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Liquid Crystalline Side-Chain Polymers [and Discussion]

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Liquid crystalline side-chain polymers

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Liquid crystalline side-chain polymers are polymers that have linked conventional low molecular mass liquid crystals (l.c.) as side chains to a polymer backbone. Their properties are experimentally compared with the corresponding low molecular mass l.c. (i) Beginning with a monomeric l.c., with increasing degree of polymerization an increase of the phase transformation temperature of l.c. to isotropic is observed. (ii) The nematic order parameter of the monomers is about 10% higher than the order parameter of the polymers. Owing to the linkage of the rigid mesogenic molecules to the polymer backbone, their rotation around the long molecular axis differs strongly from that of the monomers. (iii) Owing to the high viscosity of the polymers their response times in the electric field are much larger than the response times of the monomers. If a sufficient length of the flexible spacer that connects the mesogenic molecule to the polymer main chain is assumed, the threshold voltages of the monomers and polymers are of comparable magnitude.

1. Introduction

During the last few years, polymers exhibiting a liquid crystalline state have become of increasing theoretical and technological interest because of their properties, which are a combination of polymer-specific properties and the anisotropic behaviour of liquid crystals (l.cs). Like the monomeric l.c. (m.l.c.) the polymeric l.c. (p.l.c.) can be differentiated by their chemical constitution (figure 1).

If we look at the monomer units of the polymer backbone, in most cases we can identify these units as having the same chemical constitution as m.l.cs. Three different structures are known: (i) non-amphiphilic cylindrical, (ii) non-amphiphilic disc-like and (iii) amphiphilic monomer units. To form a polymeric main chain these mesogenic elements can be connected in two different ways: (i) head to tail, forming 'l.c. main-chain polymers', and (ii) head to head, resulting in 'l.c. side-chain polymers' (figure 1).

While polymers consisting of disc-like monomers have not yet been achieved, the four remaining polymer types are known. By analogy with m.l.cs, thermotropic phase behaviour is almost only observed for the non-amphiphilic polymers.

In this paper I shall focus on the l.c. side-chain polymers. In their chemical constitution these polymers consist of two elements. One element is the polymer backbone, which can be widely varied in chemical and physical properties. The other element is the mesogenic side chain, for which also a large number of chemical constitutions are conceivable. One principal aspect of these polymers is whether polymer-specific properties are influenced by the anisotropic state of order of the mesogenic side chains and vice versa.

Compared with the monomeric l.c., in principle the only change of the mesogenic moiety is the restriction of translational and rotational motions due to the linkage to the backbone. These restrictions should be more or less influenced by the physical properties of the main chain and in which way the rigid mesogenic moiety is linked to the backbone.

With some experimental results in this paper I shall discuss the influence of the degree of polymerization on the l.c. phase behaviour of the polymers. Thereafter the state of order of m.l.cs will be compared with that of the chemically very similar polymers. Finally the behaviour of the polymers in an electric field will be compared with the behaviour of m.l.cs.

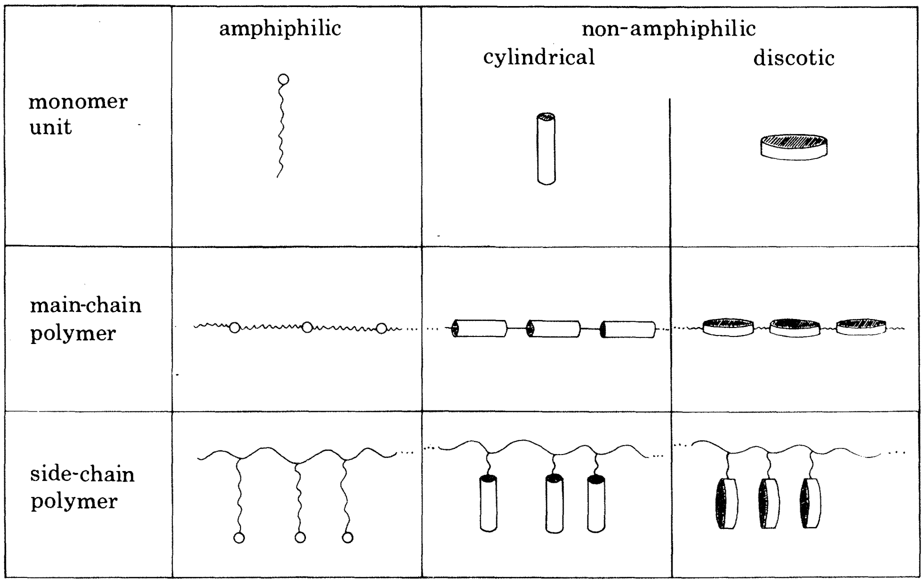
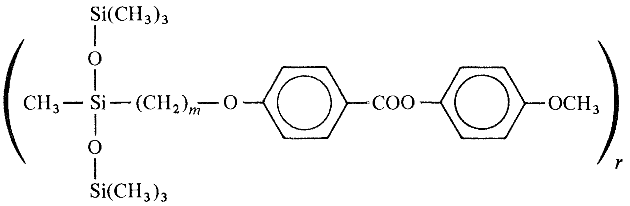


