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Molecular Weight Dependence of the Rotational Diffusion Constant and the Rotational Viscosity of Liquid Crystalline Side-Group Polymers

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ABSTRACT: Nematic side-group polymethacrylates with different molecular weights were studied by a combination of dielectric relaxation spectroscopy and measurements of the rotational viscosity by director reorientation experiments. The rotational diffusion constant obtained by relaxation frequency determinations allows the estimation of the contribution γ_1^m of the mesogenic groups to the total rotational viscosity γ_1^t on the basis of Marrucci's theory. γ_1^m then is used to separate the contribution $\Delta\gamma_1$ of the friction due to rearrangements of anisotropic ordered polymer backbones to γ_1^t. The molecular weight dependence of $\Delta\gamma_1$ can be described by a power law, as predicted by Brochard's theory. The resulting exponent gives evidence for the presence of nonentangled random-coil conformations. A model for the director reorientation shows the possibility of biexponential time dependencies for systems containing flexible chains with anisotropic conformations.

Introduction

The properties of nematic liquid crystals and flexible polymers can be combined in different types of systems: (1) solutions of polymer chains in low molecular weight nematic solvents,[1] where the fraction of polymer is limited because of the poor miscibility, (2) liquid crystalline side-group polymers, where phase separation is suppresed by coupling the mesogenic groups chemically with flexible spacer groups onto the main chain,[2–5] and (3) mixtures of these liquid crystalline polymers with low molecular weight liquid crystals.[6–8]

Comparison of the properties of polymeric with low molecular weight liquid crystals shows no difference in the general phase behavior. Smectic and nematic phases also occur in liquid crystalline side-group polymers and mixtures, with structures similar to those of low molecular weight compounds. The big difference is given by the viscosity, which is much higher for polymeric liquid crystals.[5,7] In this paper we discuss the different factors which determine the rotational viscosity γ_1. This viscosity coefficient is of special importance, since it controls the time scale of director reorientations.

In low molecular weight liquid crystals γ_1 is mainly determined by the rotational diffusion constant D_r associated with rotational movements about a short axis of the mesogenic group. As predicted by several theories,[9–11] an inverse proportionality between the rotational viscosity γ_1 and the rotational diffusion constant D_r is observed.

The additional degrees of freedom contributed by the backbone chains in liquid crystalline side-group polymers result in a pronounced increase in γ_1.[12] This increase is not only caused by the decrease of the rotational diffusion constant following from the upward shift of the glass transition temperatures. Brochard[13] has shown in a theoretical treatment that there exists an additional contribution $\Delta\gamma_1$ to the rotational viscosity, which follows from the reorientation of the backbone chains. As shown for liquid crystalline side-group polymers by neutron[14,15] and X-ray scattering experiments,[16] the anisotropic interaction between the polymer chain and the ordered nematogens causes anisotropic conformations of the polymer coil. The shape of the coil may be prolate or oblate. When the nematic director rotates in reorientation experiments, the anisotropic chain has to follow and go into a new equilibrium. These translational motions of the backbone units cause an additional contribution to the rotational viscosity. Brochard showed that for the case of dilute solutions of polymer chains in a low molecular weight nematic solvent this increase depends on the anisotropy of the chain conformation, i.e., on the difference in the radii of gyration parallel and perpendicular to the director. de Gennes pointed out that the theory should also be applicable for nonentangled melts of liquid crystalline polymers.[17] For melts with a high entanglement density reptation arguments suggest a strong molecular weight dependence of the viscosity coefficients.

The predicted dependence of $\Delta\gamma_1$ on the polymer concentration c (the geometrical parameters $R_\parallel$ and $R_\perp$ describe the anisotropy of the chain conformation)

$$\Delta\gamma_1 \sim ckT\frac{(R_\parallel^{\,2} - R_\perp^{\,2})^2}{R_\parallel^{\,2} R_\perp^{\,2}} \tag{1}$$

has been verified experimentally for mixtures of nematic side-group polymers with low molecular weight nematic solvents in the dilute regime.[6] At the concentration where the polymer coils begin to overlap, a change in the concentration dependence is noted. One observes a nonlinear increase of the rotational viscosity with increasing polymer fraction.

In the present study we analyze the effect of the molecular weight of nematic side-group polymers on the rotational viscosity. The analysis is based on a combination of rheological measurements, which yield the total rotational viscosity, with dielectric spectroscopy, which allows the determination of the rotational diffusion constant D_r of the mesogenic units. A simple model for the director reorientation is presented to discuss the changes in behavior due to the presence of polymer chains. On the basis of the experiments, we propose an explicit expression for the rotational viscosity of liquid crystalline

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Table I
Molecular Weights, Degrees of Polymerization, and Transition Temperatures

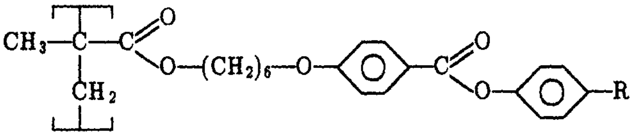
sample	$M_n{}^a$	$M_w/M_n{}^b$	N	T_{ni}, °C	T_g, °C
PMCO-9	3 500	1.19	8.5	96	30
PMCO-17	7 150	1.46	17.5	103	36
PMCO-88	36 000	1.58	88	117	45
PMCO-190	78 000	1.48	190	118	45

[a] By osmometry. [b] M_w by gel permeation chromatography of solutions in dimethylformamide.

side-group polymers of different molecular weight, using the results of theories of Marrucci[11] and Brochard.[13]

Experimental Section

Materials. In order to obtain nematic polymers with high values of the dielectric constant parallel to the director, copolymers were synthesized containing equimolar amounts of two comonomers attached to a polymethacrylate backbone:



PMCO-N, R = CN, OCH$_3$

One comonomer possesses a terminal cyano group, which produces strong signals in the dielectric spectra. The other comonomer, with terminal methoxy groups, suppresses the formation of smectic phases.

The polymerization behavior and the distribution of the comonomers along the polymer backbone was investigated by a determination of the monomer reactivity ratios.[18] The analysis of the copolymer composition as a function of the comonomer composition indicates an ideal polymerization behavior with equal reactivity ratios $r_1 = r_2 = 1$. Therefore, the two monomers are arranged randomly along the chain.

Copolymers PMCO-N with different degree of polymerization N were obtained by radical polymerization using dodecanethiol as a chain-transfer agent. The chain-transfer constant $c_s = 0.54 \pm 0.05$ (conditions: 0.25 mol/L monomer in benzene, 1 mol % azobis(isobutyronitrile), $T = 60$ °C) was evaluated according to well-known methods.[19]

Four samples with degrees of polymerization $9 \leq N \leq 190$ were synthesized. They show broad nematic regions above the glass transition at T_g. Their properties are listed in Table I.

