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# The synthesis and thermal properties of polyepichlorohydrin side-chain liquid crystal polymers

Xiangen Han [a], Robert A. Shanks [a,*], Dumitru Pavel [a,b]

[a] School of Applied Science, RMIT University, GPO Box 2476V, Melbourne, Vic. 3001, Australia
[b] National Research Council of Canada, Ottawa, Ontario, Canada A1B 3X7

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## Abstract

The synthesis and characterization of a new series of side-chain liquid crystal polyepichlorohydrin (PECH) polymers are described. The structures and thermal properties of the synthesized polymers were investigated using IR, NMR, polarized optical microscopy and differential scanning calorimetry. A substantial increase of the glass transition temperature with the degree of substitution of side-chain groups was observed. Polymers with a degree of substitution of side groups, of at least 60%, exhibited thermotropic liquid crystalline behaviour. The polymers present thermal liquid crystalline behaviour and form Schlieren and thread texture upon cooling from the isotropic phase, after annealing for 120 min at different temperatures. In addition, the thermal decomposition of PECHOPhPhCN was studied by thermogravimetry under both nitrogen and air environments. The temperature of the maximum decomposition rate was about 340 °C. Weight loss decreased considerably after 350 °C and was approximately 98% at 700 °C. Chemical modification of functional polymers offers a simple method for obtaining liquid crystalline polymers whose transition temperature can be tailored by varying the amount of substitution, however complete substitution cannot be achieved.

*Keywords:* Liquid-crystal polymers; Modification; Phase behaviour; Thermal properties

## 1. Introduction

Since the first introduction of side-chain liquid-crystal polymers (SCLCPs) by Finkelmann et al. [1], SCLCPs continue to be the focus of much research interest. This arises not only as a result of their properties as materials in a range of advanced electro-optical technologies, but also because they present a demanding challenge to our understanding of self-assembly in molecular systems. The main reason is that SCLCPs can combine the unique properties of low-molar mass liquid crystals and polymers together, which made it easier to form films during material processing. So far, many studies have been reported on the potential applications of SCLCPs in a wide range of advanced electro-optical technologies, such as information storage [2–6], holographic imaging, and non-linear optics [7–10].

The advantages of side-chain LCPs over low-molar-mass liquid crystals as image storage materials are as follows: (1) Because of the glass transition phenomenon ($T_g$), segmental motion of the polymer chains can be

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[*] Corresponding author. Tel.: +61 399 252 122; fax: +61 396 391 321.
*E-mail address:* robert.shanks@rmit.edu.au (R.A. Shanks).

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frozen in; thus it is expected that the stored image can be kept stable below $T_g$ for a long time. (2) Good film-forming properties of the polymers allow cell-free performance of the image storage materials, which is evidently favourable from the application viewpoint. (3) Low fluidity of the polymers is favourable for the long-term stability of the stored image.

The side-chain liquid crystalline properties depend on the polymer chemical structure (the nature of the polymer backbone, the flexibility and length of spacer group, and the mesogenic unit), molar mass, polydispersity, and tacticity. The spacer connecting the mesogenic unit to polymer backbone is regarded as an important constituent, in order to decouple the motion of backbone component from the arrangement of the mesogenic side-chains. Because of the complexity of the system, it is difficult to determine the effect of individual variables on liquid crystalline behaviour. Until now, there have been several systematic investigations into the correlation between the above-mentioned variables and liquid crystalline behaviour [11–13].

For conventional side-chain liquid crystalline polymers, mesogenic units based on homologs of low molecular weight liquid crystals were attached to polymer backbones as pendent groups through flexible aliphatic spacers using covalent bonding. The most frequently used side-chain mesogens have cyano, nitro, or alkoxy groups as terminal units because these groups induce dipole–dipole intermolecular interactions, which contribute to the overall stability of the mesophase. When these polymers are used for electro-optic devices, the presence of such dipoles is also of great importance in aligning the mesogens in an applied electric field. The most frequently used polymers in this research area have been polyacrylate [14,15], poly(methyl acrylate) [16,17] polyurethane [18] and polystyrene [19–22] and there has been only limited research on the polyepichlorohydrin-based SCLCPs polymers [23,24]. Few examples of liquid crystalline polyethers have been reported.

