

Rheo-optical Fourier transform infrared spectroscopy of a liquid-crystalline block copolymer

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SUMMARY

In the present rheo-optical experiments FTIR polarization spectroscopy was used to investigate the orientational behaviour of the different constituents of an LC block copolymer (copolyester imide) during uniaxial elongation at different temperatures. The results exhibit differences in the degree of alignment as well as in the response to the application of the mechanical load. With increasing temperature the level of the applied stress and the induced orientation decrease, while the differences in the orientational behaviour of the mesogen and the flexible spacer are retained.

INTRODUCTION

Segmented block copolymers consisting of crystallizable, aromatic hard blocks and flexible soft domains play an important role in the field of thermoplastic elastomers (1). Among these, elastomers composed of aromatic polyester units combined with aliphatic polyether or aliphatic polyester segments are of growing commercial significance (2). The elastomeric properties of such block copoly(ether-esters) are discussed in terms of an intermolecular association of the crystallized hard segments, which are connected with each other by flexible poly(THF) tie-molecules. Therefore, we have dealt with the question whether substitution of crystallizable aromatic units by mesogenic aromatic groups in block copolymers containing flexible poly(THF) segments results in elastomers with thermotropic behaviour (3, 4). Such block copolymers could also be interesting with respect to compatibilization in polymer blends of thermotropic liquid-crystalline polymers and conventional flexible polymers (5, 6). In the block copolymers with mesogenic aromatic polyester segments, a phase separation into a well ordered, frozen-in, nematic liquid crystalline phase formed by the mesogenic segments and an amorphous phase formed by the poly(THF) units was observed by WAXS, DSC, TEM and AFM (4, 7).

Due to the elastomeric properties of such block copolyesters, their orientational behaviour in external mechanical fields is of special interest. Therefore, the orientational behaviour of the individual constituents in these LC block copolymers was investigated by rheo-optical FTIR measurements as a function of temperature.

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EXPERIMENTAL

The LC block copolymer under discussion contains segments of flexible poly(THF) linked by a trimellitimide bridge to mesogenic aromatic polyester blocks consisting of 3 phenylene rings connected by ester groups. The copoly(esterimides) were synthesized by melt transesterification polycondensation of trimellitimide-terminated poly(THF) with 1,4-phenylenebis(oxycarbonyl-1,4-phenylene) diacetate (O-H-O) as described elsewhere (4). It was found that the structure of the aromatic blocks was slightly randomized by transesterification reactions during melt polycondensation. The chemical structure of the polymer under discussion (Polymer 1) is given in Fig. 1.

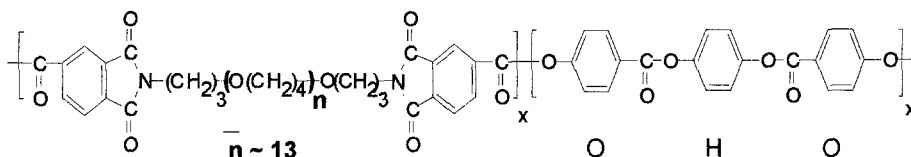


Fig. 1 Chemical structure of the investigated block copolymer
[O ... Oxybenzoate; H ... Hydroquinone]

For the purpose of comparison a second polymer with an increased length of the aromatic blocks obtained by copolycondensation with *p*-acetoxybenzoic acid was investigated (Polymer 2). In this case the mesogen/spacer ratio increases, however in principle no significantly different effects on the behaviour under mechanical deformation of the copolyesters could be observed. Therefore, only the polymer sample shown in Fig. 1 is discussed here in detail, representative for this class of polymers.

The composition, the molecular weights and the phase behaviour of the investigated polymers are summarized in Tab. 1 and 2.

Tab. 1: Characterization of the investigated block copolymers (GPC: gel permeation chromatography, using poly(styrene) calibration)

No.	\bar{M}_n	P(THF)		O-H-O		O		\bar{M}_n	\bar{M}_w	$\frac{\bar{M}_w}{\bar{M}_n}$
	P(THF) [g/mol]	[mol%][wt%]	[mol%][wt%]	[mol%][wt%]	[mol%][wt%]	GPC [g/mol]	GPC [g/mol]			
1	1000	50	74.2	50	25.8	0	0	10 900	32 200	2.95
2	1000	25	63.1	25	21.9	50	15.1	34 100	55 100	1.62

