

Functional polythiiranes

8. Influence of the terminal group on the thermotropic behaviour of side chain liquid crystalline polythiiranes and identification of a crystalline phase

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Summary

Three new side chain liquid crystalline polythiiranes were prepared with new substituents on the mesogenic groups. Their thermotropic liquid crystalline behaviour was studied by the usual techniques (DSC, X-ray diffraction and polarized optical microscopy). Unlike the polyoxiranes described in the literature, the size of the terminal group has no influence on the nature of the mesophases of polythiiranes; only slight changes of the transition temperatures were observed. In this series of polymers, a phase, denoted X, appeared at temperatures below the smectic E phase, and could not be identified by usual characterization techniques. An isothermal kinetic study for the smectic E / X phase transition resulted in an Avrami exponent close to 1, suggesting a one-dimensional ordering occurred during the transformation from the smectic phase. This result, combined with other observations, helped us to assign the X phase to the crystalline phase.

Introduction

In a previous paper in this series (1), we synthesized and characterized polythiiranes bearing mesogenic biphenyl units in the side chain. Smectic A (S_A) and smectic E (S_E) mesophases were observed with these polymers. Methoxy and butoxy groups were tested as terminal groups on the biphenyl and this difference did not influence the nature of the mesophases. S_A and S_E mesophases were also observed with the polyoxiranes described in the literature bearing the same butoxybiphenyl units (2) but in this case a S_B mesophase appeared between the S_E and S_A mesophases. In this study, Akiyama *et al.* also described the thermotropic behaviour of polyoxiranes with biphenyl side chains substituted with branched and asymmetric alkoxy groups: (S)2-methylbutoxy and 1-methylheptyloxy groups, which resulted in S_C mesophases. The similarity of the mesophases obtained with both main chains and identical butoxybiphenyl mesogens prompts us to test the thermotropic properties of polythiiranes bearing biphenyl units substituted, in the 4' position, with the 2-methylbutoxy group (R+S) **P13** and (S) **P14**. A larger group octyloxy was also tested: **P12**. The results obtained with classical methods (DSC, X-ray diffraction and polarizing optical microscopy) will complete those of our previous study.

Furthermore, for many polymers in this series, upon cooling a transition from S_E mesophase to another phase named X was observed from DSC. Although a change of texture for this transition was observed for most polymers from polarizing microscopy observations, this low-temperature phase could not be identified with certainty because the X-ray diffraction measurements showed little change when passing from S_E to the X phase. In this paper, we also report the results of a kinetic study for the S_E / X transition on polymer **P7**, and show that the measured Avrami exponent could help the identification of this phase.

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Table 1 Results of the polymerizations (solvent: DMF ; temperature: 30°C)

Polymer	[M] ₀ (mol.l ⁻¹)	[M] ₀ / [I] ₀ a	Yield	M _n calculated (g.mol ⁻¹)	M _n ^b (g.mol ⁻¹)	M _w ^b (g.mol ⁻¹)	I _p ^b (M _w / M _n)
P12	0,25	50	93	27200	12200	29800	2,45
P13	0,45	50	90	25100	12500	17300	1,40
P14	0,51	50	93	25100	19700	29100	1,48

^a calculated assuming a living polymerization : $DP_n = [M]_0 / [I]_0$

^b obtained from size-exclusion chromatography (THF) and expressed in equivalent polystyrene

Results and discussion

The synthesis of the polymers **P12**, **P13**, **P14** (Scheme 1) was performed using the methodology previously described: synthesis of the suitable monomer and polymerization with tetramethylammonium dithiobenzoate as an initiator in DMF as a solvent. We choose the spacer length in order to establish a comparison with the polymers previously prepared. The scheme 1 describes the synthetic route leading to the monomers. Further details and characterization of the monomers, intermediates and polymers are presented in the experimental section.

