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## Liquid Crystals

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## An infrared spectroscopic study of photo-induced reorientation in dye containing liquid-crystalline polymers

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Infrared spectroscopy is used to study simultaneously the orientational behaviour of different segments of dye containing liquid-crystalline side group copolymers in sandwich type films of about  $2\ \mu\text{m}$  thickness. Under continuous irradiation with polarized light above and below  $T_g$  of the polymers both azobenzene and phenyl benzoate side groups reorient preferentially normal to the film plane leading to a strongly biaxial orientation distribution. The analysis of the kinetics reveals that the reorientation is essentially a mono-exponential process with an additional faster process only found for the azobenzene dye and assigned to the initial *trans* to *cis* isomerization step. Investigation of an isotropic copolymer system containing azobenzene in the side groups shows that an anisotropy can be induced through irradiation with polarized light that is strongly dependent on temperature.

### 1. Introduction

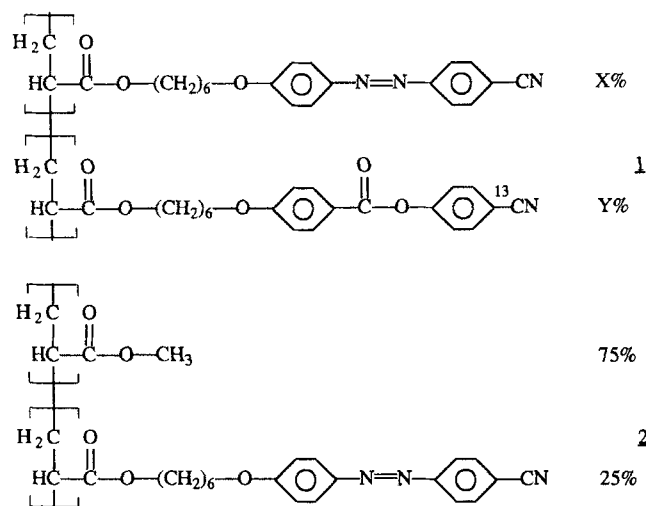
Side group liquid-crystalline polymers are materials combining the functionality of conventional liquid crystals with the properties of macromolecules. The concept of attaching a mesogenic unit via a flexible spacer to a polymer backbone offers a wide scope for molecular engineering. Many aspects of the synthesis and behaviour of these materials have already been examined and a number of reviews exist [1,2].

The mesomorphic state of liquid-crystalline polymers is characterized by the anisotropy of the structure and properties as a result of one or two dimensional ordering. This ordering can easily be achieved using mechanical, electric, or magnetic fields leading to unique physical characteristics. In contrast to low molar mass liquid crystals, the mesophase order can be frozen in at the glass transition [3,4]. These ordered glasses constitute a new and interesting class of materials with possible technical applications in non-linear optics [5], optical data storage [6–8] and separation and complexation techniques [9,10]. Consequently the knowledge of molecular parameters such as order and dynamics for the solid state is of great interest in order to relate molecular properties to macroscopic behaviour. To this end we have used different physical methods to investigate one particular side group liquid-crystalline copolymer **1**. It consists of an acrylate backbone with various amounts of a cyanoazobenzene dye in one of the comonomeric units and a cyanophenylbenzoate mesogen in the other [11,12]. This system has been proposed as a medium for reversible optical data storage based on the reversible *trans*–*cis* isomerization of the azobenzene dye [13].

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Using forced Rayleigh scattering we have investigated the dynamics of the photo-induced isomerization of azobenzene and revealed strong influences of the liquid-crystalline matrix on the relaxation processes occurring in the glassy state after irradiation [14]. With  $^{13}\text{C}$  NMR on thin films of a selectively labelled isomer of copolymer **1** we have further shown that through the photo-induced conformational transition of azobenzene, the order of the liquid-crystalline matrix was changed irreversibly once the system had been irradiated in the mesophase and subsequently cooled below  $T_g$  [15]. Using polarized infrared spectroscopy on films of the labelled material we detected that under continuous irradiation with polarized light a coupled reorientation of both azobenzene and phenylbenzoate side groups takes place *above* and *below*  $T_g$  that is strongly dependent on dye concentration and temperature [16].

In this paper a full account of these infrared spectroscopic studies is given leading to a better understanding of the coupled reorientation process occurring under irradiation. The investigations were performed with the statistical copolymer system **1** with 50 or 30 mol% of the side groups containing cyanoazobenzene. The cyano group of the phenylbenzoate mesogen in the second comonomeric unit was selectively labelled with  $^{13}\text{C}$  in order to distinguish between the azobenzene dye and what in the following will be called the liquid-crystalline matrix, due to the isotopic shift of the cyano stretching vibration in the infrared spectrum. In particular we concentrate on the photoinduced biaxiality observed for this system. In addition we investigate an isotropic copolymer **2** in which the azobenzene containing comonomer unit is statistically copolymerized with methyl acrylate. This system forms no mesophase and a comparison of the behaviour under irradiation should reveal the influence of the microscopically or even macroscopically ordered liquid-crystalline matrix on the reorientation process.



## 2. Experimental

### 2.1. Materials

The syntheses of the compounds investigated are described elsewhere [11, 12, 15]. Molecular weights and transition temperatures are listed in the table. The molecular weights were estimated using gel-permeation chromatography with polystyrene standards. The transition temperatures were measured through DSC using a Mettler DSC 30 at a heating rate of  $20\text{ K min}^{-1}$ .

### 2.2. Preparation of the samples

Optical cells were constructed consisting of two quartz substrates separated by a polyimide spacer of 2  $\mu\text{m}$  thickness with the liquid-crystalline polymer sandwiched between them. To achieve a uniform homogeneous orientation throughout the samples, a combination of magnetic field and surface effects was used. A detailed description of the preparation is described in [14, 16]. Optical cells of the isotropic system **2** were constructed in an analogous way by sandwiching the polymer between two untreated quartz substrates.

### 2.3. Experimental set up

The essential components of the experimental set up are shown in figure 1. The light beam of a Xenon lamp XBO 500 W was focused on the films in the sample compartment of a Nicolet 60 SX FTIR spectrometer. Thus infrared spectra of the polymers **1** and **2** were measured under continuous irradiation. A 448 nm filter of 40–60 nm bandwidth was used to select the desired irradiation frequency and the light intensity at the sample spot was approximately 10 mW/cm<sup>2</sup>. The geometry of the incoming light and infrared beam at the sample as well as the definition of the axis system are given in figure 2. The liquid-crystalline films were mounted on the sample holder so that the director  $\mathbf{n}$  was parallel to the polarization direction of the incoming light beam which was along the Z axis. By pneumatically rotating the IR wire grid polarizer the spectra were measured with polarization parallel (ZZ) and perpendicular (YY) to the director. Typically 100 scans were collected for each spectrum at a resolution of 4 cm<sup>-1</sup>. To control the sample temperature two 60 W Peltier elements

Weight average molecular weight  $M_w$ , ratio of weight to number average molecular weights  $M_w/M_n$ , and transition temperatures of the systems investigated.

