nematic structures at room temperature. Based on these advantages, they could become commonly used liquid crystal materials for liquid crystal displays[3,4,6-9,12,13,17]. In this study, we will introduce disiloxane and trisiloxane moieties at the end of the spacer to examine how the presence of siloxane groups affects both the liquid crystal phase and the temperatures associated with liquid crystal phase transitions.

MATERIAL AND METHODS

To identify and characterize intermediate products or monomers, the following testing instruments were employed:

1. Nuclear Magnetic Resonance Spectroscopy (NMR): A Varian 300 MHz NMR instrument was used.
2. Differential Scanning Calorimeter (DSC): A SEIKO SSC5200 DSC equipped with a Computer/Thermal Analyzer was utilized, and liquid nitrogen cooling was employed. The scanning rate was set at 10°C/minute. Phase transition temperatures of the test samples were determined from the extremum of the DSC curves, and the enthalpy change (H) was determined by analyzing the area under the peaks.
3. Optical Polarization Microscope: A Zeiss Axiophot optical microscope with magnifications ranging from 40 to 1000 times was used. A Mettler FP82 temperature controller was also employed.

All chemicals were purchased from Merck, Aldrich, TCI, Janssen, and Petrarch companies and used without purification. All solvents were obtained from Merck or Fisher companies. Anhydrous CH_2Cl_2 was dried over calcium hydride, anhydrous toluene, and tetrahydrofuran (THF) were dried over sodium metal. All drying processes involved the use of drying tubes containing calcium chloride, and the solvents were heated under reflux with nitrogen gas for several hours. After distillation under nitrogen gas, the solvents were used immediately or sealed and stored in a desiccator.

Synthesis
4-Bromo-l-butene (compound 1)
5-Bromo-1-pentene (compound 2)
6-Bromo-1-hexene (compound 3)

The synthesis method for compounds 1 to 3 is the same. To illustrate, we will use the synthesis of compound 3 as a representative example: 1,6-dibromohexane (15 mL, 0.0975 moles) is placed into a 100 mL two-neck flask and stirred while purging with nitrogen gas. The mixture is then heated to 200°C. Slowly, HMPT (hexamethylphosphortriamide, 14 mL, 0.0805 moles) is added dropwise to the reaction flask. During this process, the formation of brown carbon residues and white smoke may be observed. Subsequently, a concentrated, transparent, colorless liquid is obtained. One more vacuum distillation is performed, resulting in a 53% yield of compound 3. The chemical structure of the compound was verified through ^{1}H-NMR spectroscopy. 3-Bromo-1-propene was purchased from Merck, Aldrich.

10-Undecenyl-l-tosylate (compound 4)
The synthesis of compound 4 involves placing p-toluene sulfonyl chloride (27g, 0.142 moles) into a 500 mL two-neck flask and adding 50 mL of anhydrous pyridine and 100 mL of anhydrous dichloromethane. After thorough stirring, 10-undecen-1-ol (20 g, 0.118 moles) is slowly added dropwise under ice bath conditions. The reaction is allowed to proceed for 24 hours. Afterward, the precipitate is filtered, and the filtrate is extracted with a CH_2Cl_2/6N HCl solution. The organic phase is then dehydrated using anhydrous magnesium sulfate, followed by filtration and concentration. Then, 50 mL of n-hexane is added, and the precipitate is allowed to form. After filtration and concentration, a transparent oil-like compound 4 is obtained with a yield of 80%. The compound's chemical structure was confirmed using 1H-NMR spectroscopy.
4-(2-Propenyloxy)phenol(compound 5)
4-(3-Butenyloxy)phenol (compound 6)
4-(4-Pentenyloxy)phenol (compound 7)

4-(5-Hexenyloxy)phenol (compound 8)
4-(10-Undecenyloxy)phenol (compound 9)

The synthesis method for compounds 5 to 9 is the same. To illustrate, we will use the synthesis of compound 7 as a representative example: Hydroquinone (3 g, 0.0272 moles), KOH (2 g, 0.0357 moles), and KI (0.2 g) are placed into a 500 mL two-neck flask with 300 mL of C_2H_5OH as the solvent. The mixture is heated under reflux for half an hour, then 5-bromopentene (2.7 g, 0.0182 moles) is added, and the reflux is continued for approximately 48 hours. After cooling and concentrating the reaction mixture, it is extracted with a CH_2Cl_2/6N HCl solution. The organic phase is then dehydrated using anhydrous magnesium sulfate, followed by filtration and concentration. The mixture is then passed through a silica gel column and eluted using a combination of n-hexane and ethyl acetate. This yields a white solid compound 7 with a 43% yield and a melting point of 50.3°C. The compound's chemical structure was confirmed using ^{1}H-NMR spectroscopy.

