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Ferroelectric liquid crystal siloxane homo and copolymers

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Several new chiral liquid crystal siloxane homopolymers and copolymers have been synthesized and studied as to their mesomorphic and ferroelectric behaviour. Almost all of them exhibit chiral smectic C phases over wide temperature ranges. DSC and X-ray measurements are presented; spontaneous polarizations, response times and tilt angles are also given. Some of the spontaneous polarizations are very high, more than 100 nC/cm^2 , and the response times are found to be among the fastest for liquid-crystalline polymers, less than 1 ms.

1. Introduction

Low molecular weight liquid crystals exhibiting S_C^* phases have now been widely studied because of their ferroelectric properties [1, 2] and their very fast response times towards an applied electric field [3]. This makes them particularly suitable, for example, for electro-optic applications [3, 4]. Liquid crystal polymers exhibiting S_C^* phases have been studied quite recently [5-27] and few of them have shown ferroelectric properties. In this case, a ferroelectric liquid crystal polymer can be obtained which can combine the properties of polymers (a glassy state in which the ferroelectric structure may be frozen, the capacity of making films, specific mechanical properties, etc.) with the properties of ferroelectric liquid crystals in the S_C^* phase. So, the study of such polymers seems promising. However, the nature of polymeric materials is likely to increase the transition temperatures and the response times. These features are unfavourable for materials exhibiting interesting ferroelectric properties at room temperature, which is often needed for applications.

One of the aims of our work was to prepare ferroelectric liquid crystal side chain polymers with broad S_C^* temperature ranges including room temperature and with fast switching times. We have achieved these requirements by combining two main features.

- (i) Partial fixation of mesogenic groups on polymer backbones using methylhydrogeno-dimethyl siloxane copolymers. This dilution of the mesogenic groups on the polymer backbone lowers the transition temperatures and the viscosities of the polymers [28].
- (ii) Polar mesogenic side chains with one or two asymmetric carbon atoms. This kind of chiral moiety provides high spontaneous polarization values and short switching times [29-32].

The general formula of the polysiloxanes (II) synthesized is given in figure 1.

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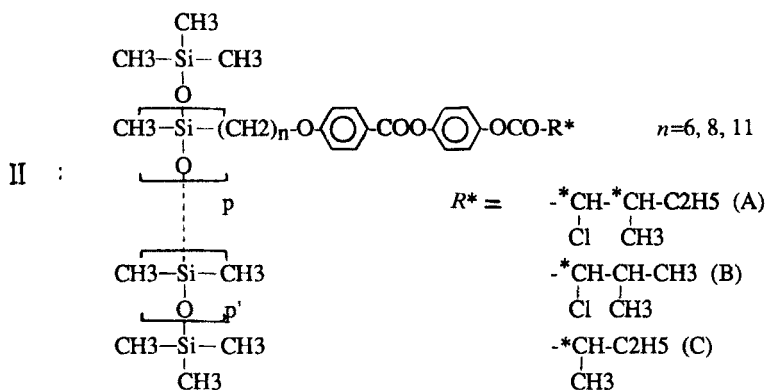


Figure 1. General formula of the synthesized polysiloxanes (II). The substitution rate x , i.e. the percentage of mesogenic groups on the siloxane chain is defined as:

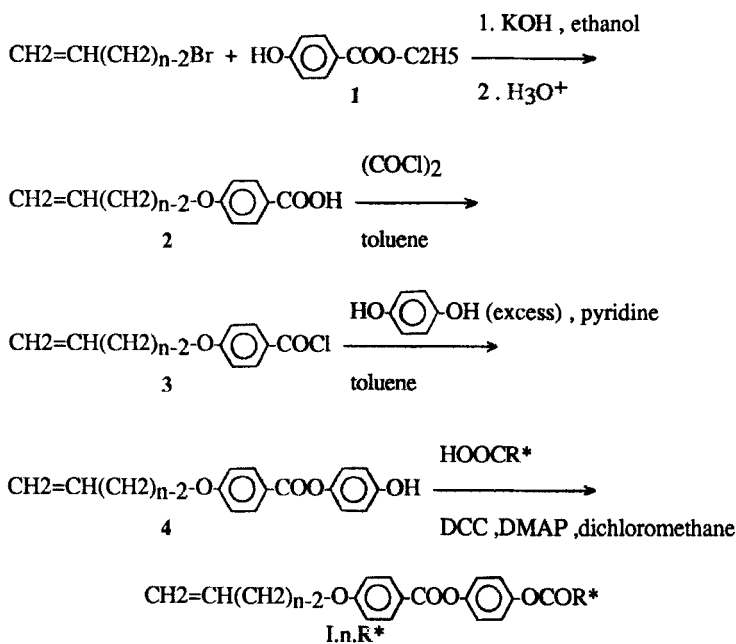
$$x = \frac{p}{p + p'}$$

$x=9$ per cent, 17 per cent, 30 per cent, 100 per cent. General labelling of polymers: II. n . x %. R^* . Example of labelling: II.11.30%.A.

2. Experimental

2.1. Synthesis of the mesogenic side chains (I)

Vinyl low molecular weight mesogenic moieties (I) were prepared following the general scheme



Synthesis scheme for the vinyl mesogenic groups (I).

An example of the synthetic method is given for I.11.A.

2.1.1. Synthesis of 4-(10-undecenyl-oxy) benzoic acid: (2)

25.6 g (0.11 mol) of 11-bromo-1-undecene (obtained from 10-undecen-1-ol following the details in [33]) were added dropwise to a solution of 16.6 g (0.1 mol) of commercial ethyl 4-hydroxybenzoate (**1**) and 6.16 g (0.11 mol) of potassium hydroxide in 300 ml of ethanol. The mixture was refluxed for 4 h. Then, 6.16 g (0.11 mol) of potassium hydroxide were added and the mixture was refluxed for 1.5 h. After cooling, the ethanol was completely removed and the residue was hydrolyzed with 8 g (0.22 mol) of concentrated hydrochloric acid in crushed ice. The resulting precipitate was filtered off and recrystallized from ethanol and dried under vacuum to obtain 11.6 g (0.04 mol) of **2**. Yield: 40 per cent.