Tab. 2 Phase behaviour of Polymer 1 and 2 (T_{v-LC} : transition temperature from the viscoelastic state to the liquid crystalline melt; T_{LC-i} : transition temperature from the liquid crystalline to the isotropic state ; DSC: Differential Scanning Calorimetry; micr.: polarization microscopy)

No.	T_{v-LC} [°C] micr.	T_{LC-i} [°C] micr.	melting range [°C] (DSC)	peak maximum [°C] (DSC)
1	125	155	107- 185	150
2	205	220	100-255	194

The liquid crystalline phase shows a nematic texture under the polarization microscope. Dynamic mechanical analysis (DMA) revealed a glass transition temperature T_g at $-64\text{ }^\circ\text{C}$ (Polymer 1) and $-50\text{ }^\circ\text{C}$ (Polymer 2), respectively.

For the rheo-optical experiments film samples were obtained by casting the polymers from chloroform solutions (0.05 g polymer in 1 ml solvent) on surface-roughened glass plates and subsequent evaporation of the solvent in vacuum at room temperature. Then, the film samples were peeled off the glass plates in water, transferred onto Teflon[®] plates and finally dried in vacuum. The film thickness obtained by this preparation procedure was approximately 20 μm and film specimens of 7 mm length and 7 mm width were elongated at a draw rate of 21% / minute up to fracture at different temperatures (27 $^\circ\text{C}$, 50 $^\circ\text{C}$, 75 $^\circ\text{C}$, 100 $^\circ\text{C}$ and 125 $^\circ\text{C}$).

The rheo-optical FT-IR experiments were performed with a miniaturized variable-temperature stretching machine which fits into the sample compartment of a Bruker IFS 88 FT-IR spectrometer as described in detail elsewhere (8). This device allows the simultaneous acquisition of FT-IR polarization spectra and stress-strain diagrams during uniaxial elongation of the film sample under examination. During the mechanical treatment 20-scan spectra were recorded at a resolution of 4 cm^{-1} in 2.85-second intervals (1% strain intervals) with radiation polarized alternately parallel and perpendicular to the drawing direction. Polarization of the IR beam was accomplished by using a pneumatically driven wire grid KRS-5 polarizer.

RESULTS AND DISCUSSION

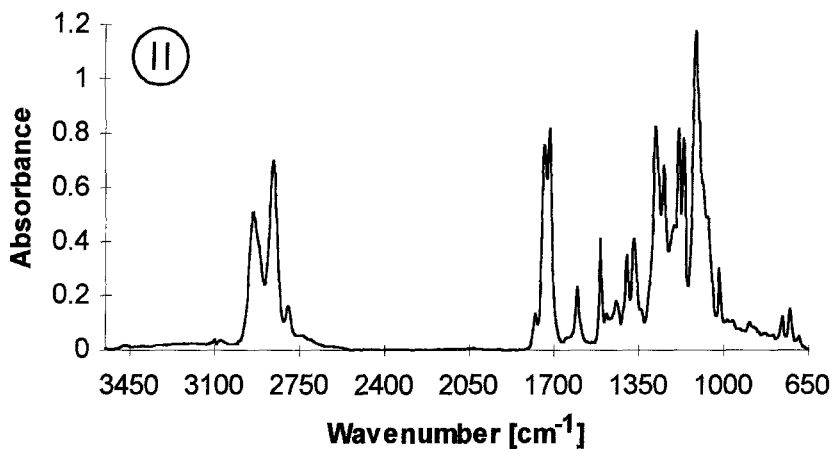
Polarization spectra of the original as-casted film specimens do not exhibit any dichroism due to the isotropic nature of the undrawn samples. When such films are drawn uniaxially intensity differences resulting from the mechanically induced anisotropy can be observed in the FT-IR spectra taken with radiation polarized parallel and perpendicular, respectively, to the drawing direction (Fig. 2).

In order to characterize the orientational behaviour of the hard and the soft segments of the investigated polymer during mechanical treatment at different temperatures specific absorption bands had to be assigned to the mesogen and the spacer, respectively. Based on the analysis of monomers and model compounds, the band assignments summarized in Tab. 3 have been established (5).

Tab. 3 Band assignment, structural origin and polarization properties of selected absorption bands (w = weak, s = strong, sh = shoulder).

