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Dielectric properties of side chain liquid crystalline elastomers: influence of crosslinking on side chain dynamics

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Abstract. Dielectric response, from 1 Hz to 10 MHz, of liquid crystalline side chain elastomers has been compared to the one of analogous uncrosslinked materials. Results are discussed in terms of mobility of the mesogens. Two different systems have been investigated: smectic A elastomers allow to determine the influence of crosslinking on the δ relaxation (*i.e.* the reorientation of the whole mesogen around the chain), a S_C^* elastomer shows the drastic influence of the polymer network on the Goldstone mode.

PACS. 61.30.v Liquid crystals – 61.41.+e Polymers, elastomers, and plastics – 77.84.Nh Liquids, emulsions, and suspensions; liquid crystals

1 Introduction

Liquid crystalline elastomers combine mechanical properties due to the chain elasticity to electro-optical properties of liquid crystals. Since de Gennes [1] pointed out that new remarkable effects would take place on these systems (mechanical critical points, shifts of the phase transition temperature, jumps in the stress-strain relationships), many works have been done concerning their synthesis and physical properties. Special attention has been payed on the influence of a static mechanical stress on liquid crystal order [2–4]. Since it was theoretically predicted that cholesteric and S_C^* elastomers should display a piezoelectric response [5,6], such materials were investigated [7–9] and they appeared as new interesting piezo-sensors. In spite of the amount of work done on liquid crystalline elastomers, dynamics characterizations have scarcely been performed.

Rheological experiments on side chain liquid crystalline polymers (LCP) and elastomers (LCE) [10,11] showed an original dynamic behavior and asked the question of its microscopical origin.

Broadband dielectric spectroscopy has been used to study liquid crystalline polymer dynamics [12–16]. Experiments realized by systematically changing one molecular parameter allowed the authors to point out the main molecular motions involved on these systems. But to our knowledge, only few experiments [17] have been performed on the homologous crosslinked materials. Dielectric spectroscopy experiments are yet of great interest in order to evaluate the influence of crosslinking on the liquid crystalline group motions. One can indeed imagine that in elastomers, all movements correlated at larger scale than the network mesh size have to experience an additional energetical barrier due to the elastic network.

In this paper, we describe the dielectric response of several achiral liquid crystalline elastomers with various proportions of mesogen and crosslinking agent, as well as different crosslinker lengths. An elastomer bearing a chiral mesogenic group is also studied. These responses are compared with those obtained from uncrosslinked samples with very close chemical composition. By this way we observe the modifications brought by the tridimensional network to the dynamical behavior of the liquid crystalline pending groups.

2 Experimental section

The dynamic of the systems represented in Figure 1 has been investigated on the frequency range 1 Hz–10^7 Hz. Elastomers are noted in the following way: $R^{n;p\%}_{\mathrm{mes};m\%}$, where $m\%$, $p\%$, n, and mes. are defined in Figure 1. For polymers, the notation is reduced to $P_{\mathrm{mes};m\%}$, since $p\% = 0$. Samples are prepared by a one-step hydrosilylation reaction [4]. A mixture of crosslinking agents, mesogenic groups and copoly(hydrogenmethyl-dimethylsiloxane) was dissolved at 60 °C in dry toluene. The concentration is strictly fixed at 2 mmol/ml of siloxane units. Use of original copolysiloxane chains synthesized at

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Table 1. Thermostructural characteristics of samples bearing the 4-1 mesogen. d is the layer thickness of the smectic phase (S_A).

		T_g (°C)	T_{S_A-N} (°C)	T_{N-I} (°C)	T_{S_A-I} (°C)	ΔH_{S_A-N} (J/g)	ΔH_{N-I} (J/g)	ΔH_{S_A-I} (J/g)	d (Å)
A	$R^{10;5\%}_{4-1;25\%}$	−28			9			1.6	46.3
B	$R^{10;10\%}_{4-1;25\%}$	−25			8			1.4	47.6
C	$R^{10;15\%}_{4-1;27\%}$	−23			17			2	45.9
D	$R^{22;10\%}_{4-1;25\%}$	−25			4			1.6	47.5
E	$R^{10;15\%}_{4-1;85\%}$	5	50	76		< 0.01	0.8		35
N	$P_{4-1;100\%}$	7	74	104		*	1.6		33
O	$P_{4-1;30\%}$	−26			19.5			3.0	44.4

* undetermined.

