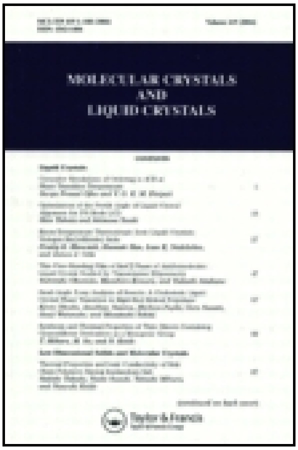

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State of Order in Liquid Crystalline Elastomers

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State of Order in Liquid Crystalline Elastomers

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The orientation behavior of crosslinked liquid crystal-line side chain polymers is determined by IR-dichroism measurements. In stretched samples the conformation of the polymer main chain and the chemical constitution of the rodlike side chain determine the position of the director in relation to the axis of stress. The order parameter S has the same temperature dependence and is of the same magnitude as in the corresponding uncrosslinked liquid crystalline polymers. The order parameter and the nematic to isotropic phase transformation temperature are independent of the applied mechanical stress under the experimental conditions (elongation up to 50%).

Keywords: liquid crystalline polymers, state of order, orientation by mechanical stress

INTRODUCTION

Liquid crystalline (l.c.) elastomers have been known for some years.[1-2] They can be synthesized by crosslinking linear l.c.-side chain polymers. Owing to the network formation, the macro-Brownian motion of the polymer chains is prevented, leading to a form-retaining material. These materials can, however, be considered as liquid crystals because the micro-Brownian motion of the chain segments is hardly influenced by the crosslinking of the polymer chains. The liquid crystalline properties are the same as in the corresponding uncrosslinked l.c.-side chain polymers. It is possible to realize elastomers with nematic, smectic or chiral nematic phases. The combination of these properties, the stability of shape, the elasticity and the liquid crystallinity, offers new materials.

Conventional low molar mass liquid crystals and uncrosslinked l.c.-polymers can be macroscopically ordered by external electric or magnetic fields. This process is limited to samples with a thickness of less than about 100 μm because of thermal fluctuations of the director. In the case of l.c.-elastomers there exists an additional possibility to obtain a macroscopic orientation. By applying a mechanical stress, the deformation of the network leads to a macroscopic orientation of the l.c.-side chains in the entire sample. Owing to the deformation of the sample, the possible conformations of the main chain segments are restricted. This leads to a deviation from the statistical chain conformation towards an anisotropic structure of the polymer main chains. According to the anisotropic main chain conformation, the director of the mesogenic side chains becomes uniformally ordered with respect to the direction of the external stress. This orientation mechanism has the advantage that samples of larger dimensions can be ordered, e.g., samples with a thickness of 1 cm can be ordered without problems. The qualitative orientation behavior of l.c.-elastomers has been examined earlier.[1-2] The direction of the orientation of the mesogenic groups relative to the axis of stress depends on the length of the flexible linkage (spacer) between the polymer backbone and the rodlike mesogenic side chains.

Up to now there exist no quantitative measurements of the nematic order parameter S for l.c.-elastomers. The question is, whether the order parameter of l.c.-elastomers and that of usual l.c.-polymers are of the same magnitude. A further interesting aspect is whether the order parameter S depends on the magnitude of the applied stress. In this paper we will describe the stress-induced orientation behavior of a series of l.c.-siloxane elastomers with different spacer length and IR-dichroism measurements of the order parameter S.

EXPERIMENTAL

1. Samples

The elastomers were prepared by addition reaction of the mesogenic molecules and the crosslinking agent with linear poly(methylhydrogensiloxane) in the presence of a Pt-catalyst, as shown in Figure 1. All components were mixed in a toluene solution and allowed to react in a mold for 48 h at 50°C. The samples were deswollen with n-hexane and dried in vacuo. Thin films with a thickness of 120 μm were obtained. The l.c.-elastomers investigated in this paper and their phase behavior are listed in Table I.

