



Synthesis and Characterization of Liquid Crystalline Organosiloxanes Containing 4-Methoxyphenyl 4-(2-alkenyloxy)benzoate

CHENG-CHIH CHEN¹ and CHIH-HUNG LIN^{1,2,*}

¹Center for General Education, Chang Gung University of Science and Technology, Kweishan, Taoyuan, Taiwan

²Research Center for Industry of Human Ecology, Chang Gung University of Science and Technology, Kweishan, Taoyuan, Taiwan

*Corresponding author: E-mail: chlin@mail.cgust.edu.tw

Received: 6 October 2015;

Accepted: 9 January 2016;

Published online: 29 February 2016;

AJC-17789

A series of new organosiloxane liquid crystalline materials based on the 4-methoxyphenyl-4-(ω -alkenyloxy)benzoate as mesogenic units have been synthesized and their mesomorphic and physical properties have been characterized. A series of new disiloxanes and trisiloxanes contain 4-methoxyphenyl 4-(ω -alkenyloxy)benzoate as mesogenic these were synthesized by addition of 4-methoxyphenyl 4-(ω -alkenyloxy)benzoate moiety to pentamethylhydrodisiloxane or heptamethylhydrotrisiloxane catalyzed by platinum divinyl-tetramethyldisiloxane complex. The thermal properties of this new series of thermotropic liquid-crystalline siloxanes were studied by differential scanning calorimetry and polarized optical microscope. Disiloxane series compounds were not showed any liquid crystal phase. Trisiloxanes series compounds exhibited nematic liquid crystal phase. The siloxane molecule helped to reduce the melting temperature. The thermal properties of the new siloxane series exhibited a pronounced odd-even effect with the length of alkyl segment.

Keywords: Siloxane, Odd-even, Nematic liquid crystal phase.

INTRODUCTION

Much work has been done on the research of organosiloxane low molar mass (LMM) liquid crystals with electro optic properties suitable for use at ambient temperatures. Organosiloxane low molar mass liquid crystals have demonstrated fast switching times in the nematic, smectic phases [1-5]. Because the fast switching time relies on a co-operative molecular reorientation, consideration has been focused on the synthesis of low mean viscosity small molecules [6-15].

Side-chain liquid-crystalline polymers display effects similar to those of the low molar mass materials [16]. However, the presence of the polymer backbone leads to a broader mesophase temperature range, reduction of the tendency to form crystalline phases by inducing glassy phases and an increase in the mesophase clearing temperature in comparison with the equivalent low molar mass mesogenic side group moiety. Generally, the polymers have a much higher elastic constants and higher viscosity than chemically equivalent low molar mass materials. As a result, the electro-optic switching times of polymeric liquid crystals are several orders of magnitude slower than for the low molar mass analogues. Work carried out on side-chain liquid-crystalline polysiloxanes containing the 4-methoxyphenyl 4-(ω -alkenyloxy)benzoate mesogenic moiety show them to possess interesting electro-optic and

storage properties. Polysiloxanes have several advantages over their more rigid poly acrylate and methacrylate counterparts, particularly because of the greater flexibility of the backbone which results in relatively low glass temperature (T_g). To date less work has been done on low molar mass mono-dispersed siloxane systems. Materials had been prepared of the AB type, where A refers to the mesogenic unit and B refers to the dimethylsiloxane and trimethylsiloxane chain [2]. The materials chosen for the present study were siloxane-containing liquid crystals based on 4-methoxyphenyl 4-(2-alkenyloxy)benzoate, four new materials were found to have excellent electro-optic properties.

In this paper, a study had been made on the influence of a highly flexible disiloxane and trimethylsiloxane terminal group on the liquid-crystalline behaviour of a homologous series of 4-methoxyphenyl 4-(2-alkenyloxy)benzoate mesogenic moieties. It was thought that the presence of the siloxane tail might lead to lower melting temperatures and interesting physical properties. Thus, a series of mesogenic compounds (**1M-4M**, **1A-4A**, **1B-4B**) were synthesized and characterized.