Figure 1. Scheme of liquid crystalline polymers.

2. Degree of polymerization

During the past few years it has been proved that nematic, cholesteric and smectic l.c. side-chain polymers can be made, exhibiting a thermodynamically homogeneous l.c. state (Finkelmann 1982). Starting from an l.c. monomer it has always been observed that because of the polymerization the extent of the l.c. phase of the monomer is strongly different from that of the polymer. To get a detailed insight into these mechanisms, Stevens *et al.* (1983) have investigated the phase behaviour as function of the degree of polymerizations of polysiloxanes:



A mixture of oligomers with different degrees of polymerization, r, were separated by gel permeation chromatography into monodisperse oligomers with defined r. The phase behaviour of these defined oligomers as function of r is shown in figure 2 for oligomers with spacer lengths $m = 3$ and $m = 6$. Polymers with $m = 3$ exhibit a nematic phase and polymers with $m = 6$ have additionally a low-temperature smectic phase. For both systems the same characteristic behaviour is observed. While the derivatives with $r = 1$ and $r = 2$ are not (or only metastable) liquid crystalline, for $r > 3$ the phase transformation temperatures from nematic to isotropic, T_{NI}, increase sharply with r and remain nearly constant for $r \approx 10$. The same behaviour is also observed for the transformation temperature T_{SN}, but r does not affect the transformation temperatures as much as for T_{NI}.

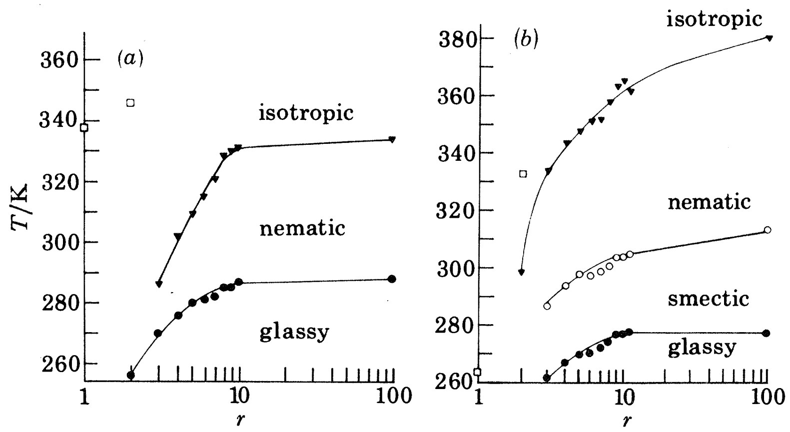


FIGURE 2. Phase behaviour of monodisperse oligomers as a function of the degree of polymerization, r: (a), $m = 3$; (b), $m = 6$. Squares: phase transformation crystalline to isotropic.

The change of the l.c. phase transformation temperatures towards higher temperatures with increasing r has been observed for all monomer–polymer systems investigated so far and can be established as a principal rule. Very often a change from nematic to the higher-ordered smectic phases is also observed. This 'stabilization' of the l.c. state by polymerization can be easily understood by the restriction of translational and rotational motions of the mesogenic molecules when they are linked to the polymer backbone.

