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Preparation and characterization of side-chain liquid crystalline polymer thin films aligned on PTFE friction-transferred layers

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Annealing of a side-chain LC polymer (SC-LCP) and a fluorescent dye containing copolymer deposited on friction-transferred PTFE substrates is found to yield macroscopically aligned glassy films. The results obtained by electron diffraction, u.v.-visible and *FT*i.r. spectroscopy clearly demonstrate that the mesogenic side-groups as well as the fluorescence dye orient with their long axes parallel to the PTFE chain axis. Thus, the SC-LCP aligned thin films adopt a near perfect bookshelf geometry in which the smectic layers are oriented edge-on and perpendicular to the alignment direction. The order parameter P_2 increases from 0.60 to as high as 0.85 when the annealing temperature in the smectic mesophase approaches the smectic to nematic phase transition temperature.

(Keywords: side-chain liquid crystal polymer; PTFE; smectic layers)

INTRODUCTION

Liquid crystalline polymers can be broadly divided in two classes of compounds, the main-chain (MC-LCP's) and the side-chain LC polymers (SC-LCP's), respectively. The later are distinct from the former in that the mesogenic units are covalently bonded (via flexible spacers) laterally to the polymer backbone. SC-LCP's are mainly synthesized with the aim of producing special materials with potential in the area of optics, display technology and information storage, since they combine specific isotropic polymer properties with the anisotropic properties of low molar mass liquid crystals[1–3]. Furthermore, as shown by various authors, the range of applications can be further extended by incorporating functional guest molecules such as dichroic dyes[4–6]. The orientation of the guest molecules can be easily achieved via the alignment of the liquid crystalline phase. In the particular case of a mesogenic group/dichroic dye copolymer, the induced orientional order can be frozen-in by cooling the polymer below its glass transition temperature so as to produce thin dichroic polymer films with dichroic ratios depending, among others, on the degree of the LC alignment. These dye-containing SC-LCP's can be macroscopically oriented by surface effects, by magnetic or electric fields in a manner similar to more conventional liquid crystals[4,7].

The present paper is aimed at demonstrating that highly ordered thin films of thermotropic liquid crystalline side-chain polymers and its corresponding dye-containing copolymers can be obtained by using friction transferred poly(tetrafluoroethylene) (PTFE) thin layers as orientation layers. As reported previously, PTFE substrates have the capacity of inducing the oriented growth of a wide variety of crystalline materials as well as the alignment of low molar mass liquid crystalline materials[8–12]. They offer several interesting advantages, including the transparency required for most optical or opto-electronical devices for which the polymeric compounds studied herein are aimed. In addition to the characteristics of the SC-LCP's used in this study, investigations by means of optical and electron microscopy, electron diffraction and u.v.-visible and i.r. spectroscopy of the LC polymer thin films aligned on PTFE are presented. Our results demonstrate that SC-LCP thin films align homogeneously on PTFE substrates. The films display a uniform and highly birefringent texture with a near-perfect bookshelf geometry in which the mesogenic side-chains in the 'edge-on' smectic layers are oriented parallel to the PTFE chain axis.

EXPERIMENTAL

Materials

The chemical structure of the liquid crystalline side-chain homopolymer 1[5] and the fluorescent dye containing copolymer 2 are illustrated in *Figure 1*. Both polymers are based on polyacrylates with methoxyphenylbenzoate mesogenic side-groups which are attached to the polymer backbone by a flexible spacer of six methylene units. Copolymer 2 contains 1% by weight of a covalently attached tetrachlorosubstituted perylene chromophore. The chromophore is a fluorescent dye with an excellent light stability and high fluorescence efficiency. The homopolymer, as well as the copolymer, were synthesized by a free radical polymerization of the corresponding monomers in dioxane at 70°C with 0.5 mol% of AIBN as initiator[13]. The polymers were precipitated in cold methanol and further purified by preparative GPC with THF as eluent.