In our previous paper [25], we have studied the effect of spacer length on the thermal and physical properties of polymers. This paper reports the synthesis and characterization of a series of polyepichlorohydrin-based side chain liquid crystalline polymers prepared by nucleophilic substitution with different mesogenic groups and their thermotropic properties. All of the mesogens were chosen to be used in this research because they were the most widely used mesogenic groups and they have been attached to a wide range of polymer backbone types. Polyepichlorohydrin (PECH), chosen as the polymer backbone has $CH_2Cl$ groups that facilitate nucleophilic substitution by alkoxy, and more important is that PECH has a flexible backbone and had seldom been used in this research area.

## 2. Experimental

### 2.1. Materials

Polyepichlorohydrin (Aldrich, $[\eta] = 0.1580$ dl/g, DMF, at 25 °C) was purified by precipitation with methanol from chloroform solution. $^1H$ NMR ($CDCl_3$, $\delta$, ppm): 3.7 (s, $-CH_2O$, $-CH-$, $-CH_2Cl$). Tetrabutylammonium hydrogen sulfate (TBAH), 4-phenylphenol (PhPh) (98%), 4-phenylazophenol (PhN=NPhOH); *N*-(4-hydroxybenzylidene)-4-cyanoaniline (HOPhCH=NPhCN), 4-cyano-4′-hydroxybi-phenyl (HOPhPhCN) and other reagents (all from Aldrich) were used without further purification, *N*,*N*-dimethylformamide (DMF) (Aldrich) was treated with potassium hydroxide, then dried by azeotropic distillation with benzene and distilled under reduced pressure.

### 2.2. Synthesis of the sodium salts of monomers

The sodium salts of monomers were prepared by modification of the method described previously [26] using an exchange reaction in dry ethanol containing sodium ethoxide. Ethanol was removed under vacuum and the salt was dried in vacuo.

### 2.3. Substitution of PECH

The general procedure, shown in Fig. 1, for the grafting of PECH with different sodium salts of mesogens (*p*-phenylphenol (PhPhOH) (98%), 4-phenylazophenol (PhN=NPhOH); *N*-(4-hydroxybenzylidene)-4-cyanoaniline (HOPhCH=NPhCN), 4-cyano-4′-hydroxybiphenyl (HOPhPhCN). Table 1 summarizes the experimental conditions and the results of substitution of PECH for all reactions performed. An example is as follows.

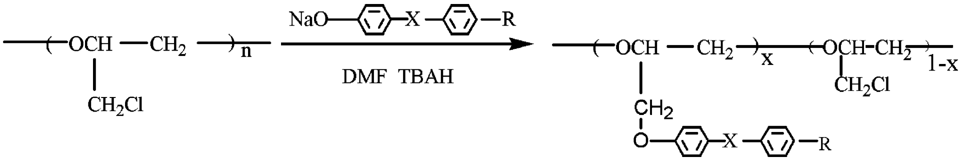


Fig. 1. Reaction scheme where R = H, CN; X = O, N=N, or CH=N; DMF = *N*,*N*-dimethylformamide; TBAH = tetrabutylammonium hydrogen sulfate.

Table 1
Results of the modification of PECH using different mesogenic groups

| Nucleophile | Nucleophile (mmol) | Reaction time (h) | Substitution $CH_2Cl$ (%) |
|---|---|---|---|
| NaOPhPh | 11.7 | 72 | 94 |
| NaOPhN=NPh | 11.8 | 72 | 93 |
| $NaOPhCH{=}NPhC_4H_9$ | 11.9 | 72 | 84 |
| NaOPhPhCN | 11.6 | 72 | 91 |

TBAH = 11.8 mmol, reaction temperature: 60 °C.

1.5 g of PECH was dissolved in DMF (50 mL) and sodium 4-phenylphenoxide (1.98 g, 11.70 mmol) and TBAH (0.40 g 1.18 mmol) were added. The reaction mixture was stirred at 60 °C under a nitrogen stream. The degree of substitution as a function of time was determined. The reaction mixture was centrifuged in order to remove sodium chloride and then the liquid was poured into methanol. The crude copolymer was purified by precipitation several times from dichloromethane into methanol and finally dried under vacuum at 40 °C for 24 h.