4-(2-Propenyloxy)phenyl trans-4-n-pentylcyclohexanoate (compound 1M)
4-(3-Butenyloxy)phenyl trans-4-n-pentylcyclohexanoate (compound 2M)
4-(4-Pentenyloxy)phenyltrans-4-n-pentylcyclohexanoate (compound 3M)
4-(5-Hexenyloxy)phenyl trans-4-n-pentylcyclohexanoate (compound 4M)
4-(10-Undecenyloxy)phenyltrans-4-n-pentylcyclohexanoate (compound 5M)

The synthesis method for compounds 1M~5M is the same. Taking the synthesis of compound 3M as an example:

4-(4-pentenyloxy)phenol (1.2 g, 0.0067 moles) and trans-4-n-pentyl-cyclohexane carboxylic acid (1.3 g, 0.0071 moles) are placed into a 250 mL two-neck flask with anhydrous dichloromethane as the solvent. Then, dicyclohexylcarbodiimide (DCC, 1.65 g, 0.008 moles) and dimethylaminopyridine (DMAP, 0.1 g) are added. The reaction is carried out at room temperature under nitrogen gas for 48 hours. After filtration and concentration, The mixture is then passed through a silica gel column and eluted using a combination of n-hexane and ethyl acetate. This yields a white solid compound 3M. The yield is 76%. The chemical shifts of compounds 1M-5M, 1M

of ^{1}H-NMR (CDCl$_3$, TMS, ppm): 0.85-2.25 (m, 20H, -CH$_2$- and -CH$_3$), 2.42(m, 1H, -OCOCH-), 4.53(t, 2H, -CH$_2$O-), 5.31(m, 2H, CH$_2$=), 6.08 (m, 1H, CH$_2$=CH-), 6.90(m, 4H, aromatic protons). 2M of ^{1}H-NMR (CDCl$_3$, TMS, δppm): 0.85-2.25 (m, 22H, -CH$_2$- and -CH$_3$), 2.42(m, 1H, -OCOCH-), 3.92(t, 2H, -CH$_2$O-), 5.01(m, 2H, CH$_2$=), 5.80 (m, 1H, CH$_2$=CH-), 6.90(m, 4H, aromatic protons). 3M of 1H-NMR (CDCl$_3$, TMS, δppm): 0.85-2.25 (m, 24H, -CH$_2$- and -CH$_3$), 2.42(m, 1H, -OCOCH-), 3.92(t, 2H, -CH$_2$O-), 5.01(m, 2H, CH$_2$=), 5.80 (m, 1H, CH$_2$=CH-), 6.90 (m, 4H, aromatic protons). 4M of ^{1}H-NMR (CDCl$_3$, TMS, δppm): 0.85-2.25 (m, 26H, -CH$_2$- and -CH$_3$), 2.42(m, 1H, -OCOCH-), 3.92(t, 2H, -CH$_2$O-), 5.01(m, 2H, CH$_2$=), 5.80 (m, 1H, CH$_2$=CH-), 6.90(m, 4H, aromatic protons). 5M of 1H-NMR (CDCl$_3$, TMS, δppm): 0.85-2.25 (m, 36H, -CH$_2$- and -CH$_3$), 2.42(m, 1H, -OCOCH-), 3.92(t, 2H, -CH$_2$O-), 5.01(m, 2H, CH$_2$=), 5.80(m, 1H, CH$_2$=CH-), 6.90(m, 4H, aromatic protons).

(5) Liquid crystal siloxane compounds (1A~5A, and 1B~5B)

Siloxane dimers, obtained from 1M~5M, are labeled as 1A~5A, while siloxane trimers are denoted as 1B~5B. Compounds 1A~5A and 1B~5B were synthesized using an identical procedure. The synthesis of compounds 3A and 3B is detailed below.

