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Fast switching films of nematic side chain copolymers

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Fast switching films of nematic side chain copolymers

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Liquid-crystalline side chain polymers may open interesting application possibilities in the area of display and optical data storage if the response times of these materials can be made sufficiently fast. Thin, well aligned films of nematic homopolymers and copolymers, containing covalently bonded dyes, have been prepared and the optical switching times for the Fréedericksz deformation depending on relevant polymer material and cell properties have been measured. It turns out that the switching times can be essentially shortened by raising the clearing temperature T_{IN}. This is due to the exponential dependence of the rotational viscosity γ_1 from the absolute temperature. We succeeded in lowering the switching time by nearly three orders of magnitude only by an enhancement of T_{IN} by 50°C, achieving the fast response of 2 ms with a nematic polymer.

1. Introduction

The research activities in the field of liquid-crystalline side chain polymers have grown steadily in recent years due to their promise in optical data storage applications [1, 2]. In these polymers the mesogenic groups are covalently bonded via flexible spacers to the polymer backbone. In addition, dichroic dyes can be covalently bonded to the polymer backbone as has been discussed recently by Ringsdorf and Schmidt [3, 4]. The mesogenic groups as well as the dichroic dyes can be well aligned and the orientational order of both can be frozen in by cooling the sample below the glass transition temperature [5]. Thin copolymer films of this kind are seriously discussed as suitable candidates for optical data storage because small micrometre-sized light scattering structures can be created and stored by laser heating followed by fast cooling [6]. These copolymers can be compared with corresponding mixtures of dichoric dyes dissolved in liquid-crystalline homopolymers [7]. Because of the covalent bonding of the dye the crystallization of the dye is sufficiently hindered to allow higher dye concentrations in the copolymers than in mixtures of dye monomers with homopolymers. Moreover, the sensitivity of the copolymer storage material can be easily enhanced and the laser energy for writing reduced further by raising the dye content of the copolymer.

The usefulness of the polymer material for optical data storage applications will, however, depend critically on the speed at which information can be written in and selectively erased. We are not yet in a position to measure the response times in thin micrometre-sized polymer spots. In a first approach we have investigated the macroscopic response times of very thin polymer films from the homogeneous planar quiescent state into a deformed quasi-homeotropic final structure. This allows us to look for the dependence of the switching speed on relevant polymer material and cell properties. In this context we have studied the influence of the mesogenic group, the dye content, the absolute temperature as well as the nematic–isotropic phase transition temperature on the optical response behaviour. Moreover, the dependence

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of the switching process from system properties such as the applied voltage and cell thickness has been explored. Earlier measurements on thick polymer samples showed response times in the minute and second range. With 2 μm thick samples we have now achieved switching times which are nearly three orders of magnitude faster, reaching the millisecond range.

2. Experimental

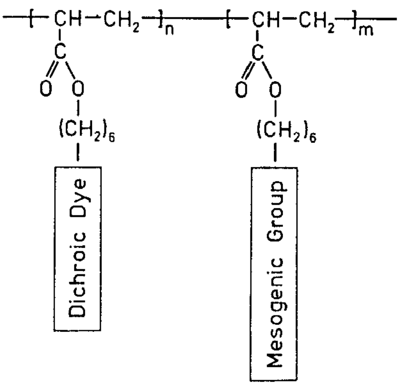
The schematic structures of the investigated liquid crystal polymers synthesized by Etzbach (BASF AG) are shown in table 1. All polymers are polyacrylates with an average molecular weight of about 15 000. The homopolymer Ben possesses a cyanophenylbenzoate as mesogenic group and has a broad nematic phase range. The homopolymer Bi includes a cyanobiphenyl as mesogenic group and contains only a narrow nematic phase, but in addition contains a smectic A and a re-entrant nematic phase [8].

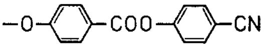
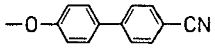
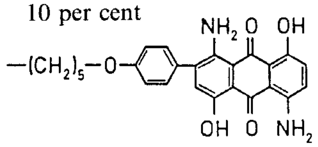
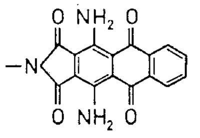
The copolymers Ben 10 DAH and Bi 10 DAH include, respectively, 10 per cent of a blue diamino-dihydroxy anthrachinone dye as shown in table 1. Evidently addition of the dye lowers the clearing temperatures of both polymers. The existence of a re-entrant nematic phase in the case of the copolymer Bi 10 DAH cannot yet be completely ruled out. Addition of 20 per cent of the blue diamino anthrachinone dye as given in table 1 further depresses the clearing temperatures of the copolymers Ben 20 DA and Bi 20 DA and suppresses completely the smectic A phase of the copolymer Bi 20 DA. The glass transition temperatures and the nematic–smectic A transition temperatures have been measured by differential scanning calorimetry (D.S.C.) studies [9]. In order to guarantee that the switching times at the temperatures nearest to the clearing temperature will be measured in the pure nematic phase and not in the biphase region, the nematic–isotropic phase transitions have been determined by polarizing microscopy. In order to achieve fast-switching samples the polymer cells must be very thin. They possess the usual symmetrical sandwich arrangement. Indium–tin oxide (ITO) was deposited on the cleaned glass substrates with a thickness of λ_{12} (λ = 0·633 μm) for maximum transmission and a sheet resistance of 10–20 Ω mm^{-2} by a sputtering technique. After this a 1000 Å thick quartz layer was coated on to the ITO layer to avoid electrical breakdown. A very good, stable, homogeneous planar alignment of the polymers with a small surface tilt angle was achieved by a rubbed polyimid layer. The small surface tilt angle avoided the appearance of domains with reverse tilts which would strongly influence the switching times.

The preparation of our cells was as follows. The polymer was melted and degased. Then a small drop of melted polymer was placed on the preheated lower glass plate and the upper plate was pressed down by a suitable cell holder, without using any spacer within the active cell area. The variation in cell thickness across the cell was minimized by carefully adjusting and regulating the pressure on the glass plates by different screws of our cell holder until at most one interference fringe was visible over an active electrode area of 0·6 cm^2. Our measuring cells were typically 2 μm thick and the precise cell thicknesses were determined by two independent methods as presented in table 2. First, the transmission as a function of wavelength of the filled cell was recorded in the isotropic phase. From the interference curve, the thickness has been calculated using isotropic refractive indices determined by a Abbé refractometer. The second method works only for the dye-containing polymers. The dye absorption of a small, well defined area of diameter 5 mm has been measured. Using the well known

Table 1. Schematic structures and phase transition temperatures of the investigated homopolyacrylates Ben and Bi, the copolymers Ben 10 DAH and Bi 10 DAH including 10 per cent of a diamino-dihydroxy-anthrachinon dye as well as the copolymers Ben 20 DA and Bi 20 DA containing 20 per cent of the diamino anthrachinone dye. The dye concentrations are given in weight percentages. The g–N, g–S_A, and S_A–N phase transitions were determined by D.S.C. studies [9]. The N–I transitions were measured by polarizing microscopy on our thin samples. The N_{re}–S_A transition originates from [8].