Dielectric Spectroscopy. Dielectric relaxation spectra were recorded using an impedance analyzer (HP 4192A) in the frequency range 100 Hz $\leq f \leq$ 10 MHz. The samples were kept in a glass plate capacitor with gold-coated electrodes and had a thickness $d = 130$ μm. For separate measurements of the components $\epsilon_\parallel{}^*$ and $\epsilon_\perp{}^*$ of the complex dielectric constant tensor ϵ^* $(=\epsilon' - i\epsilon'')$ the nematic director $\hat{n}$ was oriented parallel and perpendicular to the electric field using a magnetic field ($B \approx 1.2$ T).

Reorientation Experiments. The rotational viscosity was determined by time-dependent capacity measurements using the same sample capacitor and a lock-in amplifier at a frequency of $f_m \approx 50$ kHz. The reorientation of the director was observed after a sudden change of the angle between the plate normal and the orienting magnetic field. The measured capacity change ΔC is related to the change in the angle φ between the director and the magnetic field. For an angle $\delta = 45°$ between the magnetic and the electric field and a small initial angular displacement $\tan^2 \varphi_0 \ll 1$ one obtains[7]

$$\frac{\Delta C}{C_0} = \frac{C(t) - C(\infty)}{C_0} = \Delta\epsilon_m{}' \frac{\tan\varphi}{1 + \tan^2\varphi} \approx \Delta\epsilon_m{}' \tan\varphi_0 \exp(-t/\tau_R) \tag{2}$$

Here C_0 denotes the capacity of the empty capacitor and $\Delta\epsilon_m{}'$ the anisotropy of the real part of the dielectric constant at the measuring frequency f_m. The reorientation time τ_R depends on the rotational viscosity γ_1, the anisotropy of the diamagnetic susceptibility $\Delta\chi$ $(\Delta\chi = \chi_\parallel - \chi_\perp)$, and the magnetic field strength B. It is given by[20]

$$\tau_R = \mu_0\gamma_1/\Delta\chi B^2 \tag{3}$$

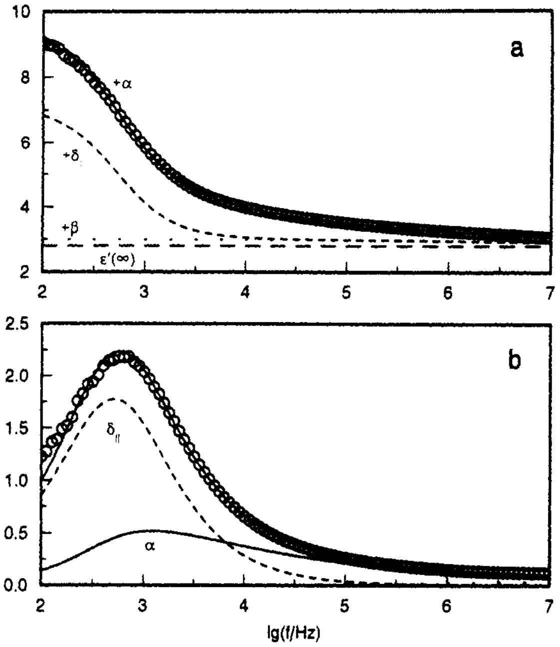


Figure 1. Dielectric spectra $\epsilon_\parallel{}'(f)$ (a) and $\epsilon_\parallel{}''(f)$ (b) of PMCO-88 in the nematic phase at 100 °C. It is shown how the different contributions sum up to give $\epsilon_\parallel{}'$.

For a determination of γ_1 a knowledge of $\Delta\chi$ is required. $\Delta\chi$ was determined by torque equilibrium experiments using a strong orienting low-frequency electric field $\vec{E}_{lf}$ ($f_{lf} \approx 1$ kHz) superposed to the magnetic field $\vec{B}$. A value of $\delta = 55°$ was chosen for the angle between $\vec{E}$ and $\vec{B}$. If $\Delta\chi$ and $\Delta\epsilon_{lf}$, the anisotropy of the real part of the dielectric constant, are both positive, the director in its equilibrium position is located in the plane set up by $\vec{E}$ and $\vec{B}$. Its orientation is given by the equilibrium of the torques per volume caused by the two external fields:

$$\frac{\Delta\chi B^2}{\mu_0} \sin\varphi\cos\varphi = \epsilon_0\Delta\epsilon_{lf}{}' E_{lf}{}^2 \sin\alpha\cos\alpha \tag{4}$$

Here φ is the angle between the director and the magnetic field, and α is the angle between the director and the electric field. With $E_{lf} = U_{lf}/d$ one obtains

$$\Delta\chi = \frac{\mu_0\epsilon_0\Delta\epsilon_{lf}{}' U_{lf}{}^2}{B^2 d^2} \frac{\sin 2\alpha}{\sin 2\varphi} \tag{5}$$

The angles α and φ are determined by measuring the change in the capacity $\Delta C = C(U_{lf}) - C(0)$ resulting from the application of the orienting field $\vec{E}_{lf}$:

$$C(U_{lf})/C_0 = \epsilon_\perp{}' + \Delta\epsilon_m{}' \cos^2\alpha \tag{6}$$

$$C(0)/C_0 = \epsilon_\perp{}' + \Delta\epsilon_m{}' \cos^2\delta \tag{7}$$

$$\rightarrow \Delta C/C_0 = \Delta\epsilon_m{}'(\cos^2\alpha - \cos^2\delta) \tag{8}$$

$$\alpha = \arccos\left[\frac{\Delta C}{\Delta\epsilon_m{}' C_0} + \cos^2\delta\right]^{1/2} \tag{9}$$

$$\varphi = \delta - \alpha \tag{10}$$

Results

Dielectric Relaxation. Nematic side-group polymers exhibit complex dielectric spectra with contributions of different relaxation processes.[3,4,7] Figures 1 and 2 show

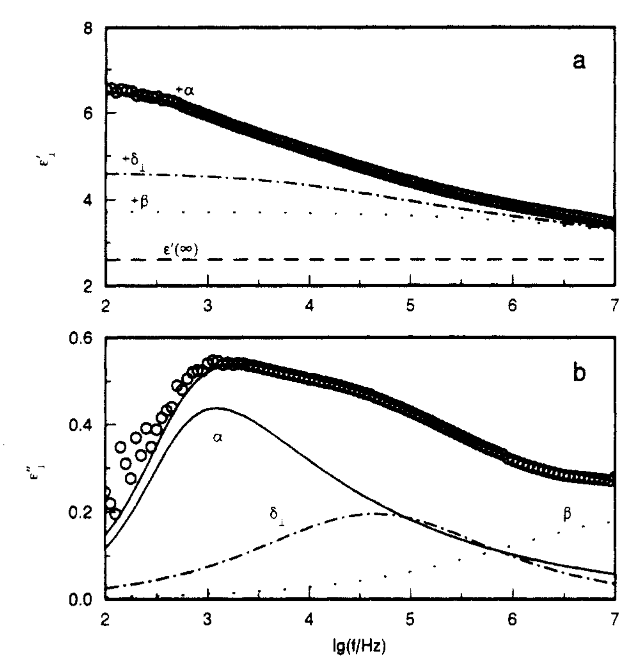


Figure 2. Dielectric spectra $\epsilon_\perp'(f)$ (a) and $\epsilon_\perp''(f)$ (b) of PMCO-88 in the nematic phase at 100 °C. It is shown how the different contributions sum up to give $\epsilon_\perp'$.

