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Synthesis and characterization of side-chain liquid-crystalline poly(ethyleneimine)s with cyanobiphenyl groups

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A series of polyethyleneimine-based side-chain liquid-crystalline polymers substituted with different ratios of cyanobiphenyl as pendent mesogenic groups has been synthesized in which the spacer length varies between two and six methylene units. The structures of the synthesized polymers are confirmed by infrared and ^1H nuclear magnetic resonance spectroscopy. The thermal properties of these polymers have been investigated using differential scanning calorimetry, polarized optical microscopy and X-ray diffraction. The results indicate that the thermal behaviour of the polymers is strongly dependent on the degree of substitution. Polymers containing more than 69% of mesogenic groups exhibit nematic-type thermotropic liquid-crystalline behaviour with schlieren textures. Below this limit, the polymers are amorphous. Polymers with a higher degree of substitution present the crystalline states. The phase transition temperatures increase and the mesomorphic temperature ranges widen with increasing degree of substitution. The clearing temperatures decrease as the spacer length increases. An odd-even effect in the clearing temperatures is observed and the odd members display the higher values.

1. Introduction

Side-chain liquid-crystalline polymers (SCLCPs) have attracted growing interest not only because of their great potential in a wide range of applications, but also because they present a demanding challenge to our understanding of self-assembly in molecular systems [1–5]. Their unique behaviour is caused by the specific structure that comprises three distinct units: a polymer backbone, a flexible spacer and a mesogenic unit [6–8]. Polysiloxanes [9, 10], polyacrylates [11, 12] and polymethacrylates [13–16] are common main-chain components of side-chain liquid crystalline polymers. Polyethyleneimine (PEI) is a water-soluble polymer which contains nitrogen lone-pair electrons and acts as a chelating agent for many metals. The use of PEI as a main chain appears interesting because the backbone with amine function offers many possibilities for chemical modification. By alkylation and quaternization, various bulky, ionic or interactive groups may be introduced onto the backbone to generate attractive non-ionic or ionic SCLCPs [17–21]. Ujiie and Iimura [18] reported a linear poly(ethyleneimine) (LPEI) bearing mesogenic 4-substituted azobenzene attached as a pendant group via six methylene spacers exhibited

nematic phase. This behaviour is in contrast to the exclusive existence of a crystalline phase in LPEI samples consisting of 4-methoxy-4'-biphenyloxy with six and twelve methylene spacers described by Masson *et al.* [20]. None of these LPEI samples show the liquid-crystalline phase with the substitution ratios increasing from 50% to 100%. Stebania and Lattermann [22] presented the synthesis of 3,4-bis(alkoxy)benzoyl substituted PEI via cationic polymerization. The lack of classical rod-like side groups or the lower molar mass of the LPEI backbone, or both, lead in their case to polymers exhibiting a liquid-crystalline phase which is in the glassy state at room temperature. The results show that the chemical architecture of the LPEI chain alone could not be responsible directly for the development of crystalline order. In addition, Rodriguez-Parada and Percec [23] and Kawakami *et al.* [24] reported that side-chain liquid-crystalline PEIs were obtained by cationic polymerizations with biphenyl derivatives as the mesogenic groups. Here the polymerizations were carried out very slowly and some chain transfer reactions might have occurred to give low molecular weight oligomers. In general, it is difficult to control the molecular weight of the polymers and polymers with low molecular weights could not reveal liquid-crystalline behaviour. Moreover, the alkylation of LPEI with 4-cyano-4'-(4-bromobutoxy)biphenyl was

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also conducted by Kawakami *et al.* [24]. The degree of substitution is too low to exhibit liquid-crystalline behaviour and the quaternization of the amino group in the polymer backbone has a strong effect on the thermal behaviour of the polymer. In all, the molecular weight of the polymer and the degree of substitution are shown to be important factors in the formation of liquid crystals, but the relationship between these factors (and the LC formation) is complicated. Owing to the complexity of the system, it is difficult to determine the effect of individual variables on liquid-crystalline behaviour. Subsequently, there has been only limited research on the PEI-based SCLCPs.

As an incomplete substitution of the amino units leaves some secondary amino groups in the LPEI backbone, the system can be intrinsically a compound of copolymers. The effect of chain structure on the liquid-crystalline behaviour is as yet unknown. Therefore, a series of PEI-based SCLCPs substituted with different ratios of cyanobiphenyl as pendent mesogenic groups, in which the spacer length varies between two and six methylene units, has been synthesized in this work. The study is focused on how the thermal properties of polymers are affected by alkylene spacers of different lengths and the relationship between the different substitution ratios and the thermal properties of these polymers.

