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Liquid Crystals

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Liquid-crystalline side chain polymers by chemical modification of poly(chloroalkylvinylether)s

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The synthesis of polyalkylvinylethers with pendant 4-cyano-4′-oxybiphenyl groups gives thermotropic liquid-crystalline polymers. The new method developed here consists of the living cationic polymerization of chloroalkylvinylethers and the subsequent modification of the polymer by the mesogenic groups. The liquid-crystalline polymers have a controlled degree of polymerisation and narrow molecular weight distributions. The influence on the mesomorphic properties of various parameters such as the degree of polymerization, the spacer length and the proportion of the mesogenic side chain content has been investigated. Binary phase diagrams with low molar mass analogues are also reported and the properties of both neat materials and binary mixtures are compared.

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1. Introduction

Polymeric liquid crystal containing mesogenic groups in the side chain have been extensively studied in recent years. Research interests have been focused mainly on the influence of the nature and structure of mesogenic groups on the mesomorphic properties of the polymers. Most of these studies were performed for polysiloxanes, polyacrylates and polymethacrylates [1, 2]. Another field of interest deals with the role of the main chain polymer on the liquid crystal properties. In this regard, the effect of the nature of other polymer backbones was the first parameter investigated: polychloroacrylates [3, 4], polyitaconates [5], polyvinylether-co-maleates [6], polybutadienes [7], polyphosphazenes [8–10], polyesters [11], polyepichlorhydrin [12], polyethylenoxides [13], polystryrenes [14] and polyacetylenes [15]. However, the study of the influence of various main chain parameters such as the degree of polymerization ($\overline{DP}_n$), molecular weight distribution, monomer unit structure, monomer unit distribution in random and block copolymers, polymer architecture,... are still scarce. This is mainly due to the low availability of the corresponding well-defined polymeric materials.

The discovery of truly living processes for the cationic polymerization of vinylethers [16] has been an important breakthrough in that direction. Living polymerization permits the control of several important primary parameters for the synthesis of well-defined structures such as molar mass, molecular weight distribution and chain ending by functional groups. Polyvinylethers with pendant mesogenic groups have been synthesized and the ability of the polyvinylether backbone to give mesomorphic phases

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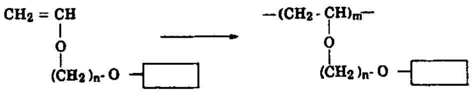
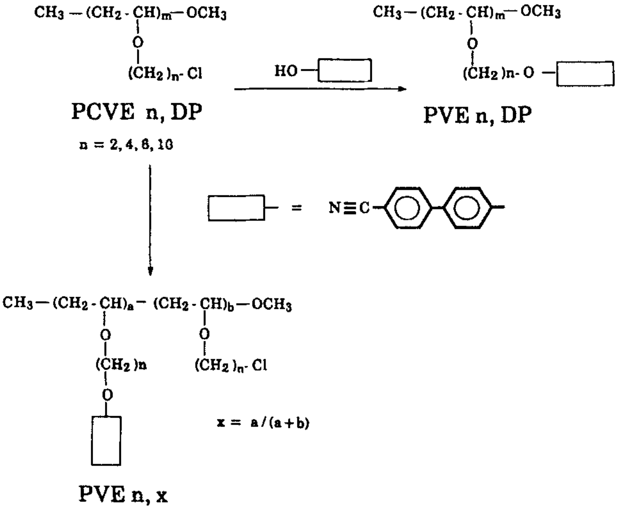
has been demonstrated [17,22]. Two different routes for the synthesis of such compounds have been proposed.

(i) The preparation in a first step of a vinylether bearing a mesogenic group, then the cationic polymerization of the functional vinylether in the presence of HI/I_2 [18] or CF_3SO_3H/Me_2S [21] (see scheme 1). Polyvinylethers with various mesogenic side groups with controlled $\overline{DP}_n$ (2 to 30) and narrow molecular weight distribution (1·01 to 1·2) have been synthesized and the influence of these parameters on mesogenic properties have been investigated [17–19, 21].



Scheme 1.

(ii) A different approach has been developed in our laboratories. It consists, firstly of the cationic polymerization of *n*-chloroalkylvinylethers initiated by HI/weak Lewis acid systems (see scheme 2).



Scheme 2.

Total or partial substitution of the chlorine is then possible. Various groups have been anchored on the polychloroalkylvinylether main chain, such as azide, carboxylic acids, alcohols, mesogens. In most of the cases, the chemical modification proceeds without detectable degradation of the side chain or main chain and without crosslinking.

In a preliminary report [20], the synthesis, according to these two procedures, of poly(4-cyano-4′-oxybiphenyl)alkylvinylethers with various spacer lengths *n* ($n = 2, 4, 6$ methylene groups) has been briefly reported and some of the properties of the polymers compared. Here we describe in the first section, the synthesis of poly(*n*-chloroalkylvinylether)s (labelled as PCVE*n*) with various $\overline{DP}_n$ having 2, 4, 6 and 10 methylene groups in the spacer and their chemical modification into the corresponding poly(4-cyano-4′-oxybiphenyl)alkylvinylethers (denoted by PVE*n*). The characteristics of the polymers are also reported. The second section deals with the evolution of the

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mesomorphic properties as a function of different molecular parameters. Finally this study is aimed at the thermodynamic behaviour of phase diagrams by mixing the polymers with low molar mass compounds.