EXPERIMENTAL

¹H NMR spectra were recorded on a Varian VXR-300 or Bruker 300 MHz spectrometer. Thermal transitions and thermodynamic parameters were determined using a Seiko SSC/5200 differential scanning calorimeter (DSC) equipped

with a liquid nitrogen cooling accessory. Heating and cooling rates were 10 °C/min. Thermal transition reports were collected during the second heating and cooling scans. A Nikon Microphot-FX polarized optical microscope (POM) equipped with a Mettler FP 82 hot stage and a FP 80 central processor was used to observe the thermal transitions and analyze the anisotropic textures. Polymerization reactions were traced using a Nicolet 520 FT-IR spectrometer.

The general synthetic routes of intermediates and target molecule were shown in **Scheme-I**. The purity and chemical structures of the intermediates and target compounds could be easily verified by TLC and ¹H NMR spectroscopy.

All the four compounds *viz.*, ethyl-4-(2-propenyloxy)benzoate (**1**), ethyl-4-(3-butenyloxy)benzoate (**2**), ethyl-4-(4-pentenyl oxy)benzoate (**3**) and ethyl-4-(5-hexenyloxy)benzoate (**4**) were prepared by the similar method.

The synthesis of ethyl-4-(5-hexenyloxy)benzoate (**4**) is described as follows: Ethyl-4-hydroxybenzoate (2.0 g, 0.012 mol), 6-bromo-1-hexene (1.96 g, 0.012 mol) and potassium carbonate (8.0 g, 0.058 mol) were dissolved in 100 mL of anhydrous ethyl-methyl ketone in a 250 mL two-neck flask. The solution was heated to reflux for 48 h. The solution was cooled and filtrated. Following the solvent being evaporated, the residue was purified by column chromatography (silica gel, using *n*-hexane/ethyl acetate as an eluent) to yield 2.53 g (85 %) of oil liquid. ¹H NMR (300 MHz, CDCl₃, δ, ppm): 1.27-2.10 (m, 11H, $-(CH_2)_4-$ and $-CH_2-CH_3$), 3.96 (t, 2H, $-CH_2O-$), 4.03 (t, 2H, $-COO-CH_2-$), 5.02 (m, 2H, $CH_2=CH-$), 5.84 (m, 1H, $CH_2=CH-$), 6.86 (m, 2H, aromatic protons), 7.83 (m, 2H, aromatic protons).

Compounds **5-8** *viz.*, 4-(2-propenyloxy)benzoic acid (**5**), 4-(3-butenyloxy)benzoic acid (**6**), 4-(4-pentenyl oxy)benzoic acid (**7**) and 4-(5-hexenyloxy) benzoic acid (**8**) were prepared by the similar method.

The synthesis of 4-(5-hexenyloxy)benzoic acid (**8**) is described as follows: Ethyl-4-(5-hexenyloxy)benzoate (1.2 g, 0.0048 mol) was added to a solution of sodium hydroxide (1.2 g, 0.030 mol) in 90 % methanol (30 mL). The solution was heated to reflux for 3 h. The solution was cooled and poured into 10 mL of 6 N HCl and the solution was then extracted with 30 mL of dichloromethane. The extraction solution was dried over anhydrous magnesium sulfate. Following removal of the solvent by evaporation under reduced pressure, the residue was purified by recrystallization from ethanol to yield 1.00 g (95 %) of white crystal. ¹H NMR (300 MHz, CDCl₃, δ, ppm): 1.50-2.20 (m, 4H, $-(CH_2)_3-$), 3.96 (t, 2H, $-CH_2O-$), 5.02 (m, 2H, $CH_2=CH-$), 5.84 (m, 1H, $CH_2=CH-$), 6.86 (m, 2H, aromatic protons), 7.96 (m, 2H, aromatic protons).

Compounds **1M-4M** *viz.*, 4-methoxyphenyl 4-(2-propenyloxy)benzoate (**1M**), 4-methoxyphenyl 4-(3-butenyloxy)benzoate (**2M**), 4-methoxyphenyl 4-(4-pentenyl oxy)benzoate (**3M**) and 4-methoxyphenyl 4-(5-hexenyloxy)benzoate (**4M**) were prepared by the similar method.

