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Measurement of the orientational elastic constants and the twist viscosity of nematic side chain polymers

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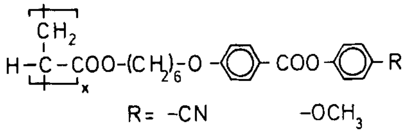
The temperature dependence of the three elastic constants k_{ii} ($i = 1, 2, 3$) and the twist viscosity γ_1 of two nematic side chain polyacrylates and one comparable low molecular weight compound have been measured by means of the Freedericksz effect. The change from the low to the high molecular liquid crystal causes a change of the ratio k_{33}/k_{11} from greater to less than unity, but the order of magnitude of the elastic constants remains the same. In contrast, the twist viscosity of the polymeric liquid crystal is about 1000 times greater in magnitude than that of a comparable low molecular weight liquid crystal. The activation energy for the viscosity of the polymer differs by a factor 3–4 from that of the low molecular weight liquid crystal. The elastic constants as well as the twist viscosity show a quadratic dependence on the order parameter S over a wide temperature range.

1. Introduction

Several theories describe the nematic phase of low molecular weight liquid crystals, for example the Maier–Saupe theory [1] and the Landau expansion proposed by de Gennes [2]. These theories yield the order parameter S, the orientational elastic constants k_{ii} ($i = 1, 2, 3$), the clearing temperature T_c and the associated volume change ΔV as a function of phenomenological parameters. To test theories, which are based on microscopically defined parameters, such as molecular shape, interaction energies and rotational states (one is outlined in [3]) It is necessary to know the influence of the orientational order on typical liquid-crystalline properties, as well as their dependence on temperature. We have therefore measured the elastic constants k_{ii} ($i = 1, 2, 3$) and the twist viscosity coefficient γ_1 of two liquid-crystalline side chain polymers and one comparable low molecular weight compound.

2. Samples

Several polyacrylates and polymethacrylates with mesogenic side chains have been prepared at the University of Mainz and already investigated by X-rays [4], N.M.R. [5], and dielectric measurements [4, 6, 7]. For our investigations two polyacrylates were kindly supplied by Dr. H. W. Schmidt and Dr. R. Zentel:



P/H/6/R

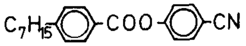
with $R = -\mathrm{CN}$ and $-\mathrm{OCH_3}$; known as P/H/6/CN and P/H/6/OCH3, respectively. The connection between the polyacryl main chain and the mesogenic group

Some properties of the samples investigated (after [4])

Short name	M_n/g mol^{-1}	x	Phase transition temperature °C	Nematic–isotropic enthalpy difference kJ mol^{-1}
P/H/6/CN	20 000	51	g 33 N 133 I	0·4
P/H/6/OCH3	43 000	108	g 35 S_A 97 N 123 I	1·1
L/7/CN	321		C 45 N 56 I	1·0

g = glassy, C = crystalline, S_A = smectic A, N = nematic, I = isotropic

(phenyl benzoate) is called the spacer and consists in both cases of six methylene groups. The behaviour of the compounds is given in the table. The phase transitions at the clearing point were sharp; the experimental error is estimated to be ±0·5°C. The degree of polymerization x was calculated from the molecular weights determined by vapour pressure osmometry by Zentel [4]. Additionally, the low molecular weight liquid crystal 4-cyanophenyl-4-heptylbenzoate



L/7/CN

with the short name L/7/CN was studied for comparison.

In order to measure k_{ii} (i = 1, 2, 3) and γ_1 it is necessary to have macroscopically oriented samples. These were obtained as usual by glass plates with polyimide coating, rubbed with a cloth in one direction. For good orientation it is necessary to keep the polymeric liquid crystal samples more than 10 hours at a temperature a little below the clearing point. The orientation process was observed with a polarizing microscope and is described in [8].

3. Measurements

The homegeneous orientation of the samples is deformed by a magnetic field H (Freedericksz transition [9]) and the change of optical birefringence is observed between crossed polarizers. The experimental set-up is illustrated in figure 1.

