# Influence of Polymer Molecules on the Rotational Viscosity and Backflow Effect at the Bend Freederiks Transition in Nematic Liquid Crystals

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ABSTRACT: Reorientation of the nematic director at the bend Freederiks transition has been studied for dilute solutions of side-chain mesogenic polymethacrylates in a low molecular weight nematic liquid crystal, pentylcyanobiphenyl (5CB). The temperature dependences of the pure twist viscosity coefficient $\gamma_1$ and bend elastic constant $K_3$ were obtained for nematic solutions containing polymers with different degrees of polymerization ($N$ = 34, 88, and 312). The increment of twist viscosity $\delta\gamma_1$ increases with $N$ according to the power law $\delta\gamma_1 \propto N^{\alpha}$ with an exponent $0.67 < \alpha < 0.87$ for temperatures of solutions $T$ = 23−33 °C. This result corresponds to nondraining chains in a good solvent. The study of the dynamics of bend deformation shows a more rapid increase in the shear Miesowicz viscosity coefficient $\eta_c$ in comparison to the twist viscosity coefficient $\gamma_1$ with increasing polymer concentration. This observation was supplemented by measurements of the ratio $\gamma_1/\eta_c$ over a wide range of the degree of polymerization $N$. This ratio was found to depend on $N$ according to the power law $\eta_c/\gamma_1 \propto N^{0.162}$.

## Introduction

Reorientation of the nematic director may induce a flow of liquid. This effect is caused by the coupling between rotation of the director and flow (backflow effect). Hydrodynamic motion affects the reorientation rate by reducing strongly the effective rotational viscosity of liquid crystals (LC).

The reorientation of nematic LC is well studied in the Freederiks transition experiment. This transition occurs when an external magnetic (or electric) field is applied to a uniformly aligned nematic LC in a direction perpendicular to the initial orientation. The dynamics of transition has been studied by Pieranski, Guyon, and Brochard[1] for splay, twist, and bend geometries. It was shown that backflow is very pronounced for bend deformation, and the effective twist viscosity $\gamma_1^*$ decreases with increasing magnetic field $H$. More recently, Guyon, Meyer, and Salan[2] and Lonberg et al.[3] showed that backflow plays an important role in the formation of transient periodic patterns for the splay and twist Freederiks transitions. A uniform rotation of the director is replaced by the opposite rotation of adjacent zones of the sample. In this case backflow reinforces the rotation of zones, and the effective rotational viscosity decreases.[3] A particularly strong effect of the backflow on the effective rotational viscosity is observed for polymer lyotropic nematics containing long rodlike molecules.[4] This fact is manifested by the high anisotropy of viscosity for these systems.

Coupling between the director rotation and the flow is controlled by the ratio of twist to shear viscosity of a liquid crystal. High values of this ratio produce a very strong backflow at reorientation of the director.

Polymer molecules dissolved in nematic liquid crystals may contribute strongly to viscous properties of nematic polymer solutions. As was shown by Brochard,[5] this effect depends on the anisotropy of the shape of macromolecules in the nematic environment. The contribution of chains with a small anisotropy of shape to the rotational viscosity is smaller than that to the shear viscosity coefficients.

For example, Gu et al.[6] have found that the contribution of polymethacrylate chains with side mesogenic groups to the bend viscosity $\eta_{bend}$ was higher than that to the twist viscosity coefficient $\gamma_1$. This result shows that the backflow connected with the bend deformation mode of the director is damped by polymer molecules.

The occurrence of the damping effect may depend on different factors such as the chemical structure of macromolecules, molecular weight, and polymer concentration. For example, no damping effect of polyacrylate side-chain polymer molecules on the backflow was observed in our previous work.[7] This result was ascribed to the very compact conformation of polymer coils in the nematic solution and their relatively small contribution to the shear viscosity.

This paper is focused on the study of the molecular weight dependences of the damping effect for solutions of polymer samples with mesogenic side groups, poly[4-[4-[(4-methoxyphenyl)azo]phenoxy]butyl methacrylate] (PMC-$N$), in a low molecular weight nematic liquid crystal, pentylcyanobiphenyl (5CB). It is shown that the degree of polymerization $N$ plays a crucial role in the occurrence of the damping effect.

These measurements demonstrate a possibility of reducing the backflow by adding polymer samples of high molecular weight ($N$ = 312) to 5CB.

This result might be interesting for suppressing instabilities which can play a negative role in some applications of LC, because the appearance of instabilities is a result of the backflow. For example, ripple instabilities can destroy performance of high-contrast devices based on supertwist cells. In some cases, instabilities are also observed at shear flow of rodlike polymer solutions (so-called band textures) where they reduce the mechanical performance of fibers or films processed from these solutions. We believe that the study of the damping effect for nematic liquids containing flexible polymer molecules can be used to improve the LC polymer processing technology.

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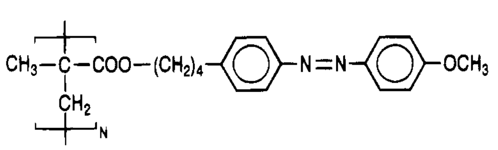
**Table 1. Molar Masses, Polydispersity, Degrees of Polymerization, Concentrations, and Clearing Temperatures of Polymer Solutions in 5CB**

| $\bar{N}_n$ | $\bar{M}_n \times 10^{-3}$ | $\bar{M}_w/\bar{M}_n$ | $C$, wt % | $T_{NI}(p)$, °C | transition temperatures[a] |
|---|---|---|---|---|---|
| 33.8 | 11.9 | 1.18 | 3.22 | 36.7 | G 84 N 127 I |
| 88.0 | 31.0 | 1.09 | 3.05 | 35.5 | G 83 N 136 I |
| 312.5 | 110 | 1.12 | 1.75 | 35.5 | G 86 N 144 I |
| | | | 3.33 | 35.5 | |

[a] Bulk polymers. G, N, and I denote glassy nematic, nematic, and isotropic phases, respectively.