2. A synthesis and characterization of the polymers

2.1. *Experimental*

The synthesis of the monomers was described in a previous paper [20]. The polymerizations of *n*-chloroalkylvinylethers were performed under dry nitrogen, at $-30^\circ C$ in toluene or methylene dichloride. HI/ZnI_2, HI/Bu_4NClO_4 [23] were used as initiating systems. At the end of the polymerization, the living polymer ends were deactivated by a mixture of cold methanol and ammonia. The substitution of the pendant chlorine by 4-cyano-4′-hydroxyphenyl was performed according to the Williamson etherification reaction. The mesogenic group (20 per cent excess with respect to chlorine) was reacted overnight with the polymer in dimethylformamide, in the presence of a caesium carbonate, at 85°C. The modified polymers were then precipitated in hot methanol to avoid the co-precipitation of unreacted mesogenic groups, washed several times with methanol and dried under high vacuum.

2.2. *General methods of characterization of the polymers*

The molecular weight and the molecular weight distribution of PCVE and PVE were determined by steric exclusion chromatography in THF at room temperature on a Varian 5500 chromatograph fitted with 4 TSK gel columns, calibrated with polystyrene standards. In addition, in order to check the validity of the steric exclusion chromatography molecular weight calibration curve, tonometry measurements were also performed on some low mass PCVE and on modified polymers. Good agreement between the two methods was observed, at least for the low molar masses range (5000). ^1H and ^{13}C NMR spectra were recorded on a Brucker AC250 spectrophotometer in $CDCl_3$ at room temperature. T_g measurements were carried out on a Perkin–Elmer DSC7 apparatus with polymer samples of about 15 mg and at a scanning rate of $10^\circ C\,min^{-1}$.

2.3. *Characterization of the poly(chloroalkylvinylether)s*

The possibility to synthesize well-defined PCVE ($n=2, 4, 6, 10$, see scheme 2) with controlled molecular weight and molecular weight distribution by cationic polymerization using HI: weak Lewis acid initiating system is outlined in table 1. A very good control of the polymer main chain parameters up to high molecular weight polymers ($\overline{DP}_n$ from 4 to 100) is possible. The experiment $\overline{M}_n$ are in good agreement with those predicted theoretically, assuming the relation

$$\overline{M}_n = \frac{n_M}{n_{HI}} \cdot m_M \cdot \text{conversion}$$

and the molecular weight distributions are very narrow ($\overline{M}_W/\overline{M}_n = 1{\cdot}1$ to $1{\cdot}2$). This may be considered as an indicator of the living character of the polymerizations. PCVE are amorphous materials; tacticity measurements of PCVE have been performed by ^{13}C NMR using the main chain methylene carbon. This latter is resolved into two peaks located near 40 ppm, corresponding to diads effect [20]. All polymers exhibit both meso and racemic diads with a percentage of about 40 to 60, whatever the number of methylene groups in the side chain.

Table 1. Some results concerning the cationic polymerization of vinylethers with various spacer lengths.

n	M/A	Conv. %	$\overline{M}_n$ (Th)	$\overline{M}_n$ (Exp)	$\overline{DP}_n$ (Exp)	$\overline{M}_w/\overline{M}_n$
2	50	90	5300	4800	45	1·2
	100	95	10650	10100	95	1·1
4	15	95	2000	1880	14	1·2
	38	95	5100	4900	37	1·2
6	14	90	2300	1950	12	1·1
	25	90	4050	3580	22	1·1
	38	95	6200	6000	37	1·1
	54	95	8800	8450	52	1·1
10	8	100	1700	1700	8	1·2
	25	90	5460	4800	22	1·2
	32	95	7000	6500	30	1·1
	45	100	9800	9800	45	1·1

M = mole of monomer.
A = mole of initiator.

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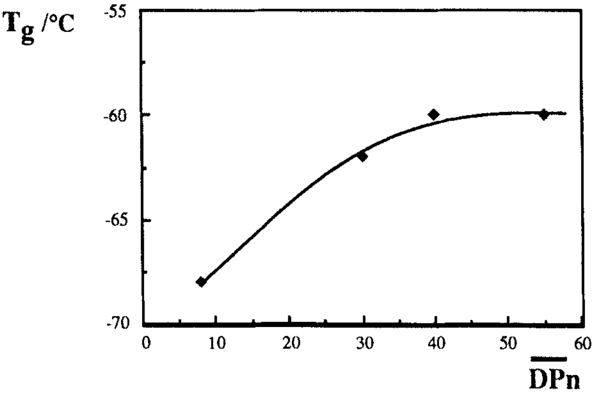

Figure 1. Evolution of the glass transition temperature T_g as a function of the degree of polymerization $\overline{DP}_n$ of the polychlorohexylvinylethers PCVE.

The influence of $\overline{DP}_n$ and of the number of methylene groups in side chain on the glass transition temperatures has been examined by differential scanning calorimetry. The dependence of T_g on $\overline{DP}_n$ is observed for polymer chains of less than 30 vinylether units. A typical example is shown in figure 1. Then, T_g levels of suggesting that the high polymer domain corresponding to constant T_g is reached. In addition, as may be seen in figure 2, at constant $\overline{DP}_n$, T_g decreases with increasing number of methylene groups in the side chain.