Polymer code	$M_w$	$M_w/M_n$	Transition temperatures/K
1 50 mol%	7500	1.7	g 304 N 374 I
2 25 mol%	11800	1.7	g 303 I
3 30 mol%	24600	1.6	g 305 N 402 I

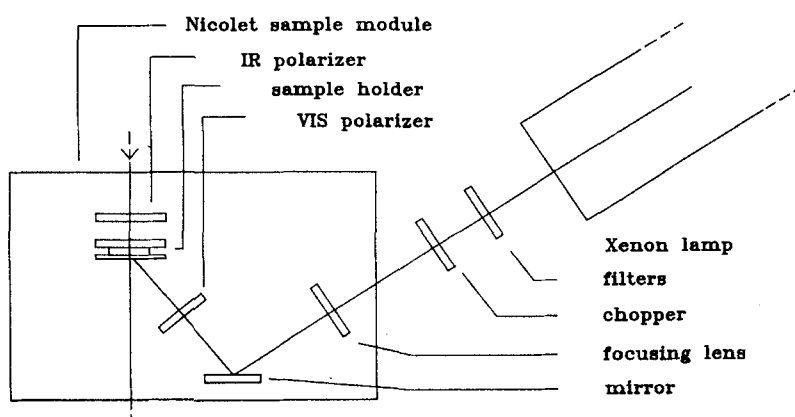


Figure 1. Essential components of the experimental set-up.

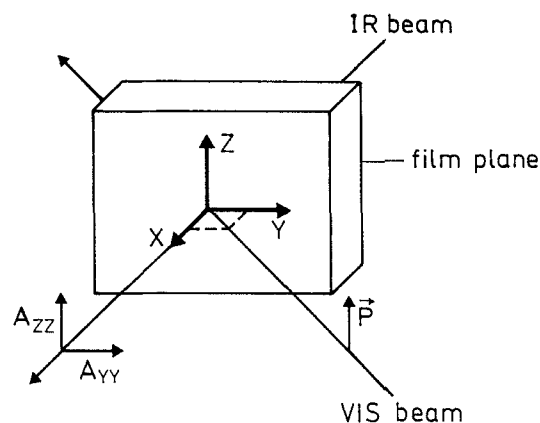


Figure 2. Geometry of incoming light beam (VIS) and IR beam at the sample as well as a definition of the axis system used in the description of the experiments. The angle between VIS and IR beam was approximately  $50^\circ$ .

were used in the range from 263–333 K with an accuracy of  $\pm 0.1$  K. To ensure that no heating of the films occurred through the continuous irradiation, the light beam was chopped at a frequency of 3 Hz.

#### 2.4. Data analysis

To determine the orientation of the mesogenic units the absorbance of the CN stretching vibration with transition dipole moment parallel to the long axis of the mesogen was used [17]. In addition the orientation of the spacer  $\text{CH}_2$  groups was determined using the asymmetric CH stretching vibration with the transition dipole moment perpendicular to the alkane chain [17]. The absorbances  $A_{ZZ}$  and  $A_{YY}$  were calculated after cubic spline interpolation around the peak as integrated intensities with a straight baseline through absorption minima adjacent to the peak.

### 3. Results and discussion

#### 3.1. Order parameter before irradiation

In order to find out whether the order in the films investigated was uniaxial prior to irradiation, the structural absorbance spectrum  $(A_{ZZ} + 2A_{YY})/3$  of the oriented liquid-crystalline polymer **1** was compared with the spectrum of an isotropic sample prepared in a KBr pellet. The result is presented in figure 3. The intensities were normalized to the aromatic CH stretching bands between  $3000$  and  $3100\text{ cm}^{-1}$  that are not strongly sensitive to orientation. In the infrared spectrum of the  $^{13}\text{C}$  labelled material two nicely resolved CN stretching bands appear at  $2227$  and  $2176\text{ cm}^{-1}$ , the lower frequency band being assigned to the labelled cyano group of the phenylbenzoate mesogen. At  $2942$  and  $2864\text{ cm}^{-1}$ , respectively, we observed the strong asymmetric and the slightly weaker symmetric CH stretching bands. The ratio between spacer and main chain  $\text{CH}_2$  groups in the system investigated was 6:1. Therefore as a good approximation these vibrational bands reflect the orientation of the spacer in the oriented film.

For a uniaxial orientational distribution of the different segments of the polymer the two spectra in figure 3 should be identical. Inspection clearly shows that this is not the case. Whereas the CN stretching bands essentially overlap, there is a pronounced deviation in those of the  $\text{CH}_2$  groups. Thus the long axes of the mesogenic groups,

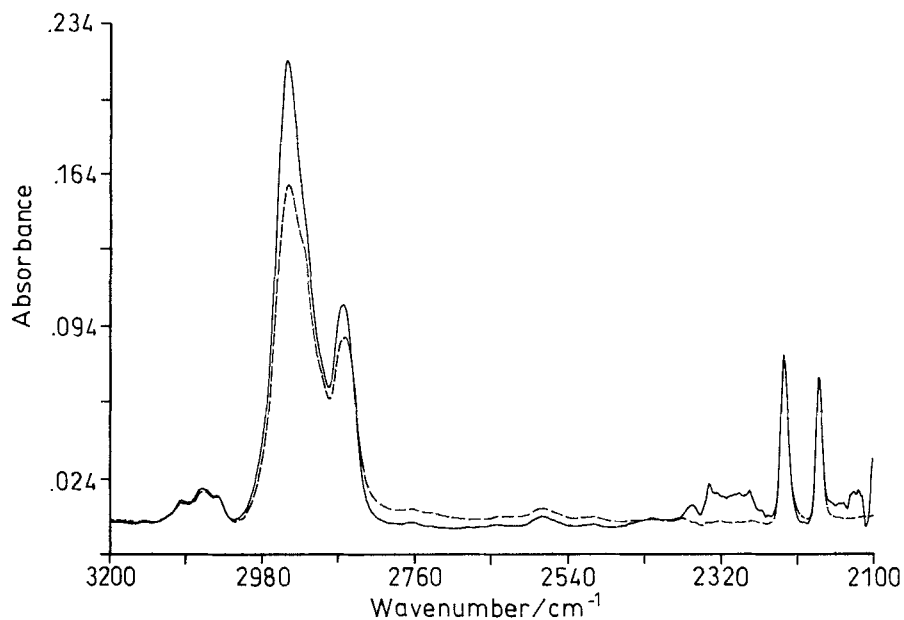


Figure 3. Comparison of the structural absorbance spectrum  $(A_{ZZ} + 2A_{YY})/3$  (solid line) with the spectrum of an isotropic KBr pellet (dotted line) of the liquid-crystalline copolymer 1. The intensities were normalized to the aromatic CH stretching bands between 3000 and 3100  $\text{cm}^{-1}$  that are not strongly sensitive to orientation.

where the orientation is probed via the cyano stretching vibration are uniaxially ordered, whereas the spacer is not. Here the ratio of the intensities of the asymmetric to the symmetric band is increased for the ordered system showing that there is a tendency for the  $\text{CH}_2$  groups to point along the surface normal. By comparing the intensities of the asymmetric stretching band of the anisotropic film with that of the isotropic sample we were able to determine the biaxiality in the  $XY$  plane to be about 20 per cent.