The synthesis of 4-methoxyphenyl 4-(5-hexenyloxy)benzoate (**4M**) is described as follows: 4-(5-Hexenyloxy) benzoic acid (**8**) (1.6 g, 0.0081 mol) and 4-methoxyphenol (1 g, 0.0081 mol) dissolved in dry dichloromethane (100 mL), N,N-dicyclohexylcarbodiimide (DCC, 2.0 g, 0.0097 mol) and

4-(N,N-dimethylamino)pyridine (DMAP, 0.2 g) were added to react under nitrogen. The reaction mixture was stirred for 24 h at room temperature. The solution was filtered. After removal of the solvent by evaporation under reduced pressure, the residue was purified by recrystallization from ethanol to yield 1.74 g (66 %) of white crystal. m.p.: 71.7 °C. ¹H NMR (300 MHz, CDCl₃, δ, ppm): 1.50-2.20 (m, 6H, $-(CH_2)_3-$), 3.80 (s, 3H, $-OCH_3$), 4.03 (t, 2H, $-CH_2O-$), 5.02 (m, 2H, $CH_2=CH-$), 5.84 (m, 1H, $CH_2=CH-$), 6.92 (m, 4H, aromatic protons), 7.10 (m, 2H, aromatic protons), 8.11 (m, 2H, aromatic protons). Compound **3M** was obtained as white solid (56 %). m.p.: 94.2 °C. ¹H NMR (300 MHz, CDCl₃, δ, ppm): 1.50-2.20 (m, 4H, $-(CH_2)_2-$), 3.80 (s, 3H, $-OCH_3$), 4.03 (t, 2H, $-CH_2O-$), 5.02 (m, 2H, $CH_2=CH-$), 5.84 (m, 1H, $CH_2=CH-$), 6.92 (m, 4H, aromatic protons), 7.10 (m, 2H, aromatic protons), 8.11 (m, 2H, aromatic protons). Compound **2M** was obtained as white solid (69 %). m.p.: 87.4 °C. ¹H NMR (300 MHz, CDCl₃, δ, ppm): 1.83 (m, 2H, $-CH_2-$), 3.80 (s, 3H, $-OCH_3$), 4.03 (t, 2H, $-CH_2O-$), 5.02 (m, 2H, $CH_2=CH-$), 5.84 (m, 1H, $CH_2=CH-$), 6.92 (m, 4H, aromatic protons), 7.10 (m, 2H, aromatic protons), 8.11 (m, 2H, aromatic protons). Compound **1M** was obtained as white solid (72 %). m.p.: 101 °C. ¹H NMR (300 MHz, CDCl₃, δ, ppm): 3.80 (s, 3H, $-OCH_3$), 4.49 (t, 2H, $-CH_2O-$), 5.31 (m, 2H, $CH_2=CH-$), 6.03 (m, 1H, $CH_2=CH-$), 6.92 (m, 4H, aromatic protons), 7.10 (m, 2H, aromatic protons), 8.11 (m, 2H, aromatic protons).

Liquid crystal siloxane compounds 1A-4A and 1B-4B: Siloxane dimer synthesized from **1M-4M** are marked as **1A-4A** and siloxane trimer from **1M-4M** are marked as **1B-4B**. Compounds **1A-4A** and **1B-4B** were prepared using the same method. The synthesis of compound **4A** is described below.