2. Experimental details

2.1. Materials

PEI was purchased in aqueous solution (PEI, 50 wt% polymer, $\bar{M}_w=75,000$) from BDH Laboratory Supplies, Poole, England. 4-cyano-4'-hydroxybiphenyl (C.P.) was purchased from Trademax Pharmaceuticals and Chemicals Co., Ltd, Shanghai, China. 1,2-bibromoethane, 1,3-bibromopropane, 1,4-bibromobutane, 1,5-bibromopentane and 1,6-bibromohexan (C.P.) were purchased from Yixing East Fine Chemical Factory, China. Alkyl bromides and 1,4-dioxane were distilled under reduced pressure. Tetrahydrofuran (THF) was dried over a Na wire and distilled onto calcium hydride. All other reagents were used as commercially obtained.

2.2. Instruments

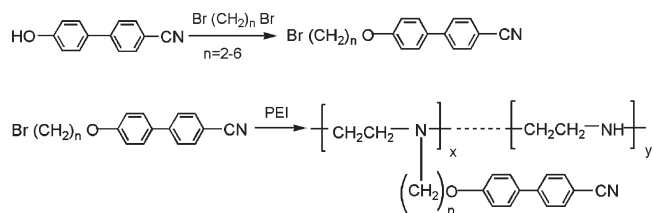
Infrared (IR) spectra were recorded using a Nicolet-60SXB FTIR spectrometer. ^1H nuclear magnetic resonance (NMR; 300 MHz) spectra were recorded on a Varian Mercury VX-300 in CDCl_3 solutions, using tetramethylsilane (TMS) as an internal standard. Thermal characterization was performed by means of differential scanning calorimetry (DSC) on the TA DSC-Q10 instrument. Measurements were carried out with heating and cooling rates at $10^\circ\text{C min}^{-1}$ under a dry nitrogen purge. The second heating and cooling runs were evaluated. The optical textures of the mesophases were studied with polarizing optical microscopy (POM; magnification 10×20 ; Olympus BH-2) fitted with a Linkam THMSE 600 type heating stage with a heating or cooling rate of 5°C min^{-1} . The X-ray diffraction (XRD) patterns were obtained through a D/MAX-III A diffractometer (Rigaku, Tokyo, Japan) with nickel-filtered Cu $K\alpha$ radiation, at a scanning rate of 8° min^{-1} .

2.3. Synthesis

The synthetic route is outlined in scheme 1. The polymers are abbreviated PCN n , where n denotes the number of methylene units in the spacer. The following numbers indicate the degree of substitution by the mesogenic groups as described in table 1.

4-cyano-4'-(ω -bromoalkyloxy) biphenyls. These were synthesized using a modified procedure as described by Attard *et al.* [25]. 1,2-Bibromoethane (0.02 mol) and anhydrous K_2CO_3 (2.76 g, 0.02 mol) were added to ethanol (20 ml). 4-cyano-4'-hydroxybiphenyl (1.95 g, 0.01 mol) was dissolved in ethanol. The solution was added dropwise into the mixture, which was refluxed with stirring for 16 h. The reaction mixture was filtered while hot and the filtrate was poured into petroleum ether. The resulting white precipitate was filtered and washed thoroughly with water. The product was recrystallized twice from ethanol with hot filtration.

- 4-cyano-4'-(2-bromoethoxy) biphenyl: melting point $77\text{--}78^\circ\text{C}$, yield 53%, IR (KBr, cm^{-1}): 1267 (CH_2Br), 644 ($\nu_{\text{C-Br}}$). ^1H NMR (CDCl_3 , δ in ppm):



Scheme 1. Synthesis of mesogens and SCLC polymers.

Table 1. The conditions and results of the preparation of PCN*n*.

Sample	Solvent	Molar ratio of PEI to mesogenic group	Time (h)	Yield (%)	Degree of Substitution (%)
PCN2-86	THF:dioxane (1:1)	1:1	96	31	86
PCN3-82	THF:dioxane (1:1)	1:1	96	38	82
PCN4-79	THF:dioxane (1:1)	1:1	96	42	79
PCN5-76	THF:dioxane (1:1)	1:1	96	59	76
PCN6-74	THF:dioxane (1:1)	1:1	96	62	74
PCN5-48	Ethanol	1:1	96	47	48
PCN5-56	THF:dioxane (1:1)	1:0.8	96	54	56
PCN5-69	THF:dioxane (1:1)	1:0.9	96	57	69
PCN5-83	THF:dioxane (1:1)	1:1	150	53	83
PCN6-81	THF:dioxane (1:1)	1:1	150	56	81

7.5, 6.9 (m, aromatic, 8H); 4.2 (t, PhOCH₂, 2H); 3.6 (t, CH₂Br, 2H).