### 2.4. Characterization techniques

Fourier Transform IR measurements were made on a Perkin–Elmer spectrometer 1725×. Samples were prepared as KBr pellets or by casting films from solutions onto NaCl plates. NMR spectra were recorded at room temperature on a Varian Gemini-200 spectrometer using $CDCl_3$ as the solvent. Thermal properties of the generated polymeric materials were investigated by differential scanning calorimetry (DSC, Perkin–Elmer Pyris 1) Calibration of temperature was performed with indium and zinc while enthalpy was calibrated with the melting of indium; a furnace calibration was performed as recommended by the manufacturer. The samples were heated and subsequently cooled in the range between −20 and 150 °C, heating and cooling rates were 10 °C/min. After the first heating cycle, the samples were held at 150 °C for 5 min to obtain identical thermal histories for all polymers before a second heating/cooling cycle. The glass transition temperature ($T_g$) was measured at the middle of the change in the heat capacity.

A Nikon Labophot 2 polarizing optical microscope, equipped with a Mettler FP-82 hot stage and Sony CCD-IRIS colour video camera was used to inspect the optical texture. Images were captured with a Nikon Coolpix 5000 digital camera. Thermal decomposition studies were performed using a Perkin–Elmer TGA7 under nitrogen atmospheres at a heating rate of 10 °C/min. The temperature scale was calibrated by high purity standards (nickel, iron) using the Curie temperature and mass was calibrated using a standard mass.

### 2.5. Structure characterization

The structure of the synthesized polymers was confirmed by IR, $^1H$ NMR and $^{13}C$ NMR spectroscopy. All of the polymers were obtained by nucleophilic displacement of the halide of polyepichlorohydrin (PECH) according to the previously developed synthetic approach [26]. All of the purified chemical modification products gave satisfactory data corresponding to their expected molecular structures. An example of the IR spectrum of PECH and PECH—PhPhCN is given in Fig. 2. The spectrum of PECH and the monomer are shown in the same figure for comparison. The —CN stretching and bending vibrations of the monomer (2221 cm$^{-1}$) were observed at 2230 cm$^{-1}$ from the PECH—PhPhCN IR spectrum, demonstrating that the monomer was successfully grafted to the polymer backbone. NMR analysis proved that the monomers have been attached to the polymer backbone. Fig. 3 shows

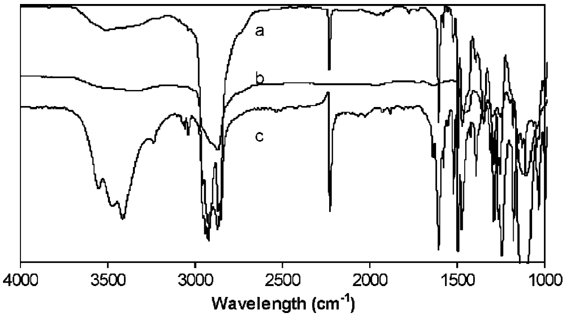


Fig. 2. Infrared spectra of (a) PECH—PhPhCN (b) PECH (c) HOPhPhCN.

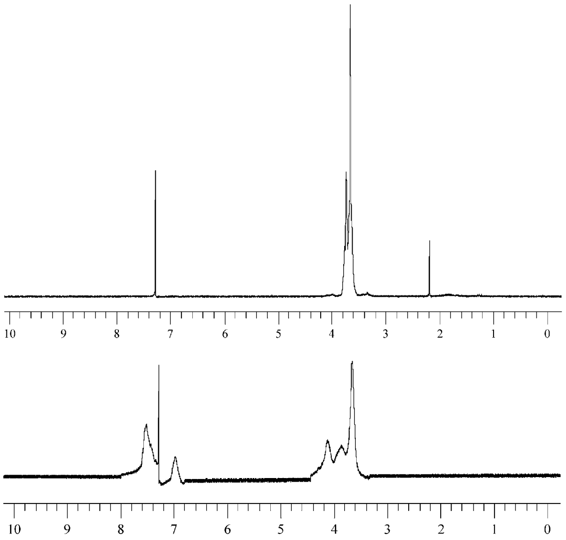
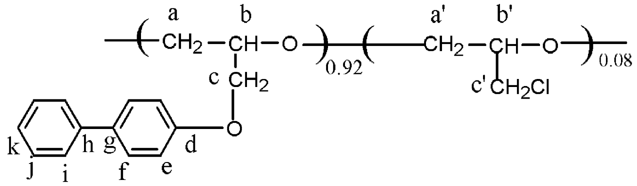


Fig. 3. $^1H$ NMR spectra of PECH (a) and PECH—PhPhCN (b) in $CDCl_3$.

