

Electro-rheological behavior of liquid crystal polymers (LCPs) dissolved in a nematic solvent: dependence on temperature and LCP structure

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Abstract

The viscosity increments $\delta\eta_{\text{on}}$ and $\delta\eta_{\text{off}}$, upon dissolving a liquid crystal polymer (LCP) in a thermotropic nematic solvent, were determined by rheometry in the presence and absence, respectively, of a saturation electric field. Four species of molecular architectures were studied, a rigid main-chain LCP, two types of flexible main chain LCP, one with mesogens oriented perpendicular to the backbone, the other with mesogens parallel to the backbone, and a flexible side-chain LCP with mesogens attached side-on to the backbone. For all mixtures, $\delta\eta_{\text{on}}$ and $\delta\eta_{\text{off}}$ exhibit a similar Arrhenius dependence on temperature, determined by the viscous activation energy of the nematic solvent. However, the temperature dependence of the ratio $\delta\eta_{\text{on}}/\delta\eta_{\text{off}}$ and of the intrinsic viscosities, $[\eta_{\text{on}}]$ and $[\eta_{\text{off}}]$, is different for each LCP, and is strongly dependent on the flexibility of the LCP. By equating η_{on} and η_{off} to the Miesowicz viscosities, η_c and η_b , respectively, these results can be interpreted in terms of the ratio of the LCP chain dimensions parallel and perpendicular to the nematic director, R_{\parallel} and R_{\perp} (since theory predicts $\delta\eta_c/\delta\eta_b = R_{\parallel}^4/R_{\perp}^4$). The results indicate that the conformation of each LCP is strongly prolate, i.e. $R_{\parallel} \gg R_{\perp}$. For the rigid main-chain LCP, R_{\parallel}/R_{\perp} changes very little with temperature; for the flexible LCPs, R_{\parallel}/R_{\perp} decreases strongly with increase of temperature, indicative that the conformation becomes more spherical. The behavior of R_{\parallel}/R_{\perp} is compared with recent theoretical models of LCP conformation. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Nematic liquid crystal materials with positive dielectric anisotropy exhibit a small electro-rheological (ER) effect because, in the absence of a field, the nematic director tends to align parallel to the flow, whereas, when a field is applied perpendicular to the flow, the director rotates along the field direction. Thus the viscosity with the field on, η_{on} , is larger than that with the field off, η_{off} . We have recently investigated [1–5] the changes in these viscosities, $\delta\eta_{\text{on}}$ and $\delta\eta_{\text{off}}$, which occur when a liquid crystal polymer (LCP) is dissolved in a low molar mass nematic solvent (NS). We find that the intrinsic viscosities $[\eta_{\text{on}}]$ and $[\eta_{\text{off}}]$ have different values which depend on the molecular weight and molecular architecture of the LCP (e.g. side-chain versus main-chain). The influence of dissolved polymer on the ER response of a low molar mass nematic is of practical as

well as fundamental interest because certain materials with promise for application in electro-optic switching devices are prepared by polymerization of a reactive monomer dissolved in a nematic solvent [6,7]. This process produces phase-separated mixtures whose switching rates are determined by the viscosities of the LC phase which may contain small amounts of dissolved polymer.

The magnitude of the ER response of flow-aligning nematics is determined essentially by the values of the so-called Miesowicz viscosities η_b and η_c . Thus the asymptotic field-on viscosity η_{on} is exactly equal to η_c , which has the nematic director fixed along the shear gradient, perpendicular to the flow. The field-off viscosity, η_{off} , is approximately equal to η_b , where the director is fixed parallel to the flow. Therefore we can equate the intrinsic viscosities $[\eta_{\text{on}}] = [\eta_c]$ and $[\eta_{\text{off}}] \approx [\eta_b]$. As discussed in more detail below, theory indicates that the ratio $\delta\eta_c/\delta\eta_b$ can be directly related to the conformational anisotropy of the LCP, which we define as the ratio R_{\parallel}/R_{\perp} of the root mean square end-to-end distances, respectively, parallel and perpendicular to the director. In contrast to the intrinsic viscosity of isotropic

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solutions, the magnitudes as well as the temperature and molecular weight dependence of $[\eta_b]$ and $[\eta_c]$ may be quite different and depend strongly on the molecular architecture of the LCP, because the conformation of the LCP chain is anisotropic, i.e. R_{\parallel} and R_{\perp} are not equal.

In this paper, we investigate the temperature dependence of $[\eta_{on}]$ and $[\eta_{off}]$ of dilute LCP/NS solutions as a function of LCP molecular architecture. Gahwiller [8] showed experimentally that the Miesowicz viscosities η_b and η_c of nematic solvents such as *p'*-methoxybenzylidene-*p-n*-butylaniline (MBBA) and *p-n*-hexyl-oxybenzylidene-*p'*-aminobenzylidene (HBAB) exhibit an exponential decrease with temperature, each having essentially the same activation energy. Pashkovskii and Litvina [9] applied dynamic Freedericksz transition measurements on dilute LCP/NS solutions of an LCP to investigate the variation of the twist viscosity with temperature, and found Arrhenius dependence characterized by a viscous activation energy comparable to that of the solvent.

Here, we focus on the expectation that the temperature dependence of the viscosities of dilute LCP/NS solutions should contain a small contribution from the change in LCP conformation. Specifically, the temperature dependence of the intrinsic viscosities $[\eta_{on}]$ and $[\eta_{off}]$ should be determined predominantly by the temperature variation of the corresponding molecular hydrodynamic volumes of the LCP. Our experimental results show that $[\eta_{on}]$ and $[\eta_{off}]$ exhibit quite different dependences on temperature. By equating $[\eta_{on}] = [\eta_c]$ and $[\eta_{off}] \approx [\eta_b]$, we are able to directly relate these differences to the temperature dependence of the conformational anisotropy of the LCP.