- 4-cyano-4'-(3-bromopropoxy) biphenyl: melting point 100–101°C, yield 57%, IR (KBr, cm⁻¹): 1267 (CH₂Br), 644 (ν_{C-Br}). ¹H NMR (CDCl₃, δ in ppm): 7.5, 6.9 (m, aromatic, 8H); 4.1 (t, PhOCH₂, 2H); 3.6 (t, CH₂Br, 2H); 2.2 (q, CH₂, 2H).
- 4-cyano-4'-(4-bromobutoxy) biphenyl: melting point 62–63°C, yield 76%, IR (KBr, cm⁻¹): 1267 (CH₂Br), 644 (ν_{C-Br}). ¹H NMR (CDCl₃, δ in ppm): 7.5, 6.9 (m, aromatic, 8H); 4.0 (t, PhOCH₂, 2H); 3.5 (t, CH₂Br, 2H); 2.2–2.0 (m, CH₂, 4H).
- 4-cyano-4'-(5-bromopentyloxy) biphenyl: melting point 76–78°C, yield 72%, IR (KBr, cm⁻¹): 1267 (CH₂Br), 644 (ν_{C-Br}). ¹H NMR (CDCl₃, δ in ppm): 7.5, 6.9 (m, aromatic, 8H); 4.0 (t, PhOCH₂, 2H); 3.5 (t, CH₂Br, 2H); 2.0–1.6 (m, CH₂, 6H).
- 4-cyano-4'-(6-bromohexyloxy) biphenyl: melting point 68–69°C, yield 64%, IR (KBr, cm⁻¹): 1267 (CH₂Br), 644 (ν_{C-Br}). ¹H NMR (CDCl₃, δ in ppm): 7.5, 6.9 (m, aromatic, 8H); 4.0 (t, PhOCH₂, 2H); 3.5 (t, CH₂Br, 2H); 1.9–1.2 (m, CH₂, 8H).

Poly[N-(4-cyano-4'-biphenyloxyalkyl)ethyleneimine]s.

PCN*n* were synthesized using methods similar to those reported in [18, 20, 26]. A 50% aqueous solution of PEI 0.86 g (0.01 mol) and 4-cyano-4'-(ω-bromoalkoxy) biphenyl (0.01 mol) were dissolved in a mixture of freshly distilled THF and 1,4-dioxane. Then 0.02 mol of sodium hydrogen carbonate was added to the mixture. The reaction mixture was stirred at the reflux temperature under a dry nitrogen stream for 96 h. After the reaction, the product was filtered while hot and the filtrate was concentrated. The product was reprecipitated by adding *n*-hexane. Finally the polymers were filtered off and dried under vacuum at 60°C for 48 h.

- PCN2: yield 31%, degree of substitution 86%. ¹H NMR (CDCl₃, δ in ppm): 7.7–6.9 (m, aromatic,

8H); 4.0 (t, PhOCH₂, 2H); 3.0–2.4 (m, NCH₂, 6H).

- PCN3: yield 38%, degree of substitution 82%. ¹H NMR (CDCl₃, δ in ppm): 7.7–6.9 (m, aromatic, 8H); 4.0 (t, PhOCH₂, 2H); 3.0–2.4 (m, NCH₂, 6H); 1.8–1.5 (m, CH₂, 2H).
- PCN4: yield 42%, degree of substitution 79%. ¹H NMR (CDCl₃, δ in ppm): 7.7–6.9 (m, aromatic, 8H); 4.0 (t, PhOCH₂, 2H); 3.0–2.4 (m, NCH₂, 6H); 1.8–1.5 (m, CH₂, 4H).
- PCN5: yield 59%, degree of substitution 76%. ¹H NMR (CDCl₃, δ in ppm): 7.7–6.9 (m, aromatic, 8H); 4.0 (t, PhOCH₂, 2H); 3.0–2.4 (m, NCH₂, 6H); 1.9–1.4 (m, CH₂, 6H).
- PCN6: yield 62%, degree of substitution 74%. ¹H NMR (CDCl₃, δ in ppm): 7.7–6.9 (m, aromatic, 8H); 4.0 (t, PhOCH₂, 2H); 3.0–2.4 (m, NCH₂, 6H); 1.8–1.4 (m, CH₂, 8H).

(The degree of substitution was calculated from ¹H NMR.)

3. Results and discussion

3.1. Synthesis

In the synthesis of 4-cyano-4'-(ω-bromoalkoxy) biphenyls, the formation of disubstitution byproduct was avoided by adding excess dibromoalkane and reducing the addition rate of 4-cyano-4'-hydroxybiphenyl.