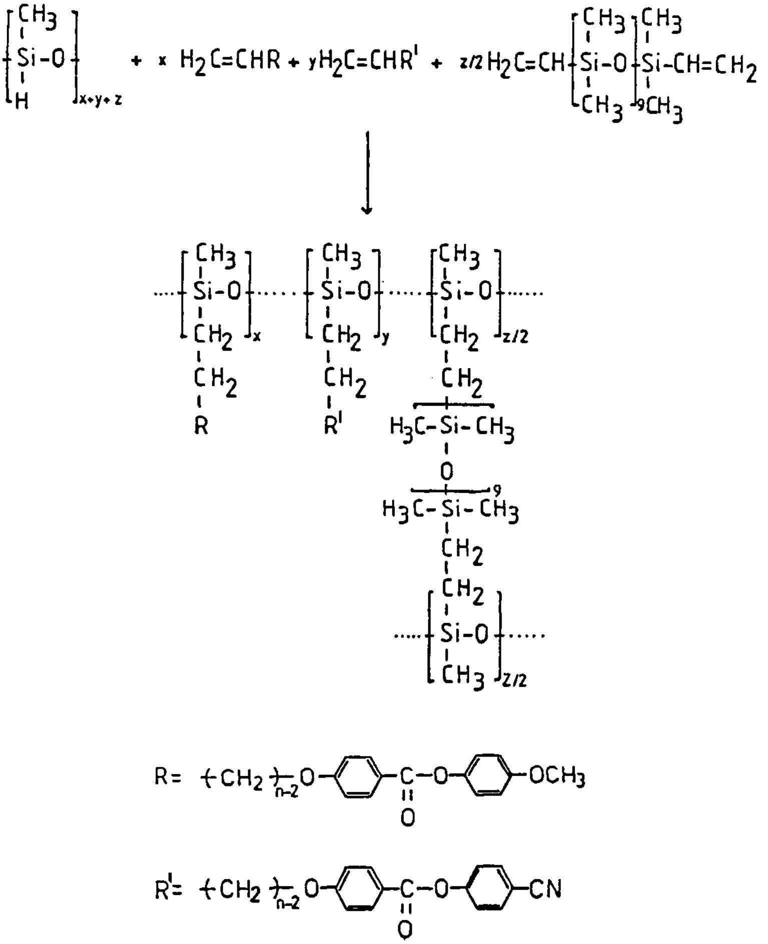

FIGURE 1 Synthesis of liquid crystalline polymer networks.

The elastomers C30 and C40 have been synthesized earlier but without the small amount of side chains with a CN-end group.[1-2] With the aid of x-ray diffraction and stress-optical measurements, the orientation behavior of these homopolymers was determined. In the case of homopolymer C30 the mesogenic side chains are oriented perpendicular, and in the case of elastomer C40, parallel to the axis of stress.

For the IR-dichroism measurements it was necessary to synthesize copolymers with a small amount of mesogenic side chains with CN-end groups as probe molecules. Both comonomers are very similar

TABLE I

Chemical constitution and phase behavior of liquid crystalline elastomers.
g: glassy s: smectic n: nematic i: isotropic

Sample	n	Phase behavior (K)
C30	3	g278n322i
C40	4	g280n343i
C50	5	g275s357n368i

x = 0.76 y = 0.04 z = 0.20

in shape. It can be assumed that the small amount of probe mesogens will not disturb the order of the other side chains. In order to analyse whether the small amount of CN-groups changes the stress-induced orientation behavior, we also synthesized a homopolymer C40 without the probe mesogen. Parts of this sample were swollen in two solutions with different concentrations of the corresponding monomer with the CN-end group. After the elastomers were deswollen, the monomers rested physically bonded in the sample.

2. IR-dichroism measurements

IR-spectra were recorded with a Bruker IFS 100 FTIR-spectrometer in polarized light. After the films were stretched by λ ($\lambda = z/z_0$, z: length of the stretched film, z_0: length of the unstretched film) in the isotropic phase, the dependence of the IR dichroism of the CN-stretching mode at 2229 cm^{-1} on the position of the polarizer, with falling temperature was determined. The evaluation of the measurements of the linear dichroism is based on the relation between the anisotropic absorption and the order parameter S which has been derived for low molar mass nematic LCs by Maier and Saupe:[3]

$$S = \frac{\epsilon_{\|} - \epsilon_{\perp}}{(\epsilon_{\|} + 2\epsilon_{\perp})(1 - 3/2\,\sin^2\alpha)} \qquad (1)$$

$\epsilon_{\|}$ and $\epsilon_{\perp}$ are the absorption coefficients along and perpendicular to, respectively, the long axis of the molecule. The angle α denotes the angle between the long molecular axis and the transition moment.

In the case of the CN- stretching mode the long molecular axis and the transition moment are parallel. Equation (1) is reduced to equation (2):

$$S = \frac{\epsilon_{\parallel} - \epsilon_{\perp}}{\epsilon_{\parallel} + 2\epsilon_{\perp}} \tag{2}$$

The spatial arrangement of the elastomer in the IR-experiment is shown in Figure 2, where z denotes the axis of stress, φ denotes the angle between the electric field vector of the incident beam and the z-axis. The thin film is fixed with its surface parallel to the x-z- plane. The beam hits the elastomer parallel to the y-axis.