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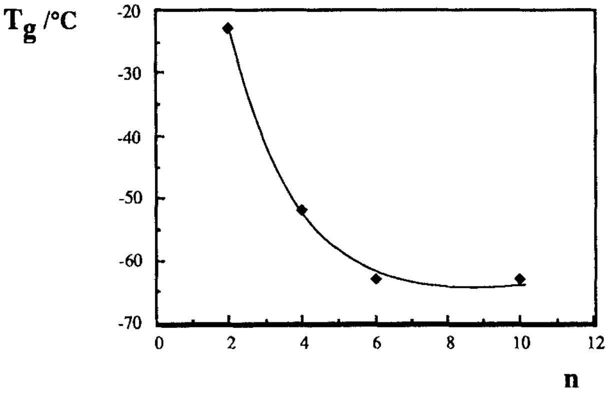

Figure 2. Evolution of the glass transition temperature T_g as a function of the number *n* of methylene in the side chain of the polychloroalkylvinylethers PCVE.

2.4. *Characterization of the poly(4-cyano-4′-oxyphenyl)alkylvinylethers*

As described in the experiment, anchoring the mesogenic group, 4-cyano-4′-hydroxybiphenyl, on the polymer chain can be achieved by chemical substitution of the pendant chlorine. According to the relative molar ratio between chlorine and mesogenic group, either completely or partially substituted polymers could be prepared.

Typical steric exclusion chromatography curves of PCVE and of the corresponding modified polymers PVE are presented in figure 3: the molecular weight distribution of the final polymer remains narrow and unchanged by the reaction procedure applied. Molecular weights, determined by steric exclusion chromatography and by tonometry

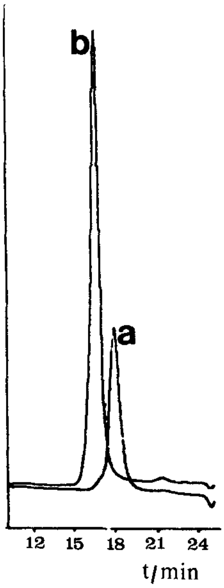

Figure 3. Typical steric exclusion chromatograms: a, PCVE10; b, the corresponding modified polymer PVE10.

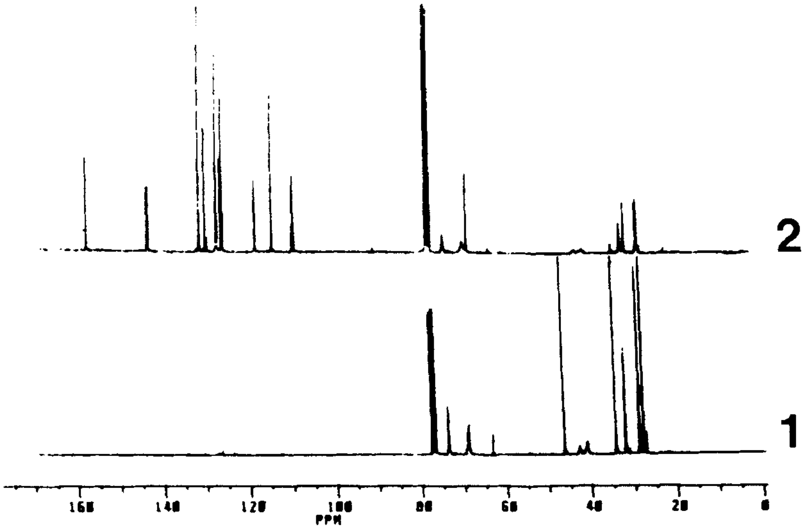

Figure 4. Typical ^{13}C NMR spectra, 1, PCVE6; 2, the corresponding modified polymer PVE6.

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(for low masses) closely correspond to the theoretical values calculated from the molecular weight increase of the monomer unit. A typical ^{13}C NMR spectra of a PCVE and of the corresponding modified polymers PVE is presented in figure 4. These results show that the substitution proceeds readily and cleanly without the occurrence of side reactions, such as dehydrochlorination, chain degradation or crosslinking.

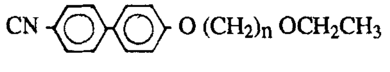
3. Mesomorphic properties

The characterizations were achieved through microscopic observations with a polarizing Leitz microscope equipped with a hot stage (Mettler FP 52) and thermal analysis on a Perkin–Elmer DSC 7. Additional X-ray diffraction experiments were performed on powder samples (Hüber Guinier camera) using a monochromatic Co–K_{α_1} radiation.

We describe the influence on the liquid-crystalline properties of three parameters, namely the degree of polymerization ($\overline{DP}_n$), the spacer length n and the proportion of mesogenic groups x.

3.1. *Influence of* $\overline{DP}_n$

Investigations of the phase behaviour of side chain liquid-crystalline polymers as a function of the degree of polymerization $\overline{DP}_n$ of the polymer backbone emphasise two general trends: a change in the phase behaviour is observed for oligomers, and then for larger $\overline{DP}_n$ (>20), the liquid-crystalline polymorphism becomes almost independent of this parameter [1]. As we have mentioned (see table 1), the PVE obtained by chemical modification of polychloroalkylvinylethers exhibit rather well-defined molecular weights. Thus the evolution of the mesomorphic behaviour as function of $\overline{DP}_n$ can be determined and compared to the transition temperatures of the mesogenic units



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Two series of polymers have been investigated: the poly(4-cyano-4′-oxybiphenyl) hexylvinylethers (PVE6 for short) and the poly(4-cyano-4′-oxybiphenyl) decylvinylethers (PVE10 for short). The transition temperatures are reported in table 2 (PVE6) and in table 3 (PVE10). All of these samples exhibit mesomorphic properties. They are purely amorphous (since no crystallinity is evident). The glass transition temperatures have been determined by DSC (heating rate 10° min^{-1}). The other transition temperatures were obtained through microscopic observations: they correspond to the first appearance of the mesophase upon cooling. In agreement with the low polydispersity index, all of the biphasic domains are narrow (~4°C).

