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New Ferroelectric Liquid Crystal Polysiloxanes

Introduction. Ferroelectric liquid crystals (FLC's) and polymeric liquid crystals are at the moment the fastest developing subjects in the domain of the technical applications of mesomorphic states.

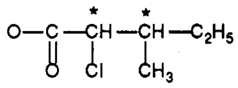
For instance the new FLC technology definitively extends the use of liquid crystals by virtue of speed and bistability.[1-3] Moreover new applications of LC systems that combine the mechanical properties of polymeric materials and structural features of liquid crystals are in progress.

Therefore it was natural to attempt to synthesize ferroelectric liquid crystal polymers and to explore their application potentialities. These polymers are comblike polymers with a flexible main chain bearing chiral mesogenic side chains.[4-10]

Our paper reports on the synthesis and characterization of new ferroelectric liquid crystalline polysiloxanes whose originality comes from combining the following features: methylhydrogeno–dimethyl siloxane copolymers as the main chain; polar mesogenic side chains with two asymmetric carbon atoms.

So far, the chiral side chains which gave S_{C^*} phases were built with one asymmetric carbon atom bearing a methyl group.

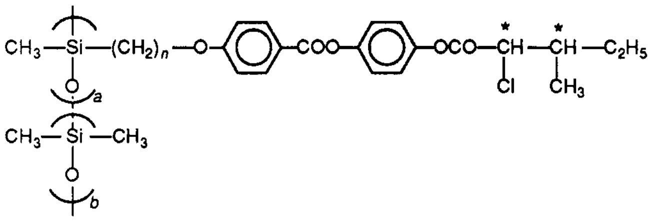
However, Scherowsky et al. have recently reported on a three-ring side-chain polysiloxane with the chiral end group



$$\mathrm{O-\underset{\displaystyle \overset{\|}{O}}{C}-\overset{*}{\underset{\displaystyle Cl}{CH}}-\overset{*}{\underset{\displaystyle CH_3}{CH}}-C_2H_5}$$

but without any S_{C^*} mesophase.[9] This kind of chiral moieties has been chosen in order to provide high spontaneous polarization values and short switching times.

Besides, our kind of polymeric chains allows a partial fixation of mesogenic groups depending on their methylhydrogeno unit percentage. This *dilution* of the mesogenic groups on the main chain lowers the transition temperatures and the viscosities of our compounds

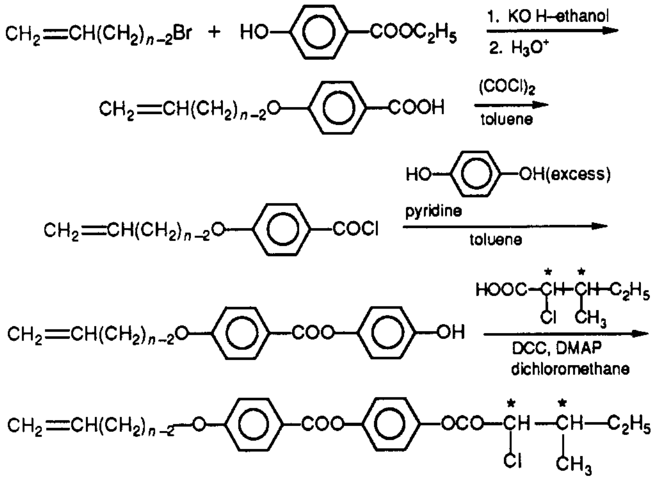


where $n = 8$ or 11 and $x = 9\%, 17\%, 30\%$, or 100%.

$$x = \frac{a}{a+b} \times 100 \qquad a + b = 30$$

Experimental Section. Synthesis. Vinyl mesogens with chiral end groups were synthesized via Scheme I. The complete synthesis of I is described elsewhere.[13] (2*S*,3*S*)-2-Chloro-3-methylpentanoic acid was prepared from the corresponding L-isoleucine by a Sandmeyer reaction (L-isoleucine is a commercially available amino acid with an optical purity higher than 98%). This reaction is performed with retention of configuration.[14,15] On the other hand, the NMR spectra of the ferroelectric liquid crystals obtained with the corresponding L-isoleucine showed a maximum of 3% racemization.[16] I were then linked to methylhydrogeno–dimethyl siloxane statistical copolymers by standard methods.[12] The initial copolymers are commercial oligomers from Petrarch Systems Inc. ($\bar{M}_n = 2200$) or were synthesized by Dr. Coqueret[11] and fractionated by gel permeation chromatography.