(*a*) *Static behaviour for the determination of the elastic constants* k_{ii} (i = 1, 2, 3)

For the static measurements the magnetic field H is changed slowly, so that balance always exists between the magnetic and the deformation energy. The maximum

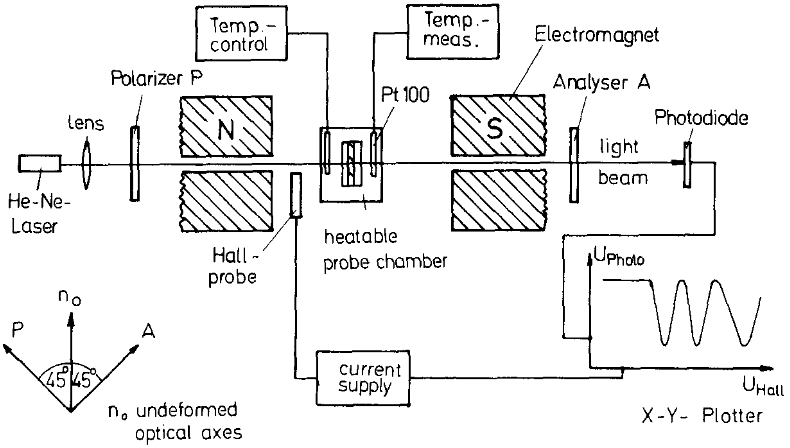


Figure 1. Experimental set-up.

possible velocity of the magnetic field change is investigated in [8] and was never exceeded in our experiments. The intensity I of the transmitted light can then be measured as a function of the applied magnetic field strength H.

Saupe [10] calculated the change of the phase difference δ between the ordinary and extraordinary light beams on the basis of the Frank elasticity theory of nematic liquid crystals [11] to be

$$\delta = 2\pi \frac{n_e x_0}{\lambda}\left[1 - \frac{2H_0}{\pi H}\int_0^{\varphi_0} \frac{(1 + \kappa \sin^2\varphi)^{1/2}}{(1 + \nu \sin^2\varphi)^{1/2}(\sin^2\varphi_0 - \sin^2\varphi)^{1/2}}\, d\varphi\right], \quad (1)$$

where

$$\kappa = \frac{k_{33} - k_{11}}{k_{11}}; \quad \nu = \frac{n_e^2 - n_o^2}{n_o^2}$$

and the threshold magnetic field

$$H_0 = \frac{\pi}{x_0}\left(\frac{k_{11}}{\mu_0 \Delta\chi}\right)^{1/2}.$$

The maximum deformation angle φ_0 is obtained from

$$\frac{H}{H_0} = \frac{2}{\pi}\int_0^{\varphi_0}\left(\frac{1 + \kappa \sin^2\varphi}{\sin^2\varphi_0 - \sin^2\varphi}\right)^{1/2} d\varphi,$$

$$\frac{x}{x_0} = \frac{1}{\pi}\frac{H_0}{H}\int_0^{\varphi(x)}\left(\frac{1 + \kappa \sin^2\theta}{\sin^2\varphi_0 - \sin^2\theta}\right)^{1/2} d\theta,$$

where x_0 is the thickness of the liquid crystalline layer, λ is the wavelength of light n_e and n_0 are the refractive index of extraordinary ordinary light, respectively and $\Delta\chi(\equiv \chi_{\parallel} - \chi_{\perp})$ is the anisotropy in the magnetic susceptibility. $\delta(H)$ is measured by means of the intensity of light $I(H)$ behind the crossed polarizers and is given by

$$I = I_0 \sin^2(\delta/2).$$

The theoretical curve (see equation (1)) is fitted to the experimental δ-data, where the threshold field H_0 and the ratio of the elastic constants κ are used as the fitting parameters. From H_0 we find k_{11} and from κ we obtain k_{33}.