Halperin and Williams [10] have carried out a theoretical analysis of the conformational behavior of a main chain LCP in a nematic solvent. They conclude [10] that R_{\parallel} and R_{\perp} each exhibit Arrhenius exponential dependence on inverse temperature. However, R_{\parallel} decreases whereas R_{\perp} increases with increasing temperature, i.e. the chain becomes more spherical. Within this model [10], the temperature dependence of the chain dimensions is determined by the activation energy required to form a hairpin in the flexible spacer groups of the LCP. As will be discussed below, this activation energy should be reflected in the temperature dependence of the intrinsic Miesowicz viscosities $[\eta_b]$, and $[\eta_c]$, as well as in the ratio of the viscosity increments, $\delta\eta_c/\delta\eta_b$.

Recently a new theoretical analysis of R_{\parallel} and R_{\perp} of LCPs in nematic solvents was reported by Carri and Muthukumar [11]. These authors employ the worm-like chain model of Kratky-Porod, with incorporation of a nematic coupling constant, D , which characterizes the strength of the orientational interaction between a polymer chain segment and a nematic solvent molecule. D varies smoothly between $D = -1$, corresponding to a strong tendency to align the segment along the director, through $D = 0$, implying the nematic field is turned off, to $D = +1$, indicative of a strong tendency for the polymer segment to align perpendicular to

the director. As explained below, analysis of the temperature dependence of $[\eta_b]$ and $[\eta_c]$ yields information on the corresponding variation of the coupling constant D . Note that the results of Carri and Muthukumar [11], as they apply to the conformation of main-chain LCPs, appear in certain aspects similar to those presented in an earlier theoretical discussion by Warner et al. [12].

Previously, we have carried out experimental studies [1–5] of the ER behavior of LCPs dissolved in nematic solvents such as 4'-(pentyloxy)-4-cyanobisphenyl (5OCB, $T_{NI} = 67^{\circ}\text{C}$) or 4'-pentyl-4-cyanobisphenyl (5CB, $T_{NI} = 35^{\circ}\text{C}$). We demonstrated that the ER response of these solutions is strongly dependent on LCP molecular weight and molecular architecture. For a flexible main-chain LCP, with mesogens parallel to the backbone, dissolved in 5OCB, we found [1] $[\eta_c] \gg [\eta_b]$, and $[\eta_c] \sim M^{\alpha}$ with $\alpha \approx 1$. Because of the low values of η_b , it was not possible to determine its molecular weight dependence [1]. In contrast, for a flexible side-chain LCP, with mesogens attached end-on to the back-bone, we observed [3] $[\eta_b] \approx [\eta_c]$, with $[\eta_b] \sim M^{0.4}$, and $[\eta_c] \sim M^{0.1}$. Qualitatively, a physical interpretation of these observations is clear. A main-chain LCP has a conformation [10–12] that is highly extended along the nematic director ($R_{\parallel} \gg R_{\perp}$). Thus the molecular hydrodynamic volume corresponding to $[\eta_c]$, where the long axis of the chain is pinned by the field perpendicular to the flow, is much larger than that corresponding to $[\eta_b]$, where the chain axis aligns with the flow. On the other hand, a side-chain LCP with end-on mesogens has a compact quasi-spherical conformation ($R_{\parallel} \approx R_{\perp}$), and hence similar hydrodynamic volumes for $[\eta_b]$ and $[\eta_c]$.

A quantitative molecular interpretation of the previous results was obtained via a hydrodynamic model developed by Brochard [13]. Brochard derived the following results for the increments in Miesowicz viscosities on dissolving LCP:

$$\delta\eta_c = (cN_A kT/M)(R_{\parallel}^2/R_{\perp}^2)\tau_R \quad (1)$$

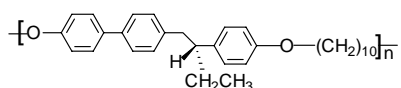
$$\delta\eta_b = (cN_A kT/M)(R_{\perp}^2/R_{\parallel}^2)\tau_R \quad (2)$$

where c is the LCP concentration, N_A is Avogadro's number, k is Boltzmann's constant, T is absolute temperature, M is the molecular weight of the LCP, and R_{\parallel} and R_{\perp} are the rms end-to-end distances parallel and perpendicular to the director. Taking the ratio of these two equations, we obtain:

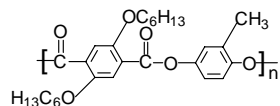
$$\delta\eta_c/\delta\eta_b = R_{\parallel}^4/R_{\perp}^4. \quad (3)$$

By identifying $\delta\eta_c$ equal to the ER viscosity with the field on, and $\delta\eta_b$ equal to the viscosity with the field off, we see that the effect of LCP on the magnitude of the ER response can be related directly to the chain anisotropy. These predictions are supported by our experimental observation [2] that the magnitude of the change in ER response produced by dissolving LCPs of different molecular architectures decreases in the order: main-chain LCP \gg side-on side-chain

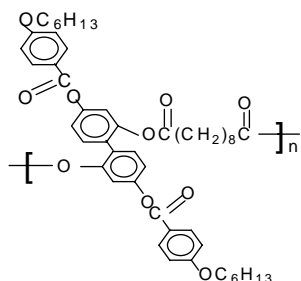
TPB 10:



ND-3-1-19:



TT-2-35A:



SA-1-75A

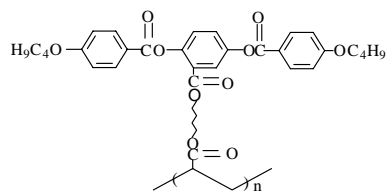


Fig. 1. The chemical structures of the liquid crystal polymers.