Wavenumber [cm^{-1}]	Assignment	Structural origin	Polarization
2940 s	$\nu_{\text{as}}(\text{CH}_2)$	spacer	σ
2860 s	$\nu_{\text{s}}(\text{CH}_2)$	spacer	σ
1775 w, sh	$\nu_{\text{as}}(\text{C}=\text{O})_{\text{imide}}$	linkage/extender	π
1740 s	$\nu(\text{C}=\text{O})_{\text{ester}}$	mesogen	σ
1715 s	$\nu_{\text{s}}(\text{C}=\text{O})_{\text{imide}}$	linkage/extender	σ
1605 s	$\nu(\text{C}=\text{C})_{\text{ar}}$	mesogen	π
1510 s	$\nu(\text{C}=\text{C})_{\text{ar}}$	mesogen	π
1115 s	$\nu(\text{C}-\text{O}-\text{C})$	spacer	π

a)



b)

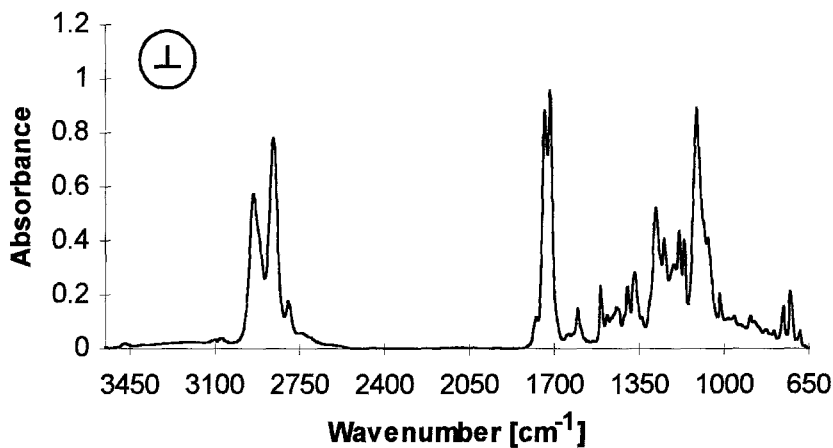


Fig. 2 FTIR Polarization spectra of a sample elongated to 94% strain at 27 °C [a) parallel and b) perpendicular to the drawing direction]

From these assigned bands we have selected the 2940 cm^{-1} ($\nu_{\text{as}}(\text{CH}_2)$) and 1605 cm^{-1} ($\nu(\text{C}=\text{C})_{\text{ar}}$) bands to monitor the orientation of the spacer and the mesogen, respectively. Assuming a uniaxial chain alignment, an orientation function f can be calculated from the polarization spectra taken during the mechanical treatment (9-12). For absorption bands whose transition moments are parallel or perpendicular to the polymer chain axis the Eqs. 1 and 2 can be applied:

$$f_{\parallel} = (R - 1) / (R + 2) \quad \langle \text{Eq. 1} \rangle$$

and

$$f_{\perp} = -2(R - 1) / (R + 2) \quad \langle \text{Eq. 2} \rangle$$

where the dichroic ratio is defined as $R = A_{\parallel} / A_{\perp}$, and A_{\parallel} and A_{\perp} are the absorbance values in the polarization spectra taken with light polarized parallel and perpendicular to the stretching direction, respectively.

The temperature range for the rheo-optical measurements (27 °C - 120 °C) was limited by the phase transition into the nematic phase at 125 °C beyond which mechanical load cannot be applied. The stress-strain diagrams of the rheo-optical experiments at different temperatures in this range are shown in Fig. 3 and clearly reflect the temperature dependence of the mechanical properties. Generally, the stress increases up to about 20% strain and then levels off into a plateau region up to fracture.

Apart from a decrease of the stress level with increasing temperature the maximum extensibility decreases until 75 °C to reincrease remarkably close to the transition into the nematic phase (125 °C).

The different orientational behaviour of the mesogen and the spacer at the experimental temperatures is illustrated in Fig. 4. Thus, generally at higher elongations the mesogens show a better alignment in the direction of stretch than the flexible spacers. A detailed analysis of the 0-20 % strain region reveals, that the flexible poly(THF) spacer responds immediately to the applied stress whereas the rigid LC domains require a minimal stress which corresponds approximately to the strain value, at which the plateau region starts (Fig. 3). Only beyond higher strains the orientation function of the mesogen rapidly exceeds the corresponding values of the flexible spacer. Raising the temperature leads to a decrease of the order parameters of both constituents, and above 100 °C no alignment can be observed for the spacer.