In a separate experiment, using a twisted nematic cell (where the glass plates are twisted by an angle of 90°), the twist constant k_{22} was determined analogously. A relation between the threshold field H_0^{TN} for the TN-cell and the elastic constants is given [12] as

$$H_0^{\mathrm{TN}} = \frac{\pi}{x_0}(\mu_0 \Delta\chi)^{-1/2}(k_{11} + \tfrac{1}{4}k_{33} - \tfrac{1}{2}k_{22})^{1/2}.$$

(*b*) *Dynamic behaviour for the determination of the twist viscosity* γ_1

γ_1 describes the rotation of the director **n** relative to the surrounding fluid. In order to measure this coefficient we observed the time dependence of δ (via that of the light intensity I) after a sudden application of a magnetic field $H > H_0$ (*rise*) or after switching off the field (*decay*). For small deformations the relaxation of the maximum deformation angle φ_0 can be replaced by the relaxation of a mean deformation angle

$\bar{\varphi}$, which is calculated from the measured change of the phase difference δ according to (d = phase difference between the ordinary and extraordinary light beam):

$$\begin{aligned}\delta(H) &= d(H=0) - d(H)\\ &= 2\pi n_e \frac{x_0}{\lambda}\left[1 - \frac{n_o}{(n_e^2 \sin^2\bar{\varphi} + n_o^2\cos^2\bar{\varphi})^{1/2}}\right].\end{aligned} \qquad (2)$$

The relaxation times τ for switch on τ_r and switch off τ_o are [13]

$$\frac{1}{\tau_r} = \frac{1}{\tau_o}\left[\left(\frac{H}{H_0}\right)^2 - 1\right], \quad \text{rise}$$

$$\tau_o = \frac{\gamma_1}{\mu_0 \Delta\chi}\frac{1}{H_0^2}, \quad \text{decay},$$

When measuring the time dependence of the intensity I, we obtain by means of equation (2) the time dependence of the mean deformation angle $\bar{\varphi}$, and from this exponential function the relaxation times τ_r and τ_o can be obtained. With knowledge of these relaxation times τ it is possible to determine γ_1.

(*c*) *Errors*

A precise consideration of all effects of error [8] yields the relative uncertainties k_{11} : 3 per cent; k_{33} : 7 per cent; k_{22} : 10 per cent; γ_1: 8 per cent.

4. Results and discussion

(*a*) *Orientational elastic constants*

Since the anisotropy of the magnetic susceptibility $\Delta\chi$ is not known for P/H/6/CN and P/H/6/OCH3, we have used $\Delta\chi$ measured on polymers with a similar structure [14]. Because the susceptibility is determined mainly by the two phenyl rings there is no significant difference in the magnetic behaviour of these substances. $\Delta\chi$ for L/7/CN was measured by Buka *et al.* [15].

The results of the measurement of the elastic constants k_{11} and k_{33} is shown in figures 2 and 3. For all three substances the twist deformation is the deformation with the lowest energy, this means that k_{22} has the lowest value of all the three elastic

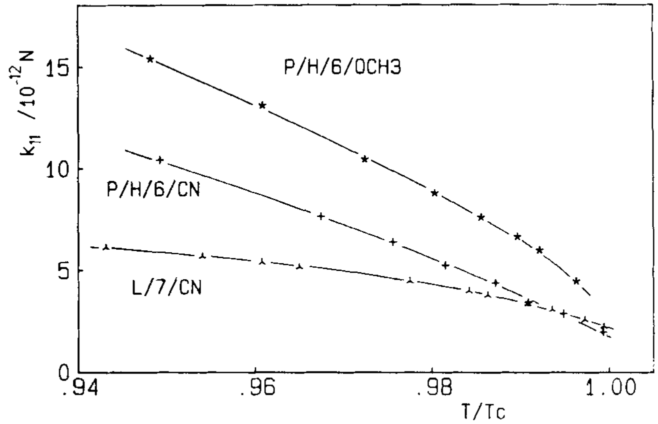


Figure 2. The temperature dependence of the elastic constant k_{11}.