LCP > end-on side-chain LCP. This is consistent with the theoretical expectation [10–12] that main-chain LCPs will have highly prolate conformations ($R_{\parallel} \gg R_{\perp}$), side-on side-chain LCPs will be moderately prolate [11] ($R_{\parallel} > R_{\perp}$), and end-on side-chain LCPs will be quasispherical [11] ($R_{\parallel} \approx R_{\perp}$). Our observations of the molecular weight dependence of the intrinsic viscosities of main-chain and side-chain LCPs were also rationalized [1,3] via the Brochard model, by assuming that the main-chain LCP has dominant free-draining hydrodynamics, whereas the side-chain LCP has dominant non-draining hydrodynamics. As will be discussed later, in the context of the conformational model of Halperin and Williams [10], Eq. (3) implies

Table 1
Molecular weights and chain contour lengths of TPB-10 polymers

	Tetramer	No. 5	No. 8
$M_{w,GPC}^a$	3070	13 330	45 820
M_w/M_n^a	1.00	1.18	1.28
M_w^b	1966	8440	28 990
L_w (nm)	14.93	62.99	215.66

^a Determined by GPC using chloroform as a solvent and polystyrene as a standard.

^b True molecular weight obtained by correcting $M_{w,GPC}$ via the ratio between $M_{w,GPC}$ and the calculated value of the tetramer, $M_c = 1966$.

that the temperature dependence of the ratio of viscosity increments, $\delta\eta_c/\delta\eta_b$, can be directly related to the hairpin formation energy, which determines the variation of R_{\parallel} and R_{\perp} with temperature. Alternatively, within the analysis of Carri and Muthukumar [11], R_{\parallel}/R_{\perp} , and consequently the ratio $\delta\eta_c/\delta\eta_b$, is determined solely by the coupling strength D .

In the present study, E48 is used as a nematic solvent to investigate the effect of temperature on the ER behavior of LCP/NS solutions. E48 is a proprietary mixture of alkyl-4-cyanobiphenyls which has a very wide nematic temperature range from room temperature to the clearing transition at $T_{NI} = 85^\circ\text{C}$. Its nematic temperature range encompasses that of the nematic solvents previously used by us, 5OCB and 5CB. Four different species of LCP are investigated in this study: two main chain LCPs, one having a flexible spacer group in the backbone, the other having a rigid polyester backbone; these LCPs are compared with data on a flexible main-chain LCP with mesogens oriented perpendicular to the backbone, and a side-on side chain LCP. It is pertinent to note that all four LCP species are expected to form prolate conformations in nematic solution, and hence are expected to exhibit flow-aligning behavior which simplifies the rheological interpretation. We determine the intrinsic viscosities $[\eta_c]$ and $[\eta_b]$ which represent the contributions to the ER behavior of a single LCP chain. Applying the hydrodynamic model of Brochard [13], we gain molecular insight into the change in ER behavior with temperature. Specifically, the conformational anisotropy, R_{\parallel}/R_{\perp} , and the conformational relaxation time, τ_R , can be calculated from the viscosity increments $\delta\eta_c$ and $\delta\eta_b$ via Eqs. (1)–(3).

2. Experimental

2.1. Materials

Three main-chain and one side-chain LCP, whose structures are shown in Fig. 1, were studied in this work. The synthesis and molecular weight characterization of the main chain LCP designated TPB10 which has a mesogenic group, 1-(4-hydroxy-4'-bisphenyl)-2-(4-hydroxyl phenyl)-butane, linked by flexible decamethylene spacer ($n = 10$), is described elsewhere [14]. The molecular weights of three fractions of TPB10 are listed in Table 1.

The second main chain LCP utilized was a low molecular weight, rigid polyester, designated ND3-1-19 ($M_w = 4500$; 57.6n115.4i), which has no spacer groups linking the mesogens. Polymer ND-3-1-19 was prepared by mixing 2,5-dihexyloxy-1,4-dicarboxylic acid chloride (500 mg, 1.36 mmol), 2-methylhydroquinone (169 mg, 1.36 mmol), 0.42 ml of triethylamine and 3.25 ml of dichloromethane in a round-bottom flask and stirred at room temperature and nitrogen atmosphere for 4 days. The reaction mixture was heated to reflux for 1 h before dilution with tetrahydrofuran (THF). The polymer was precipitated into methanol,

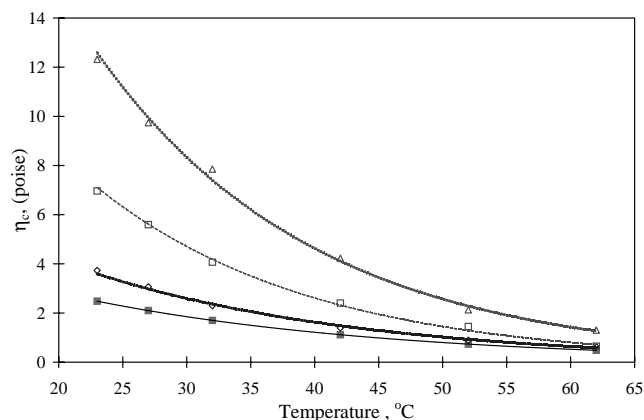


Fig. 2. The temperature dependence of the Miesowicz viscosity η_c of TT-2-35A dissolved in low molar mass nematic solvent E48: (■) pure solvent; (◇) 1 wt% solution; (□) 3 wt% solution; (△) 6 wt% solution.

filtered and re-precipitated from THF into methanol three more times until TLC showed no monomers. The polymer was dried and 491 mg of polymer (79.5% yield) was obtained. The polymer was characterized by ^1H NMR (CDCl_3 ppm: 7.61 (s, 2H), 7.20 (m, 3H), 4.12 (t, 4H), 2.31 (s, 3H), 1.70–2.00 (m, 4H), 1.62–1.20 (m, 12H), 1.00–0.80 (t, 3H)).