Dye Containing Liquid Crystalline Copolymers



	Mesogenic group	
Homopolymers	 Ben g 34 N 136 I	 Bi g 46 N_{re} 82 S_A 126 N 133·8 I
Copolymers with dichroic dye 10 per cent 	Ben 10 DAH g 33 N 127 I	Bi 10 DAH g 42 N_{re} 7 S_A 115 N 126·5 I
20 per cent 	Ben 20 DA g 50 N 106·5 I	Bi 20 DA g 41 N 116·5 I

extinction coefficient of the dye-containing polymer as determined by a calibration measurement on a thicker cell, the cell thickness has been evaluated. We estimated that the variation in cell thickness across the active electrode area should not exceed 0·1 μm. The interference measurement was made on a small area of diameter 1 mm, which is identical with the spot around which the laser beam detects switching of the

Table 2. Cell thickness (in μm) of the polymer cells as evaluated by two independent methods.

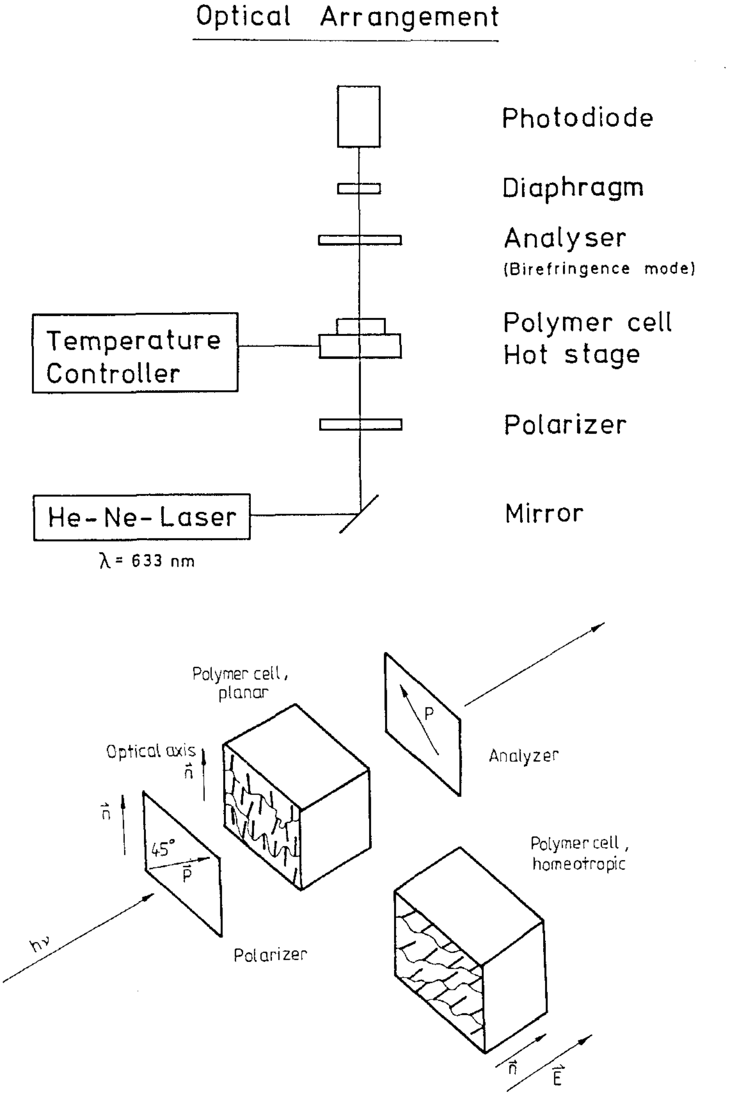
Polymer	Interference	Absorption
Bi	2·55	
Ben	2·24	
Bi 10 DAH	2·23	2·07
Ben 10 DAH, A	2·33	2·48
Bi 20 DA	1·62	1·50
Ben 20 DA	1·56	1·61
Ben 10 DAH, B	1·35	1·29
Ben 10 DAH, C	1·94	1·71
Ben 10 DAH, D	5·25	5·46
Ben 10 DAH, E	3·42	
X	2·25	

cell. We therefore prefer the thickness values from the interference measurements whose maximum error should not exceed 5 per cent. The thickness values as determined by the absorption method may have a larger error, because an average was taken over an larger measuring area. Nevertheless, the agreement between the results as evaluated by the two methods is satisfactory and amounts at most 10 per cent. No attempt has been made to correct the response times for the differences in cell thicknesses especially for the polymers Bi 20 DA and Ben 20 DA (see table 2). The homogeneity of the alignment as well as the switching behaviour of the measuring cells were always checked by microscopic observation and only high quality cells were used for the switching experiments.

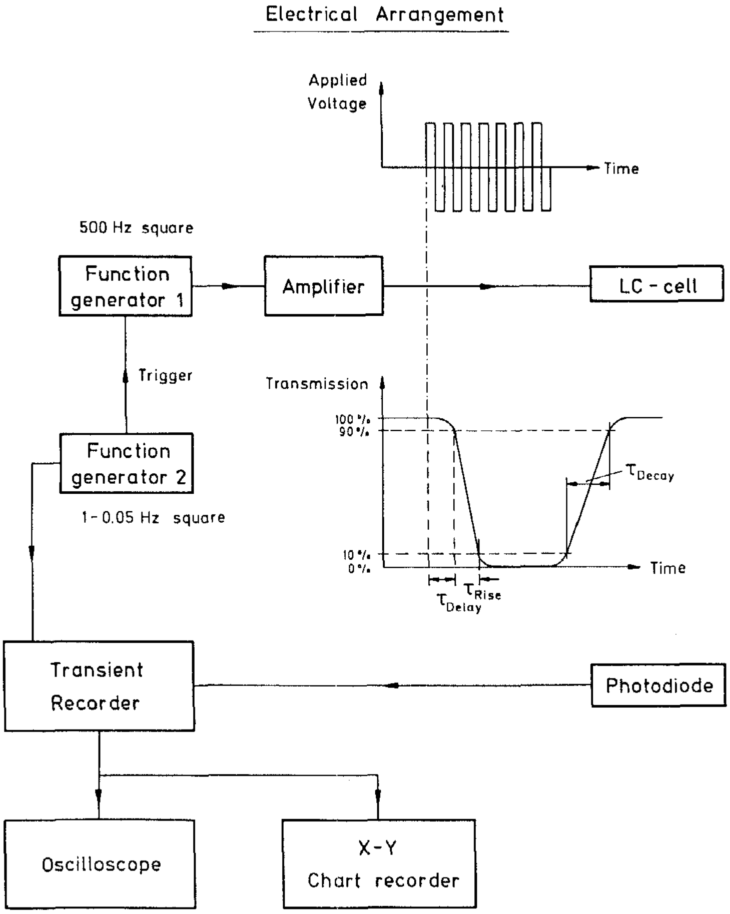
Figure 1 (*a*) shows the optical arrangement for measuring the switching time from the homogeneous planar quiescent state into a deformed quasi-homeotropic final state, well known from the literature as Fréedericksz deformation. The light of a 2 mW continuous wave He–Ne laser ($\lambda = 633$ nm) is plane polarized by a polarizer. The direction of polarization makes an angle of 45° with the optical axis of the polymer slab possessing birefringence Δn. The cell is placed between two polarizers and the temperature of the cell is controlled in a hot stage system with a stability of about 0·05°C. In order to achieve a good contrast ratio we always tried to adjust our cell thicknesses d for the lowest measurable temperature as near as possible to $d = \lambda/2\Delta n$, corresponding to the first transmission maximum between crossed polarizers. Applying an electric field perpendicular to the glass plates, the optical axis turns parallel to the electric field direction and the birefringence as well as the transmission diminishes. The change of the transmission is detected by a fast photodiode. The response times of the dye-containing polymers can alternatively be measured by observing the change in the dye absorption during application of the electric field. This can be done because our blue dyes absorb the light of the He–Ne laser very well. In this case only one polarizer is used and the direction of polarization is chosen parallel to the optic axis, which coincides with the direction of maximum absorption of the anthrachinone dyes. The response times of all the dye-containing polymers have been measured by detecting the alternation of the dye absorption. However, some care must be taken because optical response times evaluated from birefringence or absorption measurements can lead to very different results [10]. We have therefore determined additionally, at some representative temperatures and for various voltages, the rise times of all our copolymers in the birefringence mode, and found a satisfactory agreement with the results from the absorption measurements.

