Macromolecules **2002,** *35,* 5459−5465

Influence of Molecular Parameters on the Elastic and Viscoelastic Properties of Side-Chain Liquid Crystalline Elastomers

J. J. Zanna,[†,‡] P. Stein,[†] J. D. Marty,[§] M. Mauzac,[§] and P. Martinoty*,[†]

Laboratoire de Dynamique des Fluides Complexes, Unité Mixte de Recherche U.L.P.-C.N.R.S. No. 7506, Université Louis Pasteur, 4 rue Blaise Pascal, 67070 Strasbourg Cedex, France; Centre de Recherche Paul Pascal, Unité Propre de Recherche C.N.R.S. No. 8641, Université Bordeaux 1, Avenue du Dr. Schweitzer, 33600 Pessac, France; and Laboratoire des Intéractions Moléculaires et Réactivité Chimique et Photochimique, Unité Mixte de Recherche U.P.S.- C.N.R.S. No. 5623, Université Paul Sabatier, 118 Route de Narbonne, 31062 Toulouse Cedex 4, France

Received January 17, 2002; Revised Manuscript Received March 22, 2002

ABSTRACT: We investigated the influence of molecular parameters (amount of mesogen, cross-linking density, cross-linker length) on the complex shear modulus $G^* = G' + iG''$ of polydomain smectic-A side-chain liquid crystalline elastomers composed of side-chain polysiloxane cross-linked by aliphatic chains. G' presents two components in the isotropic phase. One is independent of the frequency and reflects the presence of the permanent network; the other is frequency-dependent and is characterized by a scaling law behavior $G' = G'' \sim f^{0.5}$ of the Rouse type, where f is the frequency. We show that this scaling law is independent of the molecular parameters except when the amount of mesogen becomes very small. In contrast, the crossover frequency between the elastic and the Rouse regime is a function of the cross-linking density and the cross-linker length but is independent of the amount of mesogen, except when the latter is very small. The elastic plateau follows the same behavior as the crossover frequency. It is no longer visible in the smectic-A phase, and the dynamics of this phase are essentially governed by a transient network characterized by a $f^{0.3}$ scaling law which is independent of the cross-linking density.

I. Introduction

Side-chain liquid crystalline networks are composed of polymer backbones, essentially polyacrylate or polysiloxane, bearing pendent mesogenic groups, and chemically linked together by flexible or mesogenic-like chains.[1] If the cross-linking density is low enough, these networks preserve the mesomorphic order of the liquid crystalline phases.[1,2] The mesogenic groups can be macroscopically disoriented in the liquid crystalline state (so-called polydomain elastomers) or macroscopically ordered (so-called monodomain elastomers). Because of this mesomorphic order, this new type of rubber has remarkable elastic properties;[3,4] for example, a transition from a polydomain to a monodomain can be induced by a strain field directly linked to the mesomorphic order. This transition is commonly used to prepare macroscopically ordered liquid crystalline elastomers.[5]

While there exists a lot of theoretical[3,6,7] and experimental[8−13] investigations of their static properties, their dynamical properties are less well-known.[14−18] Rheological experiments made over a wide frequency range have begun in the past few years. Gallani et al.[19] studied the behavior of various polydomain elastomers exhibiting nematic and smectic-A phases, and Weilepp et al.[20,21] studied that of polydomain and monodomain samples which only have a smectic-A phase. More recently, Stein et al.[22] have investigated the rheological properties of polydomain and monodomain samples exhibiting only a nematic phase and have shown that the monodomain samples present a marked anisotropy of the shear modulus. This anisotropy stems from the fact that the director is coupled to the shear strain when the sample is sheared in a direction parallel to the director and not when it is sheared perpendicularly to the director. These observations have been confirmed by Clarke et al.[23] For all the samples studied, whether they are polydomain or monodomain, the results obtained in the isotropic and nematic phases show that the real part of the shear modulus is the sum of two terms: one is frequency-independent and reflects the permanent network; the other depends on the frequency and gives rise to a scaling behavior ($G' \sim G'' \sim \omega^{0.5}$). The dynamic behavior of the smectic-A phase is completely different; it is governed by a transient smectic network with a very long lifetime, whose contribution to the shear modulus is greater than that of the permanent network. This network, characterized by an $\omega^{0.3}$ scaling law, stems from the fact that different polymeric backbones are connected through their mesogenic groups, which are trapped in different smectic layers or smectic domains.[20]

The aim of this paper is to determine the influence of the different molecular parameters, i.e., the amount of mesogen (from 3% to 95%), the cross-linking density (from 5% to 15%), and the cross-linker length (from 6 to 22 methylene groups), on the shear properties of polydomain samples composed of side-chain polysiloxanes cross-linked by aliphatic chains. We find that the $\omega^{0.5}$ scaling law characterizing the isotropic phase and the $\omega^{0.3}$ scaling law associated with the transient smectic network are independent of the cross-linking density. The $\omega^{0.5}$ scaling law is also independent of the cross-linker length and of the amount of mesogen, except when the latter becomes very small. The values of the rubbery plateau and the crossover frequency between the elastic and the viscoelastic regimes are both dependent on the cross-linking density and the cross-linker length but are independent of the amount of mesogen, except when the latter is very small.