Another important aspect resulting from the formation of the polymer main chain can be performed from figure 2. While the monomer and dimer ($r = 1$ or 2) crystallize, for $r > 3$ a crystallization is no longer observed at low temperatures but there is instead a transition into the glassy state. With increasing r the glass transition temperature also increases. This is well known for polymers. For this transition it should be noted that the structure of the l.c. phase observed at higher temperatures is converted into the glassy state without any macroscopically recognizable changes. This will be discussed in more detail in the next section.

3. DEGREE OF ORDER

On the basis of polarizing microscopic observations, nematic and cholesteric l.c. side-chain polymers qualitatively behave very similarly to m.l.cs. Textures and optical character (nematic phases, uniaxial positive; cholesteric phases, uniaxial negative) do not differ. On the other hand it is of interest whether the state of order is influenced when an m.l.c. is linked to a polymeric backbone. If a cylindrical symmetry of the mesogenic moieties is assumed, the state of order of the nematic phase can be described by the orientational order of the mesogenic molecules with respect to their long molecular axis $S = \frac{3}{2}(\cos^2\theta - \frac{1}{3})$, where θ is the angle between the long molecular axis and the director. The director is the symmetry axis of the orientational distribution function of the long molecular axis. In case of the polymers we refer S not to the whole macromolecule but to the mesogenic side chains of the monomer units of the macromolecule. By this way we neglect the polymer backbone. In figure 3 the chemical constitution is shown for three different systems, which will be compared with respect to S. S has been determined by Benthack *et al.* (1983) for a dye probe which is (*a*) dissolved in a monomer (M1), (*b*) dissolved in a polymer (P1) and (*c*) linked to the polymer (P2). The results are shown in figure 4. It is obvious that the m.l.c. and the p.l.cs show the same temperature dependence of S. At T_{NI} ($T^* = 1$), S vanishes discontinuously, indicating the first

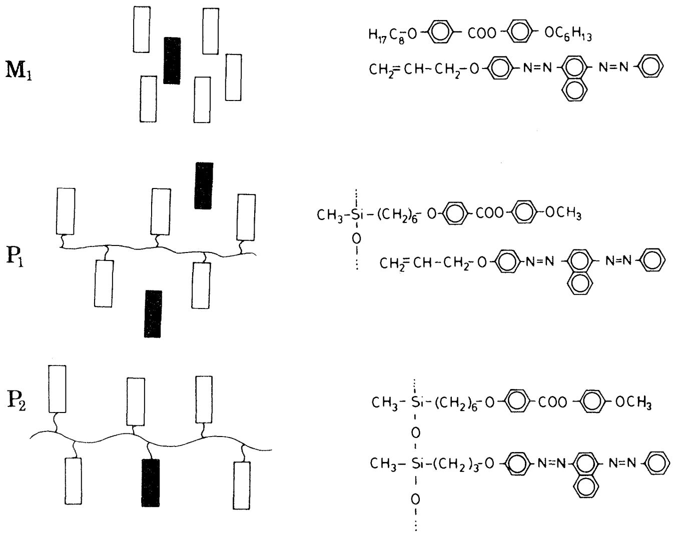


FIGURE 3. Chemical constitution of nematic phases incorporating a dye probe: M_1, a mixture of m.l.c. and dye; P_1, a mixture of p.l.c. and dye; P_2, copolymer of p.l.c. and dye.

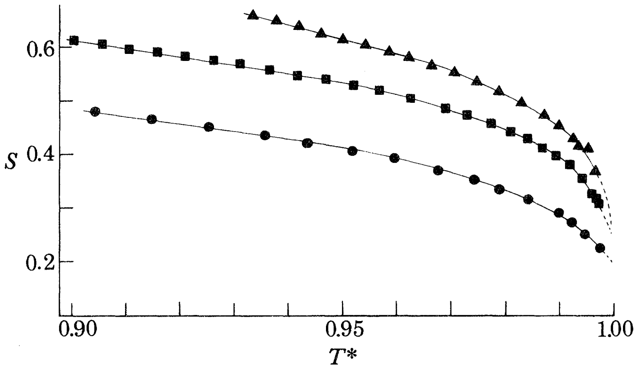


FIGURE 4. Temperature dependence of the order parameter, S, for three systems described in figure 3 ($T^* = T_m/T_{c1}$; T_m is measuring temperature; T_{c1} is phase transformation temperature, nematic to isotropic): ▲, M_1; ■, P_1; ●, P_2.

