

SYNTHESIS OF NOVEL LIQUID CRYSTALLINE POLY(METH)ACRYLATES CONTAINING SILOXANE SPACER AND TERPHENYLENE MESOGENIC UNIT*

Zhi-qian Zang, Yu-fei Luo, Dong Zhang, Xin-hua Wan and Qi-feng Zhou**

Department of Polymer Science & Engineering, College of Chemistry, Peking University,
Beijing 100871, China

Abstract Novel side-chain liquid-crystalline poly(meth)acrylates were synthesized using 1-(3-hydroxyl-propyl)-3-[(4''-cyano-*p*-terphenyloxycarbonyl)alkyl]-1,1,3,3-tetramethyldisiloxane as the key intermediate. The polymers used a disiloxane moiety as decoupling spacer with cyano-*p*-terphenyl as mesogenic unit. The products were characterized by NMR, GPC, DSC and polarizing optical microscopy. All the polymers with cyano-*p*-terphenyl mesogens formed a stable mesophase. However, if the mesogenic unit is replaced by cyano-*p*-biphenyl, the liquid crystalline character will be lost. The results also showed that the decoupling is incomplete even if a complex and very flexible decoupling spacer is deliberately incorporated to obtain the highest possible decoupling effect.

Keywords Liquid crystalline polymers, Polyacrylates, 4''-Cyano-*p*-terphenyl

INTRODUCTION

The side-chain liquid crystalline polymers (SLCPs) have become the object of intensive investigation to meet the fast developing market of the liquid crystal displays (LCD), because they are relatively inexpensive, thermally stable, and can be fabricated into films^[1, 2]. For most of their applications, liquid crystal materials are required to have a broad operating temperature range as well as high anisotropy in dielectric and optical properties. The design and synthesis of new materials with more suitable properties have been challenging tasks for liquid crystal synthetic chemists^[3].

In our previous study^[4], we synthesized a series of new liquid crystalline compounds with cyano-*p*-terphenylene moiety as mesogenic core. The high degrees of conjugation and polarization of this aromatic rod-like structure are desirable properties for LCD and other optoelectronic applications. The unique structure of this mesogenic unit causes these compounds to show very stable liquid-crystallinity in wide temperature ranges. A further study of these cyano-*p*-terphenylene derivatives as materials used in LCD or other information-processing applications is under consideration.

On the other hand, it is well known that the flexible spacer between a polymer main chain and a mesogenic side group plays an important role in decoupling the motion of the main chains from that of the side groups, and thus helps the formation of a liquid crystalline phase^[5]. In particular, Engel and coworkers^[6] have found that the incorporation of a disiloxane segment in the spacer can effectively enhance the decoupling effect. The resulting polymers have low glass-transition temperatures (as low as -20°C) desirable for LCD applications. They also found that if a disiloxane segment is used in the spacer, certain additional modification should be made so as to stabilize the mesophase. In other words, the disiloxane segment does not fit well with the orientation of the neighboring mesogenic units. As an additional modification Engel introduced a long segment of $-(CH_2)_n-$ between the disiloxane segment and the mesogenic unit. This idea of molecular design permitted Engel to

* This work was supported by NNSFC (No. 59873001).

** Corresponding author: Qi-feng Zhou (周其凤); E-mail: qfzhou@pku.edu.cn

Received April 4, 1999

successfully synthesize side-chain type liquid crystalline polymers with a T_g as low as -20°C and a nematic phase of moderate thermal stability ($T_i \sim 37^\circ\text{C}$).

In this work, we used both Engel's concept of disiloxane decoupling and our own findings obtained from the study of cyano-*p*-terphenylene derivatives in the design and synthesis of liquid crystalline polymers. As a mesogenic unit, the cyano-*p*-terphenylene moiety in our polymers has higher degree of conjugation, higher degree of polarization, and higher value of the length-to-diameter ratio than the *p*-cyanophenylloxycarbonylphenyl used by Engel *et al.* By using this mesogenic unit we are indeed able to synthesize polymers with a rather stable liquid crystalline phase. We expect that these new polymers will be useful in optoelectronic applications.