Figure 1 (*b*) shows the electrical arrangement of our experiment. The polymer cell is switched by a 500 Hz square voltage impulse produced by the function generator 1. The repetition rate of the voltage impulse is determined by the second function generator 2, which also starts the transient recorder to store the electrical signal from the photodiode.

The response time τ_{Rise} is defined in the birefringence mode as shown in figure 1 (*b*). Taking the maximum (field-free state) and minimum values of transmission (field-on state) as 100 and 0 per cent, respectively, τ_{Rise} is the time required to change the relative transmission from 90 to 10 per cent. In the absorption mode τ_{Rise} is conversely defined going from 10 to 90 per cent transmission. Here we report exclusively measurements



(*a*)



(*b*)

Figure 1. (*a*) Schematic diagram of the optical arrangement used to study the optical response of liquid-crystalline polymer samples in the birefringence mode. (*b*) Schematic diagram of the electrical arrangement and definition of the optical response times τ_{Delay}, τ_{Rise} and τ_{Decay}.

of the rise times. The experimental error of τ_{Rise} should not exceed 20 per cent. The response time τ_{Rise} for the transition from the homogeneous planar state into the deformed quasi-homeotropic structure is given approximately by [11]

$$\tau_{\mathrm{Rise}} = \alpha \frac{\gamma_1 d^2}{\pi^2 K_{11}(U^2/U_0^2 - 1)}, \tag{1}$$

where γ_1 represents the rotational viscosity, d the cell thickness, K_{11} the splay elastic constant, U the applied voltage and α is a proportionality constant, not known exactly because of the approximations included in equation (1). With the threshold voltage $U_0 = \pi(K_{11}/\varepsilon_0 \Delta\varepsilon)^{1/2}$, equation (1) can be rewritten as

$$\tau_{\mathrm{Rise}} = \alpha \frac{\gamma_1 d^2}{\varepsilon_0 \Delta\varepsilon} \frac{1}{(U^2 - U_0^2)}, \tag{2}$$

where $\Delta\varepsilon$ denotes the dielectric anisotropy. According to this relationship the rise time for a given material should be made shorter by applying high voltages and using thin cells. Equation (1) was derived with the following assumptions.

(*a*) Only small deformations (low voltages) are assumed.
(*b*) Surface pre-tilt is not considered.
(*c*) Surface and anchoring effects are not taken into account properly.
(*d*) τ_{Rise} is derived for the director's reorientation time and need not agree with the optical response time as defined in figure 1 (*b*) measured in the birefringent or in the absorption mode. Depending on the phase retardation, the optical response may differ from the director's reorientation time up to a factor of four [12]. Because of all these approximations, τ_{Rise} is only determined up to a proportionality constant and it is in general not possible to evaluate material properties such as γ_1 from measurements of the optical response times. Moreover, optical response times as evaluated from birefringence or absorption measurements can lead to very different results [10].

We have made the following checks of equation (2).

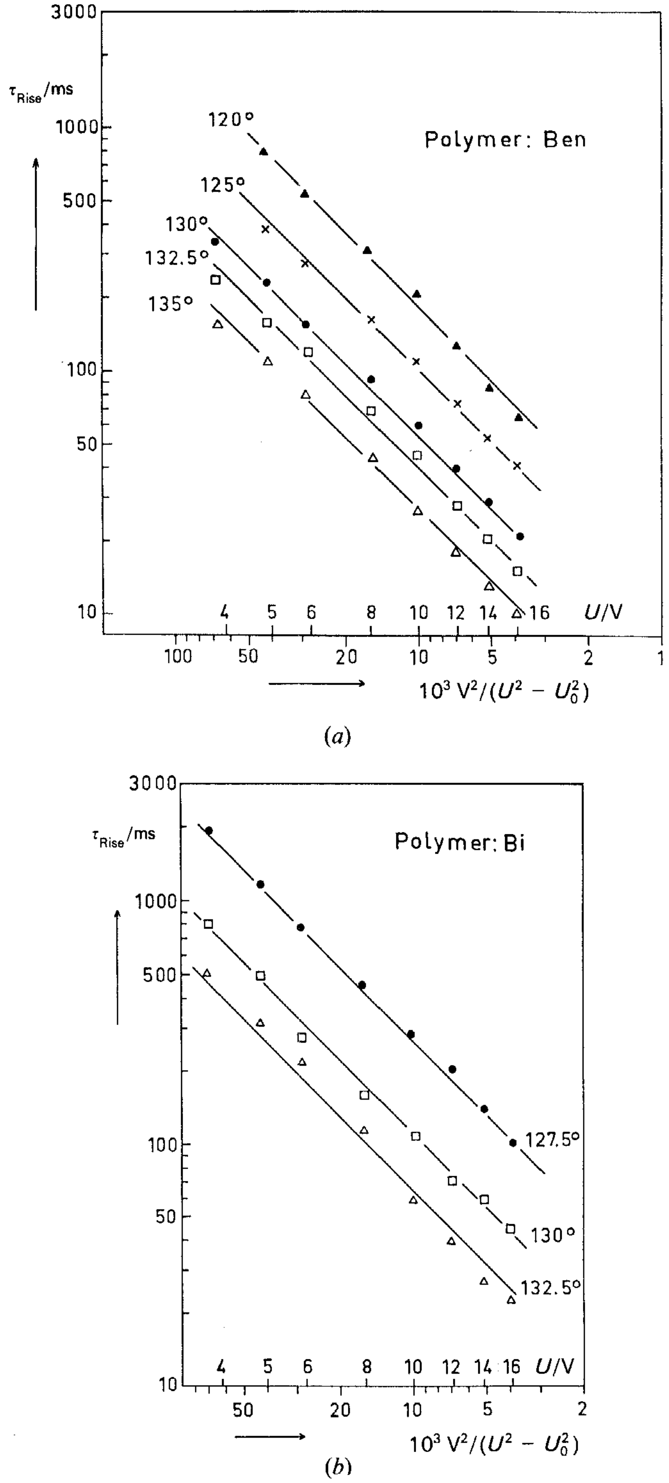
(*a*) The voltage dependence of τ_{Rise}.
(*b*) The temperature dependence of τ_{Rise}. Because the investigated temperature ranges are always relatively narrow and far from the glass transition temperature, it is sufficient to assume in a first approximation an exponential temperature dependence of γ_1 according to an Arrhenius function:

$$\gamma_1 \sim \exp(B/T) \quad \text{or} \quad \log\gamma_1 \sim B/T, \tag{3}$$

where T is the absolute temperature and B is a constant. Sufficiently far from the nematic–isotropic phase transition (about 5°C) the temperature dependence of γ_1 becomes dominant over that of $\Delta\varepsilon$ and U_0 [13] and, according to equations (2) and (3), an approximately linear relationship is expected between $\log\tau_{\mathrm{Rise}}$ and $1/T$.
(*c*) The thickness dependence of τ_{Rise}.

