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Liquid crystal comb polymer with polar mesogenic and aliphatic side groups

II. Noise of the scattered light

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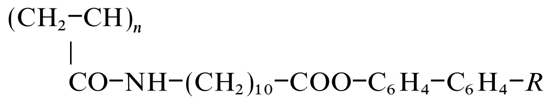
Measurements of static light scattering and of the stationary noise of the scattered light have been performed as functions of temperature on the comb polymer whose synthesis and static structural properties are discussed in the preceding paper, Part I. The intrinsic optical noise strongly increases when the nematic phase is entered. An additional maximum in the noise, observed at lower temperatures, is attributed to a rearrangement of optical domains, introducing boundary regions where the fluctuations of loosely packed side groups are enhanced. The spectral density of the observed noise is definitely non-Lorentzian and can be fitted by the superposition of two pure Lorentzian components with different cut-off frequencies, attributed to the statistically independent random motion of mesogenic and aliphatic side chains. The noise level is reduced at all temperatures by an applied electrical field; in particular, the field is effective in selectively damping the fluctuations of polar side groups.

1. Introduction

Liquid crystalline comb polymers corresponding to the general formula:



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

(where either $R = \mathrm{H}$, or $R = \mathrm{CN}$) have been optically characterized in recent years [1, 2]. The structures and physical properties of mesophases are conveniently investigated by optical measurements [3]; in particular, the analysis of the stationary (thermal) noise of monochromatic light scattered by a liquid crystal is very effective in determining physical parameters such as the relaxation times of molecular fluctuations and the viscoelastic constants of liquid crystals [3–5]. This technique, applied to comb polymers, has been instrumental in studying particular aspects of the Brownian motion of molecules (e.g. the observation of distinct contributions from side groups and main chains) and in determining additional microscopic properties, such as the temperature behaviour of damping coefficients related to material viscosity [6, 7]. However, no information on the response of this type of material to an applied electric field has so far been provided by optical analysis. In fact, although the comb homopolymer termed SP in Part I [8] is characterized by a sequence of identical side groups holding the remarkably polar CN group at their ends, neither the time average of the light scattered at any angle, nor the related noise were significantly affected by an electric field.

The recently prepared CP copolymer [8] should behave quite differently. In this material, two types of side group are present, as described in Part I: the first type, referred to as the 'long' side group, holds a CN polar group at its end (in fact, it is exactly the same as the side group of the SP polymer), whereas the second type, labelled as the 'short' side group, is non-polar and aliphatic. In this way, the response of the polar side groups to an external field should be increased by

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keeping the CN groups at a larger (average) distance apart. In fact, after polymerization, mesogenic and aliphatic side chains occur in a random sequence along the whole main chain length, remaining parallel to each other. This arrangement is shown in figure 1, while the structure of the homopolymer is sketched in figure 2 for comparison. Optical measurements confirm that the spacers reduce the thermal stability of the material and enhance the mobility of the side groups; the increased mobility results not only in a higher noise of the scattered light in the absence of an electric field, but also in a definite reduction of the noise level when an ordering electric field is applied. Thereafter, the optical measurements described in this paper complement the results discussed in Part I, allowing us to draw a detailed microscopic picture of this new comb polymer.

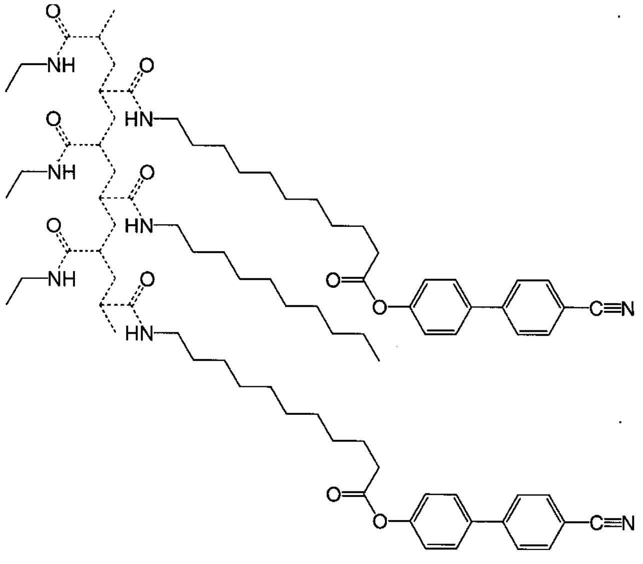

Figure 1. Disposition of the mesogenic groups in the CP polymer; the main chain is represented by the dashed line. The sequence of spacers and mesogenic groups is random; the drawing is to scale.