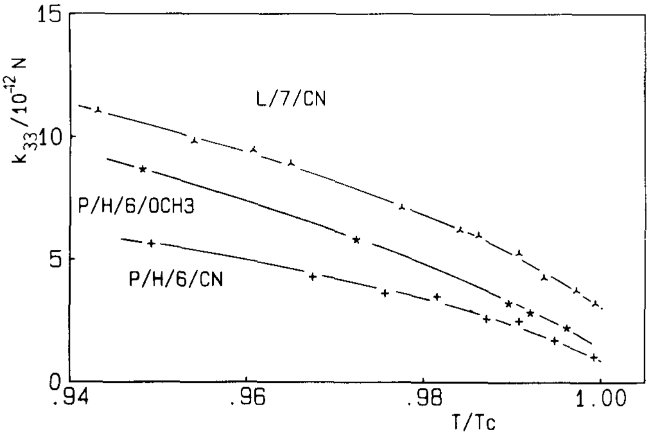


Figure 3. The temperature dependence of the elastic constant k_{33}.

constants. Moreover there is no significant difference between the k_{22} values of the three samples.

According to the results in figures 2 and 3 the order of magnitude of the elastic constants is the same for the liquid-crystalline side chain polyacrylates and for the low molecular weight liquid crystal. Measurements on liquid-crystalline polymers with a polymethylsiloxane main chain yield the same result [16]. A different situation occurs for main chain polymers, where an average of the elastic constants is about 100 times larger for the polymers than for the low molecular weight liquid crystals [17]. Consideration of the individual elastic constants of the substances investigated shows that the ratio k_{11}/k_{33} changes from less than to greater than unity when going from the low molecular weight liquid crystal to the polymeric liquid crystal: for both polymers k_{11} is larger than k_{33} in contrast to L/7/CN. The increase of the splay-constant k_{11} with increasing chain length was explained by de Gennes [18] with a model of *partly flexible chains*. This theory is applicable to polymers with mesogenic groups in the main chain, and not to the side chain polymers used here. Maier and Saupe [1] reduced the temperature dependence of the elastic constants by a molecular statistical mean field theory to the temperature dependence of the order parameter S and the molar volume V_{mol}

$$k_{ii} = \frac{S^2}{V_{\mathrm{mol}}^{7/3}} C_{ii}; \quad i = 1, 2, 3;$$

here C_{ii} are the reduced elastic constants which are temperature independent. In particular the ratio $k_{11} : k_{22} : k_{33}$ should be independent of temperature if there is no change in the short range order of the molecules. The ratio k_{33}/k_{11} for the liquid crystal L/7/CN is plotted in figure 4. However this ratio shows a rather strong dependence on temperature particularly at the nematic–isotropic transition, which means according to the Maier–Saupe theory, that there would be a strong change in the short range order. A detailed discussion of possible short range order in low molecular weight liquid crystals is given by Gruler [19]. For P/H/6/CN the reduced elastic constants C_{11} and C_{33} are shown in figure 5. The strong increase of the reduced elastic constants when approaching the clearing point ($T = T_c$) is a consequence of the increase of the thermal volume expansion coefficient, which is nearly constant over a wide temperature range and increases, about 4°C below T_c, by a factor of 3 [20]. This suggests

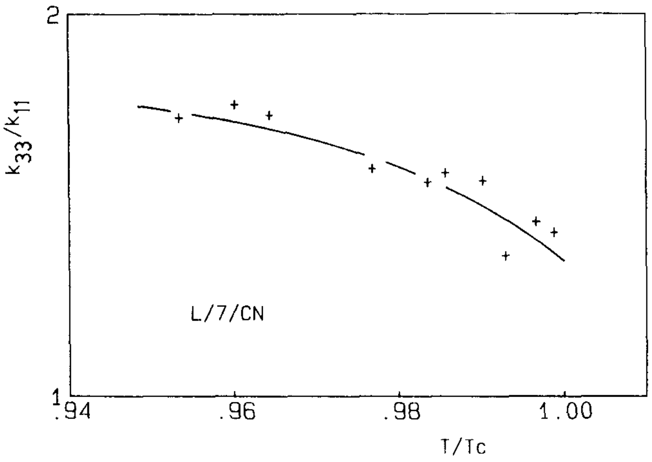


Figure 4. The dependence of the ratio k_{33}/k_{11} for L/7/CN on the reduced temperature, T/T_c