order phase transformation. Looking at a defined reduced temperature, T^*, we find that the dye dissolved in the monomer (M1) exhibits the highest-order parameter. For the dye dissolved in the polymer (P1) the order parameter is reduced for about 10%, which indicates that the polymer backbone disturbs the order of the nematic host. Birefringence measurements of S confirm these results. Furthermore it could be shown that S is not affected if the same mesogenic group is linked by flexible spacers of different lengths to the polymer main chain. An interesting effect is observed when the voluminous dye probe is also linked to the backbone in the copolymer (P2). Here the order of the dye is smaller than in the solution (P1). The decrease

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in S can be understood because of the direct linkage of the dye to the backbone. Owing to this linkage the dye cannot adapt the order of the host phase in the same way as in solution.

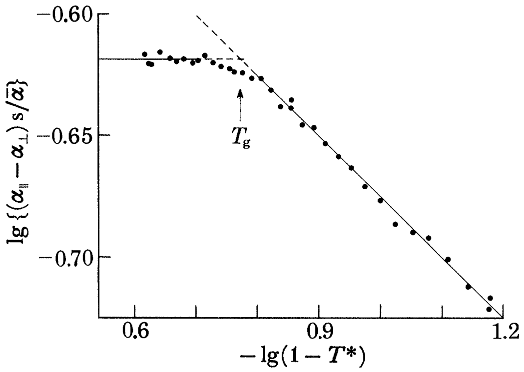


FIGURE 5. Temperature dependence of the order parameter, S, for a nematic polymer (Haller plot: $\alpha_\parallel$, $\alpha_\perp$ are molecular polarizabilities parallel and perpendicular to the molecular axis; $\bar{\alpha}$ = mean polarizability, for T^* refer to figure 4).

In figure 4 the order parameter S is shown for the polymers in the l.c. state. As mentioned before, in contrast to most m.l.cs the polymers very often exhibit at low temperatures a glass transition, which does not affect the optical properties of the system macroscopically. More detailed information is obtained if the temperature dependence of S is analysed passing through the glass transition. Following Haller *et al.* (1973), the graph of lg S against lg $(1-T^*)$, where $T^* = T_m/T_c$ (T_m being the measuring temperature and T_c the phase transformation temperature l.c.–isotropic), yields a straight line. This is demonstrated for a polymer in figure 5 from birefringence measurements.

In figure 5 the ordinate is the logarithm of $S\,\Delta\alpha/\bar{\alpha}$, which is directly proportional to S. As expected for high temperatures, the straight line indicates a normal change of S with temperature. At low temperatures, however, a bend in the curve indicates a change in the function $S(T)$. The straight line becomes parallel to the abscissa, which means that S is constant and no longer changes with temperature. By thermodynamic measurements the bend in the curve can be attributed to the glass transition. These optical measurements prove that not only the texture but also the nematic order freezes in at T_g. With these properties interesting applications are conceivable, e.g. the production of optical storage material.

For the nematic order parameter, the orientational distribution of the long molecular axis with respect to the director is considered by assuming a cylindrical symmetry of the mesogenic molecules or the mesogenic moieties linked as side chains to the backbone. At least for chiral molecules, however, no cylindrical molecular shape can be assumed. Following the theory of Goossens (1979), additional order parameters have to be considered, which also include the rotation of the mesogenic moieties around their long molecular axis.

An experimental method, which directly reflects on the rotation of the mesogenic molecules around their long molecular axis, is the induced twist observed if chiral molecules are dissolved in a nematic host phase. The induced twist depends directly on the concentration of the chiral guest molecules, their chemical constitution and on an order parameter S_r, which describes their rotation around the long molecular axis. If there is a free rotation ($S_r = 0$), no cholesteric twist will be induced. With increasing hindered rotation an increasing twist will be obtained.