For a uniaxially ordered sample the Saupe order parameter  $S_{zz}$  before irradiation can be calculated for the different segments of the oriented liquid-crystalline polymer 1 from the polarized infrared spectra  $A_{ZZ}$  and  $A_{YY}$  using [18–20]

$$S_{zz} = \frac{(R_0 + 2)(R - 1)}{(R_0 - 1)(R + 2)} \quad (1)$$

Here  $R$  is the measured dichroic ratio  $A_{ZZ}/A_{YY}$  and  $R_0$  is the dichroic ratio for perfect alignment and is equal to  $2 \cot^2 \alpha$ ,  $\alpha$  being the angle between the transition moment vector for the vibration and the local order axis. For the CN group  $\alpha \approx 0^\circ$  yielding  $S_{zz} = 0.6 \pm 0.02$  for the mesogenic units. That the mesogens are uniaxially oriented initially was further checked in an experiment in which the films were rotated around the  $Z$  axis, i.e. around the preferential orientation axis of the liquid crystal. A rotation up to  $30^\circ$  did not significantly change the order parameter  $S_{zz}$  measured from the dichroic ratio of the CN stretching bands of the mesogenic units.

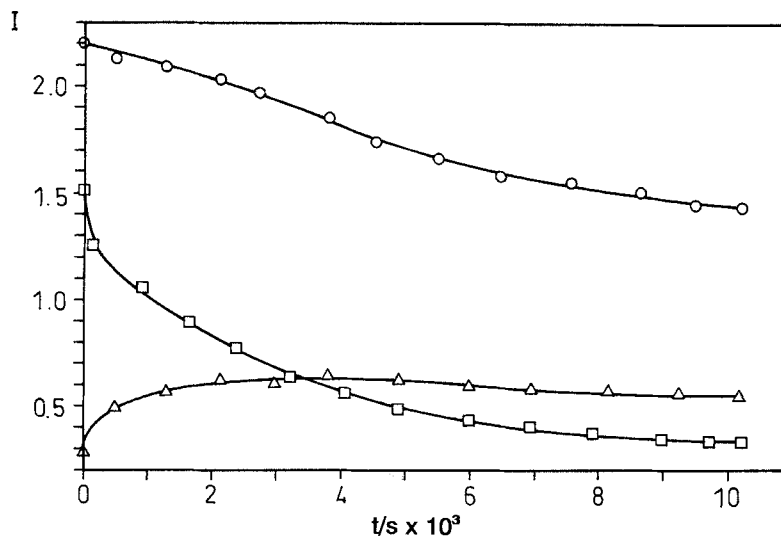
Since the spacer exhibits biaxial order, equation (1) is not strictly valid in that case. From NMR data of similar systems [21] we expect that the order parameter should decrease by about 50 to 60 per cent by going from the mesogen to the spacer. With

$\alpha = 90^\circ$ ,  $S_{zz} = 0.3$  is obtained for this segment by use of equation (1), which falls very well into the range expected for such a nematic polymer. This shows that the error introduced by using equation (1) for the analysis of the spacer orientation is not large. Further analysis of the orientational behaviour under irradiation will therefore be made under the assumption of an initial uniaxial orientational distribution for all molecular segments.

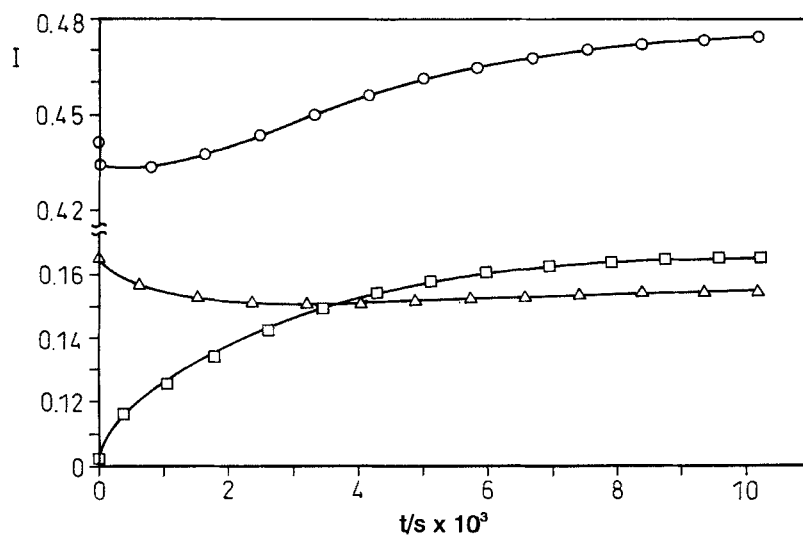
### 3.2. Photoinduced biaxiality

In figure 4(a) the integrated intensity of the cyano stretching vibration in the azobenzene unit is shown for the 50 mol% copolymer 1 as a function of irradiation time for infrared polarizer positions ZZ and YY. The measurements were performed at 273 K which is about 30 K below the caloric glass transition temperature  $T_g$  of the polymer. The observed decrease of the intensity for polarization ZZ and the increase for polarization YY results from a reorientation of the dye molecules from the Z axis into the XY plane [16, 22]. The rotation of the azobenzene away from the polarization direction of the incoming visible light beam is a consequence of angular dependent photoselection. Those dye molecules initially pointing along the Z axis preferentially isomerize since the optical transition moment of the trans species lies essentially along the long molecular axis. Through the continuous irradiation process a dynamic back and forth isomerization is induced. Its probability, however, decreases with the cosine squared of the angle between the transition moment and the polarization direction of the light. This constitutes a mechanism driving the long axis of the azobenzene molecules away from the Z axis into the XY plane. As we have shown in our preliminary communication [16] this reorientation is closely coupled with the reorientation of the phenylbenzoate mesogens occurring at the same time and depends on dye concentration and temperature, with a faster and more efficient reorientation process occurring for higher percentages of azobenzene in the side groups, and for higher temperatures. Upon reorientation, the uniaxial order is not maintained, however. Instead a biaxial orientational distribution develops in which the mesogens are preferentially aligned along the X direction, i.e. normal to the film plane. A first indication of this result is obtained from a plot of  $(A_{ZZ} + 2A_{YY})$  as a function of irradiation time for the azobenzene dye as also depicted in figure 4(a). If uniaxial order was to be maintained this quantity should remain constant with time. Instead, it decreases by about 30 per cent revealing a rather pronounced deviation from the initially observed uniaxial order. The same conclusion is reached from the analysis of the spacer orientation. In figure 4(b) the integrated intensity of the asymmetric stretching vibration of the spacer CH<sub>2</sub> groups is shown as a function of irradiation time. Since the transition moment of this vibration is perpendicular to the preferential orientation axis of the liquid crystal, the intensity increases for polarization ZZ whereas for polarization YY it decreases. As for the azobenzene the quantity  $(A_{ZZ} + 2A_{YY})$  does not stay constant but, for this band, rises with time.