Thermal transitions: C 107.5°C S_C 123°C N 137°C I.

¹H NMR (270 MHz, CDCl₃): δ_{TMS} = 1.2–1.6 ppm (m, 12 H, CH₂(CH₂)₆CH₂CH₂-O); 1.85 ppm (m, 2 H, CH₂CH₂-O); 2.1 ppm (m, 2 H, CH₂=CHCH₂); 4.05 ppm (t, 2 H, CH₂-O); 5.00 ppm (m, 2 H, vinyl H); 5.85 ppm (m, 1 H, vinyl H); 6.97 ppm (d, 2 H, Ar-H); 8.15 ppm (d, 2 H, Ar-H).

IR (nujol): 3000–2500 cm⁻¹, 1670 cm⁻¹, 920 cm⁻¹.

2.1.2. Synthesis of 4-hydroxyphenyl 4-(10-undecenyl-oxy) benzoate: (4)

7.83 g (0.027 mol) of **2** were dissolved in 25 ml of toluene with two drops of *N,N*-dimethylformamide (DMF). 8 ml (0.04 mol) of oxalyl chloride were added and the resulting solution was stirred at room temperature for 1 h. Then, the mixture was refluxed for 2.5 h. The toluene and the remaining oxalyl chloride were evaporated until complete removal to provide the acid chloride (**3**). A solution of 15.85 g (0.14 mol) of hydroquinone and 40 ml pyridine in 300 ml of toluene was made. **3** (0.027 mol) was added dropwise to the previous solution which was then heated at 70°C for one hour and left at room temperature overnight. The solvent was evaporated; the creamy residue was hydrolyzed and washed several times with water to remove the excess of hydroquinone, then acidified with hydrochloric acid, washed again and filtered. The precipitate was recrystallized from ethanol and dried to obtain 5.35 g (0.014 mol) of **4**. Yield: 35 per cent; m.p. = 96.2–98.2°C.

¹H NMR (270 MHz, CDCl₃): δ_{TMS} = 1.2–1.6 ppm (m, 12 H, CH₂(CH₂)₆CH₂CH₂-O); 1.85 ppm (m, 2 H, CH₂CH₂-O); 2.1 ppm (m, 2 H, CH₂=CHCH₂); 4.05 ppm (t, 2 H, CH₂-O); 5.00 ppm (m, 2 H, vinyl H); 5.85 ppm (m, 1 H, vinyl H); 6.80 ppm (d, 2 H, Ar-H); 7.02 ppm (2d, 4 H, Ar-H); 8.17 ppm (d, 2 H, Ar-H).

IR (Nujol): 3350 cm⁻¹, 1720 cm⁻¹, 920 cm⁻¹.

2.1.3. Synthesis of 4-((2*S*,3*S*)-2-chloro-3-methylpentanoyloxy)phenyl 4-(10-undecenyl-oxy)benzoate (I.11.A)

3.55 g (0.0093 mol) of **4** and 1.4 g (0.0093 mol) of (2*S*,3*S*)-2-chloro-3-methylpentanoic acid were stirred, at room temperature, for 24 h in 20 ml of dichloromethane with 1.6 g *N,N'*-dicyclohexylcarbodiimide (DCC) and 0.05 g of 4-dimethylaminopyridine (DMAP). The solution was filtered and the dichloromethane was evaporated. The final product was purified by chromatography of silica gel with toluene as eluent, recrystallized from ethanol and dried under vacuum at room temperature to obtain 1.43 g (0.0028 mol) of I.11.A. Yield: 30 per cent.

Thermal transitions: C 58°C (S_C 22.6°C) (S_A 46.9°C) I. (): monotropic transition.

¹H NMR (270 MHz, CDCl₃): δ_{TMS} = 1.00 ppm (t, 3 H, CH₂-CH₃); 1.15 ppm (d, 3 H, CH*-CH₃); 1.3–1.6 ppm (m, 14 H, CH₂(CH₂)₆CH₂CH₂-O + CH₂-CH₃); 1.85 ppm

(m, 2H, $\text{CH}_2\text{CH}_2\text{-O}$); 2.1 ppm (m, 2 H, $\text{CH}_2 = \text{CHCH}_2$); 2.25 ppm (m, 1 H, CH^*-CH_3); 4.05 ppm (t, 2 H, CH_2-O); 4.40 ppm (d, 1 H, CH^*-Cl); 5 ppm (m, 2H, vinyl H); 5.85 ppm (m, 1 H, vinyl H); 7.00 ppm (d, 2 H, Ar-H); 7.25 ppm (2d, 4H, Ar-H); 8.17 ppm (d, 2 H, Ar-H).

2.1.4. Chiral acids (HOOCR^*)

(a) The chiral acids (2*S*,3*S*)-2-chloro-3-methyl pentanoic acid (A) and 2-(*S*)-chloro-3-methylbutanoic acid (B) were prepared from *L*-isoleucine and *L*-valine, respectively, by a Sandmeyer reaction. *L*-isoleucine and *L*-valine are commercially available amino acids with optical purities higher than 98 per cent and the Sandmeyer reaction is performed with retention of configuration [34, 35]. Besides, $^1\text{H NMR}$ spectra of the ferroelectric liquid crystals, obtained with *L*-isoleucine, showed a maximum of 3 per cent racemization [36].

(b) (*S*)-(+)-methylbutyric acid (C) is commercially available and was used without further purification.