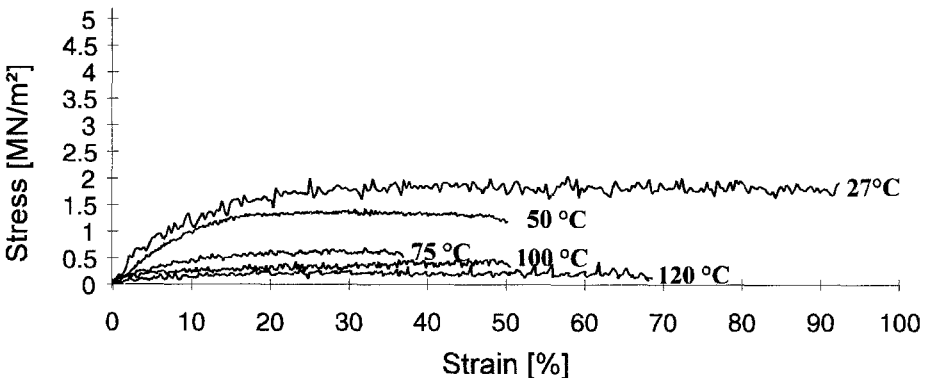


Fig. 3 The stress-strain diagrams of the investigated polymer for different temperatures

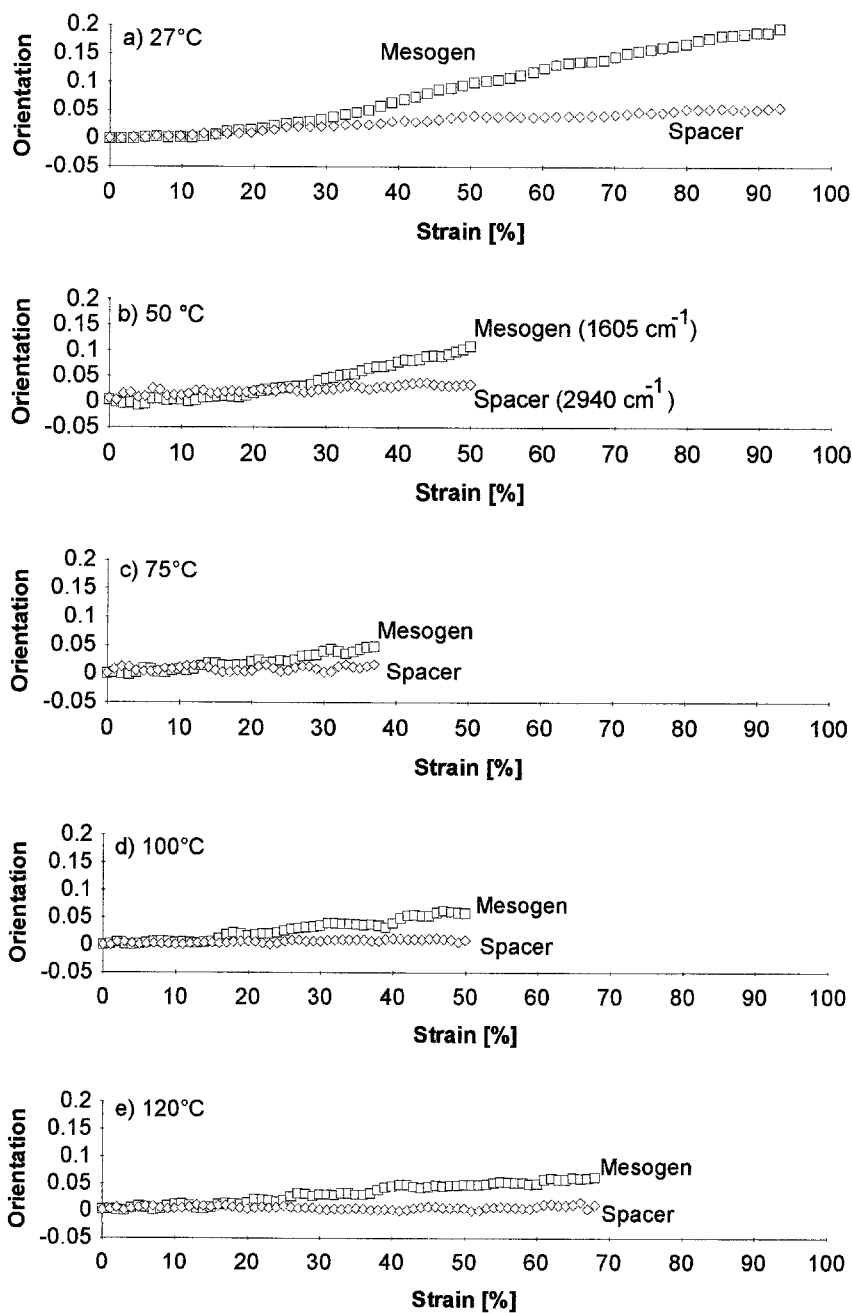


Fig. 4 Orientation function/strain plots for the spacer and the mesogen for different temperatures.

According to the obtained data the following interpretation of the orientation mechanism can be given: During the uniaxial elongation of the film specimens an alignment of the spacer chains of the amorphous poly(THF) matrix and the LC domains is induced in the drawing direction. Due to the high mobility of the spacer molecules (the measurements were carried out in the viscoelastic state and at the experimental temperatures the poly(THF) matrix exists in the form of a melt) only small order parameters could be observed, although the alignment starts directly after the application of stress. To orient the rigid LC domains a minimal stress is required which is achieved after a certain elongation. Beyond this threshold value further deformation takes places at about constant stress. This behaviour corresponds to the appearance of a diffuse yield point. At this stage of deformation LC domains (with a certain prealignment) are rotated as a whole into the drawing direction. Therefore, the order parameter obtained at high strain exceeds that of the spacer molecules. An increase in the temperature reduces the viscosity of the amorphous spacer matrix and increases the thermal mobility of the molecules resulting in a decrease of the deformational stress and the achieved orientation. The rigid LC domains resist against the deformation and the film sample breaks at lower strain. The reincrease of fracture strain near the transition temperature into the nematic phase can be related to a higher mobility of these domains. As a result a lower order parameter is observed upon elongation.