3.1.1. $\overline{DP}_n > 20$ (*in the polymer regime*)

Typical DSC thermograms are shown in figure 5: the first heating trace gives a glass transition and two narrow endotherms. The first cooling scan exhibits two corresponding exothermic peaks and the glass transition. No modification is observed in subsequent runs.

The existence of two mesophases is confirmed through microscopic observations. The textures are established after annealing just below the mesophase–isotropic transition. The high temperature mesophase exhibits a fan shaped texture suggesting smectic A phase. The transition to the low temperature mesophase corresponds to a reversible change from a uniform fan texture to a schlieren texture: it suggests either a low temperature nematic phase (as in polyacrylates with the same cyanobiphenyl side chain mesogen [24]) or a smectic C phase. In fact the X-ray diffraction experiments give evidence for the existence of a S_C–S_A sequence in both series. Indeed, in contrast with nematics, the patterns exhibited at small angles 001 Bragg reflections are indicative of a layered arrangement. Moreover a diffuse ring at wide angles denotes liquid-like short range order within the layers indicating disordered smectics (A or C).

Table 2. Evolution of the mesomorphic properties as a function of the degree of polymerization for the (4-cyano-4′-oxybiphenyl)hexylvinylethers. [ ] denotes monotropic transition.

$\overline{DP}_n$	T_g/°C	T_m/°C	S_C		S_A		N		I
1		53					●	[50°C]	●
8	6		●	30°C	●	77°C	●	85°C	●
12	16		●	40°C	●			108°C	●
22	27		●	60°C	●			117°C	●
37	34		●	74°C	●			122°C	●
55	34		●	75°C	●			125°C	●

Table 3. Evolution of the mesomorphic properties as a function of the degree of polymerization for the (4-cyano-4′-oxybiphenyl)decylvinylethers. [ ] denotes monotropic transitions.

$\overline{DP}_n$	T_g/°C	T_m/°C	S_C		S_A	N		I
1		69			●		[59°C]	●
8	4		●	17°C	●		133°C	●
22	9		●	55°C	●		145°C	●
30	14		●	57°C	●		153°C	●
45	14		●	57°C	●		148°C	●

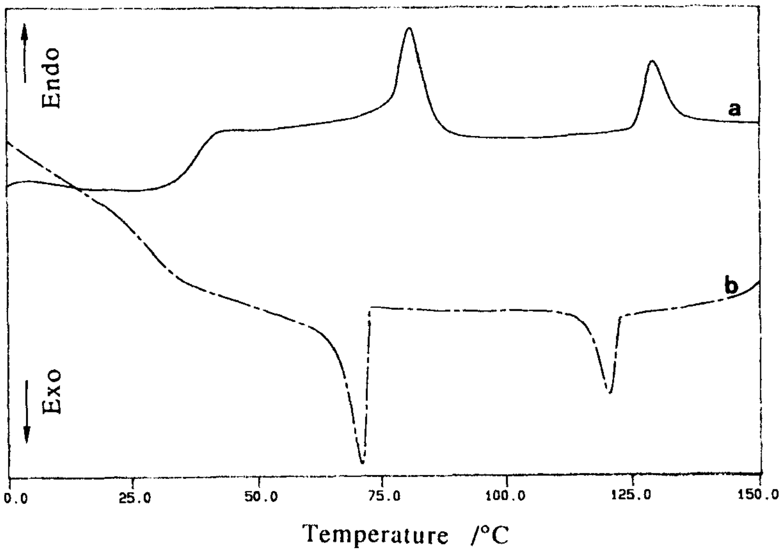

Figure 5. DSC thermograms observed for the poly(4-cyano-4'-oxybiphenyl)hexylvinylethers PVE6 ($\overline{DP}_n = 55$). Similar thermograms were observed for all the other mesomorphic polymers, a, first heating scan; b, first cooling scan.

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3.1.2. $\overline{DP}_n < 20$ *(in the oligomer regime)*

As usually observed there is an increase of order from monomer to polymer: indeed, the monomeric unit M6 ($\overline{DP}_n = 1$, see table 2) is only nematic and by increasing the degree of polymerization ($\overline{DP}_n = 8$) two smectic phases (A and C) occur in addition to the nematic phase. For $DP_n = 12$, the nematic domain has disappeared and the polymer displays the S_C–S_A–I sequence observed for higher $\overline{DP}_n$.

For decylethers, the monomeric unit M10 ($\overline{DP}_n = 1$, see table 3) possesses a smectic A and for $\overline{DP}_n = 8$, a smectic C occurs below the S_A giving rise to S_C–S_A polymorphism. Thus, as shown in figures 6 and 7, we note that on increasing $\overline{DP}_n$ the clearing temperature first increases and the polymorphism is regularly affected by the evolution of the degree of polymerization leading to a strong stabilization of the smectic phases

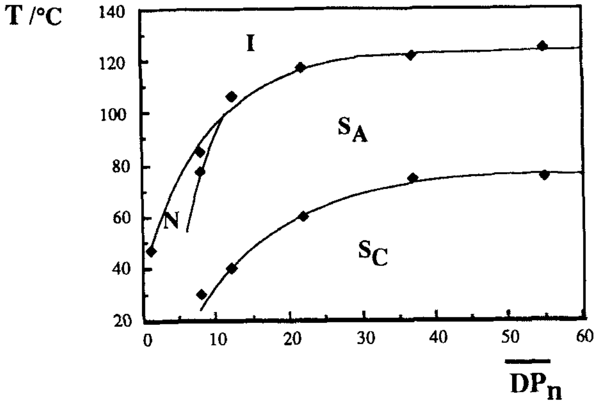

Figure 6. Evolution of the polymorphism and of the transition temperatures as a function of the degree of polymerization $\overline{DP}_n$ for the PVE6 series. The lines are guides for the eye.