3. Results

The rise time τ_{Rise} is depicted versus $1/(U^2 - U_0^2)$ in figure 2 on a doubly logarithmic scale for different temperatures and for the homopolymers Bi and Ben. Look first at the results for the polymer Bi. For a given temperature the voltage dependence can be approximated well by a straight line with slope 1, confirming the $1/U^2$ dependence of τ_{Rise} on the applied voltage. The lines for different temperatures show the same slope. This is expected from the doubly logarithmic depiction. The described features are also observed for the homopolymer Ben. Comparing the rise times of the polymers Bi and Ben at an applied voltage of 16 $\mathrm{V_{rms}}$ and at the temperature $T = T_{\mathrm{IN}} - 1$°C we measured a rise time of 25 ms for the polymer Bi but a faster rise time of 10 ms for the polymer Ben. To our knowledge this is the fastest response time which has yet been measured for a nematic side chain polymer, but as we will see later a further enhancement of the response speed has been achieved. It is worthwhile to compare the results for the polymers Bi and Ben with corresponding low molecular weight liquid crystals. Combining the results for the ratio γ_1/K_{11} given in [14, 15] a binary mixture of cyanobiphenyls shows a lower ratio of γ_1/K_{11} and therefore a faster response than a mixture of cyanophenylbenzoates. The corresponding polymers Bi and Ben



(a)

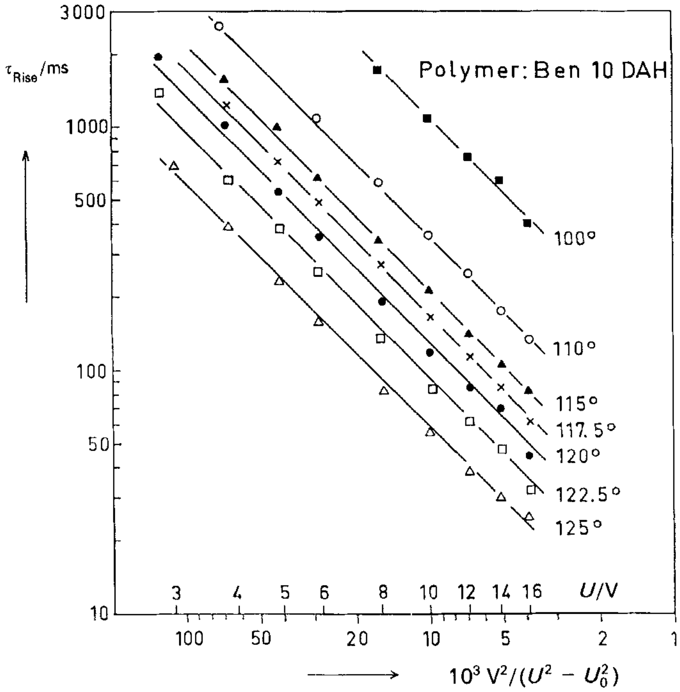
(b)

Figure 2. Voltage dependence of τ_{Rise} for the homopolymers (a) Ben and (b) Bi at different temperatures. In the figure τ_{Rise} is shown as a function of $1/(U^2 - U_0^2)$ on a doubly logarithmic scale.

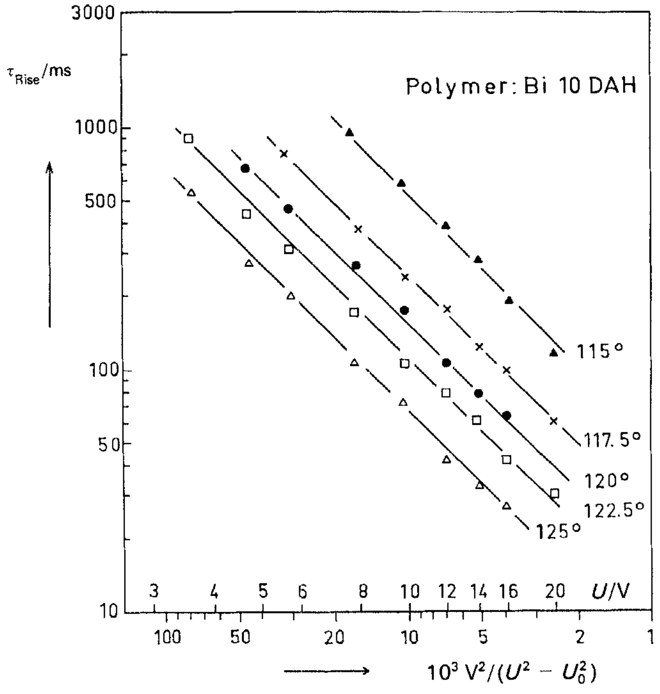
evidently reveal the opposite behaviour. This may be explained mostly by the narrow nematic phase and the neighbouring S_A phase of the polymer Bi, which strongly extend the rise times.

The response time τ_{Rise} as a function of $1/(U^2 - U_0^2)$ is given comprehensively in figures 3 (*a*)–3 (*d*) for the dye-containing copolymers Ben 10 DAH, Ben 20 DA, Bi 10 DAH and Bi 20 DA. For all copolymers and at all temperatures the inverse square dependence of the rise time on the applied voltage holds with a precision of about 10 per cent. Looking at the influence of the dye on the response times, we first compare τ_{Rise} ($16\,V_{rms}$, $T = T_{IN} - 1°C$) of Ben 10 DAH and Bi 10 DAH. For both polymers we observe about the same rise time of 25 ms. Addition of the dye broadens the nematic phase and suppresses the influence of the S_A phase on the rise times in the case of the cyanobiphenyl copolymer. Probably because of this the rise time is nearly unchanged by addition of the dye. In contrast to this behaviour, the rise time of the copolymer Ben 10 DAH, which possesses a broad nematic phase, is lengthened by a factor of 2·5 by addition of the dye. We now compare the response times of the polymers Bi 20 DA and Ben 20 DA, each containing 20 per cent of dye. Both polymers possess similarly broad nematic phases, which makes the comparison more suitable. About 1°C below the clearing temperature and with an applied voltage of $16\,V_{rms}$ we observe for the polymer Ben 20 DA a rise time of about 300 ms and for the polymer Bi 20 DA the faster rise time of 140 ms. No attempt has been made to correct these response times for the differences in cell thicknesses (table 2) as the dyes of the 10 per cent and 20 per cent dye containing polymers distinguish from each other and we are only interested in observing the essential features. In figure 4 the influence of the dye content on the rise times is summarized for $T = T_{IN} - 1°$. Both the cyanophenylbenzoate polymer and the cyanobiphenyl polymer show a strong enhancement of the rise times if the dye concentration is increased. However, the dependence is weaker in the case of the cyanobiphenyl polymer. This may be explained mainly by the narrow nematic phase and the neighbouring S_A phase, which lengthen the rise times of the cyanobiphenyl polymers without dye and with dye content of 10 per cent.

