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Optical noise and dynamical properties of liquid crystal comb polymers with different mesogenic groups

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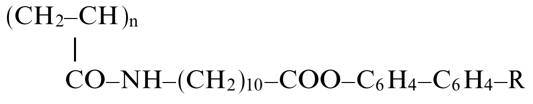
The light scattered by a comb polymer with a polyacrylamide main chain and biphenyl-based mesogenic units containing the substituent $R=\mathrm{CN}$ in the biphenyl core is characterized by a stationary noise which has been measured between 70°C and 140°C in the frequency interval $5\times10^{-2}\leqslant\nu\leqslant10\,\mathrm{Hz}$. This optical noise is analysed by means of a specific procedure introduced to clarify the role of random movements of segments of the main chains on the side chain fluctuations. The RMS amplitude of the random molecular movements, the relaxation times of the side chain and main chain fluctuations, and the damping coefficients governing their motion are investigated as functions of temperature. The results are compared with those recently obtained on a similar polymer characterized by $R=\mathrm{H}$. Common features and differences are brought into evidence and discussed in terms of the different mesophase structures exhibited by the two polymers in the temperature interval considered.

1. Introduction

Liquid crystal comb polymers exhibiting thermotropic and lyotropic properties are being extensively studied owing to their fascinating structural and physical properties and to the prospects for their applications as constituents of electro-optical devices. These systems, composed of rigid mesogenic units linked through flexible spacers to a polymeric backbone, are characterized by a variety of mesophase structures. Comb polymers with a polyacrylamide main chain, spacers containing ten methylene groups, and biphenyl-based mesogenic units were recently prepared [1, 2]. They correspond to the general formula:



$$\begin{array}{l}(\mathrm{CH_2{-}CH})_n\\ \qquad\quad|\\ \qquad\;\mathrm{CO{-}NH{-}(CH_2)_{10}{-}COO{-}C_6H_4{-}C_6H_4{-}R}\end{array}$$

where the substituent in the biphenyl core may be: $R=\mathrm{H}$, CN, $\mathrm{OCH_2CH(CH_3)C_2H_5}$ [2].

Although the characteristics of the various mesophase structures displayed by these polymers may be determined by X-ray diffraction [1, 2], considerable interest exists in techniques providing information on the dynamical properties of the constituent molecules and the parameters governing their motion, in view of the potential electro-optical applications of these materials. Dynamical properties may conveniently be studied, for instance, by detecting and analysing the Brownian motion of molecules as a function of temperature.

In a previous paper [3], optical techniques were introduced to study the Brownian movements of the main chains and side chains in the comb polymer with $R=\mathrm{H}$, obtained by polymerization in THF and exhibiting a tilted, ordered bilayer smectic phase $\mathrm{S_{I_2}}$ followed by a tilted, disordered bilayer smectic phase $\mathrm{S_{C_2}}$ above 105°C. The glass transition of this polymer occurs at $T_g=83\pm3$°C. The dynamical properties of the system were studied by measuring and analysing the stationary noise of the light scattered by the system at low angles. This technique has been successfully applied in recent years to the study of the visco-elastic constants of liquid crystals [4–6]. However, the peculiar features of the scattered light noise in these comb polymers required a novel procedure of analysis to be introduced [3]. In this way, a detailed picture of the response of both side chains and main chains to random disturbances of thermal origin was obtained.

In the present paper, the same procedure is applied to study the comb polymer with an undecanoyloxycyanobiphenyl side chain, where the substituent in the biphenyl core is the highly polar carbonitrile group $R=\mathrm{CN}$. This polymer is characterized by two disordered

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bilayer smectic phases (tilted, S_{C_2} followed by S_{A_2} above 95°C). The dynamical properties of the constituent molecules are expected to differ, to some extent, from those observed in the polymer with $R = H$, because of the different properties of the substituent and the different degree of liquid crystalline order in the corresponding mesophases. Moreover, the length of the main chains is higher than in the previous polymer. A comparison between the results obtained for the two polymers allows common features and specific differences to the conveniently checked. The good correspondence between the picture emerging from the present research and the structural information gathered on these polymers gives further support to the adopted procedure of analysis.

2. Experimental

A liquid crystal comb polymer with undecanoyloxycyanobiphenyl side chains, corresponding to the formula reported above with $R = CN$, was prepared under vacuum by radical polymerization of acrylamidoylundecanoyloxycyanobiphenyl at $T = 73$°C (346 K) in chloroform solution, with AIBN as initiator, as described elsewhere [2]. The polymer's molecular characteristics (M_n, M_w and their ratio), as determined by light scattering from chloroform solutions and Gel Permeation Chromatography, are reported in the table. The structure of the polymer was determined by X-ray diffraction [2]. The results of interest for the present study are now briefly summarized. For this polymer, as well as for the polymer with $R = H$ [2], d is the same on heating and cooling and remains constant in the whole domain of existence of each mesophase. A disordered, double layer smectic structure of the S_{C_2} type is observed below 95°C (368 K). The side chains are tilted at 24·7° with respect to the normal to the smectic layers, which contain the main chains. The distance between smectic layers is $d = 51{\cdot}8$ Å. At temperatures above 95°C, a second, disordered double layer smectic structure (of the S_{A_2} type) appears, characterized by a sudden increase in the layer spacing to 59·0 Å, and by a corresponding reduction in the tilt angle from 24·7° to 0°. The temperature of isotropization of the material, as determined by X-ray diffraction, occurs at $T = 168$°C (441 K). These results are summarized in the table, where they are compared with the corresponding data obtained on the different comb polymer, with $R = H$, previously submitted to the same type of optical analysis.