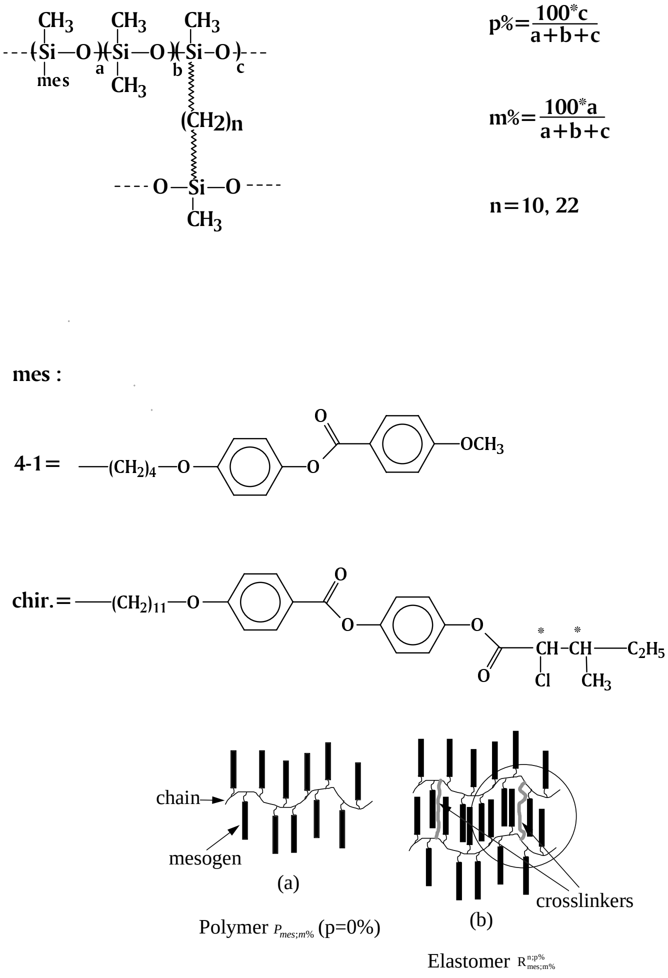

Fig. 1. Chemical structure of the materials investigated. The polymers are labelled $P_{\mathrm{mes};m\%}$; the elastomers are labelled $R^{n;p\%}_{\mathrm{mes};m\%}$. In polymers (a) all the mesogens are equivalent. In elastomers (b) mobility is reduced for mesogens which are close to a crosslinking point.

Table 2. Thermostructural characteristics of samples bearing the chiral mesogen. T_{m1} and T_{m2} correspond to the melting temperatures of the polymer. d is the layer thickness of the smectic phase (S^*_C).

		T_g (°C)	T_{m1} (°C)	T_{m2} (°C)	$T_{S^*_C-I}$ (°C)	$\Delta H_{S^*_C-I}$ (J/g)	d (Å)
K	$R^{10;10\%}_{\mathrm{chir.};25\%}$	−28			73	*	43
P	$P_{\mathrm{chir.};30\%}$	−25	−5	15	76	3	41

* undetermined.

the laboratory [18] allows to change as much as desired the proportion of the mesogenic group $m\%$ or of the crosslinking agent $p\%$. After reaction, the elastomer is carefully washed in an excess of toluene for one week with the solvent being renewed each day. This ensures a full removal of unreacted molecules. The sample is then deswollen in successive mixtures of toluene and methanol with the methanol fraction being increased in each step. As synthesis of the elastomer is performed in solution, the final material (after removal of the solvent) shows no macroscopic orientation. Polymers are obtained *via* the same reaction scheme (without crosslinking agent, $p = 0\%$) and purified by two precipitations in methanol. Polymorphism of the samples, as determined by optical microscopy, X-ray diffraction and differential scanning calorimetry, is presented in Tables 1 and 2. All the samples bearing the achiral mesogenic substituent exhibit a S_A phase. A nematic phase appears at higher temperature for the largest amount of mesogens (Tab. 1). The chiral substituent generates a smectic C* phase.

Elastomers are cut up with a microtome. Thin slides (50–100 μm) obtained are placed into a lab-designed cell composed of two circular brass electrodes ($\phi = 5$ mm).