An increase of the ratio between mesogen and spacer (Polymer 2), as caused by an extension of the mesogenic polyester block by additional oxybenzoate sequences leads to an increase of the LC domains relative to the surrounding amorphous poly(THF) spacer matrix. Therefore, it is possible to observe higher order parameters during elongation of the less entangled spacer molecules. This is illustrated in Fig. 5 (which compares the orientation function/strain plots of the spacer for the two different block copolymers). The film specimens of Polymer 2 are more brittle than those of Polymer 1. Thus, the stress required for elongation increases, while the maximum strain decreases. Concerning the alignment of the mesogens significant differences cannot be detected up to 50 °C. At higher temperatures the fracture of the film occurs at such low strains that no differences in orientation can be detected between mesogen and spacer.

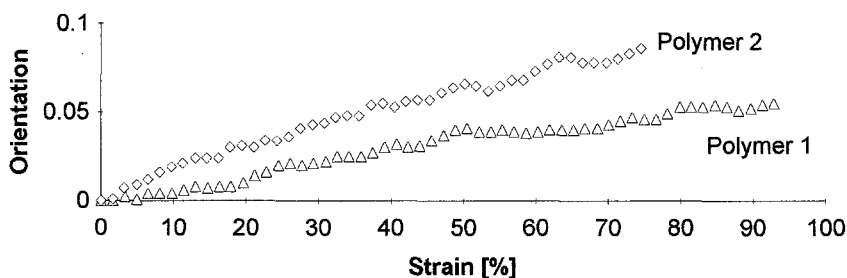


Fig 5. Orientation function/strain plot of the spacer of Polymer 1 and Polymer 2 at 27°C.

CONCLUSION

The results show that rheo-optical FTIR polarization spectroscopy is a useful tool to characterize the segmental mobility of the different constituents of LC block copolymer during uniaxial elongation at different temperatures. The spectroscopic data allow a differentiation of the alignment of the soft segments and the mesogenic segments and their dependence on temperature. Furthermore, it was possible to correlate the spectroscopic and mechanical data.

Thus, a minimum stress is required to align the rigid LC domains, which is obtained after a certain elongation. In contrast, the flexible spacer molecules responded directly to the application of stress. At maximum strain, the orientation parameters observed for the flexible poly(THF) spacers were lower than those of the rigid mesogens.

With increasing temperature the stress level as well as the observed segmental orientation is reduced significantly; nevertheless the differences between spacer and mesogen are retained.

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