A change of the rotation around the long molecular axis of an m.l.c. molecule should occur on varying the temperature. A much stronger effect on S_r, however, should be obtained, if the rigid mesogenic molecule is linked by different flexible alkyl chains to a polymer backbone. Whereas for the monomeric l.c. molecule their motions are only restricted by the anisotropic interactions with the neighbours, the motions of the mesogenic molecules, which are linked to a polymer backbone, are additionally restricted by this covalent linkage. With increasing length of the flexible spacer from the backbone to the rigid mesogenic moiety, increasing mobility and therefore a falling S_r and a falling induced twist are expected. This has been experimentally established (Finkelmann & Rehage 1980).

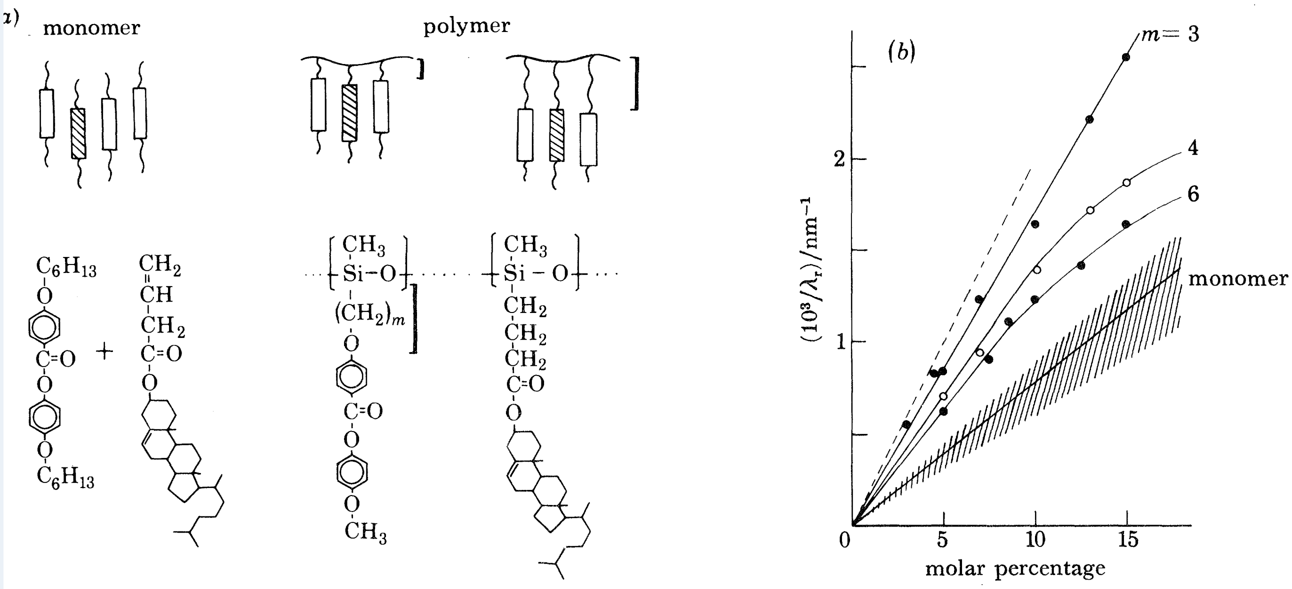


FIGURE 6. Inverse wavelength of reflexion, $1/\lambda_r$, of the induced cholesteric phase as a function of the concentration of chiral guest molecules (m is the length of the flexible spacer).

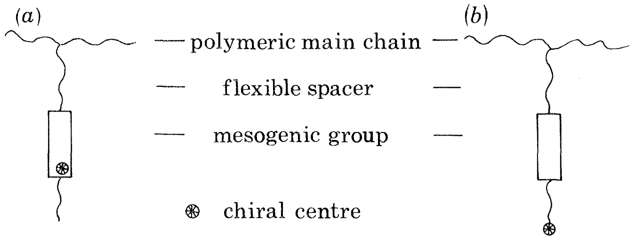


FIGURE 7. Scheme of chiral molecules with a chiral centre (*a*) within the rigid mesogenic group, and (*b*) linked by a flexible linkage to the rigid mesogenic group.