Table. Comparison between the properties and the mesophase structures of two liquid crystal comb polymers with polyacrylamide main chain and different substituents R in the mesogenic groups. Interlayer distances and angles of tilt remain constant over the whole range of existence of each reported mesophase [2].

Parameter	Mesogenic group Biphenyl ($R = H$)	Cyanobiphenyl ($R = CN$)
Low temp. phase	Ordered, S_{I_2}	Disordered, S_{C_2}
Interlayer distance/Å	53	51·8
Angle of tilt	18·8°	24·7°
Transition temp./°C	105	95
High temp. phase	Disordered, S_{C_2}	Disordered, S_{A_2}
Interlayer distance/Å	53	59
Angle of tilt	18·8°	0°
Isotropization temp./°C	150	168
M_n	24 500	68 800
M_w	42 300	88 100
M_w/M_n	1·73	1·28

The sample cell used in the optical measurements on the comb polymer with $R = CN$ consisted of two parallel glass plates with a constant spacing of 50 μm ensured by mylar spacers and was assembled using a thermoresistant glue. The sample thickness was not however measured independently, and the reported value should be considered as being merely indicative.

The experimental set-up for the light scattering measurements between room temperature and 150°C has been described in detail elsewhere [3, 6]. The monochromatic light scattered by the polymer at different angles and the associated optical noise were detected by means of a photodiode mounted on a rotating platform. The optical noise was observed in the frequency interval 5×10^{-2} Hz $< \nu <$ 10 Hz. At higher frequencies, the noise originating from the sample merged into the background noise.

All measurements were performed under normal incidence of light. The optical noise of the scattered light was sufficiently strong to be detected by the photodiode only at low scattering angles; the smallest angle of scattering compatible with the requirement of excluding the direct beam from the photodiode's active area was $\theta_s = 4$° (in air). All reported data refer to this scattering angle.

The optical measurements were performed in the temperature interval 70–140°C at an average heating rate of 0·5°C min^{-1} (including measurement time). Each power spectrum is an average taken at constant temperature over a set of five independent samples of the fluctuating voltage provided by the photodiode. No significant differences were found between the first and the fifth spectrum in each measurement. It can therefore be stated that the noise has been measured in stationary conditions.

All results obtained on the comb polymer with $R = CN$ (referred to as sample CN in the following text) will be discussed in comparison with the corresponding results for the comb polymer with $R = H$ (referred to as sample H).

3. Results

The intensity of monochromatic light scattered by sample CN at $\theta_s = 4°$ is reported in figure 1 as a function of temperature T (full symbols). At low T, this intensity is rather weak, and begins to increase steadily above 80°C, exhibiting a tendency towards saturation in the 130–140°C interval. The effect of temperature on the scattered light intensity in sample CN is much smoother than in sample H, where the order–disorder transition is marked by a sudden increase of the scattered signal (open symbols in figure 1). The lower isotropization temperature of the polymer with $R = \mathrm{H}$ makes it possible to observe a distinct decrease in the intensity of the scattered light (expected to disappear in the isotropic phase), while in sample CN such a feature is displaced to higher temperatures. Note the difference in vertical scales between the two samples. Such a difference is mainly ascribed to (*a*) slightly different thicknesses of samples, and (*b*) a different attenuation of the incident light. It is interesting to remark that, merely by multiplying all data for sample CN by the constant numerical factor 2·86, the curves of figure 1 take the same values at both low and high temperatures, supporting the hypothesis that the difference in the measured curves originates from different experimental conditions, rather than from intrinsic differences between the polymers.

Two representative spectral density curves $S(\nu)$ of the scattered light noise (at $\theta_s = 4°$) are reported in figure 2. The low temperature spectra are well described by a single Lorentzian function, while a steeper high frequency decay is observed at higher temperatures, as expected in these polymers [3]. After subtraction of the background noise, the spectral density curves were integrated over the measurement frequency interval, in order to study the evolution with temperature of molecular fluctuations [4, 7]. The square root of the area

$$A = \int_{\nu_1}^{\nu_2} S(\nu)\,\mathrm{d}\nu, \quad \text{with } \nu_1 = 0{\cdot}1\,\mathrm{Hz}, \quad \nu_2 = 10\,\mathrm{Hz}$$

(i.e. the RMS noise) is shown in figure 3 (open symbols). A steady increase with temperature of the molecular fluctuations is observed, although no particular feature emerges from this analysis in the proximity of the transition temperature. The scattered light intensity is reported for comparison (full symbols in figure 3).