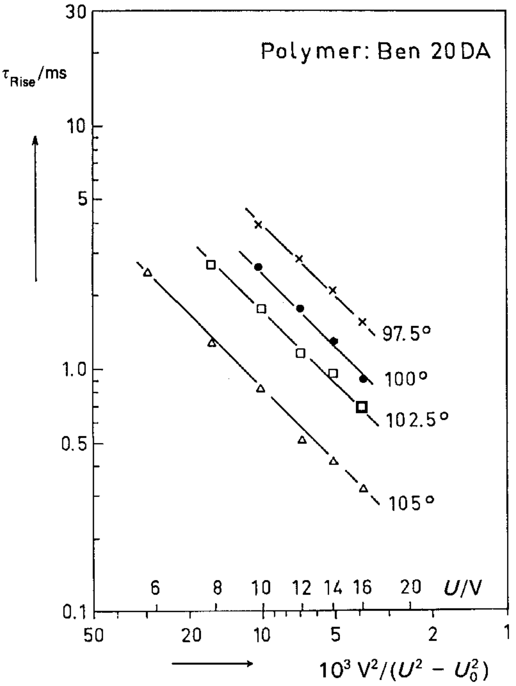
The temperature dependence of the rise times for different voltages is shown in figure 5 for the polymer Ben. We have depicted τ_{Rise} on a logarithmic scale as a function of the reciprocal of the absolute temperature. Except near the nematic–isotropic phase transition temperature, a linear relationship between $\log \tau_{Rise}$ and $1/T$ can be seen. The dielectric anisotropy $\Delta\varepsilon$ as well as U_0 for all of the polymers investigated depend only weakly on temperature for $T \leqslant T_{IN} - 5°C$ [13]. This implies that the temperature dependence of the ratio $\gamma_1/\Delta\varepsilon$ is mainly governed by the rotational viscosity γ_1 and the linear relationship between $\log \tau_{Rise}$ and $1/T$ as shown in figure 5 confirms the exponential law for γ_1 according to equation (3) if we are sufficiently far from the nematic–isotropic phase transition. The slight bending down in the neighbourhood of the clearing temperature may be due to the decrease of the degree of order. This means that by approaching to the clearing point the rotational viscosity decreases more strongly than the dielectric anisotropy $\Delta\varepsilon$. The corresponding temperature dependences of the rise times for the dye-containing cyanophenylbenzoate copolymers Ben 10 DAH and Ben 20 DA are presented in figures 6 (*a*) and 6 (*b*). Ben 10 DAH also shows the linear relationship between $\log \tau_{Rise}$ and $1/T$ as well as the slow bending down near the clearing temperature. The same is true for the copolymer Ben 20 DA but the bending down of the curve is stronger and the straight line holds for only a very narrow temperature range. It cannot be followed to lower


Polymer: Ben 10 DAH
τ_{Rise}/ms
3000
1000
500
100
50
10
100°
110°
115°
117.5°
120°
122.5°
125°
3 4 5 6 8 10 12 14 16 U/V
100 50 20 10 5 2 1
$10^3\,V^2/(U^2-U_0^2)$

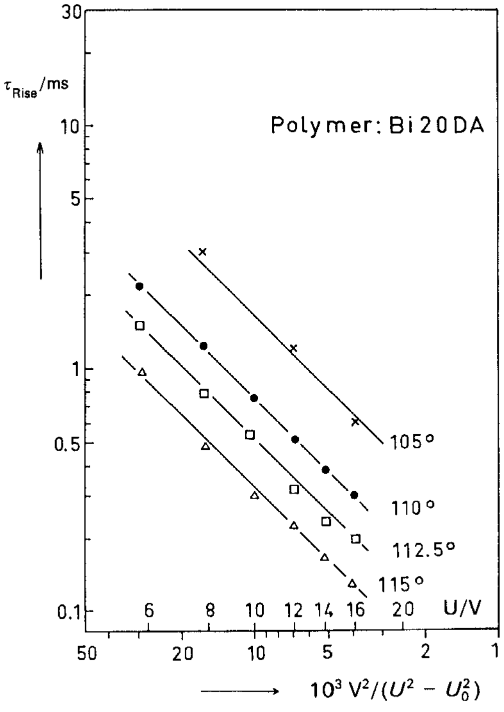
(*a*)


Polymer: Bi 10 DAH
τ_{Rise}/ms
3000
1000
500
100
50
10
115°
117.5°
120°
122.5°
125°
3 4 5 6 8 10 12 14 16 20 U/V
100 50 20 10 5 2 1
$10^3\,V^2/(U^2-U_0^2)$

(*b*)



(*c*)



(*d*)

Figure 3. Voltage dependence of τ_{Rise} for the various dye-containing copolymers (*a*) Ben 10 DAH, (*b*) Bi 10 DAH, (*c*) Ben 20 DA and (*d*) Bi 20 DA. τ_{Rise} is given as a function of $1/(U^2 - U_0^2)$ at different temperatures on a doubly logarithmic scale.

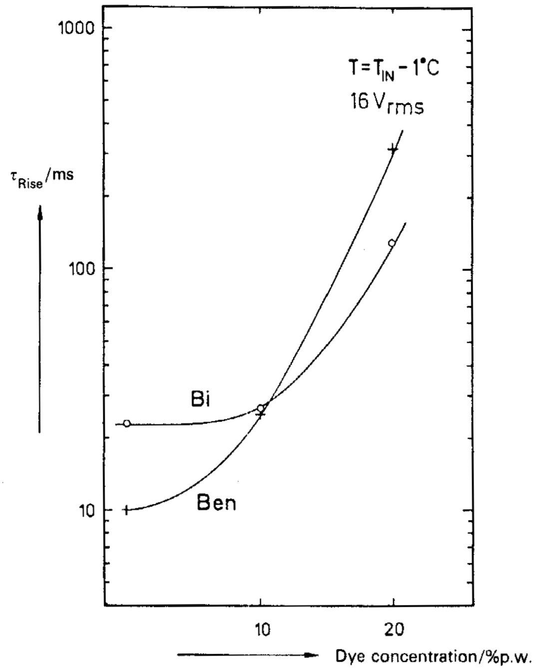


Figure 4. Variation of the rise time depending on the dye content for the polyacrylates containing two different mesogenic groups (Bi and Ben).