Table 2
$^1H$ and $^{13}C$ NMR spectroscopic data for PECH-based biphenyl derivatives



| $^1H$ NMR data | | $^{13}C$ NMR data | |
|---|---|---|---|
| Resonances (ppm) | Assignment | Resonances (ppm) | Assignment |
| 3.5, 4.2 | a, b, a′, b′, c′ | 43.5 | c′ |
| 4.5 | c | 65.1 | c |
| 6.8 | j | 69.6–70.1 | a, a′ |
| 7.4 | k, i, f | 77.0–77.5 | b, b′ |
| 7.9 | e | 115.2 | j |
| | | 126.4 | f |
| | | 128.3 | d |
| | | 129.3 | i |
| | | 130.1 | e |
| | | 139.4 | h |
| | | 128 | k |
| | | 145.4 | g |

the $^1H$ NMR spectra of PECH and PECH—PhPhCN in d-chloroform. There are no peaks in the acetylene and aromatic ring-H absorption region ($\delta \sim 2.0$, 6.0–8.0 ppm, respectively) in the spectrum of the PECH. Instead, a new broad peak appeared in the aromatic absorption region ($\delta = 6.0$–8.0 ppm).

NMR data are also summarized and showed in Tables 2 and 3 for the synthesised PECHOPhN=NPh, and PECHOPhCH=NPhCN.

IR data (KBr pellet, $cm^{-1}$) of modified polymers were as follows:

PECH modified with 4-hydroxybiphenyl (PECHOPhPh): 3078 $cm^{-1}$ (C—H aromatic), 1617 $cm^{-1}$ (C=C, aromatic).

PECH modified with 4-phenylazophenol (PECHOPhN=NPh): 3068 $cm^{-1}$ (C—H aromatic), 1607, $cm^{-1}$ (C=C aromatic), 1680 $cm^{-1}$ (—N=N—).

PECH modified with *N*-(4-hydroxybenzylidene)-4-butylaniline (PECHOPhCH=NPhCN): 3059 $cm^{-1}$ (C—H aromatic), 1610 $cm^{-1}$ (C—C aromatic), 2231 $cm^{-1}$ (—CN), 1496 $cm^{-1}$ (—CH=N—).

PECH modified with 4-cyano-4′-hydroxybiphenyl (PECHOPhPhCN): 3079 $cm^{-1}$ (C—H aromatic), 1605 $cm^{-1}$, (C=C aromatic), 2230 $cm^{-1}$ (—CN).

## 3. Results and discussion

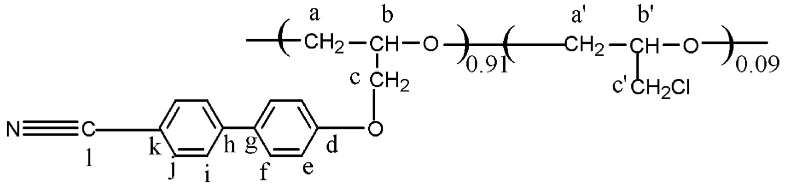
### 3.1. Kinetics of substitution

The results for the modification of PECH summarized in Table 1 demonstrate that 84–94% substitution of the $CH_2Cl$ group was obtained. As shown in Fig. 4, the analysis of the substitution reaction curves was carried out using second-order kinetics. In the case of PECHOPhPhCN, the second-order rate law was followed until about 91% substitution while for the polymer PECHOPhPhCN, a deviation was observed after 70% substitution when the reaction rate decreased. Under the chosen experimental conditions, the chemical modification of PECH was an $S_N2$ reaction, as an elimination reaction would lead to the formation of double bonds, which were not been detected in the modified polymers either by IR or by $^{13}C$ NMR.