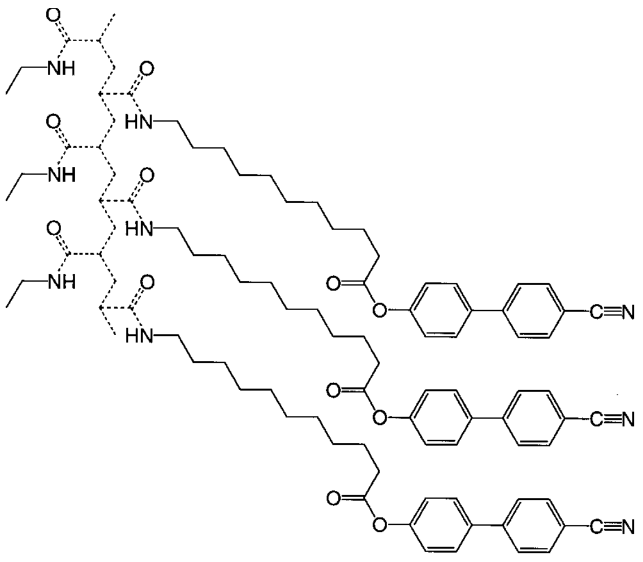

Figure 2. As in figure 1, for the SP polymer.

2. Experimental

Light-scattering experiments were performed in the temperature range 20–100°C using an experimental set-up discussed in detail elsewhere [5] and essentially consisting of a He-Ne laser, a sample holder and an amplified photodiode mounted on a rotating platform. All measurements were performed at normal incidence of light.

The samples for optical measurements were prepared by depositing on a clean glass surface a thin layer of a solution of the comb polymer in chloroform. After evaporation of the solvent, a cell was obtained by applying a second clean glass to the free surface of the polymer. Both clamping glasses carried a transparent ITO film in order to apply a d.c. electric field across the sample; the maximum applied voltage was 120 V.

The intensity of the scattered light was measured as a function of both the scattering angle θ_s and of the measuring temperature T at a fixed scattering angle. The noise of the light scattered at low angles (just off the direct beam) was measured in the interval 0.25–100 Hz. The sample temperature was changed by an electrically controlled heater. All measurements were performed under thermally stable conditions, the average heating rate (including measurement time) being of the order of $1^\circ\mathrm{C\,min}^{-1}$.

3. Results

The temperature dependence of the intensity $I_S(\theta_s)$ of the light scattered by the sample at different angles θ_s is reported in figure 3. At low scattering angles ($\theta_s = 3^\circ$, open and full squares in figure 3), I_S exhibits a typical increase at high temperatures, as is usually observed in such materials [6, 7]. A minimum in the I_S vs. T curve as found at $T = 50^\circ$C in a first temperature run (open squares). In order to check the degree of reproducibility of these measurements, a second run was performed immediately after completion of the first (full squares in figure 3). The temperature of the minimum was found to be lowered by about 5°C. The sample was then submitted to a third heating to check the temperature behaviour of the intensity of the light scattered at high angles; a scattering angle of 25° was chosen. As expected, I_S (25°) [full triangles] is much lower than I_S (3°) [note the different left and right scales in figure 3] and decreases with temperature; however, a bump is observed at $T = 40^\circ$C, i.e. five degrees below the minimum observed for I_S (3°) during the second heating cycle.