The results of the polymerizations are summarized in table 1. With tetramethylammonium dithiobenzoate as an initiator, the initiation step is slower than the propagation step and large I_p values are usually obtained (3). The low solubility of polymer **P12** in the polymerization mixture explains the large polydispersity index of this sample.

The thermotropic behaviour of the polymers is reported on table 2. DSC curves for the polymers **P12**, **P13**, **P14** exhibited three transitions corresponding to three enantiotropic mesophases. Glass transitions were not easily assigned. The textures observed on polarizing optical microscopy were identical for the three polymers. In the higher temperature range, typical focal conic texture of S_A mesophase was observed; in the middle range of temperatures, the focal conic texture appeared striated and this confirmed the characterization of a S_E mesophase deduced from X-ray diffraction pattern. On cooling, as previously reported in this series, we observed an unidentified striated texture corresponding to the phase X, in which focal conics are hidden. The S_A and S_E mesophases were also well characterized by means of X-ray studies for the three samples. From the X-ray patterns the d-spacing of both smectic mesophases could be evaluated : 58.1 Å and 62.3 Å respectively for **P12**; 31.7 Å and 31.2 Å for **P13** ; 32.5 Å and 32.7 for **P14**. The values of the d-spacing can be compared with the length of the side chain calculated from a computer drawn model for a polymer with the same spacer and a butoxy terminal group : 27,9 Å. Like the others polymers of the series, **P13** and **P14** are arranged in single layer but **P12** with the larger terminal group in the series is arranged in double layer.

Apparently, no difference could be evidenced in the X-ray diffraction patterns between the S_E and X mesophases. As the low-temperature X phase is more ordered than S_E, we suspect that it is the crystalline phase or something very close. Therefore, we made an isothermal kinetic study for the transition S_E / X in order to get more insights into the nature of this transition. Such measurements could not be realized for **P12**, **P13** or **P14**, because the hysteresis in their S_E / X transitions is too narrow. The previously prepared polymer **P7** (Scheme 1) which exhibits a broader hysteresis for this transition (1), was selected for this study. An erroneous thermotropic behaviour of **P7** was reported in reference (1) : after

Table 2 Phase transition temperatures in °C (enthalpy in J.g⁻¹)

P7	X	$\xleftrightarrow[100,5 (1,97)]{114,6 (5,42)}$	S _E	$\xleftrightarrow[133 (13,74)]{136,8 (15,03)}$	S _A	$\xleftrightarrow[145 (15,16)]{150,6 (15,62)}$	Iso
P12	X	$\xleftrightarrow[94,3 (5,35)]{97,5 (5,22)}$	S _E	$\xleftrightarrow[118,8 (14,5)]{124,4 (11,5)}$	S _A	$\xleftrightarrow[150,0 (20,6)]{155,6 (16,3)}$	Iso
P13	X	$\xleftrightarrow[93,4 (3,85)]{96,2 (3,64)}$	S _E	$\xleftrightarrow[98,7 (3,97)]{101,5 (3,77)}$	S _A	$\xleftrightarrow[109,8 (9,78)]{114,9 (10,28)}$	Iso
P14	X	$\xleftrightarrow[93,2 (4,18)]{95,8 (3,68)}$	S _E	$\xleftrightarrow[98,1 (4,18)]{101 (3,68)}$	S _A	$\xleftrightarrow[110,6 (10,41)]{114,7 (10,03)}$	Iso

