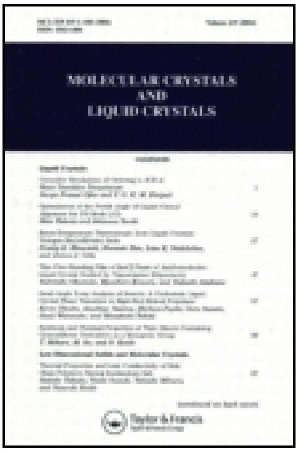

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Polymorphism and Thermoelastic Behavior of Some Crosslinked Mesogenic Polysiloxanes

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Polymorphism and Thermoelastic Behavior of Some Crosslinked Mesogenic Polysiloxanes

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A series of crosslinked liquid crystalline polysiloxanes has been realized by successively modifying the crosslinking density, the chemical nature of the linkage and the nematogenic or smectogenic character of the mesogen. All these parameters affect the polymorphism of the network, especially the ordered smectic A phases which have been proved more sensitive to crosslinking than the nematic phases. The mechanical measurements confirm the influence of the structure of the material and show that, in the smectic state, the mesogenic side groups build up ordered structures which create much more important retractive forces than in a purely nematic material.

INTRODUCTION

Liquid crystalline networks have been the subject of an important amount of work since the first synthesis was reported by Finkelmann *et al.*[1] in 1981. The crosslinked materials include comblike polyacrylates or polysiloxanes,[1-7] main chain polymers,[3] and also materials with more complex structures including mesogenic groups both in the main chain and as part of the side groups.[3,9,10]

These materials lead to new types of elastomer which combine rubber elasticity and the ordered character of liquid-crystalline phases. Their mechanical orientability[10-18] is of great interest with respect to theoretical research[19-21] and technological applications.[15,17]

The previous studies have pointed out that the behavior of the elastomers was connected with the chemical structures and composition of the material: the degree of crosslinking,[1,4,6,7] the length of the spacer in the mesogenic group,[2,5,7,12] and the length of the crosslinking agent[7] have been proved to have an effect on the mesogenic properties or on the thermoelastic behavior. To extend this study we were interested in the influence of other structural parameters. For this purpose, we selected polysiloxanes with classical mesogenic moieties in the side groups and modified systematically the following components of the system: (i) the nature of the mesogen (nematogen and/or smectogen), (ii) the nature of the crosslinking agent (mesomorphic or not and more or less flexible), (iii) the degree of crosslinking (from about 1% to 15%).

The fabrication process was also selected with intent to determine the gelation conditions and to define the physical characteristics of the materials.

We focus on the mesomorphic and mechanical properties of the elastomers as a function of the parameters indicated above.

MATERIALS

Description

In a previous study,[22] we examined a series of side-chain polymethylsiloxanes with the same mesogenic rigid core, but various substituents. Among these materials we have chosen two mesogenic groups (see Scheme I, $m = 1$ or $m = 4$) able to produce uncrosslinked polymers with different properties: the homopolymer corresponding to the methoxy free tail is a fully amorphous material which gives both the nematic and the smectic phase; the other one ($m = 4$) has a semicrystalline character and only exhibits a smectic phase.

Three crosslinking agents have been successfully inserted (Scheme I): the first one (4-4) corresponds to a bifunctional mesogenic group, the second (10) is a flexible linkage and the last one (3.3) is an intermediate non-mesogenic crosslink. a and b are respectively the average numbers of free and linked monomeric units in a macromolecule:

The degree of crosslinking, x, is defined as the mole ratio of linkage over linkage plus free mesogen: $x = (b/2)/(a+b/2)$.

The corresponding networks are labeled "$R_{4-m}^{\text{linkage},x\%}$," 4 referring to the length of the spacer in the mesogen.