In the case that the director is in a position perpendicular to the surface of the polymer film, the absorption of the CN-group corresponds to $E_{\perp}$, and is independent of the direction of the polarized

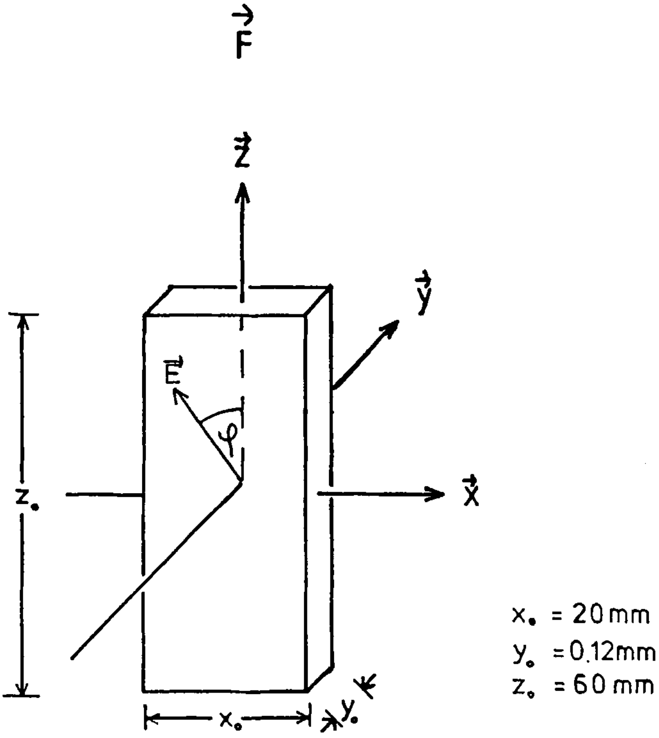

FIGURE 2 Spatial arrangement in the IR-experiment.

light. Under this condition, it is not possible to determine the value of $E_{\parallel}$ in a direct way. $E_{\parallel}$ can be calculated indirectly if E_i, which is the isotropic absorption, is known. E_i can be determined as a function of the temperature in the isotropic state and can be extrapolated into the region of the liquid crystalline phase. Neglecting the volume jump at the isotropic to nematic phase transformation, the absorption $E_{\parallel}$ can be calculated by equation (3):

$$\epsilon_i = 1/3(\epsilon_{\parallel} + 2\epsilon_{\perp}) \qquad (3)$$

RESULTS AND DISCUSSION

Elastomer C30

For the elastomer C30, which has the very short propyloxy-spacer between polymer main chain and the l.c.-side chain, we examined the dependence of the absorption of the CN-group on the direction of the polarizer in order to determine the position of the director. With these results, the absorptions $E_{\parallel}$ and $E_{\perp}$ were measured as a function of the temperature.

A typical absorbance spectrum of elastomer C30 is shown in Figure 3. E_0 is the spectrum with $\varphi = 0°$, E_{90} the spectrum with $\varphi = 90°$ (see Figure 2). The strong dichroism of the stretching mode of the CN-

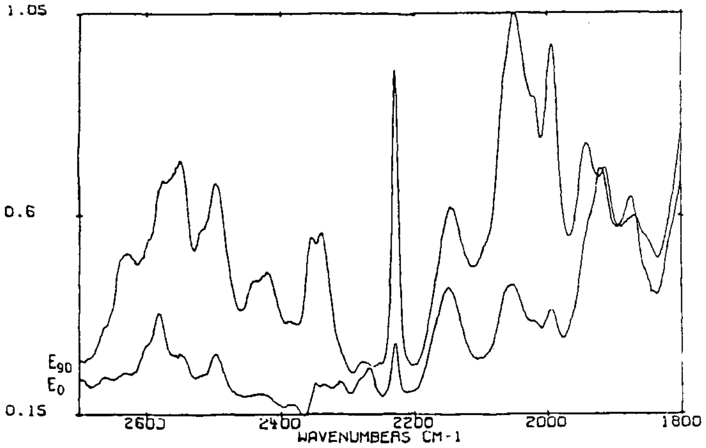

FIGURE 3 IR absorbance spectrum of elastomer C30 with the E-vector of the polarized light parallel (E_0) and perpendicular (E_{90}) to the axis of stress. $\lambda = z/z_0 = 1.23$ z_0: original length of the sample
z: length of the stretched sample

groups at 2229 cm^{-1} indicates an ordered sample. If the absorbance of the CN-group is plotted versus φ, the maximum of the absorption appears at $\varphi = 90°$, the minimum at $\varphi = 0°$ (see Figure 4). This indicates that the director lies parallel to the x-axis and therefore parallel to the surface of the elastomer film. The l.c.-side chains are oriented perpendicular to the axis of stress as schematically shown in Figure 5. Knowing the position of the director, $E_{\parallel}$ and $E_{\perp}$ can be determined as a function of the temperature, which is shown in Figure 6. In the nematic phase, E_{90} decreases with increasing temperature, whereas E_0 increases. In the isotropic phase both absorptions are equal.