From this discussion it follows that equation (1) can no longer be used to determine the order parameter  $S_{zz}$  for the different molecular segments of copolymer 1 under irradiation. Instead, in order to obtain a complete description of the orientational behaviour under irradiation it is necessary to define a macroscopic order tensor  $Q$  as shown in the Appendix. From its definition this tensor is traceless and in our case has diagonal form. The three resulting diagonal elements  $Q_{XX}$ ,  $Q_{YY}$  and  $Q_{ZZ}$  quantify the order along the three laboratory axes X, Y and Z, respectively. The element  $Q_{ZZ}$  is equal



(a)



(b)

Figure 4. (a) Integrated intensity of the cyano stretching vibration in the azobenzene unit as a function of irradiation time for copolymer 1 taken with the incoming VIS light beam polarized along the Z direction for the IR polarizer position ZZ (□) and YY (△) at 273 K. Also shown is the quantity  $(A_{ZZ} + 2A_{YY})$  as a function of irradiation time (○) as a measure for the photoinduced biaxiality. (b) Integrated intensity of the asymmetric stretching vibration of the spacer CH<sub>2</sub> groups for the polarizer position ZZ (□) and YY (△) and the quantity  $(A_{ZZ} + 2A_{YY})$  (○) as a function of irradiation time collected under conditions described in (a).



to the Saupe order parameter  $S_{zz}$  and in the analysis of the CN stretching vibration bands the equation

$$Q_{ZZ} = S_{zz} = \frac{A_{ZZ} - 1/2(A_{XX} + A_{YY})}{A_{XX} + A_{YY} + A_{ZZ}}, \quad (2)$$

derived in the Appendix, can be used for its determination. In the analysis of the spacer orientational behaviour the right side of this equation has to be multiplied by an additional factor of  $-2$  originating from the term  $(R_0 + 2)/(R_0 - 1)$  in equation (1) considering the angle  $\alpha \approx 90^\circ$  of the  $\text{CH}_2$  transition moment to the local chain axis of the spacer. As we have shown  $A_{ZZ}$  and  $A_{YY}$  are measured in the experiment.  $A_{XX}$  can be calculated at any irradiation time  $t$  by subtracting  $A_{ZZ}(t)$  and  $A_{YY}(t)$  from the total absorption before irradiation at  $t = t_0$ :  $A_{\text{tot}}(t_0) = A_{ZZ}(t_0) + 2A_{YY}(t_0)$ , where the distribution of the various molecular segments around the optical axis is essentially uniaxial, as we have described. The result is presented in figure 5, where the order parameter  $Q_{ZZ} = S_{zz}$  for the two different mesogens and for the spacer is plotted versus irradiation time at 273 K. For both azobenzene and phenylbenzoate mesogens  $Q_{ZZ}$  drops from an initial value of about 0.6 to a value of about  $-0.25$ . The order parameter for the spacer decreases from 0.3 to about  $-0.1$  in the same time interval. Figure 5 reveals the strong coupling between dye and matrix mesogens. Through the photo-induced isomerization the azobenzene molecules start to reorient first and the order parameter drops slightly faster than for the phenyl-benzoate mesogens. The latter are following the reorientation process and in the end the order parameters of both side chains become equal.

As derived in the Appendix the elements  $Q_{XX}$  and  $Q_{YY}$  of the macroscopic order tensor  $Q$  can be related to the measured absorptions by cyclic permutation of the indices  $X$ ,  $Y$  and  $Z$  in equation (2). The result is presented in figure 6 where the three quantities  $Q_{XX}$ ,  $Q_{YY}$  and  $Q_{ZZ}$  are plotted versus irradiation time for the azobenzene unit at 273 K. For a reorientation process conserving the initially uniaxial symmetry  $Q_{ZZ}$  would decrease with time whereas  $Q_{XX}$  and  $Q_{YY}$  would increase equally the sum of all

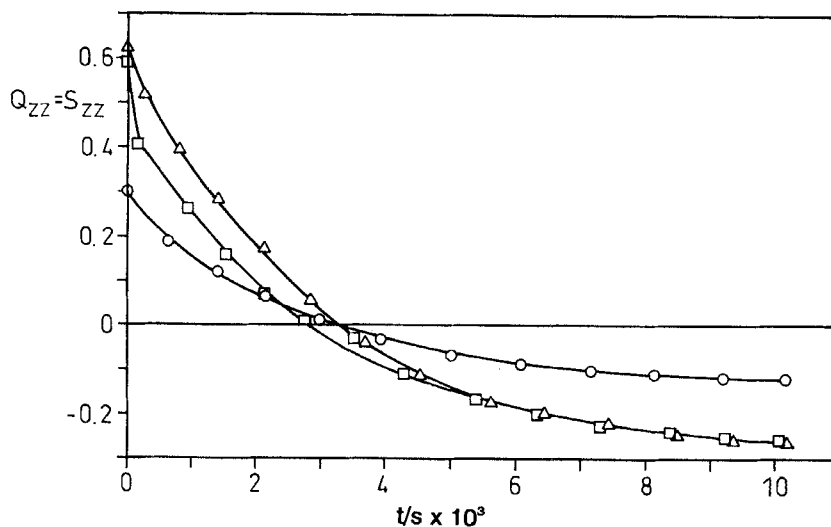


Figure 5. Order parameter  $S_{zz}$  calculated from equation (2) for the azobenzene (□) and phenylbenzoate (△) mesogens and for the spacer (○) versus irradiation time for copolymer **1** at 273 K.