To a degassed solution of compound **4M** (0.26 g, 0.0008 mol) and pentamethyl-hydrodisiloxane (0.14 g, 0.0009 mol) in 10 mL of dry and freshly distilled toluene was added divinyl-tetramethyldimethylsiloxyl (2.5 mg) as catalyst. The reaction mixture was stirred at 75 °C under nitrogen for 48 h. After the solvent being evaporated, the residue was purified by column chromatography (silica gel, using *n*-hexane/ethyl acetate as an eluent) to yield 0.33 g (76 %) of white crystals. ¹H NMR (CDCl₃, δ, ppm): 0.0 (m, 15H, $-Si-CH_3$), 0.53 (m, 2H, $-Si-CH_2-CH_2-$), 1.50-2.20 (m, 8H, $-CH_2-$), 3.80 (s, 3H, $-O-CH_3$), 4.03 (t, 2H, $-O-CH_2-$), 6.92 (m, 4H, aromatic protons), 7.10 (m, 2H, aromatic protons), 8.11 (m, 2H, aromatic protons). Compound **3A** was obtained as white solid (78 %). ¹H NMR (CDCl₃, δ, ppm): 0.0 (m, 15H, $-Si-CH_3$), 0.53 (m, 2H, $-Si-CH_2-CH_2-$), 1.50-2.20 (m, 6H, $-CH_2-$), 3.80 (s, 3H, $-O-CH_3$), 4.03 (t, 2H, $-O-CH_2-$), 6.92 (m, 4H, aromatic protons), 7.10 (m, 2H, aromatic protons), 8.11 (m, 2H, aromatic protons). Compound **2A** was obtained as white solid (76 %). ¹H NMR (CDCl₃, δ, ppm): 0.0 (m, 15H, $-Si-CH_3$), 0.53 (m, 2H, $-Si-CH_2-CH_2-$), 1.50-2.30 (m, 4H, $-CH_2-$), 3.80 (s, 3H, $-O-CH_3$), 4.03 (t, 2H, $-O-CH_2-$), 6.92 (m, 4H, aromatic protons), 7.10 (m, 2H, aromatic protons), 8.11 (m, 2H, aromatic protons). Compound **1A** was obtained as white solid (67 %). ¹H NMR (CDCl₃, δ, ppm): 0.0 (m, 15H, $-Si-CH_3$), 0.53 (m, 2H, $-Si-CH_2-CH_2-$), 1.87 (m, 2H, $-CH_2-$), 3.80 (s, 3H, $-O-CH_3$), 4.49 (t, 2H, $-O-CH_2-$), 6.92 (m, 4H, aromatic protons), 7.10 (m, 2H, aromatic protons), 8.11 (m, 2H, aromatic protons). Compound **4B** was obtained as white solid (81 %). ¹H NMR (CDCl₃, δ,

ppm): 0.0 (m, 21H, -Si-CH₃), 0.53 (m, 2H, -Si-CH₂-CH₂-), 1.50-2.20 (m, 8H, -CH₂-), 3.80 (s, 3H, -O-CH₃), 4.03 (t, 2H, -O-CH₂-), 6.92 (m, 4H, aromatic protons), 7.10 (m, 2H, aromatic protons), 8.11 (m, 2H, aromatic protons). Compound **3B** was obtained as white solid (57 %). ¹H NMR (CDCl₃, δ, ppm): 0.0 (m, 21H, -Si-CH₃), 0.53 (m, 2H, -Si-CH₂-CH₂-), 1.50-2.20 (m, 6H, -CH₂-), 3.80 (s, 3H, -O-CH₃), 4.03 (t, 2H, -O-CH₂-), 6.92 (m, 4H, aromatic protons), 7.10 (m, 2H, aromatic protons), 8.11 (m, 2H, aromatic protons). Compound **2B** was obtained as white solid (70 %). ¹H NMR (CDCl₃, δ, ppm): 0.0 (m, 21H, -Si-CH₃), 0.53 (m, 2H, -Si-CH₂-CH₂-), 1.50-2.30 (m, 4H, -CH₂-), 3.80 (s, 3H, -O-CH₃), 4.03 (t, 2H, -O-CH₂-), 6.92 (m, 4H, aromatic protons), 7.10 (m, 2H, aromatic protons), 8.11 (m, 2H, aromatic protons). Compound **1B** was obtained as white solid (72 %). ¹H NMR (CDCl₃, δ, ppm): 0.0 (m, 21H, -Si-CH₃), 0.53 (m, 2H, -Si-CH₂-CH₂-), 1.87 (m, 2H, -CH₂-), 3.80 (s, 3H, -O-CH₃), 4.49 (t, 2H, -O-CH₂-), 6.92 (m, 4H, aromatic protons), 7.10 (m, 2H, aromatic protons), 8.11 (m, 2H, aromatic protons).

RESULTS AND DISCUSSION

For the synthesis of liquid crystalline siloxane derivative various derivatives of 4-methoxyphenyl-4-(2-alkenyloxy)-benzoate were used. **Scheme-I** presented synthesis steps of target molecule. Table-1 showed the phase transition of these alkene(methylene units spacer, n = 3, 4, 5, 6) precursors (**1M-4M**). This series of compounds had a small enthalpy of isotropic transfer nematic phase that enthalpy could not be measured by the differential scanning calorimeter, it could only be measured by a polarized optical microscope. These followed the usual structural dependence pattern for the low molar mass liquid crystals. **1M-4M** compounds were exhibited monotropic nematic liquid crystal phase. **1M-4M** compounds with shorter spacer length showed a higher melting point and liquid crystal temperature and they had odd-even effect.