Scheme I



I

Phase Identification. Phase identifications were performed by classical methods: polarizing microscope, DSC, and X-ray measurements.

Electrooptical Measurements. The samples were sandwiched between two ITO-coated glass (Balzers 30 $\Omega/\square$) whose surfaces were spin-coated with polyvinyl alcohol and then rubbed by a velvet. The sample thickness was estimated to be between 5 and 10 μm according to the Newton color method. The planar alignment was achieved by shearing at the S_{C^*}–isotropic phase transition under a ± 50 V voltage at a few hertz. The temperature dependence of the spontaneous polarization (P_s) and the switching time (τ) was measured from the induced polarization current obtained by applying a rectangular wave voltage. The spontaneous polarization corresponds to the integration of the current bump versus time, its maximum to the response time (τ). In our experimental set up, the current is accumulated and recorded versus time with a Kontron SMRII digital oscilloscope. An example of the diagram is given in Figure 1.

Results and Discussion. Polymorphism. Some of these polymers exhibit uncharacteristic textures under microscope; on the contrary other ones give typical S_{C^*} textures. Anyway, miscibility studies, polarization measurements, and X-ray patterns assess the existence of a S_{C^*} phase in all the samples except for the lowest substituted homologue (9%) which is devoid of any mesomorphic properties. The S_{C^*} ferroelectric phase temperature ranges are very broad and include room temperature (Table I).

The glass transition temperatures are 0 °C for the 100%, −23 °C for the 30%, and much lower for the 17%. However, on DSC thermograms, an additional peak was observed below room temperature, at 3 °C, for 30%. This behavior can be assigned to a semicrystalline character as the thermal annealing of the sample significantly increases the enthalpy of this peak (annealing allows the crystalline areas to grow).

The isotropic–S_{C^*} transition temperatures are considerably lowered going from 100%, 30%, and 17% and the corresponding apparent viscosity decreases: at room temperature, the 17% is a fluid, cream-like material while the 100% is almost a solid. Apparent viscosity measure-

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Table I
Phase Transition Temperatures of the Different Polymers (°C)

polymer	spacer *n*	fixation rate *x*	T_g	T_m	S_C*		S_A		*I*
1a	8	9%					nonmesomorphic		
1b	8	17%	*a*	-5	•	30			•
1c	8	30%	-23	3	•	63			•
1d	8	100%	0		•	95			•
2c	11	30%	-26	18	•	75		85	•

[a] Not yet determined.

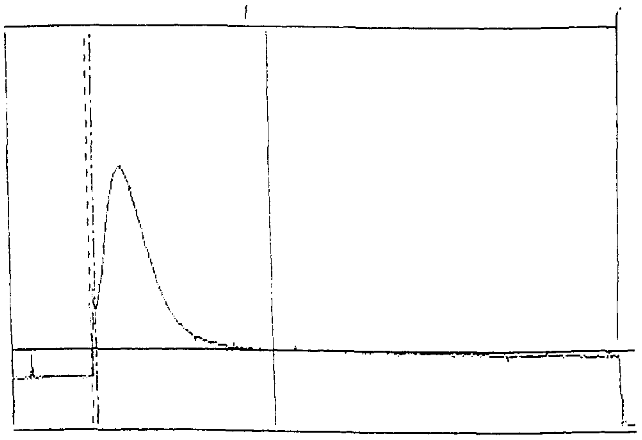


Figure 1. Measured current versus time: sample **1c**, 40 °C, 30 V, cell thickness 5 μm.

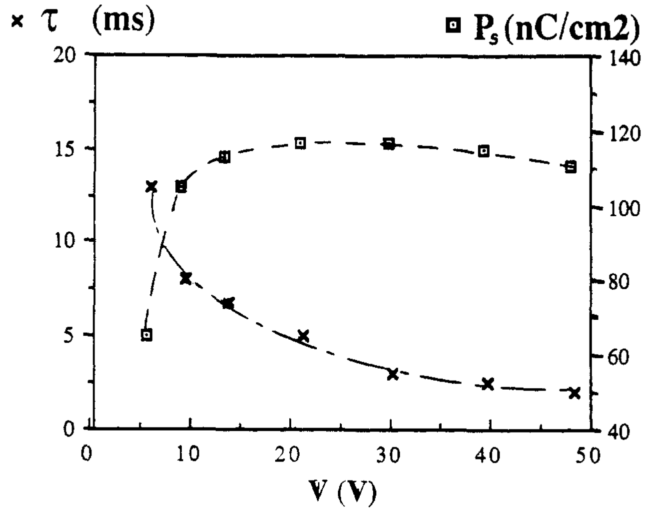


Figure 2. Spontaneous polarization (□) and response time (×) versus voltage (5 Hz): sample **1c**, 50 °C, cell thickness 5 μm.