The results of the polymerizations under various conditions are presented in table 1. The degree of substitution is found to be dependent on the solvent. The product was insoluble in ethanol: precipitation occurred during the reaction so that part of the reaction took place in a heterogeneous medium. Most of the alkylation of PEI with mesogenic alkyl bromides was realized in the mixture of THF and 1,4-dioxane. It is worthwhile to point out that fully alkylated polymers could not be obtained even though the reaction is

quantitative at moderated ratios of transformation. For PCN5, the degree of substitution of mesogenic groups depends on the solvent in which the polymerization is carried out and the reaction time (compare samples PCN5-48, PCN5-76 and PCN5-83). A 7% increase in the degree of substitution is obtained as the reaction time increases by 54 h. When the reaction is carried out in a homogeneous medium, using the mixture of THF and 1,4-dioxane as the solvent, the degree of substitution increases. In addition, the degree of substitution of mesogenic groups is observed to decrease with increasing spacer length under identical reaction conditions. This effect agrees well with Han *et al.*'s [27] recent study of the chemical modification of polyepichlorohydrin: the degree of substitution of the chloromethyl groups decreases with increasing spacer length. It seems that the poor swelling of the polymer backbone and the large size of the mesogenic groups are the causes. This effect is consistent with the study conducted by Masson *et al.* [20] on the alkylation of LPEI with 4'-methoxybiphenyl. Fully alkylated samples could not be obtained when the polymerization was carried out in a homogeneous medium using sulfolane as the solvent. Some quaternization reactions of the amino group in the polymer backbone might have occurred. The effect of the quaternization of the amino group in the backbone on the thermal properties will be a topic investigated in our future work.

3.2. IR and ^1H NMR characterization

Preparation of PCN n was conducted according to the reaction shown in scheme 1. The chemical structures of all products mentioned previously were verified by IR and ^1H NMR spectroscopy. The IR and ^1H NMR

spectra of PCN n polymers are in full agreement with the expected structures.

The IR absorption spectra of PEI and the corresponding PCN n polymers were obtained to characterize the interaction between the PEI main chain and the mesogenic groups. Figure 1 presents the characteristic absorption bands of the reactant and PCN5 (a representative example for PCN n). The appearance and disappearance of key vibrations can be seen clearly. In the IR spectrum of PCN5, the major NH band at 3400 cm^{-1} attributed to the N–H band with bonded hydrogen becomes much smaller. In addition, absorption bands due to the mesogenic groups appear at 2940 cm^{-1} (CH_2 stretching vibration) and 2223 cm^{-1} (CN stretching vibration).

NMR analyses of the PCN n products confirm the attachment of the synthesized mesogenic groups onto the PEI backbone, which is in agreement with the reaction shown in scheme 1. The ^1H NMR spectra of all PCN n samples are similar, and their shift data are given in the section 2.3. The spectrum of PCN5 is provided as a representative example (see figure 2). The ^1H NMR spectrum shows that alkylation has not proceeded quantitatively; some secondary amino groups have not reacted (2.8 ppm , NHCH_2) and the quaternization has

occurred to some extent (3.6 ppm , $\text{—}\overset{+}{\text{N}}\text{—CH}_2$).

3.3. Thermal properties

Thermal properties of the polymers were examined by DSC measurement. All of the phase transitions are reversible during repeating heating and cooling cycles. The phase transition temperatures determined by DSC are consistent with those observed by POM. The data

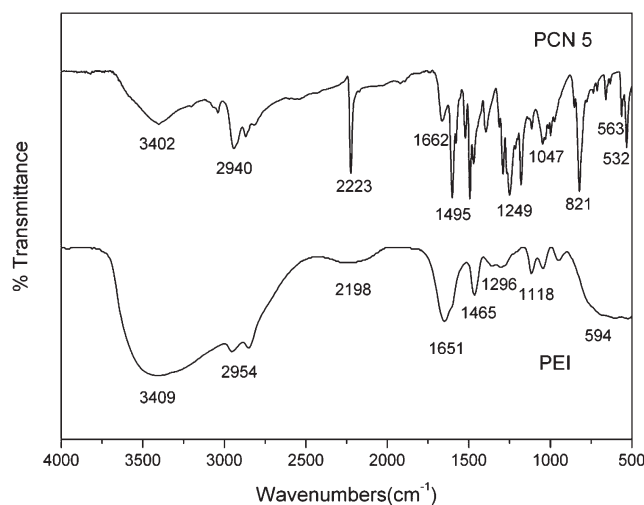


Figure 1. IR spectra of PEI and PCN5 (a representative example for PCN n).