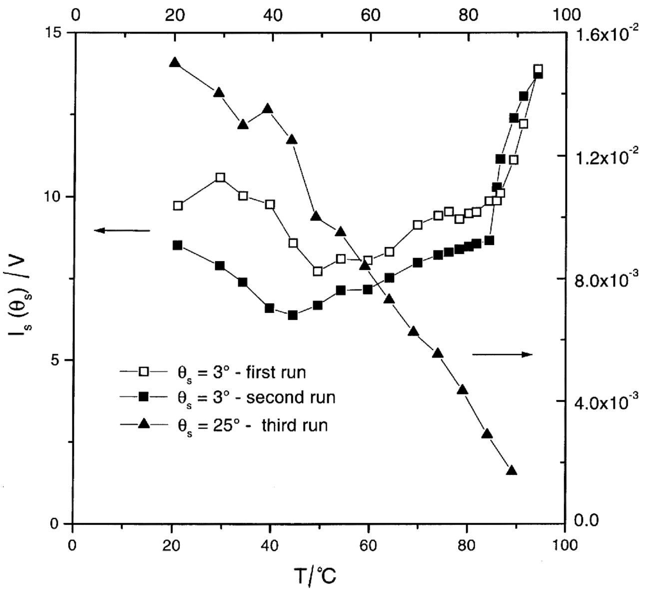

Figure 3. Temperature behaviour of the intensity of light scattered at $\theta_s = 3°$ (open and full squares) and at $\theta_s = 25°$ (full triangles) by the CP polymer.

Dynamical effects in comb polymers, such as the thermally activated random fluctuations of their side groups, may be investigated by performing optical noise measurements [6, 7]. The power spectrum (spectral density) $S(\nu)$ of the light scattered at $\theta_s = 3°$ at $T = 96°C$ is shown in figure 4; this behaviour is representative of all measured spectra. Spurious noise components around 50 and 100 Hz were present in all measurements. The spectral density of the CP polymer has a definitely non-Lorentzian shape, while it is well described by a single Lorentzian function for the SP polymer, as shown in figure 5 where two normalized spectra taken at nearly the same temperature have been compared (the normalization is performed by dividing each spectrum by its area).

The spectral density $S(\nu)$ has been integrated between the frequency limits ($\nu_1 = 0.25$ Hz, $\nu_2 = 100$ Hz) after subtracting all spurious contributions to noise. The resulting quantity $P_N = \int_{\nu_1}^{\nu_2} S(\nu)\,d\nu$ is a measure of the r.m.s. power dissipated by the random relaxation processes (polymer chain fluctuations) responsible for the noise of the scattered light. The ground noise (primarily caused by the laser and by the electronic detector and amplifier), integrated over the same frequency interval, is always lower than P_N by more than three orders of magnitude. The results are reported in figure 6 as functions of temperature, in the form of the ratio of the square root of P_N to the total intensity of the light I_S scattered at the same angle. Such a ratio (a pure number) gives information on the intrinsic variation in the noise level, giving evidence of changes not merely reflecting those of the signal intensity. The reported curve is actually the result of an average over measurements made for different samples. In the absence of an electric field, both P_N and $P_N^{1/2}/I_S$ steadily increase when the temperature rises towards the isotropization point, indicating a strong increase in the fluctuations of the polymer side groups. Such a behaviour is typical of comb polymers [6, 7]; here, however, an additional maximum at about 45°C

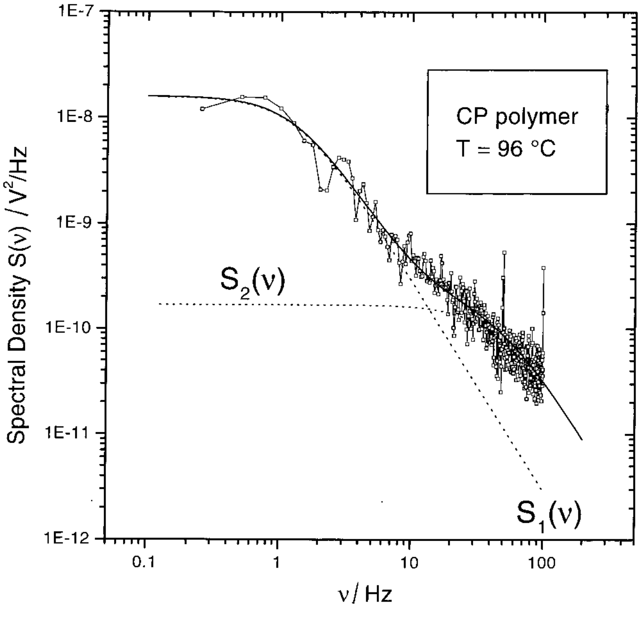

Figure 4. Spectral density $S(\nu)$ of the scattered light noise observed at $T = 96°C$ in a sample of the CP polymer. Dotted lines: Lorentzian functions S_1 and S_2 (see text); full line: best-fit curve.