The temperature dependence of the nematic order parameter *S* determined by Eq. (2) is shown in Figure 7. The order parameter of elastomer C30 has the same temperature dependence and is of the same magnitude as in the corresponding linear LC polymer.[4] According to the experimental results, at the clearing point the order parameter seems to decrease continuously to zero although the ne-

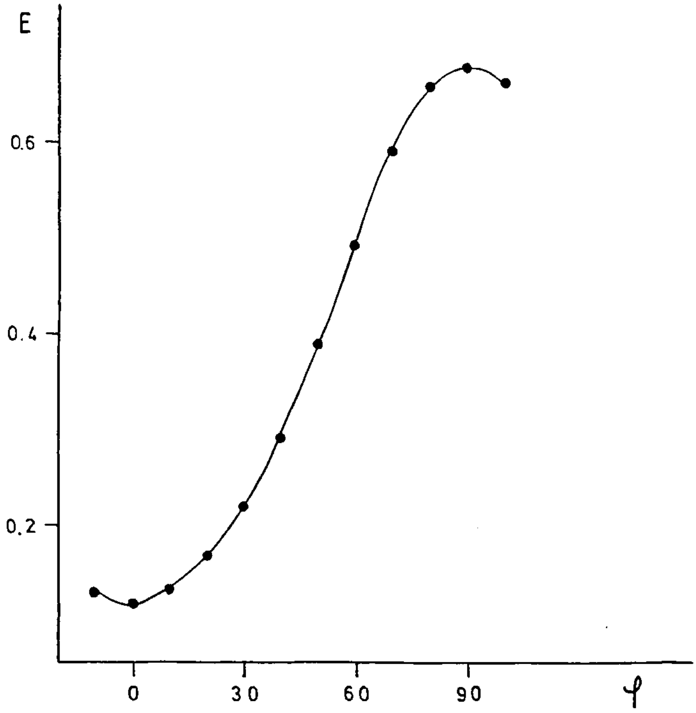

FIGURE 4 Absorbance of the CN-stretching mode in dependence of the angle φ between the position of the polarizer and the axis of stress. $\lambda = 1.23$

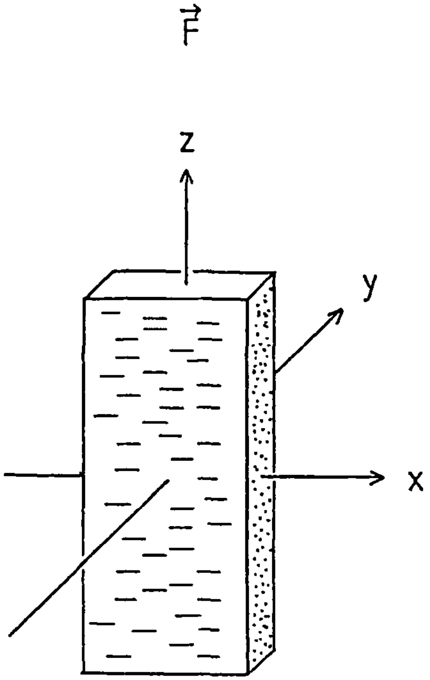

FIGURE 5 Position of the director in an oriented film of elastomer C30.

matic to isotropic phase transformation is of first order. An explanation for the measured continuous slope of the curve is the existence of a broad biphasic region at the clearing point. The reasons for this broad biphasic region are the following. The crosslinking agent itself has no liquid crystalline properties. Consequently the rubber can be considered as a two component system which always displays a biphasic gap at all phase transformations. Furthermore, there are restrictions on the possible conformations of the polymer main chains in the neighbourhood of the crosslinkages. Both effects may broaden the biphasic gap.

A further question is the influence of the magnitude of the applied stress on the clearing point and on the order parameter *S*. As a consequence of the interaction between polymer main chain and l.c.-side chains the extent of the anisotropic deformation of the network should affect both parameters. In the case of l.c.-main chain elastomers, de Gennes predicted a shift of the clearing point and the order parameter when varying the mechanical stress.[5] In our system, we could not find this effect. After applying a minimum stress of

$\lambda = 1.1$, the mesogenic side groups are oriented macroscopically. An increase in the stress up to $\lambda = 1.5$ has no influence on the quality of the orientation within the experimental error (ΔS: ±2%). Also the clearing point is not affected detectably (ΔT_c: ±3K) by stretching the network. This indicates that the motions of mesogenic side groups and polymer backbone are essentially decoupled.