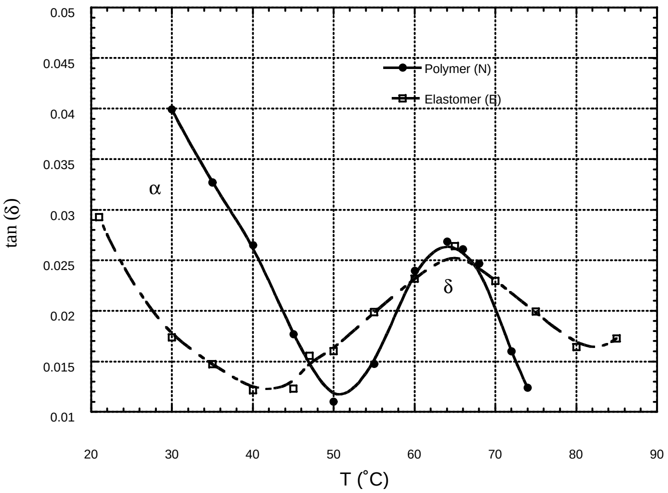

Fig. 2. Loss tangent for the polymer $P_{4-1;100\%}$ (N) (close circles) and the elastomer $R^{10;15\%}_{4-1;85\%}$ (E) (open squares).

Interelectrode spacing can be adjusted by a micrometer screw, in order to fit to the elastomer thickness. Sample temperature is controlled between −50 to +150 ℃ by using an Eurotherm 818 regulator (±0.05°). Impedance measurement is performed with two different set-up: a Chelsea dielectric interface connected to a Solartron 1250 impedance meter is used for low frequency measurements. This apparatus allows high impedance measurements. For the range 1 kHz–13 MHz, an HP4192 A impedance meter is connected to the cell.

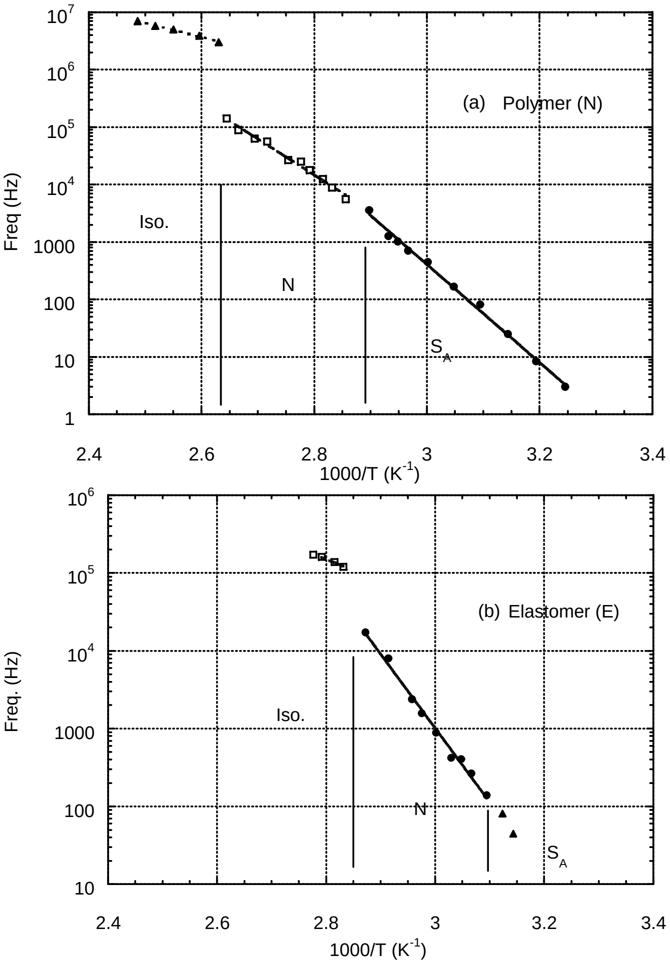

Fig. 3. Arrhenius plot for samples $P_{4-1;100\%}$ (a) and $R^{10;15\%}_{4-1;85\%}$ (b).

3 Results

3.1 Samples bearing the 4-1 mesogenic group

The first series studied in this paper concerns samples bearing an achiral 4-1 mesogenic group. Attention is focused on the δ relaxation mechanism which involves the reorientation of the mesogenic group as a whole. This motion, which follows an Arrhenius law, is a good probe of the way the mesogenic groups interact with the network.