the components $\epsilon_\parallel^*(f)$ and $\epsilon_\perp^*(f)$ of the dielectric constant for PMCO-88 in the nematic phase. Decomposition of the spectra seems to be difficult but can be achieved by a simultaneous fit of the four spectra to relaxation functions. The resulting fits give a good representation of the data. Systematical errors in ϵ^* occur at low frequencies, when the sensitivity of the technique is low due to the low capacitance of the sample. The origin of these deviations is unknown. The contributions of the different processes, denoted α, β, $\delta_\parallel$, and $\delta_\perp$, are shown in the figures.

The α-process shows up in both orientations of the director and can be described by an asymmetric Cole–Davidson relaxation function

$$\epsilon^*(f) = \epsilon'(\infty) + \frac{\epsilon'(0) - \epsilon'(\infty)}{(1 + if/f_0)^b} \tag{11}$$

with $b = 0.25$. Curves with similar shapes are found for ordinary polymers too, where the α-process is understood as a cooperative process which is associated with the glass transition.

The β-process, which gives a contribution at the high-frequency end, also shows up in both orientations and can be represented by a Cole–Cole function

$$\epsilon^*(f) = \epsilon'(\infty) + \frac{\epsilon'(0) - \epsilon'(\infty)}{1 + (if/f_0)^{1-a}} \tag{12}$$

with a value of $a \approx 0.6$, indicating a broad distribution of relaxation times.

The δ-process reflects the rotational diffusion of the mesogenic groups about a short molecular axis. In the isotropic phase its relaxation frequency f_δ is proportional to the rotational diffusion constant D_r:

$$f_\delta = D_r/\pi \tag{13}$$

In the nematic phase it is split into two processes, $\delta_\parallel$ and $\delta_\perp$, which can be separately observed choosing different orientations of the director.[21]

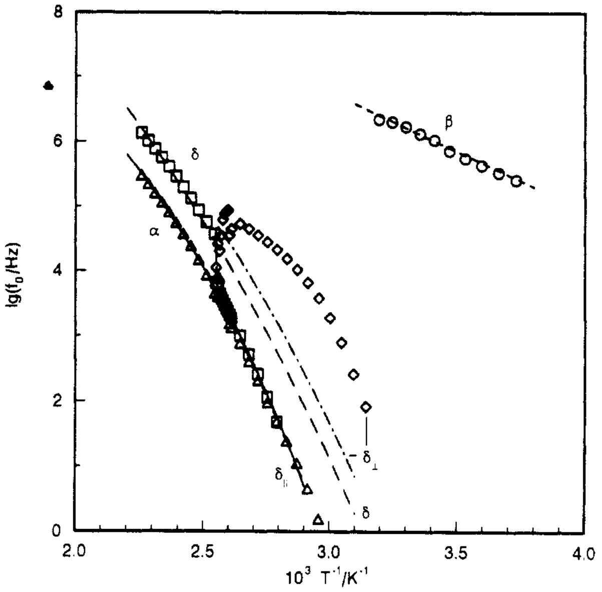


Figure 3. Temperature dependence of the relaxation frequencies of the different processes (α, β, δ) observed in the dielectric spectra of PMCO-88.

The $\delta_\parallel$-process shows up in the $\epsilon_\parallel$-spectra. It is nearly Debye-like. A fit by a Cole–Cole relaxation function at 100 °C yielded a value $a = 0.11$.

The $\delta_\perp$-process is found in the $\epsilon_\perp$-spectra. It is located at higher frequencies and can also be fitted by a Cole–Cole function, but with a broader distribution of relaxation times ($a = 0.48$). This is in agreement with observations reported in the literature for nematic polymers[4] and low molecular weight nematics.[22]

Figure 3 collects the results of the temperature-dependent measurements on PMCO-88, showing the relaxation frequencies of all observed processes.

The β-process shows an Arrhenius-like behavior with an activation energy $E_A = 35$ kJ/mol. It originates from intramolecular motions which do not freeze at the glass transition.

The α-process is essentially unaffected by the nematic–isotropic phase transition. His temperature dependence can be described by a Vogel–Fulcher law:

$$f_0 = f_0^\infty \exp\left(-\frac{A}{T - T_0}\right) \tag{14}$$

The same temperature dependence is found for the relaxation frequency of the δ-process in the isotropic phase; hence, for the rotational diffusion constant

$$D_r = D_r^\infty \exp\left(-\frac{A}{T - T_0}\right) \tag{15}$$

For the δ-processes in the nematic phase, $\delta_\parallel$ and $\delta_\perp$, the effect of the nematic potential has to be taken into account. As discussed in the work of Martin, Meier, and Saupe,[21] it leads to a retardation of $\delta_\parallel$ and an acceleration of $\delta_\perp$:

$$f_{\delta\parallel} = \frac{D_r}{\pi g_\parallel(S)} \quad (g_\parallel > 1) \tag{16}$$

$$f_{\delta\perp} = \frac{D_r}{\pi g_\perp(S)} \quad (g_\perp < 1) \tag{17}$$

Numerical values for $g_\parallel$ and $g_\perp$ were derived from the work of Martin, Meier, and Saupe, using approximations which are valid for $S \leq 0.8$:

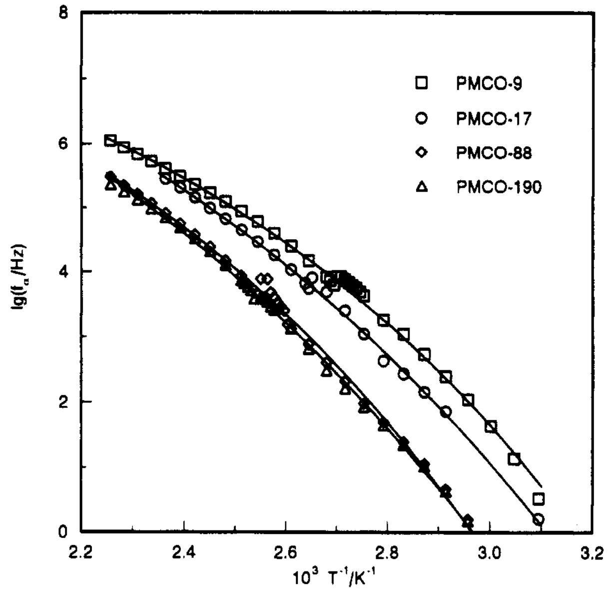


Figure 4. Temperature dependence of the relaxation frequency of the α-process observed for samples with different molecular weight. The lines represent fits to eq 14.

