Preparation of ordered, crosslinked and thermally stable liquid crystalline poly(vinyl ether) films*

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Highly ordered liquid crystalline polymer films have been prepared by cationic polymerization of a mesogenic vinyl ether monomer, oriented in its mesophase. The degree of orientation of the mesogenic groups was calculated from wide-angle X-ray scattering measurements. The maximum value of the Herman orientation function was found to be 0.94. Thermally stabilized ordered films were prepared by polymerization of an oriented monomer mixture, consisting of a mesogenic monofunctional monomer and a mesogenic bifunctional monomer. The films maintained orientation up to temperatures of 200°C.

(Keywords: orientation; thermal stabilization; liquid crystalline polymers; vinyl ether; crosslinking)

INTRODUCTION

Liquid crystalline polymers (LCPs) have received considerable attention during the past decade and polymers of greatly varying molecular architecture fall into this category. Side-chain liquid crystalline polymers (SCLCPs) are one class of compounds in this field and the synthesis and structure of these polymers have been reviewed[1–3]. By the incorporation of a flexible spacer group in the molecules, the orientation of the mesogenic groups will not be affected by the motion of the main chain, as was reported by Finkelmann *et al.*[14]. In order to produce thin films of functional LCP materials, useful in electro-optical applications, there are two major requirements to be met. Liquid crystalline materials are by nature opaque and to possess transparency and good optical quality, a high degree of order must be obtained. Furthermore, for film utilization at elevated temperatures, the mesophase has to be thermally stable.

About 60 years ago, Vorländer realized the possibility of preparing liquid crystalline resins and lacquers that were stable for a long time at both low and high temperatures[5]. It was shown that extensive crosslinking should be avoided in order to prevent the formation of a fully amorphous polymer. For acrylate monomers with short spacer groups, Strzelecki and Liébert reported a 'locking-in' for organization of the liquid crystalline phase[6]. A monofunctional monomer was mixed with a bifunctional monomer of similar structure and polymerization was carried out in the mesophase that the two monomers formed together. Uniformly oriented polymer films were also obtained by polymerization of monomers in the presence of a magnetic field[7]. The latter increases the rate of the polymerization reaction[8].

A feasible method of producing highly oriented polymer films from acrylate monomers with long spacer groups was described by Broer *et al.*[9,10]. These authors reported on orientation of the monomer in its mesophase using a rubbed polyimide film followed by *in situ* polymerization. The use of photoinitiation allowed the polymerization temperature to be extensively varied. The use of this technique, for cationic polymerization, has been reported in a previous paper[11].

Earlier work[12] has shown that cationic bulk polymerization of liquid crystalline vinyl ether monomers at elevated temperatures results in high molar mass polymers with narrow molar mass distributions. In addition, reactions are fast and give high yields. Thermally initiated polymerization performed at different temperatures exhibited a simple Arrhenius behaviour, completely unaffected by the state of order of the monomer (isotropic or mesomorphic). However, these results are contradictory to those obtained by Hoyle *et al.*[13], who reported a rate enhancement in the liquid crystalline phase upon laser polymerization of acrylate monomers. This difference between acrylate and vinyl ether systems is probably a result of the different termination mechanisms involved in the polymerization of the monomers.

This paper presents the preparation and structure of thermally stable smectic polymer films with a high degree of orientation using a monofunctional liquid crystalline vinyl ether monomer in a mixture with low concentrations of a bifunctional liquid crystalline vinyl ether monomer.

EXPERIMENTAL

Materials

α-Methylbenzyltetramethylenesulphonium hexafluorophosphate was used as thermal initiator and phenacyltetramethylenesulphonium hexafluoroantimonate was

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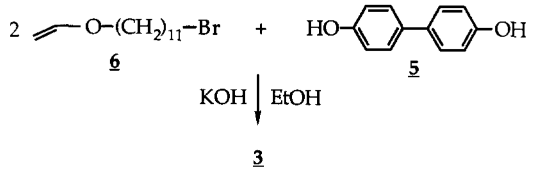
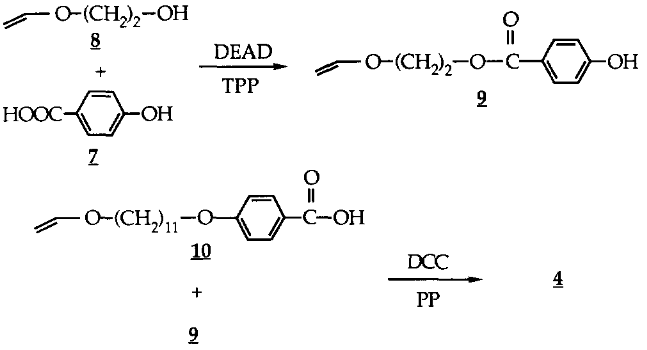
used as photoinitiator. The syntheses of these initiators are described elsewhere[14,15].