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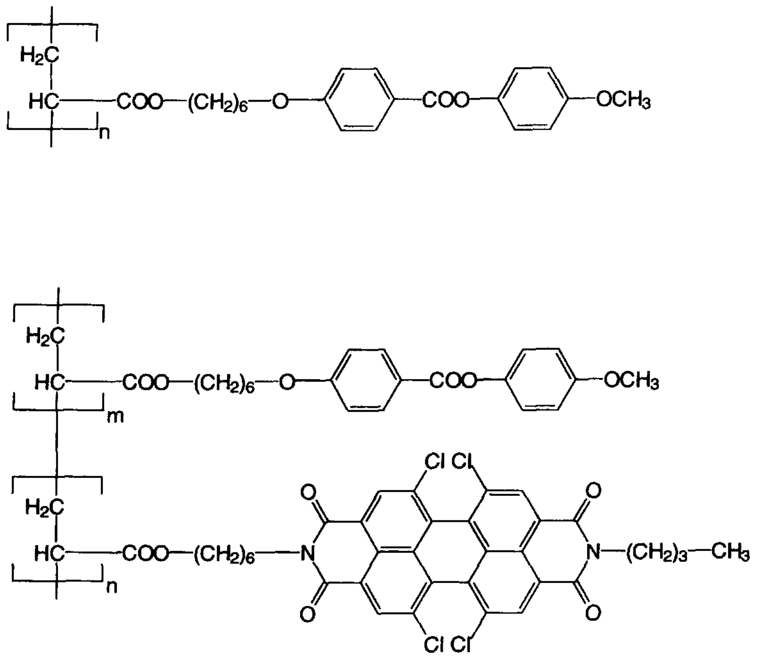
The phase behaviour was investigated with d.s.c. and polarized optical microscopy. The d.s.c.-curves (second heating, 10 K min^{-1}) are shown in *Figure 2*. Homopolymer 1 presents a glass transition at 30°C and a smectic A mesophase up to 93°C followed by a nematic mesophase. The clearing transition to the isotropic state occurs at 119°C. The incorporation of 1% by weight of the perylene dye in copolymer 2 has a minor influence on the transition temperatures. The glass transition is at 28°C, the smectic to nematic transition at 92°C and the nematic to isotropic transition at 117°C. The structure of the smectic A mesophase is preserved upon cooling below the glass transition temperature resulting in a glass with smectic A order.

The chemical structure of homopolymer 1 is closely related to a side-chain LCP (hereafter called BPB) used by Voigt-Martin and Durst[14,15] in their pioneering work on the structural analysis of side-chain liquid crystal polymer films by electron microscopy. The polymer backbone is a polymethacrylate instead of a polyacrylate and the terminal substituent of the mesogenic side group is a butoxy group instead of a methoxy group. The phase behaviour of BPB is: glass 30°C smectic$_A$ 110°C nematic 113°C isotropic.

Sample preparation

The PTFE substrates were prepared by the friction transfer method which has been described in detail elsewhere[8,10,16]. In brief, it consists in sliding, at a rate of ~1 mm s^{-1}, a rod of a commercial grade PTFE across a freshly cleaned glass slide held at 300°C (the rod axis is parallel to the glass slide and perpendicular to the friction direction). During this process, a thin highly oriented layer of PTFE is transferred on the glass slide. Electron diffraction and AFM imaging of the layer surface clearly show that PTFE chains are fully extended in the friction direction[8,10,16–18].

With the PTFE/LC polymers wetting affinity being low, macroscopically aligned uniform dichroic polymer thin films were prepared by a three-step procedure. Firstly, thin films of the homopolymer or copolymer were made by casting a 0.1% (w/w) solution in chloroform on glass slides. Secondly, after drying, the films were floated on water and subsequently redeposited on the PTFE covered glass slides, and then carefully dried under vacuum. Finally, the films in contact with the PTFE substrate were annealed at around 80°C (i.e. in the smectic phase range) for 15 min, then



1

2

Figure 1 Chemical structure of the side-chain LC-homopolymer 1 and the fluorescent dye containing copolymer 2