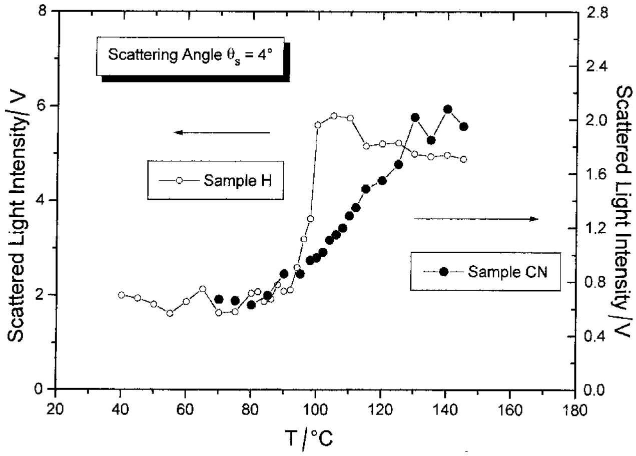


Figure 1. Temperature behaviour of the intensity of the light scattered at $\theta_s = 4°$ by sample CN (full circles), compared with data from sample H (open circles).

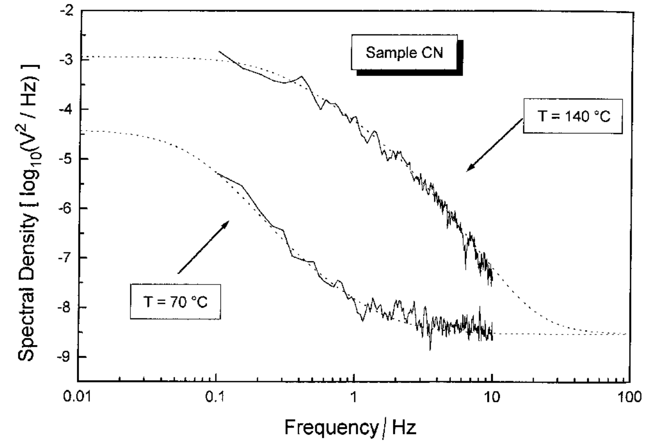


Figure 2. Typical spectral density curves of the optical noise displayed by sample CN at two different temperatures. Dotted lines: best-fit curves.

Valuable information on the molecular fluctuations may be extracted by analysing the ratio between low frequency and high frequency integrated spectral density curves. Let us define

$$A_{\mathrm{low}} = \int_{\nu_1}^{\nu_1'} S(\nu)\,\mathrm{d}\nu, \quad \text{with } \nu_1 = 0{\cdot}1\,\mathrm{Hz}, \quad \nu_1' = 0{\cdot}5\,\mathrm{Hz}$$

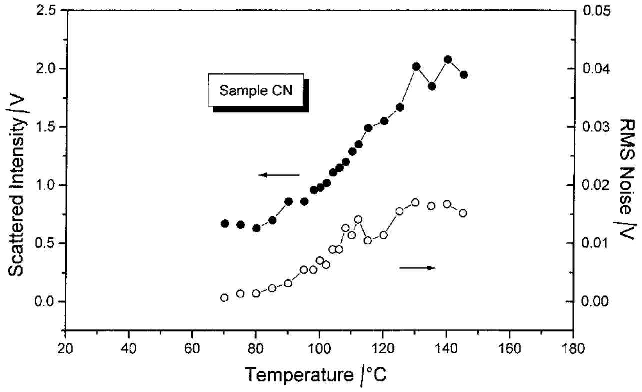


Figure 3. Effect of temperature on the RMS optical noise in sample CN (open circles) compared with scattered light intensity (full circles).

and

$$A_{\mathrm{high}} = \int_{\nu_2'}^{\nu_2} S(\nu)\,\mathrm{d}\nu, \quad \text{with } \nu_2' = 5\,\mathrm{Hz}, \quad \nu_2 = 10\,\mathrm{Hz}.$$

The square root of the ratio $R = A_{\mathrm{low}}/A_{\mathrm{high}}$ is reported in figure 4 as a function of temperature. The quantity $R^{1/2}$ is a measure of the predominance of low frequency effects in the spectrum of the molecular fluctuations. A peak in $R^{1/2}$ is observed at $T = 95°\mathrm{C}$, in good agreement with general concepts concerning fluctuation modes in the proximity of a phase transition (the slow relaxing modes must substantially increase around the transition temperature).