Preparation and Characterization

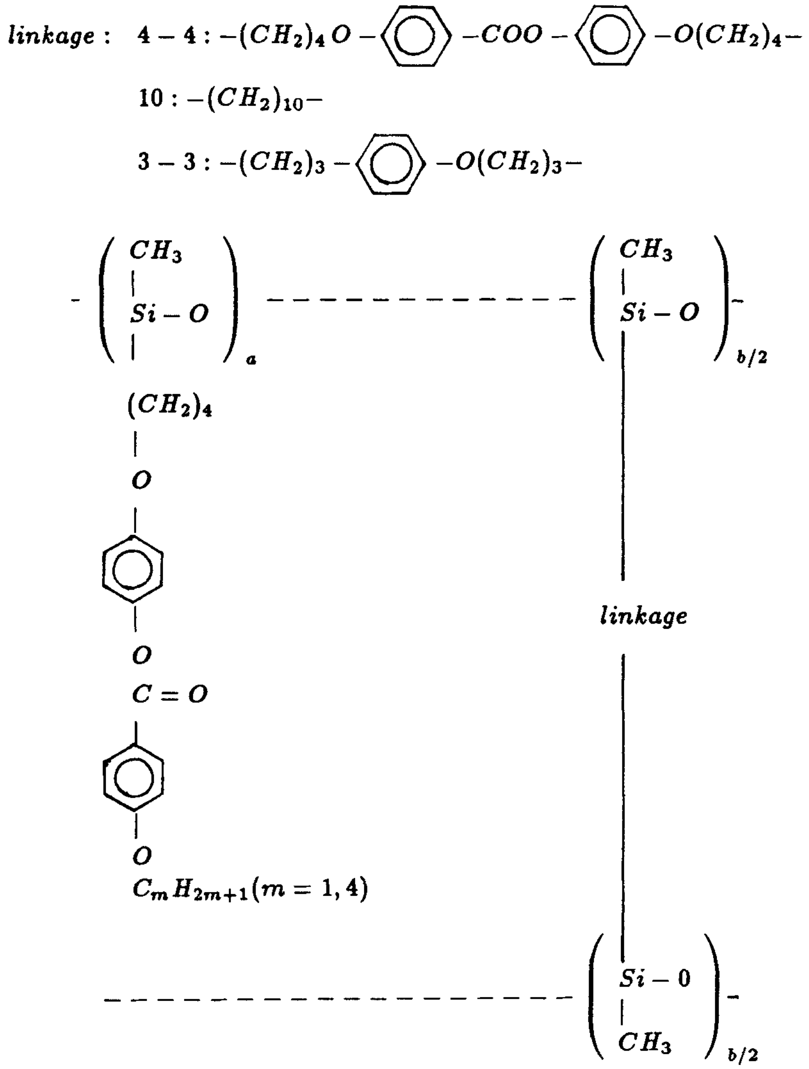
The samples were prepared by a one-step hydrosilylation reaction[1] between the hydrogenosiloxane units and the vinyl end groups of the substituents.

After drying the apparatus with a stream of nitrogen, a mixture of free mesogenic group, crosslinking reagent and poly(methylhydrogen) siloxane (3 mmoles from Petrarch, degree of polymerization of 70 units) was dissolved at 60°C in dry toluene. The vinyl groups are in excess of ten percent with regard to the siloxane units. About 0.5 mg of solid $H_2PtCl_6,6H_2O$ (from Merck) is added and the reaction is kept at 60°C for eight hours.

The concentration of the compounds has a major effect on the consistency of the final product: due to the short length of the backbone, complete gel formation needs a high concentration of the polymer in the solvent. At a low concentration, i.e. under the gel point, the formation of an infinite network is not achieved, and the samples remain soluble.

To study the influence of this parameter, networks were prepared at various concentrations in the reaction vessel (Table I).

At the end of the synthesis, the soluble materials were fully precipitated using methanol, purified by twice dissolving in tetrahydrofuran and precipitating with methanol, then dried by heating under vacuum. The gels were washed several times



SCHEME I

with toluene until the dissolution of the low molecular weight molecules was complete. Afterwards the samples were carefully deswollen by slow evaporation of the solvent during a whole week. These precautions are necessary to obtain suitable materials with regard to mechanical measurements. It has to be noted that extraction with toluene in a Soxhlet apparatus is not used because this method produces some degradation of the materials. The purity of the samples and the x values were assessed by ^{1}H NMR (270 MHz): the gels were swollen by $CDCl_3$; the other products were analyzed in solution in the same solvent. The relative accuracy on the x values is about ten percent.

