

# Smectic A organisation in copolymers of *i*-butyl vinyl ether and 11-[(4'-cyano-4-biphenyl)oxy]undecanyl vinyl ether as assessed by X-ray scattering

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## Summary

Liquid crystalline copoly(vinyl ether)s based on *i*-butyl vinyl ether and 11-[(4'-cyano-4-biphenyl)oxy]undecanyl vinyl ether of various compositions were synthesized. The copolymers exhibited smectic A mesomorphism with a layer thickness strongly increasing with increasing *i*-butyl vinyl ether content. The intermesogenic distance remained unchanged. A model of the layer structures is given based on structural assessments from small-angle X-ray scattering data.

## Introduction

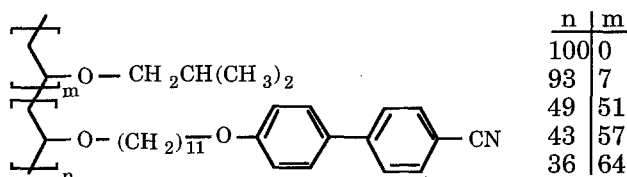
Side-chain liquid crystalline polymers (SCLCP) have been extensively studied, primarily because of their combined low-molar-mass liquid crystalline and polymer properties (1). One way of lowering the glass transition temperature of SCLCPs is to include monomers lacking the ability to show mesomorphism. It is generally depicted that the periodic structure of polymer smectic LC phases consists of organised layers with the mesogens confined between less organised domains consisting of a polymer backbone and a flexible spacer, i.e. a two-phase system of alternately ordered and disordered regions. The trajectory of the polymer backbone in SCLCPs has been clarified by small-angle neutron scattering showing that the backbones of polymethacrylates (2) and poly(vinyl ether)s (3) are mostly located between the planes of the mesogenic groups. According to Diele *et al* (4-5), the smectic layer distance increases with the content of non-mesogenic moieties in LC copolysiloxanes. Dimethylsiloxane was copolymerized with monomers consisting of phenylbenzoate mesogenic groups linked by seven-methylene spacers to the siloxane backbone. The thickness of the disordered regions increased with increasing content of dimethylsiloxane. A similar behaviour of copolysiloxanes containing other mesogenic groups has been reported by Percec *et al* (6).

This paper presents X-ray scattering data of copolymers of *i*-butyl vinyl ether (IBVE) and 11-[(4'-cyano-4-biphenyl)oxy]undecanyl vinyl ether (CBPUVE), indicating a considerable change in thickness of the smectic (A) layers depending on the comonomer composition.

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## Experimental

The copolymers studied were prepared by living cationic polymerisation according to Ref. (7). The CBPUVE and IBVE were charged in the proportions 100:0, 90:10, 60:40, 50:50 and 40:60 yielding copolymers, according to NMR, with compositions 100:0, 93:7, 49:51, 43:57 and 36:64. The chemical structure of the copolymers is shown in Figure 1. Small-angle X-ray scattering patterns of the different samples, used for determining the layer structures, were recorded in a Statton camera using Cu K $\alpha$  radiation generated by a Philips PW 1830 generator. Non-oriented samples were studied at different temperatures using a PID-controlled resistive oven inside the camera. Thermal characterisation was carried out using differential scanning calorimetry (Perkin-Elmer DSC-7) and polarized light microscopy (Leitz Ortolux Pol BK II).



**Figure 1.** Chemical structure of the side-chain liquid crystalline copoly(vinyl ether)s studied. The percentage of the repeating units in the copolymers are represented by n and m.

## Results and discussion

Table 1 shows the thermal behaviour of the different copolymers. An enantiotropic smectic A phase was found in all samples. The glass transition temperature ( $T_g$ ) decreased with increasing IBVE content. The degree of polymerization (DP) varied between 23 and 48 and the number average molar masses ( $M_n$ ) were about 10 000 g/mol. The decrease in glass transition temperature with increasing content of IBVE is expected because of the dilution of the constraining mesogenic groups with increasing IBVE content.