Elastomer C40

Elastomer C40 has a butoxy- spacer, which is one methylene unit longer than that in elastomer C30. Earlier measurements with the homopolymer network showed that the extension of the spacer length from a propyloxy- to a butyloxy chain alters the position of the director from perpendicular (C30) to parallel (C40) to the axis of stress. The measurements with the C40 copolymer network yielded, however, the following results: in the nematic phase, only a small dichroism appears if the elastomer film is in a position perpendicular

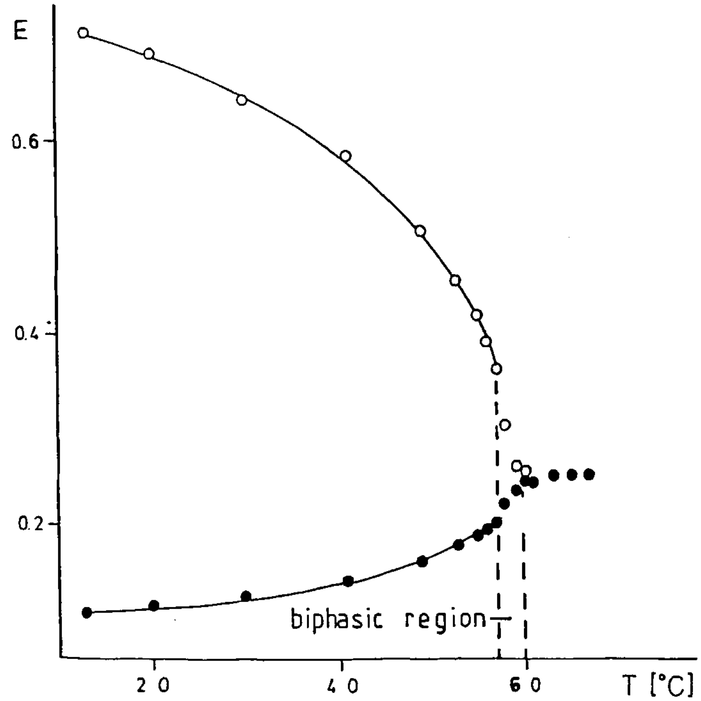

FIGURE 6 Temperature dependence of the absorption E_0 and E_{90} of the CN-stretching mode. Elastomer C30.
$\lambda = 1.37$ ●: E_0 O: E_{90}

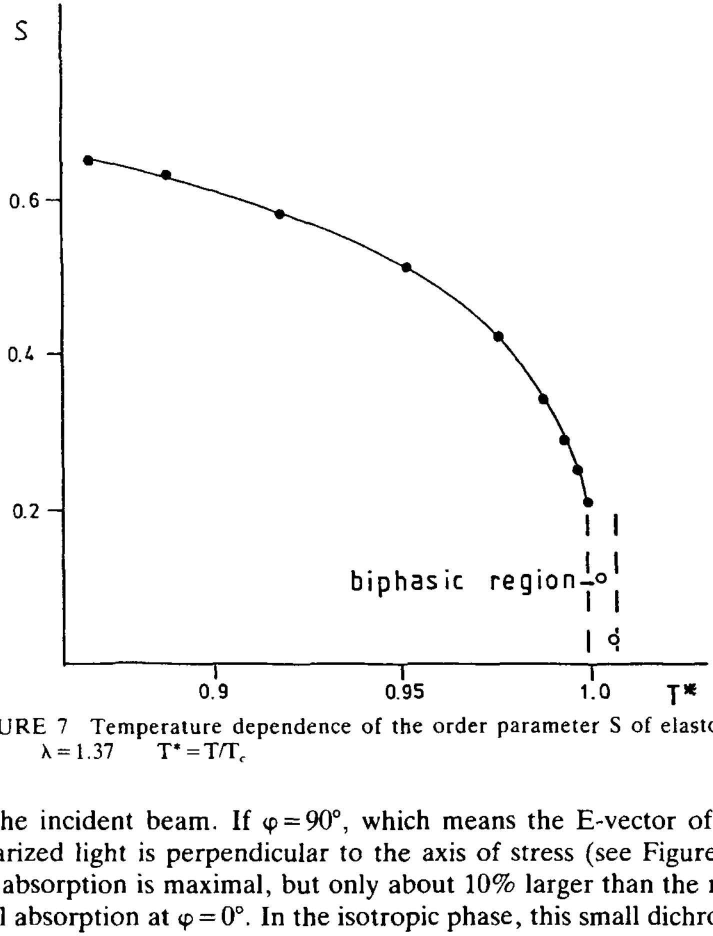

FIGURE 7 Temperature dependence of the order parameter S of elastomer C30. $\lambda = 1.37$ $T^* = T/T_c$

to the incident beam. If $\varphi = 90°$, which means the E-vector of the polarized light is perpendicular to the axis of stress (see Figure 2), the absorption is maximal, but only about 10% larger than the minimal absorption at $\varphi = 0°$. In the isotropic phase, this small dichroism disappears. The absorption at 2229 cm^{-1}, with the polarizer parallel (E_0) and perpendicular (E_{90}) to the axis of stress, is plotted versus the temperature in Figure 8. Both E_0 and E_{90} increase with increasing temperature. The shape of the plots is similar to the plot of E_0 of C30 in Figure 6, which is the absorption perpendicular to the long molecular axis of the l.c.-side chain.