EXPERIMENTAL

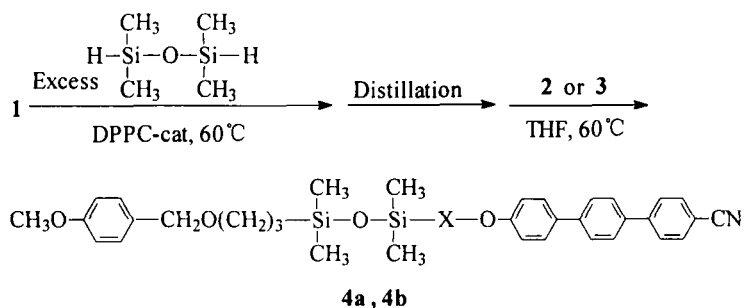
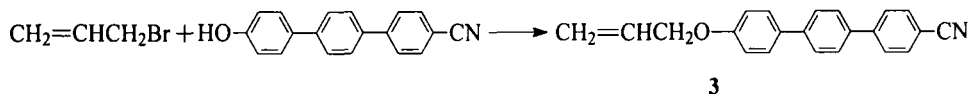
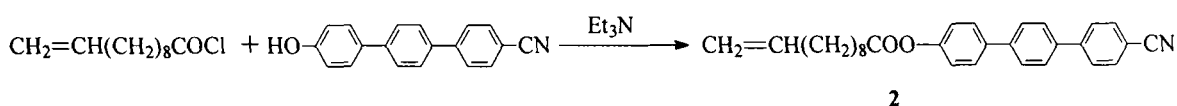
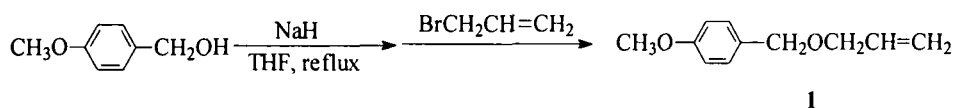
Materials and Equipment

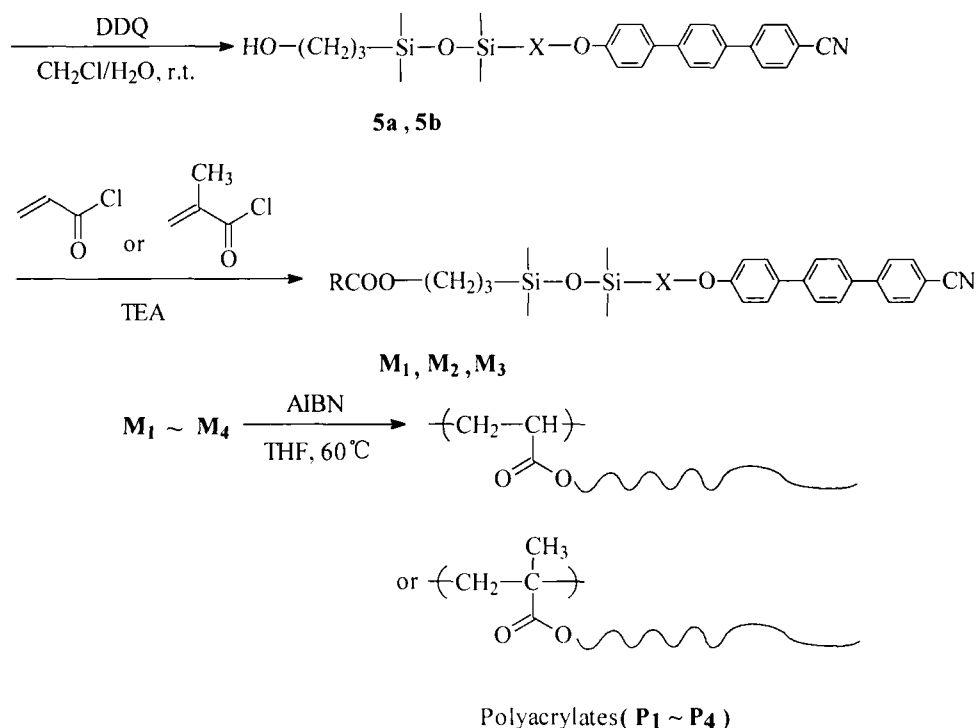
4-Methoxybenzyl alcohol, 1,1,3,3-tetramethyldisiloxane (TMDS) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) were supplied by Acros Inc. and used without further purification. Dicyclopentadienyl-platinum(II) chloride catalyst (DPPC) was prepared referring to literature^[7]. 4-Hydroxy-4''-cyano-*p*-terphenyl was prepared in our previous work^[4]. All other chemicals and reagents were purchased from chemical companies of Beijing. All solvents were refluxed with CaH_2 before use.