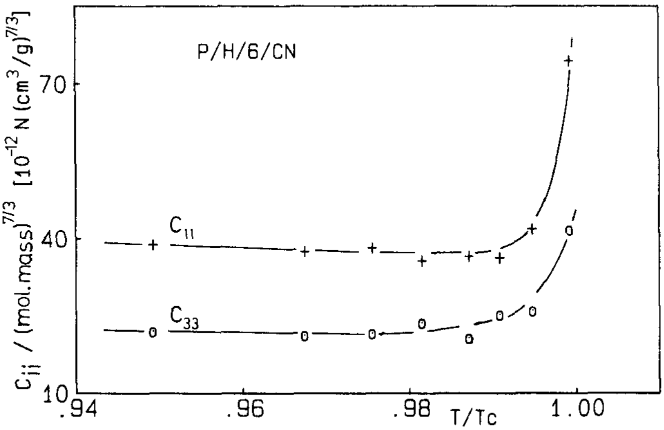


Figure 5. Reduced elastic constants C_{11} and C_{33} of P/H/6/CN.

a strong change in the molecular arrangement at temperatures just below the nematic–isotropic transition, which influences the elastic constants k_{ii} ($i = 1, 2, 3$). A problem for the future will be to explain this behaviour with a elasticity theory of nematic liquid crystals, based on microscopically defined parameters. A possible concept will be the introduction of dislocations, which has been applied successfully to the melt transition phenomena of metals and polymer crystals [3].

(*b*) *Twist viscosity γ_1 and activation energies*

γ_1 was determined from rise as well as from decay experiments: both methods agreed well [8]. The temperature dependence of the twist viscosity is shown in figures 6, 7 and 8. A comparison of the orders of magnitudes yields the result, and γ_1 of the polymer P/H/6/CN is about three decades higher than that of the comparable low molecular weight liquid crystal L/7/CN. This reflects the strong influence of the main chain on the ability of side chain orientation in an external (magnetic) field. Moreover the constitution of the main chain plays a decisive role, because a polysiloxane liquid crystal [16] with the same molecular weight and mesogenic group shows, at the

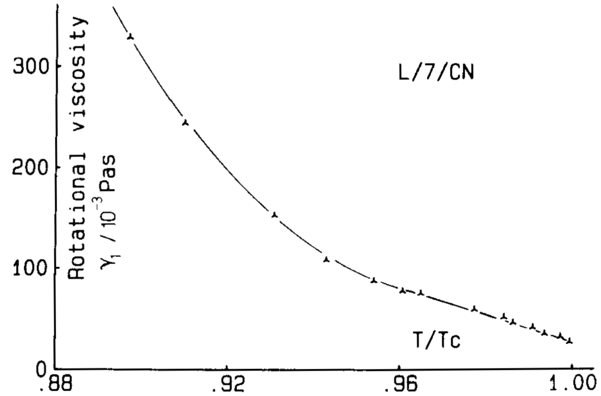


Figure 6. The temperature dependence of γ_1 for L/7/CN.

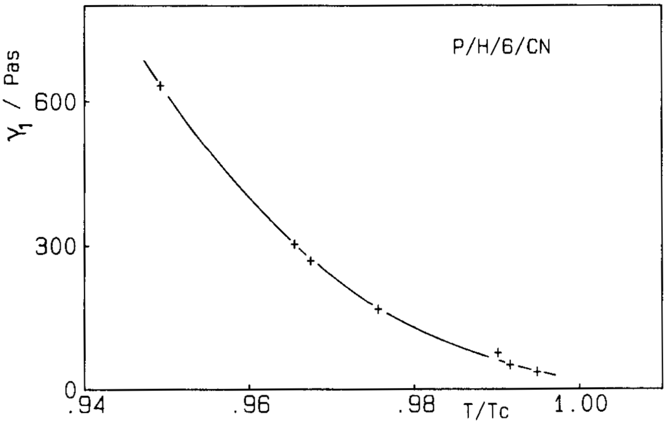


Figure 7. The dependence of γ_1 for P/H/6/CN on the reduced temperature.