[†] Université Louis Pasteur.

[‡] Université Bordeaux 1.

[§] Université Paul Sabatier.

10.1021/ma020083z CCC: $22.00

Table 1. Characteristics of the Samples[a]

sample	m%	n	p%	T_G (°C)	T_{SA-N} (°C)	T_{N-I} (°C)	T_{SA-I} (°C)	ΔH_{SA-N} (J/g)	ΔH_{N-I} (J/g)	ΔH_{SA-I} (J/g)	d (Å)
E_1	95	10	5	5	73	93		0.07	1.2		34
A	25	10	5	−28			9			1.6	46.3
B	25	10	10	−25			8			1.4	47.6
C	27	10	15	−23			17			2	45.9
D	20	10	10	−35			−7			0.6	50.5
E	32	10	10	−19			20			2	45
F	3	10	5	−95							
G	5	10	5	−75							
E_0	0	10	13	−120							
H	25	22	10	−25			4			1.6	47.5
I	25	6	10	−25			4			1.4	47

[a] T_G is the glass transition temperature, ΔH the transition enthalpy, and d the layer spacing of the smectic-A phase.

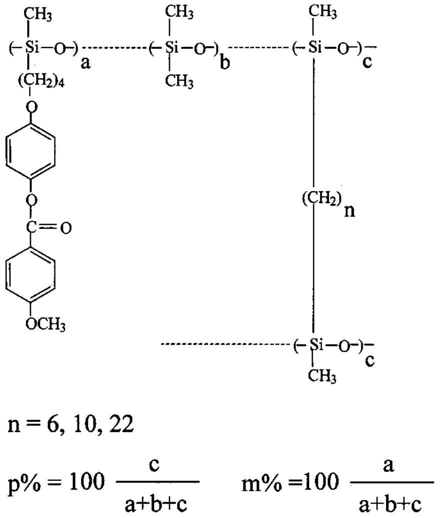

Figure 1. Chemical structure of the samples. They all have the same mesogenic unit with a spacer length of four methylene groups and a methoxy end group. p% and m% represent the cross-linking density and the proportion of mesogenic units, respectively. n is the number of methylene groups in the aliphatic cross-linker.

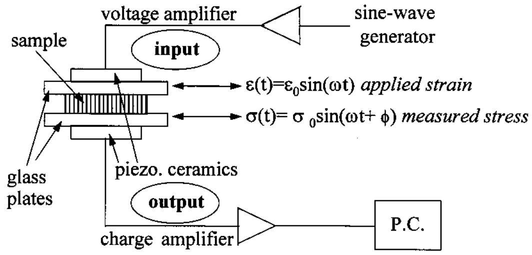

Figure 2. Schematic representation of the experimental setup.

II. Experimental Section

2.1. Materials. The elastomers studied correspond to the general formula given in Figure 1. The samples were prepared by a one-step hydrosilylation reaction.[11] A mixture of cross-linking agents, mesogenic groups, and copoly(hydrogenmethyl−dimethylsiloxane) was dissolved at 60 °C in dry toluene. The concentration was strictly fixed at 2 mmol siloxane units/mL. Several copolysiloxane precursor chains were synthesized[24] in order to allow large changes of the amount of mesogenic group (m%) or cross-linking agent (p%). These copolymers were prepared to be of virtually identical lengths (the averaged number degree of polymerization is 80 ± 5, as checked by steric exclusion chromatography) and with a statistical distribution of the two different types of units. The cross-linking density as indicated in Table 1 is the amount of cross-linker introduced during synthesis without taking into account the effective cross-linkage. After reaction, the sample was carefully washed in an excess of toluene for 1 week with the solvent being renewed each day. This ensured full removal of unreacted molecules. The sample was then deswollen in successive mixtures of toluene/methanol (solvent/nonsolvent), increasing the methanol fraction in each step. As synthesis was performed in solution, the final dry elastomer showed no macroscopic orientation of the liquid crystalline domains.

The characteristics of the elastomers studied are given in Table 1. The phase transitions were determined by differential scanning calorimetry (Perkin-Elmer DSC7). The temperatures reported correspond to those determined from the position of the DSC peak as the temperature fell at 5 °C/min. The glass transition temperatures (T_g) were obtained as the temperature increased at 10 °C/min. The smectic-A structure was established by X-ray measurements taken on samples orientated by mechanical stretching.[25] It should be noted that the smectic layer thickness increased as the amount of mesogen decreased. This phenomenon, due to a microphase separation between the unsubstituted dimethylsiloxane units and the siloxane units substituted by the mesogens, was previously observed in the non-cross-linked smectic polymers.[26]

Elastomers A, B, C, D, E, H, and I containing amounts of mesogen ranging from 20% to 32% showed a S_A−I transition. Elastomers F and G bearing a very low amount of mesogen, 3% and 5%, respectively, did not exhibit any liquid crystalline phase. Sample E_0 was a mesogen-free network synthesized for comparison. Sample E_1 with 95% amount of mesogen displayed a nematic and a smectic-A phase. The viscoelastic properties of samples E_1 and A have been reported in refs 19 and 20, respectively.