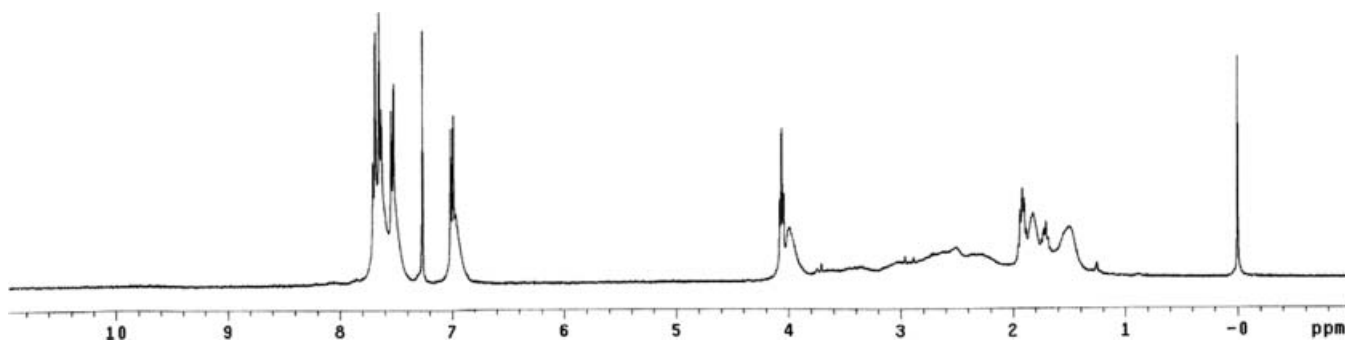


Figure 2. ^1H NMR spectrum of PCN5 (a representative example for PCN n).

listed in table 2 are extracted from the second heating and cooling cycle and these traces are shown in figures 3 and 4, respectively. As seen in Figure 3, when the degree of substitution varies from 74% to 86%, the DSC heating curve shows a broad peak (or a baseline shift) for the PCN n sample, which is ascribed to a complex behaviour arising from several transitions. We identify the behaviour as a possible glass transition (T_g). The DSC heating trace for the PCN n sample exhibits a single endothermic peak. All of the polymers reveal liquid-crystalline phase to isotropic transitions due to their flexible backbones. In the cooling scan, there is one exothermic peak for the PCN n sample, which corresponds to the isotropic to liquid-crystalline phase transition. In the lower-temperature region, no crystallization peak of the side chain is observed for the sample. This is confirmed by POM investigations.

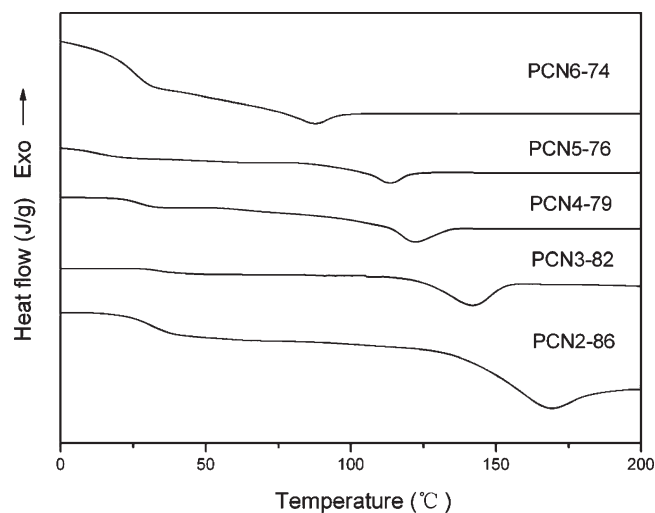
Based on the DSC analyses for PCN5 samples, the results show that the thermal behaviour of the polymers is strongly dependent on the degree of substitution. It is particularly interesting to observe that the thermal behaviour changes with the changing degree of substitution in the side chain (figure 4). There is a minimum degree of substitution for liquid crystal formation,

below which the polymers are amorphous (PCN5-48 and PCN5-56) and present only the glass transitions. From the phase transitions of PCN5-69 and PCN5-76, it is observed that the glass transition temperature (T_g) and the clearing temperature (T_i) increase as the degree of substitution increases. The DSC heating traces show endothermic peaks at 112.1°C ($\Delta H=1.81\text{ J g}^{-1}$) and 138.9°C ($\Delta H=2.94\text{ J g}^{-1}$), respectively. The glass transition temperature T_g reflects the mobility of chain segments and increases as the mobility of chain segments decreases. Obviously, the free ethyleneimine moieties plasticize the copolymers. The clearing temperature T_i increases more than T_g and ΔH increases with increasing degree of substitution. This suggests that a higher ratio of substitution leads to a wide mesomorphic temperature range (ΔT) and stabilizes the mesomorphic properties. The existence of the crystalline phase in samples PCN5-83 and PCN6-81 was determined by DSC. For PCN5-83, the DSC heating curve shows a melting transition peak at 132.4°C ($\Delta H=27.83\text{ J g}^{-1}$) and a nematic–isotropic transition at 172.8°C ($\Delta H=3.27\text{ J g}^{-1}$). The crystalline state of LPEI with 4'-methoxybiphenyl was also described by Masson *et al.* [20]. However, the chemical architecture