**Table 1.** Characteristics of the copolymers studied.

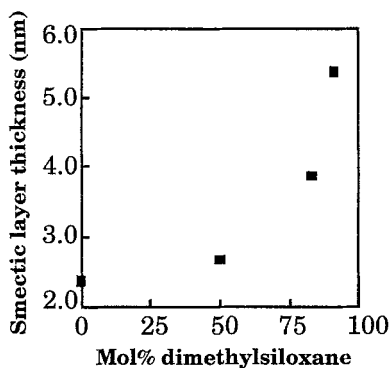
CBPUVE:IBVE	$M_n^1$ (g/mol)	$DP_n$	$M_w/M_n$	Phase transitions <sup>2</sup> (°C)	
				Heating	Cooling
100:0	9600	24	2.4	g8s <sub>A</sub> 140i	i133s <sub>A</sub> 4g
93:7	8700	23	1.5	g5s <sub>A</sub> 131i	i123s <sub>A</sub> -1g
49:51	11400	47	1.4	g3s <sub>A</sub> 79i	i78s <sub>A</sub> -2g
43:57	10900	48	1.5	g2s <sub>A</sub> 73i	i68s <sub>A</sub> -4g
36:64	8700	42	1.6	g-2s <sub>A</sub> 46i	i43s <sub>A</sub> -12g

1. In polystyrene equivalents

2. Obtained by DSC, polarized light microscopy and X-ray diffraction. g; glass; s<sub>A</sub>; smectic A; i; isotropic phase

The relationships between  $T_g$ , molar mass and the heat of isotropisation ( $\Delta h_i$ ) in SCLC poly(vinyl ether)s have been thoroughly described by Gedde *et al* (8), who showed that  $T_g$  and  $\Delta h_i$  for poly (vinyl ether)s are dependent

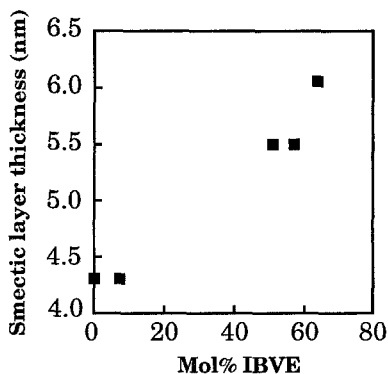
on molar mass, which is not the case for polysiloxanes and polymethacrylates. X-ray diffraction measurements of the different copolymers in the smectic A phase showed that the intermesogenic distances were 0.47 nm independent of composition.



**Figure 2.** Graph drawn after results in Ref. (4) showing the smectic A layer thickness as a function of the percentage of dimethylsiloxane in the backbone of a side-chain liquid crystalline copolysiloxane.

The independence of the lateral mesogenic distance on the content of mesogenic groups is in accordance with data reported for diluted polysiloxanes (4). The thickness of the smectic A layers increased with increasing dimethylsiloxane content in a SCLC copolysiloxane, whereas the intermesogenic distance remained constant. The thickness of the smectic layers increased in a linear manner with increasing number of inserted dimethylsiloxane units, which in a plot of layer thickness vs. molar composition conforms to the graph shown in Figure 2. The magnitude of the increase in smectic layer thickness was relatively small, from 2.4 nm for the polymer with 0% dimethylsiloxane to 2.6 nm in the polymer with 50% dimethylsiloxane, i.e. an increase of 8%. It was proposed (4) that the disordered phase between the smectic layers expanded linearly with increasing content of dimethylsiloxane. The increase in thickness of the smectic A layers of the SCLC copoly(vinyl ether)s with IBVE content was much greater than for the polysiloxanes (cf. Figures 2 and 3): from 4.3 nm (0% IBVE) to 5.5 nm (50% IBVE) for the poly(vinylether)s which is an increase of 28%. The homopolymer of CBPUVE exhibited a smectic A layer structure with a 4.3 nm layer spacing which is larger than the thickness of a monolayer of the side-chains. It is known that mesogenic groups containing strong polar groups, such as the cyano-biphenyl mesogenic group, form interdigitated smectic bilayers (9). The spacer, consisting of eleven methylene units, has an end-to-end distance including the backbone chain of  $1.2 \pm 0.1$  nm according to calculations in Ref. (10). The fraction of bonds in the *trans* state ( $x_t$ ) was estimated by Boltzman weighting:  $x_t = 1/(1 + 2\exp(-\Delta E/RT))$ .  $x_t$  had a value of  $0.6 \pm 0.1$  when  $\Delta E$ , representing the energy difference between *trans* and *gauche* states, was set to  $2500 \text{ J mol}^{-1}$  (Ref. 11). This was an average value based on a simulation of 200 spacer group chains. The calculated length of the mesogenic group including the cyano tail group is  $1.1 \pm 0.1$  nm. Thus an interdigitated bilayer packing, with a 25 per cent overlap of the mesogenic groups, is proposed for the 100:0 and

93:7 samples. The proposed model implies an overlap of the cyano group and the adjacent outer phenyl rings. A further increase in the content of IBVE (49:51 and 43:57 samples), led to an increase in smectic layer thickness which cannot be accounted for by a linear expansion of the disordered phase of the backbone. It is necessary also to consider a change of mesogenic organisation from an interdigitated bilayer to a bilayer packing (Figure 4). The further increasing in IBVE content supposedly also caused a more moderate increase in the thickness of the disordered regions between the layers of the mesogens.