2.2. Synthesis of the polymers (II)

The vinyl mesogens (I.n.R*) were linked to the methylhydrogeno siloxane units of the copolymer backbones by a standard hydrosilylation reaction. The initial copolymers are either commercial products from Petrarch Systems Inc. and were used as received or were synthesized by Dr Coqueret [37] and fractionated by gel permeation chromatography before use (Waters, Ultrastyrigel 500 Å column, 19×300 mm, toluene). The characteristics of the initial copolymers are given in table 1.

All polymers were obtained according to the example of polymer II.11.30%.A. In a dry apparatus, 0.5145 g (0.001 mol) of vinyl mesogen I.11.A and 194 μl (0.00087 mol Si-H bonds) of poly (30 per cent methylhydrogeno-70 per cent dimethyl) siloxane copolymer were dissolved in 10 ml of dry toluene under nitrogen. About 0.5 mg of solid hexachloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, Merck) were then added and the system was kept at 70°C for 20 h (or 48 h for 100 per cent polymers). The resulting polymer was purified by gel permeation chromatography (Waters, Ultrastyrigel 10000 Å-500 Å columns, 19×300 mm, toluene) and dried under vacuum at 40°C for 12 h.

All polymers were checked by $^1\text{H NMR}$ (Bruker WH 270 MHz, CDCl_3). An example spectrum is given for compound II.11.100%.A in figure 2. The disappearance of the Si-H spectral lines (4.72 ppm) and the integration of the various lines prove that, in every case, all of the Si-H bonds have been grafted with a mesogenic group.

Table 1. Characteristics of the initial co and homo polysiloxanes.

$x(\%)$	\bar{M}_n	\overline{DP}_n	p
9	1900 ± 200	26 ± 3	2.2 ± 0.3
17	1950 ± 150	27 ± 2	4.2 ± 0.3
30	2050 ± 150	29 ± 2	8.1 ± 0.6
100	2300 ± 200	36 ± 1	34 ± 1

x , percentage of methylhydrogeno units per chain; \bar{M}_n , average number molecular weight determined by vapour phase osmometry; \overline{DP}_n , average number degree of polymerization; p , average number of methylhydrogeno units per chain.

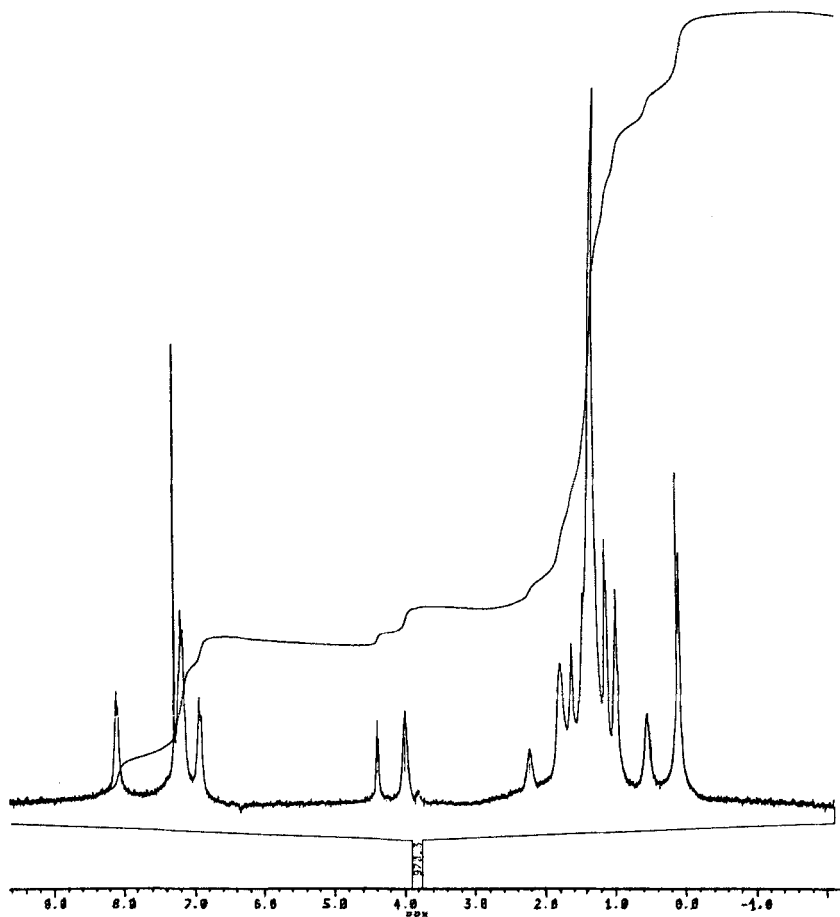


Figure 2. ^1H NMR spectrum of IL.11.100%.A (270 MHz, CDCl_3).

3. Identification of the phases

The identification of the phases requires several techniques such as microscopic observations, X-ray analysis, differential scanning calorimetry and polarization measurements.

3.1. Microscopic observations

A polarizing microscope coupled with a hot stage (Mettler FP 52) was used to determine the transition temperatures and to characterize the mesophases. The mesophases of the vinyl moieties (I) were clearly determined by microscopic observations. For example, on cooling from the isotropic phase of compound I.8.C, the cholesteric phase appeared with an oily streak texture and further cooling led to the homeotropic and focal conic textures of a S_A phase. Below the S_A phase, the ferroelectric S_C^* phase appeared with striated focal conic or schlieren textures. The transition temperatures of the vinyl moieties (I) and their corresponding hydrogenated homologues (I') are given in table 2. On the other hand, some polymers, with short spacers ($n=6$ and 8), exhibit uncharacteristic textures whatever the thermal treatment. In this case, the nature of the mesophases was assigned by X-ray and polarization