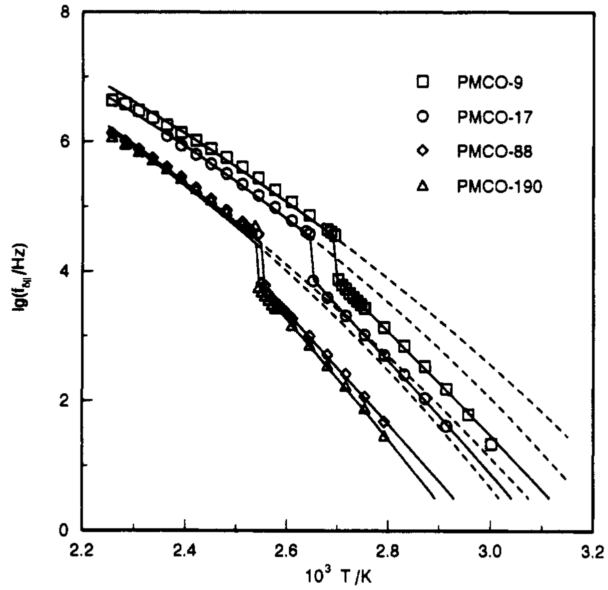


Figure 5. Temperature dependence of the relaxation frequency of the $\delta_\parallel$-process observed for samples with different molecular weight. The lines represent fits to eqs 13 and 15. The broken lines show the values of D_r/π in the nematic phase.

$$\log(g_\parallel) = 0.954S + 0.1615[(1 - S)^{-1.431} - 1] \qquad (18)$$

$$\log(g_\perp) = -0.508S - 0.0951[(1 - S)^{-1} - 1] \qquad (19)$$

The temperature dependence of the order parameter S was assumed to be in accordance with the Maier–Saupe theory, being approximately described by[23]

$$S(T) = (1 - 0.98T/T_{ni})^{0.22} \qquad (20)$$

The comparison of the measured values $f_{\delta\parallel}(T)$ and $f_{\delta\perp}(T)$ with the theoretical curves shows a good agreement for the $\delta_\parallel$-process but clear deviations for the $\delta_\perp$-process. The experimental values of $f_{\delta\perp}$ are higher than predicted by the theory. The broad distribution of relaxation times also cannot be explained within the framework for the theory. Possible reasons for the broadening are contributions of intramolecular processes to the relaxation of the longitudinal component of the dipole moment. In the theory the mesogenic groups are treated as stiff rods.

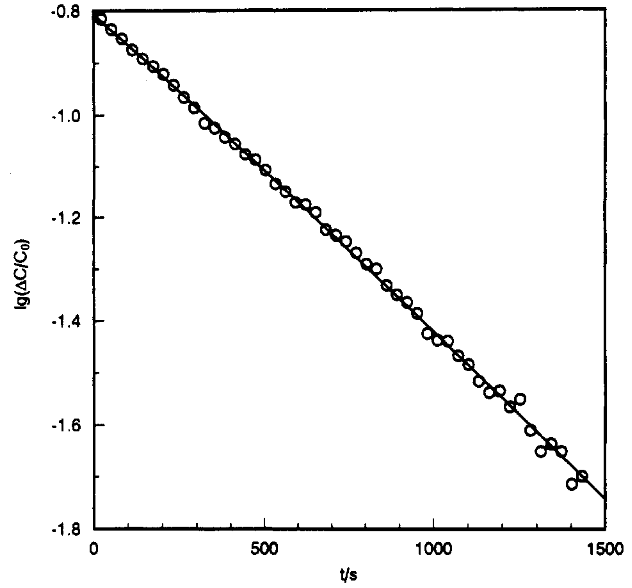


Figure 6. Time dependence of the relative capacity change of a PMCO-88 sample at 115 °C after a sudden rotation of the sample by φ_0 = 10°. The line represents a fit to eq 2.

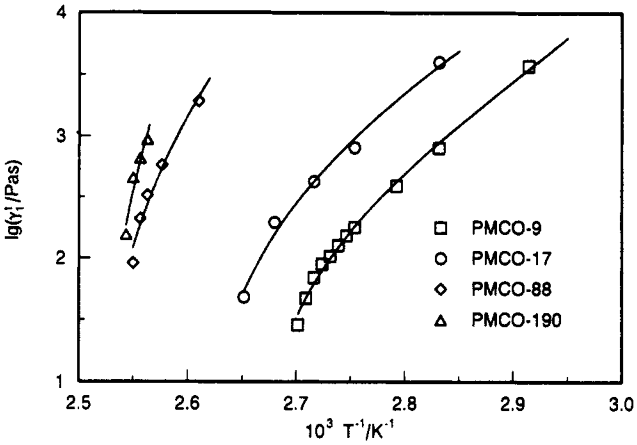


Figure 7. Temperature dependence of the rotational viscosity γ_1^t.

The relaxation frequencies of the α-process with dependence on the temperature are shown in Figure 4 for all samples. Obviously T_g is the essential parameter; the curves for samples with similar values of T_g (see Table I) approach each other closely.

Figure 5 shows $f_{\delta\parallel}$ and $D_r(T)$ for all samples. The data are well described by eqs 15, 16, 18, and 20, fitting the three parameters D_r^∞, A, and T_0.

Director Reorientation. In Figure 6 the time dependence of the capacity change is shown for the nematic side-group polymer PMCO-88. The data are well described by the exponential decay (eq 2). As will be shown in the discussion, this must not be necessarily the case. The elastic properities of polymer coils could also lead to more complex time dependencies.

Figure 7 shows the effective rotational viscosities as determined by the use of eq 2. As expected,[5,7] the viscosities are very high compared to those of low molecular weight nematics. The values exhibit a pronounced dependence on the degree of polymerization N. For the samples with N = 88 and N = 190 measurements were only possible in a small range just below T_{ni}.