3.1.1 Comparison between a polymer $P_{4-1;100\%}$ and an elastomer $R^{10;15\%}_{4-1;85\%}$ of similar composition

These two samples carry a high amount of mesogens ($m = 100\%$ and $m = 85\%$). The elastomer studied is the most highly crosslinked one. First of all, examination of Figure 2 shows that the same two mechanisms are involved in both systems. The lower temperature one is related to the glassy transition and is noted α. The second mechanism, δ, has nearly the same amplitude in both systems. It can be related to the reorientation of the dipole carried by the liquid crystalline group. The peak related to δ is wider in the case of the elastomer but this will be commented afterwards. It is interesting to note here that, even for the highly crosslinked elastomer $R^{10;15\%}_{4-1;85\%}$, mesogen reorientation is not locked. This is coherent with the fact that this sample displays a liquid crystalline behavior which requires indeed a certain degree of freedom for the pendant groups. The crosslinking process used to synthesize our elastomers prevents macro-Brownian movements (chains are no more free to slip and the sample is solid) but let micro-Brownian one to take place.

Activation energy and Arrhenius plots for the δ mechanism in samples $P_{4-1;100\%}$ and $R^{10;15\%}_{4-1;85\%}$ are presented in Table 3 and Figure 3. In the isotropic phase, a slight increase of the activation energy is observed in the elastomer (0.57 eV compared to 0.49 eV for the polymer). At the isotropic-nematic transition, the δ frequency undergoes a significant drop. This was already observed in similar systems [13,19] and was ascribed to the appearance of a nematic potential. In the nematic phase, the δ activation energy is found to be significantly higher in the elastomer than in the polymer (1.67 eV compared to 1.24 eV). In this phase, where movements are correlated at large scale by liquid crystalline interactions, the δ movement clearly requires more energy while it has to experience

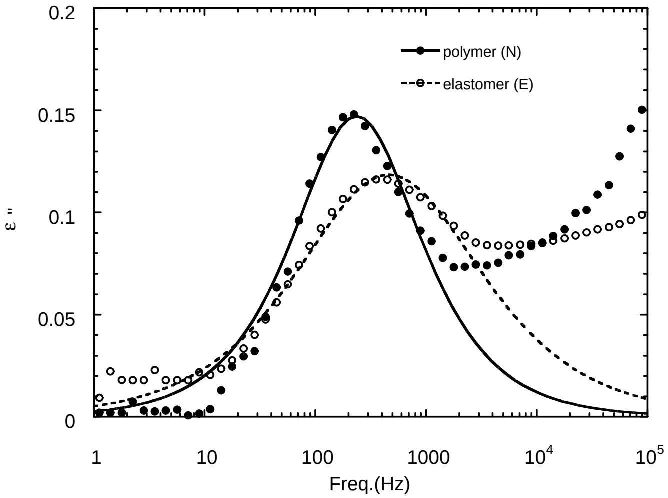

Fig. 4. Cole-Cole fits for the δ relaxation peak at 55 °C. Open symbols correspond to $\mathrm{R}^{10;15\%}_{4-1;85\%}$ (E) and close symbols to $\mathrm{P}_{4-1;100\%}$ (N).

the elastic network. In the $\mathrm{S_A}$ phase of the crosslinked sample, the δ peak cannot be resolved with enough accuracy to determine an activation energy.

The distribution of relaxation times in the mesomorphous state is worth comparing. Figure 4 shows the δ relaxation peaks for both systems at 55 °C. After subtraction of the $1/f$ low frequency conductivity tail, data were fitted by the following Cole-Cole function:

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon}{1 + (j\omega\tau)^\alpha} \tag{1}$$

where ε_∞ is the high frequency permittivity, $\Delta\varepsilon$ the difference between the static permittivity and ε_∞; ω is the angular frequency defined as $\omega = 2\pi f$; τ is the characteristic relaxation time; α is a fitting parameter that allows to take into account a distribution of relaxation time. If $\alpha = 1$, equation (1) is the Debye function describing a single relaxation time mechanism. Any deviation from unity $(0 < \alpha \leq 1)$ reflects a distribution of relaxation time. For the polymer, α is found to be equal to 0.93, which is very close to unity. On the contrary, the elastomer displays an α value of only 0.68 which clearly shows a distribution of relaxation times. This distribution can be discussed in terms of mesogen mobility. Indeed, in the case of elastomers, all mesogenic pending groups are not equivalent as they are in the case of polymers (see Fig. 1). In elastomers, their mobility is a function of their distance from a crosslinking point. Furthermore, one can imagine the network tridimensional structure forces some mesogens to move in a cooperative manner, since it creates additional correlations between mesogens.