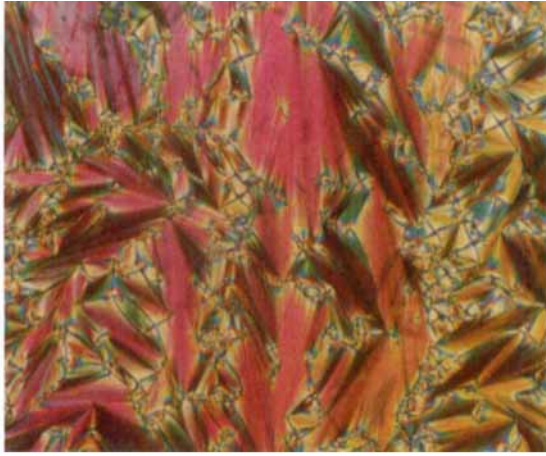
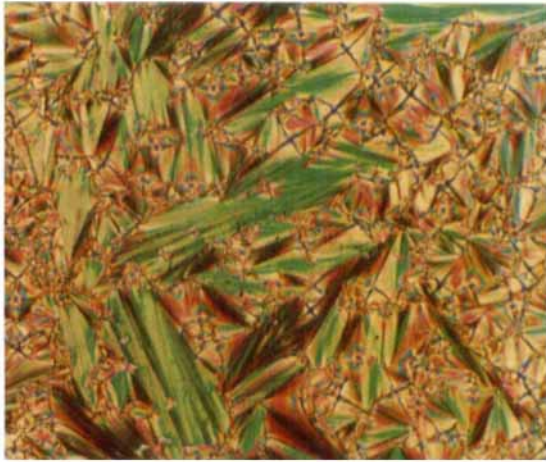
**(a)****(b)****(c)**

Figure 3. (a) Optical photograph of the S_A texture of polymer II.11.100%.A (119°C). (b) Optical photograph of the S_C^* texture of polymer II.11.100%.A (80°C). (c) Optical photograph of the S_C^* texture of polymer II.11.30%.A (75°C).

measurements. Nevertheless, other polymers, with long spacers ($n = 11$), present rather typical textures: fan shaped texture in the S_A phase (see figure 3 (a)), broken fans in the S_C^* phase (see figures 3 (b) and (c)). The mesophase transition temperatures of the polymers (II), determined on cooling, are reported in table 3.

Table 2. Transition temperatures ($^{\circ}\text{C}$) of vinyl moieties (I) and their hydrogenated homologues (I').

Name	n	C	S_C	S_A	N^*	I
I.6.A	6	●	57	—	—	●
I'.6.A	6	●	62.5	—	—	●
I.8.A	8	●	46	—	● (34.4)	●
I'.8.A	8	●	69.5	—	● (48.4)	● (48.6)
I.11.A	11	●	58	● (22.6)	● (46.9)	●
I'.11.A	11	●	69.2	● (38)	● (54.4)	●
I.11.B	11	●	59	● (28)	● (57)	●
I'.12.B	12	●	68	● (44)	● (67)	●
I.8.C	8	●	43	● (30.3)	● (39.9)	● (42.6)
I'.9.C	9	●	53	● (46)	● (49)	●
I.11.C	11	●	53.4	● (36.2)	● (39)	●
I'.12.C	12	●	60	● (52)	● (53)	●

(), monotropic phase.

Table 3. Transition temperatures ($^{\circ}\text{C}$) of polymers (II).

Name	n	$x(\%)$	T_g	T_m	S_C^*	S_A	I
II.6.30%.A	6	30	-24	—	● 35	—	●
II.8.9%.A	8	9			Non-mesomorphic		
II.8.17%.A	8	17	+	—	● 29	—	●
II.8.30%.A	8	30	-23	6	● 63	—	●
II.8.100%.A	8	100	0	—	● 95	—	●
II.11.17%.A	11	17	+	12	● 54	—	●
II.11.30%.A	11	30	-26	-1/18	● 85	—	●
II.11.100%.A	11	100	3	26	● 105	● 133	●
II.11.9%.B	11	9			Non-mesomorphic		
II.11.17%.B	11	17	+	-3	● 63	—	●
II.11.30%.B	11	30	—	10	● 102	—	●
II.8.30%.C	8	30	-30	—	● 45	—	●
II.11.30%.C	11	30	-18	15	● 74	—	●
II.11.100%.C	11	100	—	48	● +	+ 130	●

+, not determined.

3.2. DSC analysis

The DSC analysis of the ferroelectric liquid crystal polysiloxanes was performed with a DSC 7 Perkin-Elmer apparatus at $10^{\circ}\text{C min}^{-1}$ on heating and $5^{\circ}\text{C min}^{-1}$ on cooling. In this study, the smectic A-isotropic or chiral smectic C-isotropic transitions

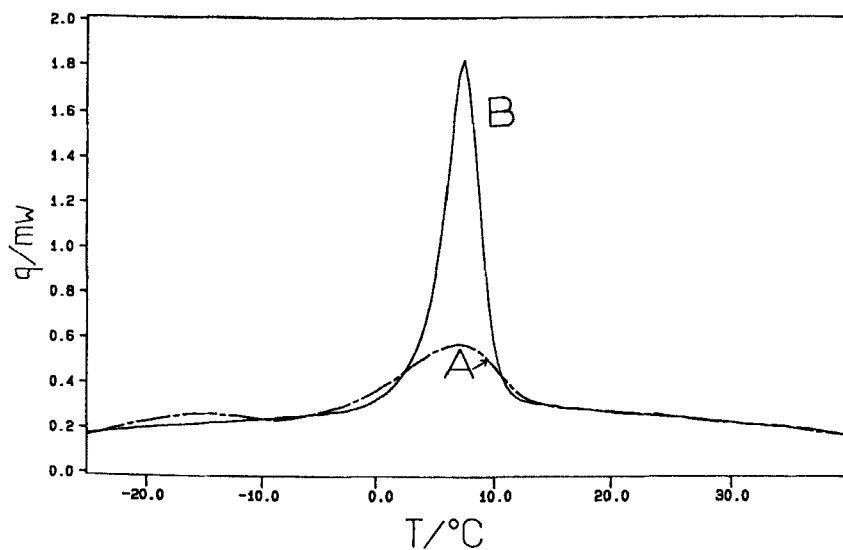


Figure 4. DSC thermogram of polymer II.8.30%.A showing its crystalline character. A: first heating scan; B: second heating scan after annealing at -7°C .