2.2. Experimental Setup. The complex shear modulus $G^* = G' + iG''$ was measured as a function of frequency and temperature, using the piezo-rheometer used previously[19−22] (Figure 2). The principle of this apparatus consists of applying slight strain to the sample by means of a piezo-electric ceramic vibrating in the shear mode and measuring the stress transmitted through the sample by a second piezo-electric element. The strain imposed on the sample is given by

$$\epsilon = \delta/L \approx V_{\text{in}} = (V_0)_{\text{in}} e^{i\omega t} \tag{1}$$

where V_{in} is the tension applied to the emitting ceramic, δ the resulting displacement, and L the thickness of the sample. The stress measured on the receiving ceramic is given by

$$\sigma = f/S \approx V_{\text{out}} = (V_0)_{\text{out}} e^{i(\omega t+\varphi)} \tag{2}$$

where f is the force transmitted by the sample, S the sample surface area, and V_{out} the tension given by the ceramic.

Measurement of the complex shear modulus

$$G^* = \sigma/\epsilon \approx ((V_0)_{\text{out}}/(V_0)_{\text{in}}) e^{i\varphi} \tag{3}$$

enables the nature and mechanical properties of the compound to be determined. Phase change φ can vary from zero (perfectly elastic solid) to $\Pi/2$ (Newtonian liquid) and is related to the real G' and imaginary G'' parts through the relation

$$\tan \varphi = G''/G' \tag{4}$$

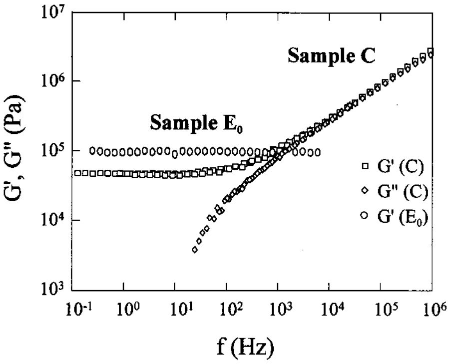

Figure 3. Master curves of G' and G'' in the isotropic phase for the mesogen-free elastomer E_0 and sample C ($m = 27\%$). The reference temperature is $T_{ref} \sim T_g + 100$ °C.

In practice, the compound is placed between two glass slides, one of which is stuck to the emitting ceramic and the other to the receiving ceramic. All the experiments were carried out using the same experimental procedure: the sample was placed in the cell at room temperature and then heated to 100 °C. It was then cooled step by step after 30 min of annealing at each temperature of measurement. The applied strain ϵ_0 never exceeded 10^{-3}. For these strain amplitudes the validity of the linear response was checked experimentally. Before the experiments, the cell was calibrated using solid or liquid materials whose shear modulus and viscosity are accurately known. The sensitivity of the setup does not allow G' and G'' values smaller than 10^3 Pa to be measured. G' and G'' were determined to within 10% for values around 10^3 Pa. The accuracy increases when the G' and G'' values increase and can be estimated to be smaller than 1% for values higher than 10^4 Pa.

III. Results and Discussion

3.1. Time−Temperature Superposition Method. The variation of the shear modulus over a frequency range larger than the one given by the apparatus (10^{-1}−10^4 Hz) can be obtained by using the empirical time−temperature superposition principle.[27,28] By using this method, master curves were obtained for G' and G'' for the isotropic and smectic phases, but it was not possible to obtain master curves composed of data taken both in the isotropic and the smectic phase. In other words, the time−temperature superposition does not hold across the smectic−isotropic transition. The description of the full mechanical behavior of samples presenting a smectic phase therefore needs two master curves, confirming our previous studies.[19−21]

3.2. Comparison between Liquid Crystalline Elastomer and Classical Elastomer. Figure 3 compares the response, at $T \sim T_g + 100$ °C, of the mesogen-free elastomer E_0 to that of the liquid crystalline elastomer C. The latter, with 27% mesogen, had the same cross-linker and a cross-linking density quite similar to that of E_0, as shown in Table 1. It can be seen that sample E_0 had an elastic response over the whole frequency range investigated. For sample C, the behavior of G' was also frequency independent at low frequency but became viscoelastic above 100 Hz. In this frequency range, G' and G'' increased strongly with frequency and became equal at higher frequencies with a phase shift ϕ of around 45°. For these frequencies, G' and G'' followed the scaling law $G' = G'' \sim f^{0.5}$. This behavior has been observed for all the side-chain liquid crystalline elastomers studied up to now.[19−22] It corresponds to that predicted by the Rouse model, which describes, in its general formulation, the dynamics of Brownian particles interacting with their nearest neighbors.[28] The interpretation of the results with this model[20] assumes that the interaction between the mesogens leads to transient bulky clusters, which interact with each other and are weakly coupled to the polymer backbone via the flexible spacer.