For a more detailed examination of the spatial position of the director, we measured the absorption of the CN-stretching mode with the sample tilted relative to the incident beam. In the IR-experiment, the sample holder is rotated around the *z*- and the *x*-axis (see Figure 2). Rotating the sample around the *z*-axis, the ratio E_{90}/E_0 increases with increasing tilt angle β as shown in Figure 9. The minimum of the curve is not exactly at the origin of the co-ordinates. This proves that the position of the director is perpendicular to the axis of stress and is slightly twisted to the surface of the elastomer film. From the position of the minimum in the plot of Figure 9, the tilt angle can be estimated to be about 5°. This small deviation from a perpendicular position of the director to the surface of the film causes the appearance of the small dichroism shown in Figure 8. When the sample is rotated along the x-axis, the ratio E_{90}/E_0 decreases with increasing tilt angle β (Figure 10). This result is in agreement with the position of the director described above.

The orientation behavior of the copolymer C40 is quite different from that of the respective homopolymer. In the case of the homopolymer, the director lies parallel to the axis of stress, and in the case of the copolymer, perpendicular to this direction. Obviously the addition of a small amount of the polar CN-substituted probe completely alters the stress-induced orientation behavior. To get more detailed information about the influence of the polar additive on the orien-

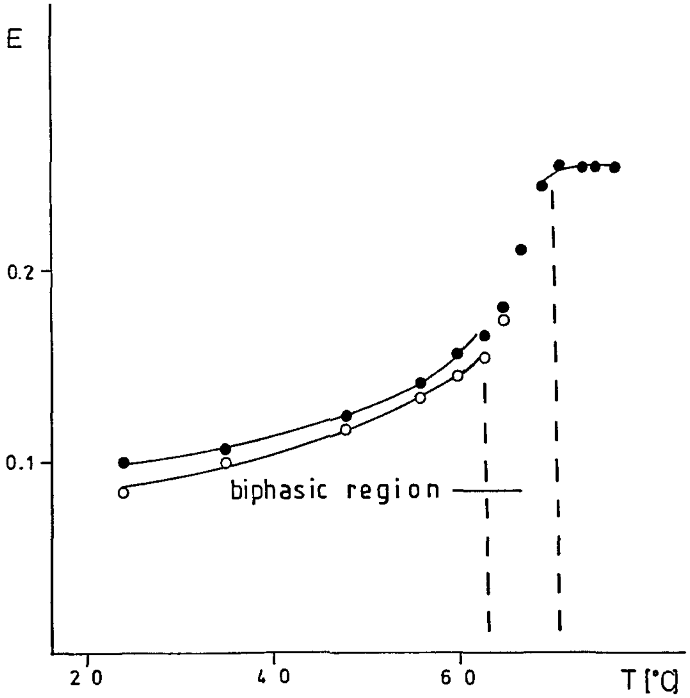

FIGURE 8 Temperature dependence of the absorption E_0 and E_{90} of the CN-stretching mode. Elastomer C40.
$\lambda = 1.20$ ○: E_0 ●: E_{90}

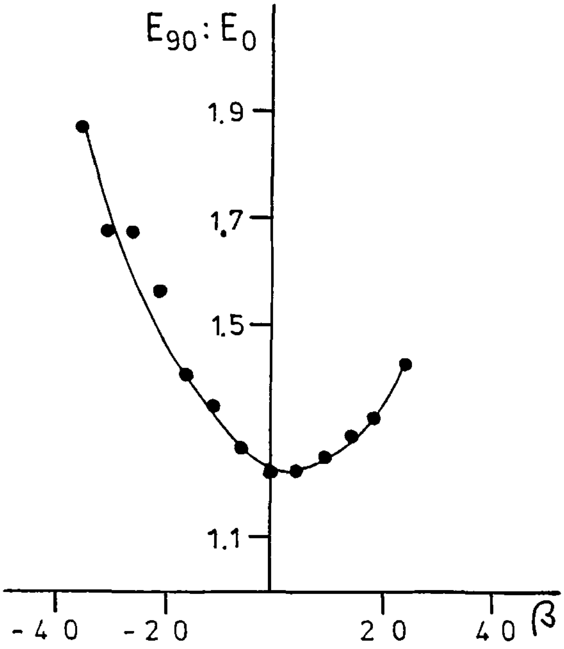

FIGURE 9 Ratio E_{90}: E_0 after the rotation of sample C40 around the z-axis. β denotes the angle between the y-axis and the direction of the incident beam.