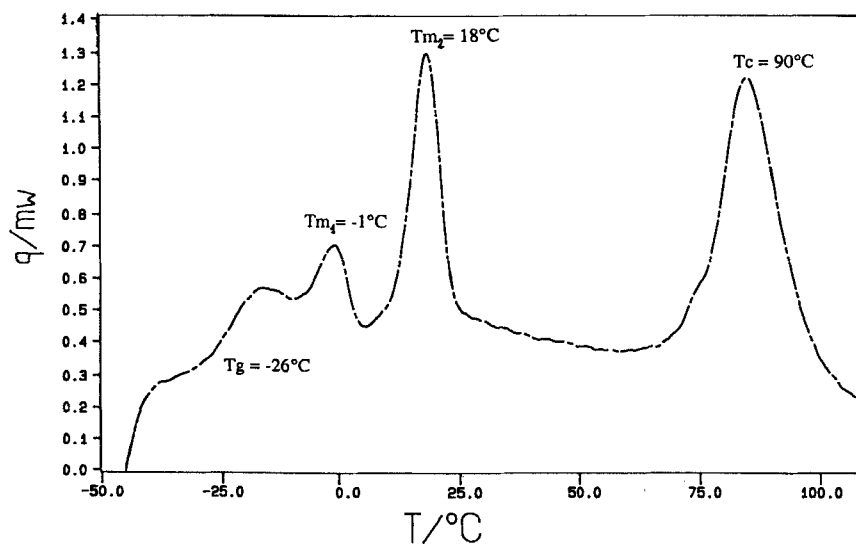


Figure 5. DSC thermogram of a semi-crystalline polymer (II.11.30%.A) (heating scan).

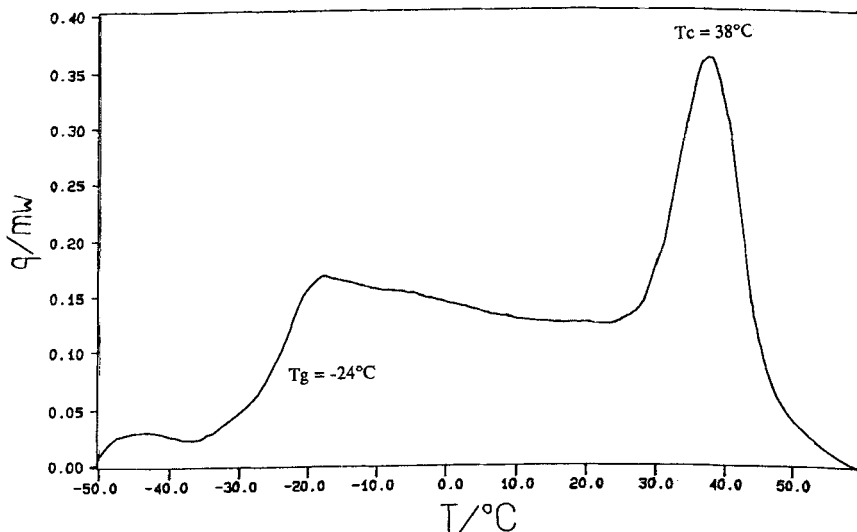


Figure 6. DSC thermogram of an amorphous polymer (II.6.30%.A) (heating scan).

were confirmed but the $S_C^*-S_A$ transitions were never detected. The amorphous and/or crystalline characters were also determined. Glass transition temperatures (T_g) and melting temperatures (T_m) (determined on heating) are given in table 3.

The initial siloxane polymers are totally amorphous materials ($T_g < -120^\circ\text{C}$) but our liquid crystal polysiloxanes may exhibit a crystalline character. This character is shown by annealing the samples (see figure 4). As to the glassy state, it was seen that glass transition temperatures are about 0°C for polymers with $x=100$ per cent, between -30 and -20°C for $x=30$ per cent and could not be reached for $x=17$ per cent whatever the chiral end-group or the spacer length. Thermograms of semi-crystalline (II.11.30%.A) or totally amorphous (II.6.30%.A) polymers are shown in figures 5 and 6.

3.3. X-ray diffraction

X-ray diffraction patterns for powder samples were obtained with a high temperature Guinier camera using monochromatic Co- K_α radiation. In our case, they assess the existence of smectic phases and give their layer spacing, d , as a function of temperature (see figures 7, 8 and 9).

4. Results and discussion

4.1. Mesomorphism

It can be seen from table 2 that the vinyl (I) and saturated moieties (I') exhibit monotropic S_A and S_C^* phases except for the shortest chain ($n=6$). However, as it is well-known for liquid-crystalline polymers to form more ordered mesophases, the polysiloxanes (II) mostly show enantiotropic S_C^* (see table 3) phases even with a non-mesogenic vinyl moiety (I.6.A). The S_A phase is only observed with a long spacer ($n=11$) for fully substituted polymers ($x=100$ per cent). We can explain this behaviour if we consider that in these homopolymers there is not enough free space for the mesogenic moieties so that they lie close together giving rise to a S_A phase. Finally, we note that these polymers are devoid of any cholesteric phase. In fact, all of our polymers, except

the lowest substituted copolymers ($x=9$ per cent), display an enantiotropic ferroelectric S_C^* phase with a very broad temperature range; for example, from 18°C to 85°C for compound II.11.30%.A.