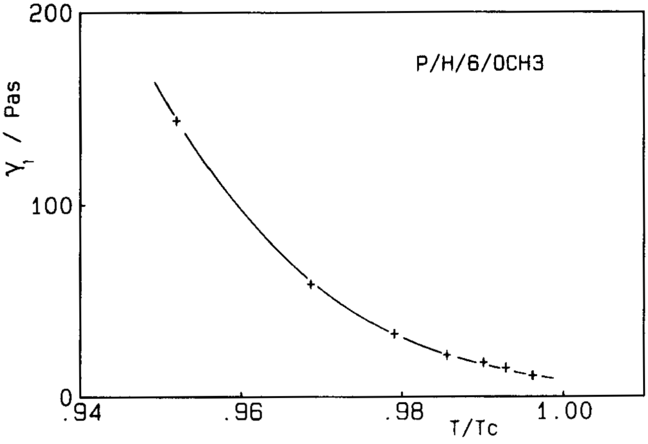


Figure 8. The temperature dependence of γ_1 for P/H/6/OCH3.

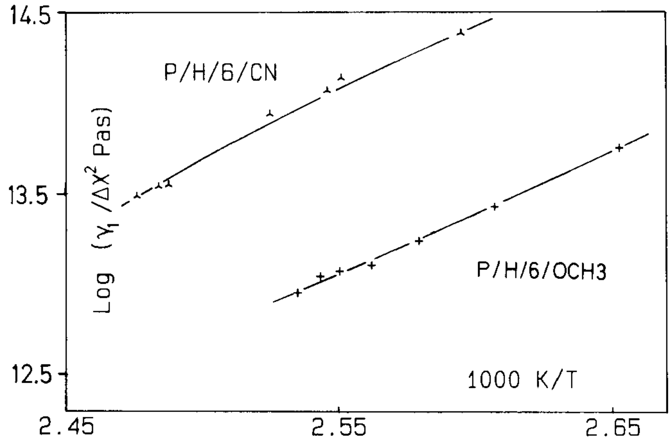


Figure 9. Quadratic order parameter dependence ($S \sim \chi$)

same reduced temperature ($T/T_c = 0{\cdot}95$), a twist viscosity γ_1 three times smaller than the polyacrylate P/H/6/CN investigated here.

A comparison of both polymers P/H/6/CN and P/H/6/OCH3 elucidates the influence of the mesogenic side group on γ_1. Though the molecular weight of P/H/6/OCH3 is twice as high as that of P/H/6/CN, the polymeric liquid crystal with the end cyano group (P/H/6/CN) possesses a γ_1 which is four times higher than that of the polymer with the end methoxy group (P/H/6/OCH3). This behaviour can be explained by molecular association of the polar cyano molecules. Dielectric [21] and X-ray [22] investigations support the model of an antiparallel arrangement of the polar molecules, which corresponds to an electrostatic energy of about 10 kJ/mol. The temperature dependence of γ_1 is described by several theories [23], which all lead to an equation of the form

$$\gamma_1 = f(S(T))\, g(T),$$

where $f(S)$ is of type S^x where x is either 1 or 2 and $g(T)$ is in general an exponential function of temperature. We have also investigated our measurements using this equation and find good agreement with an exponent of 2 (see figure 9). Hess [24] treats the non-equilibrium orientation of liquid crystals by means of irreversible thermodynamics and finds

$$\gamma_1 = 15 S^2 \frac{\varrho RT}{M} \tau(T), \qquad (3)$$

where S is the equilibrium order parameter, ϱ is the density, R is the gas constant and τ is the relaxation time of deviations from the equilibrium order parameter. Equation (3) yields the relaxation time τ

$$\begin{aligned}\tau &= \frac{M}{15R}\frac{\gamma_1}{S^2\varrho T}\\ &= \tau_0 \exp(E/RT).\end{aligned}$$

In figures 10 and 11 this relaxation time τ_{visc} and the dielectric relaxation time τ_{diel}, which is determined from the maximum frequency $f_{\max}$ of the δ-relaxation according to $2\pi f_{\max}\tau_{\text{diel}} = 1$ are plotted logarithmical against the reciprocal temperature.