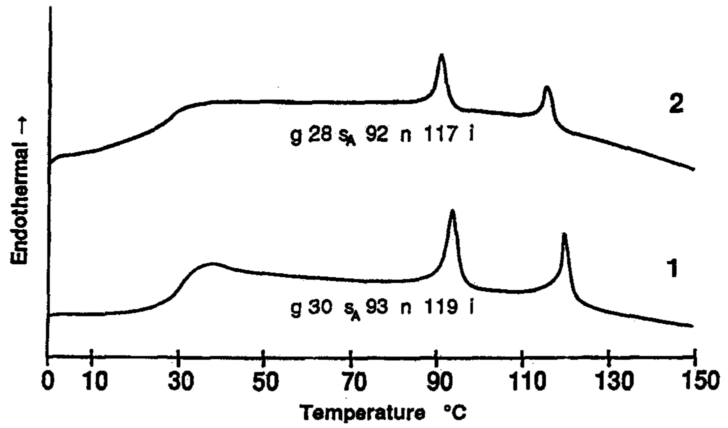


Figure 2 DSC heating curve of homopolymer 1 and copolymer 2 (heating rate: 10 K min^{-1}. i = isotropic, n = nematic, S$_A$ = smectic A and g = glass)

cooled to room temperature below the glass transition temperature, thus preserving the LC side-chain and the chromophore orientation induced during the orientation and annealing step.

Characterization of the aligned LC polymer thin films

Optical and electron microscopy and calorimetry. Optical microscopy observations were carried out using a Zeiss photomicroscope II. For the electron microscopy investigations, the PTFE/LC polymer bilayers were coated with a carbon film, floated on a dilute hydrofluoric acid–water solution in order to prevent deformation of the bilayer and then mounted on EM copper grids before examination in transmission and selected area diffraction modes using a Philips CM12 electron microscope operating at 120 kV.

Differential scanning calorimetry (d.s.c.). d.s.c. measurements were carried out with a Perkin-Elmer d.s.c. 7. The heating and cooling rate was 10 K min^{-1}. The transition temperatures (peak maximum) were determined from the second heating run.

*Polarized FT*i.r. and u.v.-visible spectrometry. The degree of orientation of the mesogenic side-groups and of the dichroic dye in macroscopically aligned SC-LCP glasses was determined by polarized *FT*i.r. and u.v.-visible dichroism measurements, respectively.

The dichroic ratio R and the order parameter P_2 are calculated using the following equations:

$$R = \frac{A_{/\!/}}{A_{\perp}}$$

and

$$P_2 = \left(\frac{R_0+2}{R_0-1}\right)\left(\frac{R-1}{R+2}\right)$$

where $A_{/\!/}$ and $A_{\perp}$ represent the absorbances measured with the radiation polarization direction parallel and perpendicular to the PTFE sliding direction. Assuming an uniaxial orientation, R_0, the ideal dichroic ratio is given by $R_0 = 2\cot g^2\alpha$ where α is the angle between the transition moment of the modes used for the dichroic measurement and the reference axis, i.e. the PTFE sliding direction. When they are parallel, as is the case for the dye side-group in aligned films of copolymer 2 (see below), α is equal to 0 and the above equation reduces to:

$$P_2 = \left(\frac{R-1}{R+2}\right)$$

Polarized *FT*i.r. spectra of the thin films deposited on EM grids were recorded using a Bruker IFS 113 V spectrometer fitted with a microscope operating in transmission mode. Polarization of the beam was produced with an Al wire-grid polarizer. At least 500 interferrograms with a resolution of 2 cm^{-1} were added for each spectrum. The polarized u.v.-visible absorption spectra of copolymer 2 were determined with a Shimadzu u.v.-PC2101 spectrometer using a cell made of two parallel PTFE-covered glass walls spaced by ~10 μm using short Kevlar fibres.

RESULTS AND DISCUSSION

Morphological investigations

Optical microscopy observations in polarized light of the thin films of 1 and 2 directly after redeposition on PTFE covered glass slides show no relevant texture. Once annealed in the smectic state (30°C < 92°C) textures typical of a LC phase are observed on the PTFE-uncovered glass surface (*Figure 3*a) while on the PTFE covered part of the slide, uniform highly birefringent films are formed (*Figure 3*b) proving that, as expected, the PTFE layers act as very efficient alignment substrates for LC side chain polymers. *Figure 3*b has been selected intentionally with a few small defects in the aligned film, since films aligned on nearly perfect PTFE layers are absolutely featureless.

The alignment of the smectic phase, frozen-in by rapid quenching of the samples after annealing, has been further characterized by electron diffraction. No attempt has been made to directly observe the smectic layers by high-resolution microscopy following the procedure used by Voigt-Martin and Durst[14].