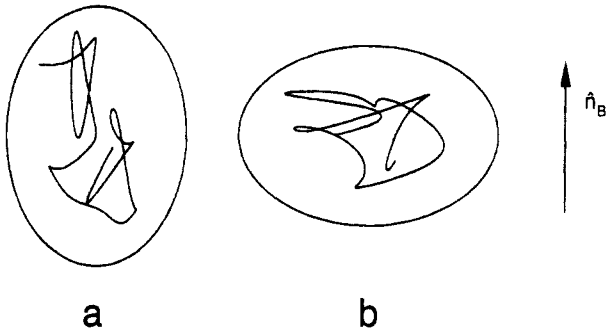


Figure 8. Anisotropic chain conformations in a nematic matrix: (a) prolate and (b) oblate shape.

Discussion

Model Considerations. In the following we present a simple model description for the director reorientation in nematic systems containing polymer chains.

Due to the interaction with the ordered mesogenic groups the chain configuration in general will also be anisotropic (Figure 8). We introduce a polymer backbone director $\hat{n}_B$, given by the axis of symmetry of the (prolate- or oblate-shaped) ellipsoids. In equilibrium $\hat{n}_B$ is parallel to the nematic director $\hat{n}$ of the mesogenic groups.

It can be assumed that an orienting magnetic field $\vec{B}$ acts directly only on the nematic director. The interaction force is determined by the diamagnetic anisotropy of the mesogenic groups. The effect of $\vec{B}$ on $\hat{n}_B$ is of indirect nature, being produced by a coupling between $\hat{n}$ and $\hat{n}_B$. If a linear coupling is assumed, producing a torque proportional to the angle $\varphi - \varphi_B$ between $\hat{n}$ and $\hat{n}_B$, it can be specified by a torsional modulus G_B. The geometry is shown in Figure 9.

The equations of motion for the two directors, oriented at angles φ and φ_B, are

$$\dot{\varphi} = -\frac{\Delta\chi B^2}{\mu_0\gamma_1^m}\sin\varphi\cos\varphi + \frac{G_B}{\gamma_1^m}(\varphi_B - \varphi) \tag{21a}$$

$$\dot{\varphi}_B = \frac{G_B}{\Delta\gamma_1}(\varphi - \varphi_B) \tag{21b}$$

Here γ_1^m and $\Delta\gamma_1$ are the rotational viscosities connected with the motions of $\hat{n}$ and $\hat{n}_B$, respectively.

For small angles φ ($\sin\varphi \ll 1$) the equations can be linearized:

$$\dot{\varphi} = -(a + b)\varphi + b\varphi_B \tag{22a}$$

$$\dot{\varphi}_B = c\varphi - c\varphi_B \tag{22b}$$

with

$$a = \Delta\chi B^2/\mu_0\gamma_1^m, \quad b = G_B/\gamma_1^m, \quad c = G_B/\Delta\gamma_1$$

The solutions are

$$\varphi = A_1\exp(-t/\tau_1) + B_1\exp(-t/\tau_2) \tag{23a}$$

$$\varphi_B = A_2\exp(-t/\tau_1) + B_2\exp(-t/\tau_2) \tag{23b}$$

with

$$1/\tau_{1,2} = \frac{a+b+c}{2} \mp \left[\left(\frac{a+b+c}{2}\right)^2 - ac\right]^{1/2} \tag{24}$$

Hence, in general biexponential time dependencies are expected for the relaxatory motion of both directors.

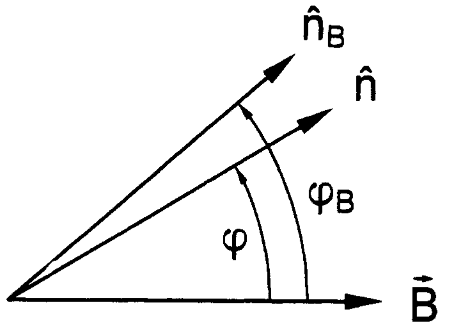


Figure 9. Orientation of the nematic director $\hat{n}$ and the director $\hat{n}_B$ of the polymer backbone in a reorientation experiment using a magnetic field $\vec{B}$.

Starting the reorientation experiment from an equilibrium

$$\varphi_B(t{=}0) = \varphi(t{=}0) = \varphi_0 \tag{25}$$

we obtain

$$A_1/\varphi_0 = \frac{\tau_2^{-1} - a}{\tau_2^{-1} - \tau_1^{-1}}, \quad B_1/\varphi_0 = 1 - A_1/\varphi_0 = \frac{a - \tau_1^{-1}}{\tau_2^{-1} - \tau_1^{-1}} \tag{26a}$$

$$A_2/\varphi_0 = \frac{\tau_2^{-1}}{\tau_2^{-1} - \tau_1^{-1}}, \quad B_2/\varphi_0 = 1 - A_2/\varphi_0 = -\frac{\tau_1^{-1}}{\tau_2^{-1} - \tau_1^{-1}} \tag{26b}$$

As is shown in the Appendix, under normal conditions for comparable angular displacements the torque produced by the magnetic field is small compared to the torque due to G_B; i.e., $a \ll b, c$. We therefore obtain

$$\tau_1 \approx \frac{1 + b/c}{a} = \frac{\mu_0}{\Delta\chi B^2}(\gamma_1^m + \Delta\gamma_1) \tag{27a}$$

$$\tau_2 \approx \frac{1}{b + c} = \frac{1}{G_B/\gamma_1^m + G_B/\Delta\gamma_1} \tag{27b}$$

For $\varphi_B(t{=}0) = \varphi(t{=}0) = \varphi_0$ we obtain

$$A_1/\varphi_0 \approx 1 - \frac{ab}{(b + c)^2} \approx 1 \tag{28}$$

$$B_1/\varphi_0 \approx \frac{ab}{(b + c)^2} \ll 1 \tag{29}$$

We conclude that the contribution of the component with τ_2 can be neglected. The director reorientation experiment essentially shows a single-exponential decay which is associated with the slow component $\varphi_0\exp(-t/\tau_1)$. Only in the case of high magnetic or electric fields ($a_{el} = \epsilon_0\Delta\epsilon E^2/\gamma_1^m$) together with high dielectric, diamagnetic, or paramagnetic anisotropies one can expect to observe a biexponential decay.

In the framework of Brochard's theory,[13] the total rotational viscosity for nematic systems, which contain polymer chains, is given by

$$\gamma_1^t = \gamma_1^m + \Delta\gamma_1 \tag{30}$$

Here γ_1^m denotes rotational viscosity of the mesogenic units, and $\Delta\gamma_1$ is the additional contribution due to the rearrangement of the polymer coil. Using γ_1^t the reorientation time measured in a director reorientation experiment would be given by the equation

$$\tau_{R} = \frac{\mu_0 \gamma_1^{t}}{\Delta\chi B^2} \tag{31}$$

Setting up our model with the equations of motion (eq 21), we have also used the two viscosities γ_1^{m} and $\Delta\gamma_1$ and arrived at the same result for the reorientation time (eq 27a) in the usually realized case of strongly coupled directors $\hat{n}\|\hat{n}_B$.