The terminal alkenyl precursor compound 3M (0.2864 g, 0.0008 moles) and pentamethyldisiloxane (0.14 g, 0.0009 moles; if 3B was added with 1,1,13,3,5,5-heptamethyltrisiloxane 0.21 g, 0.0009 moles) were placed in a 50-milliliter two-neck flask and connected to a reflux condenser. Nitrogen gas was passed through the flask, and about 10 mL of anhydrous toluene was included as the solvent. The mixture was stirred to dissolve, and a catalyst complex consisting of platinum and divinyltetramethyldisiloxane was prepared in a separate 10 mL of anhydrous toluene, yielding a diluted solution. A syringe was used to extract 0.25 mL of the solution and placed into a reaction vial. The reaction was heated to 80°C and allowed to continue for 48 h with continuous monitoring of its progression using TLC (Thin-Layer Chromatography).

Following the reaction's conclusion, the toluene solvent was evaporated, and the product was subjected to purification via column chromatography on a silica gel column, employing ethyl acetate/n-hexane as the elution solvent. The residual solvent was eliminated in a vacuum oven, yielding the

white solid product 3A. The yield was 67%. ^{1}H-NMR (CDCl$_3$, δppm): 0.0(m, 15H, Si(CH$_3$)$_3$O-Si(CH$_3$)$_2$O-), 0.53(m, 2H, -Si(CH$_3$)$_2$-CH$_2$-), 0.85-2.25(m, 26H,-CH$_2$- and -CH$_3$), 2.42(m, 1H, -OCOCH-), 3.92(t, 2H, -CH$_2$O-), 6.90(m, 4H, aromatic protons). Compound 3B yield was 59%, ^{1}H-NMR (CDCl$_3$, δppm): 0.0 (m, 21H, Si(CH$_3$)$_3$O-Si(CH$_3$)$_2$O-Si(CH$_3$)$_2$O-), 0.53 (m, 2H, -Si(CH$_3$)$_2$-CH$_2$-), 0.85-2.25(m, 26H,-CH$_2$- and -CH$_3$), 2.42(m, 1H, -OCOCH-), 3.92(t, 2H, -CH$_2$O-), 6.90(m, 4H, aromatic protons).

RESULTS AND DISCUSSIONS

In the course of this research, we successfully created three series of liquid crystalline compounds featuring the trans-cyclohexane structure. Each series consisted of five distinct spacer lengths, specifically containing 3, 4, 5, 6, and 11 methylene units. Compounds of 1M~5M included a terminal double bond in their molecular structure. Compounds of 1A~5A, the double-bond tail end was replaced with a dimethylsiloxyl group. Compounds of 1B~5B, the end-tail group was substituted with a trimethylsiloxyl group. The structures of the synthesized compounds were identified using NMR spectroscopy, while their liquid crystalline behavior was characterized using thermal analysis and polarized optical microscopy. The study explored the impact of siloxane groups and flexible spacer lengths on the temperature ranges, transition temperatures, and phase transitions of liquid crystal phases.

The molecular structure and the overall synthetic methods for these compounds are depicted in Scheme 1. Compounds 1M-5M were reacted with pentamethyl disiloxane and heptamethyl trisiloxane using a hydrosilylation reaction catalyzed by a platinum divinyltetramethyldisiloxane complex in an anhydrous toluene environment. The advancement of the reaction was tracked through thin-layer chromatography (TLC), and the resulting products

were subsequently purified through silica gel column chromatography. After hydrosilylation of the precursor, the signals between 5~6 ppm corresponding to the alkene position disappeared, resulting in saturated alkyl groups. The ester group on trans-cyclohexane is more stable at the equatorial position due to steric hindrance, while the hydrogen at the 1,4 position is in the axial position and exhibits axial-axial hydrogen coupling on the 1~2.4 ppm signal peak in the spectrum, consistent with the coupling situation.
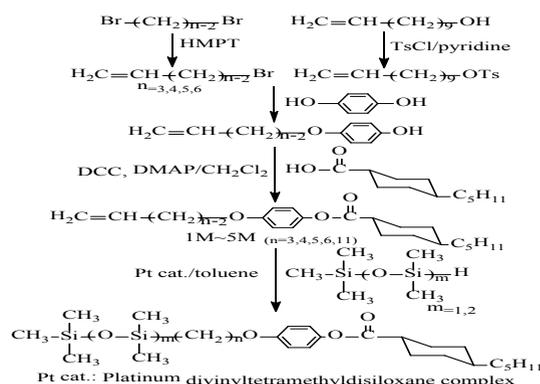
Scheme 1. Synthesis of compounds