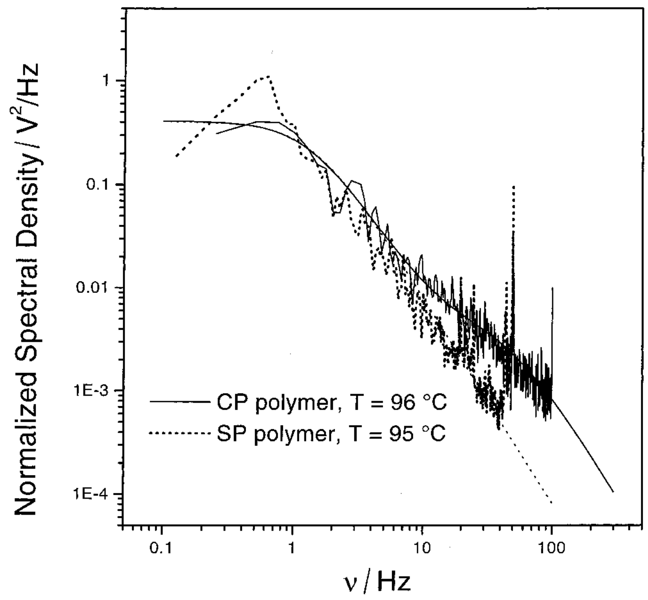

Figure 5. Comparison between normalized spectral densities observed at the same temperature in the SP and CP polymers (dotted and full lines, respectively).

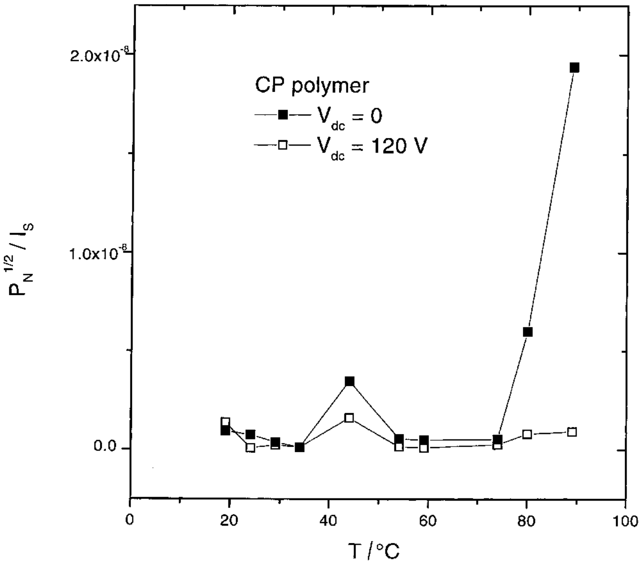

Figure 6. Temperature dependence of the optical noise-to-signal ratio $P_{\mathrm{N}}^{1/2}/I_{\mathrm{S}}$ (see text) without and with an electric field (full and open symbols, respectively).

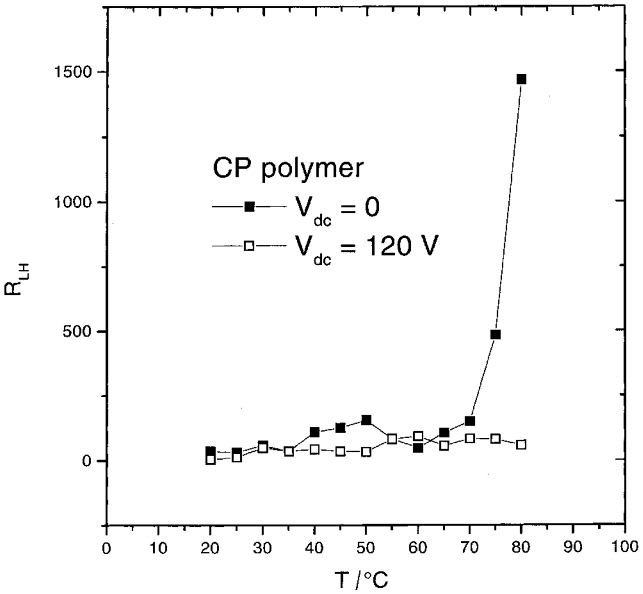

Figure 7. Temperature dependence of the low frequency to high frequency noise ratio R_{LH} (see text) without and with an electric field (full and open symbols, respectively).

is observed. It is interesting to note that the applied electric field dramatically quenches the high temperature fluctuations, also reducing the intensity of the low temperature maximum.