An increase of the director reorientation time in polymeric systems was also predicted and discussed in a work of Pleiner and Brand.[12] Their approach in considering rotations of backbone segments relative to the nematic director was based on a similar, but more detailed, model.

Brochard's theory yields an explicit expression for $\Delta\gamma_1$. The contribution of the polymer chains to the rotational viscosity depends on the anisotropy of the coil shape given by the parameters $R_\parallel$ and $R_\perp$:

$$\Delta\gamma_1 = \frac{\rho_p kT}{N}\frac{(R_\parallel^{\,2} - R_\perp^{\,2})^2}{D_\perp R_\parallel^{\,2} + D_\parallel R_\perp^{\,2}} \tag{32}$$

$D_\parallel$ and $D_\perp$ are the translational diffusion constants of the chain associated with motions parallel and perpendicular to the nematic director $\hat{n}$.

Using eqs A8a and A8b, the shape parameters $R_\parallel$ and $R_\perp$ can be expressed by the backbone order parameter S_B and the average R^2 (see Appendix). This leads to

$$\Delta\gamma_1 = \frac{\rho_p kT}{N}\frac{3R^2 S_B^{\,2}}{D_\perp(1 + 2S_B) + D_\parallel(1 - S_B)} \tag{33}$$

Molecular Weight Dependence of $\Delta\gamma_1$. Theories for low molecular weight nematics describe γ_1 as the product of a temperature-dependent and an order-parameter-dependent term (ρ_p: particle density of the mesogenic groups):

$$\gamma_1 = \frac{\rho_p kT}{D_r} g(S) \tag{34}$$

There are slight differences in the theories with regard to $g(S)$. Hess[9] proposes

$$g(S) = 5S^2/2 \tag{35}$$

Marrucci[11] gives

$$g(S) = 3S^2/(2 + S) \tag{36}$$

and Tseber[10] derives

$$g(S) = \frac{3S^2}{2 + S - 0.88989T/T_{ni}} \tag{37}$$

One cannot expect that eq 34 holds for the system under study, a liquid crystalline polymer, since it does not include the effect of the chains. However, it should give a good description for the part γ_1^{m} associated with the mesogenic groups, as it becomes a clear regarding the definition of γ_1^{m} in eq 21. We therefore set

$$\gamma_1^{t} = \frac{\rho_p kT}{D_r} g(S) + \Delta\gamma_1 \tag{38}$$

Data analysis can be based on this equation. It enables a separate determination of γ_1^{m} and $\Delta\gamma_1$.

The change of the measured rotational viscosity γ_1^{t} with increasing molecular weight shown in Figure 8 is due to different factors:

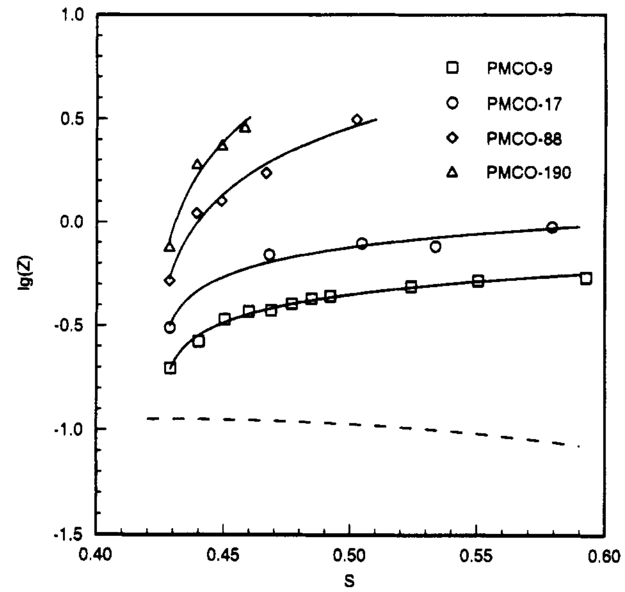


Figure 10. Dependence of the product quantity Z^t (eq 34) on the order parameter S as calculated from γ_1^{t} and $f_{\delta\parallel}$. Broken line: Z^m according to Marrucci's theory[11] (eq 40).

(i) T_g shifts to higher values. Consequently D_r decreases (eq 15).

(ii) The contribution $\Delta\gamma_1$ caused by the rearrangement of the polymer backbone exhibits a pronounced molecular weight dependence. For dilute solutions of nonentangled flexible chains in low molecular nematic solvents $\Delta\gamma_1$ is expected to scale as the degree of polymerization N, assuming simple random walk and free draining.[13,17]

(iii) γ_1^{t} is also affected by the order parameter, which changes between different samples at a given temperature. S affects γ_1^{m} via the factor $g(S)$. In addition, a change in S will also change the coil anisotropy $R_\parallel^{\,2} - R_\perp^{\,2}$ and therefore $\Delta\gamma_1$.

In order to eliminate the T_g-effect, it is convenient to introduce and discuss the product quantity Z, defined by[7]

$$Z^t = 2\pi f_{\delta\parallel}\gamma_1^{t}/\rho_p kT \tag{39}$$

Using Z^t eliminates D_r with its strong temperature dependence. Insertion of eqs 16 and 34 and, for example, Marrucci's expression (eq 36) shows that for low molecular weight nematics Z should depend on temperature only via the order parameter S:

$$Z^m(S) = \frac{2}{g_\parallel(S)}\frac{3S^2}{2 + S} \tag{40}$$

For some low molecular nematics, we in fact found a quite good agreement of the data with eq 40.[24] In the following we therefore use Marrucci's expression for the order parameter dependence of γ_1^{m}.

In Figure 10 the values of Z^t obtained by inserting the experimental values of γ_1^{t} and $f_{\delta\parallel}$ are compared with eq 40 using eqs 18 and 20 to calculate S and $g_\parallel(S)$. The experimental values are higher than Z^m due to the additional viscosity $\Delta\gamma_1$. As expected, these differences increase with an increase in the degree of polymerization. There is also an increase with an increase in the values of S. This effect is stronger for the samples with higher molecular weight.