## Experimental Section

**Materials.** The polymer samples utilized in this study were synthesized by Professor H. Finkelmann and Dr. R. Bohnert.[8] The structure of the poly[4-[4-[(4-methoxyphenyl)azo]phenoxy]-butyl methacrylate] (PMC-$N$, $34 \leq N \leq 312$) samples was



PMC-N

The molecular weights, polydispersities, and transition temperatures of the samples are given in Table 1. The polymers were dissolved in a low molecular weight nematic liquid crystal, pentylcyanobiphenyl (5CB) (Merck, Poole, clearing temperature $T_{NI}$ = 35.5 °C), for 30 min at $T$ = 120 °C. The homogeneity of the resulting nematic solutions was checked by conoscopic observations with a MIN-8 polarizing microscope (LOMO, St. Petersburg). Careful determination of the clearing temperatures of the nematic solutions was made with a hot stage equipped Boetius polarizing microscope (VEB Analytik). The biphasic nematic–isotropic range was observed for nematic solutions. Therefore, the pseudotransition temperatures $T_{NI}(p)$ located between the upper and lower temperature boundaries of the biphasic range were measured. The determination of $T_{NI}(p)$ is described in ref 7.

The concentration range of the solutions was $1.75 \leq C \leq 3.33$ wt %. This range corresponds to the dilute regime because in this range the dependence of $\gamma_1$ on $C$ is linear.

**Experiments. (A) Theory.** The dynamics of the bend transition has been described in detail by Pieranski et al.[1] Here we discuss the main results of this theory, which are necessary for the determination of the material parameters of the polymer solutions. The initial orientation of the nematic director $\mathbf{n}_0$ is perpendicular to the glass plates (homeotropic orientation). The magnetic field $\mathbf{H}$ is perpendicular to $\mathbf{n}_0$. The Freederiks transition takes place when the magnetic torque is higher than the torque produced by the elastic forces. The balance of elastic and magnetic forces determines the value of the Freederiks threshold:

$$H_F = \frac{\pi}{d}\left(\frac{K_3}{\chi_a}\right)^{1/2} \qquad (1)$$

where $\chi_a$ is the diamagnetic anisotropy of the nematic liquid crystal, $d$ is the cell thickness, and $K_3$ is the bend elastic constant. The dynamics of the Freederiks transition involves viscous forces which depend on the configuration of the director. In the case of pure rotation of the director (i.e., without the hydrodynamic motion of molecules) viscous torque has the simplest form, expressed as a product of the twist viscosity coefficient and the reorientation rate: $\gamma_1 \partial\theta/\partial t$. However, in the bend geometry a flow of liquid along $\mathbf{H}$ occurs during the reorientation; therefore an additional viscous term appears.

For axes $z$ parallel to $\mathbf{n}_0$ and $x$ parallel to $\mathbf{H}$, the balance of elastic, magnetic, and viscous forces is given by

$$K_3\frac{\partial^2\theta}{\partial z^2} + \frac{1}{2}\chi_a H^2 \sin 2\alpha = \gamma_1\frac{\partial\theta}{\partial t} + \frac{\gamma_2 - \gamma_1}{2}\frac{\partial V_x}{\partial z} \qquad (2)$$

where $\theta$ is the angle between the director and $z$, and $V_x$ is the velocity of the liquid in the $x$-direction.

The equation of motion for a given geometry is written as (neglecting inertial terms)

$$\frac{\partial}{\partial z}\left(\eta_c\frac{\partial V_x}{\partial z} + \alpha_2\frac{\partial\theta}{\partial t}\right) = 0 \qquad (3)$$

where $\alpha_2$ is the Leslie twist viscosity coefficient which is normally $|\alpha_2| \approx \gamma_1$. Equation 3 shows the coupling between the director rotation and the velocity gradient; i.e., the faster the reorientation, the stronger the flow of liquid (backflow).

When the magnetic field is high ($h = H/H_F \gg 1$), an additional reinforcement of the backflow takes place because the wavelength $\lambda$ of the bend distortion decreases. Note that $\lambda = 2d$ for values of the field near $H_F$, $h \geq 1$, whereas for $h \rightarrow \infty$ $\lambda = {}^2/_3 d$ owing to the spatial director modulation along the $z$-axis.

Solutions taking into account this modulation of the director field $\theta(z)$ and $V_x(z)$ are given by the following expressions:

$$\theta(z,t) = \theta_0\left(\cos kz - \cos\frac{kd}{2}\right)\exp(t/\tau) \qquad (4)$$

$$V_x(z,t) = V_0\left(\sin kz - \frac{2z}{d}\sin\frac{kd}{2}\right)\exp(t/\tau) \qquad (5)$$

Equations 2–5 lead to the following equations which express the relationship between the wavenumber $k$ of the distortion and the time constant $\tau$ (the value of $\tau$ characterizes the reorientation rate)

$$(1 - A)\frac{\tau_0}{\tau(h)}\left(1 - \frac{1}{h^2}\right) = 1 - \frac{4X^2}{\pi^2 h^2} \qquad (6)$$

$$h^2 = \frac{4X^2}{\pi^2}\frac{\tan X - X/A}{\tan X - X}$$

where $A = \alpha_2^2/(\eta_c\gamma_1)$ and $X = (kd)/2$. The ratio of $(\tau_0/\tau(h))(1 - 1/h^2) = \gamma_1/\gamma_1^*(h)$ shows that the effective viscosity $\gamma_1^*(h)$ is small compared to the pure twist viscosity $\gamma_1$.