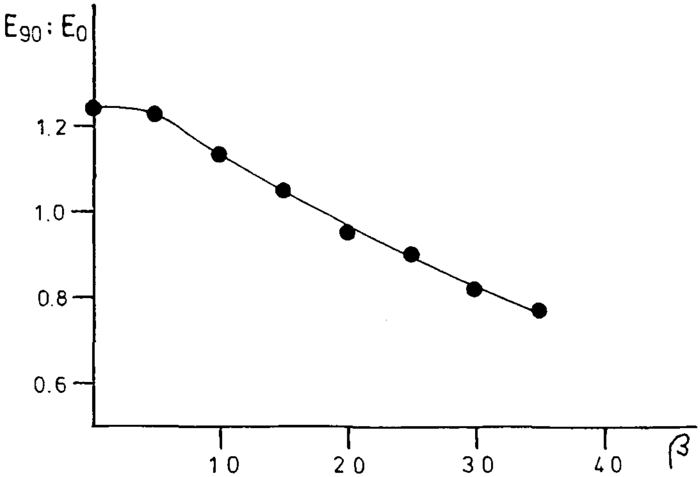

FIGURE 10 Ratio E_{90}: E_0 after the rotation of sample C40 around the x-axis. β denotes the angle between y-axis and the direction of the incident beam.

tation behavior, we performed swelling experiments with the C40 homopolymer. X-ray experiments showed that in the homopolymer, the director lies parallel to the axis of stress, in agreement with earlier results.[1-2] In a sample which contains about 1% by weight of probe monomers dissolved in the network, the stress-induced orientation of the side chains remained unchanged. If, however, the concentration of the monomers with CN-end groups was greater than 10% by weight, the stress-induced orientation changed. The director now lies perpendicular to the axis of stress (see Figure 11). The influence of the polar monomers is the same whether they are chemically bonded as in the copolymers or only dissolved in the network. The swelling experiments with the probe monomer proved that the exchange of only 4% by weight of the l.c.-side chains against a chemically similar probe mesogen is responsible for this drastic variation of the orientation behavior.

The reason for this unusual behavior might be explained by a pair formation due to charge transfer interaction of the l.c.-side chains containing a methoxy end group with those containing a nitrile end group. This effect will stiffen the polymer backbone and reduce the probability of various chain conformations. The same stiffening effect can appear in the case of elastomer C30 due to the short spacer. It is possible that both effects, the stiffening by pair formation in the case of copolymer C40 and the stiffening as a consequence of the short spacer in the case of homopolymer C30, cause the orientation

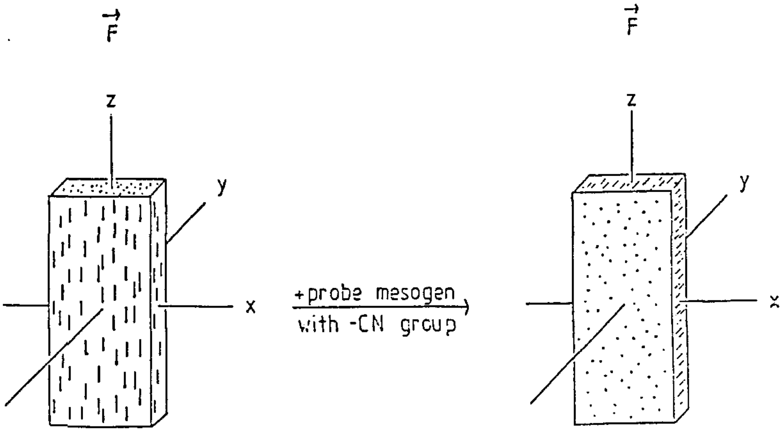

FIGURE 11 Changed behavior of orientation after the addition of a small amount of mesogenic units with a CN-end group instead of a OCH_3-end group.

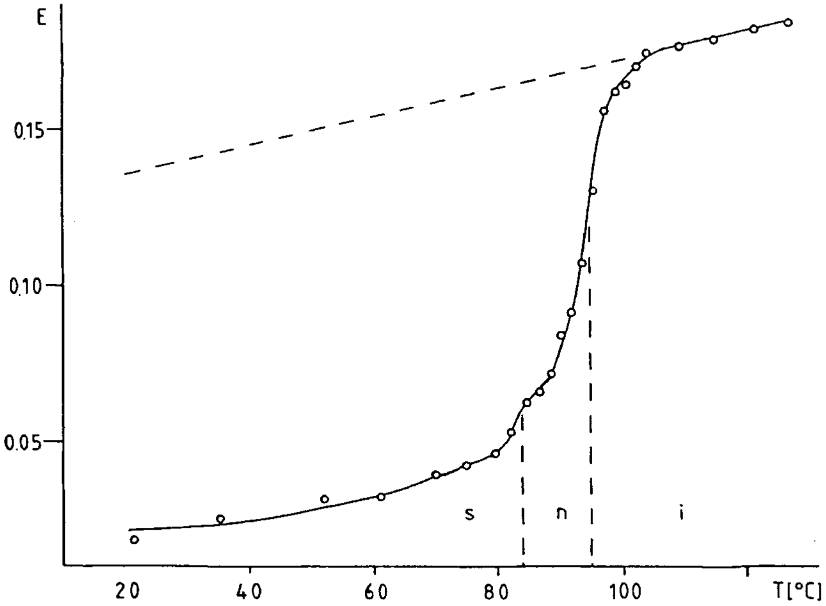

FIGURE 12 Temperature dependence of the absorption E of the CN-stretching mode. Elastomer C50. $\lambda = 1.20$

of the director perpendicular to the axis of stress and therefore perpendicular to the polymer main chain.