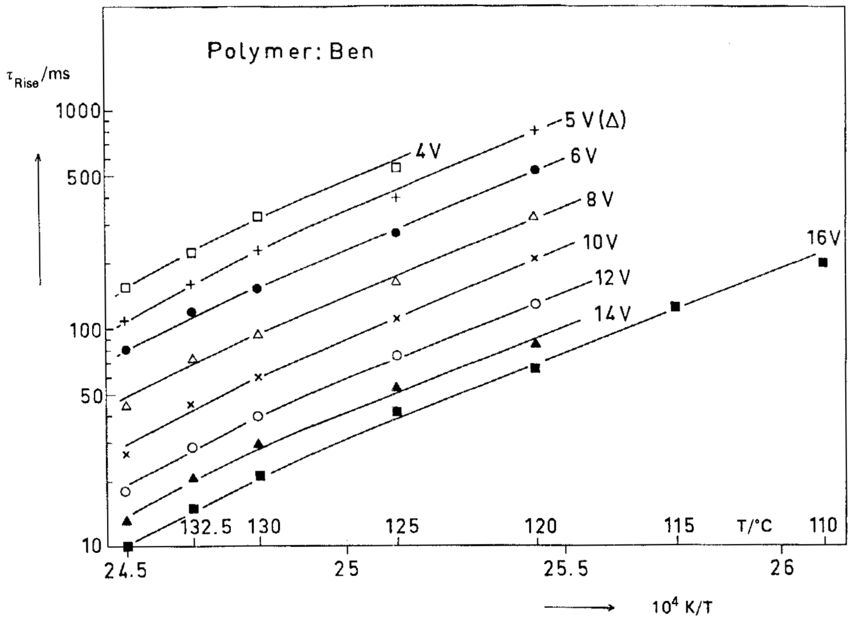
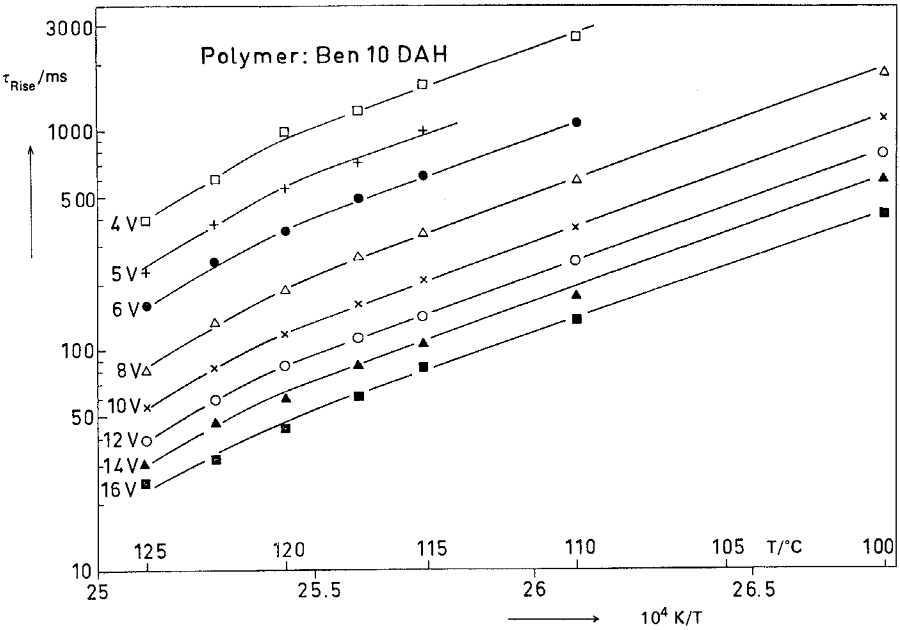
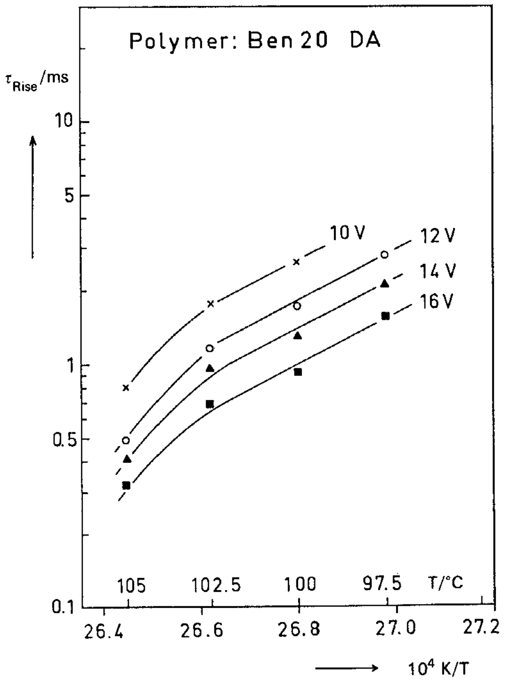


Figure 5. Variation of the rise time as a function of the reciprocal of the absolute temperature T for the homopolymer Ben. τ_{Rise} is shown on a logarithmic scale versus $1/T$ for different voltages.



(a)



(b)

Figure 6. Variation of the rise time as a function of the reciprocal of the absolute temperature T for the dye-containing copolymers (a) Ben 10 DAH and (b) Ben 20 DA. τ_{Rise} is plotted on a logarithmic scale versus $1/T$ for different voltages.

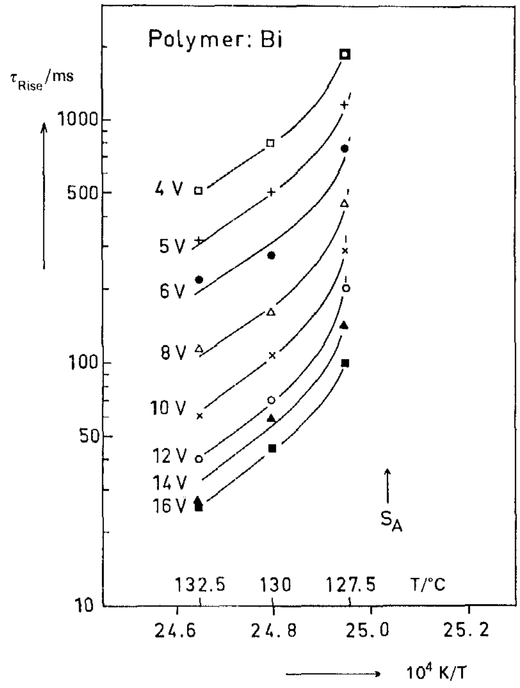


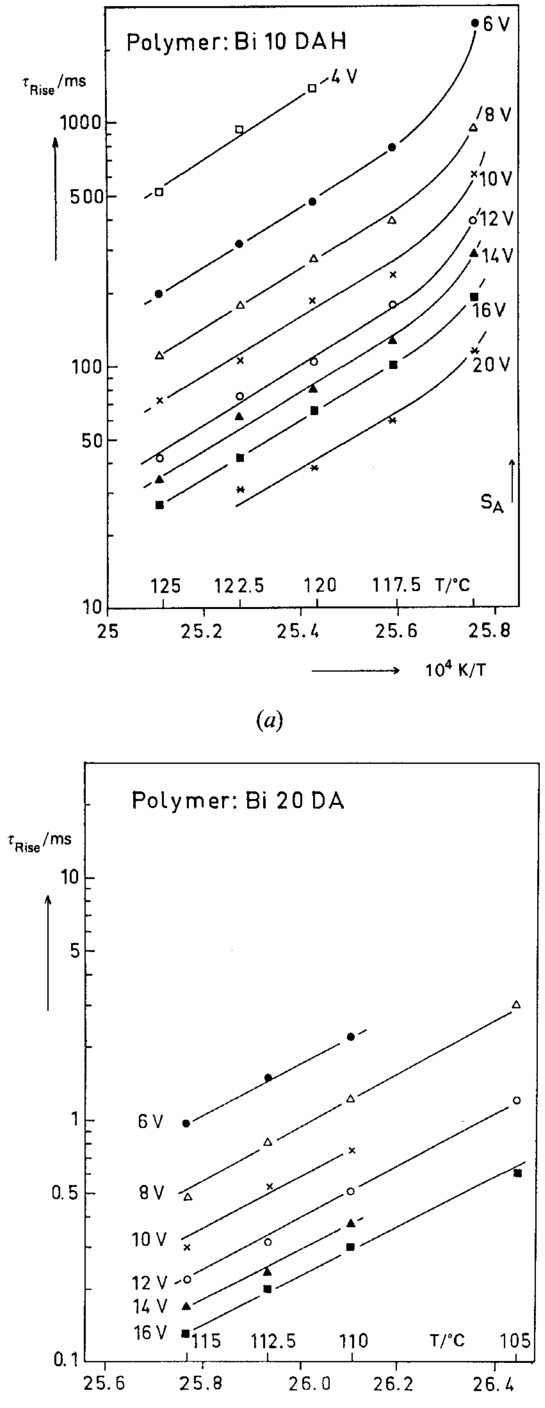
Figure 7. Variation of the rise time as a function of the reciprocal of the absolute temperature T for the homopolymer Bi. τ_{Rise} is depicted on a logarithmic scale versus $1/T$ for different voltages.

temperatures because the switching times became too slow to be measured and the switching no longer occurs in an uniform manner.