**(B) Measurements.** The effective twist viscosity coefficients and bend elastic constants were measured by using Freederiks transition experiments for bend deformation. The preparation of cells with homeotropic boundary conditions has been described elsewhere.[7,9]

The values of the bend elastic constant $K_3$ were obtained from eq 1.

A linear dependence of the ratio of the time constants $\tau_0/\tau(h)$ on $H^2$ was used to obtain the vlaue of the threshold field $H_F$, because $\tau_0/\tau(h) \rightarrow 0$ at $H = H_F$. This method of determination of $H_F$ is very precise, especially when experimental values of $H$ are chosen in the vicinity of $H_F$.

Time constants $\tau(h) = s^{-1}(h)$ and $\tau_0 = s_0^{-1}$ were determined by using a conoscopic method.[7,9] The values of $d$ were measured with a high accuracy by using the interference method. The values of diamagnetic anisotropy $\chi_a$ obtained by Buka and de Jeu[10] for 5CB were used in our study.

The effective twist viscosity coefficient $\gamma_1^*(0)$ for relaxation in zero field was calculated from the equation

$$\gamma_1^*(0) = 2\chi_a H_F^2 \tau_0 \qquad (7)$$

The value of $\gamma_1^*(0)$ is smaller than the twist viscosity coefficient $\gamma_1$ for pure twist deformation.

The value of the pure rotational viscosity was obtained from the equation

$$\gamma_1 = \frac{\gamma_1^*(0)}{1 - A/6} \qquad (8)$$

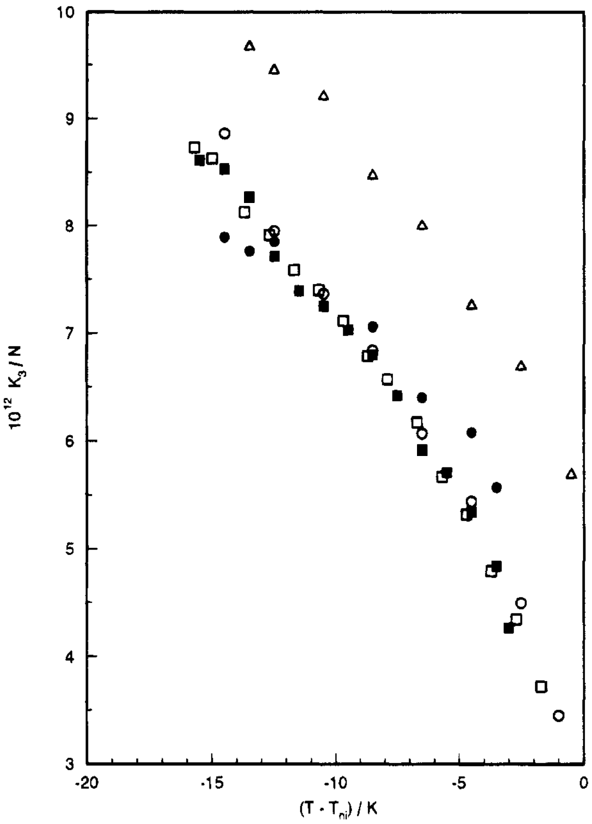


**Figure 1.** Temperature dependences of the bend elastic constant for 5CB (○) and PMC-34 (□), PMC-88 (△), PMC-312, $C$ = 1.75% (■), and PMC-312, $C$ = 3.33% (●) solutions.

The parameter $A$ in eq 8 was determined by fitting the experimental dependences of $\tau_0/\tau(h)$ on $h$ to eq 6.

## Results and Discussion

**Measurements of the Bend Elastic Constant.** Flexible polymer molecules usually do not change the elastic properties of nematic solutions.[11] Figure 1 shows that the values of $K_3$ for all solutions of PMC-$N$ in 5CB are similar to those for 5CB.[12] This result is consistent with theoretical predictions[13] that give the dependence of $K_3$ on the axial ratio or the shape of molecules. The mesogenic groups of PMC-$N$ are geometrically similar to the molecules of 5CB, and, therefore, the resulting contribution of macromolecules to the bend elastic constant is negligible. However, an increase in $K_3$ for dilute solutions of polyacrylates with cyanobiphenyl mesogenic side groups was observed.[7] The values of $K_3$ for solutions were twice as high as those for pure 5CB. This fact was explained in terms of macromolecular conformation. A compact globular conformation of polymer molecules in the nematic environment was suggested. This conformation is consistent with a large contribution of macromolecules to $K_3$. The idea of a globular conformation of polyacrylates was supported by measurements of the twist viscosity coefficient $\gamma_1$ as a function of the degree of polymerization $N$:

$$\delta\gamma_1/(\gamma_1^0 C) \propto N^{0.11}$$

Here $\gamma_1^0$ is the twist viscosity of the pure solvent and $\delta\gamma_1$ denotes the twist viscosity increment of the solution. This weak dependence is expected for a quasi-globular conformation of the coils, with a dimension scaled as $R \propto N^{0.37}$.