A comparison between the RMS noise curves for samples CN (full symbols) and H (open symbols) is shown in figure 5. The curves have been corrected for the experimental difference in the level of scattered light (see figure 1). In particular, all data referring to sample CN have been multiplied by the constant numerical factor 2·86, as previously discussed. Sample CN is characterized by a continuous increase in the RMS fluctuation amplitude, which starts from a very small value, and is followed by a saturation region above 120°C. In sample H, the fluctuation amplitude remains instead very small and constant up to about 100°C; for higher temperatures, a steep increase is observed, and the high-T portion of the curve reaches the same values as for sample CN. Once again, these differences may be naturally explained in terms of the different types of molecular arrangements at low and high temperatures; the correspondence of the curves (after rescaling) is however remarkable, and definitely points to a common origin of the optical noise in both polymers, as is indeed expected.

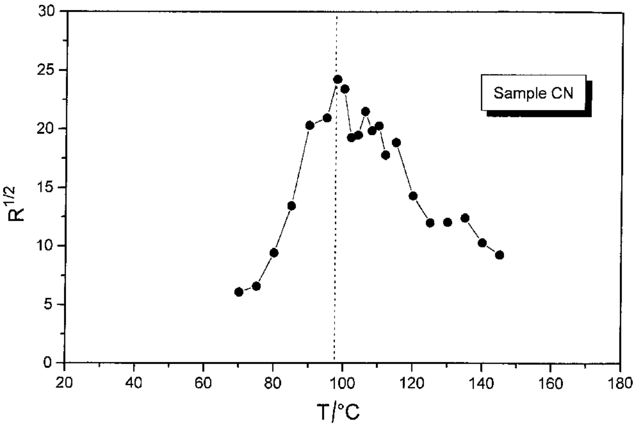


Figure 4. Temperature behaviour of the square root of the ratio R between lower frequency and higher frequency contributions to the optical noise in sample CN (see text for details).

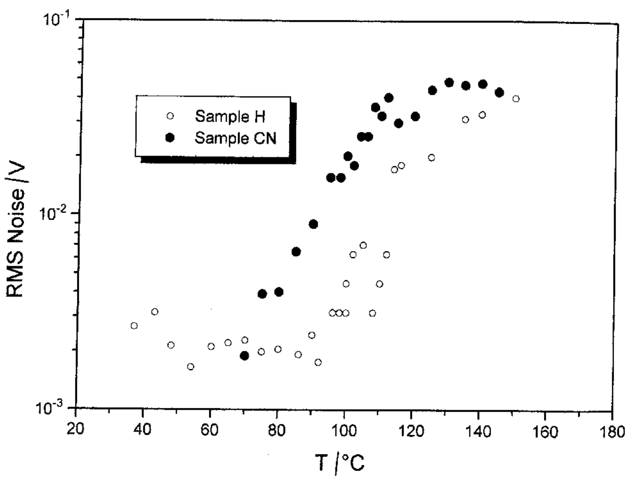


Figure 5. Comparison between RMS optical noise measured for sample CN (full circles) and for sample H (open circles).

4. Analysis of the spectral-density curves

A dynamical model of the fluctuations responsible for the optical noise in comb polymers has been recently proposed [3]. A brief account of its basic assumptions and consequences follows. The molecular fluctuations may be described as pure relaxational phenomena, involving massless, heavily damped oscillators submitted to random external forces [4, 5]. The optical noise is assumed to arise, at all temperatures, mostly from fluctuations of the side chains. Main chains however play a significant role at high temperature, because the random forces acting on side chains partly arise also from random movements of segments of the main chains. This fact brings about a change of the $S(\nu)$ curve from a nearly pure Lorentzian behaviour to the weighted sum of a pure Lorentzian and the product of two Lorentzians, according to the expression:

$$S(\nu) = S_0(T) + \left(P_1 + \frac{P_2}{\nu^2 + \gamma_2^2}\right)\frac{1}{\nu^2 + \gamma_1^2} \qquad (1)$$

where $S_0(T)$ is the background noise.

Both terms in equation (1) describe thermally excited fluctuations of the side chains; the Lorentzian term, with the weight $P_1(T)$, is related to their spontaneous fluctuations, while the product of the two Lorentzians, with the weight $P_2(T)$, accounts for fluctuations induced by random movements of segments of the long chains. The quantities $\gamma_1^{-1}, \gamma_2^{-1}$ are relaxation times for side chain and main chain fluctuations, respectively.