### 3.2. Thermal properties and liquid crystal textures of the polymers

The polymers obtained showed remarkably different DSC patterns depending on their different mesogens. As an example shown in Fig. 5, the thermal properties of PECHOPhPhCN were strongly dependent on the degree of substitution. It was found that there was a minimum substitution limit of approximately 60% necessary for liquid crystal formation. Below this limit, the copolymers all resemble typical amorphous polymers. The DSC curves were characterized by a marked glass transition temperature. There was a sharp increase in the glass transition temperature with increasing amount of substitution (as shown in Fig. 5). It is evident that the bulky side groups cause severe hindrance to main chain motions. Such a linear dependence of the glass transition temperature was observed for other amorphous modified PECH [23,24].

Table 3
$^1$H and $^{13}$C NMR spectroscopic data for PECH-based cyanobiphenyl derivatives



| $^1$H NMR data | | $^{13}$C NMR data | |
|---|---|---|---|
| Resonances (ppm) | Assignment | Resonances (ppm) | Assignment |
| 3.4, 4.4 | a, b, a′, b′, c′ | 43.4 | c′ |
| 4.6 | c | 64.3 | c |
| 6.9 | j | 69.6–70.1 | a, a′ |
| 7.5 | k, i, f | 77.0–77.5 | b, b′ |
| 7.9 | e | 114.5 | j |
| | | 124.5 | f |
| | | 127.4 | d |
| | | 129.3 | i |
| | | 130.1 | e |
| | | 132 | h |
| | | 139 | k |
| | | 143.3 | g |

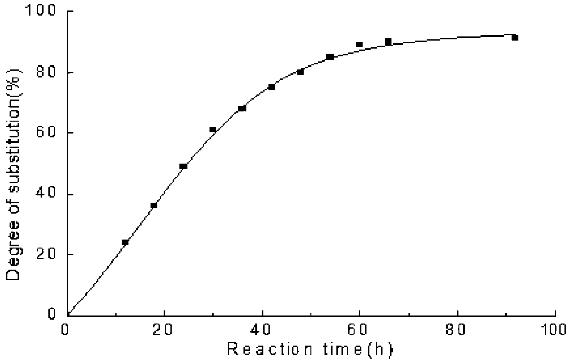


Fig. 4. Plot of the amount of —$CH_2Cl$ of PECH substituted by sodium 4-cyano-4′-biphenyloxide versus reaction time.

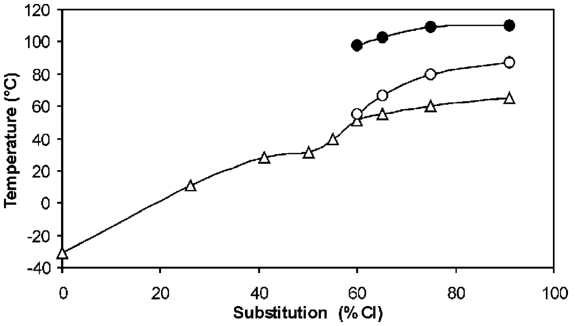


Fig. 5. The effect of substitutions of chlorine on the thermal properties of side-chain liquid crystal PECHOPhPhCN polymers: (–●–) isotropic temperature; (–○–) melting temperature; (–△–) glass transition temperature.

The physical and thermal data of all synthesised polymers are listed in Table 4. The thermal data were extracted from a second heating cycle of the DSC temperature–heat flow profile. It was observed that different mesogenic group attached to the same polymer backbone have different thermal behaviour. For the polymer PECHOPhPh, there was only one transition peak at 89 °C. It showed no liquid crystalline properties when PhPh was attached to the polyepichlorohydrin backbone and this was confirmed by POM. Fig. 6 shows DSC curves of PECHOPhN=NPh, PECHOPhN=NPhCN, and PECHOPhCH=NPhCN. The DSC curves of all the synthesised polymers (except PECHOPhPh) contained two endothermic peaks. Optical microscopy observations of PECHOPhN=NPh are shown in Fig. 7 (at 70 °C after annealing for 120 min), the phase was assigned as a grainy texture. Optical microscopy observations of PECHOPhPhCN are shown in Fig. 8, and the texture was formed upon cooling from an isotropic phase, and the phase was assigned as nematic Schlieren texture. Optical micrography of PECHOPhCH=NPhCN is shown in Fig. 9, and the texture was formed upon cooling from an isotropic phase and annealing for 120 min at 95 °C.