Figure 7 presents in an analogous way τ_{Rise} as a function of $1/T$ for the cyanobiphenyl polymer Bi. The deviation from the linear relationship can be seen clearly. Because of the neighbouring S_A phase, the rise times are strongly enhanced near the nematic–S_A phase transition. The splay deformation is not forbidden in the S_A phase and the splay elastic constant K_{11} shows no extraordinary behaviour near the nematic–S_A phase transition [16]. Therefore, the strong increase of τ_{Rise} described may be due to a diverging behaviour of the rotational viscosity γ_1, which is a well known fact from low molecular weight liquid crystals [17].

The corresponding results for the temperature dependence of the rise times for the dye-containing cyanobiphenyl copolymers Bi 10 DAH and Bi 20 DA are depicted in figures 8 (*a*) and 8 (*b*). For both polymers we can observe in a narrow temperature range a linear relationship between $\log \tau_{Rise}$ and $1/T$. In the case of the polymer Bi 10 DAH a strong enhancement of τ_{Rise} is again ascertained near the nematic–S_A phase transition. However, no slow bending down behaviour of τ_{Rise} has been observed near the nematic–isotropic phase transition for any of the cyanobiphenyl polymers.

It is interesting to look at the thickness dependence of the rise time. Preliminary results are given in figure 9, where τ_{Rise} is plotted versus the cell thickness d on a doubly logarithmic scale. The straight lines with $x = 1$ and $x = 2$ represent a theoretical, linear or square dependence of τ_{Rise} on d. According to equation (1) τ_{Rise} should be proportional to d^2. Conversely, our measurements suggest that in the thickness range 1–3·5 μm a linear dependence on d seems more probable. However, we can only



(a)

(b)

Figure 8. Variation of the rise time as a function of the reciprocal of the absolute temperature for the dye-containing copolymers (a) Bi 10 DAH and (b) Bi 20 DA. τ_{Rise} is depicted on a logarithmic scale versus $1/T$ for different voltages.

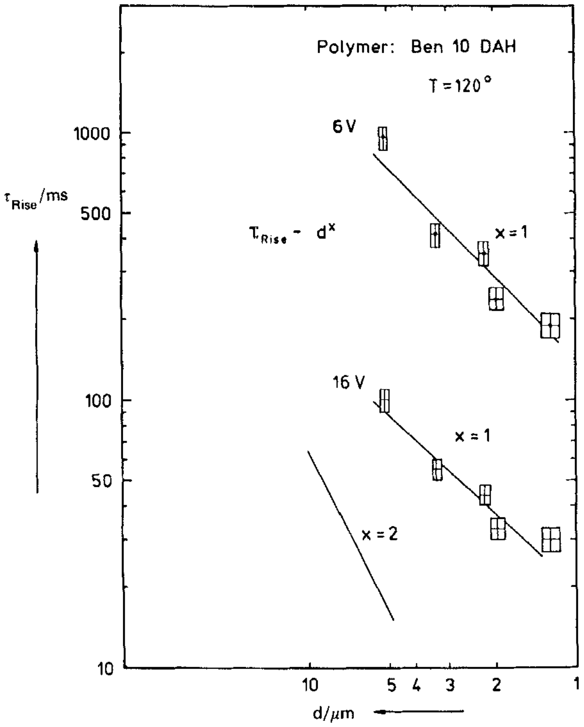


Figure 9. Variation of the optical rise time as a function of the cell thickness *d*. Results are presented for the polymer Ben 10 DAH, measured at 120°C and with 6 and 16 V_{rms} applied voltage. τ_{Rise} is depicted versus **d** on a doubly logarithmic scale. The straight lines with the slope $x = 1$ and $x = 2$ represent the theoretical linear or square dependence, respectively, of the rise time on the cell gap.

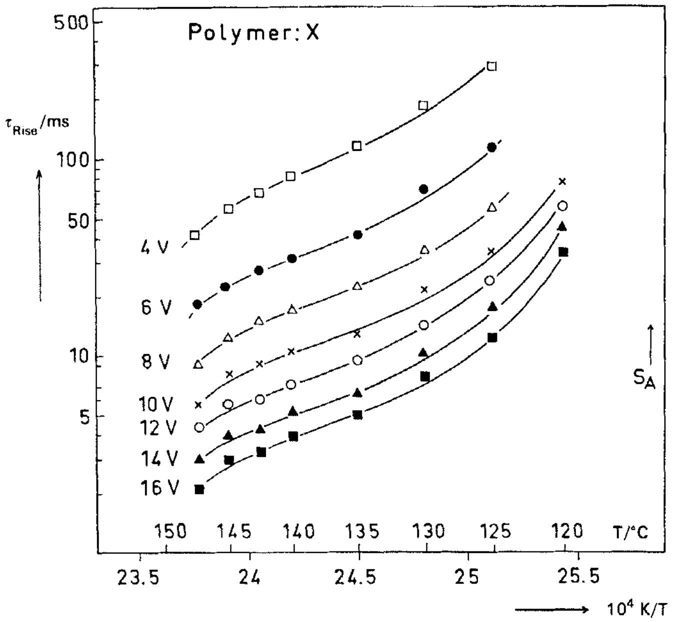


Figure 10. Variation of the rise time as a function of the reciprocal of the absolute temperature *T* for the polymer X. τ_{Rise} is depicted on a logarithmic scale versus $1/T$ for different voltages.