Remark: the $1/f$ low frequency conductivity tail appears very commonly in polymer materials, whatever the electrodes employed. It is due to the fact the materials are never pure dielectrics and carry some ionic impurities.

Table 3. Modification of the activation energy for the δ mechanism from the polymer to the elastomer.

	E_a (eV)		
	Smectic	Nematic	Isotropic
$\mathrm{P}_{4-1;100\%}$ (N)	1.70 ± 0.08	1.24 ± 0.06	0.49 ± 0.04
$\mathrm{R}^{10;15\%}_{4-1;85\%}$ (E)	*	1.67 ± 0.07	0.57 ± 0.04

* undetermined.

Table 4. Activation energy for the δ mechanism as a function of the crosslinking ratio.

	E_a (eV) (Isotropic)
$\mathrm{P}_{4-1;30\%}$ (O)	0.81 ± 0.05
$\mathrm{R}^{10;5\%}_{4-1;25\%}$ (A)	0.85 ± 0.05
$\mathrm{R}^{10;10\%}_{4-1;25\%}$ (B)	0.90 ± 0.05
$\mathrm{R}^{10;15\%}_{4-1;27\%}$ (C)	0.91 ± 0.05

3.1.2 Influence of the mesogen amount

The mesogen amount $m\%$ controls the polymorphism of the sample and also plays the main rule on the stiffness of the chain, as can be seen from the evolution of the T_g values (Tabs. 1 and 2). This implies that, the study of the effect of crosslinking must be realized with samples containing close amount of mesogens. Nevertheless, an interesting feature can be observed when comparing samples with very different mesogen amount. The activation energy of the δ mechanism in the isotropic phase (Tabs. 3 and 4) is significantly lower for polymers with high $m\%$ (N and E) than for samples with less mesogens (O, A, B, C). This could be attributed to the presence of a large volume fraction of polysiloxane chains making the δ movements more difficult.

3.1.3 Influence of the crosslinking rate

Elastomers $\mathrm{R}^{10;5\%}_{4-1;25\%}$, $\mathrm{R}^{10;10\%}_{4-1;25\%}$ and $\mathrm{R}^{10;15\%}_{4-1;27\%}$ present nearly the same mesogen ratio but differ by their crosslinking amount. Arrhenius plots for these three samples and for the analogous polymer $\mathrm{P}_{4-1;30\%}$ are reported in Figure 5. The δ mechanism has not been resolved with sufficient accuracy in the $\mathrm{S_A}$ phase so that activation energy, presented in Table 4 is only given in the isotropic phase.

$\mathrm{P}_{4-1;30\%}$ and $\mathrm{R}^{10;5\%}_{4-1;25\%}$ nearly present the same Arrhenius plot. However, one can observe a regular decrease of the relaxation frequency from 5 to 15% crosslinking which shows the progressive loss of mobility of the side groups. The activation energy of the δ mechanism appears to be

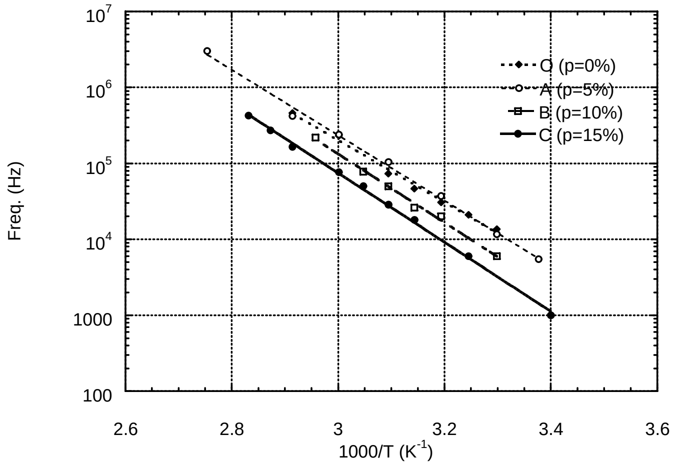

Fig. 5. Influence of the crosslinking ratio on the δ mechanism: Arrhenius plot for samples $P_{4-1;100\%}$ (O), $R^{10;5\%}_{4-1;25\%}$ (A), $R^{10;10\%}_{4-1;25\%}$ (B) and $R^{10;15\%}_{4-1;27\%}$ (C).