In order to understand whether this fact is a result of the specific chemical structure of the polyacrylate with cyanobiphenyl mesogenic side groups, the dependence of $\delta\gamma_1$ on $N$ for PMC-$N$ with methoxyazobenzene mesogenic groups in the same nematic solvent, 5CB was studied.

**Twist Viscosity Measurements.** According to the theory of Brochard[5] for polymer chains in a nematic medium, the contribution of chains to the twist viscosity, $\delta\gamma_1$, is given by

$$\delta\gamma_1 \equiv \gamma_1^{\text{solution}} - \gamma_1^{\text{solvent}} = (CkT/N)\tau_R \frac{(R_\perp^2 - R_\parallel^2)^2}{R_\perp^2 R_\parallel^2} \quad (9)$$

where $R_\perp$ and $R_\parallel$ are the coil dimensions perpendicular and parallel to the director, $C$ is the volume fraction of polymer segments, and $\tau_R$ is the rotational relaxation time of the chain. The value of $\tau_R$ may be given as a combination of two relaxation times associated with motions of a chain parallel and perpendicular to the director:

$$\frac{1}{\tau_R} = \frac{1}{\tau_\parallel} + \frac{1}{\tau_\perp} \quad (10)$$

Relaxation times of a nondraining chain are scaled as

$$\tau_\parallel \propto R_\parallel^\zeta \quad \text{and} \quad \tau_\perp \propto R_\perp^\zeta \quad (11)$$

where $\zeta$ is the critical dynamic exponent.[14] This exponent is usually $2.8 < \zeta \leq 3$ ($\zeta = 3$ in Zimm's nondraining limit).

The shape anisotropy of a chain $f(R) = (R_\perp^2 - R_\parallel^2)^2/(R_\perp^2 R_\parallel^2)$ in eq 1 does not depend on the degree of polymerization because both $R_\perp$ and $R_\parallel$ are supposed to change with $N$ in a similar way:

$$R_\perp \propto N^\beta \quad \text{and} \quad R_\parallel \propto N^\beta \quad (12)$$

Therefore, combining eqs 9–12 we obtain for $\delta\gamma_1$

$$\delta\gamma_1 \propto \frac{C}{N}\tau_R \propto \frac{C}{N}\frac{R_\parallel^\zeta R_\perp^\zeta}{R_\parallel^\zeta + R_\perp^\zeta} \propto N^{\beta\zeta - 1} \quad (13)$$

The value of the exponent $\beta$ for a chain with a compact globular conformation is $\beta = 1/3$, and $\delta\gamma_1$ does not depend on $N$. For macromolecules in a good solvent, one might expect a strong dependence of $\delta\gamma_1/\gamma_1^0$ on $N$ because $\beta = 3/5$ (assuming $\zeta = 3$):

$$\delta\gamma_1/\gamma_1^0 \propto N^{0.8} \quad (14)$$

The simple analysis given here is valid only for large $N$ for which eq 12 is fulfilled. Because in our experiment we used samples with $34 < N < 312$, the conditions given by eq 12 may be incorrect. However, experimental dependences of $\ln(\delta\gamma_1/\gamma_1^0)$ on $\ln N$ are consistent with prediction (14) as can be seen below.

Figure 2 shows the temperature dependences of $\gamma_1$ for dilute solutions of PMC-$N$ in 5CB. A strong increase in $\gamma_1$ with $N$ is clearly seen; this result is quite different from data presented in ref 7, where the values of $\gamma_1$ are similar for polymer samples with different values of $N$. Figure 3 gives the dependences of $\ln(\delta\gamma_1/\gamma_1^0 C)$ on $\ln(N)$ for different temperatures of solutions. The values of the slope $\alpha = \beta\zeta - 1$ of these linear dependences change from 0.87 to 0.67 in the temperature range 23–33 °C (see Table 2). In the approximation of the nondraining regime ($\zeta = 3$) this range of $\alpha$ corresponds to the

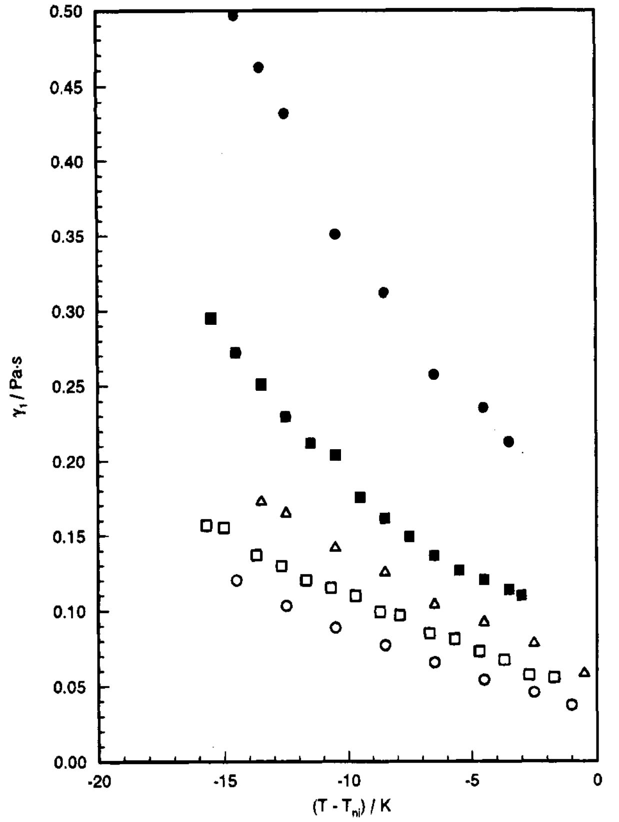


**Figure 2.** Temperature dependences of the twist viscosity coefficient for 5CB (○) and PMC-34 (□), PMC-88 (△), PMC-312, $C$ = 1.75% (■), and PMC-312, $C$ = 3.33% (●) solutions.