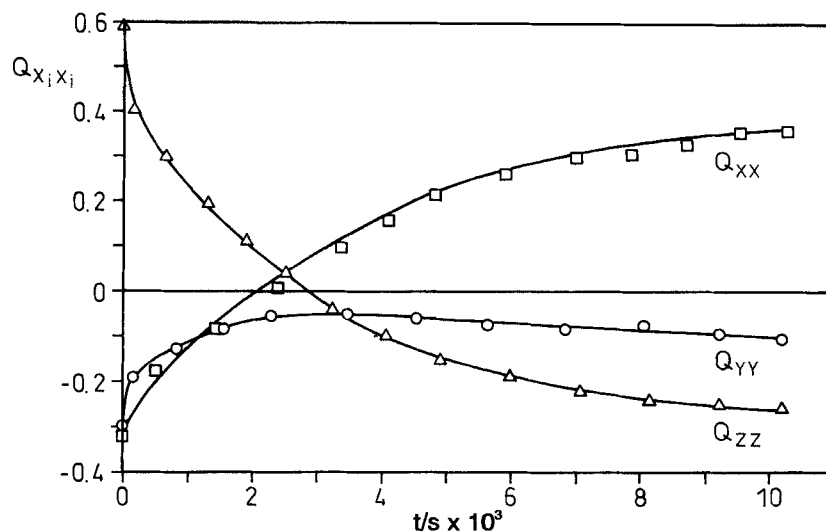


Figure 6. The diagonal elements  $Q_{XX}$  (□),  $Q_{YY}$  (○) and  $Q_{ZZ}$  (△) of the macroscopic order tensor  $Q$  calculated from equation (13), (14) and (15), respectively, as a function of irradiation time for the azobenzene mesogens of the 50 per cent copolymer 1 at 273 K.

three quantities always being equal to zero because of the traceless nature of the  $Q$  tensor. This is clearly not the case. Whereas  $Q_{YY}$  after about 3000 s stays almost constant at a value slightly below zero,  $Q_{XX}$  increases to a value of about 0.4 as the  $X$  direction becomes the new order axis. Figure 6 reveals that, as indicated before, a pronounced biaxiality develops through continuous irradiation.

As outlined in the experimental part we have oriented our films through a combination of surface and magnetic field effects in order to achieve a uniform homogeneous orientation throughout the samples. For the surface treatment the glass slides were spincoated with a polyimide film which was then microstructured by unidirectional brushing with a carbon fibre brush. We have proved that this procedure alone is sufficient to orient the liquid-crystalline polymer by cooling the optical cells slowly through the clearing temperature of the material into the glass. This shows that the surface forces are strong enough to impose a well-defined orientation of the director  $\mathbf{n}$  at the surface which is called strong anchoring [23].

We can try to relate the development of biaxial order during the reorientation process to the elastic constants of the material. With the brushing direction being along the  $Z$  axis a reorientation of the mesogens into the  $Y$  direction involves the twist constant  $K_2$  whereas a reorientation into the  $X$  direction involves a mixture of the splay and bending constants  $K_1$  and  $K_3$ , respectively. From these constants,  $K_3$  is usually the largest whereas  $K_2$  is the smallest [23]. To minimize the elastic energy we should, therefore, expect the mesogens to reorient into the  $Y$  direction. Since this is not the case for our system we can conclude that if the boundary conditions along the surface stay constant throughout the irradiation process, the reorientation is not a hydrodynamic process depending on the force constants of the liquid-crystalline material. To prove that the direction of the surface treatment really has no influence on the reorientation process we prepared a sample with the brushing direction along the  $Y$  axis whereas the

liquid crystal was aligned along the  $Z$  axis using a 7 T magnet. Under continuous irradiation with light polarized along  $Z$ , again a biaxial orientational distribution was formed with most of the mesogens aligned along the  $X$  direction.

Ichimura *et al.* [24] have recently reported on photo-induced alignment changes of low molar mass liquid crystals when the liquid crystal is sandwiched between two glass plates, the surfaces being modified with an azobenzene monolayer. The phenomenon involves the reversible change between homeotropic and homogeneous modes induced by the *trans* form and the *cis* form of the azobenzene monolayer, respectively. They showed that in their system two azobenzene units command about 15 000 liquid-crystalline molecules to change the alignment and therefore introduced the term command surface. An equivalent effect may be responsible for the photo-induced biaxiality observed here. Prior to irradiation the azobenzene molecules lie parallel to the surface. Through strong anchoring and the additional use of a magnetic field the liquid-crystalline polymer is homogeneously aligned and subsequently cooled below  $T_g$ . Under irradiation, isomerization from *trans* to *cis* azobenzene takes place propagating from the surface into the film plane. For the *cis* conformation there is a high probability for one of the phenyl rings to have a component along the surface normal. This might impose a new boundary condition such that the system reorients preferentially into the  $X$  direction, i.e. normal to the surface in order to minimize the energy. An illustration of the suggested mechanism is presented in figure 7. At this point we want to stress that the driving force of this reorientation is a single photon single molecule process and not the surface although the latter might impose a boundary condition on the system that determines which path it follows to minimize the energy.

If the suggested mechanism were true the observed biaxiality of the liquid-crystalline matrix should be dependent on the amount of dye per unit surface area and therefore on the composition of the copolymer. We, therefore, compared the degree of biaxiality observed for the 50 per cent system with that in a copolymer 3 having 30 per cent of the side groups containing azobenzene. The measurements were taken at 318 K which is about 10 K above  $T_g$  of both polymers. This temperature was chosen since the 30 per cent copolymer does not reorient completely below  $T_g$  within a reasonable time period [16]. The result is shown in figures 8(a), (b) where the three order parameters  $Q_{XX}$ ,  $Q_{YY}$  and  $Q_{ZZ}$  are presented as a function of irradiation time for the phenylbenzoate mesogens of the 50 and 30 per cent copolymer, respectively. We have chosen this

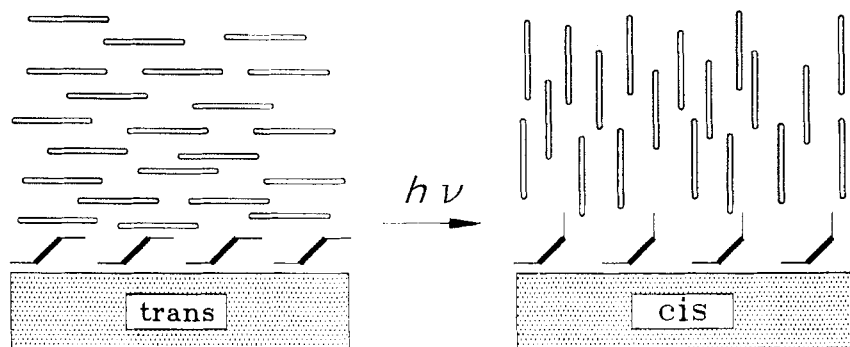


Figure 7. Illustration of how the first surface layer offers different boundary conditions for the alignment of the liquid crystal before and during irradiation. In this illustration only the azobenzene units of the surface layer are drawn with a different shape to stress the argument.