Phenothiazine was obtained from Aldrich and used as photosensitizer for u.v. polymerizations. 2-Hydroxyethyl vinyl ether was supplied by Nisso Maruzen Chemical Co. All other reagents and solvents were obtained from Aldrich and Merck.

Synthesis of monomers



Scheme 1 Synthesis of 3



Scheme 2 Synthesis of 4

4-[11-(Vinyloxy)undecyloxy]-4-methoxyphenylbenzoate (*1*) was synthesized as reported elsewhere[16].

2,2-Bis[4-(2-(vinyloxy)ethoxy)phenyl]propane (2) was synthesized according to a literature procedure[17].

4,4′-Bis[11-(vinyloxy)undecyloxy]biphenyl (*3*, *Scheme 1*). 4,4′-Bishydroxybiphenyl (**5**, 0.26 g, 1.38 mmol), KOH (0.19 g, 3.32 mmol) and 11-bromoundecanyl vinyl ether (**6**, 0.78 g, 2.83 mmol) were dissolved in ethanol (30 ml). The reaction mixture was heated at reflux for 24 h. The solvent was evaporated after cooling to room temperature. The resulting solid was washed with water and 1 M KOH and then recrystallized from ethanol to yield white crystals (0.4 g, 50%). M.p. (d.s.c.) 75°C. ^{1}H n.m.r. ($CDCl_3$, TMS, δ, ppm): 1.31–1.48 (28 protons, $-(C\underline{H}_2)_7-$, m), 1.60–1.69 (4 protons, $-CH_2-C\underline{H}_2-O-CH=CH_2$, p), 1.77–1.83 (4 protons, $-C\underline{H}_2-CH_2-OPh$, p), 3.68 (4 protons, $-C\underline{H}_2-O-CH=CH_2$, t), 3.97–4.02 (6 protons, 4 from $-C\underline{H}_2-OPh$ and 2 from $C\underline{H}_2=CH-O-$ *trans*, m), 4.15-4.21 (2 protons, $C\underline{H}_2=CH-O-$ *cis*, d), 6.44–6.52 (2 protons, $CH_2=C\underline{H}-O-$, q), 6.95 (4 aromatic protons, o from –O– of ether group, d), 7.46 (4 aromatic protons, m from –O– of ether group, d).

4-[4-(11-(Vinyloxy)undecycloxy)benzoyloxy]-2-(vinyloxy)ethylbenzoate (*4*, *Scheme 2*). A mixture of diethyl azodicarboxylate (5.48 g, 31.6 mmol) and 4-hydroxybenzoic acid (**7**, 4.0 g, 31.8 mmol) in dry ether (50 ml) was slowly added to a solution of 2-hydroxyethyl vinyl ether (**8**, 2.8 g, 29 mmol) and triphenylphosphine (8.36 g, 31.8 mmol) in dry ether (100 ml). The reaction mixture was stirred for 2 days and then stored in a refrigerator overnight. The resulting precipitate was filtered and the solvent was evaporated in a rotavapor. The resulting oil was purified by column chromatography (silica gel) using a gradient of hexane/ethyl acetate. Recrystallization from xylene/hexane produced white crystals (**9**, 2.2 g, 36%).