While elastomer C possessed a cross-linking density comparable to that of its mesogen-free counterpart E_0, it had a lower elastic plateau value (5×10^4 instead of 10^5 Pa). The conventional rubber elasticity[29] predicts that the static elastic modulus G_e is inversely proportional to M_e, where M_e is the molecular weight of chain between two cross-linking points. Adding mesogenic side groups leads to an increase in M_e and in turn to a decrease in G_e. But other explanations are possible: for example, the presence of the mesogenic side groups can create steric obstacles, making the creation of effective cross-linkers more difficult and thus lowering the value of G_e.

3.3. Influence of the Cross-Linking Density on the Complex Shear Modulus *G, Keeping the Amount of Mesogen and the Cross-Linker Length Identical.** The influence of the cross-linking density (p%) was checked on samples A, B, and C, which contain the same cross-linker ($n = 10$) and a very similar amount of mesogen ($m \sim 25\%$). The amounts of cross-linker introduced during synthesis were 5%, 10%, and 15%, respectively. This parameter is called the cross-linking density although the true cross-linking density is probably lower than that given by the cross-linkers concentration, because the cross-linking efficiency is decreased by the presence of the mesogen.

3.3.1. Variations of *G′* and *G″* vs Frequency. The master curves of G' and G'' associated with the isotropic phase of each compound were determined using the empirical time−temperature superposition principle. They are plotted in Figure 4a−c at the same reference temperature $T_{ref} \sim T_g + 100$ °C to allow comparison between them. For the three samples the variations of G' and G'' vs frequency show the same behavior characterized by a low-frequency regime, for which G' is frequency-independent (equal to G_e, the static elastic modulus) and G'' linearly increases with frequency, and a high-frequency viscoelastic regime of the Rouse type. Inspection of the figure shows that the cross-linking density has no effect on the viscoelastic behavior (same 0.5 power-law exponent) but only affects the value of G_e and that of the crossover frequency f_1 between elastic and viscoelastic behavior. The values of f_1 were calculated from the equation

$$G'' = G_e f / f_1 \qquad (5)$$

which is given by the low-frequency limit of the Mooney model.[27] Figure 5a,b shows the variations of G_e and f_1 as a function of the cross-linking density. It can be seen that G_e and f_1 increase with the cross-linking density and that the behavior of G_e is roughly proportional to p%.

Figure 6a−c gives the master curves obtained in the smectic-A phase at the reference temperature of 0 °C (approximately T_g + 25 °C). Three characteristic regimes can be observed: In the low-frequency range, G' and G'' follow a power law with an exponent of about 0.3. This result is observed for the three samples and is therefore independent of the amount of cross-linker. It confirms that the smectic structure induces a particular dynamic behavior as previously observed[20] and

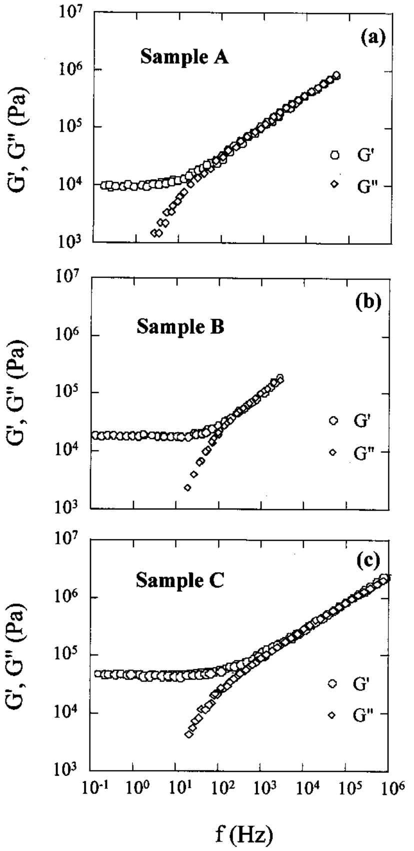

Figure 4. Master curves of G' and G'' in the isotropic phase for samples A–C. The reference temperature is $T_{\mathrm{ref}} \sim T_g + 100$ °C.

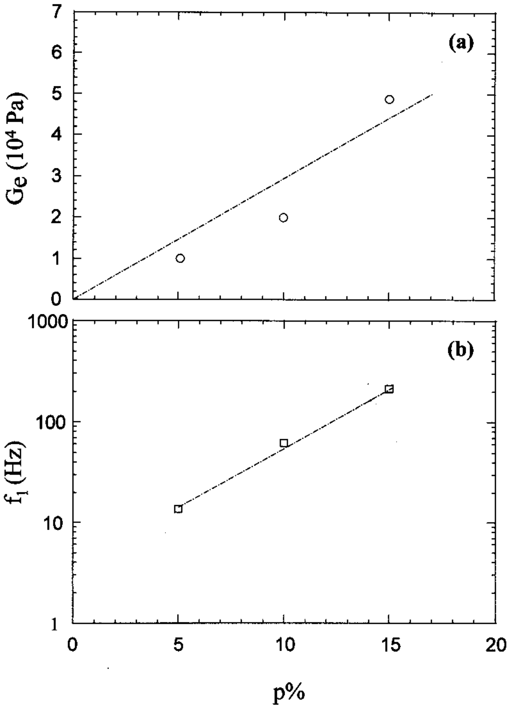

Figure 5. Variation of the static modulus G_e and the characteristic frequency f_1 vs the cross-linking density for samples A–C. The amount of mesogen ($m \sim 25\%$) and the cross-linker length ($n = 10$) are the same for the three samples.

explains why the time–temperature superposition principle cannot be applied through the S_A–I transition. After a crossover region, G' and G'' become equal and follow a power law with an exponent of about 0.5. This behavior is observed for most conventional polymers and is probably not related to the liquid crystalline properties of the compounds. Finally, at very high frequencies, G' tends toward a constant value, the glassy plateau, and G'' tends toward zero. So qualitatively, the three samples show the same frequency behavior.