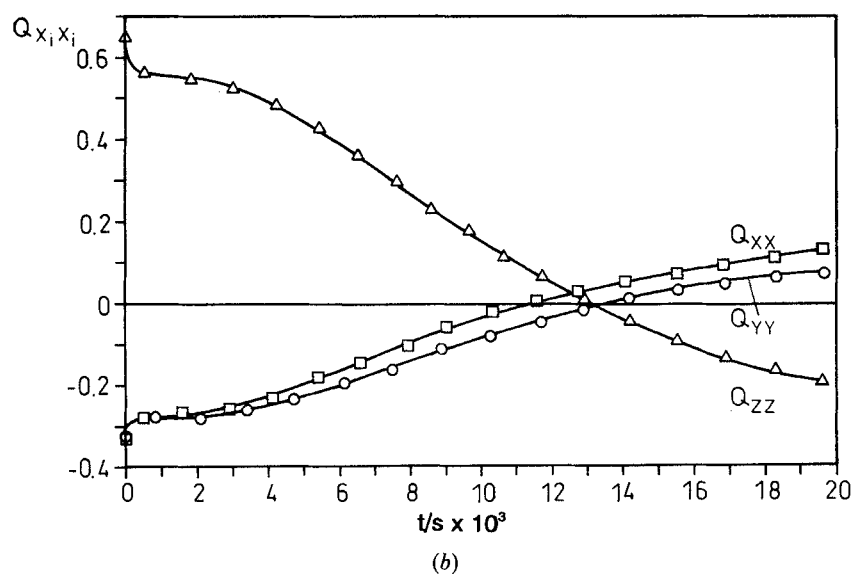
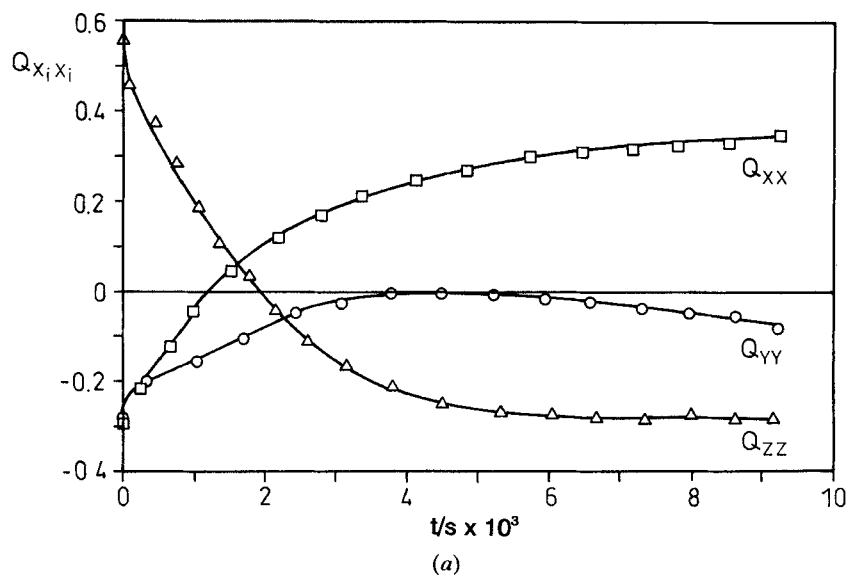


Figure 8.  $Q_{XX}$  ( $\square$ ),  $Q_{YY}$  ( $\circ$ ) and  $Q_{ZZ}$  ( $\triangle$ ) versus irradiation time for the phenylbenzoate mesogen of (a) the 50 per cent copolymer 1 and (b) the copolymer 3 with 30 per cent of the side groups containing azobenzene both measured at 318 K.

segment for quantification in order to stress that the same orientational behaviour is found for both, dye and matrix mesogens. Whereas for the 50 per cent copolymer the same result is obtained as below  $T_g$  (comparison with figure 6), the 30 per cent azobenzene containing polymer hardly shows any biaxiality. Here both quantities  $Q_{XX}$  and  $Q_{YY}$  increase in an almost equal manner as is expected for a reorientation conserving a uniaxial symmetry.

This result agrees with the mechanism suggested here. However, the alignment of liquid-crystalline material through surface treatment is an empirical method and clear cut molecular explanations are lacking in most cases. It is suggested that the intrinsic

biaxiality of the spacer segment prior to irradiation may also result from interactions with the cell surface. Further experimental evidence, however, is needed to prove this conjecture.

A closer look at the course of the order parameter  $Q_{YY}$  for the 50 per cent copolymer in figure 8 (a) reveals that after reaching a maximum at about 4500 s it decreases slightly again. Since at the same time  $Q_{ZZ}$  reaches its equilibrium value this indicates that some of the side groups initially reorienting into the  $Y$  direction finally reorient into the  $X$  direction. This behaviour was found for all segments of the 50 per cent copolymer under irradiation.

### 3.3. Kinetics of the reorientation process

In figure 9 the logarithm of the integrated intensities of the cyano stretching vibrations in the azobenzene and phenylbenzoate unit for polarizer position  $ZZ$  are presented as a function of irradiation time. The curves are representative of the kinetics found above and below the glass transition. It is apparent from figure 9 that the reorientation of the phenylbenzoate mesogens is essentially a mono-exponential process which levels off after an equilibrium state has been reached. This is also largely true for the azobenzene moiety. In this case it is interesting, however, to take a closer look at the short time behaviour. This shows that in contrast to the liquid-crystalline matrix the dye molecules themselves exhibit a fast process that leads to the initial, relatively fast drop of the order parameter that can also be seen in figure 5. Since this faster process is not observed for the phenylbenzoate mesogens it is assigned to the isomerization step of the azobenzene in which one of the phenyl rings undergoes a rotation around the nitrogen double bond of about  $43^\circ$  [25,26]. This behaviour contains useful information about the coupling between the dye and the liquid-crystalline matrix. The fact that the fast process is not found for the matrix mesogens

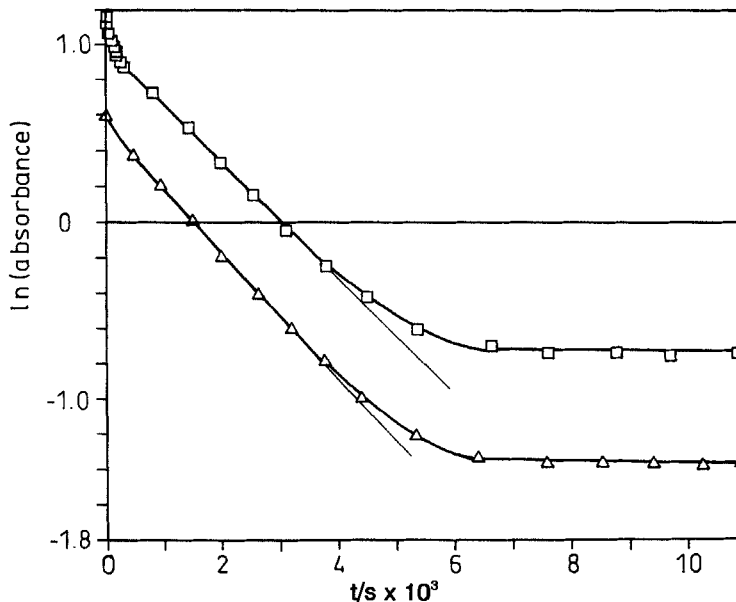


Figure 9. Logarithm of the integrated intensity of the cyano stretching vibration in the azobenzene (□) and phenylbenzoate (△) unit for polarizer position  $ZZ$  as a function of irradiation time.

leads to the conclusion that single isomerization steps do not appreciably change the orientation of these segments. Only the overall reorientation of the long molecular axis of the azobenzene molecules through the dynamic back and forth isomerization induced through continuous irradiation leads to a significant change in the orientational distribution of the phenylbenzoate side groups.