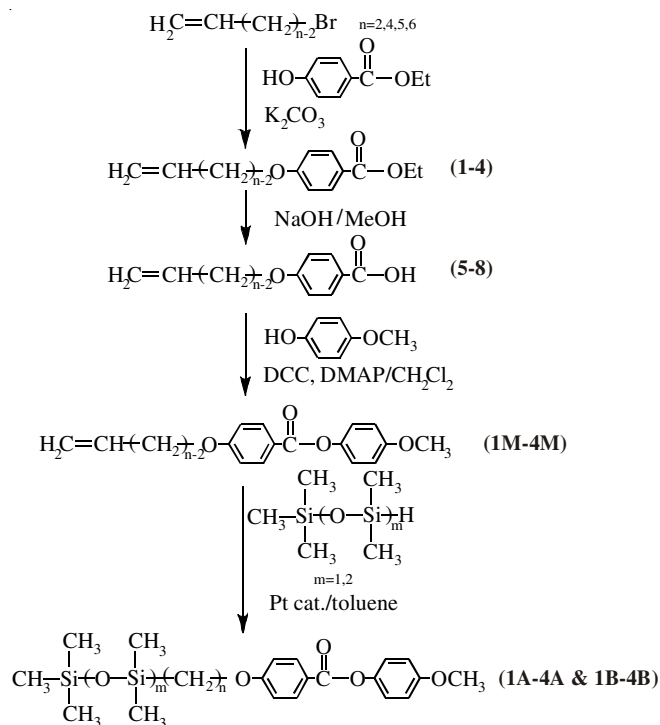
TABLE-1
THERMAL TRANSITIONS OF COMPOUNDS **1M-4M**

Compd.	Spacer	Phase transitions °C (corresponding enthalpy changes, Kcal/mol)	
		heating	cooling
1M	3	K 101 (6.75) I I 77.6(-) ^a N 69.7(-6.01) K	
2M	4	K 87.4(8.03) I I 54.1(-) ^a N 41.5(-6.47) K	
3M	5	K 94.2(6.67) I I 82.3(-) ^a N 73.5(-7.24) K	
4M	6	K ₁ 29.4(1.28) K ₂ 71.7(5.82) I I 57.3(-) ^a N 55.1(-4.71) K	

K = crystal, N = nematic A, I = isotropic

^aDetermined by optical polarizing microscopic observation.

The disiloxane and trisiloxane derivatives were synthesized by the addition of pentamethylhydrodisiloxane or heptamethylhydrotrisiloxane to the 4-methoxyphenyl 4-(2-alkenyloxy)-benzoate mesogenic moiety catalyzed by a platinum divinyl-tetranlethyldisiloxane complex. Table-2 showed the phase



Scheme-I: Synthesis of compounds **1M-4M**, **1A-4A** and **1B-4B**

TABLE-2
THERMAL TRANSITIONS OF COMPOUNDS **1A-4A**

Compd.	Spacer	Phase transitions °C (corresponding enthalpy changes, Kcal/mol)	
		heating	cooling
1A	3	K 92.1(8.95) I I 66.6(-9.18) K	
2A	4	K 63.2(9.55) I I -12.6(-2.63) K	
3A	5	K 71.2(8.20) I I 36.3(-8.55) K ₁ 5.8(-0.42) K ₂	
4A	6	K 48.1(6.40) I I 24.4(-5.28) K	

K = crystal, I = isotropic

transition of **1A-4A** disiloxane compounds. All disiloxane compounds did not show any liquid crystal phase. Table-3 showed the phase transition of **1B-4B** trisiloxane compounds. **1B** compound did not exhibit any liquid crystal phase. **2B-4B** compounds showed a monotropic nematic liquid crystal phase. Fig. 1 presented the polarized optical microphotograph of **4B** compound. Fig. 1 showed schlieren texture of nematic. Fig. 2 depicted the DSC analysis diagram of compound **4B** compound. As to the cooling process, two exothermal transitions appeared at 12.1 and -42.1 °C with respect to the endothermal transition temperature on the cooling scan.