The clearing temperatures usually increase with the spacer length [38]. At the same time, glass transition temperatures are lowered by the spacer lengthening according to the well-known plasticizing effect of long spacers. However, this latter effect is slight because of a parallel increase in crystallinity. As can be seen in table 3, II.8.30%.C is amorphous whereas II.11.30%.C is semi-crystalline. In the same way, II.6.30%.A is amorphous but II.8.30%.A and II.11.30%.A are semi-crystalline.

Let us now point out the strong influence of dilution on all the transition temperatures, including T_g and T_m , which are reduced when decreasing the substitution rate; (compare compounds II.11.100%.A, II.11.30%.A and II.11.17%.A). In addition, dilution seems to favour the S_C^* phase since the S_A temperature range is reduced and even disappears for small substitution rates ($x=17$ and 30 per cent).

4.2. Layer spacing

The X-ray diffraction experiments allow for the determination of the thermal variations of the layer spacing in the smectic phases (see figures 7, 8 and 9).

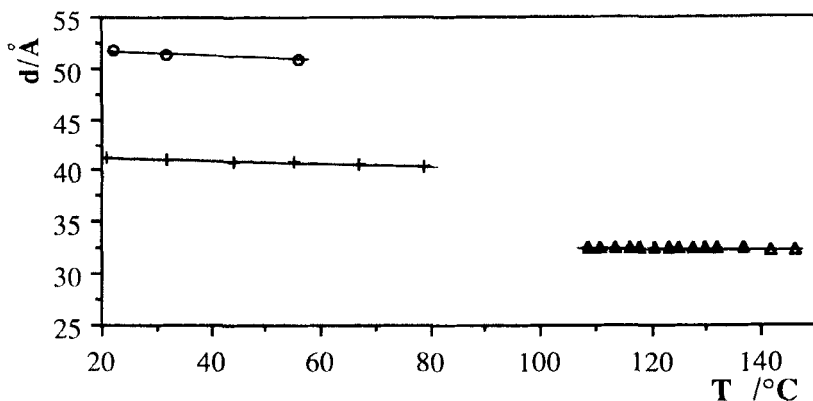


Figure 7. Layer spacing versus temperature for polymers of the II.11.x%.A series. \circ , II.11.17%.A; +, II.11.30%.A; \triangle , II.11.100%.A.

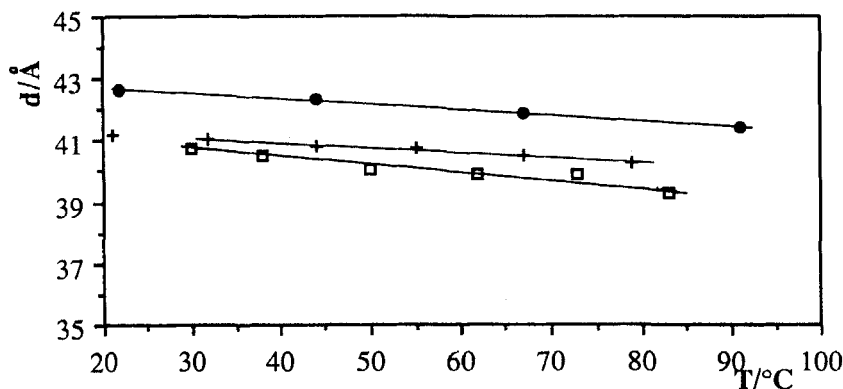


Figure 8. Layer spacing versus temperature for polymers II.11.30%.R*. R* = A, B and C. +, II.11.30%.A; \bullet , II.11.30%.B; \square , II.11.30%.C.

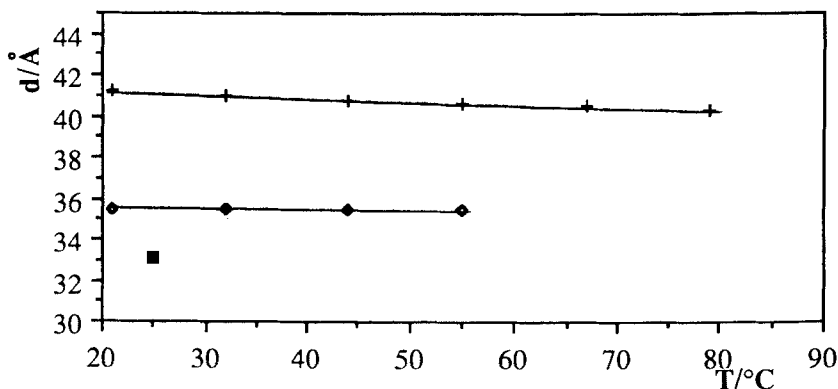


Figure 9. Layer spacing versus temperature for polymers II.*n*.30%.A. *n* = 6, 8 and 11. ■, II.6.30%.A; ◇, II.8.30%.A; +, II.11.30%.A.

We have mentioned in the previous part that the S_A phase is only observed in the homopolymers with a long spacer ($n = 11$). For instance, the polymer II.11.100%.A exhibits both S_A and S_C^* phases but X-ray measurements do not show any difference in layer spacing at the transition $S_A-S_C^*$ (see figure 7). The length, l , of the mesogenic group, in its most extended conformation (SASM stereo model, including the Si-CH₃ length), is 38 Å for this polymer. This value is slightly longer than the corresponding layer spacing of 32.4 Å. As $d/l < 1$, we can think that this compound only exhibits a S_C^* phase but some X-ray studies on several non-polar homopolysiloxanes give evidence of such values of $d/l < 1$ in the S_A phase [39]. Furthermore, our microscopic observations correspond to typical fan shaped textures for the S_A phase (see figure 3 (a)) and broken fan shaped textures for the S_C^* phase (see figure 3 (b)). The existence of the S_A phase is also confirmed by electro-optic measurements which show no switching and no polarization in polymer II.11.100%.A between 105°C and 133°C.