To a solution of **9** (0.31 g, 1.5 mmol) and **10** (0.5 g, 1.5 mmol) in dry CH_2Cl_2 (30 ml) at 0°C were added 1,3-dicyclohexylcarbodiimide (0.34 g, 1.65 mmol) and 4-pyrrolidinopyridine (0.22 g, 1.5 mmol). The reaction mixture was heated at reflux temperature for 5 days. The resulting precipitate was filtered and the solvent was evaporated in a rotavapor. The resulting solid was purified by column chromatography (silica gel) using a gradient of hexane/ethyl acetate. Recrystallization from ethanol produced white crystals (0.2 g, 25%). Purity (h.p.l.c.) 99.9%. M.p. (d.s.c.) 45°C. ^{1}H n.m.r. ($CDCl_3$, TMS, δ, ppm): 1.23–1.54 (14 protons, $-(C\underline{H}_2)_7-$, m), 1.64–1.76 (2 protons, $-CH_2-C\underline{H}_2-O-CH=CH_2$, p), 1.80–1.90 (2 protons, $-C\underline{H}_2-CH_2-OPh$, p), 3.68 (2 protons, $-C\underline{H}_2-O-CH=CH_2$, t), 3.97–4.29 (8 protons, 2 from $C\underline{H}_2=CH-O-$ *trans*, 2 from $C\underline{H}_2=CH-O-$ *cis*, 2 from $Ph-COO-CH_2-C\underline{H}_2-$ and 2 from $-C\underline{H}_2-OPh$, m), 4.58 (2 protons, $Ph-COO-C\underline{H}_2-CH_2-$, t), 6.42–6.60 (2 protons, $CH_2=C\underline{H}-O-$, m), 7.0 (2 aromatic protons, o from –O– of ether group, d), 7.3 (2 aromatic protons, o from –O– of ester group, d), 8.14 (4 aromatic protons, 2 m from –O– of ether group and 2 m from –O– of ester group, d).

Methods

The initiator was added to the monomer as a dilute CH_2Cl_2 solution. The monomer–initiator blend was then dissolved in CH_2Cl_2 and thoroughly mixed while allowing the solvent to evaporate. The resulting solid was dried *in vacuo* overnight. The monomer to initiator concentration ratio was in all cases 250, except for polymerizations prior to s.e.c. measurements where it was 500.

Polymerizations were performed under isothermal conditions either in aluminium pans in the differential scanning calorimeter or between glass slides in a microscope hot-stage. When polymerizations were performed in the mesophase of the monomer, the monomer–initiator blend was first heated up to the isotropization temperature and then cooled to the actual polymerization temperature.

Orientation of the liquid crystalline monomer was achieved by the use of a rubbed polyimide film, coated on the inside of the cover glass. Polyethylene fibre (Spectra) was used as a spacer between the glass slides to give the polymerization cell a uniform thickness of 30 μm.

Instrumentation

Molar mass measurements were performed by s.e.c. (Waters model 510, WISP 710B and differential refractometer 410), using Styragel® columns (500, 105, 104, 103 and 100 Å) and polystyrene standards with tetrahydrofuran as eluent. A differential scanning calorimeter (Perkin Elmer DSC-7, scanning rate 10°C min^{-1}) was used for thermal characterization. Hot-stage polarized light microscopy (Leitz Ortholux POL BKII equipped with a Mettler hot stage FP 82) was used for morphological and thermal characterization. An Osram Ultra-Vitalux lamp (300 W) served as the u.v. source for photopolymerization. Wide-angle X-ray scattering was performed on a Stadi/P instrument equipped with a curved position-sensitive detector (radius 220 mm). Strictly monochromatized Cu Kα_1 radiation with $\lambda = 0.154$ nm was used. ^{1}H n.m.r. was performed on a Bruker 250 MHz and ^{13}C n.m.r. on a Bruker 200 MHz.

RESULTS AND DISCUSSION

The monomers used (*Figures 1* and *2*) were cationically polymerized under isothermal conditions in the bulk state using either thermal or photochemical initiation. Sulphonium salt initiators in very low concentrations resulted in a final material of high purity. As reported earlier[11,12], this type of polymerization results in high molar mass polymers with narrow molar mass distributions. The reactions are very fast and give high yields. An increase in polymerization temperature leading to higher monomer mobility increases the reaction rate, for both photochemical and thermal initiation.