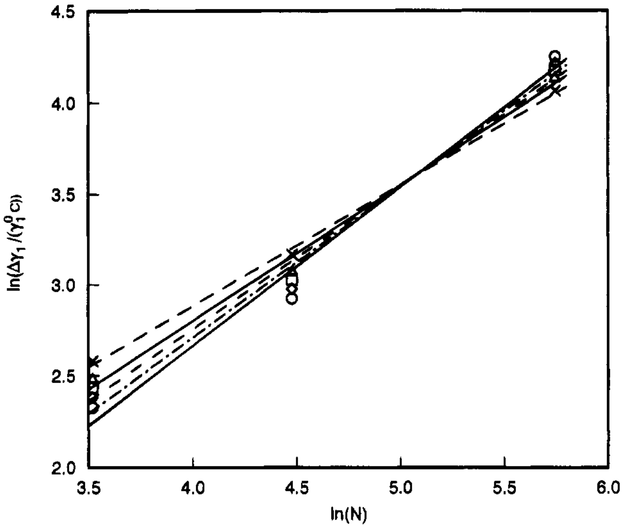


**Figure 3.** Dependences of $\ln(\delta\gamma_1/(\gamma_1{}^0C))$ on ln $N$ for $T$ = 23 (○), 25 (◇), 27 (□), 29 (△), and 33 °C (×).

**Table 2. Values of the Exponent α in Dependences of $\delta\gamma_1/\gamma_1{}^0$ on $N$ for Different Temperatures of Solutions**

| $T$, °C | α | $T$, °C | α |
|---|---|---|---|
| 23 | 0.87 ± 0.12 | 29 | 0.75 ± 0.06 |
| 25 | 0.83 ± 0.10 | 31 | 0.71 ± 0.04 |
| 27 | 0.79 ± 0.08 | 33 | 0.67 ± 0.03 |

exponent $0.56 < \beta < 0.62$. Therefore, chains of PMC-$N$ may be considered to be flexible macromolecules in a good solvent ($\beta$ = 0.6 in this case[14]).

It should be noted that the interval of exponent $0.67 \leq \alpha \leq 0.87$ is similar to the values of α for the side-chain copolymethacrylate with cyano- and methoxy-terminated mesogenic side groups in the melt.[15]

**Table 3. Values of the Apparent Activation Energy for 5CB and Polymer Solutions**

| sample | $W$, K |
|---|---|
| 5CB | 5473 ± 77 |
| PMC-34 | 4849 ± 123 |
| PMC-88 | 4609 ± 144 |
| PMC-312 ($C$ = 175 wt %) | 6366 ± 191 |

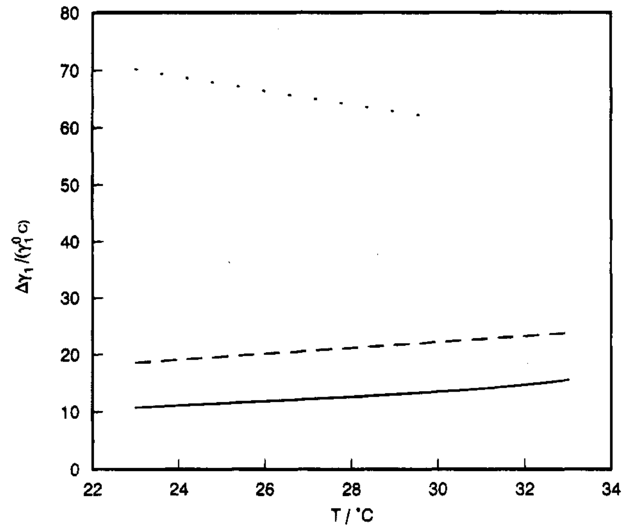


**Figure 4.** Temperature dependence of $\delta\gamma_1/(\gamma_1{}^0C)$ for PMC-34 (—), PMC-88 (– – –), and PMC-312 (···) solutions.

An intercept of the straight lines in Figure 3 can be seen at $\ln(N) \approx 5$ ($N \approx 150$). This intercept shows that a positive temperature coefficient of $\delta\gamma_1/\gamma_1{}^0$ for PMC-34 and PMC-88 is replaced by a negative coefficient for PMC-312.

The values of $\delta\gamma_1/\gamma_1{}^0$ given in Figure 3 were calculated from previously fitted temperature dependences of $\gamma_1$ for 5CB and polymer solutions according to the equation

$$\gamma_1/\chi_a = \text{const} \times \exp(W/T) \tag{15}$$

The values of the apparent activation energies for 5CB and solutions of PMC-$N$ obtained from the Arrhenius plot $\ln(\gamma_1/\chi_a)$ vs $1/T$ are listed in Table 3. These values of $W$ were used to calculate $\delta\gamma_1$ at the same absolute temperatures $T$. A correction of $\gamma_1$ for the solution of PMC-34 was made to take into account the difference between $T_{NI}(p)$ of the solution and $T_{NI}$ of 5CB:

$$\gamma_1(\text{corrected}) = \gamma_1(\text{measured}) \times \left(\frac{1 - 0.9995(T/T_{ni}(p))}{1 - 0.9995(T/T_{ni})}\right)^{0.141}$$

A decrease in the activation energy for PMC-34 and PMC-88 is observed; however, $W$ for PMC-312 is higher than $W_0$ for 5CB.