Figure 7 also shows the effect of dilution on the layer spacing which increases from about 30 Å for homopolysiloxanes to 40 Å for a 30 per cent substitution rate to 50 Å for a 17 per cent substitution rate. Such behaviour has already been observed and interpreted [40, 41]. The influence of the chiral chain length on the layer spacing is shown in figure 8. The longer the chiral chain, the smaller the layer spacing is, as observed previously [39]. Finally, from figure 9, we can mention that the layer spacing also increases with the spacer length.

5. Ferroelectric properties

5.1. Electro-optic measurements

The samples were sandwiched between two ITO coated glass plates (Balzers 30 Ω) whose surfaces were spin-coated with polyvinylalcohol or polyimide and then rubbed with velvet. The sample thickness was estimated to be between 5 and 10 μm, according to the Newton colour method. Planar alignment was achieved by shearing at the S_C^*-I or $S_C^*-S_A$ transitions under a voltage of ±50 V at a few Hz. The temperature dependence of the spontaneous polarization (P_s) and the switching time (τ) was measured from the induced polarization current obtained with a rectangular wave voltage. In our experimental set up, the current is accumulated and recorded versus time with a Kontron SMR II digital oscilloscope. The spontaneous polarization corresponds to the integration of the current bump versus time, its maximum to the

response time. Thus, this response time is defined as the time between field reversal and the maximum of the current peak. Most papers use another definition (optical rise time τ_{op}) corresponding to the time between 10 per cent and 90 per cent of the transmitted optical intensity. Experimentally τ_{op} is always shorter than τ [42] and so, our values of the response times are certainly overestimated.

5.2. Results and discussion

The spontaneous polarization and the response time were measured both as a function of temperature and of voltage at 5 Hz.

5.2.1. Influence of voltage and temperature

Figure 10 shows the saturation of the spontaneous polarization with voltage, at constant temperature, for polymers of the II.11.x%A series. The voltage allowing this saturation depends, of course, on temperature, on the substitution rate and also on the

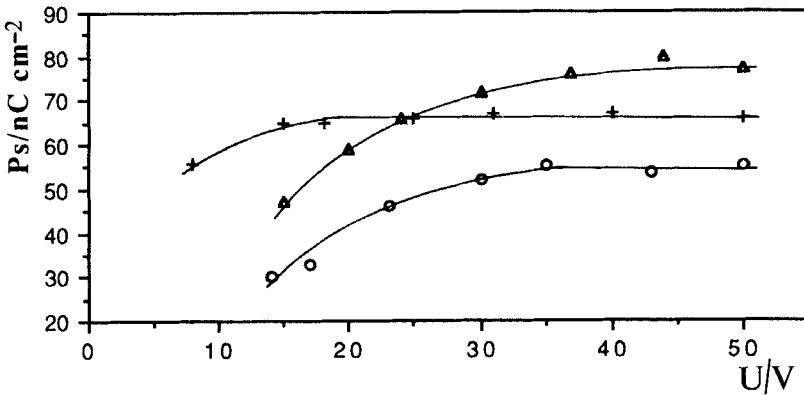


Figure 10. Polarization versus voltage at 5 Hz for polymers of the II.11.x%A series. II.11.17%A (23°C); II.11.30%A (65°C); II.11.100%A (70°C). ○, II.11.17%A; +II.11.30%A; △, II.11.100%A.

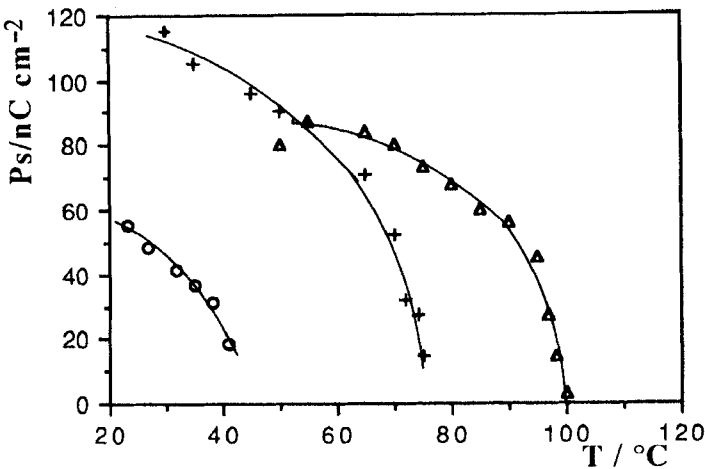


Figure 11. Polarization (saturation) versus temperature (50 V, 5 Hz) for polymers of the II.11.x%A series. ○, II.11.17%A; +II.11.30%A; △, II.11.100%A.