TABLE I

Characteristics of a crosslinked polymer $R_{4-1}^{10,10\%}$, synthesized at various concentrations in the solvent

Polymer concentration in the reaction bath		Consistency of final product	Weight swelling ratio** in toluene	Thermal characteristics of dry network °C**	
mmoles of units/ cm^3 of toluene	Weight %*			T_g	T_c
0.24	8	Soluble	-	9	82
0.87	23.5	Gel	4.1 - 4.6	8	80
1.2	29	Gel	3.8 - 4.3	0	79
1.6	35	Gel	3.3 - 3.9	1	85
1.8	37.5$^+$	Gel	3.4 - 3.9	0	85

* the concentration expressed in weight % represents the weight of the network divided by the total weight of the reactants.

** average values obtained after four measurements.

$^+$ insolubility of reagents precluded measurements at higher weight % values.

The swelling ratio of the gels is evaluated by dividing the weight ratio of the sample (swollen to saturation) by the weight of the dry network. Four determinations were made for each material.

The glass transition (T_g), the melting temperature (T_m) and the clearing temperature (T_c: isotropic phase to mesophase) were determined by differential scanning calorimetry.

The characterization of the mesophases was achieved for the more fluid materials through microscopic observations (Leitz-Dravert polarizing microscope).

The comparison between networks synthesized at different concentrations in the reaction vessel (Table I) leads to the two following observations:

(i) High concentrations in the reaction vessel are absolutely necessary to obtain gel samples. The calculated swelling ratios, despite the lack of accuracy, achieve a constant value when the weight percentage of the network during reaction reaches about 35%. For a defined gel system of solvent and network, the swelling ratio is only related to the average molecular weight of the polymer section between the two junction points.[23,24] In the networks studied, the above mentioned concentration seems to be a reasonable evaluation of the gel point.

(ii) The mesomorphic phase transition seems to be unconnected with the gelation phenomenon. The observed variations in T_c exhibit a random character and might be due for example to some changes in the crosslinking density. This result means that the liquid crystalline organization occurs on a scale below that of the gelation phenomenon.

Therefore, for any study linked to the mechanical properties of the rubber, the concentration in the reaction vessel must be carefully selected to be above the gel point. On the contrary, characterization of the mesophases can be achieved for fluid materials obtained in dilute solution.

PHASE BEHAVIOR

The polymorphism of the networks depends on the crosslinking density as well as the nature of both the mesogenic group and the linkage.

Influence of the Level of Crosslinking

For this study we have selected the "$R_{4-4}^{4-4,x\%}$" network in which the degree of crosslinking, x, is increased up to 15% (Table II). In these materials the crosslinking agent is identical to the free mesogenic group, so that the number of mesomorphic moieties is the same for all the samples.

The uncrosslinked polymer ($x = 0\%$) is semi-crystalline. Samples of low crosslink densities preserve this character. However the degree of crystallinity decreases as x increases, inducing a drop in T_g value. On the contrary, samples with higher concentrations of crosslinking chains are completely amorphous and present an usual increase in the temperature of the glass transition with x.

On the other hand, the effect of the crosslinking is to lower the clearing temperatures though, as previously observed,[4,6,7] high degrees of crosslinking may be introduced without disrupting the liquid crystal phase. These levels of crosslinking (up to 15% molar concentration in the present example) are very large compared with those of conventional elastomers.

The smectic A phase displayed by the uncrosslinked polymer is strongly influenced by the crosslinking agent, and only remains in samples of low crosslink density. Its layer spacing, determined by X-ray diffraction on powder samples, is not modified (27 Å). With 5% of crosslinking reagent, the sample exhibits both a smectic A phase and a nematic phase at higher temperature. For the most heavily crosslinked samples, only a nematic phase is observed.

Influence of Both the Mesogenic Group and the Crosslinking Reagent

The influence of the nature of the crosslinking reagent has been observed on the two above mentioned polymers with m equal to one or four (Table III). The two nonmesogenic crosslinking chains exhibit the same effect on both the amorphous character and the mesogenic behavior. The polymorphism of the uncrosslinked polymer is preserved with only a shift of the transition temperatures towards lower

TABLE II

Phase transitions as a function of the crosslink density x (molar %) in the $R_{4-4}^{4-4,x\%}$ network

				Phase transition temperature (°C)		
x%	T_g (°C)	T_m (°)	$\Delta^* Hm (Jg^{-1})$	S_A	N	I
0	19	79	19	. 149		.
2	13	72	13	. 144		.
5	12	47	9	. 95	. 128	.
10	14	51	6		. 127	.
15	17	-	-		. 116	.

* melting enthalpies determined by differential scanning calorimetry.