Orientation

Ordered thin (30 μm) polymer films were obtained by polymerization of **1** at different temperatures into the s_A phase of poly(**1**). A rubbed polyimide film, coated on the inside of the polymerization cell, induced the orientation. X-ray diffraction measurements were performed to verify the high degree of order obtained in these films. The intensity of the equatorial scattering corresponding to a *d*-spacing of 4.3 Å, which corresponds to the intermesogenic distance, was measured and the Herman orientation function (f) calculated as follows:

$$f = \frac{3\langle \cos^2 \Phi \rangle - 1}{2} \qquad (1)$$

$$\langle \cos^2 \Phi \rangle = \frac{\int_0^\pi I(\Phi) \sin \Phi \cos^2 \Phi \, d\Phi}{\int_0^\pi I(\Phi) \sin \Phi \, d\Phi} \qquad (2)$$

where $I(\Phi)$ is the intensity of the scattering at the azimuthal angle Φ, the summation being performed over $\Phi = 0$–$180°$. It is assumed that scattering at $\Phi = -10°$ equals scattering at $\Phi = 170°$, and so on.

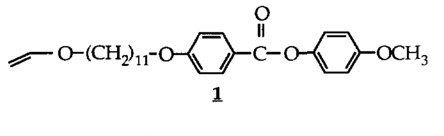


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Figure 1 Mesogenic monofunctional vinyl ether monomer **1**

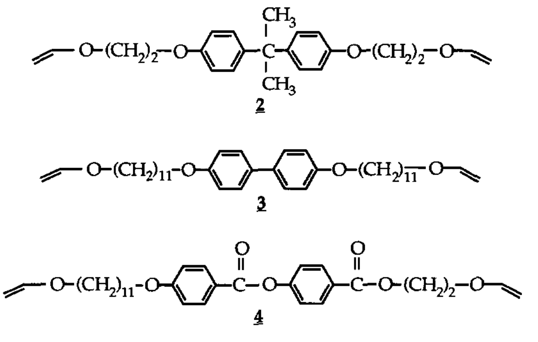

Figure 2 Bifunctional vinyl ether monomers **2**, **3** and **4**

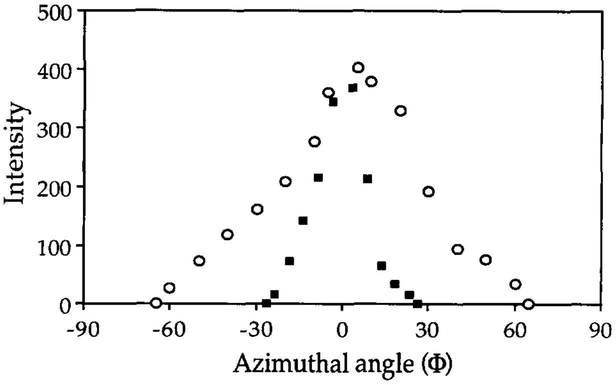

Figure 3 X-ray diffraction intensity as a function of azimuthal angle (Φ) for poly(**1**), obtained from photopolymerization of **1** in a 30 μm thick glass cell coated with a rubbed polyimide film: (○) polymerization from the isotropic state; (■) polymerization from the nematic phase

Table 1 Values of the Herman orientation function (f) for poly(**1**), obtained from photopolymerization of **1** at different temperatures (T_p) in a 30 μm thick glass cell, coated with a rubbed polyimide film

Monomer phase	T_p (°C)	f
Isotropic	80	0.66
Nematic	54	0.93
Smectic	41	0.94

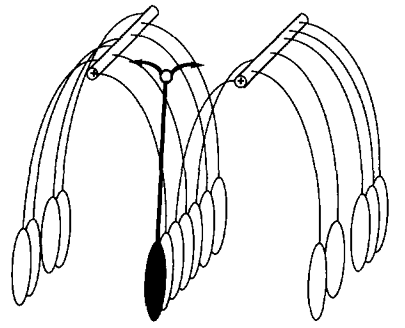

Figure 4 Schematic polymerization model

A significantly higher degree of orientation was obtained (*Figure 3* and *Table 1*) with *in situ* polymerization from the liquid crystalline phase of the monomer ($f = 0.93$–0.94) compared to polymerizing the isotropic monomer ($f = 0.66$). In the second case the rubbed polyimide film directed the growing oligomer/polymer molecules. In the first case the small monomer molecules were easily oriented and polymerization conserved the order. As reported earlier[11], the films obtained from *in situ* photopolymerization of **1** were completely transparent.

S.e.c. measurements (*Table 2*) show that photopolymerizations of **1** in 30 μm thick glass cells gave polymers with reasonably high molar mass values and narrow molar mass distributions. The polymerization giving ordered thin films resulted in a polymer of a lower molar mass than of the unordered equivalent. The uniformity index, however, remained unchanged. The decrease in molar mass of the ordered polymer systems may be due to impurities, present in the rubbed polyimide film, terminating the polymerization.