To prove that a single isomerization step of a dye molecule does not change the orientational distribution of the local liquid-crystalline environment we have investigated a 14 per cent dye containing copolymer system **1** in which the azobenzene molecule was exchanged by a fulgimide, which is a thermally irreversible photochromic group. This polymer was first synthesized and characterized under irradiation with light by Cabrera *et al.* [27]. The dye undergoes an irreversible conformational change under irradiation. This system which forms nematic mesophases was irradiated above and below  $T_g$  and the orientation of the phenylbenzoate mesogens was simultaneously monitored using the CN stretching vibration in the infrared spectrum. Under irradiation no change in the IR dichroism could be detected for the matrix mesogens, as expected. This fits well with the observations made for the azobenzene containing copolymer and gives useful directions for the future design of media with high writing speed for optical information storage.

#### 3.4. Comparison of liquid-crystalline and isotropic amorphous matrix

In order to reveal the influence of the ordered liquid-crystalline matrix on the reorientation process we have investigated copolymer **2** which forms no mesophase. From studies of similar amorphous polymer systems below  $T_g$  [22] it is known that the angular dependent photoselection of the isomerizing azobenzenes under irradiation with polarized light induces an optical axis perpendicular to the polarization direction of the writing light beam. We have, therefore, investigated copolymer **2** at 298, 293 and 263 K, all temperatures lying below the  $T_g$  of 303 K. The result is presented in figure 10(a), where the order parameter  $S_{zz}$  of the CN band of the azobenzene unit is plotted versus irradiation time for the three different temperatures. The observed order parameters are all negative which confirms that the induced optical axis lies perpendicular to the polarization plane of the incoming light beam. As described in [22] the measured anisotropies are much smaller than those generated in the liquid-crystalline material after irradiation. A closer examination of figure 10(a) reveals that the induced order increases when irradiating at lower temperatures. At 263 K  $S_{zz}$  reaches a value of about  $-0.08$  which is substantial for irradiation of an initially isotropic system. The same result is obtained from the analysis of the spacer orientation which is depicted in figure 10(b) although here, as expected, the order parameters are smaller overall. This indicates that the thermal mobility of the system competes with the tendency to form an anisotropic medium. If this conjecture is correct we should expect that above  $T_g$  no anisotropy is formed since the mobility strongly increases at this transition. We therefore irradiated copolymer **2** at 318 K which is about 15 K above its glass transition. As predicted no anisotropy in the orientation of the azobenzene unit or the spacer segment could be detected.

For the ordered liquid-crystalline copolymer **1** a temperature dependence of the reorientation could not be detected for a temperature range from  $T_g$  to 40 K below. Any slight changes observed are of the order of those resulting from variations in sample thickness which also effects the kinetics. Above  $T_g$ , however, acceleration of this process by a factor of about two (comparison of figure 6 with figure 8(a) and a slightly higher efficiency than in the glassy state of the polymer was found [16]. At first sight, the fact

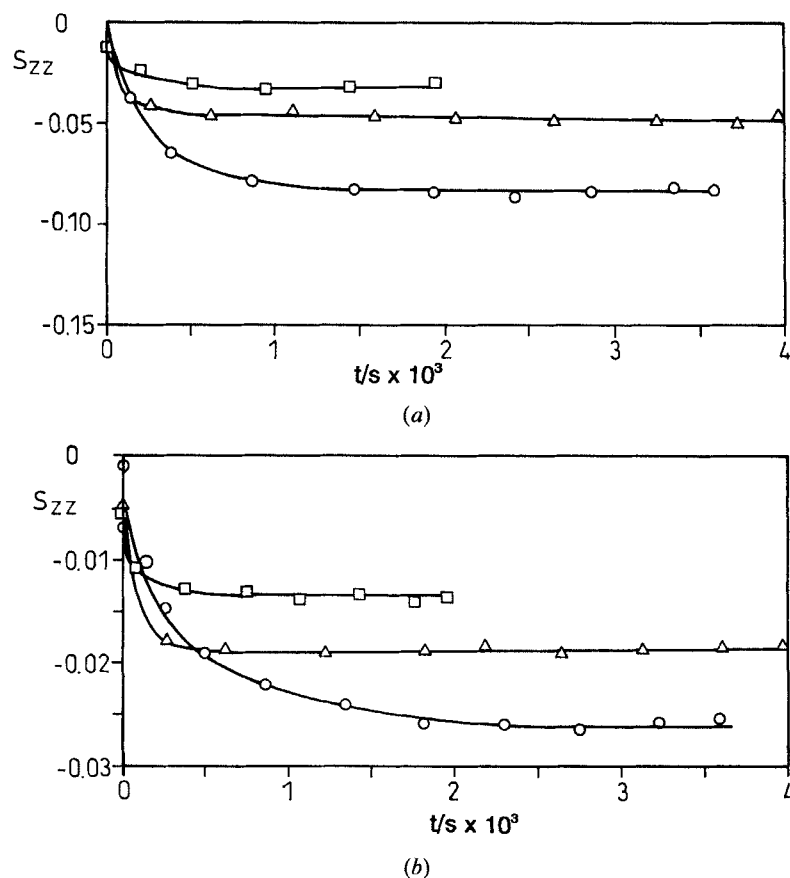


Figure 10. Order parameter  $S_{zz}$  for (a) the azobenzene unit and (b) the spacer unit in copolymer 2 as a function of irradiation time for 298 ( $\square$ ), 293 ( $\triangle$ ) and 263 K ( $\circ$ ), all temperatures lying below the glass transition of this system which was at 303 K.

that matrix reorientation actually takes place below  $T_g$  may be surprising. It should be noted, however, that through continuous irradiation the system experiences a non-linear perturbation and is driven away from equilibrium. That relaxations of such non-equilibrium states occur even well below the glass transition of polymers is known especially from non-linear optics where through corona and contact poling created non-equilibrium states that are frozen in the glass of polymer films show a significant loss of orientation of the dopant reflected in a reduction of second harmonic generation [28]. On the other hand the result that at  $T_g$  the kinetics is only slightly changed and does not show the usual WLF behaviour [29] found for polymer dynamics, whose correlation times change several orders of magnitude within, for example, 20 K indicates that the reorientation process does not couple directly to the segmental motion of the polymer chain which is activated at the glass transition.

The observation that above and below the glass transition temperature a coupled reorientation of azobenzene and phenylbenzoate mesogens takes place in the liquid-crystalline system can be understood by considering its free energy. If only the dye molecules would rotate away from the  $Z$  axis and the matrix mesogens keep their initial positions the energy of the system would be increased as a consequence of the elastic

forces between neighbouring mesogens of different orientation. In the case of a rotation of the phenylbenzoate mesogens which do not take part in the photoreaction, not the sum of bulk and surface energies but essentially only the surface energy term has to be taken into account to calculate the change in free energy. The magnitude of the surface energy contribution, however, can be assumed to be much smaller than that of the bulk term in the case of a different behaviour of dye and matrix mesogens. Since, in addition, the overall macroscopic order is decreased, the process is entropically favoured and a coupled reorientation of azobenzene and phenylbenzoate side groups is observed.