Differential scanning calorimetry (DSC) was performed with a TA Instruments DSC 2010. Polarizing optical microscopy (POM) was carried out with a Leitz Laborlux 12 Pol microscope with a Leitz 350 heating stage. Nuclear magnetic resonance spectra were obtained with a Bruker ARX400 spectrometer by using TMS as internal standard. Molecular weight was determined by GPC with a Waters 201 instrument.

Synthetic Procedure

The synthetic route is shown in Scheme 1^[8-10]. The structural details of the intermediates and the monomers and the polymers are further described in Table 1. The procedure of synthesis is described below with the synthesis of polyacrylate **P₁** as an example.





Scheme 1 Synthesis of intermediates, monomers and polymers; refer to Table 1 for more structure details

Synthesis of 4-methoxybenzyl allyl ether (1)

Under an argon atmosphere, a solution containing 4-methoxybenzyl alcohol (2.0 g, 14.5 mmol) in 3 mL of dry THF was added dropwise to sodium hydride (19.6 mmol) in 20 mL of dry THF and 20 mL of hexane. The mixture was heated at reflux for 11 h. A solution of 3-bromopropene (2.0 g, 17.3 mmol) was then added to the solution, and the mixture was heated at reflux overnight. After the solvent had been removed in a rotary evaporator, the residue was extracted with diethyl ether, and purified by column chromatography on silica gel with diethyl ether/n-hexane (1/5 vol) as eluent to yield 2.0 g transparent colorless liquid. Yield: 75%. $^1\text{H-NMR}$ δ (in CDCl_3): 3.8 (s, 3H), 4.0 (d, 2H), 4.4 (s, 2H), 5.1~5.3 (m, 2H), 5.8 (m, 1H) and 6.8~7.2 (m, 4H).

Synthesis of 1-(10-undecenoyloxy)-4''-cyano-p-terphenyl (2)

4-Hydroxy-4''-cyano-*p*-terphenylene (0.17 g, 0.62 mmol) and pyridine (0.4 mL, 4.9 mmol) were dissolved in 5 mL of THF. 10-Undecenyl chloride (0.2 mL, 0.9 mmol) was added to the mixture which was stirred overnight. After the solvent had been removed in a rotary evaporator, the residue was purified by column chromatography on silica gel with chloroform as eluent and recrystallized from ethyl acetate to yield 0.263 g of **2** as white crystals. Yield: 95.9%. ¹H-NMR δ (in CDCl₃): 1.3~1.4(*m*, 10H), 1.7(*m*, 2H), 2.0(*m*, 2H), 2.6(*m*, 2H), 4.9~5.0 (*m*, 2H), 5.8 (*m*, 1H) and 7.1~7.7(*m*, 12H).

Synthesis of 1-allyloxy-4''-cyano-p-terphenyl (3)

4-Hydroxy-4''-cyano-*p*-terphenyl (0.386 g, 1.4 mmol) and 3-bromopropene (0.400 g, 2.8 mmol) were dissolved in 100 mL of acetone. Potassium carbonate (0.407 g, 2.8 mmol) and potassium iodide (0.040 g) were then added to the mixture. After heating at reflux overnight, the precipitated salts were removed by filtration. The solvent was removed by a rotary evaporator, and the residue was purified by column chromatography on silica gel with chloroform as eluent to yield 0.405 g of **3** as white crystals. Yield: 91.4%. ¹H-NMR δ (in CDCl₃): 4.5~4.6 (*m*, 2H), 5.2~5.5 (*m*, 2H), 6.1 (*m*, 1H) and 7.0~7.7 (*m*, 12H).