TABLE III

Phase transitions as a function of the nature of both the crosslinking agent and the mesogenic group

Sample	T_g (°C)	T_m (°C)	ΔHm (Jg^{-1})	Phase transition temperature (°C)			d** (Å)
				S_A	N	I	30°C
* $R_{4-4}^{-,0\%}$	19	79	19	. 149		.	27
$R_{4-4}^{4-4,10\%}$	14	51	6		. 127	.	
$R_{4-4}^{10,10\%}$	13	62	6	. 137		.	28
$R_{4-4}^{3-3,10\%}$	13	59	6	. 137		.	28
* $R_{4-1}^{-,0\%}$	7	-		. 74	. 104	.	33
$R_{4-1}^{4-4,10\%}$	13	-			. 100	.	
$R_{4-1}^{10,10\%}$	9	-		. 50	. 79	.	35
$R_{4-1}^{3-3,10\%}$	11	-		. 43	. 74	.	34

* Samples corresponding to uncrosslinked polymers.

** d : layer spacing of the smectic phase.

values and the layer spacing of the smectic A phase remains the same. It has to be noted that the number of mesogenic groups is 10% lower in the network than in the uncrosslinked polymer, so the drop in temperature cannot be quantitatively connected with crosslinking.

The mesogenic crosslinking group, used at the same x ratio, causes more drastic changes. The glass transition increases, reflecting the increasingly restricted motion available to the polymer chain. The ordered smectic A phase vanishes and only a nematic phase can be observed.

In conclusion of this study relating to the polymorphism we note: (i) that a large amount of crosslink can be inserted without destroying the mesomorphic behavior, (ii) that the smectic phases are more sensitive than the nematic phases, (iii) that this last point is more marked with a mesogenic crosslinking reagent.

MECHANICAL PROPERTIES

For this study we have selected four elastomers combining the two free liquid crystalline groups with either the mesogenic crosslink or the aliphatic one.

Experimental Conditions

All the samples were synthesized so as to be above the gel point. Their characteristics are given in Table IV.

TABLE IV

Characteristics and applied stress concerning the different elastomers

Sample	Weight swelling ratio in toluene	Thermal characteristics °C					Applied Stress (Nm^{-2})
		T_g	T_m	$S_A^{(1)}$	N	I	
$R_{4-4}^{4-4,10\%}$	4.5 - 4.8	17	-		. 133	.	6.08 10^4
$R_{4-4}^{10,10\%}$	10 - 12	14	60	. 137		.	2.2 10^4
$R_{4-1}^{4-4,10\%}$	2.8 - 3	14	-		. 102	.	1.05 10^4
$R_{4-1}^{10,10\%}$	3.4 - 3.9	0	-	. 50	. 85	.	5.6 10^3

(1) $N \rightarrow S_A$ transition temperatures can only be determined on non gel samples. The values have been compared to the gels for guidance.

We note that the swelling ability unexpectedly depends on both the free mesogenic group and the crosslinking agent. In particular it seems to be favored by the aliphatic linkage; this may reflect a lower effective crosslink density due, for example, to intramolecular crosslinkages. However the usual interpretation[23] of the swelling ratio as a function of the crosslinking density values is complicated by the ordering nature of the mesogenic substituents that modifies the interactions with the solvent.

The elastic properties were measured using a Dynamic Mechanical Analyzer (Perkin-Elmer DMA 7). The samples under compression between two parallel plates, were analyzed as a function of temperature. Frequency (1 Hz) and stress were held constant over the full course of the experiment. For each sample, stress was selected with intent to induce strains of the same order of magnitude for all the samples (from 0.1% to 6%) over the selected temperature range (from T_g − 30 to T_c + 30). Changes in modulus (G) and in tan δ (δ: phase lag between stress and strain) are recorded in Figures 1 and 2.