The third main-chain LCP, designated TT-2-35A ($M_w = 21\,400$, $M_w/M_n = 1.71$; 30n134i), is a polyester with mesogenic groups oriented perpendicular to the backbone linked by octamethylene spacers. Polymer TT-2-35A was prepared by mixing decandioyl chloride (1.6 mmol) and 2,2'-dihydroxy-4,4'-bis(4''-hexyloxybenzoyloxy)-1,1'-biphenylene (1.6 mmol), triethylamine (0.46 ml, 3.5 mmol) and 10 ml of dichloromethane. The mixture was stirred at room temperature for 3 days and the polymer was precipitated from dichloromethane into methanol three times. The polymer was dried and characterized by ^1H NMR (CDCl_3 ppm: 8.10 (d, 4H), 7.30 (d, 2H), 7.14 (dd, 2H), 7.08 (d, 2H), 6.94 (d, 4H), 3.99 (t, 4H), 2.66 (t, 4H), 1.76–1.83

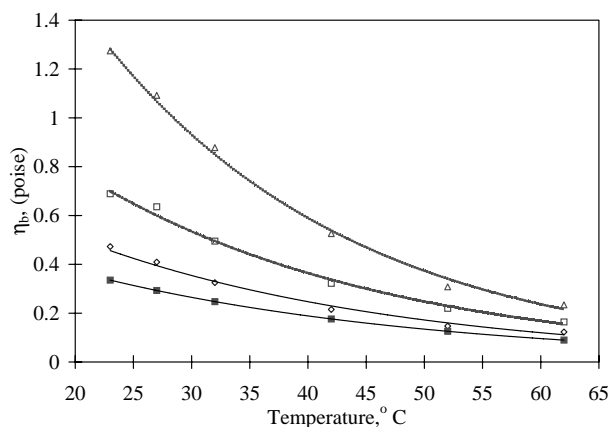


Fig. 3. The temperature dependence of the Miesowicz viscosity η_b of TT-2-35A dissolved in nematic solvent E48: (■) pure solvent; (◇) 1 wt% solution; (□) 3 wt% solution; (△) 6 wt% solution.

(m, 4H), 1.18–1.57 (m, 24H), 0.90 (t, 4H)). A side-on side chain LCP, designated SC-1-75A ($M_w = 28\,900$; $M_w/M_n = 3.2$; c50n114i), with mesogens attached side-on via tetramethylene spacers, is also studied for comparison. Polymer SC-1-75A was prepared by polymerizing 2-[bis(4-butoxybenzoyl)-1',4'-dihydroxybenzene] carbonyloxybutoxy acrylate with 2 wt% of AIBN in toluene at 65°C for 24 h. The polymer was obtained by precipitation from dichloromethane into hexane five times, dried, and characterized by ^1H NMR (CDCl_3 ppm: 8.14 (dd, 4H), 7.92 (d, 1H), 7.5 (dd, 1H), 7.34 (m, 6H), 4.21 (t, 2H), 4.01 (t, 2H), 2.70 (m, 4H), 1.61 (m, 3H), 1.43 (m, 8H), 0.94 (t, 6H)).

The nematic solvent used in this study is a proprietary mixture of alkylcyanobiphenyls designated E48 ($T_{\text{NI}} = 85^\circ\text{C}$) and was obtained from BDH Ltd. All materials were used without further purification.

2.2. Methods

A specified weight of LCP was dissolved in E48 at a temperature above its clearing temperature. Equilibration was continued for 24 h until LCP completely dissolved. No evidence of phase separation was found on cooling into the nematic range as evaluated by optical microscopy between crossed polarizers. Thirty microliters of this solution was placed between the gap of a Carri-Med controlled shear rheometer with cone-and-plate geometry (tip gap = $15\ \mu\text{m}$, diameter = 2 cm, angle = 0.5°) and maintained at the desired temperature for at least 10 min. The shear stress sweep mode was applied to measure the viscosity response in the presence and absence of a saturation electric field ($E = 2.2\ \text{kV/mm}$). As described elsewhere [1,2], we extrapolate the field-on viscosity to low shear rate to obtain the Miesowicz viscosity η_c , and assume the steady high-shear viscosity with the field off is the Miesowicz viscosity η_b . The latter is only approximately correct, since, for flow-aligning nematics, the director will be aligned at a small angle to the flow direction [1–5].

3. Results

The viscosities of the nematic solvent E48 and the LCP/E48 solutions were determined in the presence and absence of a saturation electric field yielding, respectively $\eta_{\text{on}} = \eta_c$ and $\eta_{\text{off}} \approx \eta_b$, over the nematic temperature range 23 – 72°C . An example is shown in Figs. 2 and 3 for solutions of the flexible main-chain LCP with mesogens orthogonal to the backbone, TT-2-35A. Experimental data on η_c (Fig. 2) and η_b (Fig. 3) for the pure solvent are compared with those for the solutions containing, respectively, 1, 3, and 6% w/w TT-2-35A. Addition of the LCP progressively increases both η_c and η_b . As indicated by the solid lines, the results for both η_c and η_b can be well described by least-squares fits to an exponential function of temperature. From these exponential fits, we determine the intrinsic viscosities at each temperature in the usual way, by extrapolation to zero

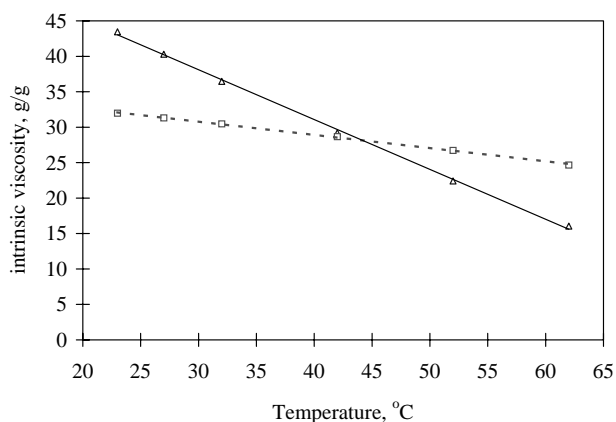


Fig. 4. The temperature dependence of the intrinsic Miesowicz viscosities $[\eta_c]$ and $[\eta_b]$ of TT-2-35A dissolved in nematic solvent E48: (Δ) $[\eta_c]$; (\square) $[\eta_b]$.

concentration of the reduced specific viscosity using the Huggins equation:

$$\eta_{sp}/C = [\eta] + K_1[\eta]^2 C. \quad (4)$$

The results for TT-2-35A are shown in Fig. 4. We see that $[\eta_c]$ and $[\eta_b]$ each decrease with increasing temperature, but that the rate of decrease is more rapid in the case of $[\eta_c]$. Thus, a cross-over occurs in the temperature dependence such that, at low temperatures, $[\eta_c] > [\eta_b]$, whereas, at high temperatures, $[\eta_b] > [\eta_c]$.