Synthesis of 1-[3-(4-methoxy-benzyloxy)propyl]-3-[10-(4''-cyano-p-terphenyloxy carbonyl) decyl]-1,1,3,3-tetramethyl-disiloxane (4a)

Under an argon atmosphere, 4-methoxybenzyl allyl ether (0.44 g, 2.32 mmol) and TMDS (8.2 mL, 4.7 mmol)

and DPPC (3.0 mg) were stirred for 12 h at 60°C. The solvent was removed in a rotary evaporator below 60°C. Under an argon atmosphere, **2** (0.437 g, 1.0 mmol) in 5 mL of dry THF was added to the residue, and the mixture was stirred again overnight at 60°C. After the solvent had been removed in a rotary evaporator, the residue was purified by column chromatography on silica gel with dichloromethane/*n*-hexane as eluent to yield 0.725 g of **4a**, as a white waxy solid. Yield: 96.8%. ¹H-NMR (δ in CDCl₃): 0.1 (*m*, 12H), 0.4–0.5 (*m*, 4H), 1.2 (*m*, 14H), 1.6 (*m*, 2H), 1.7 (*m*, 2H), 2.5–2.6 (*m*, 2H), 3.3–3.4 (*m*, 2H), 3.8 (*s*, 3H), 4.4 (*m*, 2H) and 6.8–7.7 (*m*, 16H).

1-[3-(4-Methoxybenzyloxy)propyl]-3-[3-(4''-cyano-*p*-terphenyloxy)propyl]-1,1,3,3-tetramethyl-disiloxane (**4b**) was synthesized using a procedure similar to that for **4a**, but with **3** instead of **2** in the second step. Yield: 81.9%. ¹H-NMR (δ in CDCl₃): 0.1 (*m*, 12H), 0.4–0.6 (*m*, 4H), 1.6 (*m*, 2H), 1.7 (*m*, 2H), 3.3–3.4 (*m*, 2H), 3.8 (*s*, 3H), 4.0 (*m*, 2H), 4.4 (*m*, 2H) and 6.8–7.7 (*m*, 16H).

*Synthesis of 1-(3-hydroxypropyl)-3-[10-(4''-cyano-*p*-terphenyloxycarbonyl)decyl]-1,1,3,3-tetra-methyl-disiloxane (5a)*

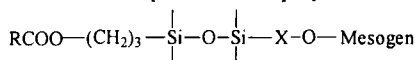
4a (0.360 g, 0.48 mmol) was dissolved in 10 mL of dichloromethane and 1 mL of water. DDQ (0.131 g, 0.58 mmol) was added to the mixture and stirred for 1 h at room temperature. The product was purified by column chromatography on silica gel with dichloromethane as eluent to yield 0.178 g of **5a** as a white waxy solid. Yield: 58.9%. ¹H-NMR (δ in CDCl₃): 0.1 (*m*, 12H), 0.5 (*m*, 4H), 1.2 (*m*, 14H), 1.6 (*m*, 2H), 1.7 (*m*, 2H), 2.5–2.6 (*m*, 2H), 3.6 (*m*, 2H) and 6.7–7.7 (*m*, 12H).

1-(3-Hydroxypropyl)-3-[3-(4''-cyano-*p*-terphenyloxycarbonyl)propyl]-1,1,3,3-tetramethyl-disiloxane (**5b**) was similarly obtained from **4b**. Yield: 25.8%. ¹H-NMR (δ in CDCl₃): 0.1 (*m*, 12H), 0.4–0.6 (*m*, 4H), 1.6 (*m*, 2H), 1.7 (*m*, 2H), 3.6 (*m*, 2H), 4.0 (*m*, 2H) and 6.7–7.7 (*m*, 12H).