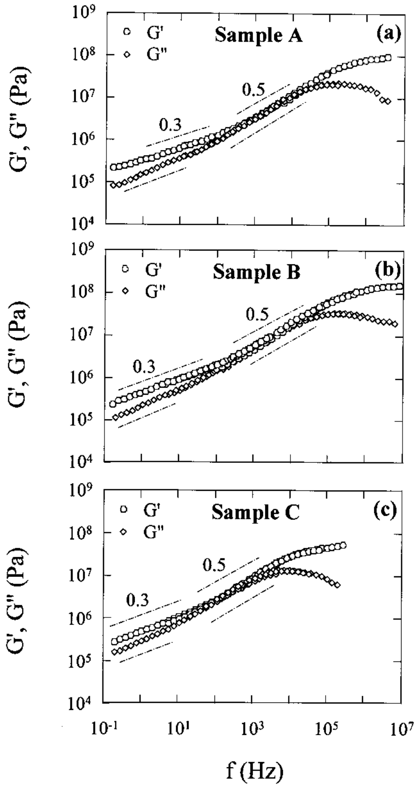

Figure 6. Master curves of G' and G'' in the smectic phase for samples A–C. The reference temperature is $T_{\mathrm{ref}} \sim T_g + 25$ °C.

3.3.2. Variation of *G'* vs Temperature. Figure 7a–c shows the temperature dependence of the real part G' of the shear modulus at 1, 100, and 1000 Hz for samples A, B, and C. As can be seen, G' is essentially controlled by the dynamics of the glass transition over the whole temperature range under study, with a small anomaly near the S_A–I transition for the lowest frequency. For a given frequency, the end of the relaxation range is related to the temperature for which the phase defined by eq 4 becomes zero. Above this temperature, the frequency is lower than all the relaxation frequencies of the system, and the behavior of G' characterizes the permanent network in its hydrodynamic regime. At 1 Hz, this regime is reached at $T \sim T_g + 70$ °C. Since the mesomorphic domain between the glass transition and the isotropic phase was typically of the order of 40 °C for the three samples, the hydrodynamic regime is not reached at the clarification temperature, even for frequencies as low as 1 Hz. This explains why the anomaly in G' observed at 1 Hz in the transition region is nearly hidden by the dynamic glass transition, in contrast to the results obtained for a sample exhibiting a very broad smectic-A phase.[20] This anomaly, which is not observed near the nematic–isotropic transition,[19,22] reflects the disappearance of the lamellar structure associated with the smectic-A phase. It has also been observed at the nematic–smectic-A transition on samples exhibiting a nematic phase,[19] such as compound E_1. In the hydrodynamic regime, G' measured at 1 Hz increases with

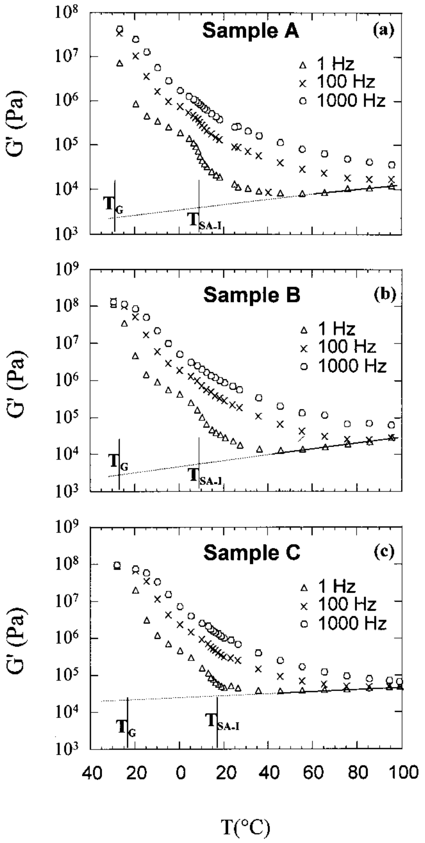

Figure 7. Temperature dependence of G' for samples A−C taken at various frequencies. The solid straight lines represent the hydrodynamic behavior. The transition temperatures were determined by DSC.

temperature, in qualitative agreement with the classical rubber elasticity theory.[29]

3.4. Influence of the Amount of Mesogen on the Complex Shear Modulus G^*, Keeping the Density and the Length of the Cross-Linkers Identical. As seen in the previous section, all the elastomers bearing 25% of mesogen exhibit, in their isotropic phase, a power law behavior ($G' = G'' \sim f^u$) characterized by an exponent $u = 0.5$. The same behavior has also been observed[19] on the same series of elastomers substituted by at least 85% mesogen. To determine the threshold of mesogen from which this behavior appears, samples F and G with very small amounts of mesogen were synthesized. Note that these samples did not present any liquid crystalline phase (see Table 1). They can be compared with samples A and E_1, since for these four compounds the density and the length of the cross-linkers are the same ($p = 5\%$, $n = 10$).