ments on similar diluted polymers show a strong decrease by 2 orders of magnitude.[17]

Spontaneous Polarization and Switching Time. The polarizations and switching times were measured as a function of temperature and voltage.

At a given temperature, the polarization shows an asymptote with increasing voltage corresponding to the saturation of the polarization (P_s) (Figure 2).

The minimum voltages allowing this saturation are very low (2–6 V/μm according to temperature) in comparison with those given by Suzuki et al.[7] and Uchida et al.[6] at comparable temperature.

Figure 3 represents the polarization (P_s) and the response time (τ) as a function of temperature for one sample.

P_s reaches a maximum with decreasing temperature. At room temperature, its value is fairly large and comparable with that of analogous low molecular weight ferroelectric liquid crystals (around 100 nC/cm^2).

Let us point out that the switching times are the fastest ever found for ferroelectric liquid crystal polymers under so low voltages: 300 μs under 2 V/μm at 73 °C for compound **2c**.

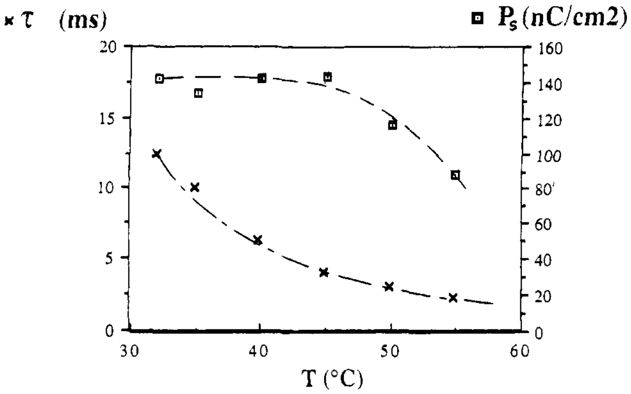
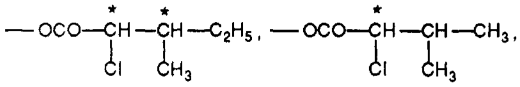


Figure 3. Spontaneous polarization (□) and response time (×) versus temperature: sample **1c**, 30 V, cell thickness 5 μm.

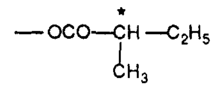
At room temperature, those times are still fast: around 15 ms for compound **1c** under 6 V/μm. This behavior is probably due to the low viscosity of the 30% polymers in connection with their fairly large polarization according to the well-known relation $\tau = \gamma_\phi / P_s E$ where γ_ϕ is the rotational viscosity and E the applied electric field.

Conclusion. The combination of new polar chiral mesogenic side chains with copolymeric main chains leads us to build up a new series of smectic C* ferroelectric polymers with large spontaneous polarizations and fast switching times.

This series is being completed with all the homologous for different spacers (n = 5, 6, 8, 10, 11), different fixation rates (9, 17, 30, 100%), and different chiral end groups:



$$-OCO-\underset{Cl}{\overset{*}{C}H}-\underset{CH_3}{\overset{*}{C}H}-C_2H_5,\quad -OCO-\underset{Cl}{\overset{*}{C}H}-\underset{CH_3}{CH}-CH_3,$$



$$-OCO-\underset{CH_3}{\overset{*}{C}H}-C_2H_5$$

The systematic investigation of their physical properties (including tilt angles) is in progress and will be published and discussed elsewhere.

Several other attempts using three ring mesogenic chains with two chiral carbons will also be investigated as well as other types of polymeric chains such as polyacrylates.

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Relaxation Time Distributions of Entangled Polymer Solutions from Dynamic Light Scattering and Dynamic Mechanical Measurements

Recent Laplace inversion analyses of dynamic light-scattering (DLS) data on semidilute solutions of high molecular weight polystyrene (PS) at the Θ temperature established the existence of a distribution of slower relaxation times, which was independent of the wave vector ($\mathbf{q}$) of the incident light, in addition to the fast $\mathbf{q}^2$-dependent relaxation time which describes the cooperative diffusion of the polymer chains.[1-4] Although the contribution of the slower relaxational modes to the correlation function persists at temperatures well above the Θ temperature and is even detectable in thermodynamically good solvents, their relative amplitude is only considerable (dominant) at temperatures in the vicinity of Θ.