X = crystalline ; S_A = smectic A ; S_E = smectic E ; Iso : isotrope liquid

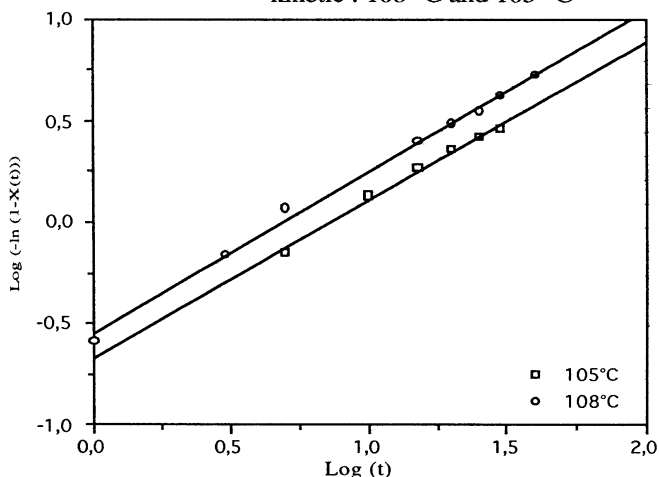
further purifications in order to remove any impurities, which sometimes are difficult to eliminate (4), the reproducible mesomorphism reported in table 2 was finally obtained.

The kinetics of a crystallization process, either from liquid or liquid crystalline states, is often described by the Avrami equation (5–9): $X(t) = 1 - \exp(-b t^n)$, where $X(t)$ is the transformed fraction, and b and n are two constants whose values dependent on the nucleation mechanism and the geometry of the growing domains. The development of $X(t)$ with time was measured for **P7** through the usual DSC method (9). As shown in Figure 1, the kinetic data for the S_E / X transition at two temperatures, 105°C and 108°C, were well fitted with the Avrami equation, resulting in an exponent $n \sim 0.8$. This low value close to 1 implies that the S_E / X transition is an ordering process along one direction. As S_E differs from the crystal by the weak attachment between the layers in their stacking, which is the origin of the plastic deformation of S_E under the effect of external forces, it is likely that the one-dimensional ordering during the S_E / X transition gives rise to more order along the stacking direction of the smectic layers, i.e., in the direction perpendicular to the planes. This analysis suggests that the X phase is actually the crystalline phase. This assignment is also supported by some orientation measurements (10). When **P7** was mechanically stretched in different phases, a strong orientation of the mesogens was obtained for both S_A and S_E resulting from the alignment of the smectic planes, but only little orientation was induced when the stretching was made in the X phase. These results indicate that the certain degree of mobility or fluidity for S_A and S_E was lost for the X phase. Finally, for this series of polymers which have a long flexible spacer connecting the main chain and the mesogenic side chain, such a one-dimensional ordering from S_E to crystal might not be easily observable from the X-ray diffraction measurements. The amorphous halo in both diffraction patterns of S_E and the X phase could be originated from the polymer main chains which remain disordered even with the crystallization of the mesogenic side chains.

Conclusion

The data of the literature about liquid crystalline polyoxiranes with side chain having biphenyl units showed a change in the nature of the mesophases when 2-methylbutoxy group was put in place of terminal butoxy group. Expecting the same modification, we

Figure 1 : S_E / X transition, Avrami's Plot from isothermal transition kinetic : 108 °C and 105 °C



introduced 2-methylbutoxy group on the para position of biphenyl units in side chain liquid crystalline polythiiranes; the larger octyloxy group was also tested. We can now conclude that in the polythiiranes the modification of the alkoxy terminal group has no effect on the nature of the mesophases; only slight variations of the transitions temperatures were observed. These results evidence the role played by the main chain in the building of mesophases.

On the other hand, a low-temperature phase, X, transformed from S_E was detected for most of the polymers in this series. This phase could not be identified from the usual characterization techniques such as X-ray diffraction. We made a kinetics measurement using DSC for the S_E / X phase transition. The obtained Avrami exponent n was about 0.8 suggesting a one-dimensional ordering during this transition. Our analysis led to the conclusion that this phase could be the crystalline phase.