Using the dielectric relaxation data, it is possible to determine the contributions $\Delta\gamma_1$ and γ_1^{t} to the rotational viscosity. γ_1^{t} is obtained directly from director reorientation experiments; γ_1^{m} can be derived from $f_{\delta\parallel}$ using eqs

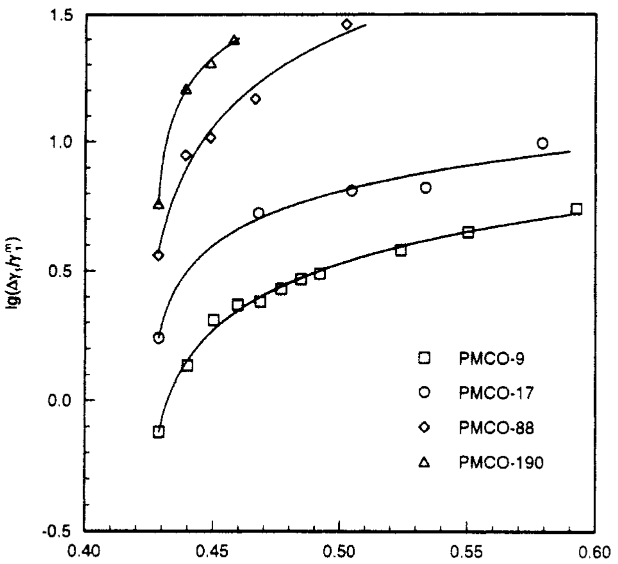


Figure 11. Dependence of the relative increase $\Delta\gamma_1/\gamma_1^m$ of the rotational viscosity (eq 42) on the order parameter S.

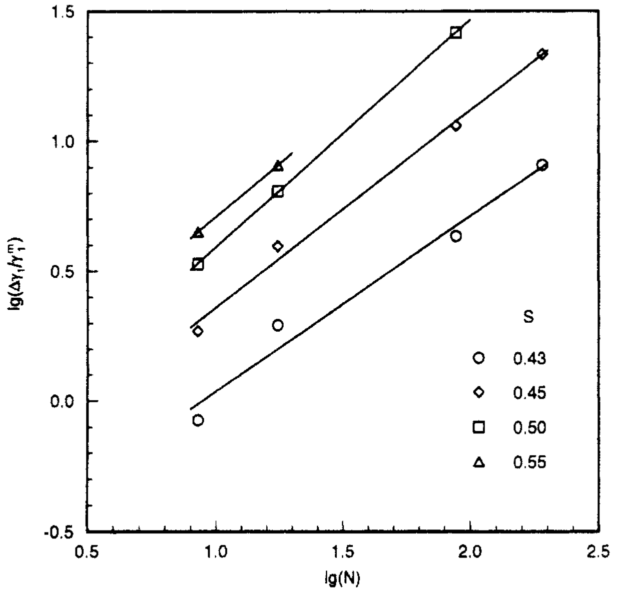


Figure 12. Dependence of the relative increase $\Delta\gamma_1/\gamma_1^m$ on the rotational viscosity (eq 42) on the degree of polymerization N.

18, 20, 34, and 36. The ratio γ_1^t/γ_1^m can be directly derived from the Z-functions:

$$\frac{\gamma_1^t}{\gamma_1^m} = \frac{\gamma_1^m + \Delta\gamma_1}{\gamma_1^m} = \frac{Z^t}{Z^m} \qquad (41)$$

Figure 11 shows the order parameter dependence of the ratio

$$\frac{\Delta\gamma_1}{\gamma_1^m} = \frac{Z^t}{Z^m} - 1 \qquad (42)$$

The continuous lines in Figure 11 were obtained by a fit to the empirical equation

$$\log(\Delta\gamma_1/\gamma_1^m) = A + B\log(S - C) \qquad (43)$$

The curves can be used to get interpolating values of $\Delta\gamma_1/\gamma_1^m$ for given values of S. Figure 12 shows for different constant values of S the dependence of $\Delta\gamma_1/\gamma_1^m$ on the degree of polymerization N. The fit by straight lines in a double-logarithmic plot suggests a power law

$$\Delta\gamma_1/\gamma_1^m \sim N^\mu \qquad (44)$$

The values obtained for the exponent are located in the range $0.7 \le \mu \le 0.9$. Also observed is a pronounced increase of $\Delta\gamma_1/\gamma_1^m$ with S.

It is interesting to compare these results with the theoretical predictions. In the free-draining limit the translational diffusion constants are related to the monomeric translational friction constants $\zeta_\parallel$ and $\zeta_\perp$ by

$$D_\parallel = kT/N\zeta_\parallel, \quad D_\perp = kT/N\zeta_\perp \qquad (45)$$

Using the rotational friction coefficient $\zeta_r = kT/D_r$, the ratio $\Delta\gamma_1/\gamma_1^m$ is obtained from eqs 33, 34, and 36:

$$\Delta\gamma_1/\gamma_1^m = R^2(S_B/S)^2 \frac{2 + S}{(1 + 2S_B)\zeta_r/\zeta_\perp + (1 - S_B)\zeta_r/\zeta_\parallel} \qquad (46)$$

Assuming that S_B and the ratios $\zeta_r/\zeta_\parallel$ and $\zeta_r/\zeta_\perp$ do not depend on N, $\Delta\gamma_1/\gamma_1^m$ should depend on the molecular weight like R^2. Thus, for ideal chains one expects $\mu = 1$, which is slightly higher than the obtained values. The observed dependence on S appears to be more pronounced than predicted by eq 46.

As known for conventional branched polymers, in nematic side-group polymers one can expect an enhanced entanglement density. Here, in addition, the aligning nematic potential may stabilize entanglement points.[17] Therefore, the entanglement threshold N_e for the degree of polymerization might be relatively low. For the case $N > N_e$ one would expect a stronger molecular weight dependence of $\Delta\gamma_1/\gamma_1^m$ (compare the change of the power law for the shear viscosity of conventional polymers from $\eta \sim N$ to $\eta \sim N^{3.4}$ at the entanglement threshold[25]). Obviously the resulting low values for the exponent μ do not indicate high entanglement densities in the polymers under study. Also Figure 12 shows no change of the power law in the given range of N. It appears that we are dealing with the nonentangled regime.

The rotational viscosity of dilute solutions of nematic side-group polymers in low molecular weight nematic solvents was studied by Pashkovsky et al.[8] In contrast to our results, they found nearly no dependence of γ_1^t on the degree of polymerization of the solute. As pointed out, this would indicate a rather compact chain conformation. At present the reason for the difference in the results is not clear.

Conclusion

The presence of the backbone chain in nematic side-group polymers affects the dynamics of rotational motions in different ways:

(1) The rotational diffusion constant D_r, describing individual motions of the mesogenic groups, is modified by the shift of the glass transition temperature T_g. D_r can be derived from the relaxation frequency of the δ-process.