Influence of Polymorphism

As previously observed, in the isotropic and glassy states, the behavior is similar to conventional elastomers but strongly differs in the liquid-crystalline state.[5,12,17] The orientation of the mesogenic side chains in relation to mechanical deformations induces retractive forces in the mesophases of the elastomers.[10,12,13]

The evolution of the modulus over the mesomorphic temperature range strongly depends on the nature of the sample: it draws a plateau in samples with an aliphatic linkage (Figure 1a), whereas it regularly decreases in samples having a mesogenic linkage (Figure 1b). The polymers crosslinked with the aliphatic linkage exhibit a smectic A phase, whereas the others are only nematic. As the smectic phase is of higher order, a weaker modification of G in the liquid crystalline state, as well as

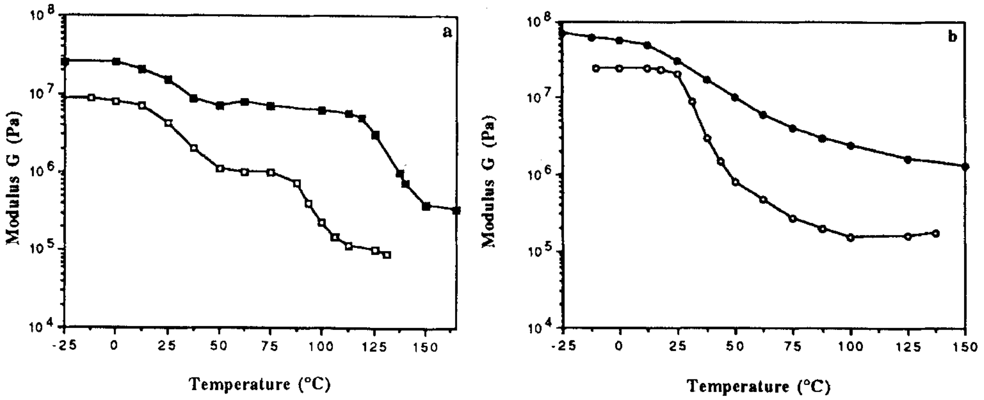


FIGURE 1 Changes in modulus over a temperature range for elastomers with a flexible linkage (Figure 1a: ■: $R_{4-4}^{10,10\%}$, □: $R_{4-1}^{10,10\%}$) or a mesogenic linkage (Figure 1b: ●: $R_{4-4}^{4-4,10\%}$, ○: $R_{4-1}^{4-4,10\%}$).

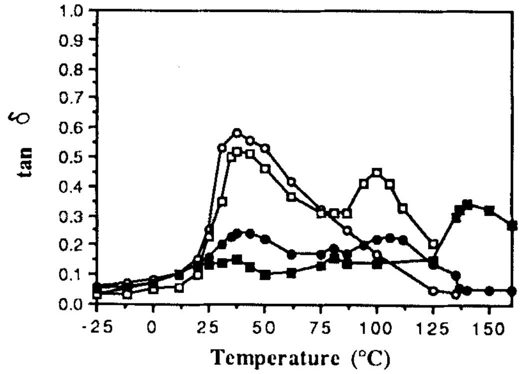


FIGURE 2 Changes in tan δ over a temperature range for different elastomers (■: $R_{4-4}^{10,10\%}$, □: $R_{4-1}^{10,10\%}$) ●: $R_{4-4}^{4-4,10\%}$, ○: $R_{4-1}^{4-4,10\%}$).

a greater step at the clearing temperature, can be expected for samples crosslinked with the 10 chain. Reported measurements, on the smectic $R_{4-4}^{10,10\%}$ compared with the nematic $R_{4-4}^{4-4,10\%}$, confirm this assumption. In the case of the $R_{4-1}^{10,10\%}$ elastomer which presents the two mesophases, the same evolution as that for $R_{4-4}^{10,10\%}$ is observed over the whole liquid-crystalline temperature range showing that the thermoelastic behavior is determined by the smectic phase.

Above the clearing temperature, in the rubber state, the modulus values also depend on the type of elastomer and does not seem connected with the swelling ratio.

All the results presented are in favor of a strong influence of the ordering of the mesogenic groups and of the mesophase structure on the elastic properties of the elastomer.

Tan δ on the other hand always has low values (Figure 2), and this confirms the highly elastic behavior of these materials.

In conclusion, the results and discussions outlined above clearly indicate that the composition of the network and the chemical structure of both the linkage and the mesogenic core strongly affect the polymorphism and the mechanical properties of the materials. The ordered character of the mesogenic parts is of great importance in the viscoelastic behavior, and the theoretical approaches used for conventional ideal rubber are unsuitable to analyze the mechanical properties of these liquid crystalline elastomers.

Complementary experiments are in progress to control the homogeneity of the materials, especially the crosslinking density, and to specify the modifications to the molecular organization under mechanical stress.

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