The isotropization temperature, recorded in the

Table 2 Results from s.e.c. measurements of poly(1) obtained from photopolymerization of 1 at different temperatures (T_p) in a 30 μm thick glass cell

Monomer state	T_p (°C)	$[M]_0/[I]_0$	M_n (g mol^{-1})	M_w/M_n
Unoriented				
Isotropic	80	500	18 100	2.35
Nematic	54	500	16 500	2.21
Smectic	41	500	20 500	2.02
Oriented				
Isotropic	80	500	13 700	2.04
Nematic	54	500	13 200	1.99
Smectic	41	500	11 600	1.95

polarized light microscope, of a macroscopically ordered film of poly(**1**) appeared to be the same as for its unordered equivalent. By lowering the temperature of the isotropic phase of the previously oriented sample a globally unordered sample was obtained. The orientation was completely lost by heating the sample above the clearing point, thus realizing the need for thermal stabilization.

Organization

^{13}C n.m.r. studies of **1**, polymerized with thermal initiation at 80°C show that the signal from the β-carbon at δ41 consists of two small almost identical peaks representing the *meso* and *racemic* dyads, respectively. Thus it can be concluded that the polymer is atactic. The side chains are randomly arranged on both sides of the main chain. In a previous publication[11] it has been shown, by X-ray diffraction, that poly(**1**) and its ordered equivalent exhibit a s_A liquid crystalline phase. The measured layer thickness was 31 Å and it is possible that smectic monolayers were formed. These results are in good agreement with the earlier data of Duran *et al*[18] and Yamaguchi and Asada[19]. From these data a model of how the polymerization proceeds can be constructed (*Figure 4*). The monomer enters the smectic polymer phase and then has two possibilities of choosing a growing chain end, thus building up an atactic polymer with a smectic single-layer structure.

Thermal stabilization

In trying to prepare a SCLCP with a thermally stable mesophase, three different types of bifunctional vinyl ether monomers, denoted **2**, **3** and **4**, respectively, were used. Each of the three compounds were mixed in relatively low concentrations (10–30%) with the monofunctional monomer **1** and the mixtures were subsequently polymerized, both thermally at 80°C for d.s.c. and photochemically in the microscope hot-stage at the same temperature. The different structures of the bifunctional monomers were believed to cause different properties in the resulting crosslinked polymers.

Compound **2** is a non-mesogenic monomer and, at low concentrations in polymerization with **1**, mainly acts as an impurity, which is demonstrated by the observed decrease in isotropization temperature with increasing **2** content (*Table 3*). Crosslinks always connect backbone chains and are probably located between the smectic layers in poly(**1**) and the side chains are free to move, however somewhat disturbed by the new compound present. At sufficiently high concentrations of **2**, the polymer became fully amorphous and no first-order transitions were observed.

Monomer **3** was considered to be more promising since its structure is similar to that of **1**. At a concentration of 10% of the bifunctional monomer **3**, the isotropization temperature of the resulting polymer was somewhat increased (*Table 3*) and at 20% no first-order transition was observed. However, the addition of almost 20% of bifunctionality to the monomer mixture obviously reduced the amount of monofunctional monomer present and accordingly any possible functional property of the final material. Thus a more efficient crosslinker was needed.

The bifunctional mesogenic monomer **4** has a structure quite similar to **1** and should fit better than **3** into the smectic structure of poly(**1**) and therefore a lower concentration would be required for the stabilization of the mesophase. The results (*Table 3*) clearly show that this is the case. Only 10% of the bifunctional monomer **4** is needed to give a thermally stable polymer. The d.s.c. traces of poly(**1**) and its crosslinked equivalent are shown in *Figure 5* and it can be seen that the endothermic isotropization peak is not present in the crosslinked polymer. This polymer showed a texture resembling focal conical domains indicative of a smectic liquid crystalline phase.

The two major differences in the structures of **3** and **4** are the short spacer on one of the sides of the mesogenic group and also the ester group between the aromatic rings, both features present only in **4**. The short spacer enables a better 'locking-in' of the mesophase formed and the similarity in mesogenic group between **1** and **4** enables better packing. This explains the lower amount of **4** needed to stabilize the mesophase of poly(**1**).