Table 1 presents enthalpy changes and phase transition temperatures for five distinct end-tail alkene precursors, denoted as 1M through 5M, each featuring varying spacer lengths. All five compounds manifest enantiotropic nematic liquid crystal phases. Compounds 1M~4M display nematic liquid crystal phases across a temperature span of approximately 40°C. In contrast, compound 5M, characterized by a lengthier spacer (11 methylene units), exhibits both a SA liquid crystal phase and a higher molecular order SE liquid crystal phase. Notably, the nematic liquid crystal phase in compound 5M is suppressed, leading to a considerably narrower temperature range of approximately 6°C as compared to compounds 1M~4M.

Table 1: The changes of enthalpy and phase transition temperature of 1M-5M

Compound	n	Phase transition, (corresponding enthalpy change, Kcal/mole)
1M	3	(K 34.0(4.31) N 70.0(0.110) I)
		I 67.1(-0.101) N 13.0(-4.43) K)
2M	4	(K$_1$ 23.0(0.691) K$_2$ 66.0(1.25) N 87.1(0.420) I
		I 77.1(-0.171) N 49.0(-1.42) K$_2$ 7.00(-0.561) K$_1$
3M	5	(K 41.0(7.14) N 75.1(0.310) I)
		I 73.1(-0.311) N 18.0(-4.02) K
4M	6	(K 20.0(4.38) N 63.1(0.201) I)
		I 63.0(-0.271) N 18.0(-0.260) K$_2$ 3.00(-2.22) K$_1$
5M	11	(K 35.0(6.21) S_E 56.1(0.921) S$_A$ 66.1(0.380) N 73.1(0.391)I
		I 72.0(-0.421) N 66.1(-0.382) S$_A$55.2(-0.961) S$_E$ 15.0(-2.39)K

K=crystal, N=nematic, S$_A$=smectic A, S$_E$=smectic E, I=isotropic

The enthalpy changes and transition temperatures for compounds 1A to 5A are shown in Table 2, and for compounds 1B to 5B, they are provided in Table 3. It is noteworthy that compound 1A does not exhibit a liquid crystal phase, while compounds 2A to 4A and 1B to 4B all display a monotropic SA liquid crystal phase. On the other hand, compounds 5A and 5B, characterized by longer spacers, exhibit enantiotropic SA and SB liquid crystal phases. Fig. 1 illustrates the results of the DSC analysis conducted on compound 5A. Additionally, Fig. 2[A] and [C] showcase the SA and SB liquid crystal textures observed under polarized light microscopy during the cooling process after heating compound 5A to the isotropic temperature. Fig. 2[B] provides the texture transition from SA to SB at 49°C, resulting in a fan-like texture with visible cracks. Notably, compounds 2A and 4A exhibit lower melting points and crystallization temperatures compared to 1A and 3A, which is indicative of the persistence of the odd-even effect.
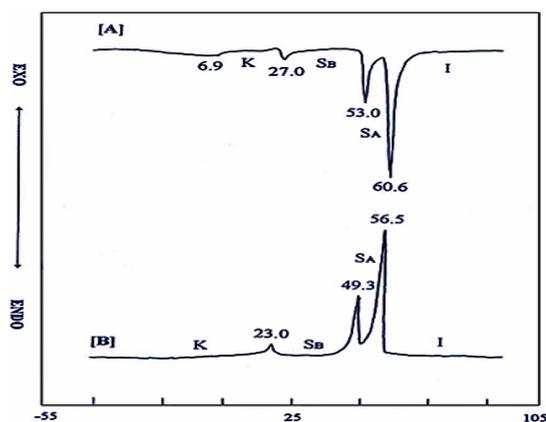

(a)

(b)

(c)