Figure 4 shows a composite diffraction pattern of a PTFE/homopolymer bilayer. The outer pair of arced reflections on the meridian are the only clearly visible reflections arising from the PTFE substrate: they can be indexed as 0015 reflections of the room temperature crystalline phase of PTFE (15_7 helix in hexagonal phase IV). The chain direction, and hence the friction direction, is


a

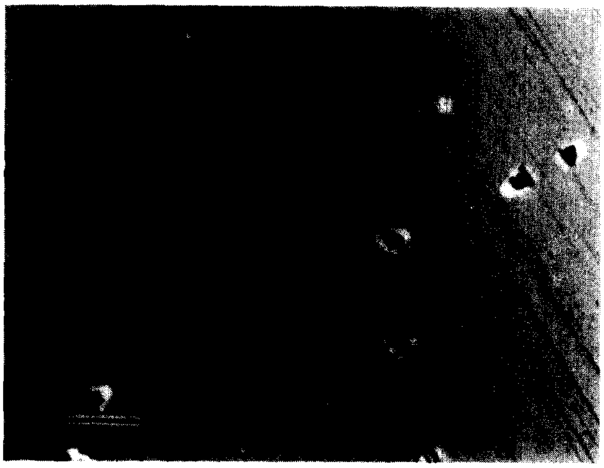

b

Figure 3 Optical micrographs in polarized light of the textures of homopolymer 1 annealed at 80°C after deposition on (a) a freshly cleaned glass surface (scale bar: 5 μm); and (b) a PTFE covered glass slide (scale bar: 10 μm) parallel to this meridional line, i.e. is vertical. On the same line, but much closer to the central spot, up to three pairs of very sharp small angle diffraction maxima (second to fourth order reflections) are observed. They clearly reveal that:

- the smectic layers are oriented edge-on, i.e. parallel to the electron beam, or perpendicular to the PTFE chain axis (bookshelf geometry);
- the measured smectic layer spacing is equal to 2.46 nm, which is in good agreement with the calculated length of an extended mesogenic side-chain ($l \approx 2.4$ nm).

On the equator, only a pair of diffuse arced halos can be distinguished at wide angles, which correspond to an average inter-side-chain spacing in the smectic layer of 0.45 nm. The same wide angle reflection has been observed for BPB polymethacrylate[14,15]. It clearly indicates a lack of order in the side-chain lateral packing within the smectic layer.

It can, thus, be concluded from the composite diffraction pattern shown in *Figure 4* that:

- The smectic layers are stacked edge-on, i.e. the layers are normal to the film plane and, therefore, parallel to the electron beam. Further, they are well ordered since they all extend in a single direction, normal to the PTFE chain direction (perfect book-shelf geometry).
- The mean orientation of the mesogenic side-chains is normal to the smectic layer planes (smectic phase A). The mesogenic groups are, therefore, perfectly aligned along the PTFE chain axis.

The PTFE/copolymer 2 composite diffraction pattern is similar to the pattern described above. However, it indicates that the introduction of a small amount of chromophoree side-chains causes a slight loss of orientation in the aligned thin films. On the meridional line only two orders of low angle reflections are observed, whereas on the equator the halo corresponding to the side-chain packing is more arced and more diffuse. Therefore, both the smectic intra- as well as inter-layer order are slightly disturbed.

In summary, after annealing of the SC-LCP's thin films, the mesogenic side-groups are aligned parallel to the PTFE chain axis, and a very uniform texture in which the smectic layers are arranged in a perfect book-shelf geometry over a very large surface ($\approx 5\ \text{cm}^2$) is obtained. Whether the strong aligning ability of PTFE substrates is due to a form of epitaxy as first suggested by Castellano[19] and Geary and coworkers[20] for mechanically buffed or rubbed polymer layers, or to the presence of an adequate substrate surface topography (presence of grooves and steps) is far from being obvious. Indeed, the average inter-side-chain spacing observed within the smectic layers is 0.45 nm. This value departs significantly from the PTFE inter-chain distance of 0.56 nm in the (100) contact surface. However, given the degree of orientational freedom of the mesogenic side-group in the smectic phase, it may well be that such liquid crystalline polymers are much less 'sensitive' to a large substrate/deposit mismatch than conventional crystalline polymers or solids, so that epitaxial alignment could, nevertheless, occur via the formation at the substrate–deposit interface of a transient layer with an inter-side-chain spacing close to 0.56 nm. PTFE substrates also present numerous steps of different heights (1–50 nm) extending all over the surface in the friction direction, i.e. the PTFE chain direction. Such steps could well act as preferential nucleation sites well fitted to induce a strong orientation of the mesogenic groups along the PTFE chains. Finally, on the basis of the present experimental evidence, it cannot be ruled out that both mechanisms may contribute to the alignment process of the liquid crystalline homopolymer and copolymer.