In contrast to the results of previous research work [14–22], this series of mesogenic units demonstrates that no spacer was required to obtain liquid crystalline behaviour from PECH (except PECHOPhPh, for which no liquid crystal properties appeared), although the thermal characteristics of the four copolymers are quiet different. On the other hand, polyacrylates and

Table 4
Thermal properties of PECH modified copolymer

| Polymer | DS (%)[a] | $T_m$ (°C)[b] | $T_i$ (°C)[b] | $T_{I-N}$ (°C)[c] | $T_{N-C}$ (°C)[c] | [$\eta$] (dl/g)[d] |
|---|---|---|---|---|---|---|
| PECH | – | – | – | – | – | 0.1580 |
| PECHOPhPh | 94 | 89 | – | – | – | 0.2475 |
| PECHOPhN=NPh | 93 | 75 | 101 | 89 | 66 | 0.2933 |
| PECHOPhCH=NPhCN | 84 | 77 | 92 | 99 | 72 | 0.3055 |
| PECHOPhPhCN | 91 | 87 | 110 | 105 | 75 | 0.2394 |

[a] Expressed in mole percent and determined from $^1$H NMR measurements.
[b] $T_m$ = melting temperature, $T_i$ = isotropization temperature.
[c] Determined by optical microscopy.
[d] [$\eta$] limiting viscosity number, solution: DMF, 25 °C.

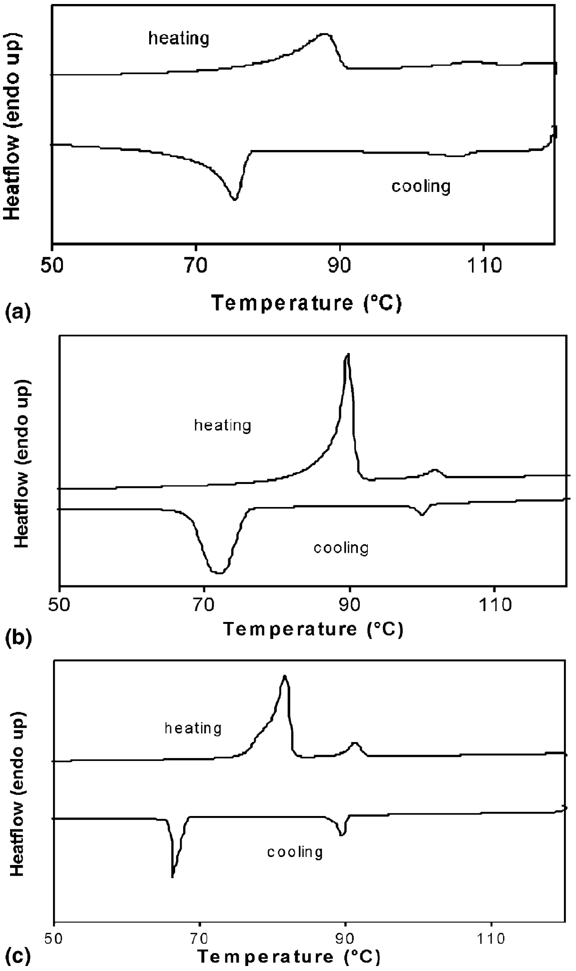


Fig. 6. Normalised second cooling and heating DSC curves of (a) PECH—PhPhCN, (b) PECH—PhCH=NPhCN and (c) PECH—PhN=NPh.

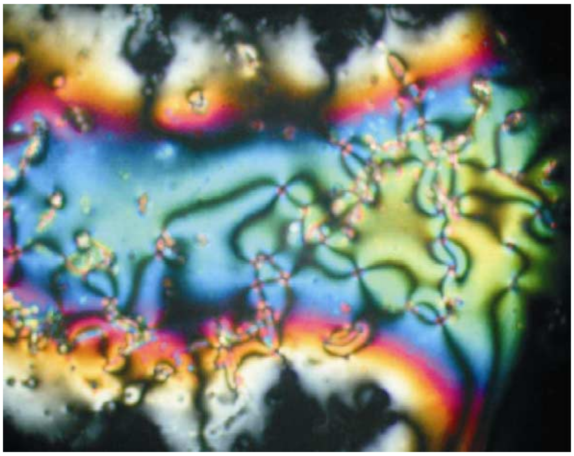


Fig. 7. Typical polarized optical micrograph of PECH-OPhN=NPh, Schlieren texture upon cooling from isotropic phase and annealing at 70 °C for 120 min, magnification: ×200.