Finkelmann and Rehage [16] synthesized polysiloxane containing 4-methoxyphenyl-4-(2-alkenyloxy)benzoate. They



Fig. 1. Polarizing optical micrographs (magnification $\times 320$) of compound **4B** in N texture obtained after cooling from isotropic phase to 0 °C

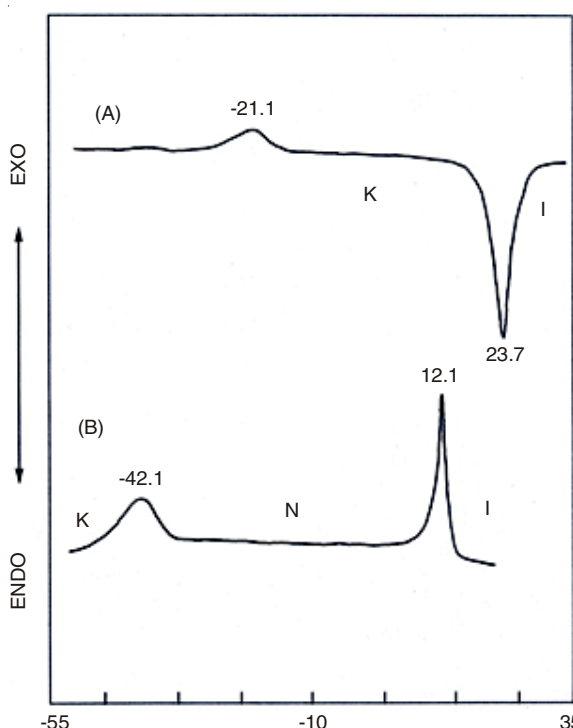


Fig. 2. DSC thermograms of compound **4B** (10 °C/min) for (A) second heating scanning and (B) cooling scanning

TABLE-3 THERMAL TRANSITIONS OF COMPOUNDS 1B-4B		
Compd.	Spacer	Phase transitions °C (corresponding enthalpy changes, Kcal/mol)
		heating cooling
1B	3	$K_1 33.0 (1.46) K_2 69.5 (7.33) I$ $I 44.8 (-7.35) K_2 21.9 (-1.50) K_1$
2B	4	$K_1 -2.7 (-1.54) K_2 18.1 (-1.60) K_3 45.9 (9.87) I$ $I -4.6 (-1.02) N -15.3 (-1.85) K$
3B	5	$K_1 11.6 (1.96) K_2 31.2 (8.73) I$ $I 29.0 (-1.36) N 19.3 (-4.69) K_2 -23.6 (-1.71) K_1$
4B	6	$K_1 -21.1 (-2.80) K_2 23.7 (7.89) I$ $I 12.1 (-0.82) N -42.1 (-1.49) K$

K = crystal, N = nematic A, I = isotropic

reported all polysiloxane (spacer length 3, 4, 5, 6) showed a monotropic mesophase nematic phase and crystal phase. The polysiloxane contain three methylene units spacer appeared nematic phase at the temperature range from 15 to 61 °C, four methylene units spacer polysiloxane appeared nematic phase at the temperature range from 15 to 102 °C, five methylene units spacer polysiloxane appeared nematic phase at the temperature range from 87 to 115 °C, six methylene units spacer polysiloxane appeared nematic phase at the temperature range from 57 to 108 °C. When siloxane unit was increase then nematic phase of 4-methoxy-phenyl-4-(2-alkenyloxy)benzoate mesogen was more stable. Polysiloxane compounds appeared nematic phase temperature range bigger than trisiloxane compounds. Disiloxane compounds didn't exhibit nematic phase. This effect was well documented in polymeric materials in which the polymer backbone stabilizes the liquid crystal phase, but it was interesting to note that these trisiloxanes also exhibit similar behaviour special spacer increase.

The bulky and highly flexible siloxane tail contain disiloxane and trisiloxane caused a reduction in the interchain interactions and the degree of crystallinity of the 4-methoxy-phenyl-4-(2-alkenyloxy)benzoate compounds. A comparison of Fig. 3 showed the melting points for the siloxane containing mesogens were lower than the alkene substituted materials. Trisiloxane compounds were low than disiloxane compounds. It was interesting to note that the melting temperature of the **1M-4M**, **1A-4A** compounds followed an odd-even effect and that the even homologues had lower melting temperatures. This presumably reflects the reduced shape anisotropy of the even-membered homologues. The melting temperature of **1B-4B** compounds showed decrease as the spacer length increased.