Spectroscopic investigations

u.v.-visible spectroscopy. The degree of orientation of the perylene chromophoree in copolymer 2 was determined by measuring the u.v.-visible dichroism of a sample aligned in the 10 μm thick PTFE/glass cell by annealing at 100°C (i.e. in the nematic phase range) for a few hours followed by slow cooling to room temperature. The spectroscopic measurements were made in the smectic glassy state. The

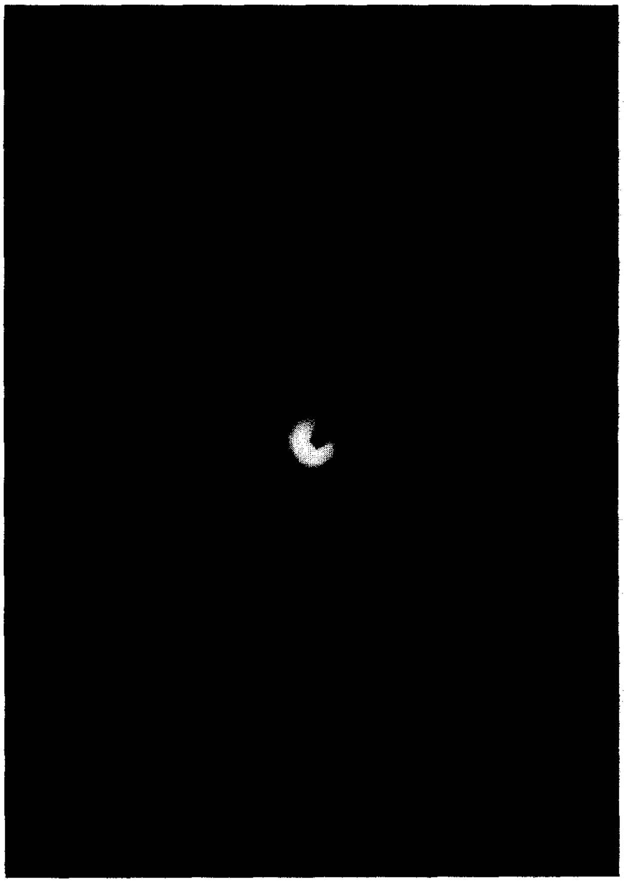


Figure 4 Composite selected area electron diffraction pattern of homopolymer 1 film aligned on a PTFE substrate by annealing at 80°C in the smectic phase followed by quenching to room temperature. The outer pair of 0015_{PTFE} reflections (arrow) on the meridional line indicates the PTFE chain axis direction and, therefore, the friction direction

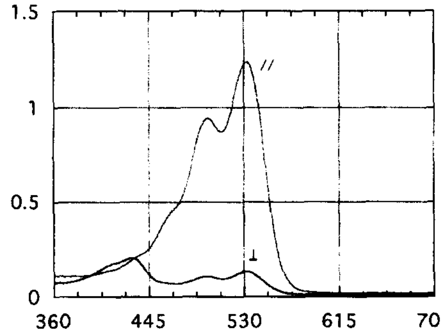


Figure 5 UV-visible absorption spectra at room temperature of the aligned dye containing copolymer 2 taken parallel ($A_{//}$) and perpendicular ($A_{\perp}$) to the alignment direction, i.e. the PTFE chain axis

absorption spectra shown in *Figure 5* were taken parallel ($A_{\parallel}$) and perpendicular ($A_{\perp}$) to the PTFE sliding direction. Maximum absorption is obtained when the polarization direction is parallel to the mesogenic group alignment direction given by the PTFE sliding direction. Thus, as expected, the dye side-group adopts the same orientation as the host mesogenic group, i.e. its main molecular axis is parallel to the PTFE chain axis.