The parameter P_1, obtained from the best fit of experimental spectra to equation (1), is reported as a function of temperature in figure 6 for sample CN (full symbols). A remarkable enhancement of P_1 is observed with increasing T. No definite structure appears in the

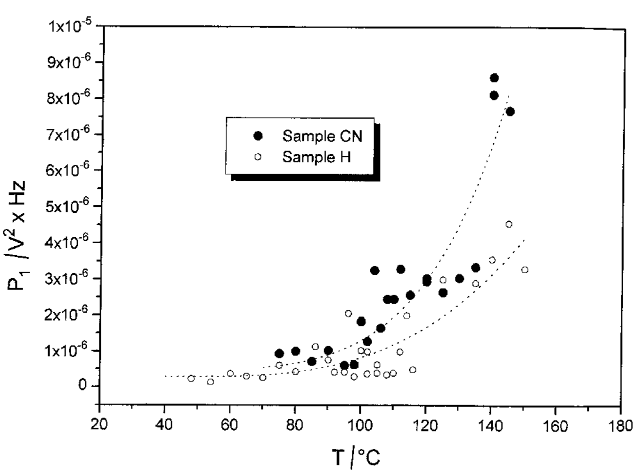


Figure 6. Weighting factor P_1 of the Lorentzian component of the $S(\nu)$ fitting function for sample CN (full circles). The P_1 values obtained for sample H under the same experimental conditions are reported for comparison (open circles).

curve around 95°. The corresponding curve for sample H exhibits similar features (open symbols). Quite interestingly, the low temperature limits of the P_1 curves are very similar; the enhancement of P_1 is however stronger in sample CN.

The temperature behaviour of P_2 is shown in figure 7 for sample CN (full symbols). At low temperatures ($T \leqslant 100°\mathrm{C}$), P_2 is very small, albeit non-zero, and dramatically increases with increasing T above 100°C, indicating a high mobility of the main chains of $\mathrm{S_{A_2}}$ phase; on the other hand, the P_2 parameter of sample H is equal to zero below 80°C (indicating that the main chains are completely frozen in their equilibrium positions), and increases at higher temperatures, although with a lower slope than in sample CN. It can be concluded that the main chains have a larger motional freedom in sample CN than in sample H. At low temperatures, such a freedom can be related to the lack of crystalline order in the $\mathrm{S_{C_2}}$ phase of sample CN, while in the high-T region, the $\mathrm{S_{A_2}}$ phase of sample CN seems to be more unstable that the $\mathrm{S_{C_2}}$ phase of sample H.

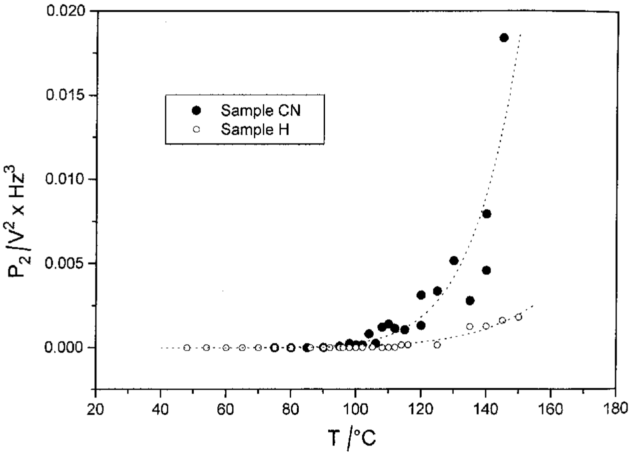


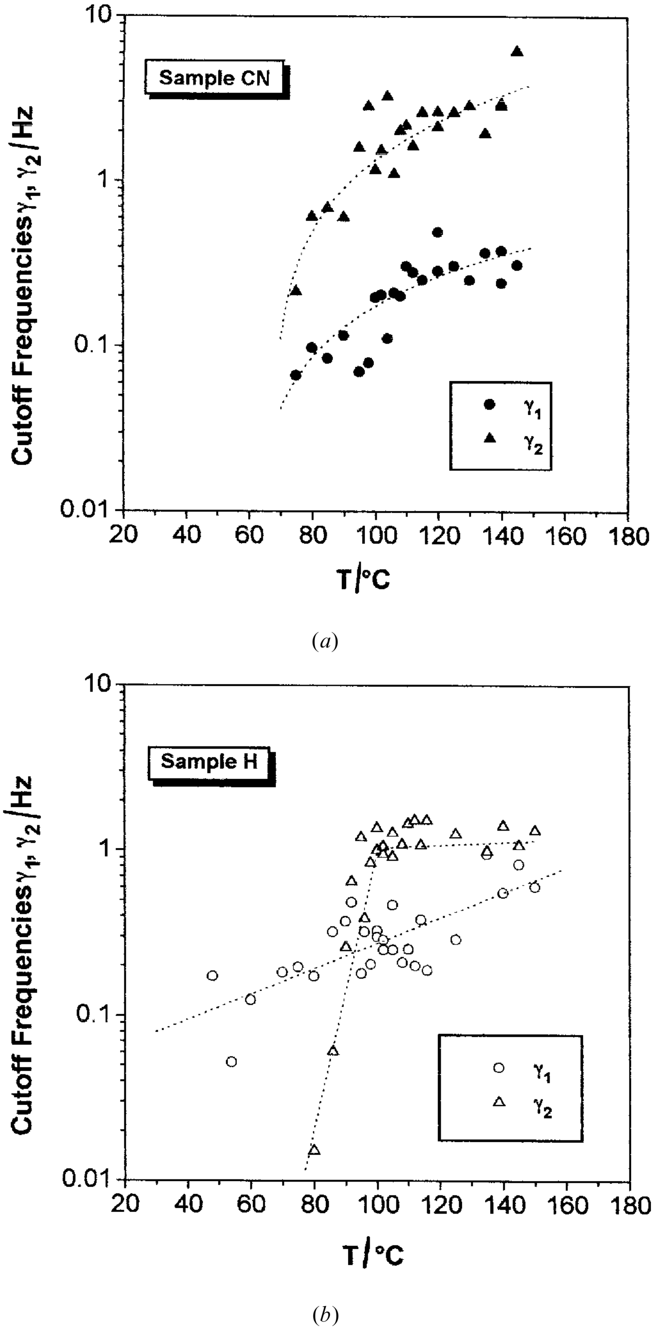
Figure 7. Weighting factor P_2 of the non-Lorentzian component of the $S(\nu)$ fitting function for sample CN (full circles). The P_2 values obtained for sample H under the same experimental conditions are reported for comparison (open circles).