Experimental Part

^1H and ^{13}C NMR spectra were recorded on a Bruker AC 400 NMR spectrometer; tetramethylsilane was used as a standard. Molecular weights of polymers were determined by size exclusion chromatography (SEC) on Styragel columns calibrated with standard polystyrene samples. A Perkin-Elmer DSC 4 differential scanning calorimeter was used to determine the thermal transitions; heating and cooling rates were $10^\circ\text{C min}^{-1}$. A Leitz Ortho-Plan polarizing microscope equipped with a Mettler FP 82 hot stage was used to observe the textures of mesophases. The X-ray diffraction patterns were obtained using a CPS-120 curved counter from inel. The localized $\text{CuK}_{\alpha 1}$ X-ray beams were produced by a XRG-2500 generator (inel). A Perkin-Elmer DSC 7 differential scanning calorimeter was used for the isothermal kinetics. Melting points were measured in capillaries on a Buchi-510 device

4'-Alkyloxybiphenyl-4-ol

4'-Octyloxybiphenyl-4-ol (**1a**) was prepared by a modification of the procedure described (11). Yield: 20 %;

m.p. 146°C ; ^1H NMR (CD_3OD): δ : 0.89 (t, 3H, CH_3); 1.31–1.49 (m, 10H, octyl); 1.78 (qt, 2H, CH_2); 4.01 (t, 2H, OCH_2); 6.88, 6.97, 7.44, 7.50 (d, ArH)

4'-(2-Methylbutoxy)biphenyl-4-ol (**1b,1c**) were prepared according to (2).

The characteristics of the products were in accordance with those described by the authors. The reactions used in the monomers synthesis were fully described in the previous work (1).

6-[(4'-Alkyloxy-4-biphenyl)oxy] hexanol

2a; Yield: 65%; m.p. 132°C; ¹H NMR (CDCl₃): δ : 0.99 (t, 3H, CH₃), 1.29–1.60 (m, 14H, CH₂), 1.62 (q, 2H, CH₂), 1.80 (m, 4H, CH₂), 3.67 (t, 2H, HOCH₂), 3.98 (t, 2H, OCH₂), 3.99 (t, 2H, OCH₂), 6.91(d, 4H, ArH), 7.45 (d, 4H, ArH).

2b, 2c: Yields: 30–40%; m.p. 111–113°C; ¹H NMR (CDCl₃): δ : 0.96 (t, 3H, CH₃), 1.00 (m, 3H, CH₃), 1.35–1.70 (m, 8H, CH₂), 1.82 (m, 3H, CH, CH₂), 3.66 (t, 2H, CH₂OH), 3.80 (m, 2H, OCH₂), 3.99 (t, 2H, OCH₂), 6.90 (d, 4H, ArH), 7.40 (d, 4H, ArH).

6-[(4'-Alkyloxy-4-biphenyl)oxy]hexyl bromoethanoates

The reactions with bromoacetyl bromide were performed in methylene chloride at room temperature.

3a : purification by silica gel chromatography (cyclohexane / acetone: 90 / 10); Yield 54%; m.p. 70°C; ¹H NMR (CDCl₃): δ : 0.89 (t, 3H, CH₃), 1.29–1.46, 1.46–1.53, 1.53–1.58 (m, 14H, CH₂), 1.72–1.80 (m, 6H, CH₂), 3.83 (s, 2H, CH₂Br), 3.98 (t, 2H, OCH₂), 3.99 (t, 2H, OCH₂), 4.19 (t, 2H, CH₂OCO), 6.93 (d, 4H, ArH), 7.45 (d, 4H, ArH).

3b, 3c : recrystallization from ethanol; Yield: 55–60%; m.p. 56°C; ¹H NMR (CDCl₃): δ : 0.96 (t, 3H, CH₃), 1.03 (d, 3H, CH₃), 1.27–1.51, 1.59–1.72 (m, 10H, CH₂), 1.82 (m, 1H, CH), 3.82 (m, 2H, CH₂O), 3.83 (s, 2H, CH₂Br), 3.99 (t, 2H, CH₂O), 4.19 (t, 2H, CH₂OCO), 6.94 (d, 4H, ArH), 7.46 (d, 4H, ArH).