Table 3 Isotropization temperatures (T_i)[a] and textures[b] for some polymers, obtained from polymerization of different monomer mixtures at 80°C, both in the differential scanning calorimeter and in the microscope hot-stage

Monomer mixture	Relative amounts (mol/mol)	T_i (°C)	Texture
1	100/0	126	Smectic
1/2	90/10	109	Smectic
1/2	80/20	–[c]	Amorphous
1/3	90/10	133	Smectic
1/3	80/20	–[c]	Smectic
1/4	90/10	–[c]	Smectic

[a] From first heating scan in the differential scanning calorimeter
[b] As observed by microscopy
[c] No transition observed

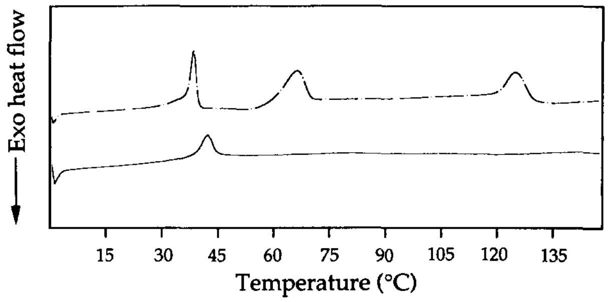

Figure 5 D.s.c. thermogram (first heating scan) of poly(1) (– ·) and its crosslinked equivalent (——), containing 10% of 4

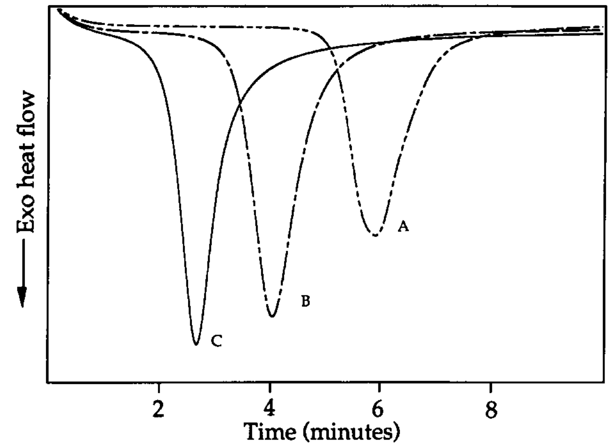

Figure 6 Polymerization exotherms for different monomer mixtures, thermally polymerized at 80°C in the differential scanning calorimeter: (A) pure **1**; (B) mixture of **1** and **4** (95/5); (C) pure **4**

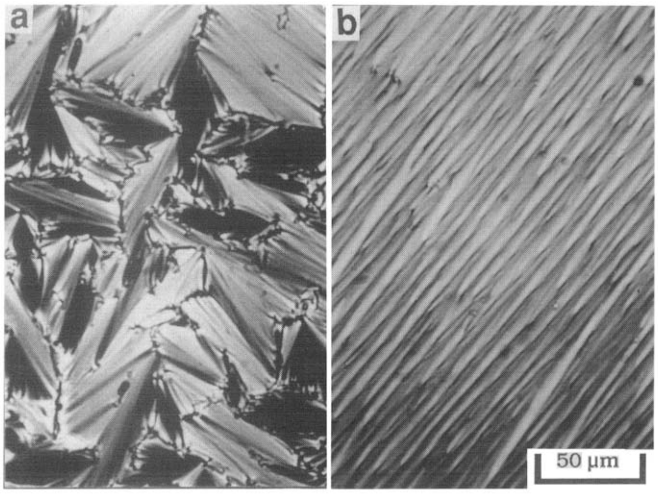

Figure 7 Polarized photomicrographs showing (a) poly(**1**), obtained from photopolymerization of **1** at 54°C in a 30 µm thick glass cell, and (b) its ordered crosslinked equivalent, obtained from photopolymerization of a mixture of **1** and **4** (90/10) at 50°C in a 30 µm thick glass cell coated with a rubbed polyimide film. The sample in (b) was heated up to 200°C and then cooled down to room temperature before the photomicrograph was taken

As expected, the rate of polymerization was also affected by adding a bifunctional monomer to the reaction mixture. Thermally initiated polymerizations of **1** and **4** were performed by d.s.c. at 80°C. The polymerization exotherms clearly show that adding only 5% bifunctional compound increases the rate of polymerization (*Figure 6*).