In figure 6*b* the inverse wavelength of reflexion, $1/\lambda_r$, of induced cholesteric phases (figure 6*a*), which are induced by chiral molecules, is shown as function of the concentration (in molar percentages) of the chiral guests. The inverse wavelength $1/\lambda_r$ is directly proportional to the induced twist.

For a constant concentration of the chiral guest the highest twist is observed if the mesogenic moieties are linked by a flexible spacer with three methylene groups ($m = 3$). With increasing length of the spacer, the twist becomes smaller. The lowest value of $(1/\lambda_r)_x$ is observed for the monomeric mixture.

To prove that the considerations of hindered rotation of the rigid mesogenic moieties are correct and that the experiments actually reflect this restriction of motions, we performed another experiment. This is presented schematically in figure 7. For the experiments mentioned above the chiral centres are within the rigid mesogenic part of the molecules (figure 7*a*). If, however, the asymmetric centre is also linked by a flexible linkage to the rigid mesogenic groups (figure 7*b*) a change in a hindered rotation of the mesogenic moiety should no longer strongly influence the chiral nematic twist. In this way it has to be presumed that the motions of the chiral groups are no longer correlated with respect to different kinds of linkages of the mesogenic moiety to the polymer main chain. These considerations are also confirmed by experiment (figure 8). If the monomer mixtures are compared with the polymer systems, only a small change in the induced twist can be observed, which might also be attributed to a change in the basic nematic order parameter. However, *no* difference is observed in the twist (i) for a mixture of the nematic polymer and the chiral monomer, (ii) for the copolymers with the nematic host and chiral guest molecules, and (iii) for the copolymers with different spacer lengths.

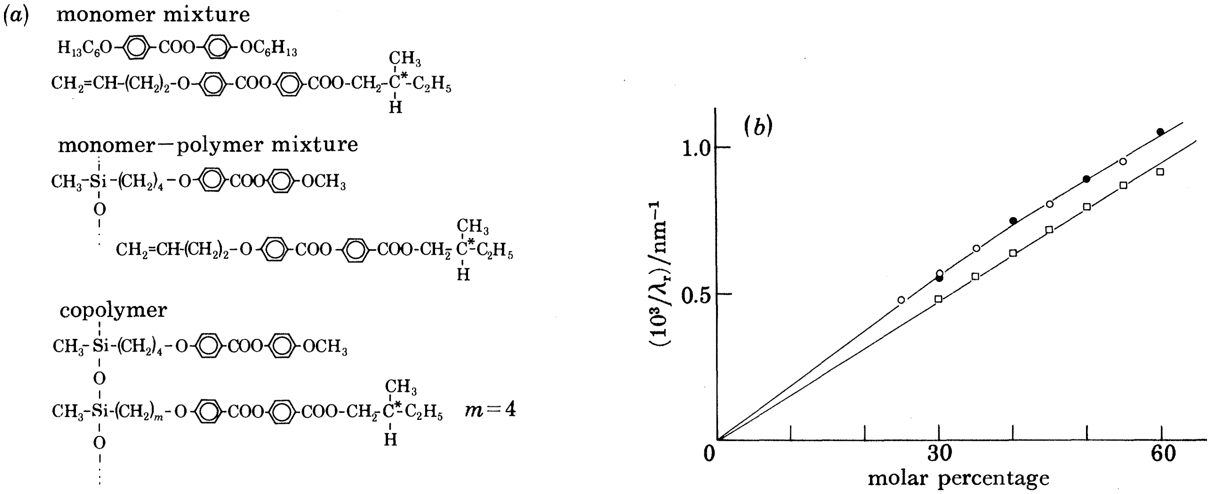


FIGURE 8. Inverse wavelength of reflexion, $1/\lambda_r$, of induced cholesteric phases as a function of the concentration of chiral guest molecules for: □, monomer mixture, ○, monomer–polymer mixture, and ●, copolymers.