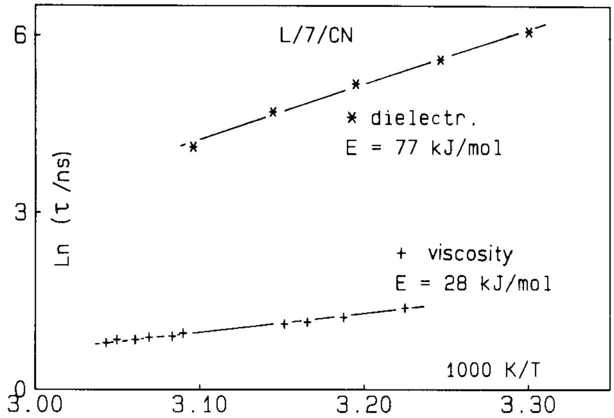


Figure 10. The temperature variation of the relaxation times for L/7/CN.

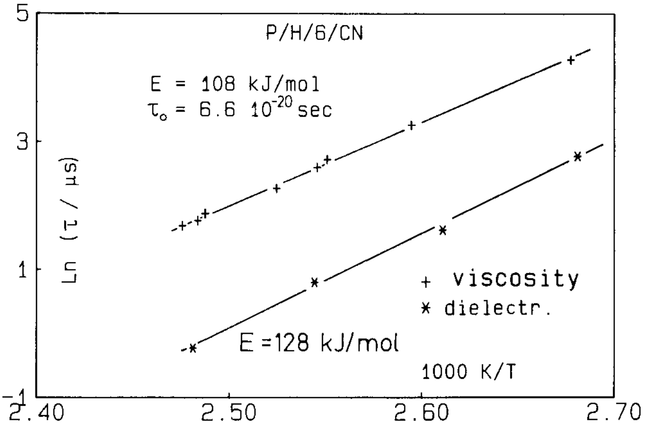


Figure 11.. The variation of the relaxation times for P/H/6/CN with temperature.

The plotted straight lines are fits of exponential temperature relations for the relaxation times to the experimental data. For all experiments we obtain good agreement with an exponential law and find the activation energies

$$\text{P/H/6/CN}: \quad E_{\text{visc}} = 108\,\text{kJ/mol}, \quad E_{\text{diel}} = 128\,\text{kJ/mol};$$

$$\text{L/7/CN}\ : \quad E_{\text{visc}} = 28\,\text{kJ/mol}, \quad E_{\text{diel}} = 77\,\text{kJ/mol}$$

For the polymeric liquid crystal P/H/6/CN the activation energy for orientational relaxation E_{visc} is about four times greater than that for the comparable low molecular weight liquid crystal L/7/CN, which is characteristic of the influence of the main chain on typical liquid-crystalline properties.

The great difference between the activation energies for the low molecular weight liquid crystal L/7/CN ($E_{\text{diel}} = 77$ kJ/mol, $E_{\text{visc}} = 28$ kJ/mol) can be explained qualitatively again by the association of the polar molecules in clusters: for reorientation of the cluster a rotation of the whole cluster is necessary and therefore the electrostatic interaction plays no role, but for a change in polarization (dielectric relaxation) the interaction between the dipoles has to be overcome which increases the total potential barrier.

For the liquid-crystalline polymer P/H/6/CN the difference in the activation energies is not so great (E_{visc} = 108 kJ/mol E_{diel} = 128 kJ/mol). An explanation for this fact may be that the electrostatic interaction has to be overcome for the reorientation of the side group (→ twist viscosity) as well as for the dipole-orientation polarization (→ dielectric δ-process). For more accurate quantitative statements model calculations based on this molecular association are necessary.

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