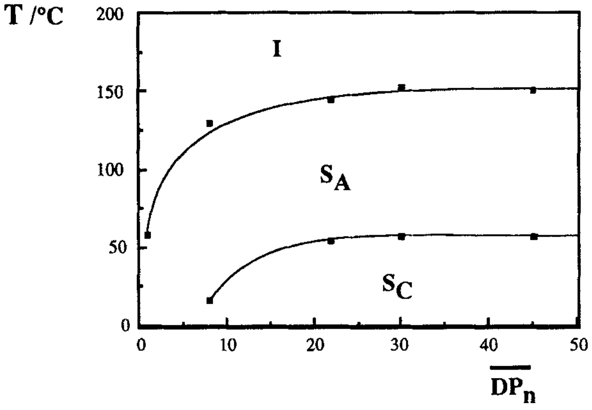

Figure 7. Evolution of the polymorphism and of the transition temperatures as a function of the degree of polymerisation $\overline{DP}_n$ for the PVE10 series. The lines are guides for the eye.

which replace the nematic state. Then, for larger $\overline{DP}_n$, the liquid-crystalline properties are slightly affected by a modification of the length of the backbone. In both series, this plateau is reached from $\overline{DP}_n = 20$. These results agree closely with the classical evolution of the mesomorphic properties as a function of the degree of polymerization as observed previously for main chain polymers [25] or different side chain polymers: polysiloxanes [1], polyacrylates and polymethacrylates [2], polyvinylethers [20, 22].

3.2. *Influence of the spacer length n on the mesomorphic behaviour*

To study the influence of the spacer length *n* on the phase behaviour, we compare polymers with a high degree of polymerization (> 30). The transition temperatures are reported in table 4. We note first the decrease of the glass transition temperature with an increasing number of methylene groups in the spacer. Such a relationship provides evidence for the plasticizing effect of the aliphatic chain.

The first polymer of this series with two methylene groups in the spacer (PVE2) is not mesomorphous, in agreement with previous results [18], probably because of steric hindrance imposed by the main chain on the packing of the mesogenic side groups. It is also the case for polymer PVE4 with four methylene groups in the spacer which has no liquid-crystalline properties. The thermograms are reported in figure 8, the first scan shows two endothermic events (1 a and 1 b). After quenching the sample, a glass transition is easily detected, then upon heating an exothermic feature (2 b) is observed followed by an endothermic peak (3 b) which corresponds to 1 b. This can be summarized as follows: 1 a corresponds to a dynamic relaxation event, 2 b reveals a

Table 4. Evolution of the properties as function of the spacer length *n* for the (4-cyano-4′-oxybiphenyl)alkylvinylethers series.

n	$\overline{DP}_n$	T_g/°C	T_m/°C	S_C		S_A		I
2	50	70						●
4	37	52	90					●
6	37	34		●	74°C	●	122°C	●
10	45	14		●	57°C	●	148°C	●

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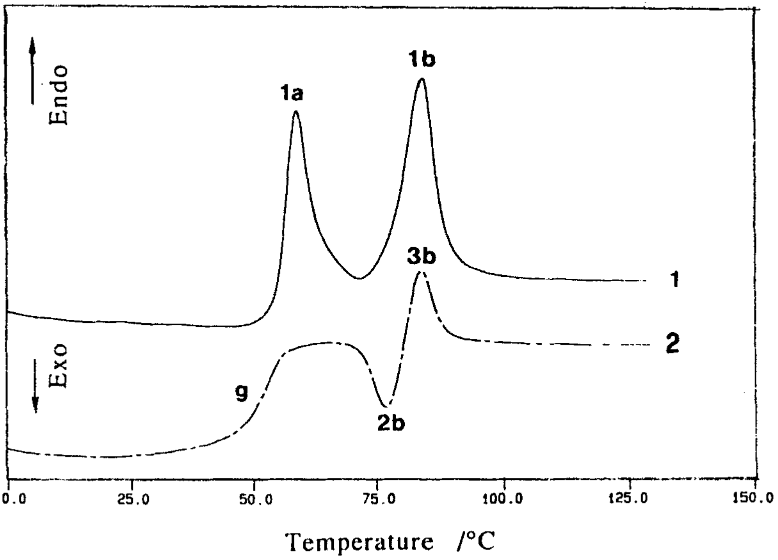

Figure 8. DSC thermograms of the PVE4 ($\overline{DP}_n = 37$): 1, first heating scan (10° min^{-1}); 2, second heating scan (10° min^{-1}) after quenching.

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crystallization upon heating and 1 b and 3 b relate to the melting. This behaviour is confirmed by microscopic observations. We can note that a polyvinylether, with four methylene groups in the spacer, obtained via the polymerization method is claimed to have nematic phase [22, 26]. Although the absence of residual-CH_2Cl has been checked within the accuracy of the ^{13}C NMR technique, a lack of complete substitution could explain the non-mesogenic character of our sample (see § 3).