Synthesis of the monomers (M₁–M₄, see Table 1 for structural details)

5a (0.475 g, 0.76 mmol) and TEA (1.0 mL, 7.2 mmol) were dissolved in 10 mL THF. Then acryloyl chloride (0.31 mL, 3.7 mmol) was added to the mixture and was stirred overnight. After the solvent had been removed in a rotary evaporator, the residue was extracted with ethyl acetate, and purified by column chromatography on silica gel with chloroform as eluent to yield 0.434 g monomer **M₁**, 1-(3-acryloyloxy-propyl)-3-[3-(4''-cyano-*p*-terphenyloxycarbonyl)propyl]-1,1,3,3-tetramethyl-disiloxane, as a white waxy solid. Yield: 84.1%. ¹H-NMR (δ in CDCl₃): 0.1 (*m*, 12H), 0.5 (*m*, 4H), 1.2 (*m*, 14H), 1.6–1.7 (*m*, 4H), 2.5 (*m*, 2H), 4.0 (*m*, 2H), 5.7–6.1 (*m*, 2H), 6.3 (*m*, 1H) and 7.0–7.6 (*m*, 12H).

Table 1. Properties of the polymers of



Polymer code	Inter-mediate	R in monomers	X	Mesogen	Phase transition (°C)	<i>M_n</i>
P₁	4a, 5a	M₁ : CH ₂ =CH-	-(CH ₂) ₁₀ CO-	-PhPhPhCN	g 54 C 110 S* 213 i	5942
P₂	4a, 5a	M₂ : CH ₂ =C(CH ₃)-	-(CH ₂) ₁₀ CO-	-PhPhPhCN	g 73 C 120 S* 228 i	5158
P₃	4b, 5b	M₃ : CH ₂ =CH-	-(CH ₂) ₃ -	-PhPhPhCN	g 104** C 198 S* 240** i	4498
P₄		M₄ : CH ₂ =CH-	-(CH ₂) ₃ -	-PhPhCN	g -8 i	1996
A^{***}		M : CH ₂ =C(CH ₃)-	-(CH ₂) ₃ -	-PhCOOPhCN	g 4 i	
B^{***}		M : CH ₂ =C(CH ₃)-	-(CH ₂) ₅ -	-PhCOOPhCN	g 0 i	
C^{***}		M : CH ₂ =C(CH ₃)-	-(CH ₂) ₁₁ -	-PhCOOPhCN	g -20 n 37 i	

* This mesophase showed a fan-shaped texture with focal-conic defect on POM, suggesting the S_B phase by comparison of this mode with plates 9 and 11 in Ref. [11]. ** This temperature was obtained from POM because the DSC peak of this transition was rather broad. *** Quoted from Ref. [6].

M₂, **M₃** and **M₄** were similarly obtained by the same method but different precursors, The yields were 84.9%, 56.8% and 29.6%, respectively.

Polymerization

The 4 polymers were synthesized by radical polymerization of their respective monomers according to the following procedure. The monomer and 2,2'-azobisisobutyronitrile (AIBN) were dissolved in dry THF in a polymerization tube. The concentration of the monomer was 0.2 mmol/mL. The molar ratio of the initiator to each monomer, $[I][M]^{-1}$, was 3%. After degassing the mixture, the tube was sealed and heated at 60°C overnight. The reaction mixture was poured into an excess amount of methanol to precipitate the polymer. The obtained polymer was reprecipitated twice from its DMF solution with excess methanol and dried in vacuum. The yield was 43.7% for **P**₁, 50.5% for **P**₂, 78.6% for **P**₃ and 31.7% for **P**₄, respectively.

RESULTS AND DISCUSSION

In this study we synthesized four monomers and their corresponding polymers which have not been described in the literature. Three of the four polymers have cyano-*p*-terphenyl and the remaining one has cyano-*p*-biphenyl as the mesogenic group attached to the end of a flexible side chain. Another unique feature of these polymers is the structure of the flexible spacer bridging the main chain and the mesogenic groups. A tetramethyldisiloxane segment is inserted in the center of a short polymethylene chain to form the spacer as shown in Scheme 1.

The syntheses of these polymers were very difficult as they involved several delicate reactions to obtain each monomer (Scheme 1) and free radical polymerization to yield the final products. Column chromatographic separation was repeatedly used to purify the intermediates as well as the monomers. Although the purity of the monomers was assured by NMR and other analyses, yet the yield of each monomer was very low and only a few hundred milligrams were obtained. The molecular weights of the polymers were also low (Table 1) probably because the polymerization conditions have not yet been optimized.