The temperature behaviour of the cut-off frequencies γ_1 and γ_2 in sample CN is shown in figure 8 (*a*). Both quantities steadily decrease with decreasing T, indicating that the relaxation times for the fluctuations of both side chains and main chains become larger. A striking difference is observed in sample H (figure 8 (*b*)), where the parameter γ_2 drops to zero below 80°C, indicating that the corresponding main chain fluctuations are becoming exceedingly slow. Such a feature does not occur in sample CN, where the disordered phase, stable at low temperature, does not bring about any freezing of main chain movements.

The parameters of equation (1) may be used to give information about the temperature behaviour of the damping parameters governing the motion of the side and main chains (β_s and β_m, respectively) [3]. In particular β_s, linearly related to an effective viscosity experienced by the side chains, is proportional to T/P_1, where T is expressed in Kelvin, while β_m, linearly related to an effective viscosity experienced by the main chains, is proportional to $(P_1/P_2)^{1/2}$ [3].

The temperature behaviour of $T/P_1 \approx \beta_s$ is shown in figure 9 for sample CN and sample H (full and open symbols, respectively). In both cases, β_s decreases with T, according to an Arrhenius law of the type $\beta_s = \beta_{so} \exp(Q/RT)$, where β_{so} is a constant, Q is an activation energy for viscous flow, and R is Meyer's constant (dotted/dashed lines in figure 9). In sample CN, the activation energy turns out to be $Q = 39{\cdot}1\,\mathrm{kJ\,mol^{-1}}$, significantly higher than in sample H ($Q = 28{\cdot}5\,\mathrm{kJ\,mol^{-1}}$ [3]). On the other hand, the pre-exponential factor β_{so} is smaller in sample CN than in sample H: $\beta_{so}(\mathrm{CN}) \cong 1/56\,\beta_{so}$ (H). The absence of any effects of main chain order on β_s indicates that these damping effects arise through the effect of localized interactions between the side chains themselves, almost certainly occurring in the interlayer region where the side chains of two adjacent polymers are in close contact. In the considered temperature range, the β_s coefficients of the two polymers are similar, owing to a balance of effects from the pre-exponential constant (larger in sample H) and from the activation energy for viscous flow (larger in sample CN).

The temperature behaviour of $(P_1/P_2)^{1/2} \approx \beta_m$ is shown in figure 10 for sample CN and sample H (full and open symbols, respectively). Both curves are



(*a*)

(*b*)

Figure 8. Cut-off frequencies γ_1 and γ_2 appearing in the $S(\nu)$ fitting function: (*a*) overall temperature behaviour for sample CN; (*b*) the same for sample H.

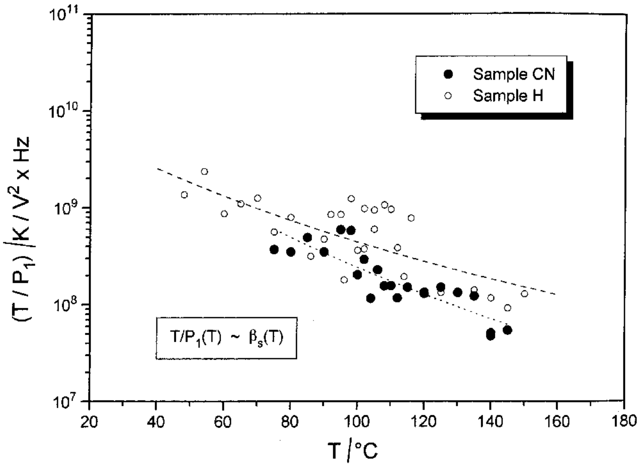


Figure 9. Behaviour of T/P_1 (proportional to the damping coefficient for side chains) for sample CN (full circles), compared with the same quantity for sample H (open circles). Dotted and dashed lines: best fit to an Arrhenius law (parameters given in the text).