Fig. 2. Optical polarizing microphotography of 5A; (A) SA texture obtained after heating to 56°C; (B) transition from SA to SB texture upon cooling to 49°C; (C) SB texture obtained after cooling to 36°C

Fig. 1. DSC thermograms of compounds 5A (10/min)
[A] second heating scan
[B] cooling scan

Table 2: The changes of enthalpy and phase transition temperature of compounds 1A-5A

Compound	n	Phase transition, (corresponding enthalpy change, Kcal/mole)
1A	3	(K52.6(4.62) I
		I 34.1(-4.58) K
2A	4	(K 19.8(4.10) I
		I 2.20(-0.561) S_A-18.8(-2.81) K
3A	5	(K 43.4(8.78) I
		I 34.1(-1.07) S_A 3.10(-5.58) K
4A	6	K_1 0.600(3.01) K_2 30.8(1.81) I
		I 20.7(-0.851) S_A-44.2(-1.70) K
5A	11	K 27.2(0.170) S_B 53.0(0.560) S_A 60.6(1.76) I
		I 56.5(-1.58) S_A 49.3(-0.500) S_B 23.0(-0.190)K

K=crystal, S_A=smectic A, S_B=smectic B, I=isotropic

Table 3: The changes of enthalpy and phase transition temperature of compounds 1B-5B

Compound	n	Phase transition, (corresponding enthalpy change, Kcal/mole)
1B	3	K13.9(5.30) I
		I -11.9(-0.160) S_A -22.0(-4.01) K
2B	4	K 9.81(3.98) I
		I-7.70(-0.731) S_A -27.8(-2.88) K
3B	5	K 17.5(7.91) I
		I 16.3(-0.800) S_A -23.6(-4.87) K
4B	6	K-8.71(2.60) I
		I 6.60(-0.461) S_A -48.2(-1.80) K
5B	11	K 29.7(0.131) S_B 43.1(0.680) S_A 55.2(2.00) I
		I 51.5(-1.81) S_A 40.2(-0.400) S_B 25.2(-0.211)K

K=crystal, S_A=smectic A, S_B=smectic B, I=isotropic

Comparing Tables 1, 2, and 3, it is evident that the introduction of disiloxane moieties at the molecular terminus disrupts or transforms the original nematic liquid crystal phases (1M~5M) into more ordered SA liquid crystal phases. The addition of disiloxane moieties appears to increase the regularity of liquid crystal alignment, leading to the formation of layered phases. In terms of melting points and liquid crystal phase transition temperatures, compounds 1A~5A exhibit lower values than 1M~5M, suggesting that the flexibility of disiloxanes contributes to the reduction of these temperature parameters. Compounds 1B~5B display liquid crystal phase behavior similar to that of compounds 1A~5A. However, a notable difference is observed between compound 1A, which contains disiloxane moieties and does not exhibit a liquid crystal phase, and compound 1B, which contains trisiloxane moieties and exhibits a SA liquid crystal phase. From Tables 2 and 3, it is apparent that the introduction of siloxane moieties at the molecular terminus helps to reduce melting points and further lowers phase transition temperatures, with trisiloxanes having a more pronounced effect than disiloxanes.

CONCLUSION

This study resulted in the successful synthesis of a range of liquid crystal compounds (1M to 5M) with trans-cyclohexane structures with terminal double bonds. Through the hydrosilylation reaction, we introduced disiloxane and trisiloxane into compounds 1M~5M, resulting in disiloxane compounds (1A~5A) and trisiloxane compounds (1B~5B). Compounds 1M~4M mainly exhibit a nematic liquid crystal phase, while compound 5M, characterized by a longer spacer unit (11 methylene units), simultaneously displayed the SA liquid crystal phase and a higher molecular order SE liquid crystal phase. The majority of siloxane liquid crystal compounds exhibit the SA liquid crystal phase, while compounds 5A and 5B, featuring longer carbon chain spacers, also demonstrate the SB liquid crystal phase. In summary, both disiloxane and trisiloxane compounds exhibit similar liquid crystal behavior, but the trisiloxane compound has a lower phase transition temperature. These findings contribute to our understanding of liquid crystal compounds and their potential applications.

Conflicts of Interest

The authors declare that there are no conflict of interest regarding the publication of this paper.

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