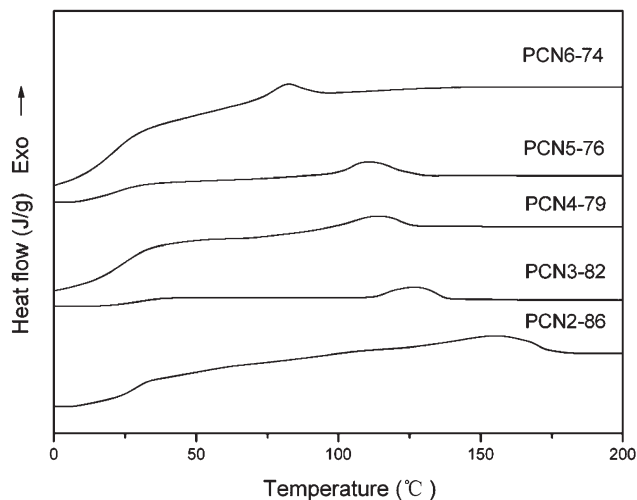
Table 2. Thermal transition temperatures and entropies of PCN n .

Sample ^a	Phase transition temperature (°C)		Corresponding enthalpy changes (J g^{-1})	
	Heating ^b	Cooling	Heating ^b	Cooling
PCN2-86	G 32.7 N 168.1 I	G 28.2 N 159.0 I	N 2.34 I	N 2.28 I
PCN3-82	G 33.9 N 145.4 I	G 23.4 N 126.6 I	N 2.69 I	N 2.54 I
PCN4-79	G 25.6 N 118.8 I	G 21.6 N 112.1 I	N 2.75 I	N 2.97 I
PCN5-48 ^c	G 3.8	G 1.1	—	—
PCN5-56	G 12.1	G 7.6	—	—
PCN5-69	G 22.3 N 112.1 I	G 20.7 N 104.4 I	N 1.81 I	N 2.56 I
PCN5-76	G 27.1 N 138.9 I	G 21.4 N 127.5 I	N 2.94 I	N 3.49 I
PCN5-83 ^d	K 132.4 N 172.8 I	K 74.0 N 163.6 I	K 27.83 N 3.27 I	K 19.16 N 3.93 I
PCN6-74	G 18.8 N 86.4 I	G 17.7 N 79.6 I	N 3.28 I	N 3.62 I
PCN6-81 ^d	K 53.0 N 116.8 I	K 4.6 N 109.5 I	K 30.85 N 4.26 I	K 28.39 N 4.34 I

^aSee section 2 for an explanation of the sample codes. ^bG, glassy; K, crystalline; N, nematic, I, isotropic. ^cIn ethanol for 96 h. ^dIn the mixture of tetrahydrofuran and 1,4-dioxane for 150 h.



(a)



(b)

Figure 3. DSC heating and cooling traces of PCN*n*: (a) heating; (b) cooling.

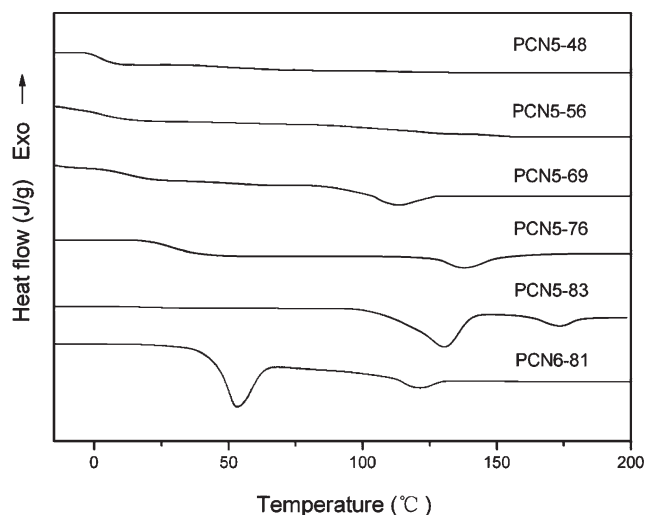
of the LPEI chain alone could not be responsible directly for the development of crystalline order [22]. The polymer condensed state is considered in relation to the degree of substitution of mesogenic groups. It is likely that the thermal transitions of the polymers are strongly affected by the degree of substitution. Polymers with a higher degree of substitution exhibit higher phase transition temperatures and wider mesomorphic temperature ranges.