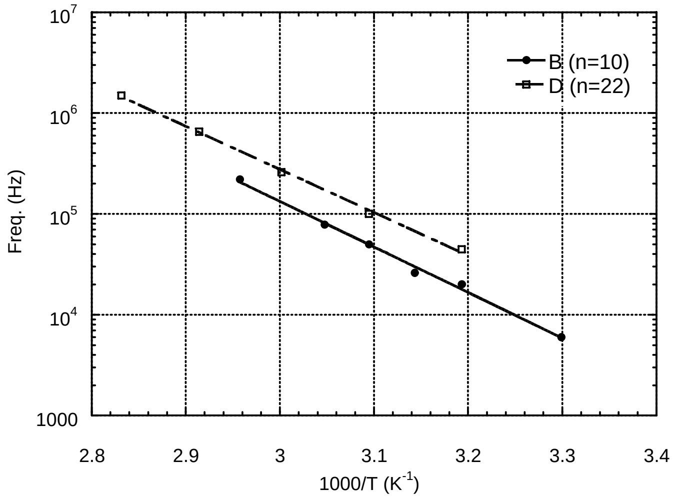

Fig. 6. Influence of the crosslinker length on the δ mechanism: Arrhenius plot for samples $R^{10;10\%}_{4-1;25\%}$ (B) and $R^{22;10\%}_{4-1;25\%}$ (D).

only slightly modified in the isotropic phase. This can be explained by the fact that, in this phase, mesogen motions are not correlated through distances larger than the network average mesh size and mesogens are nearly as free as in polymers. Below the mesh size of the network, the material can be described as a polymer (Fig. 1), then, no additional energetic barrier is expected, and the activation energy remains nearly constant.

3.1.4 Influence of the crosslinking agent length

A sample, $R^{22;10\%}_{4-1;25\%}$, analogous to $R^{10;10\%}_{4-1;25\%}$ but with a longer crosslinking agent (22 carbons) was also studied. Increasing the length of the bridge between polymer chains increases the mesh size of the network and mesogens should then experience less hindrance to motion. It is seen in Figure 6 that the δ mechanism occurs at higher frequency in $R^{22;10\%}_{4-1;25\%}$ than in $R^{10;10\%}_{4-1;25\%}$. This shows it is possible, by tuning such molecular parameters, to modify the dynamics, *i.e.* to act on the coupling between mesogens and elastic network. One can also remark, that the value of the activation energy for the δ mechanism is not significantly modified by the crosslinker length in the isotropic phase. This is in agreement with observations made in previous subsections.

3.2 Study of a S_C^* sample

Within the frequency range studied in this paper, the dielectric behavior of S_C^* materials is governed by collective relaxation modes. In particular, the Goldstone mode is characteristic of the helicoïdal structure of the S_C^* phase [20]. It is related to the fluctuations of the molecules around the smectic cone and can be very easily electrically induced. For low molecular weight molecules, this mode is observed between 10^2 and 10^4 Hz and its large amplitude remains nearly constant on the whole temperature range of the S_C^* phase. In liquid crystalline S_C^* polymers, this mode is still present but its characteristics are influenced by the polymer backbone [21–24]. Indeed, its amplitude decreases with temperature. Furthermore, its frequency is found to be typically one decade lower than for low molecular weight materials.

The study of the Goldstone mode in liquid crystalline elastomers is of special interest du to its collective nature: indeed, movements occur at higher length scale than the network mesh size and then directly interact with the elastic structure. This problem is directly related to the problem of switching with an electric field. Switching liquid crystalline ferroelectric structure is of great interest for technological applications but this mechanism is still not clear for elastomers.