Ordered and thermally stable films

The final goal of this work was to prepare an oriented SCLCP film with a thermally stable mesophase. To meet these requirements and use the procedures described, it was necessary to find a bifunctional mesogenic monomer that mixes intimately with **1** in the mesophase. Mixtures of **1** with **2** and **3**, respectively, could not be oriented since both bifunctional monomers crystallized on cooling the isotropic monomer mixtures, before any mesophase was formed. For this reason it was impossible to use these substances to prepare oriented thermally stable films.

However, it was interesting to find that on cooling an isotropic mixture of **1** with 10% of **4**, a stable potentially orientable nematic phase was formed. The occurrence of this mixed mesophase is probably due to the fact that the structures of **1** and **4** are similar. Polymerization of the mixture of **1** and **4** at 50°C with photochemical initiation in a 30 µm thick glass cell coated with a rubbed polyimide film resulted in a highly ordered polymer film that could be heated up to 200°C without losing its high degree of order. The film was completely transparent at room temperature and showed a texture of macroscopically ordered s_A focal conical domains. *Figure 7* shows a polarized photomicrograph of this polymer and, for comparison, one of poly(**1**), globally unoriented and not thermally stabilized.

CONCLUSIONS

Ordered and thermally stable SCLCP films have been prepared by the *in situ* photopolymerization of an oriented liquid crystalline monomer mixture consisting of a monofunctional vinyl ether monomer and, in low concentration, a bifunctional vinyl ether monomer.

ACKNOWLEDGEMENTS

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REFERENCES

1 Finkelmann, H. and Rehage, G. *Adv. Polym. Sci.* 1984, **60/61**, 99

2 Shibaev, V. P. and Platé, N. A. *Adv. Polym. Sci.* 1984, **60/61**, 173

3 McArdle, C. B. 'Side Chain Liquid Crystal Polymers', Chapman and Hall, New York, 1989

4 Finkelmann, H., Happ, M., Portugall, M. and Ringsdorf, H. *Makromol. Chem.* 1978, **179**, 2541

5 Vorländer, B. *Trans. Faraday Soc.* 1933, **29**, 907

6 Strzelecki, L. and Liébert, L. *Bull. Soc. Chim. Fr.* 1973, 597

7 Liébert, L. and Strzelecki, L. *CR Acad. Sci. Ser. C* 1973, **276**, 647

8 Perplies, E., Ringsdorf, H. and Wendorff, J. H. *J. Polym. Sci., Polym. Lett. Edn* 1975, **13**, 243

9 Broer, D. J., Finkelmann, H. and Kondo, K. *Makromol. Chem.* 1988, **189**, 185

10 Broer, D. J., Boven, J., Mol, G. N. and Challa, G. *Makromol. Chem.* 1989, **190**, 2255

11 Jonsson, H., Andersson, H., Sundell, P.-E., Gedde, U. W. and Hult, A. *Polym. Bull.* 1991, **25**, 641

12 Jonsson, H., Sundell, P.-E., Percec, V., Gedde, U. W. and Hult, A. *Polym. Bull.* 1991, **25**, 649

13 Hoyle, C. E., Chawla, C. P. and Griffin, A. C. *Polymer* 1990, **60**, 1909

14 Sundell, P.-E., Jönsson, S. and Hult, A. *J. Polym. Sci., Polym. Chem. Edn* 1991, **29**, 1535

15 Sundell, P.-E., Jönsson, S. and Hult, A. in 'Radiation Curing of Polymeric Materials' (Eds C. E. Hoyle and J. F. Kinstle), American Chemical Society Symposium Series no. 417, American Chemical Society, Washington DC, 1990, Ch. 32

16 Jonsson, H., Percec, V. and Hult, A. *Polym. Bull.* 1991, **25**, 115

17 Crivello, J. V. and Conlon, D. A. *J. Polym. Sci.* 1983, **21**, 1785

18 Duran, R., Guillon, D., Gramain, P. and Skoulios, A. *Makromol. Chem. Rapid. Commun*, 1987, **8**, 181

19 Yamaguchi, T. and Asada, T. *Liquid Crystals* 1991, **10**, 215