Table 1 also shows the structural features of the four polymers. The polymers **P**₁ and **P**₂ have the same cyano-*p*-terphenyl mesogenic group and the same spacers. The difference between these two polymers is in their main chain backbone, as **P**₁ is a polyacrylate and **P**₂ is a polymethacrylate. Therefore a comparison between the two will show the influence of the backbones. Polymer **P**₃ is also a polyacrylate, but has a shorter polymethylene segment inserted between the mesogenic group and the disiloxane moiety in comparison with polymer **P**₁ so that the property difference between **P**₃ and **P**₁ should originate from the difference in the spacers. In addition, **P**₄ was synthesized to show the necessity of a strong mesogenic unit for these polymers to form a stable mesophase if an Engel type spacer with a short polymethylene segment is used.

The liquid crystallinity of the polymers was studied by means of DSC together with POM. The results are shown in Table 1.

Both polymers **P**₁ and **P**₂ have a long decamethylene spacer segment and a strong mesogenic cyano-*p*-terphenyl group and each also forms a stable mesophase in a broad temperature range (over 100 degrees). The two mesophases showed fan-shaped textures with focal-conic defects on POM (Fig. 1). The typical focal-conic textures strongly suggest a smectic B phase^[11] although their definitive identification needs additional X-ray analysis. Unfortunately, the samples were too small to permit such a study.

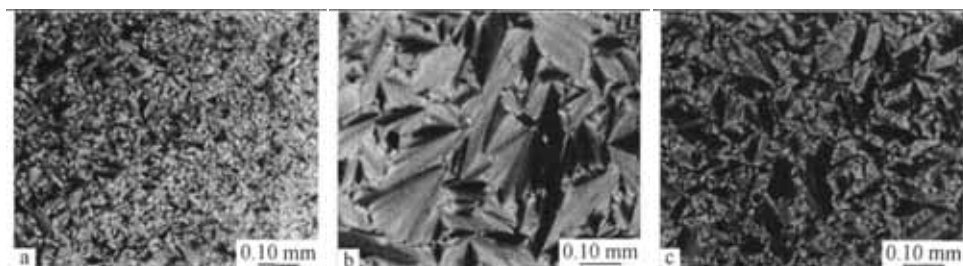


Fig. 1 The polarizing optical microscopic textures of **P**₁–**P**₃

a) **P**₁ at 149°C, b) **P**₂ at 209°C and c) **P**₃ at 203°C

The properties of P_1 and P_2 are very similar except that the polyacrylate P_1 has lower transition temperatures than the polymethacrylate P_2 . Since P_1 has a higher molecular weight than P_2 , the lower transition temperatures of P_1 can be interpreted as due to the difference in molecular structure even if the molecular weights of the two polymers are not high. Thus, the lower T_g of P_1 is understandable because the polyacrylate chain is in principle more flexible than the polymethacrylate chain, as has been demonstrated by poly(methyl acrylate) ($T_g \sim 6^\circ\text{C}$) and poly(methyl methacrylate) ($T_g \sim 105^\circ\text{C}$). On the other hand, the lower isotropization temperature (T_i) of the liquid crystalline phase of P_1 implies that the nature of the main chain still affects the property of the mesophase. In other words, the motions of the main chain and the side groups are still coupled. The argument of Percec and Pugh^[12] of incomplete decoupling is applicable in these polymers even if a complex decoupling spacer is deliberately designed to obtain the highest possible decoupling. Percec and Pugh suggested that the cooperative motion of the side groups would be independent of the main chain if a complete decoupling is achieved.

Polymer P_3 is also a polyacrylate like P_1 , but it has a significantly higher T_g (104°C) than P_1 (54°C) even if the molecular weight of P_3 is lower. In P_3 a short termethylene segment is incorporated between the mesogenic group and the disiloxane moiety, while in P_1 a longer decamethylene is used. This implies that even though the flexible polyacrylate has been used as the backbone and the flexible disiloxane moiety has been used in the spacer, the length of the polymethylene segment in the spacer still plays a significant role in affecting the property of the polymer chain. With a longer polymethylene segment the polymer chain is more flexible and has a lower transition temperature. Thus, the motion of the polymer main chain is again only partially decoupled from the motion of the anisotropically oriented mesogenic side groups even if a very flexible disiloxane segment is incorporated in the spacer. Therefore, incomplete decoupling is also demonstrated by a comparison between P_1 and P_3 .