It is of evidence that one can, by mean of crosslinking, obtain ferroelectric structures with locked orientation [8,25–27]. This orientation is preserved even if the sample is heated to the isotropic phase and brought back in the S_C^* phase. This experimental fact clearly means the network structure keeps a memory of the mesogenic groups orientation. In other terms, it is energetically favourable for the mesogens to preserve the orientation they had during crosslinking. However, certain authors [28] have synthesized oriented ferroelectric elastomers that could be switched by an electric field of the same strength that the one used in the case of a ferroelectric polymer. To reach this scope, they used a particular crosslinking technique that minimizes interactions between the network and the mesogens. Furthermore, the crosslinking ratio was chosen to be very low as the scope of the authors is to favor switching. It should be noted that crosslinking reaction takes place directly into the measurement cell, which means that the networks investigated are not washed before switching experiments are performed. It is then possible that some uncrosslinked liquid crystalline polymer chains remain in the sample and that, consequently, the switching is partly due to this free polymer part. In the case of our work, the washing treatment ensures full

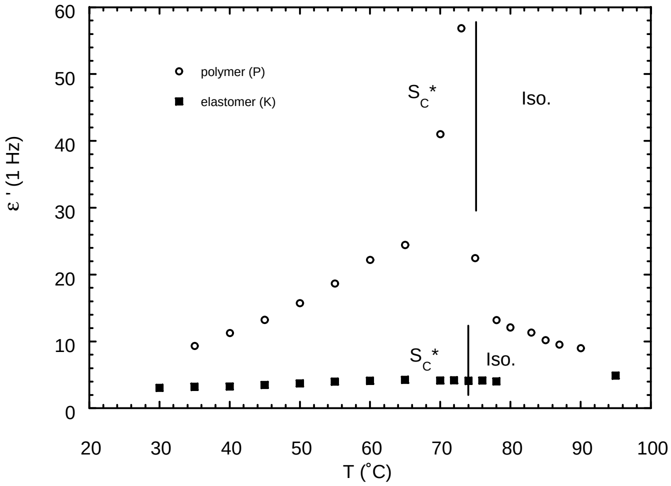

Fig. 7. 1 Hz permittivity for the chiral polymer (P) and elastomer (K).

removal of unreacted compounds and makes sure investigated sample does not present any polymer fraction unlinked to the tridimensional network.

The elastomer sample studied here shows a wide S_C^* phase and it was clearly established it possesses piezoelectric properties [9] within this phase. To compare the behavior of the elastomer with the one of an uncrosslinked system, the polymer $P_{chir;30\%}$ was also investigated.

Figure 7 shows the real part of the permittivity, at the lowest investigated frequency (1 Hz), at which the contribution of the Goldstone mode should be the highest for both systems.

In the case of the polymer, the value of the permittivity is indeed clearly influenced by the Goldstone mode, the maximum contribution of which takes place two degrees below the transition temperature. The amplitude of this mode decreases with temperature as was already observed in such polymer systems [22].

On the contrary, the elastomer shows a really flat response and no trace of a Goldstone mode is seen even near the transition temperature. Crosslinking has fully suppressed this low frequency mode. The question remains to know the reason of this disappearance. Is it due to the crosslinked nature of the material that hinders collective molecular fluctuations around the smectic cone? This would mean that the azimuthal angle would have relevance in the free energy of S_C^* elastomers. Is it due to a particular chemical composition of the sample studied? We could then imagine to synthesize samples crosslinked in such a way that the Goldstone mode would be still present.

Remark: In elastomers, the Goldstone mode manifestation would induce a macroscopic change of shape. Then, one could think that squeezing the sample between two fixed electrodes should be sufficient to suppress the Goldstone mode (the change of shape would be locked). To check this point, we renewed the experiments using an interelectrode space ten micrometers larger than the elastomer thickness. The free volume was filled by paraffinic oil to allow eventual distortion of the sample. These experiments gave the same result than the one presented here.

4 Conclusion

Several side chain liquid crystalline elastomers have been investigated by dielectric spectroscopy. These experiments allow to determine the characteristics of the side group motions. It is seen that, in the isotropic phase, the δ relaxation of the mesogens exhibits the same qualitative features than in polymer samples, which shows that crosslinking process preserves micro-Brownian motions. However, crosslinking decreases the δ relaxation rate. Through mesophases, mesogen motions are correlated due to liquid crystalline interactions. The length scale of these correlations being larger than the network mesh size, molecular motions are submitted to an additional hindrance. Consequently, the activation energy increases from the polymer to the network. The length of the crosslinking agent is also to be considered in these effects.

It was also shown that the presence of crosslinking points along the polymer chain modify the mobility of the closest mesogens. Then, all mesogens do not relax at the same frequency, which broadens the δ relaxation peak.

The behavior of the S_C^* sample is of particular interest as it shows that the Goldstone mode can be suppressed in crosslinked materials. Further investigations (experimental as well as theoretical) are required to understand the physical reasons of its disappearance.

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