The dichroic ratio R calculated for a wavelength of $\lambda = 533$ nm and the corresponding order parameter P_2 are equal to 12 and 0.79, respectively. These values which are slightly higher than the values measured for analogous liquid crystalline copolymers aligned on rubbed polyimide layers (see Table 4 in Ref.[7]), point out the high degree of ordering of the dye molecules triggered by a near perfect alignment of the mesogenic groups in the smectic A phase.

*Polarized FT*i.r. spectroscopy. The two *FT*i.r. spectra of a thin film of homopolymer 1 oriented on a PTFE friction-transferred layer by annealing at 80°C and taken with the beam polarized parallel and perpendicular to the PTFE chain direction (solid and broken line, respectively) are shown in *Figure 6*.

The vibrations observed on these spectra are of two types: (i) vibrations associated with the aromatic groups in the mesogenic side-chain; and (ii) vibrations of the backbone/mesogen spacer and the polyacrylate backbone. The mesogenic sidegroup contains two para-disubstituted aromatic rings; their normal modes correspond to three orientations of the transition moments MX, MY and MZ corresponding to the out of plane axis, the in-plane axis normal to the C1–C4 axis and the C1–C4 axis, respectively. Concerning the aromatic vibrations, the attribution of the normal modes which remain unaffected by substitution effects (modes MX: 4, 11, 10b; MY: 15; MZ: 18a, 9a, 19a, 8a)[21] can easily be made by using the Table given by Carrigou-Lagrange *et al.*[22]. Conversely, MZ modes involving the C–X stretching vibration are known to be very sensitive to substitution effects and their attribution is, therefore, less evident. Le Calvé *et al.*[23] calculated the frequency shifts for several subtituted aromatic molecules and showed that for light substituted compounds, these coupled modes correspond to 6a, 1 and 12 which become d, d′, e, e′ modes. *Table 1* lists the wavenumbers, the dichroic ratios and the proposed assignments of the various i.r. bands of the mesogenic group. The vibrations of the backbone/mesogen spacer reported in *Table 2* are of the typical alkane type (CH_2 rocking or scissoring at 730 and 1465 cm^{-1}, respectively)[24], and always of lower intensity than the mesogenic side-group i.r. bands.

Estimation of the order parameter of thin films of homopolymer 1 annealed for 15 min at 50, 60, 70 and 8O°C was made by taking into account all the vibrations of the mesogenic side-group. Note that annealing of PTFE/homopolymer 1 bilayers at higher temperatures, i.e. in the nematic phase range, were unsuccessful since, as vividly

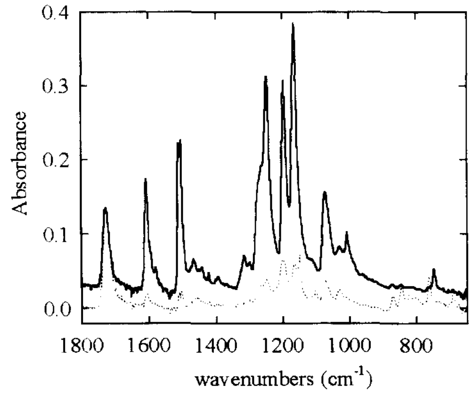


Figure 6 Transmission polarized FTIR spectra of a homopolymer 1/PTFE bilayer annealed at 80°C. The solid and broken lines represent the absorption spectra for the polarization parallel and perpendicular to the alignment direction, respectively

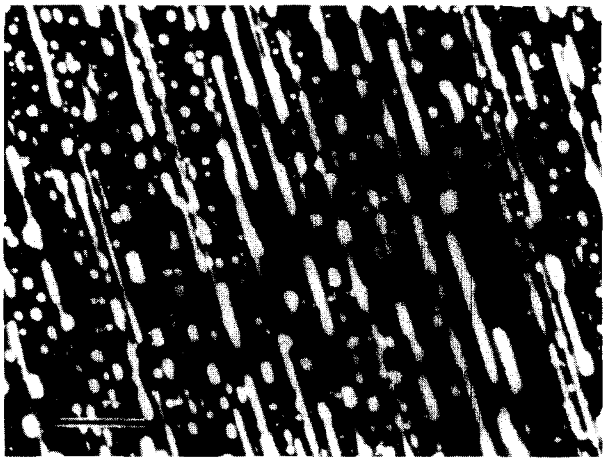


Figure 7 Optical photomicrograph showing the dewetting which occured during the annealing process at 92°C of a homopolymer 1 thin film deposited on a PTFE orientation layer (scale bar: 20 μm)