The glass transition temperatures and the clearing temperatures of PCN*n* samples with a similar degree of substitution tend to decrease as the length of the flexible alkyl spacer increases (figure 5). This could be attributed to the plasticization of the polymer backbone by the side groups. The clearing

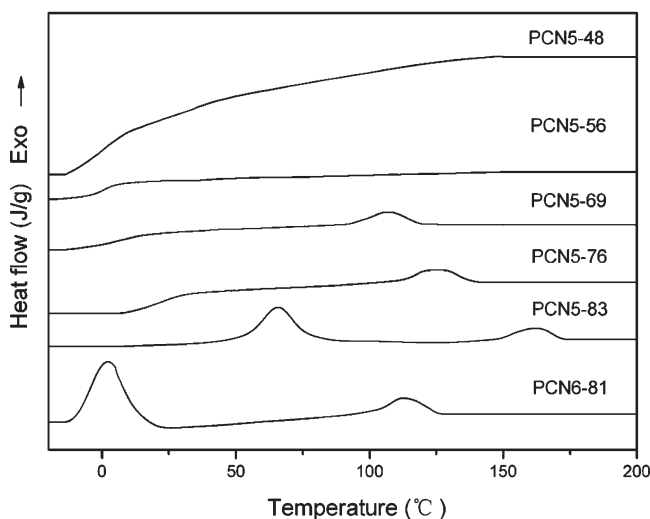
entropies (ΔH) increase as the spacer length increases. The spacer length is considered to affect the local conformation of the side chain as well as the mechanical decoupling of the mesogenic group from the main chain. An odd–even effect can be seen in the phase transition temperatures. This may be rationalized by considering the different conformations of the mesogenic groups and their influence.

3.4. Liquid crystalline textures

To identify the phase present before and after the transition peaks, texture observations were made with POM. The POM investigations reveal schlieren textures in the liquid-crystalline phase of PCN*n*, which suggest the formation of the nematic phase (figure 6).



(a)



(b)

Figure 4. DSC heating and cooling traces of PCN5 with different degrees of substitution and PCN6-81: (a) heating; (b) cooling.

The textures were obtained by cooling the isotropic phase to 150°C for PCN2-86, 130°C for PCN3-82, 122°C for PCN4-79, 100°C for PCN5-69, 129°C for PCN5-76 and 86°C for PCN6-74. All of the temperatures are close to those observed in the DSC traces. When PCN5-83 is cooled from the isotropic phase, a nematic schlieren texture is formed; when it is cooled further, the liquid-crystalline to crystalline phase transition is observed at 70°C (figure 6(b)). The crystallization temperature of PCN6-81 is too low to observe. Comparing these results with the smectic phase observed by Kawakami *et al.* [24], the molecular weight and molecular weight distribution are considered as the important factors affecting the thermal properties of the SCLCPs.

3.5. Phase behaviour

X-ray scattering was used to verify the existence of a liquid-crystalline phase and to confirm the nature of the phases observed by DSC and POM. The diffraction patterns were obtained with powder samples at room temperature. These samples were heated to the liquid-crystalline phase and then quenched in liquid nitrogen bath. The diffractograms of PCN n (figure 7) are consistent with their amorphous nature, which contain a diffuse broad halo at a periodicity of 4.3 Å in the wide-angle region ($2\theta \approx 21^\circ$). No peaks were observed in the low-angle region, indicating no lamellar order in these polymers. The location and the relative intensities indicate an orthogonal nematic

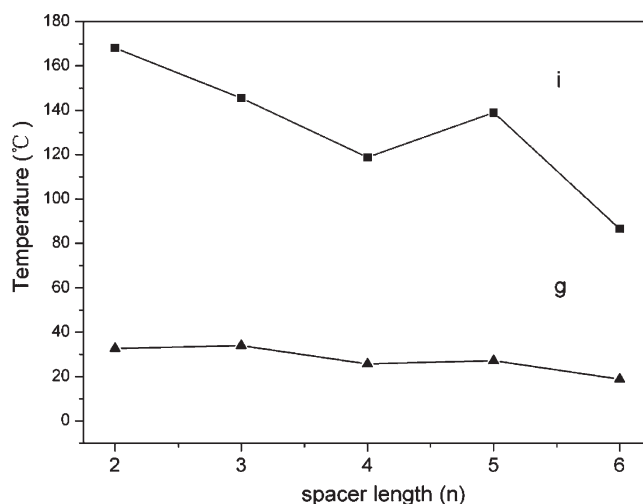


Figure 5. Dependence of the isotropic–nematic (■) and the nematic–glass (▲) transition temperatures on the number of methylene groups (n) of spacer for PCN n .