A more detailed analysis of the processes responsible for the observed noise has been performed by introducing the quantity $R_{\mathrm{LH}} = (P_{\mathrm{N,L}}/P_{\mathrm{N,H}})^{1/2}$, where $P_{\mathrm{N,L}}$ is the power noise density integrated in the lower frequency interval ($0.25 \leqslant \nu \leqslant 10$ Hz), and $P_{\mathrm{N,H}}$ represents the same quantity integrated in the higher frequency interval ($10 \leqslant \nu \leqslant 25$ Hz). The temperature behaviour of R_{LH} is shown in figure 7. Even in this case, the displayed curves result from an average over signals taken on different sample regions. In the absence of an applied field, the quantity R_{LH} exhibits a broad maximum centred at 50°C, and a steep increase in the high temperature region. The R_{LH} curve for a sample submitted to an applied field is again very flat.

4. Discussion

The optical properties of the CP comb polymer exhibit a high degree of irreversibility compared with other polymers of the same type, such as the SP polymer, where small irreversible effects were observed only after high temperature treatments (>100°C). In the present case, the polymer structure is observed to change significantly even after measurement cycles at relatively low temperature, never exceeding 100°C (see for instance figure 3). Of course, such a feature is detrimental to reaching a definite physical picture of this polymer. Taking into account this unavoidable irreversibility, it can be reasonably inferred that the structures observed in all $I_{\mathrm{S}}(\theta_{\mathrm{s}})$ curves shown in figure 3 (i.e. the minimum at low scattering angle and the bump at high scattering angle) are strictly related. Similar low temperature effects were never observed on previously studied comb polymers [6, 7]. The CP polymer thus undergoes some structural change, introducing a number of small reflecting surfaces at random angles, leading to the enhancement of high angle scattering through multiple reflections. No phase transitions were however detected by X-ray diffraction (XRD) in this temperature range (see Part I). A possible mechanism could involve structural changes on a larger scale, such as the appearance of a finer structure optical domain; however, no definite conclusion on such a domain rearrangement can be drawn from the present measurements. It is interesting to note that other optical properties exhibit similar anomalies in the same temperature interval. For example, a maximum in the intrinsic noise of the scattered light is observed around 45°C in the absence of an electric field (figure 6); moreover, in the same temperature range, the ratio of low frequency to high frequency contributions to the total noise slightly increases (figure 7), indicating that slower fluctuations of the polymer chains are favoured. All low temperature anomalies are reduced by a strong electric field.

By analysis of the overall behaviour of the entire set of noise–temperature curves, it can be concluded that: (a) the intrinsic optical noise strongly increases when the isotropization temperature is approached, as is often observed in similar comb polymers [6, 7]; such an increase is not merely proportional to the increase in the intensity of the scattered light (figure 3), but is considerably stronger (figure 6); (b) the intrinsic noise begins to increase suddenly just above the temperature (*c.* 72°C) corresponding to the smectic to nematic transition; (c) in the same temperature region, slow chain fluctuations play a dominant role (figure 7); (d) the electric field always quenches the optical noise, because it reduces the local degrees of freedom for all types of chain fluctuations (slow and fast, at high and low temperatures). It should be explicitly remarked that a significant effect of a transverse electric field on the optical properties of a comb polymer is observed here for the first time.