A theory of Brochard and de Gennes[5,6] with a modification in ref 7, is partially successful in explaining the experimental observations. Accordingly, the response of the system to spontaneous concentration fluctuations starts by diffusion of solvent molecules until an equilibrium is reached between the osmotic force and the elastic force arising from the transient network formed by topological entanglements of the polymer chains. As the entanglements are not fixed as in a permanent network, the system can continue to relax in a second stage through disentanglement of the chains.

As we have recently shown,[1] this theory successfully describes the variation of the cooperative diffusion coefficient with polymer concentration. However, contrary to the experimental findings,[1-4] the theory predicts the existence of only one $\mathbf{q}$-independent slow relaxation mode. The latter follows from the assumption that the disentanglement of the chains forming the transient network is a unique process characterized by a single relaxation time. Mechanical measurements[8] show that this is an oversimplification for most polymer systems. A comparison of the values for the slowest relaxation time from DLS measurements and dynamical shear moduli determinations on the same systems strongly suggests that these two techniques are probing closely related processes. It is therefore ventured that the distribution of relaxation times deduced from analyses of DLS data is the result of a more complex disentanglement process and moreover that this should also be reflected in similarly treated dynamic mechanical data. There have been reported very few oscillatory shear measurements on semidilute solutions. To examine the plausibility of this explanation, DLS measurements and oscillatory shear viscosity measurements have been performed on the same solutions of high molecular weight PS in the solvent dioctyl phthalate (DOP) at the Θ temperature (22 °C).[9] This solvent is convenient for rheological measurements with an open-cell geometry because of its very low vapor pressure. The Θ system is suited to present purposes since in good solvents the cooperative diffusion almost completely dominates the correlation function. The present communication is a preliminary report sketching the main findings. A paper dealing with the influence of concentration, molecular weight, and the influence of temperature on the light-scattering and dynamic mechanical distributions will follow and will include a more detailed description of the analysis methods, as well as a comparison with alternative distribution models, such as the Williams–Watts function.

The elastic storage and loss shear moduli, G' and G'', were measured on a Rheometrics RFS 8500 instrument, employing a cone and plate geometry (diameter 50 mm, 0.02 angle rad). The frequency range was 0.01–100 rad/s, and 10 points were taken per decade. The strain amplitude was between 0.05 and 0.50, and it was ensured that all measurements were made in the linear viscoelastic region. The stress relaxation shear modulus, $G(t)$, was calculated from G' and G'' by use of the approximative expression of Ninomiya and Ferry (see eq 4.48 of ref 11)

$$G(t) = G'(\omega) - 0.40G''(0.4\omega) + 0.01G''(10\omega) \qquad (1)$$

which uses G' at the frequency $1/t$ and G'' at two other frequencies. (It is not possible to accurately evaluate $G(t)$ directly by Fourier inversion since this would necessitate knowledge of G' and G'' over a much wider range of frequencies than could be measured. It is not possible to extend the frequency range in the present case by employing time–temperature superposition since it would involve changes in the thermodynamic properties of the system.)

For the DLS measurements the autocorrelator was a multi-τ model from ALV, Langen, FRG, employing 23 simultaneous sampling times and thus allowing monitoring of widely spaced decays in the same experiment. Approximately 8 decades in relaxation time could be covered. The measurements were made in the homodyne mode using a wavelength of 633 nm.

A Laplace inversion routine called REPES[10] has been used to analyze both the measured DLS correlation function, $g^2(t)$, and the square of the time-dependent shear modulus, $G(t)$. The algorithm differs from the often-used program CONTIN[12] in that it directly minimizes the sum of squared differences between the measured and calculated $g^2(t)$ function using nonlinear programming and an a priori chosen parameter P, "probability to reject" (we use $P = 0.5$). The decay time distributions were found to be closely similar to those obtained using the comparable Laplace inversion routines MAXENT[13] and CONTIN.

The basis for the proposed comparison is not immediately obvious since $g(t)$ is related to the longitudinal elastic modulus (M) and not the shear modulus.[14] The observed close similarity shown below between the dynamic

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