The master curves associated with samples F and G are reported in Figure 8a,b. As for samples A and E_1, the reference temperature is $T_{ref} \sim T_g + 100$ °C. Although both compounds have a very small amount of mesogen, it can be seen that G' and G'' present an overall behavior which is qualitatively similar to that observed for samples A and E_1. However, there are some quantitative differences. First, G' is different from G'' in the high-frequency range, and the power law exponent u is of the order of 0.4 whereas $G' = G''$ and $u = 0.5$ for samples A and E_1. Second, as shown in Table 2, the values of the crossover frequency f_1 and of the static rigidity modulus G_e are higher than those of samples A and E_1, which are nearly identical. These differences in behavior therefore suggest that there is an amount of mesogen above which this parameter no longer has an influence on the shear response of the elastomer. In this respect, samples D, E, and B, which are 10% cross-linked and respectively substituted by 20%, 25%, and 32% of mesogens, also show a 0.5 power-law behavior, which is consistent with the results found for the other samples in which the amount of mesogen is higher than 20%.

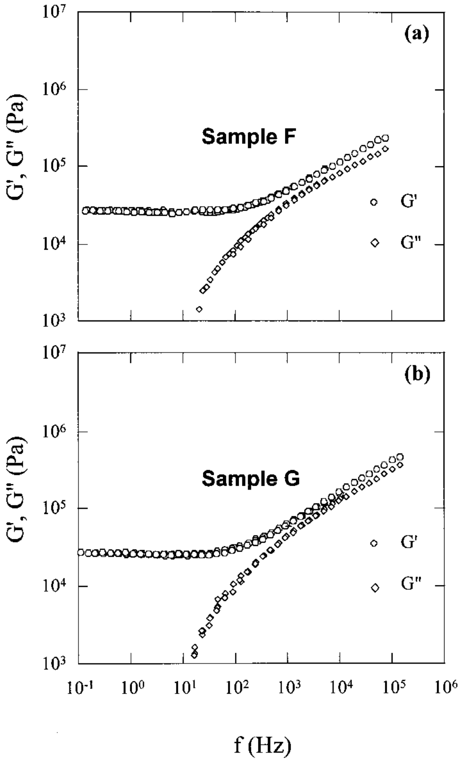

Figure 8. Master curves of G' and G'' in the isotropic phase for samples F and G. The reference temperature is $T_{ref} \sim T_g + 100$ °C.

Table 2. f_1 Frequency and G_e Modulus for Samples with Different Amounts of Mesogen[a]

sample	F	G	A	E_1
m%	3	5	25	95
f_1 (Hz)	500	300	20	30
G_e (Pa)	4×10^4	3×10^4	10^4	10^4

[a] The proportion of cross-linker (5%) and the cross-linker length ($n = 10$) are the same for the four samples. $T \sim T_G + 100$ °C.

3.5. Influence of the Cross-Linker Length on the Complex Shear Modulus G^*, Keeping the Amount of Cross-Linkers and Mesogen Identical. This study was made with samples B, H, and I. These elastomers have the same amount of mesogen ($m = 25\%$) and cross-linker ($p = 10\%$). They only differ by the length of the cross-linkers ($n = 10$, 22, and 6 methylene groups, respectively).

All the samples previously studied had cross-linker made with aliphatic chains with 10 methylene groups, i.e., shorter (∼15 Å in the most extended conformation) than the mesogen length (∼24 Å). As the cross-linking density is high, one can imagine that the motion of the mesogens is strongly hampered by the cross-linkers (cage effect). This idea can be tested with samples B and H, which are cross-linked with chains composed of 10 and 22 methylene groups, respectively. Figure 9 compares the G' behavior obtained for both samples. It shows that the increase of the cross-linker length

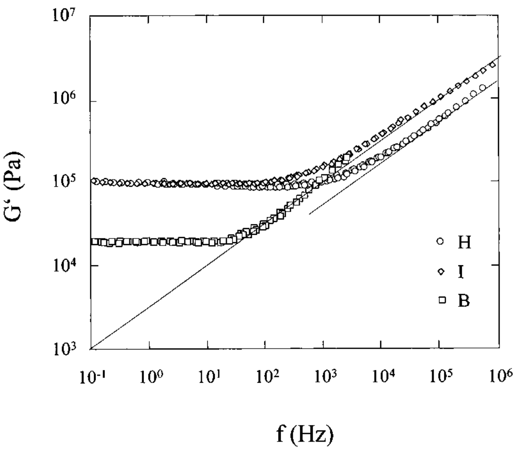

Figure 9. Influence of the cross-linker length on the master curves associated with the isotropic phases of samples H, I, and B. The cross-linking density ($p = 10\%$) and the amount of mesogen ($m = 25\%$) are the same for the three samples. The solid lines represent the $f^{0.5}$ behavior.