A more detailed picture is obtained from analysis of the spectral density curves. The presence of an inflection point for the $S(\nu)$ function at about 10 Hz is a peculiar feature of this polymer. In the cases examined so far [6, 7], almost pure Lorentzian spectra were always observed at temperatures corresponding to those used here. Pure Lorentzian spectra in comb polymers are usually related to uncorrelated, random motion of side groups; the fluctuations of segments of the main chains may gradually introduce an additional contribution depending on ν^{-4} (particularly evident at low frequencies) when the measurement temperature is increased to values significantly higher than the temperatures marking the transition to the less ordered mesophase [6, 7]. In the present case, such a gradual low frequency deformation of a Lorentzian spectrum was not observed. On the other hand, the peculiar shape of the $S(\nu)$ curves may be adequately fitted by the sum of two Lorentzian functions:

$$S(\nu) = S_1(\nu) + S_2(\nu) = \frac{P_1}{\nu^2 + \gamma_1^2} + \frac{P_2}{\nu^2 + \gamma_2^2} \qquad (1)$$

with different amplitudes P_i and cut-off frequencies γ_i, as shown in figure 4 (dotted lines). The cut-off frequencies obtained by fitting the experimental spectra to equation (1) are shown in figure 8. Both appear to increase steadily with temperature; the γ_1/γ_2 ratio is close to 30. On the other hand, the ratio of amplitudes P_2/P_1 proves to be about 10 at all temperatures. Generally speaking, a superposition of spectral components means that independent fluctuation modes are simultaneously activated. Describing the spectral density curves by means of a superposition of two Lorentzian functions implies that in the CP polymer there are two distinct, and essentially uncorrelated, fluctuation modes of the side groups. Comparing the results of figure 8 with data obtained for other comb polymers, it can be concluded that in the temperature interval considered, the random processes with cut-off frequency γ_1 are faster (by about one order of magnitude) than those responsible for the Lorentzian spectra of polymers with $R = \mathrm{H}$ and N [6, 7]; on the other hand, the additional Lorentzian component with cut-off frequency γ_2 means that even faster fluctuations are activated. These dynamical properties are related to the peculiar structure of the CP polymer, enhancing the degrees of freedom for random motion of the side groups. The appearance of two distinct Lorentzian processes could be reasonably related to the presence of 'short' and 'long' side groups in the CP polymer (the latter ending with polar groups). In fact, the SP polymer, where all side groups have the same length, is characterized by good Lorentzian spectra, at least at temperatures far from the isotropization point (see figure 5). The present hypothesis is further supported by the following order-of-magnitude calculation: as known [6], the amplitude ratio P_2/P_1 (≈ 10 in this case) is proportional at each temperature to the ratio β_1/β_2 between damping coefficients introduced to describe the overdamped motion of chains, according to the following formula [6]:

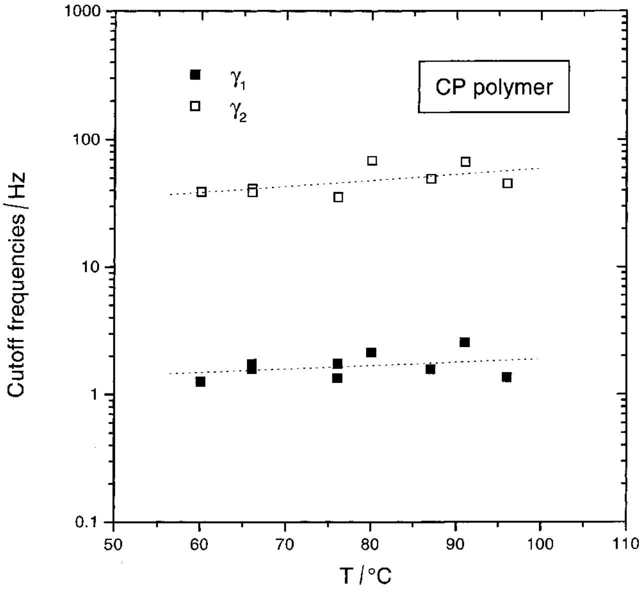

Figure 8. Temperature dependence of the cut-off frequencies γ_1 and γ_2 of the two Lorentzian spectra describing the optical noise of the CP polymer.