A quantitative interpretation of these observations is possible via Eq. (3) from the hydrodynamic model of Brochard [13]. To accomplish this, we first realize that the Brochard model applies to the Einstein limit, i.e. at sufficient dilution that intermolecular interactions can be neglected. Thus, to apply the theory, we determine the reduced viscosity increments $\delta\eta_c/c$ and $\delta\eta_b/c$ in the Einstein limit. These can be directly computed from the intrinsic viscosities:

$$\lim_{c \rightarrow 0} \delta\eta_c/c = \eta_c^0[\eta_c] \quad (5)$$

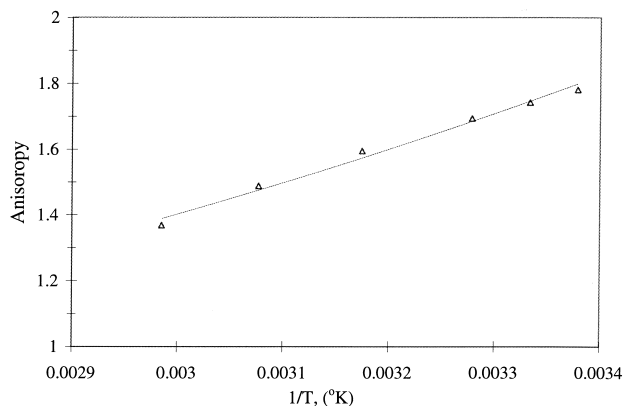


Fig. 5. The temperature dependence of the conformational anisotropy, $R_{||}/R_{\perp}$, of TT-2-35A dissolved in nematic solvent E48.

$$\lim_{c \rightarrow 0} \delta\eta_b/c = \eta_b^0[\eta_b] \quad (6)$$

where η_b^0 and η_c^0 represent the Miesowicz viscosities of the pure solvents. Taking the ratio of these equations at each temperature, and invoking Eq. (3), we directly obtain the corresponding value of the conformational anisotropy, $R_{||}/R_{\perp}$:

$$\eta_c^0[\eta_c]/\eta_b^0[\eta_b] = R_{||}^4/R_{\perp}^4. \quad (7)$$

The results are shown in Fig. 5. It is evident, first, that the chain conformation is indicated to be prolate, $R_{||} > R_{\perp}$, and that, as temperature increases, the conformation becomes less asymmetric. Recalling the structure of TT-2-35A shown in Fig. 1, we conclude that, because of the flexible spacers, the nematic interaction of the mesogens with the solvent is able to align the backbone along the director, producing a prolate conformation. As the temperature increases, Brownian motion diminishes the nematic interaction, and also weakens the coupling between mesogen and the backbone.

A similar pattern of behavior was observed for the side-on side-chain LCP, SC-1-75A. Fig. 6 shows the temperature dependence of the intrinsic viscosities, estimated following the same procedures as described above for TT-2-35A. Again, at low temperatures, $[\eta_c] > [\eta_b]$. As temperature increases, $[\eta_c]$ decreases weakly, and $[\eta_b]$ actually increases slightly so that at 52°C, $[\eta_c] \approx [\eta_b]$. Application of the hydrodynamic model [13], viz. Eq. (7), yields information on the temperature dependence of the conformational anisotropy shown in Fig. 7. The results indicate that the side-on side-chain LCP is prolate throughout the nematic range, and furthermore that the values of $R_{||}/R_{\perp}$ are at all temperatures only slightly larger for SC-1-75A than for TT-2-35A. Note, however, that the values of $[\eta_c]$ and $[\eta_b]$ are each substantially smaller for SC-1-75A, indicative that the hydrodynamic volume of the side-on side-chain LCP is considerably smaller than that of TT-2-35A. This is consistent with the observation that the molecular weight of SC-1-75A, measured by GPC relative to polystyrene standards, ($M_w = 21\,400$) is substantially smaller than that ($M_w = 28\,900$) of TT-2-35A.

The temperature dependences of the intrinsic viscosities of ND-3-19A and TPB10, which are main-chain LCPs with mesogens parallel to the backbone, are distinctly different from those of TT-2-35A and SC-1-75A. In Fig. 8, we show the temperature dependence of $[\eta_c]$ and $[\eta_b]$ for the rigid LCP, ND-3-1-19A. Here, $[\eta_c] > [\eta_b]$ at all temperatures, and each quantity changes only weakly with temperature. The corresponding variation of the conformational anisotropy, obtained via application of Eq. (7), is exhibited in Fig. 9. Evidently $R_{||}/R_{\perp}$ decreases very slightly over the experimental temperature range from a value 1.75 at $T = 22^\circ\text{C}$ to 1.70 at $T = 62^\circ\text{C}$. Clearly, this observation is consistent with the very rigid structure of this molecule shown in Fig. 1. Also, we point out that the values of $[\eta_c]$ and $[\eta_b]$ are

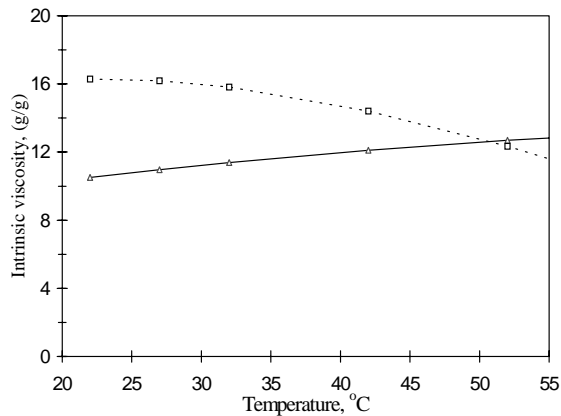


Fig. 6. The temperature dependence of the intrinsic Miesowicz viscosities $[\eta_c]$ and $[\eta_b]$ of SC-1-75A dissolved in nematic solvent E48: (\square) $[\eta_c]$; (\triangle) $[\eta_b]$.

relatively large considering the small molecular weight of this polymer specimen ($M_w = 4500$, via GPC using polystyrene standards). This is indicative that the hydrodynamic volume is relatively large, reflecting the extended rod-like nature of the chain conformation.