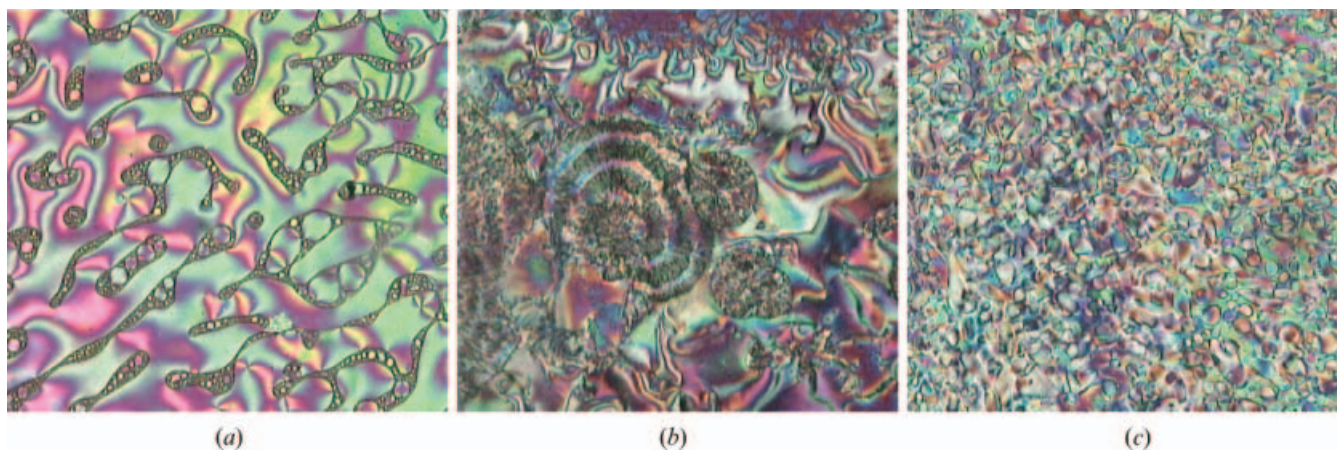


Figure 6. Polarized optical micrograph of PCN n ($\times 200$): (a) PCN2-86, schlieren texture obtained at 150°C; (b) PCN5-83, N–K phase transition obtained at 70°C; (c) PCN6-74, schlieren texture obtained at 86°C (cooling from the isotropic phase).

phase and there is no order in the direction of the molecular long axes.

4. Conclusions

A series of PEI-based SCLCPs substituted with different ratios of cyanobiphenyl as pendent mesogenic groups, in which the spacer length varies between two and six methylene units, has been synthesized in this work. DSC traces, POM investigations and wide-angle XRD studies indicate that PCN n ($n=2-6$) samples exhibit liquid-crystalline phases of nematic type. It has been shown that PEI is flexible and acts as a suitable main-chain component for SCLCPs. Polar and less bulky cyano-substituted biphenyl seems to be a good mesogenic group. The

degree of substitution in the side chain has a strong effect on the thermal properties and liquid-crystal formation of the polymers. A degree of substitution of 69% seems to be the minimum for the liquid-crystal formation. Below this limit, the polymers are in the glassy states at room temperature. The phase transition temperatures increase and the mesomorphic properties stabilize as the degree of substitution increases. In addition, polymer containing 81% or 83% of mesogenic groups exhibits the crystalline behaviour. The clearing temperatures decrease as the spacer length increases. An odd–even effect is observed and the odd members display the higher values. The results of the present work imply that the condensed states and the phase transition temperatures of the polymers can be adjusted by varying the degree of substitution.

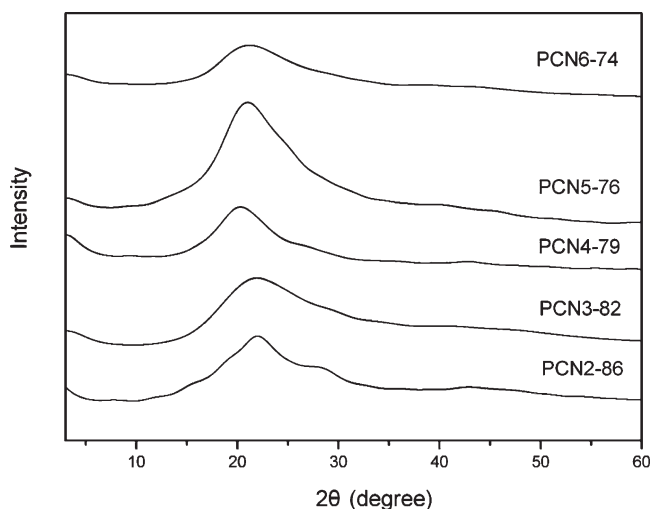


Figure 7. Wide-angle X-ray diffractograms of PCN n .

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