(2) Due to chain elasticity, director reorientation experiments in principle may exhibit biexponential time dependencies. It is possible to estimate a torsional modulus G_B which determines the torque arising for nonvanishing angular displacements of the backbone director $\hat{n}_B$ and the nematic director $\hat{n}$. For comparable angular deviations this torque is large compared to the torque originating from an external magnetic or electric field. Therefore, under usual experimental conditions the director reorientation can be described as a common

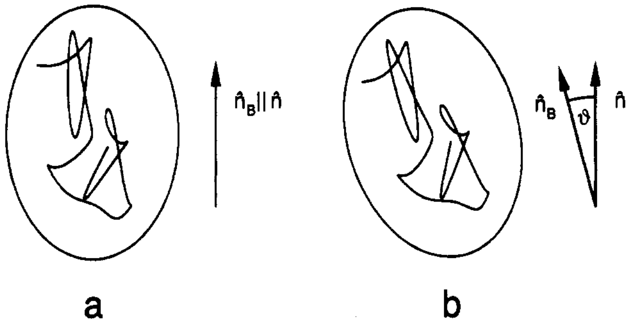


Figure 13. Chain conformations (prolate) in a nematic matrix: (a) equilibrium conformation; (b) nonparallel directors $\hat{n}$ and $\hat{n}_B$.

motion of strongly coupled directors $\hat{n}$ and $\hat{n}_B$, leading to a single-exponential time dependence.

(3) The rotational viscosity γ_1^t observed in a director reorientation experiment is set up by two parts, a contribution γ_1^m of the mesogenic groups and a contribution $\Delta\gamma_1$ of the backbone chains. γ_1^m depends on D_r, which is determined by the location of T_g, and S, as in the case of low molecular weight liquid crystals. Using Marrucci's theory,[11] γ_1^m can be obtained from D_r determined by dielectric relaxation spectroscopy. $\Delta\gamma_1$ is given by Brochard's theory. The combination of dielectric relaxation experiments enables a separate determination of γ_1^m and $\Delta\gamma_1$.

(4) $\Delta\gamma_1$ shows a molecular weight dependence $\Delta\gamma_1 \sim N^\mu$ with $\mu \approx 0.7$–0.9, near to the result predicted in Brochard's theory[13] for ideal nonentangled chains. There is no evidence for the presence of high entanglement densities, because higher values of μ are expected in this case.

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Appendix

In the following we will derive an expression for the torsional modulus G_B (see eq 18) describing the restoring torque acting on the directors $\hat{n}$ and $\hat{n}_B$ of nematics containing polymer chains.

The free energy of a deformed coil in a nematic matrix is a function of the squared values of the coordinates x, y, z of the end-to-end vector $\vec{R}$:[13]

$$F = \frac{kT}{2}\left(\frac{z^2}{R_\parallel^2} + \frac{x^2 + y^2}{R_\perp^2}\right) \tag{A1}$$

The shape parameters $R_\parallel^2 = \langle z^2 \rangle_{eq}$ and $R_\perp^2 = \langle x^2 \rangle_{eq} = \langle y^2 \rangle_{eq}$ give the equilibrium values parallel and perpendicular to the nematic director $\hat{n}$. In equilibrium ($\langle z^2 \rangle = R_\parallel^2$) we get $F = {}^3/_2 kT$.

This result of Brochard's theory, originally derived for dilute solutions of polymer chains in low molecular weight nematics, is assumed to be valid also in the case of nematic melts, because the unknown entanglement density should affect only the dynamic behavior of the system.

We calculate the change in free energy for a chain rotated by an angle ϑ in the fixed nematic field, keeping the chain conformation constant (see Figure 13). The rise in energy for an angle $\vartheta \neq 0$ between $\hat{n}_B$ and $\hat{n}$ can be determined by applying eq A1. We introduce a second coordinate system (x', y', z') which is attached to the coil, with $z' \| \hat{n}_B$. Coordinates are related by (choosing the axis of rotation parallel to x)

$$x = x' \tag{A2a}$$

$$y = y' \cos\vartheta + z' \sin\vartheta \tag{A2b}$$

$$z = -y' \sin\vartheta + z' \cos\vartheta \tag{A2c}$$

Using the equilibrium values for the chain conformation ($\langle x'^2 \rangle = \langle y'^2 \rangle = R_\perp^2$, $\langle z'^2 \rangle = R_\parallel^2$, $\langle x'y' \rangle = 0$), we obtain

$$\begin{aligned} F &= \frac{kT}{2}\left(\frac{R_\perp^2 \sin^2\vartheta + R_\parallel^2 \cos^2\vartheta}{R_\parallel^2} + \frac{R_\perp^2 + R_\perp^2 \cos^2\vartheta + R_\parallel^2 \sin^2\vartheta}{R_\perp^2}\right) = \\ &\frac{kT}{2}\left[3 + \left(\frac{R_\perp^2}{R_\parallel^2} + \frac{R_\parallel^2}{R_\perp^2} - 2\right)\sin^2\vartheta\right] = \\ &\frac{kT}{2}\left[3 + \frac{(R_\parallel^2 - R_\perp^2)^2}{R_\parallel^2 R_\perp^2}\sin^2\vartheta\right] \end{aligned} \tag{A3}$$

The torque Γ acting on the directors is given by

$$\Gamma = (\partial F/\partial\vartheta)_{\vartheta\to 0} \tag{A4}$$

which leads to the result

$$\Gamma = kT\vartheta \frac{(R_\parallel^2 - R_\perp^2)^2}{R_\parallel^2 R_\perp^2} \tag{A5}$$

The torsional modulus G_b follows as

$$G_B = \frac{\rho_p}{N}\frac{\partial\Gamma}{\partial\vartheta} = \frac{\rho_p kT}{N}\frac{(R_\parallel^2 - R_\perp^2)^2}{R_\parallel^2 R_\perp^2} \tag{A6}$$

Here ρ_p denotes the (monomer) particle density. The anisotropy of the conformation can be expressed by introduction of an order parameter S_B of the backbone links

$$S_B = 1/2(3\,\langle\cos^2\vartheta_B\rangle - 1) \tag{A7}$$

Here ϑ_B is the angle between a chain link and the backbone director $\hat{n}_B$. With

$$R\|^2 = \langle\cos^2\vartheta_B\rangle R^2 = (1 + 2S_B)R^2/3 \tag{A8a}$$

$$R_\perp^2 = 1/2(1 - \langle\cos^2\vartheta_B\rangle)R^2 = (1 - S_B)R^2/3 \tag{A8b}$$

we obtain

$$G_B = \frac{\rho_p kT}{N}\frac{9S_B^2}{1 + S_B - 2S_B^2} \tag{A9}$$

For nematic side-group polymers the chain density is given by $\rho_p/N = \rho N_A/M$ (ρ, mass density; N_A, Avogadro's constant). Inserting typical values ($M = 10\,000$, $\rho = 1$ g/cm^3, $T = 300$ K, $S_B = 0.3$), we get $G_B \approx 1.7 \times 10^5$ Pa. The corresponding "diamagnetic modulus" in eq 21a, $\Delta\chi B^2/\mu_0 \approx 0.8$ Pa (inserting $\Delta\chi = 10^{-6}$, $B = 1$ T), is small compared with G_B. In eq 26 this leads to $a \ll b$ and $a \ll c$.

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