Figure 4 shows the temperature dependences of $\delta\gamma_1/(\gamma_1{}^0C)$ for the solutions of PMC-34, PMC-88, and PMC-312. The decrease in $\delta\gamma_1/(\gamma_1{}^0C)$ with temperature for molecules of PMC-312 is similar to results obtained for other polymers with side chain[6,7] and main-chain[16,17] mesogenic groups in nematic solvents. However, the opposite result is obtained for PMC-32 and PMC-88 in 5CB; namely, $\delta\gamma_1/\gamma_1{}^0$ increases with temperature.

It should be noted that both the positive and negative temperature coefficients are very small in comparison with those for main-chain polymer solutions in 5CB[9] or in 5OCB.[17] These temperature coefficients are determined by the difference between the activation energies of the solvent and the solutions, $\Delta W = W^{\text{solution}} - W^{\text{solvent}}$. For example, for the main-chain mesogenic polymer TBP-*X*,[17] it was found that $\Delta W = 2440 - 3430$ K whereas this difference is $\Delta W = +800 - (-900)$ K for solutions for PMC-*N*. This value is only 2 times higher than the error bar (±200 K; see Table 3) for the activation energy obtained by the least squares fit of the temperature dependences of $\gamma_1/\chi_a$ to eq 15.

The high value of $\Delta W$ for main-chain polymers shows a strong coupling between the nematic order parameter (which increases when temperature decreases) and the anisotropy of the main chain. For side-chain polymers PMC-*N* this coupling is weaker because the influence of interactions between the side mesogenic groups and the nematic environment on the conformation of the main chain is small.

Nevertheless, the difference in the behavior of the solutions of PMC-34 and PMC-88 as compared to that of PMC-312 cannot be explained by the uncertainty in the determination of *W*. We suppose that the effect of the nematic interaction on the molecular shape depends on the degree of polymerization. Therefore, relatively short ($N = 34$, 88) and long ($N = 312$) chains in the nematic solvent behave in different ways.

Most theories predict a negative temperature coefficient for $\delta\gamma_1$ corresponding to the extension of chains with increasing nematic order parameter *S*. This is consistent with the behavior of PMC-312. The behavior of shorter chains, PMC-34 and PMC-88, is compatible with recent results obtained by the Monte Carlo simulation of flexible chains in a nematic medium.[18] There is a strong tendency for chains to be aligned perpendicularly to the nematic director caused by the anisotropy of the excluded volume effect. Chains with small *N* are prolate, whereas longer chains have an oblate form. This may explain our experimental observation. Short chains diminish their anisotropy as *S* increases starting from the prolate shape. Longer chains are oblate from the very beginning. Therefore, anisotropy increases with the nematic order parameter.

To summarize, the degree of polymerization of PMC-*N* affects the behavior of macromolecules in the nematic environment, changing the temperature coefficient of $\delta\gamma_1/\gamma_1^0$ and increasing the rotational viscosity. An analogy with classic dilute polymer solutions indicates a swollen conformation for molecules of PMC-*N* in 5CB.

**Viscosity Reduction.** The viscosity reduction for the bend Freederiks transition is expressed by the ratio of the twist viscosity coefficient for pure twist deformation (without backflow) $\gamma_1$ to the effective twist viscosity, $\gamma_1/\gamma_1^*$ (see eqs 6 and 7).

The ratio of time constants $\tau_0/\tau(h) = (\gamma_1/\gamma_1^*)(h^2 - 1)$ was measured as a function of field $h^2$. The obtained dependences were fitted to eqs 6 and 7 by using *A* as the only fitting parameter.

The experimental dependences of the ratio $\tau(0)/\tau$ on $h^2 - 1$ for pure 5CB and solutions of PMC-*N* in 5CB are presented in Figure 5. It can be clearly seen that the viscosity reduction for solutions of PMC-34 and PMC-88 is approximately similar to that for 5CB. However, no strong viscosity reduction occurs for solutions of PMC-312. Note that the polymer concentration for all solutions under study was approximately the same (≈3%). Therefore we may detect the effect of *N* on the backflow for polymer solutions.

Table 4 shows the values of *A* for solutions of PMC-*N* in 5CB. This value decreases from $A = 0.8$ for PMC-34 to $A = 0.56$ for PMC-312. This result shows that the molecular weight plays a crucial role in damping of the backflow. Samples with $N = 34$ and $N = 88$ do not affect the viscosity reduction; however, solutions with $N = 312$ show a very strong damping of the backflow.

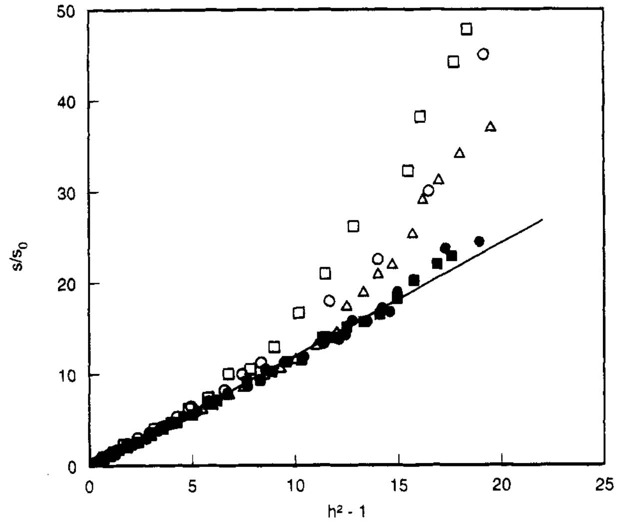


**Figure 5.** Dependence of the ratio $s/s_0$ on $h^2 - 1$ for 5CB (○) and PMC-34 (□), PMC-88 (△), PMC-312, $C = 1.75\%$ (■), and PMC-312, $C = 3.33\%$ (●) solutions.