Liquid-crystalline properties are obtained for longer spacers ($n = 6$ and 10). As shown in table 4, the clearing temperature increases with n and the S_A phase is promoted. Conversely the S_C phase is disfavoured by lengthening the spacer. These divergent trends lead to a strong increase of the temperature interval of the S_A phase (48°C for $n = 6$ and 93°C for $n = 10$). An increase of the clearing temperature with n is also observed in the corresponding low molar mass cyanobiphenyl series [27] and in the other side chain polymer series with the same mesogenic groups: polymethacrylates [28], polysiloxanes [29, 30], polyacrylates (24, 28], and polyvinylethers [21, 26, 31].

It is interesting to compare the mesophases of these different series: polymethacrylates and polysiloxanes are only smectic A. In contrast polymorphism is observed for polyvinylethers (S_C–S_A) and for polyacrylates. In this last case the polymorphism depends on the spacer length: according to [24] these polyacrylates are nematic for $n = 4$, smectic A for $n = 5$. For $n = 6$ a reentrant nematic–smectic A sequence is observed [24] as previously reported [32, 33]. Moreover for polyacrylates with a longer spacer ($n = 11$) a smectic C–smectic A sequence is detected [34]. We note that the occurrence of a smectic C phase which does not exist with the other backbones constitutes some similarity between polyacrylates and polyvinylethers (moreover we stress that the glass transitions for the bare polymers in these two series are very close). In this regard a reentrant sequence could be expected in PVE with other polar mesogenic side groups.

The X-ray diffraction experiments enable us to determine the layer thickness d of the smectic A and C phases. Figure 9 shows the temperature dependence of d for PVE6

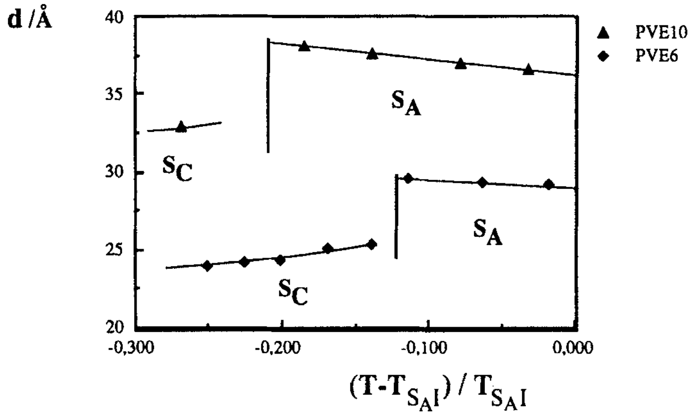

Figure 9. Evolution of the layer spacing d in the S_C and S_A phases as a function of the reduced temperature $(T-T_{S_AI})/T_{S_AI}$ for PVE6 and PVE10 in the polymer regime.

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and PVE10. These values can be compared to the length l of the monomeric unit in its most extended conformation ($l = 22$ Å for $n = 6$, $l = 27$ Å for $n = 10$, SASM stereomodels) and this comparison deserves the following comments: the S_A phases of polyvinylethers including mesogenic moieties with a highly polar end group (—CN) are partially bilayer ($d/l > 1$) as observed previously with cyanobiphenyl mesogens in low molar mass systems [35] as well as in side chain polymers such as polyacryalates and polymethacrylates [28], polysiloxanes [36, 37] or polyesters [11]. These associations of mesogenic groups vary with temperature in the S_A phase (d increases as the temperature decreases) of PVE6 and PVE10. The influence of the length of the spacer can be evaluated from figure 9 at a given reduced temperature in the S_A state: $d = 28{\cdot}5$ Å for $n = 6$ and $d = 37{\cdot}5$ Å for $n = 10$. On the basis of a linear evolution of the layer spacing versus n as found previously in polar polysiloxanes series [38], we note that the corresponding slope (9 Å/4) is close to the length of two CH_2 groups ($2 \times 1{\cdot}2$ Å). This suggests the same overlapping of the mesogens as n increases. At the S_C–S_A transition, the layer spacing decreases noticeably due to the tilt angle of the mesogenic moieties with respect to the plane of the layers.

3.3. *Influence of the proportion of mesogenic groups x on the mesomorphic properties*

It is now useful to remember that the method chosen for the synthesis of mesogenic polyvinylethers; i.e. the chemical modification of polychloroalkylvinylether allows us to study the effect of the proportion x of mesogenic side groups fixed on the same polymer chain on the liquid-crystalline properties. This partial fixation of mesogenic groups leads to copolymers with an amount of non-mesogenic moiety–$O(CH_2)_nCl$ (see scheme 2). In the case of polysiloxanes, several studies have shown that the mesomorphic properties can be preserved even for a low mesogenic group content [38–40]. Moreover, the influence of the nature of the non-mesogenic moiety on the liquid-crystalline properties has been clearly evidenced [41].