The flexible main-chain LCP with mesogens parallel to the backbone (TPB10) demonstrates a third class of temperature dependence as shown in Fig. 10(a), for $[\eta_c]$, and Fig. 10(b) for $[\eta_b]$. Three species of different molecular weights were studied (DP = 63, 16, and 4), but due to limited quantities available of the tetramer, only $[\eta_c]$ data could be obtained with sufficient precision. Comparing Fig. 10(a) and (b), we see that $[\eta_c] \gg [\eta_b]$ at all temperatures for each specimen, and further that $[\eta_c]$ and $[\eta_b]$ both decrease significantly with increase of temperature. It follows that the conformational anisotropy computed from the intrinsic viscosities via Eq. (7) also varies strongly with temperature, as displayed in Fig. 11. We see here that the chain conformation is highly prolate and can be described by an Arrhenius expression as evidenced by the linear least-squares fits shown.

Such Arrhenius behavior is consistent with a theoretical

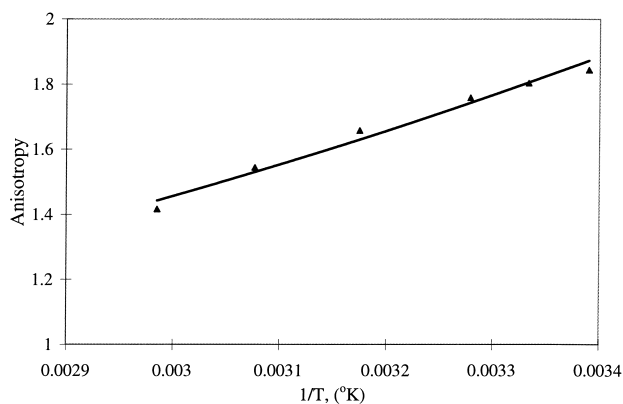


Fig. 7. The temperature dependence of the conformational anisotropy, $R_{||}/R_{\perp}$, of SC-1-75A dissolved in nematic solvent E48.

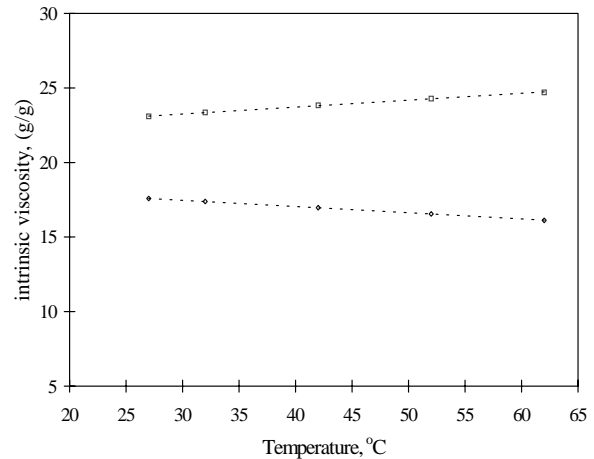


Fig. 8. The temperature dependence of the intrinsic Miesowicz viscosities $[\eta_c]$ and $[\eta_b]$ of ND-3-1-19 dissolved in nematic solvent E48: (\square) $[\eta_c]$; (\diamond) $[\eta_b]$.

analysis of the conformation of main-chain LCPs, using an Ising chain model, described by Halperin and William [10]. Their analysis leads to the conclusion that the chain dimensions, $R_{||}$, along the nematic field, and R_{\perp} , in the perpendicular direction, each exhibit exponential temperature dependence as expressed by Eqs. (8) and (9):

$$R_{||} = (la)^{4/5} \exp[2U_h/5kT] R_F; \quad (8)$$

$$R_{\perp} = (la)^{7/10} \exp[-U_h/10kT] R_F \quad (9)$$

where l (is the monomer length and a is the persistence length, R_F is the Flory phantom-chain radius of gyration of the LCP, and U_h is the energy required to form a hairpin turn in the flexible spacer groups of the main-chain LCP. These equations predict that $R_{||}$ will decrease with increasing T and R_{\perp} will increase with increasing with T . Examining Eqs. (8) and (9), it is clear that the conformational anisotropy, $R_{||}/R_{\perp}$ is predicted to decrease with increasing

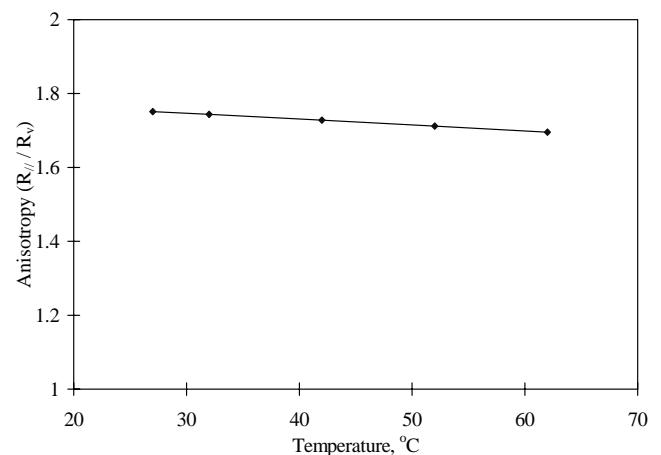


Fig. 9. The temperature dependence of the conformational anisotropy, $R_{||}/R_{\perp}$, of ND-3-1-19 dissolved in nematic solvent E48.