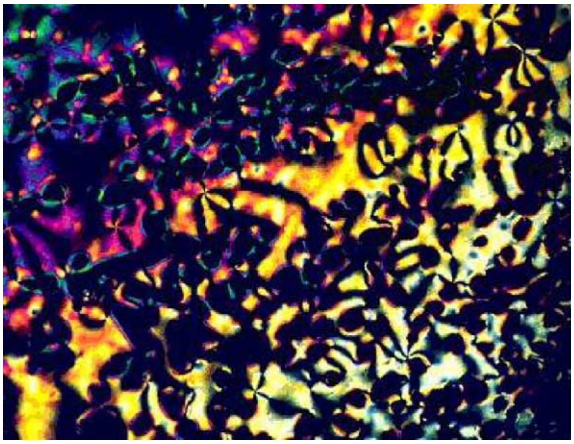


Fig. 8. Polarized optical micrograph of the nematic Schlieren texture of PECH—PhPhCN observed upon cooling from the isotropic phase and annealing at 95 °C for 120 min, magnification: ×200.

polymethacrylates connecting mesogenic side groups without flexible spaces sometimes have difficulty forming mesophases [14–17], and exhibit high transition

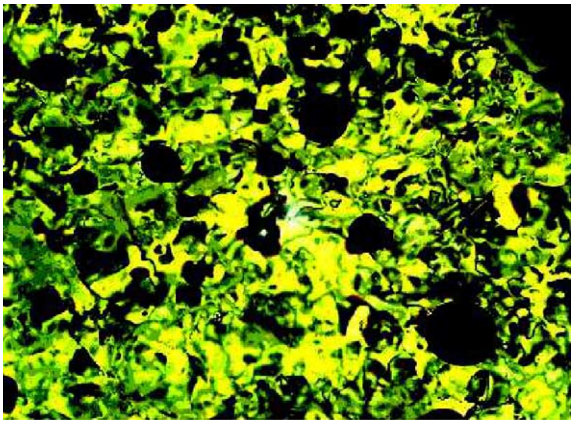


Fig. 9. Typical optical polarized light micrographs of the threaded texture for PECH—PhCH=NPhCN, Schlieren texture upon cooling from isotropic phase and annealing at 95 °C for 120 min, magnification: ×200.

temperatures, even if mesophases are formed. However, PECH-based copolymers exhibited an enantiotropically nematic phase over a moderately low transition temperature region in spite of the absence of a flexible spacer. This demonstrates that the flexibility of the ether backbone contributed to liquid crystalline ordering of the mesogenic pendant groups.

### *3.3. Thermal degradation experiments*

TGA was used to investigate the thermal degradation behaviour of a PECH-based series of copolymers. The thermal decomposition of PECH-based copolymers were studied in both nitrogen and air environments. Fig. 10 shows the TGA curves of PECH—PhPhCN as a function of temperature during dynamic heating (30–800 °C at 10 °C/min) in an inert environment (nitrogen) for the same sample. The thermal decomposition process under an inert atmosphere only involves the chain scission of polymers, and there is no interaction between the polymer and environment. The temperature at the maximum decomposition rate was about 340 °C. Weight loss decreased considerably after 350 °C and was approximately 98% at 700 °C.

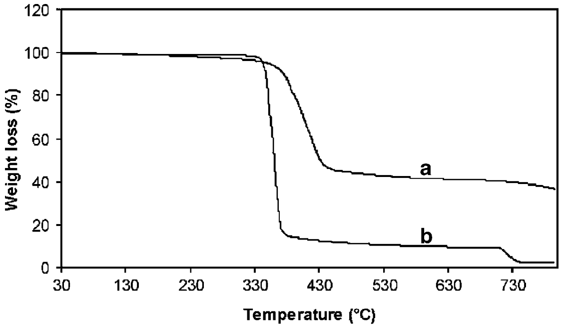


Fig. 10. Thermogravimetry curves of PECH—PhPhCN under (a) air and (b) nitrogen.