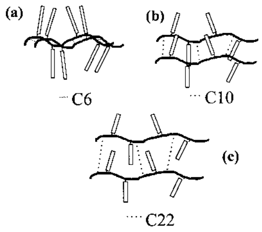

Figure 10. Schematic representation showing the influence of the cross-linker length on mesogen freedom of movement (a is associated with sample I, b with sample B, and c with sample H).

increases the values of G_e and f_1 and shifts the viscoelastic behavior toward higher frequencies. As expected, increasing the cross-linker length therefore causes more effective decoupling between the network and the mesogens. Conversely, what happens when cross-linking was a very short bridge? A priori, one could imagine that the network−mesogen interactions would be much higher than for sample B and that the viscoelastic behavior would thus take place at lower frequencies. The results obtained on sample I, which has a very short cross-linker (six methylene groups corresponding to ~7.5 Å), shows that this is not the case. Indeed, Figure 9 shows that the values of G_e and f_1 are higher than those of sample B. Thus, the use of very short cross-linker decouples the mesogens from the network. This indicates that, with very short bridges, cross-linking can only take place between close chains, thereby increasing the freedom of the mesogens, as illustrated in Figure 10. Brehmer et al.[30] have taken advantage of cross-linking with very short chains to switch the mesogens of a S_C* elastomer with an electric field of comparable strength to that used in polymers, whereas this switching was impossible with longer cross-linkers. The values of G_e and f_1 for the three samples B, H, and I are given in Table 3.

Table 3. f_1 Frequency and G_e Modulus for Samples with Different Cross-Linker Lengths[a]

sample	I	B	H
n	6	10	22
f_1 (Hz)	700	40	4000
G_e (Pa)	10^5	2×10^4	10^5

[a] The proportion of mesogen (25%) and of cross-linker (10%) are the same for the three samples. $T \sim T_G + 100$ °C.

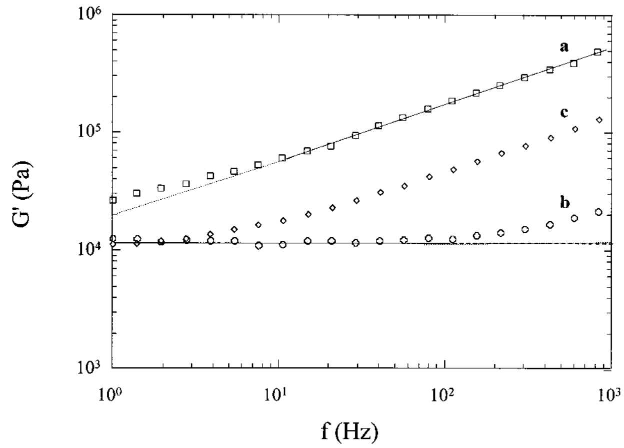

Figure 11. Behavior of G' vs frequency for sample C in the dry (a) and swollen (b) states and during deswelling (c). The solid lines represent the $f^{0.5}$ behavior (curve a) and the elastic behavior (curve b).

3.6. Influence of the Interactions between the Mesogens on the Rouse Behavior. As described in the previous sections, the samples with over 20% mesogen exhibit a Rouse behavior due to the fact that the interaction between mesogens leads to transient bulky clusters interacting with each other. If this is so, the Rouse behavior should be modified when: (i) the amount of mesogen becomes too small to develop supramolecular associations. This is what was observed for samples F and G with 3% and 5% of mesogen, respectively. There was an increase of the frequency at which their viscoelastic behavior starts and a decrease of the power law exponent; (ii) the interactions between mesogens are quenched, for example by introducing a solvent inside the elastomer. To check this point, we measured the shear modulus, in the dry and swollen states of sample C at room temperature. In the dry state, G' presented a viscoelastic response over the whole frequency range, as shown by curve a in Figure 11. Then, the sample was swollen by a mixture of ethanol 70% (poor solvent) and toluene 30% (good solvent). The proportion of poor solvent to good solvent was chosen to lead to a moderate swelling of the sample. After putting the sample into an excess of this mixture for 1 day, the shear modulus was measured. As shown in curve b of Figure 11, G' was then purely elastic from 1 to 100 Hz. The sample response was closer to that of a conventional elastomer due to the disappearance of the bulky clusters resulting from the diminution of the interactions between the mesogens. We continued the experiment by letting the sample deswell in the cell and observed that it progressively recovered its viscoelastic behavior, as shown by curve c in Figure 11. These experiments support the picture of transient macroscopic clusters formed by associations of the mesogenic side groups.