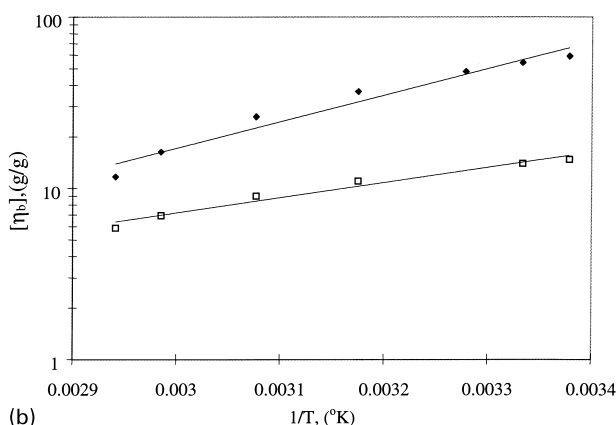
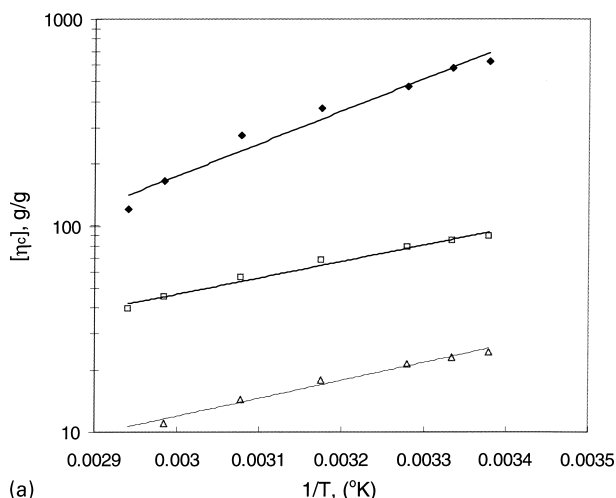


Fig. 10. (a) The temperature dependence of intrinsic Miesowicz viscosity $[\eta_c]$ of main chain LCP TPB10 polymer dissolved in nematic solvent E48: (Δ) DP = 4; (\square) DP = 18; (\blacklozenge) DP = 63. (b) The temperature dependence of intrinsic Miesowicz viscosity $[\eta_b]$ of main chain LCP TPB10 polymer dissolved in nematic solvent E48: (\square) DP = 18; (\blacklozenge) DP = 63.

temperature as:

$$R_{\parallel}/R_{\perp} = (l/a)^{1/10} \exp[U_h/2kT]. \quad (10)$$

Thus the hairpin activation energy U_h can be calculated from the Arrhenius fit to the data in Fig. 11. We find a value $U_h = 2.5$ kJ/mol for the sample with DP = 18, and $U_h = 3.6$ kJ/mol for the sample with DP = 63. These values are numerically consistent with an earlier estimate, $U_h = 2.7$ kJ/mol derived from the temperature dependence of the intrinsic twist viscosity, measured by dynamic light scattering [15]. As noted previously [15], hairpin formation requires two *trans* to *gauche* transformations each of which involves an energy expenditure of about 1 kJ/mol [16]. Thus it appears that the experimental values of U_h are of the right order of magnitude.

Our observations can also be interpreted within the theoretical description of Carri and Muthukumar [11]. In the limit of long polymers ($L \gg \lambda/(1+D)^{1/2}$), where L is the contour length and λ is the Kuhn segment length of the

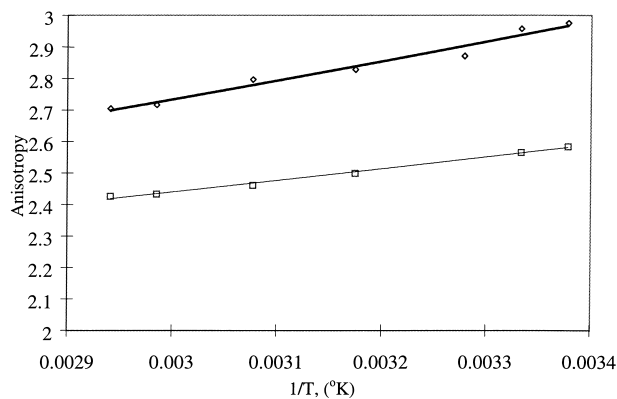


Fig. 11. The temperature dependence of conformational anisotropy, R_{\parallel}/R_{\perp} , of main chain LCP TPB10 polymer dissolved in nematic solvent E48: (\square) DP = 18; (\blacklozenge) DP = 63.

polymer, this analysis predicts that:

$$R_{\parallel}^2/R_{\perp}^2 = 1/(1+D) \quad (11)$$

i.e. the ratio R_{\parallel}/R_{\perp} depends only on the coupling strength D . Thus, for polymers TPB10, TT-2-35A, and SC-1-75A, each of which have mesogens connected by flexible spacers, the substantial decrease of the ratio R_{\parallel}/R_{\perp} with temperature (see Figs. 5, 7, and 11) indicates, via Eq. (11), that the magnitude of the coupling strength $|D|$ decreases, which is presumed to reflect the fact that the flexibility of the spacers increases, and the strength of the nematic field decreases with temperature. Moreover, our observations in Figs. 5 and 11, respectively, that, for the side-on side-chain LCP (SC-1-75A) and for the main-chain LCP with mesogens parallel to the polymer backbone (TPB10) the conformation is strongly prolate ($R_{\parallel}/R_{\perp} \gg 1$) indicates via Eq. (11), $D \ll 0$, i.e. the polymer segments align strongly with the director, which is expected for these molecular architectures [11]. Likewise, our earlier finding [2–4] that end-on side-chain LCPs have a quasi-spherical conformation, which is weakly oblate in the long polymer limit, i.e. $R_{\parallel} \leq R_{\perp}$, is also concordant with the theoretical deductions of Carri and Muthukumar [11], since, for these polymers the polymer segments align perpendicular to the director, $D > 0$. However, the present result that $R_{\parallel}/R_{\perp} > 1$ for polymer TT-2-35A, which is a main-chain LCP with mesogens orthogonal to the polymer backbone (Fig. 1), although a molecular architecture not explicitly considered by these authors, appears to conflict with their analysis, since the interaction of the mesogen with the nematic field would seem to align the backbone perpendicular to the director, i.e. it would imply that D is greater than zero, and hence, via Eq. (11), the conformation should be oblate, $R_{\parallel}/R_{\perp} < 1$.