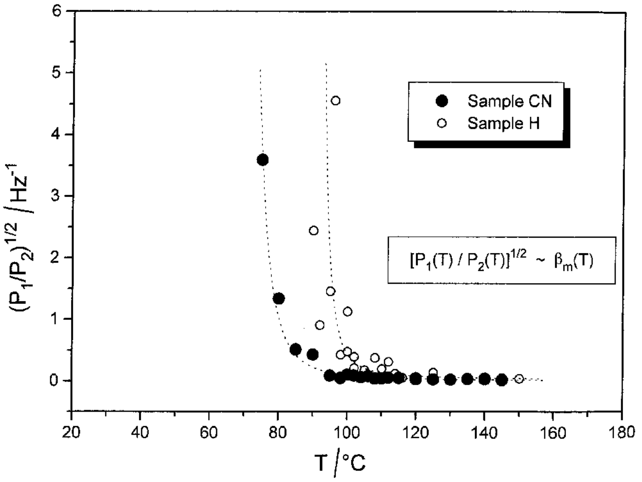


Figure 10. Behaviour of $(P_1/P_2)^{1/2}$ (approximately proportional to the damping coefficient for main chains) for sample CN (full circles), compared with the same quantity for sample H (open circles). Dotted lines: best fit to a Vogel–Fulcher–Taumann law (parameters given in the text).

described by a Vogel–Fulcher–Taumann expression: $\beta_{\mathrm{m}} = \beta_{\mathrm{mo}} \exp(\Theta/(T - T_0))$, where β_{m0}, Θ and T_0 are constants. It has been suggested that the temperature T_0, where the main chains appear to be completely frozen (both β_{m} and γ_{m}^{-1} diverge when $T \to T_0$ from above), corresponds to the glass transition of the polymer main chains [3]. In fact, T_0 in sample H, (≅85°C) turns out to be nearly coincident with the glass transition temperature T_{g} measured by calorimetric techniques (83 ± 3°C). In that polymer, T_0 is only 20°C below the temperature of the S_{I_2}–S_{C_2} transition, while in sample CN the main chains appear to maintain some short range mobility over the whole temperature interval explored. In fact, $T_0 \cong 54°\mathrm{C}$ in this case, i.e. 41°C below the temperature of the S_{C_2}–S_{A_2} transition. We can conclude that the main chains are more efficiently damped in sample H than in sample CN, where the freezing of main chains is expected to occur at a definitely lower temperature. It is worth mentioning that the polymer with $R = \mathrm{CN}$ seems to exhibit a glass transition at about 50°C, once again close to our T_0, but the existence of this transition is not yet well established on the basis of calorimetric measurements.

Finally, it may be of interest to compare the behaviour of the two polymers when they are in the same mesophase (the S_{C_2} phase). From this viewpoint, the relevant parameter is the relative separation in temperature from the glass transition. Assuming for simplicity that $T_g = T_0$ for both polymers, all data concerning the common S_{C_2} phase, may be replotted as functions of $T - T_0$. Two typical results are given in figure 11. The behaviour of the measured noise intensity, shown in figure 11 (*a*), indicates that the overall effect of random forces of a thermal nature on the molecules of both polymers is almost the same at the same temperature above T_g. A similar effect is observed for other parameters of the present analysis. The only significant difference between sample CN and sample H occurs on considering the behaviour of the quantity $(P_1/P_2)^{1/2}$, proportional to the damping coefficient for main chains, β_m, and reported in figure 11 (*b*). While in sample H this coefficient stays nearly constant over the whole existence range of the S_{C_2} phase, in sample CN, it is observed to increase for the lowest values of the parameter $T - T_0$. This behaviour is possibly related to the different chemical and physical properties of the two polymers; however, a satisfactory explanation of this behaviour is still lacking, and the present results may be a suitable starting point for future work on this subject.