## Appendix

### Theory

In general the order in liquid crystals can be described using the following super ordering matrix [23, 30]:

$$S_{UVuv} = 1/2(3\langle \cos(uU) \cos vV \rangle - \delta_{UV}\delta_{uv}), \quad (3)$$

where  $U, V = X, Y, Z$  are indices referring to the laboratory frame, while  $u, v = x, y, z$  are indices referring to the molecular frame and  $\delta_{UV}$  and  $\delta_{uv}$  are Kronecker deltas. The  $\cos(uU)$  are direction cosines of the angle between the molecular axes  $u$  and the laboratory axes  $U$ . The brackets  $\langle \rangle$  represent a thermal average.

For molecules of cylindrical symmetry in a biaxial phase each block  $S_{UV}$  has only one independent diagonal element  $S_{UVzz}$ . Therefore the matrix  $Q$  with  $Q_{UV} = S_{UVzz}$  is sufficient to describe the order;  $Q$  is called the macroscopic order matrix [30]. The elements of  $Q$  are defined by

$$Q_{UV} = 1/2(3\langle \cos(zU) \cos(zV) \rangle - \delta_{UV}). \quad (4)$$

To set up  $Q$  for our particular problem we first have to obtain some information about the symmetry of the distribution function that describes the orientational behaviour of the liquid-crystalline films of copolymer 1 under irradiation. We therefore tried to fit the spectroscopic results for the absorptions  $A_{ZZ}$ ,  $A_{YY}$  and  $A_{XX} = 1 - A_{ZZ} - A_{YY}$  after normalization to one ( $A_{XX} + A_{YY} + A_{ZZ} = 1$ ) using different normalized orientation distributions  $f(\theta, \varphi)$ ,  $\theta$  and  $\varphi$  being the polar angles between the molecular  $z$  axis and the laboratory frame

$$\int_0^{2\pi} \int_0^\pi f(\theta, \varphi) \sin \theta \, d\theta \, d\varphi = 1, \quad (5)$$

$$A_{ZZ} = \int_0^{2\pi} \int_0^\pi f(\theta, \varphi) \cos \theta \sin \theta \, d\theta \, d\varphi, \quad (6)$$

$$A_{YY} = \int_0^{2\pi} \int_0^\pi f(\theta, \varphi) \sin \theta \sin \varphi \sin \theta \, d\theta \, d\varphi, \quad (7)$$

$$A_{XX} = \int_0^{2\pi} \int_0^\pi f(\theta, \varphi) \sin \theta \cos \varphi \sin \theta \, d\theta \, d\varphi. \quad (8)$$

Good fits were obtained in terms of a biaxial, gaussian shaped orientation distribution function [4]

$$f_b(\theta, \varphi) = \exp \left[ -\frac{\cos^2 \theta}{2 \cos^2 \bar{\theta}} - \frac{\sin^2 \varphi}{2 \sin^2 \bar{\varphi}} \right]; \quad (9)$$



$\bar{\theta}$  and  $\bar{\varphi}$  being measures for the width of the distribution around the  $Z$  and  $X$  axes, respectively. From the definition of  $f_b(\theta, \varphi)$  it follows, that the corresponding distribution has the three symmetry planes  $\sigma_{XY}$ ,  $\sigma_{XZ}$  and  $\sigma_{YZ}$ . Therefore the thermal averages  $\langle X \rangle$ ,  $\langle Y \rangle$  and  $\langle Z \rangle$  as well as the averages  $\langle X, Y \rangle$ ,  $\langle X, Z \rangle$  and  $\langle Y, Z \rangle$  disappear. As a result the macroscopic order matrix  $Q$  has the diagonal form

$$Q = \begin{bmatrix} Q_{XX} & & 0 \\ & Q_{YY} & \\ 0 & & Q_{ZZ} \end{bmatrix} \quad (10)$$

$Q_{ZZ}$  being equal to the Saupe order parameter  $S_{zz}$  defined by

$$Q_{ZZ} = 1/2(2\langle \cos^2 zZ \rangle - 1) = S_{zz}. \quad (11)$$

#### Connection with experiment

Figure 11 shows the three angles  $\alpha$ ,  $\beta$  and  $\gamma$  between the molecular  $z$  axis and the axes of the laboratory frame. The squares of these direction cosines are proportional to the quantities  $A_{XX}$ ,  $A_{YY}$  and  $A_{ZZ}$  measured in the experiment:

$$\langle \cos^2 \alpha \rangle \propto A_{XX}, \quad \langle \cos^2 \beta \rangle \propto A_{YY}, \quad \langle \cos^2 \gamma \rangle \propto A_{ZZ}. \quad (12)$$

Therefore, using  $N$  as the number of molecules

$$\begin{aligned} Q_{ZZ} = S_{zz} &= 1/2(3\langle \cos^2 \gamma \rangle - 1) = 1/2 \left( 3 \frac{N \langle \cos^2 \gamma \rangle}{N} - 1 \right) \\ &= 1/2 \left[ \frac{3A_{ZZ} - (A_{XX} + A_{YY} + A_{ZZ})}{A_{XX} + A_{YY} + A_{ZZ}} \right], \\ &= \frac{A_{ZZ} - 1/2(A_{XX} + A_{YY})}{A_{XX} + A_{YY} + A_{ZZ}}. \end{aligned} \quad (13)$$

$Q_{XX}$  and  $Q_{YY}$  follow equivalently by cyclic permutation of the indices  $X$ ,  $Y$  and  $Z$  in equation (13)

$$Q_{XX} = \frac{A_{XX} - 1/2(A_{YY} + A_{ZZ})}{A_{XX} + A_{YY} + A_{ZZ}}, \quad (14)$$

$$Q_{YY} = \frac{A_{YY} - 1/2(A_{XX} + A_{ZZ})}{A_{XX} + A_{YY} + A_{ZZ}}. \quad (15)$$

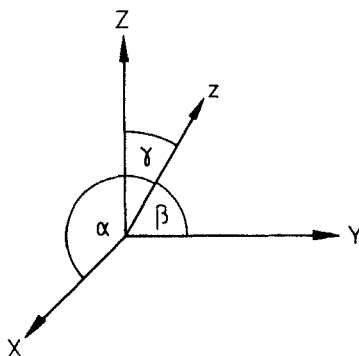


Figure 11. Coordinate system introducing the three angles  $\alpha$ ,  $\beta$  and  $\gamma$  between the molecular  $z$  axis and the laboratory axes  $X$ ,  $Y$  and  $Z$ , respectively.

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