IV. Conclusion

In this article, we have studied the influence of molecular parameters on the behavior of the shear modulus of polydomain smectic-A side-chain liquid crystal elastomers. The study was conducted on a series of elastomers with different cross-linking densities, amounts of mesogen, and cross-linker lengths. The results obtained show that the $\omega^{0.5}$ scaling law characterizing the isotropic phase is independent of the molecular parameters (cross-linking density, cross-linker length, amount of mesogen), except when the amount of mesogen is very small. In contrast, the frequency at which this scaling law starts is dependent on the cross-linking density and cross-linker length but remains independent of the amount of mesogen, except when the latter is very small. We also find that the $\omega^{0.3}$ scaling law characterizing the viscoelastic properties of the smectic-A phase is independent of the cross-linking density, which confirms that the dynamics of the smectic-A phase is governed by a transient network with a very long lifetime, whose contribution to the shear modulus is greater than that of the permanent network. The purely elastic response of the elastomers is only visible in the isotropic phase and, as expected, is a function of the cross-linking density and the cross-linker length.

Acknowledgment. It is a pleasure to thank H. Brand, H. Finkelmann, and J. Weilepp for fruitful and stimulating discussions.

References and Notes

(1) Finkelmann, H.; Ringsdorf, H.; Wendorff, J. H. *Makromol. Chem.* **1978**, *179*, 273.

(2) Küpfer, J.; Nishikawa, E.; Finkelmann, H. *Polym. Adv. Technol.* **1994**, *5*, 110.

(3) de Gennes, P. G. *C. R. Seances Acad. Sci.* **1975**, *B28*, 101.

(4) Finkelmann, H.; Brand, H. *Trends Polym. Sci.* **1994**, *2*, 222.

(5) Küpfer, J.; Finkelmann, H. *Macromol. Rapid Commun.* **1991**, *12*, 717.

(6) Weilepp, J.; Brand, H. R. *Macromol. Theory Simul.* **1998**, *7*, 91.

(7) Mao, Y.; Warner, M.; Terentjev, E. M.; Ball, R. C. *J. Chem. Phys.* **1998**, *108*, 20.

(8) Schätzle, J.; Kaufhold, W.; Finkelmann, H. *Makromol. Chem.* **1989**, *190*, 3269.

(9) Mitchell, G. R.; Davis, F. J.; Ashman, A. *Polymer* **1987**, *28*, 639.

(10) Finkelmann, H.; Koch, H. J.; Rehage, G. *Makromol. Chem., Rapid Commun.* **1981**, *2*, 317.

(11) Degert, C.; Richard, H.; Mauzac, M. *Mol. Cryst. Liq. Cryst.* **1992**, *214*, 179.

(12) Guo, W.; Davis, F. J.; Mitchell, G. R. *Polymer* **1994**, *35*, 2954.

(13) Brehmer, M.; Zentel, R. *Mol. Cryst. Liq. Cryst.* **1994**, *243*, 353.

(14) Kaufhold, W.; Finkelmann, H.; Brand, H. R. *Makromol. Chem.* **1991**, *192*, 2555.

(15) Oppermann, W.; Braatz, K.; Finkelmann, H.; Gleim, W.; Kock, H. J.; Rehage, G. *Rheol. Acta* **1982**, *21*, 423.

(16) Barnes, N. R.; Davis, F. J.; Mitchell, G. R. *Mol. Cryst. Liq. Cryst.* **1989**, *168*, 13.

(17) Pakula, T.; Zentel, R. *Makromol. Chem.* **1991**, *192*, 2401.

(18) Sigel, R.; Stille, W.; Strobl, G.; Lehnert, R. *Macromolecules* **1993**, *26*, 4226.

(19) Gallani, J. L.; Hilliou, L.; Martinoty, P.; Doublet, F.; Mauzac, M. *J. Phys. II* **1996**, *6*, 443.

(20) Weilepp, J.; Zanna, J. J.; Assfalg, N.; Stein, P.; Hilliou, L.; Mauzac, M.; Finkelmann, H.; Brand, H. R.; Martinoty, P. *Macromolecules* **1999**, *32*, 4566.

(21) Weilepp, J.; Stein, P.; Assfalg, N.; Finkelmann, H.; Martinoty, P.; Brand, H. R. *Europhys. Lett.* **1999**, *47*, 508.

(22) Stein, P.; Assfalg, N.; Finkelmann, H.; Martinoty, P. *Eur. Phys. J. E* **2001**, *4*, 255.

(23) Clarke, S. M.; Tajbakhsh, A. R.; Terentjev, E. M.; Warner, M. *Phys. Rev. Lett.*. **2001**, *86*, 4044.

(24) Leroux, N.; Mauzac, M.; Noirez, L.; Hardouin, F. *Liq. Cryst.* **1994**, *16*, 421.

(25) Degert, C.; Davidson, P.; Megtert, S.; Petermann, D.; Mauzac, M. *Liq. Cryst.* **1992**, *12*, 779.

(26) Diele, S.; Oelsner, S.; Kuschel, F.; Hisgen, B.; Ringsdorf, H.; Zentel, R. *Makromol. Chem.* **1987**, *188*, 1993.

(27) Ferry, J. In *Viscoelastic Properties of Polymers*; Wiley: New York, 1980.

(28) Strobl, G. In *The Physics of Polymers*; Springer: Berlin, 1996.

(29) Flory, P. J. In *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.

(30) Brehmer, M.; Zentel, R. *Makromol. Rapid Commun.* **1995**, *16*, 659.

MA020083Z