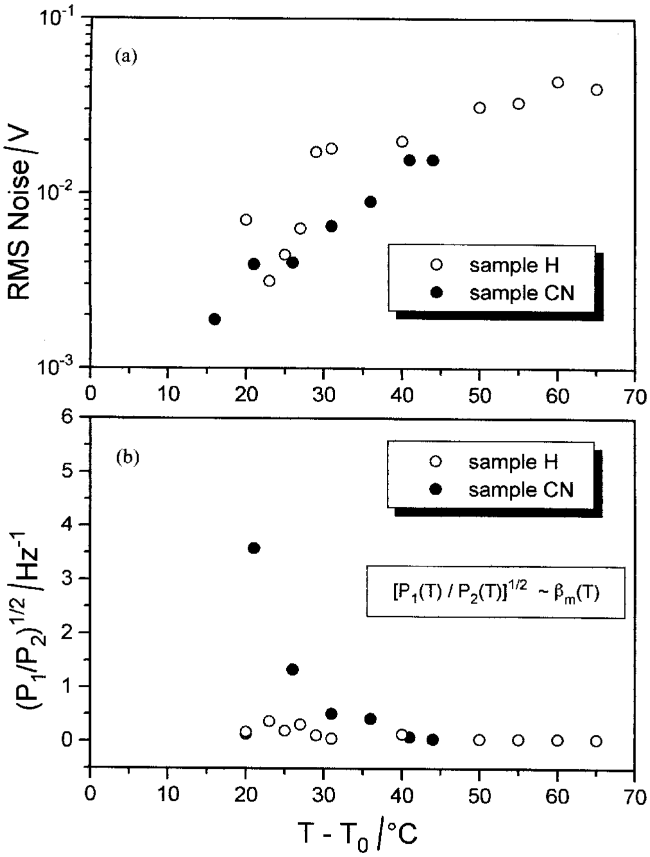


Figure 11. Selected experimental data obtained on samples CN and H in the same mesophase (S_{C_2}) plotted against the relative distance from the glass transition temperature: (*a*) RMS optical noise; (*b*) $(P_1/P_2)^{1/2}$, proportional to β_m.

5. Concluding remarks

The present results confirm the advantages of an analysis based upon optical noise measurements to derive valuable information about the dynamical properties of liquid crystalline comb polymers. In fact, the different features observed in the optical noise of two such polymers, differing chemically only by an atomic group in their side chains (H or CN), are intrinsically related to differences in the type of liquid crystalline order displayed by the polymers. These differences were independently evidenced by X-ray diffractometry: in fact, the optical noise analysis is not sufficient, by itself, to provide detailed information about the nature of liquid crystalline phases and their stability regions. However, the results discussed in § 3 indicate that such an analysis may give the correct information about the temperature at which a phase transition occurs, characterized by an increase in low frequency molecular fluctuations.

The common picture emerging from the present analysis involves thermally-excited fluctuations of the polymer side chains, submitted to stochastic forces at least partially related to random movements of segments of the main chains, whose role significantly increases with increasing T.

However, remarkable differences are observed between corresponding parameters obtained for the two polymers through noise analysis. The RMS amplitude of the optical noise related to spontaneous fluctuations of side chains grows with temperature more rapidly in sample CN than in sample H, indicating a stronger response of these chains to random disturbances in the S_{A_2} arrangement than in the S_{C_2} configuration. Likewise, the RMS high temperature fluctuations of main chains are definitely stronger in sample CN than in sample H. These fluctuations rapidly disappear with decreasing T below the transition to the ordered S_{I_2} phase of sample H, while they persist in the disordered S_{C_2} phase of sample CN.

The relaxation times for side chain fluctuations are almost the same in both materials; the main chain fluctuations are instead characterized by a marked difference occurring in the low temperature phases, with a divergence of γ_m^{-1} in sample H at $T = T_0$, while the behaviour of the corresponding quantity is regular in sample CN over the examined temperature interval.

Side chain movements are characterized by similar damping coefficients in both materials, while the main chains experience a lower damping in the S_{A_2} phase of sample CN than in the S_{C_2} phase of sample H. A dramatic difference between these damping factors is observed in the low temperature phases. In fact, the effective viscosity experienced by the main chains diverges 20°C below the S_{I_2}–S_{C_2} transition of sample H, while the same effect is estimated to be shifted to a significantly lower temperature (41°C below the S_{C_2}–S_{A_2} transition) in sample CN.

It can be concluded that both side chains and main chains of the comb polymer with $R = \mathrm{CN}$ are less stable than those of the polymer with $R = \mathrm{H}$ with respect to thermal random disturbances. This general property, substantially independent of temperature, may be explained in terms of the stricter configurational constraints characterizing the S_{I_2} phase with respect to the S_{C_2} phase, and the S_{C_2} phase with respect to the S_{A_2} phase. On the other hand, the molecular fluctuations responsible for the optical noise seem to be essentially independent of the actual degree of polymerization, almost twice as high in sample CN as in sample H. This is not a surprising result, as the considered random movements occur because of localized thermal disturbances, and do not involve large scale motion of main chain molecules.

References

[1] Gallot, B., and Monnet, F., 1996, *Eur. Polym. J.*, **32,** 147.

[2] Gallot, B., Monnet, F., and Siyuan He, 1995, *Liq. Cryst.*, **19,** 501.

[3] Allia, P., Oldano, C., Rajteri, M., Taverna, P., Trossi, L., Gallot, B., and Monnet, F., 1996, *Liq. Cryst.*, **20,** 225.

[4] De Gennes, P., 1975, *The Physics of Liquid Crystals* (Oxford: Clarendon Press), p. 59.

[5] Orsay liquid crystal group, 1969, *Phys. Rev. Lett.*, **25,** 1361.

[6] Allia, P., Oldano, C., Rajteri, M., Taverna, P., Trossi, L., and Aloe, R., 1994, *Liq. Cryst.*, **18,** 555.

[7] Papoulis, A., 1965, *Probability, Random Variables and Stochastic Processes* (New York: McGraw-Hill-Kogakusha), p. 336.