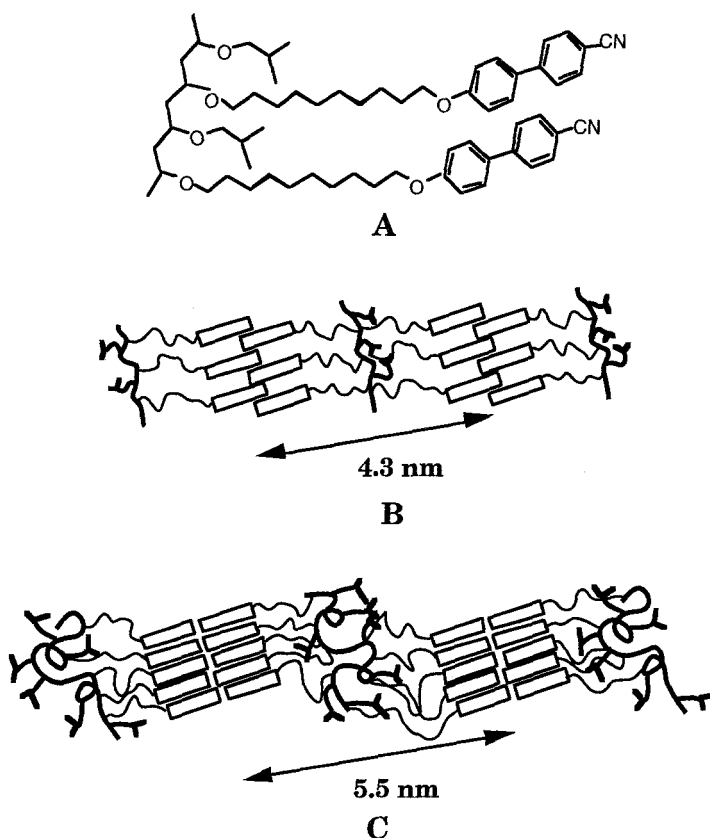
**Figure 3.** Graph showing the smectic A layer thickness as a function of the percentage i-butyl vinyl ether in the backbone of side-chain liquid crystalline copoly(vinyl ether)s.

**Table 2.** Heat of isotropisation during the smectic A -isotropic phase transition as a function of mesogenic content in copoly(vinyl ether)s

CBPUVE:IBVE	$\Delta h_i$ (kJ/mru) <sup>1</sup>	
	heating	cooling
100:0	3.30	3.26
93:7	3.30	3.01
49:51	1.59	1.34
43:57	1.42	1.25
36:64	0.67	0.54

1. mole repeating mesogenic unit

The heats of isotropisation ( $\Delta h_i$ ) for the copolymers are presented in Table 2. Comparing samples 93:7 and 49:51, the  $\Delta h_i$  dropped from 3.30 kJ mru<sup>-1</sup> to 1.59 kJ mru<sup>-1</sup> while the smectic layer thicknesses increased from 4.3 nm to 5.5 nm. Gedde *et al* (8) describes how  $\Delta h_i$  decreases with increasing molar mass for SCLC poly(vinyl ether)s. This change in  $\Delta h_i$  only becomes relevant when comparing samples in which DP varies by decades, which is not the case for the samples used in this study. It is thus proposed that the observed change in  $\Delta h_i$  is caused by the stronger interactions between the mesogenic groups in the interdigitated bilayer packing than in the bilayer packing.



**Figure 4.** A) The chemical structure of the copolymer studied. B) Schematic representation of the interdigitated bilayer packing formed in the smectic A phase of the 100:0 and 93:7 samples. C) Schematic representation of the bilayer packing formed in the smectic A phase of the 49:51 and 43:57 samples.

## Conclusions

The smectic A layer packing has been studied in a series of side-chain liquid crystalline copoly(vinyl ether)s of *i*-butyl vinyl ether and 11-[(4'-cyano-4-biphenyl)oxy]undecanyl vinyl ether. The thickness of the smectic layers increased with increasing concentration of *i*-butyl vinyl ether in the copolymer. The increase was a result not only of an expansion of the disordered regions between the layers of mesogenic groups but also of changes in the organisation of the mesogenic groups from interdigitated bilayer to bilayer packing. A considerable change in the heat of isotropization with comonomer composition can also be related to this change in the organisation of smectic layers.

## Acknowledgements

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