## 4. Conclusions

PECH-based SCLCPs have been synthesized by nucleophilic substitution. The structure of the synthesized copolymers was confirmed by IR and $^1$H and $^{13}$C NMR spectroscopy. All of the copolymers were obtained by nucleophilic displacement of the halogen of polyepichlorohydrin according to a previously developed synthetic approach. All the purified chemical modification products gave satisfactory spectroscopic data corresponding to their expected molecular structures.

There was a minimum substitution limit of approximately 60% necessary for liquid crystal formation. Below this limit, the copolymers all resembled typical polymers with bulky branch groups. Although the thermal characteristics of the four copolymers were very different, chemical modification of functional polymers offered a simple method for obtaining liquid crystalline polymers whose transition temperatures can be tailored by varying the amount of substitution, however complete substitution cannot be achieved.

In addition, the thermal decomposition of PECH—PhPhCN was studied by TGA in both nitrogen and air environments. The temperature at the maximum decomposition rate was about 340 °C. Weight loss decreased considerably at 350 °C and was approximately 98% at 700 °C.

## Acknowledgment

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## References

[1] Finkelmann H, Happ M, Portugall M, Ringsdorf H. Makromol Chem 1978;179:2541.
[2] Meng X, Natansohn A, Barrett C, Rochon P. Macromolecules 1996;29:946.
[3] Hvilsted S, Andruzzi F, Kulinna C, Siesler HW, Ramanujam PS. Macromolecules 1995;28:2172.
[4] Bao X, Tian Y, Tong WM. Organic photonic materials and devices II. Proceedings of SPIE, vol. 3939. The International Society for Optical Engineering; 2000. p. 105.
[5] Laura A, Massimo F, Marco G, Massimo H, Giancarlo G, Michele L. Molecular Cryst Liquid Cryst Sci Technol, A: Molecular Cryst Liquid Cryst 2002;37:229.
[6] Kajzar F, Noel C. Molecular Phys Rep 1999;25:51.
[7] Lee HK, Doi K, Kanazawa A, Shiono T, Ikeda T, Fujisawa T, et al. Polymer 2000;41:1757.

[8] Fan G, Zhao X, Zhou E. Polymer preprints, vol. 43. Division of Polymer Chemistry, American Chemical Society; 2002. p. 605.

[9] Trollsas M, Sahlen F, Gedde UW, Hult A, Hermann D, Rudquist P, et al. Macromolecules 1996;29:2590.

[10] Craig HA, Imrie CT. Macromolecules 1995;28:3617.

[11] Brecl M, Malavasic T. J Polym Sci: Part A: Polym Chem 1997;35:2871.

[12] Brecl M, Zigon M, Malavasic T. J Polym Sci: Part A: Polym Chem 1998;36:2135.

[13] Lacoudre N, Borgne AL, Spassky N, Vairon JP. Mol Cryst Liq Cryst 1988;155:113.

[14] Percec V, Lee M. Macromolecules 1991;24:1017.

[15] Craig AA, Winchester I, Madden CP, Larcey P, Hamley WI, Immrie TC. Polymer 1998;39:1197.

[16] Percec V, Tomazos D. Polymer 1990;31:1658.

[17] Mirceva A, Zigon M. Polym Bull 1998;41:447.

[18] Imrie TC, Karasz EF. Macromolecules 1992;25:1728.

[19] Imrie TC, Karasz EF. Macromolecules 1993;26:3803.

[20] Imrie TC, Karasz EF. Macromolecules 1993;26:545.

[21] Imrie TC, Karasz EF, Attard GS. Macromolecules 1996;29:1031.

[22] Imrie CT, Karasz EF, Attard GS. Macromolecules 1994;27:1578.

[23] Pugh C, Percec V. Polym Bull 1986;16:521.

[24] Ujiie S, Iimura K. Polym J 1992;24:427.

[25] Han X-E, Shanks RA. Macromol Chem Phys 2004;205:743.

[26] Cser F, Nyitrai K, Horvath J, Hardy G. Eur Polym J 1985;21:259.