**Table 4. Values of the Critical Fields and Parameter *A* for 5CB and Polymer Solutions**[a]

| sample | $h_c^2$ | *A* |
|---|---|---|
| 5CB | 11 (10.6)[b] | 0.74 ± 0.06 |
| PMC-34 | 10 (10.0) | 0.80 ± 0.03 |
| PMC-88 | 12 (11.3) | 0.70 ± 0.04 |
| PMC-312 ($C = 1.75$ wt %) | 16 (13.8) | 0.56 ± 0.06 |
| PMC-312 ($C = 3.33$ wt %) | 16 (13.8) | 0.56 ± 0.02 |

[a] Measurements were made at $T = 23$ °C. [b] Calculated values of $h_c^2$ are given in parentheses.

Backflow and the corresponding viscosity reduction are manifested in the experiment as a deviation of $\tau(0)/\tau$ from the $h^2 - 1$ law in Figure 5. A linear increase in $\tau(0)/\tau$ with $h^2 - 1$ is observed for relatively small values of the magnetic field, $1 < h^2 < h_c^2$, where $h_c$ is a critical field, which corresponds to the deviation from the $h^2 - 1$ law. As was pointed out in ref 1, for ordinary low molecular weight nematic LC $h_c^2 \approx 5$; i.e., this field is approximately twice as high as the Freederiks threshold field, $H_c \approx 5^{1/2}H_F$. In this range the $\gamma_1^*(0)/\gamma_1^*$ ratio is constant, because $\tau(0)/\tau = \gamma_1^*(0)/\gamma_1^*(h^2 - 1)$. Figure 5 shows a regular increase in $h_c^2$ with an increase in *N* of dissolved polymers. The values of $\tau(0)/\tau$ are approximately similar for both solutions of PMC-312 (1.75 and 3.33 wt %). Thus, the values of *A* for these solutions are similar.

This result does not agree with the observation of Gu et al.,[6] who have found a regular decrease in *A* from 0.79 to 0.37 in the concentration range 0−15%. Therefore, it may be concluded that the difference between the values of *A* for solutions with $C = 1.75$ and 3.33% is too small to be detected in our experiment.

One might expect that the deviation of $\tau(0)/\tau$ from a linear increase with $h^2 - 1$ is accompanied by a change in the reorientation mechanism. In terms of the theory of Pieranski, Guyon, and Brochard,[1] this deviation corresponds to a certain range of wavelength of the bend distortion $^2/_3d < \lambda < d$ corresponding to values of $\pi < X < 3\pi/2$.

This theory predicts two regimes of the effective twist viscosity reduction, slow and fast. There is a smooth

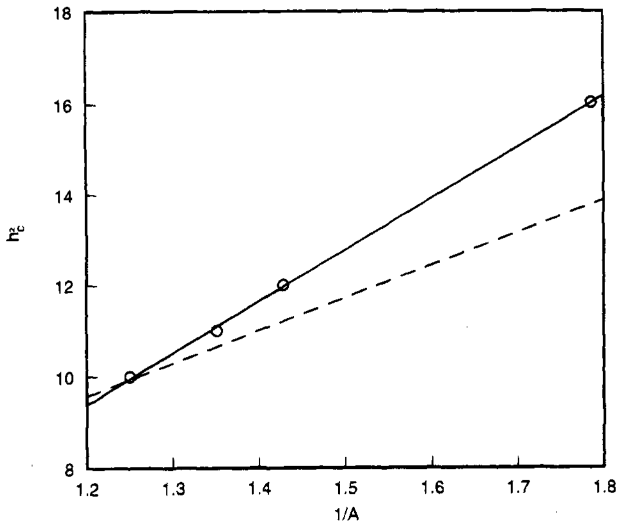


**Figure 6.** Dependence of critical field $h_c^2$ on $1/A$ (○). Broken line corresponds to calculations based on eqs 6 and 7.

transition between these regimes that occurs at some value of the magnetic field $h_c$. The value of $h_c$ may be defined as a magnetic field corresponding to the maximal curvature of the dependence $f_\gamma = \gamma_1/\gamma_1{}^*(h)$ on $h^2$ (see eq 6). Numerical calculations of the third derivative of $f_\gamma$ were made for different values of $A$ by using eq 6, because $f_\gamma{}'''(h) = 0$ at $h = h_c$ defined in this way. The calculated values of $h_c^2$ are given in Table 4 together with the experimental values of $A$ and $h_c^2$.

The experimental dependences in Figure 5 were fitted to eq 6. This fitting procedure gives the value of $A$ with a good accuracy. Critical values of the field $h_c^2$ were obtained independently by using plots for each curve, presented in Figure 5, in a large scale. The accordance between the calculated and the experimental values of $h_c^2$ is good, especially for $A \geq 0.7$. The discrepancy of the experimental and calculated values of $h_c^2$ for $A = 0.56$ is probably due to the difficulty of determination of $h_c^2$ for solutions of PMC-312 because of a small deviation of $\tau_0/\tau$ from the $h^2 - 1$ law.