These experimental results are of great interest in view of the theories of the cholesteric phase and the basic question of whether or not a hindered rotation of the molecules has to be considered. For our experiments, in principle the chemical constitution of the systems (e.g. the summation formula), which are compared, remains almost constant. Only the motions of the mesogenic moieties are changed by different kinds of flexible linkages to the polymer backbone. Following our experiments, the results are only consistent with the ideas of the theory of Goossens (1979), in which the cholesteric twist is explained by the hindered rotation of the chiral molecules around their long molecular axis.

4. BEHAVIOUR IN AN ELECTRIC FIELD

During the past few years m.l.cs have become of great commercial interest because of their applicability to display technology. A mushrooming number of new substances has been prepared, to optimize the physical properties of the material for their use in the different kinds of display cells. Here three basic parameters are of interest: the dielectric anisotropy, $\Delta\epsilon$, the elastic constants, k_{ii} and the viscosity, approximately represented by the bulk viscosity η. These parameters determine

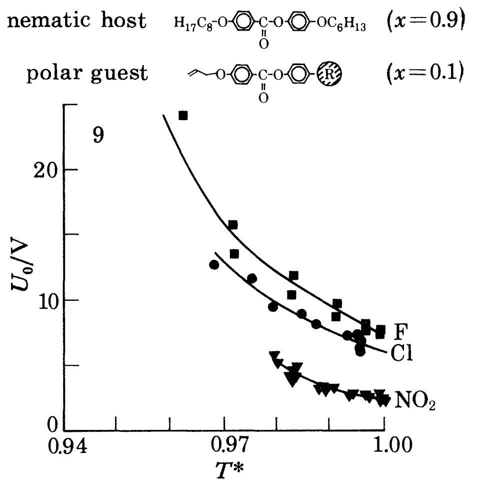
(i) the threshold voltage of the cells,

$$U_0 \propto (k_{ii}/\Delta\epsilon)^{\frac{1}{2}}, \tag{1}$$

and (ii) the response time of the display,

$$\tau_{\text{on/off}} \propto \eta. \tag{2}$$

The l.c. side-chain polymers are a completely new type of l.c. material and it is obvious to ask whether the polymers can be used in display technology or whether they bring prospects of new applications.



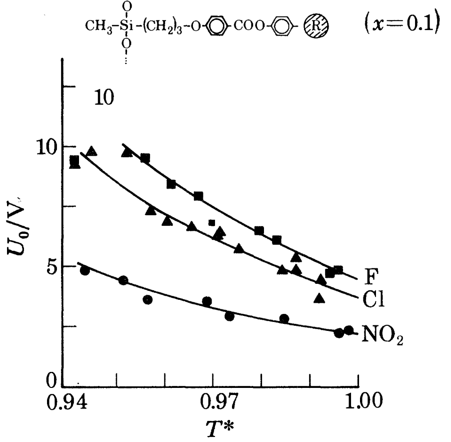


FIGURE 9. Temperature dependence of the threshold voltage of mixtures of monomers ($T^* = T_m/T_{NI}$).
FIGURE 10. Temperature dependence of the threshold voltage of copolymers.

Without doing any experiments we know that one property of the polymeric material strongly differs from that of the conventional l.c.: the viscosity of the polymer is larger by several orders of magnitude than that of the monomers. Therefore, referring to (2), we have to conclude that the response times of *pure* polymers are larger by several orders of magnitude than those of m.l.cs. Experiments confirm these considerations. If, however, the glass transition temperature T_g of the polymers is much smaller than the temperature of the experimental conditions, response times $\tau < 200$ ms have been observed (Finkelmann *et al.* 1979). With falling temperature, τ becomes infinite at T_g. To get a more detailed insight into the field effects of the polymers, Kiechle *et al.* (1983) compared the threshold voltage, U_0, of monomeric l.c. mixtures with chemically very similar copolymers in a TN display (sample thickness 15 μm, frequency 10 kHz).