Thus several PVE with $\overline{DP}_n > 30$ (to avoid the effect of this parameter) and various proportions of mesogenic groups have been synthesized. The polymorphism and transition temperatures are reported in figures 10 (for $n = 6$) and 11 (for $n = 10$). As usually observed in polysiloxanes, the I–S_A transition temperature decreases gradually

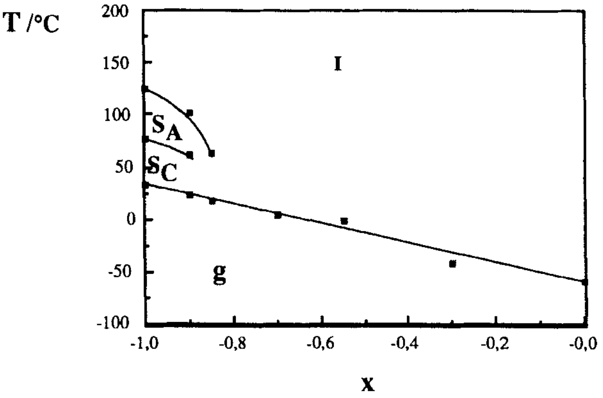

Figure 10. Transition temperatures as a function of the proportion of mesogenic groups x for the PVE6 system. The lines are guides for the eye.

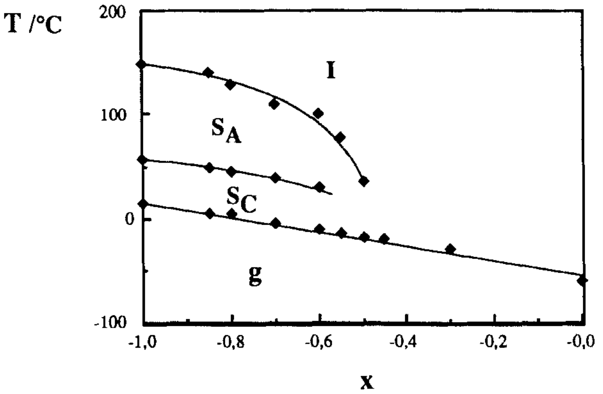

Figure 11. Transition temperatures as a function of the proportion of mesogenic groups x for the PVE system. The lines are guides for the eye.

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with decreasing x. On the other hand the S_C–S_A temperature is slowly depressed. Thus, in both cases ($n=6$ and $n=10$), the smectic A is more destabilized than the smectic C.

We have to note that the lowest proportion of mesogenic units for which mesomorphic behaviour is preserved appears highly dependent on the spacer length: the liquid-crystalline properties exist down to $x=0{\cdot}5$ for $n=10$ and only remain until $x=0{\cdot}8$ for $n=6$ (that is to say that copolymers with a proportion of mesogenic groups lower than the corresponding limit do not show any mesophase down to the glassy state). Thus a large decoupling between the side groups and the polymer backbone via a long spacer ($n=10$) favours the anisotropic packing of the mesogenic groups in partially substituted polymers. Reciprocally, the liquid-crystalline order is more especially depressed as the spacer length decreases and as the proportion of non-mesogenic moieties on the main chain increases. This suggests that complete substitution is mandatory to observe mesogenic properties with the shortest spacer ($n=4$).

The thermal evolution of the layer spacing in the smectic phases of partially substituted polyvinylethers is reported in figure 12. We note first that the smectic A

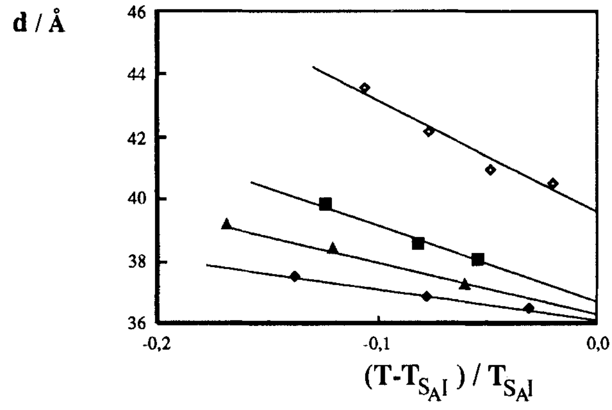

Figure 12. Layer spacing d in the S_A phase as a function of the proportion x of mesogenic groups for the PVE10 system. ◆, $x = 100$ per cent; ▲, $x = 85$ per cent; ■, $x = 70$ per cent; ◇, $x = 53$ per cent.

phase remains partially bilayer in these copolymers. We note that in all cases observed hitherto, a general trend can be emphasized by the structural comparison of a partially substituted polysiloxane with the corresponding homopolymer: the partial fixation leads to an increase of the layer spacing in the S_A phase, which corresponds to a swelling of the sublayer formed by siloxane units not substituted with mesogenic groups [39–42].

In the case of PVE, a qualitatively comparable effect is evidenced: the variation of the layer spacing of the smectic A phase as function of x shows a significant increase of d with decreasing x from 1 to 0·53. Nevertheless, it seems difficult to compare quantitatively the amplitude of this phenomenon between liquid-crystalline polymers with different backbones since the nature of the cosubstituent [41] and the nature of the mesogenic groups [38–42] influence the structural characteristics of the smectic phases. Since the packing arrangement is imposed by the cyanobiphenyl units, we can assume that the overlapping of the mesogenic cores remains unchanged with partial substitution and that the layer spacing could correspond, as in polysiloxanes, to a simple swelling of the non-mesogenic units.