The addition of the polymer to 5CB changes the parameter $A$. This makes it possible to obtain an experimental dependence $h_c^2$ *vs* $1/A$. Figure 6 shows a very good linear fit of the experimental data but with a higher slope (11.285) than that predicted in the theory of Pieranski et al.[1] (7.155).

According to our experimental data, the value of $A$ decreases with $N$

$$A = 1.93A_0N^{-0.162\pm0.01} \qquad (16)$$

where $A_0$ is the parameter for a pure nematic solvent. For $h_c^2$ we have

$$h_c^2 \propto \frac{N^{0.162}}{A_0}$$

As noted above, the parameter $A$ may be presented as a ratio of twist to shear viscosity coefficients (using $\alpha_2 \approx \gamma_1$):

$$A \approx \frac{\gamma_1}{\eta_c} = \frac{\gamma_1{}^0 + \delta\gamma_1}{\eta_c{}^0 + \delta\eta_c} = A_0\left(\frac{1 + \delta\gamma_1/\gamma_1{}^0}{1 + \delta\eta_c/\eta_c{}^0}\right) \qquad (17)$$

where superscript "0" refers to the viscosity coefficient for a pure solvent and the value of the increment of the Miesowicz viscosity $\delta\eta_c$ is given in the theory of Brochard:[5]

$$\delta\eta_c = (CkT/N)\tau_R\frac{R_\parallel{}^2}{R_\perp{}^2} \qquad (18)$$

A comparison of eqs 16 and 17 gives

$$\frac{1 + \delta\gamma_1/\gamma_1{}^0}{1 + \delta\eta_c/\eta_c{}^0} = 1.93N^{-0.162}$$

This result shows that a relative increment of the shear viscosity $\delta\eta_c/\eta_c{}^0$ increases with $N$ more rapidly than $\delta\gamma_1/\gamma_1{}^0$. The difference between these two increments can be clearly seen if eqs 9 and 18 are compared. Let us assume that we have almost spherically shaped macromolecules with $R_\parallel \approx R_\perp$. They would provide a zero contribution to the twist viscosity, $\delta\gamma_1 \approx 0$, but show a large $\delta\eta_c$.

It should be emphasized that polymer molecules dissolved in nematic liquid crystals can change markedly the combination of material parameters that influence the backflow and the viscosity reduction. One might expect that this effect would depend on the chemical structure of macromolecules. Therefore, it is interesting to obtain similar results for different side-chain mesogenic polymers in order to understand the influence of the shape of macromolecules on the damping of the backflow.

A more pronounced effect of macromolecules on the reorientation mechanism is expected for the twist Freederiks transition. In this case viscosity reduction is accompanied by the formation of periodic patterns. The value of the threshold field dividing two different regimes of reorientation—periodic and nonperiodic regimes—is proportional to the ratio $\eta_a\gamma_1/\alpha_2{}^2$:[19]

$$h_c^2 = 1 + \frac{K_3}{K_2}\frac{\eta_a\gamma_1}{\alpha_2{}^2}$$

where $K_3$ and $K_2$ are elastic constants and $\eta_a$ is the shear viscosity coefficient. We have recently obtained a very strong concentration dependence of $(\eta_a\gamma_1)/\alpha_2{}^2$ for PMC-312 in 5CB.[20]

## Conclusions

The experimental study of the bend Freederiks transition for solutions of PMC-*N* in 5CB shows a strong influence of polymer molecules on the dynamics of the transition.

It is shown that a reduced increment of the twist viscosity changes with the degree of polymerization according to the power law $\delta\gamma_1/(\gamma_1{}^0C) \propto N^\alpha$ with exponent $0.67 < \alpha < 0.87$ for different temperatures of nematic solutions. Therefore, a nematic liquid crystal, 5CB, may be considered as a good solvent for PMC-*N* in analogy with isotropic polymer solutions.

The temperature coefficient of $\delta\gamma_1/(\gamma_1{}^0C)$ is positive for PMC-34 and PMC-88, whereas this coefficient is negative for PMC-312.

A damping of the backflow for polymer solutions was found. This damping is especially strong for PMC-312. A strong decrease in the effective rotational viscosity begins for the magnetic field $h > h_c$. The value of the threshold field $h_c^2$ is found to depend on the ratio of twist to shear viscosity coefficients, $A = \alpha_2^2/(\gamma_1\eta_c) \approx \gamma_1/\eta_c$. This result agrees with the theory of Pieranski, Guyon, and Brochard:[1] $h_c^2 \propto 1/A$. It is shown that the parameter $A$ decreases with $N$ according to the power law $A \propto A_0N^{-0.162}$.

Therefore, the value of $h_c^2$ increases with $N$. This result makes it possible to shift the threshold field to higher values for nematic solutions containing polymers with a high degree of polymerization. This effect is due to the large difference in the contributions of the macromolecules to the shear viscosity $\eta_a$ and to the rotational viscosity $\gamma_1$ of the solutions; we have $\delta\eta_c > \delta\gamma_1$. This effect might be useful for the stabilization of the uniform reorientation process. In the application of liquid crystals to displays, instabilities are undesired. The addition of polymers may provide a means to suppress them considerably. Therefore, dilute polymer solutions may be of interest in all applications where convective flow destroys the device's performance.

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