In figure 9 the temperature dependence of U_0 is shown for monomer mixtures differing in the polarity of the substituent R of the polar guest molecule. According to (1), with increasing $\Delta\epsilon$ we observe a falling U_0. The same behaviour is observed for polymers with a spacer length of $m = 6$ (figure 10). If we compare the threshold voltage at a defined T^* we even observe $U_{0,\text{m.l.c.}} > U_{0,\text{p.l.c.}}$. As the chemical constitution of both systems, and thus also U_0, is very similar, the elastic constants of the m.l.c. and the p.l.c. must be of the same magnitude. Refer-

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ring to the measurements of the order parameters (§3), polymers with a spacer length $m = 6$ behave more similarly with regard to m.l.cs than polymers with $m < 6$. The rigid mesogenic, groups are less hindered by the polymer backbone than are short flexible spacers. This behaviour is also reflected by the threshold voltage, which is compared for polymers with different spacer lengths but the same chemical constitution (figure 11). Comparing U_0 at a constant T^* the threshold voltage increases strongly with decreasing spacer length and for $m = 4$ we found $U_0 > 50$ V. The copolymer with $m = 3$ did not show any field effects under the experimental conditions. Following the arguments mentioned above, we can conclude that the elastic constants of the polymers depend on the chemical constitution of the linkage of the mesogenic groups to the polymer backbone.

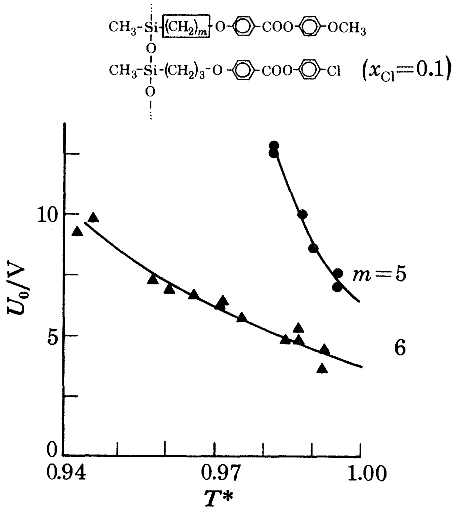

FIGURE 11. Threshold voltage U_0 as a function of the reduced temperature, T^*, for copolymers with different spacer lengths, m.

To summarize these results, an application of pure l.c. side-chain polymers in fast switching displays is not practicable. On the other hand, a characteristic property of the polymers is the glassy state and the possibility to freeze an l.c. texture in the glassy state. With this property it is possible to produce films. Above the glass transition temperature, an electric field can be used to put in information that can be durably stored at lower temperatures in the glassy state of the material.

REFERENCES

Benthack, H., Finkelmann, H. & Rehage, G. 1983 *J. Phys., Paris.* (In the press.)

Finkelmann, H. 1982 In *Polymer liquid crystals* (ed. A. Ciferri, W. R. Krigbaum & R. B. Meyer), ch. 2, p. 35. New York: Academic Press.

Finkelmann, H. & Rehage, G. 1980 *Makromol. Chem. rapid Commun.* **2**, 317.

Finkelmann, H., Ringsdorf, H. & Naegele, D. 1979 *Makromol. Chem.* **180**, 803.

Goossens, W. J. A. 1979 *J. Phys., Paris Colloq.* (Orsay, France), vol. 40, p. 158.

Haller, J., Huggins, H. A., Lilienthal, H. R. & McGuire, T. R. 1973 *J. phys. Chem.* **77**, 950.

Kiechle, U., Finkelmann, H. & Rehage, G. 1983 *Molec. Cryst. liq. Cryst.* (In the press.)

Stevens, H., Finkelmann, H., Lühmann, B. & Rehage, G. 1983 In *Liquid crystals and ordered fluids* (ed. J. S. Johnson & R. S. Porter), vol. 4. (In the press.)

Discussion

A. H. Price (*Edward Davies Chemical Laboratories, University College of Wales, Aberystwyth, U.K.*). Would Dr Finkelmann please indicate how the response times to an external stimulus vary between an 'ordinary' nematogen, a side-chain liquid crystal polymer and a main-chain polymer?

H. Finkelmann. As described in the paper, for an l.c. side-chain polymer the response time depends strongly on the vicinity of a glass transition, where a field effect can no longer be observed. With increasing distance to T_g, the response time falls and for some polymers $\tau < 200$ ms has been found at high temperatures (200 °C).

For l.c. main-chain polymers the response time depends on the degree of polymerization, r. For high molecular mass polymers, no field effects were observed. Detailed information about the response time as a function of r is not yet known.