$$\beta_i \dot{y} + \omega_i^2 y = f \quad (i = 1, 2) \qquad (2)$$

where y is a generalized displacement of a side group, f is the usual collision force per unit mass, and ω_i is the pulsation of free oscillation of the side group. The measured cut-off frequency is by definition $\gamma_i = \omega_i^2/\beta_i$. Admitting that the two Lorentzian functions arise from the motion of the two different side groups, the ratio ω_1^2/ω_2^2 must be equal to the ratio m_1/m_2 between their masses; such a ratio is about one third. As a consequence, one gets:

$$\frac{\gamma_2}{\gamma_1} = \frac{m_2}{m_1}\frac{\beta_1}{\beta_2} = \frac{m_2}{m_1}\frac{P_2}{P_1} \approx 30 \qquad (3)$$

as an estimate for the ratio between cut-off frequencies. The good agreement with the actual results (figure 8) supports the hypothesis that the motion of 'long' and 'short' side groups gives rise to the slow (γ_1) and fast (γ_2) components of the total spectrum. Our results indicate that the fluctuations of 'long' side groups are more effectively damped than those of 'short' side groups ($\beta_1 \gg \beta_2$); this fact may be related to the presence in 'long' side groups of the mesogenic polar groups whose electrostatic interactions with surrounding moieties and molecules may result in stronger damping forces.

These results allow us to interpret the low frequency component of the observed spectra as mainly connected with the motion of 'long' side groups. Considering these results together with those of figures 6 and 7, the following picture can be drawn: all fluctuation modes of side groups are enhanced by temperature; however, the Brownian motion of 'long' side groups is activated more effectively than that of the spacer-like short side groups when the sample structure becomes less ordered for any reason (e.g. either from the formation of a number of domain boundaries, as possibly observed at about 50°C, or at the transition to a looser liquid crystal arrangement, such as the nematic phase). On the other hand, the Brownian motion of 'long' side groups is selectively damped by the aligning electrical field, so that the level of the noise generated by both 'long' and 'short' side groups becomes almost the same (and quite low) at all temperatures.

5. Concluding remarks

The CP polymer was specifically designed to enhance the side group mobility and the response to an external field. The starting point was a similar system, the SP polymer, characterized by polar mesogenic groups and by regular side groups, all of the same type. The CP polymer differs from the previous one by the fact that some of the mesogenic side groups are substituted, in a random way, by shorter spacer-like side groups. Such a structural difference is enough to fulfil the initial requirements. However, the thermal stability of the CP polymer proves to be substantially lower than that of the SP system, as confirmed by structural information (evidence of a lower isotropization temperature) and optical measurements (evidence of significant irreversible processes even after low temperature cycles).

A definite effect of a d.c. electric field on the optical noise has been observed for the first time on a comb polymer. In the SP polymer the applied field had virtually no effect on the optical noise. This fact may be explained by considering that in that case the electrostatic interactions between adjacent mesogenic groups were particularly effective in reducing their thermally activated motion, and no additional effect of the external field was observed. Reducing the electrostatic interactions by insertion of the alkyl side groups increases the side group fluctuations and the level of thermal noise, which can now be strongly reduced by an external field.

The transition from the tilted smectic to the nematic structure, observed by XRD, is also shown by the sudden change in slope observed on plotting the intrinsic optical noise as a function of temperature; in the nematic phase, slower fluctuation modes of the side groups become more important. Optical noise measurements thus confirm their validity in providing a complete picture of the dynamical properties of comb polymers. Moreover, the analysis of the spectral density of the optical noise provides a unique way of demonstrating the contributions of different fluctuation modes, ascribed to the presence of the 'long' and 'short' side groups in the CP polymer. Once again, such an interpretation is supported by the fact that in the SP polymer the side group fluctuations are described by a single cut-off frequency.

In conclusion, the reduced thermal stability of the CP comb polymer with respect to similar systems implies that it cannot be considered as a good candidate for use in applications requiring a stable, stiff material, e.g. as a surface coating material. However, the remarkable response to an external electric field, as well as the improved degrees of freedom for side group reorientation, make this comb polymer interesting for its potential applications as a liquid crystal. In fact, the CP polymer should be regarded as a first step towards the preparation of novel liquid crystal systems eligible for applications in electro-optical devices; to meet this aim, its physical properties must be substantially improved.

However, it has been shown in this work that many static and dynamical properties of a comb polymer may be substantially improved by changes in the type and nature of its side groups; as a consequence, modified physical and chemical properties are to be expected when side groups of different types are combined in different proportions. In this way, comb copolymers could constitute a novel family of mesophases characterized by tuneable physical properties, and interesting both for applications and for fundamental research. The optical measurements reported in the present work give examples of the variety of physical effects induced (or enhanced) by introducing a change in the side group morphology.

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