Table 1 IR vibrations of the mesogenic side-group. The attributions correspond to the description given by Carrigou-Lagrange[22]. The orientation of the X,Y and Z axes is specified in the text

Wavenumbers[a] (cm^{-1})	Polarization	Dichroic ratio	Attribution
w 690	⊥	0.1	4, X
w 747	//	14.0	d, Z^{b}
w 763	⊥	0.1	11, X
w 822	⊥	0.1	—
w 842	//	0.08	d′, Z^{b}
w 870	⊥	0.2	10b, X
m 1008	//	20.0	18a, Z
m 1072	//	5.0	—
m 1150	⊥	—	15, Y
S 1166	//	19.0	9a, Z
S 1195	//	8.0	1, e, Z^{b}
S 1246	//	14.0	12, e′, Z^{b}
w 1420	//	—	—
S 1507	//	12.0	19a, Z
sh 1578	//	—	—
S 1609	//	12.0	8a, Z

[a] w, m, S and sh correspond to weak, medium, strong intensity and shoulder, respectively.

[b] Mode of vibrations coupled with stretching C–O, and C–C.

Table 2 Assignment of the vibrations of the backbone/mesogen spacer

Wavenumbers[a] ($^{cm^{-1}}$)	Attribution
w 731	Rocking CH2
w 1031	Stretching COC
w 1315	Wagging CH2
w 1441	Scissoring CH3
m 1465	Scissoring CH2
w 2930	Stretching CH
w 2860	Stretching CH

[a] w and m correspond to weak and medium, respectively.

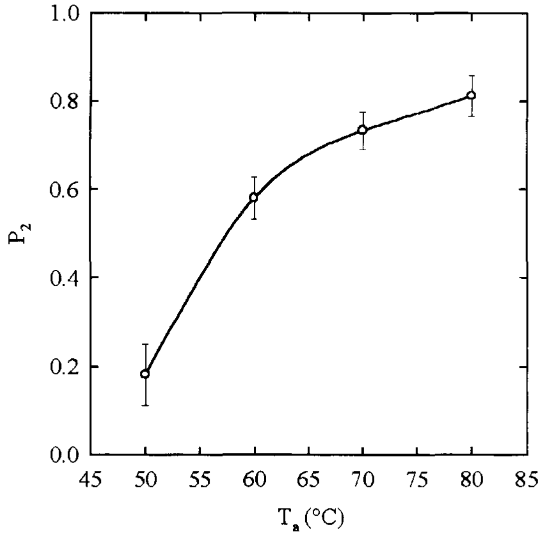


Figure 8 Variation of the order parameter P_2 of homopolymer 1 as a function of the annealing temperature T (annealing time: 15 min). The error bar at a given temperature corresponds to the standard deviation of the order parameter measured for the various mesogenic side-group vibrations

demonstrated by the photomicrograph shown in *Figure 7*, dewetting of the PTFE substrate occured rapidly as a consequence of the low viscosity of the nematic liquid crystalline phase. *Figure 8*, which represents a plot of the order parameter P_2 *versus* the annealing temperature, shows a definite increase of P_2 from 0.2 to as high as 0.85 when the annealing temperature is increased from well below the smectic–nematic transition to 80°C. Thus, the alignment of the SC-LCP thin films deposited on PTFE substrates improves significantly as the annealing temperature approaches the smectic–nematic phase transition.

CONCLUSION

In conclusion, the present results clearly demonstrate that friction-transferred PTFE layers have an alignment ability equivalent if not superior to the classical mechanically rubbed polymer layers. As deduced from the electron diffraction patterns, the mesogenic groups of the side-chain liquid crystalline polymeric glasses, and as a consequence, the chromophoree group of the dye containing copolymers orient with their long axes parallel to the PTFE chain axis. The thin films in the smectic phase adopt, therefore, a nearly perfect bookshelf geometry in which the smectic layers are all oriented perpendicular to the alignment direction. The relatively high values of the measured dichroic ratios and order parameters underline the excellent quality of the alignment induced by the PTFE substrates over large areas.

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