6-[(4'-Alkyloxy-4-biphenyl)oxy]hexyl (2,3-epithiopropyl)thioethanoates

The crude yields were quantitative. The whole monomers were purified by silica gel chromatography (cyclohexane / acetone)

4a : m.p. 62–63°C; ¹H NMR (CDCl₃): δ : 0.90 (t, 3H, CH₃), 1.28–1.40 (m, 8H, CH₂), 1.50–1.60 (m, 8H, CH₂), 1.70 (m, 2H, CH₂), 1.80 (m, 2H, CH₂), 2.28 and 2.54 (2d, 2H, CH₂ thiirane), 2.71–3.08 (m, 2H, CH₂S), 3.10 (m, 1H, CH thiirane), 3.32 (s, 2H, CH₂CO), 4.00 (t, 2H, CH₂O), 4.18 (t, 2H, CH₂OCO), 6.86 (d, 4H, ArH), 7.40 (d, 4H, ArH).

4b, 4c : m.p.50–55°C; ¹H NMR (CDCl₃) : δ : 0.88 (t, 3H, CH₃), 1.15–1.25 (m, 8H, CH₂), 1.35–1.51 (m, 8H, CH₂), 2.19 and 2.48 (2d, 2H, CH₂ thiirane), 2.62–3.02 (m, 2H, CH₂S), 2.99 (m, 1H, CH thiirane), 3.24 (s, 2H, SCH₂CO), 3.69 à 3.79 (m, 2H, CH₂O en α de CH), 3.91 (t, 2H, CH₂O), 4.08 (t, 2H, CH₂OCO), 6.86 (d, 4H, ArH), 7.37 (d, 4H, ArH).

Polymerizations and polymers

The polymerizations and the purification of the polymers were performed as previously described (1).

P12 : ¹H NMR (CDCl₃) : δ : 0.89 t, 3H, CH₃), 1.29 (m, 8H, CH₂), 1.43 (m, 6H, CH₂), 1.66 (m, 2H, CH₂), 1.76 (m, 4H, CH₂), 3.05 (m, 5H, CH₂-CHS-CH₂), 3.29 (s, 2H, SCH₂CO), 3.92 (m, 4H, OCH₂), 4.11 (m, 2H, CH₂OCO), 6.90 (m, 4H, ArH), 7.42 (m, 4H, ArH).

¹³C NMR (CDCl₃) : δ : 14.18 (CH₃), 22.73, 25.82, 25.89, 26.15, 28.62, 29.33, 29.41, 29.47, 31.90 (CH₂), 34.37, 37.15, 46.80 (CH₂-CHS-CH₂), 65.86, 67.87, 68.11 (CH₂O), 114.77, 114.79, 127.65, 127.66, 133.22, 133.33, 158.17, 158.28 (aromatic C), 170.34 (COO)

P13, P14 : ¹H NMR (CDCl₃) : δ : 0.93 (t, 3H, CH₃), 0.99 (t, 3H, CH₃), 1.25 (m, 2H, CH₂), 1.43 (m, 4H, CH₂), 1.66 (m, 1H, CH), 1.77 (m, 4H, CH₂), 3.01, 3.05, 3.12 (3m,

5H, CH₂-CHS-CH₂), 3.29 (s, 2H, SCH₂CO), 3.72–3.80 (m, 2H, CH₂), 3.91 (m, 2H, OCH₂), 4.11 (t, 2H, CH₂OCO), 6.90 (m, 4H, ArH), 7.41 (m, 4H, ArH).
 13C NMR (CDCl₃) : δ : 11.38, 16.59 (CH₃), 25.85, 25.79, 26.19, 28.60, 29.30 (CH₂), 31.49 (CH₂CO), 34.37(CH), 34.78, 36.54, 46.79 (CH₂-CHS-CH₂), 65.54, 67.86, 72.9 (CH₂O), 114.74, 114.79, 127.62, 127.64, 133.18, 133.34, 158.14, 158.44 (aromatic C), 170.34 (COO).

P14 : $[\alpha]_D^{20} = -3.6 \text{ deg.dm}^{-1} \text{ g}^{-1} \text{ cm}^3$

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