Finally, it is of interest to point out that, from the Brochard theory, with knowledge of R_{\parallel}/R_{\perp} , and the degree of polymerization, N , of the LCP, it is possible to extract information on the conformational relaxation time, τ_R , since

Table 2
Conformational relaxation time, τ_R (μs), of LCPs dissolved in nematic solvents

LCP	Temperature ($^{\circ}\text{C}$)						
	23	27	32	42	52	62	67
ND-3-1-19	–	4.69	2.96	1.47	0.77	0.72	–
TT2-35A	36.5	31.3	21.5	11.8	6.48	2.84	–
SC-1-75A	–	34.3	23.4	11.6	7.14	3.27	–
TPB10 (DP = 4)	1.85	1.20	0.57	0.36	0.20	0.14	0.13
TPB10 (DP = 18)	24.9	18.4	9.76	5.71	2.58	1.80	1.61
TPB10 (DP = 63)	240	173	99.7	37.4	24.7	19.1	15.8

one may write [3]:

$$\begin{aligned} \eta_{\text{on}} - \eta_{\text{off}} &= \eta_{\text{on}}^0 - \eta_{\text{off}}^0 + c(\delta\eta_{\text{on}}/c - \delta\eta_{\text{off}}/c) \\ &= \eta_{\text{c}}^0 - \eta_{\text{b}}^0 + (cN_{\text{A}}kT\tau_{\text{R}}/M)(R_{\parallel}^2/R_{\perp}^2 - R_{\perp}^2/R_{\parallel}^2). \end{aligned} \quad (12)$$

The resulting values of τ_R are presented in Table 2. Note that, for TT-2-35A, SC-1-75A, and ND-3-1-19, there will be a substantial error in the value of τ_R , because the molecular weight value used in Eq. (12) is based on GPC analysis relative to polystyrene standards, and so is not the true value. However, the magnitude of the variation in τ_R with temperature should be free of such errors. The τ_R values of the flexible chain LCPs, TT-2-35A, SC-1-75A, and TPB10 decrease by approximately the same amount, viz. $\times 10$, whereas that of the rigid LCP, ND-3-1-19, decreases by a slightly smaller amount, around $\times 7$, over the temperature range 27–62 $^{\circ}\text{C}$. The corresponding activation energies are 52.2 kJ/mol for the former, and 46.5 kJ/mol for the latter. As noted previously by Pashkovskii and Litvina [9], the temperature dependence of τ_R , is dominated by the viscous activation energy of the nematic solvent which is thus of the order 50 kJ/mol.

We also remark that, at a specified temperature, the magnitude of τ_R for different LCPs should scale with the molecular hydrodynamic volume of the LCP. This is indeed apparent on inspection of the results in Table 2 where, at each temperature, we find a strong correlation between the magnitude of τ_R and the GPC molecular weight of the polymer, which of course reflects its hydrodynamic volume in the GPC solvent, tetrahydrofuran. It is further interesting to point out in Table 2 that, for the main-chain LCP TPB10, the value of τ_R decreases by an order of magnitude with increase of N from 4 to 18 and from 18 to 63. This result is approximately consistent with the expectation from our previous work [1] that $\tau_R \sim N^2$, which is obtained from the Brochard hydrodynamic model with the assumption that the main-chain LCP conformation behaves as a free-draining random walk [1,15,17]. Thus, from the Brochard model [13] we have:

$$\tau_{\text{R}} = \frac{1}{kT} \left[\frac{(\lambda_{\parallel}\lambda_{\perp}R_{\perp}^2R_{\parallel}^2)}{(\lambda_{\perp}R_{\perp}^2 + \lambda_{\parallel}R_{\parallel}^2)} \right] \quad (13)$$

where λ_{\parallel} and λ_{\perp} are the translational friction coefficients of the LCP for displacements parallel and perpendicular to the director, respectively. When $R_{\parallel} \gg R_{\perp}$, this simplifies to:

$$\tau_{\text{R}} = (1/kT)[\lambda_{\perp}R_{\perp}^2] \sim M^2 \quad (14)$$

when $\lambda_{\perp} \sim M$ (free-draining) and $R_{\perp}^2 \sim M$ (Gaussian statistics). Note that this interpretation is predicated on our earlier conclusion that, for TPB10 at $M_w \geq 8440$, we are in the long polymer limit, since [17] the effective Kuhn segment $l_{\text{eff}} = L/\sqrt{(1+D)} = 3.62$ nm, and hence, from Table 1, $L/l_{\text{eff}} \geq 17 \gg 1$. Otherwise, from Eq. (14), it should be realized that some combination of partial draining and non-Gaussian (i.e. wormlike) statistics may also combine to give a molecular weight exponent ≈ 2 .

4. Conclusions

We have investigated the temperature dependence of the intrinsic Miesowicz viscosities $[\eta_{\text{c}}]$ and $[\eta_{\text{b}}]$ of several LCPs, with differing molecular architectures, in the nematic solvent E48 which has an extended nematic range. Distinct patterns of behavior were observed. For the main-chain LCPs with mesogens aligned with the backbone, $[\eta_{\text{c}}] \gg [\eta_{\text{b}}]$, and each is strongly temperature dependent in the case of the flexible backbone (TPB10), but essentially temperature-independent for the rigid backbone (ND-3-1-19). For the flexible side-chain LCP with mesogens side-on (SC-1-75A), and the flexible main-chain LCP with mesogens orthogonal to the backbone (TT-2-35A), $[\eta_{\text{c}}] > [\eta_{\text{b}}]$, but the values converge with increase of temperature, and actually cross over in the case of TT-2-35A. Application of the molecular hydrodynamic theory of Brochard indicates that the LCP chain conformation is strongly prolate in all cases, though much more so in the case of TPB10. With increase of temperature, the conformational anisotropy of the rigid LCP, ND-3-1-19, remains essentially invariant, whereas that of each flexible LCP becomes more spherical, especially for TT-2-35A and SC-1-75A.

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