Elastomer C50

The observed IR-spectra of the elastomer C50 with a pentoxy- spacer are similar to those of the sample C40. If the elastomer film is in a position perpendicular to the incident beam, the absorbance of the CN-stretching mode is independent of the direction of the polarized light. With increasing temperature the absorbance increases. The director is oriented perpendicular to the axis of stress as in sample C40 but is now exactly perpendicular to the surface of the elastomer film, in contrast to sample C40 where it was slightly tilted.

The absorption of the CN-stretching mode is plotted versus the temperature in Figure 12. In the smectic phase the absorption slowly increases with increasing temperature. At the phase transformation to the nematic phase, there is a strong increase in absorption which corresponds to a strong decrease of the order parameter. The order parameter, calculated with equation (3), is plotted versus the reduced temperature in Figure 13. As expected, in the smectic phase the order parameter *S* is about 0.2 times larger than in the nematic phase. The magnitude and temperature dependence of *S* is again very similar to linear l.c.-side chain polymers.

CONCLUSION

There still remain questions concerning the ordering mechanism by stretching l.c.-side chain elastomers. It is not possible to find a simple model which predicts the molecular order as a function of the shape of the l.c.-side chains. In a theoretical model calculation, Wang and Warner considered at least five different energetic and entropic influences which determine the orientation behavior of l.c.-side chain polymers.[6] They postulated different nematic phases by ordering the l.c.-side chain parallel or perpendicular to the polymer main chain, as experimentally found in our systems. Experiments on polyacrylate

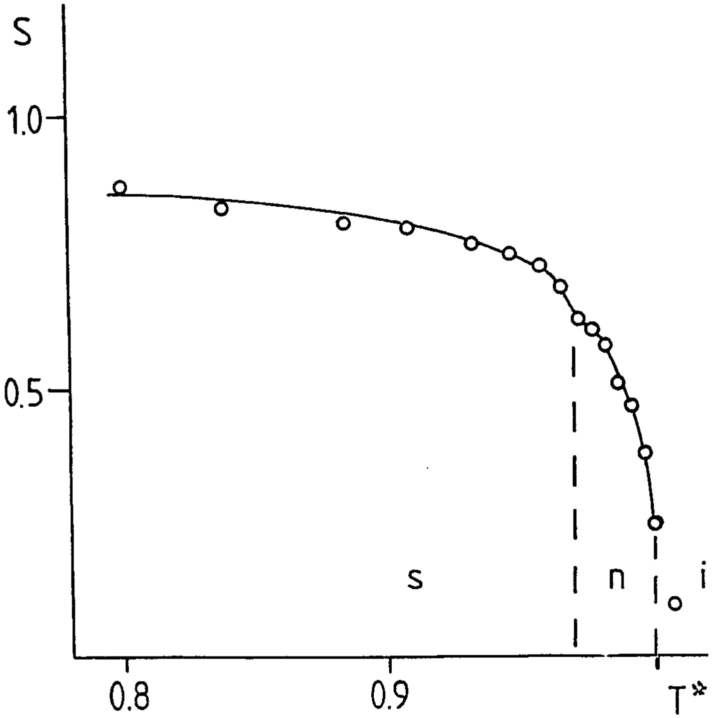

FIGURE 13 Temperature dependence of the order parameter S of elastomer C50. $T^* = T/T_c$

and polymethacrylate l.c.-side chain elastomers have shown that the shape of the polymer main chain also has an influence on the orientation behavior.[7] The change from the polyacrylate to the polymethacrylate elastomer with the same l.c.-side chain leads to another position of the director relative to the polymer main chain under stress. The fact that in the more flexible polyacrylate elastomer the orientation of the side chains is parallel to the main chain demonstrates that the flexibility of the main chain seems to have a strong influence on the orientation behavior. If this flexibility is high enough, the l.c.-side chains tend to align parallel to the main chain. Restrictions of this flexibility, as a consequence of a short spacer, rigid main chain or interactions between the l.c.-side chains lead to an orientation perpendicular to the main chain. Theoretical conformation analysis might help to understand these stress induced orientation effects.

The question of whether the magnitude of the applied stress has an influence on the nematic to isotropic phase transformation temperature and on the order parameter could not be clarified. For these experiments it is necessary to synthesize a more suitable network than the polysiloxane networks which can only be stretched up to 50%.

Acknowledgment

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