3.4. *Binary diagrams with PVE and low molar mass compounds*

In this study we frequently refer to cyanobiphenyl low molar mass compounds which constitute the mesogenic side chain of the poly(4-cyano-4′-oxybiphenyl) alkylvinylethers. To extend this comparison, we have determined by the contact method the main characteristics of several binary diagrams (cyanobiphenyls-PVE). We chose two low molar mass compounds: 4-*n*-hexyloxy-4-cyanobiphenyl (6OCB) which is only nematic and 4-*n*-octyloxy-4′-cyanobiphenyl (8OCB) which has a S_A–N sequence. With this last compound, as shown in figure 13 an ideal behaviour is observed and complete miscibility is found in the S_A domain. Moreover we can remark that the S_C is disfavoured by mixing a low molar mass cyanobiphenyl as expected since no S_C tendency exists in the cyanobiphenyl series. In the 6OCB–PVE6 binary system, a nematic reentrance is clearly evidenced (see figure 14) and we can observe at low temperature a $N_RS_AS_C$ triple point already revealed in binary systems of low molar mass liquid crystals [43, 44]. Moreover, if we refer to the 6OCB–8OCB system in which a reentrant nematic was found [45], we stress the analogy between the behaviour of the

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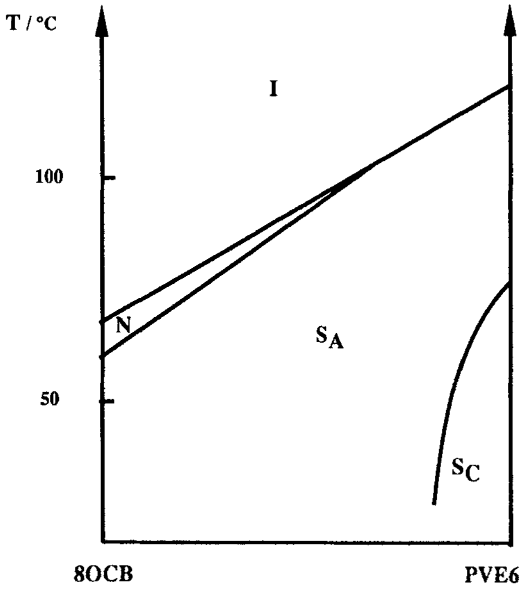

Figure 13. Schematic drawing of the phase diagram obtained by the contact method for 4-*n*-octyloxy-4′-cyanobiphenyl 8OCB–polymer PVE6 ($\overline{DP}_n = 37$) system.

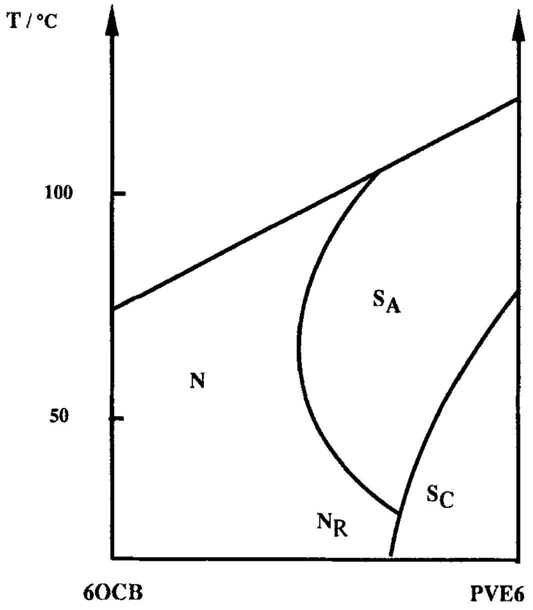

Figure 14. Schematic drawing of the phase diagram obtained by the contact method for 4-*n*-hexyloxy-4′-cyanobiphenyl 6OCB-polymer PVE6 ($\overline{DP}_n = 37$) system.

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polymer in the system 6OCB–PVE and of the 8OCB in the 6OCB–8OCB phase diagram. Although a non-ideal behaviour is observed by mixing the polymer with 6OCB and not with 8OCB, it is surprising to note that the spacer length in the polymer PVE6 corresponds to the aliphatic length of 6OCB instead of 8OCB. This last remark once more underlines the very subtle influence of the polymer chain mesogens coupling on the evolution of the mesomorphic behaviour.

4. Conclusion

This study has shown that liquid-crystalline poly(4-cyano-4′-oxybiphenyl)alkylvinylethers of controlled size ($\overline{DP}_n$ and molecular weight distribution) and structure can be obtained by living cationic polymerization of chloroalkylvinylethers and subsequent substitution of the pendant chlorine by 4-cyano-4′-hydroxybiphenyl. The influence of $\overline{DP}_n$ and spacer length on the polymorphism confirm that these PVE exhibit mesomorphic properties close to those obtained by direct polymerization of a vinylether functionalized by the corresponding mesogen. Both fully and partially substituted polymers, which can be assumed as homopolymers and random copolymers, respectively, have been prepared from the same polymer chain precursor, making easier the study of the effect on the mesomorphic properties of some parameters such as intramolecular dilution effect. Besides, the truly living character of the polymerization of chlorinated vinylethers makes possible the synthesis of polymers of original architecture such as block copolymers or model networks. The synthesis and the study of the mesogenic properties of these latter materials are under investigation and will be reported in a forthcoming paper.

Finally, PVE together with PA are unique chains which provide so far a smectic C-smectic A dimorphism with cyanobiphenyl mesogenic side groups.

Referring to mixtures with low molar mass homologues, it may well be that PVE polymers will be found to promote a reentrant nematic behaviour under appropriate conditions (hydrostatic pressure or copolymers). This suspected result would reinforce the similarities between PVE and PA liquid crystal side chains. Returning to partially substituted polymers we have revealed here how the mesomorphic states are strongly destabilized from homo to copolyvinylethers. Thus, we can claim that the PVE polymers possess a weaker mesomorphic potential than the copolysiloxanes analogues [46].

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