The polymers P_3 and P_4 have the same polyacrylate main chain and the same decoupling spacer, but their mesogenic units are different, i.e. cyano-*p*-terphenyl for P_3 but cyano-*p*-biphenyl for P_4 . While P_3 is liquid crystalline as described above, P_4 is non-liquid-crystalline. For P_4 , only a glass transition was observed at -8°C , and the phase in the temperature range above the T_g was confirmed as an isotropic phase by polarizing optical microscopy. Therefore, it seems that the side-chain type polymers with disiloxane moiety in the flexible spacer require strong mesogenic units. The rod-like mesogenic group cyano-*p*-terphenyl has a stronger potential to form a mesophase than cyano-*p*-diphenyl because the former has a larger length-to-diameter ratio and a greater conjugation. Our result agrees well with what has been reported by Engel^[6] and Nagase^[13]. These researchers found that the bulky tetramethyldisiloxane groups in the spacers would disturb the liquid crystalline order, and the mesophase was found only when longer polymethylene segments or stronger mesogenic groups were used in the side chain. For our polymers reported here, cyano-*p*-biphenyl is not strong enough to stabilize a mesophase if a termethylene is used in between the mesogenic group and the disiloxane moiety.

Compared with Engel's polymers (Table 1), polymers P_1 , P_2 and P_3 not only have a much more stable mesophase but also have a much higher T_g even if a polyacrylate main chain is used as in P_1 and P_3 . This is attributed to the different mesogenic units. Cyano-*p*-terphenyl used in our polymers has a higher degree of conjugation and polarization than cyanophenyloxycarbonylphenyl used in theirs. In order to further weaken the mutual interactions between the main chain and the mesogens, a more flexible group such as trisiloxane moiety may be introduced in the spacer.

In conclusion, we have synthesized four monomers and their corresponding polymers. The structure-property relationship of this new series of polymers agrees with the general concept of SLCPs. The three polymers with cyano-*p*-terphenyl as mesogenic groups are liquid crystals with enantiotropic phase transitions, except the one with cyano-*p*-biphenyl groups. It implies that a mesogenic unit of higher degree of conjugation and polarization is required for this series of polymers to form a stable mesophase. In addition, the properties are also influenced by the nature of the main chain and the structure of the decoupling spacers. Therefore the decoupling of the motions of the main chain and the mesogenic side groups is incomplete even if a complex and very flexible decoupling spacer is deliberately incorporated in order to obtain the highest possible decoupling effect.

REFERENCES

- 1 Geelhaar, T., *Liquid Crystals*, 1998, 24: 91
- 2 Collings, Peter J., "Liquid Crystals", Princeton University Press, Princeton, 1990, p.162
- 3 Rinsdorf, H. and Zental, R., *Makromol. Chem.*, 1979, 180: 183
- 4 Zang, Z.Q., Zhang, D., Wan, X.H. and Zhou, Q.F., Submitted to *Molecular Crystals and Liquid Crystals*
- 5 Finkelmann, H. and Rinsdorf, H., *Makromol. Chem.*, 1978, 179: 273
- 6 Engel, M. and Rinsdorf, H., *Pure & Appl.*, 1985, 57: 1009
- 7 Apfel, M.A. and Finkelmann, H., *Anal. Chem.*, 1985, 57: 651
- 8 Okawa, Tadashi and Yamada, Shuji, 1996, EP 0 693 492 A1
- 9 Akiyama, E. and Matsui, N., *Liquid Crystals*, 1997, 23: 425
- 10 西野裕二, 山本昭, 1994, 特开平6-228163 (in Japanese)
- 11 Gray, G.W. and Goodbye, J.W., "Smectic Liquid Crystals—Textures and Structures", Leonard Hill, Glasgow and London, 1984, Plate 9 and 11
- 12 Percec, V. and Pugh, C., in "Side Chain Liquid Crystal Polymers". ed. by McArdle, C.B., Blackie, Glasgow and London, 1989, p.30
- 13 Nagase, Y. and Takamura, Y., *Makromol. Chem.*, 1992, 193: 1225