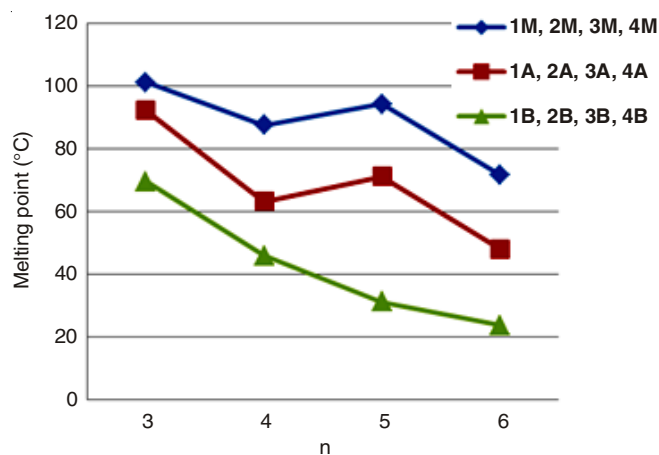


Fig. 3. Melting temperature of **1M-4M**, **1A-4A** and **1B-4B**

Conclusion

The general synthetic routes of the intermediates and target molecule were shown in **Scheme-I**. The induction of the bulky and highly flexible siloxane molecule was helpful to change the melting temperature. Trisiloxane compounds was lower melting temperature than disiloxane compounds. The siloxane molecule induction was helpful to the nematic phase formation. Polysiloxane compounds showed nematic phase temperature range bigger than trisiloxane compounds. Disiloxane compounds

didn't exhibit nematic phase. The melting temperature of the **1M-4M**, **1A-4A** compounds followed an odd-even effect and that the even homologues had lower melting temperatures.

ACKNOWLEDGEMENTS

This research was supported in part by Chang Gung University of Science and Technology, Kweishan, Taoyuan, Taiwan (grant EZRPF3E0061, EZRPF3E0071, EZRPF3E0081).

REFERENCES

1. E.A. Corsellis and H.J. Coles, *Mole. Cryst. Liq. Cryst.*, **261**, 71 (1995).
2. J. Newton, H.J. Coles, P. Hodge and J. Hannington, *J. Mater. Chem.*, **4**, 869 (1994).
3. H.J. Coles, H. Owen, J. Newton and P. Hodge, *Liq. Cryst.*, **15**, 739 (1993).
4. H.J. Coles, H. Owen, J. Newton and P. Hodge, *Proc. SPIE*, **2408**, 22 (1995).
5. P. Kloess, J. McComb, H.J. Coles and R. Zentel, *Ferroelectrics*, **180**, 233 (1996).
6. G. Scherowsky, A. Schliwa, J. Springer, K. Kuhnpast and W. Trapp, *Liq. Cryst.*, **5**, 1281 (1989).
7. V.P. Shibaev, M.V. Kozlovsky, N.A. Plate, L.A. Beresnev and L.M. Blinov, *Liq. Cryst.*, **8**, 545 (1990).
8. S.U. Vallerien, F. Kremer, E.W. Fischer, H. Kapitza, R. Zentel and H. Poths, *Makromol. Chem., Rapid. Commun.*, **11**, 593 (1990).
9. H. Kapitza and R. Zentel, *Makromol. Chem.*, **192**, 1859 (1991).
10. H. Endo, S. Hachiya, S. Uchida, K. Hashimoto and K. Kawasaki, *Liq. Cryst.*, **9**, 635 (1991).
11. S.U. Vallerien, F. Kremer, H. Kapitza, R. Zentel and E.W. Fischer, *Ferroelectrics*, **109**, 273 (1990).
12. C.H. Lin, *Mol. Cryst. Liq. Cryst.*, **552**, 33 (2012).
13. C.H. Lin, *Int. J. Mol. Sci.*, **14**, 21306 (2013).
14. J. Naciri, J. Ruth, G. Crawford, R. Shashidhar and B.R. Ratna, *Chem. Mater.*, **7**, 1397 (1995).
15. C.S. Hsu and B.S. Her, *Macromol. Chem. Phys.*, **197**, 4105 (1996).
16. G. Rehage and H. Finkelmann, *Adv. Polym. Sci.*, **60-61**, 99 (1984).