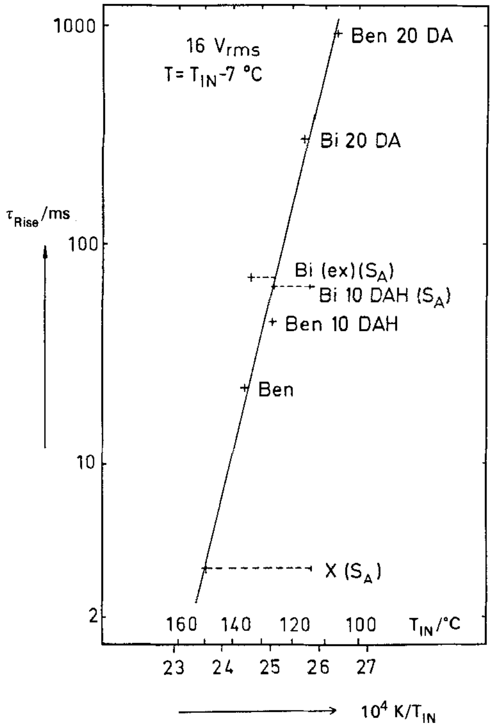


Figure 11. Variation of the rise time as a function of the reciprocal of the phase transition nematic–isotropic T_{IN} for all polymers given in table 1 and the polymer X. τ_{Rise} is depicted on a logarithmic scale versus $1/T_{IN}$ for the fixed temperature $T = T_{IN} - 7°C$ and for an applied voltage of 16 V_{rms}. The polymers Bi, Bi 10 DAH and X possess in addition S_A phases and the nematic phase ranges are indicated by a broken horizontal line ending at the nematic–S_A phase transition temperature. Because of the narrow nematic phase of the polymer Bi a more representative value τ_{Rise} has been used by extrapolating the straight line given in figure 7 to $T = T_{IN} - 7°C$.

speculate on which of the four approximations used in the derivation of equation (1) is the reason for the deviation from the theoretical prediction. Further detailed measurements are obviously required to clarify this interesing point.

Looking at equations (2) and (3), let us assume that the simplest and most effective way of shortening the response times by an order of magnitude is to lower the rotational viscosity γ_1 by switching the material at corresponding higher absolute temperatures. In order to check our assumption, polymer materials with higher nematic–isotropic transition temperatures are clearly required. Etzbach and co-workers from BASF have synthesized such a polymer denoted as X, which has the phase transition temperatures:

$$\text{g} \quad 25°\text{C} \quad \text{S}_\text{A} \quad 115°\text{C} \quad \text{N} \quad 148{\cdot}5°\text{C} \quad \text{I}.$$

It is also important that it has a broad nematic phase. Figure 10 plots the rise time of this polymer X on a logarithmic scale versus $1/T$. At the temperature $T = T_{IN} - 1°C$ and with an applied voltage of 16 V_{rms} we have achieved with this material the record rise time of 2 ms. Note that a doubling of the applied voltage and a further decrease of the cell thickness would shift the response time to the 300 μs

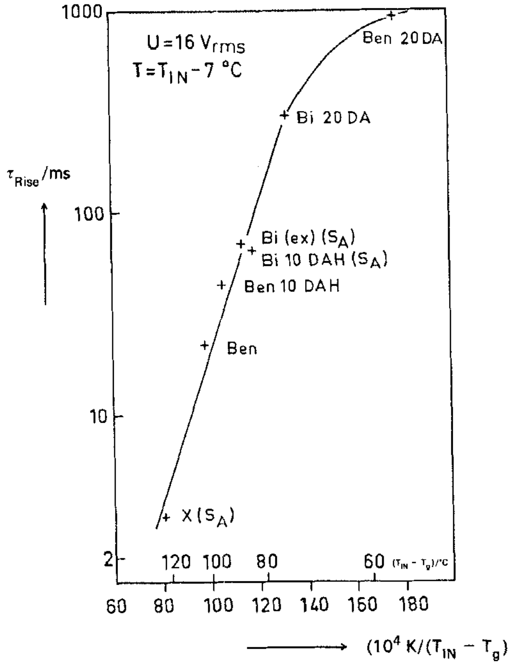


Figure 12. Variation of the rise time as a function of $1/(T_{IN} - T_g)$ for the polymers given in figure 11 ($T = T_{IN} - 7°C$ and $U = 16\,V_{rms}$).

range. Because the polymer X possesses an S_A phase, a strong non-linear increase of the response times is observed when approaching the nematic–S_A phase transition. The slight bending down of the curves in figure 10 near the nematic–isotropic phase transition can also be seen.

The rise time is governed mainly by the clearing temperature of the polymer materials. This is impressively illustrated in figure 11, where τ_{Rise} is shown on a logarithmic scale versus $1/T_{IN}$ for all of the investigated polyacrylate polymers. The measured rise times lie to a good approximation on a straight line. This is equivalent to an exponential dependence of the rise time on the clearing temperature and reflects the exponential dependence of γ_1 on the absolute temperature. According to figure 11 the switching time has been made nearly three orders of magnitude faster by raising the clearing temperature by 50°C.

We have not yet considered the influence of the glass transition temperature on the response times. It could be argued that the distance of the clearing temperature from the glass temperature is just as important for the response time as the absolute temperature, according to figure 11. We have therefore plotted τ_{Rise} versus $1/(T_{IN} - T_g)$ to check this (see figure 12). Clearly there is no essential difference between figures 11 and 12 for $T_{IN} - T_g > 70°C$. Moreover, the influence of T_g is clearly overestimated because a strong increase of τ_{Rise} must be expected if T_{IN} approaches T_g. Contrary to this, we observe in figure 12 a decrease of τ_{Rise} if we go from Bi 20 DA to Ben 20 DA. This shows that equation (3) describes our experimental results well, because our measurement have been accomplished sufficiently far from T_g.

4. Summary and conclusions

(1) The optical rise time τ_{Rise} is proportional to $1/(U^2 - U_0^2)$.

(2) Sufficiently far from the nematic–isotropic and nematic–S_A phase transitions as well as the glass transition temperature the rotational viscosity γ_1 can be approximated well by an Arrhenius function:

$$\gamma_1 \sim \exp(B/T).$$

In some cases we observe a slight bending down of τ_{Rise} approaching T_{IN} and always a diverging behaviour of τ_{Rise} approaching the nematic–S_A phase transition. The latter behaviour may be due to a divergence of γ_1.

(3) For the thickness range 1–3·5 μm our preliminary results suggest a linear dependence of the cell thickness on the optic rise time: $\tau_{\mathrm{Rise}} \sim d$. Clearly, further measurements need to be made to discover which kind of approximation in equation (2) leads to this observation.

(4) The rise times increase with increasing dye content. The influence of the dye on the rise times is stronger in the case of the cyanophenylbenzoate polymers than in the case of the cyanobiphenyl group. This may be caused mainly by the narrow nematic phase range and the neighbouring S_A phase lengthening the rise times of the biphenyl polymers Bi and Bi 10 DAH.

(5) Addition of anthrachinone dye lowers the clearing temperatures. Because of this the rise times are measured at a correspondingly lower absolute temperature. The exponential temperature dependence of the rotational viscosity γ_1 then leads to a strong enhancement of the rise times of the dye-containing polymers.

(6) The absolute temperature governs the rise times of our polyacrylates. Therefore, the rise times decrease exponentially by raising the nematic–isotropic phase transition temperature T_{IN}. This again reflects the exponential dependence of the rotational viscosity γ_1 on the absolute temperature. The glass transition temperature plays only a minor role because our switching experiments were made sufficiently far from T_g. We succeeded in lowering the response time by nearly three orders of magnitude only by an enhancement of T_{IN} by 50°C. It should be noted that these results hold only for our polyacrylates and that polymers with higher glass temperatures and different polymer main chains could show a different behaviour.

(7) With the nematic side chain polymer X we have achieved a rise time of 2 ms (2 μm thick sample, 16 V_{rms} applied voltage and 1°C below T_{IN}). It should be noted that this response time has been reached with a contrast ratio CR = 30. Doubling of the applied voltage and a further decrease of the cell gap should shift the response time into the 300 μs range.

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