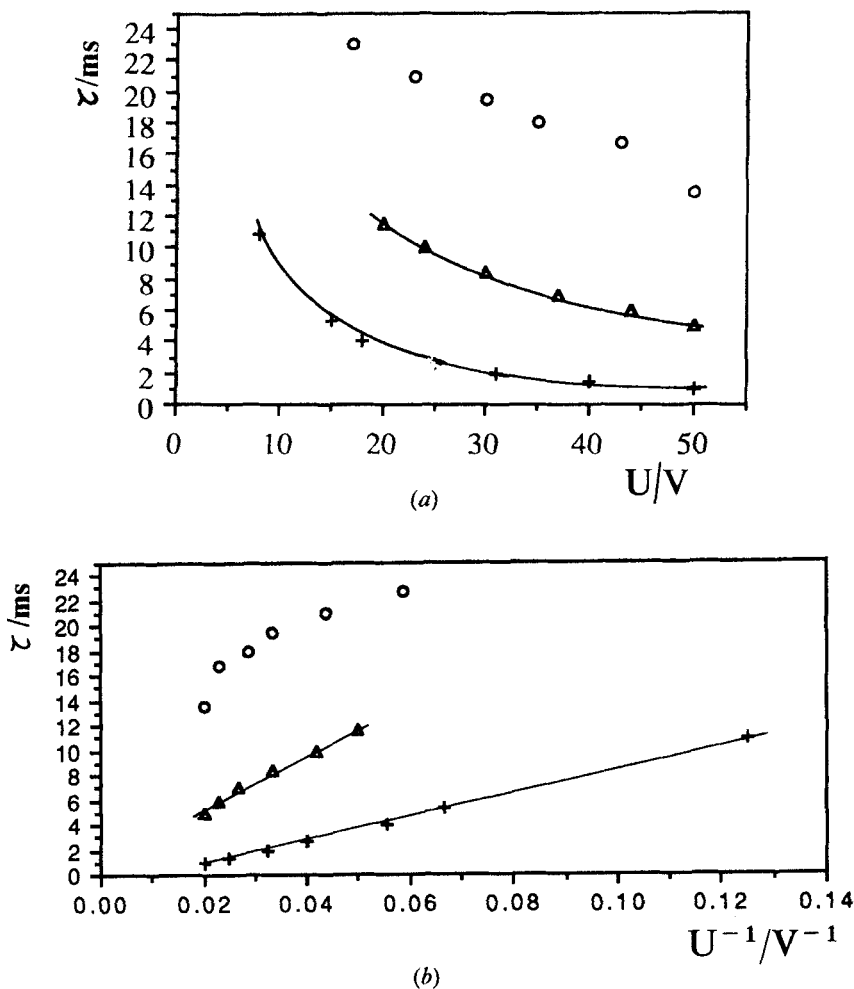


Figure 12. (a) Response time versus voltage at 5 Hz for polymers of the II.11.x%.A series. II.11.17%.A (23°C); II.11.30%.A (65°C); II.11.100%.A (70°C). \circ , II.11.17%.A; +, II.11.30%.A; \triangle , II.11.100%.A. (b) Response time versus reciprocal voltage at 5 Hz for polymers of the II.11.x%.A series. II.11.17%.A (23°C); II.11.30%.A (65°C); II.11.100%.A (70°C). \circ , II.11.17%.A; +, II.11.30%.A; \triangle , II.11.100%.A.

alignment conditions. For these reasons, saturation could not sometimes be obtained for some polymers. As we can see in figure 11, the polarization of polymer II.11.100%.A drops for temperatures below 55°C because the maximum applied voltage (50 V) no longer provides saturation of the polarization when the temperature is lower than 55°C. In contrast, for all of the copolymers, saturation of the polarization was reached with fairly low voltages: 10 to 20 V at temperatures such as $T_c - T < 10^\circ\text{C}$ (T_c is the $S_C^* - S_A$ or $S_C^* - I$ transition temperature). These values are similar to those measured for standard ferroelectric liquid crystals.

Figure 12(a) shows the voltage dependence of the response times, at constant temperature, for polymers of the II.11.x%.A series. All of the response times decrease strongly with voltage and, for polymers II.11.30%.A and II.11.100%.A, a τ versus reciprocal voltage plot reveals good agreement with the well-known relation $\tau = \nu/P_s \cdot E$

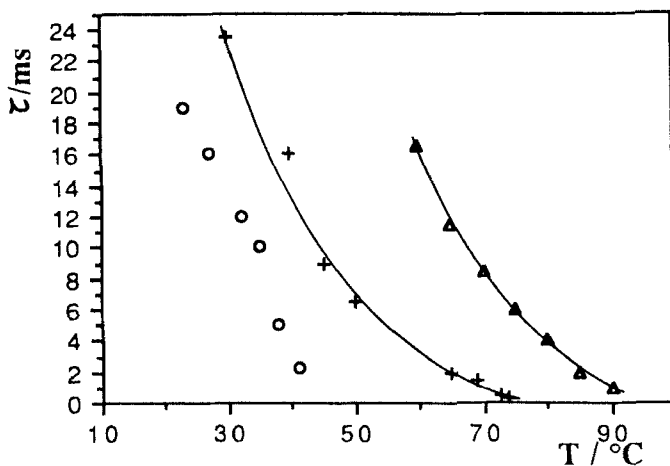


Figure 13. Response time versus temperature (30 V, 5 Hz) for polymers of the II.11.x%.A series. ○, II.11.17%.A; +, II.11.30%.A; △, II.11.100%.A.

where ν is the bulk viscosity and E is the applied electric field which is directly proportional to the voltage (see figure 12 (b)).

The thermal variations of the spontaneous polarizations for polymers of the II.11.x%.A series are shown in figure 11. At a given voltage the polarization increases and tends to an asymptotic value with decreasing temperature. However, it has to be noticed that when the viscosity becomes too important, far from the S_C^* transition, there is no switching and no measurement can be made even if the sample is still in a S_C^* phase (this is the case for the homopolymer II.11.100%.A).

5.2.2. Influence of dilution

Although they have the same chiral end-group, II.11.17%.A, II.11.30%.A and II.11.100%.A are found to have different maximum polarizations. Particularly II.11.17%.A seems to have much lower P_s values than II.11.30%.A or II.11.100%.A (no significant differences are noted between 30 per cent and 100 per cent). The very low content (see table 1) of mesogenic groups per chain of II.11.17%.A might account for these low values. The alignment conditions and the quality of the alignment could also be responsible for differences in P_s values. In fact, after several attempts, we have noticed that the following parameters do have an effect on the alignment of the sample: type of coating (polyvinylalcohol or polyimide), shearing, measuring on heating or on cooling. For instance, the values of P_s for II.11.100%.A were always found to be higher if measured on heating from room temperature than on cooling from the isotropic phase; the difference may be as large as 50 per cent. However, such a difference was never observed for copolymers which give reproducible P_s and τ values whatever the thermal treatment.

Another feature of our copolymers is their very fast response times in the field of polymer materials (see figure 13). This could be correlated with the noticeable fall in the bulk viscosities. At room temperature, 17 per cent polymers are almost fluid, cream-like materials; 30 per cent are soft, pastry-like while 100 per cent are rather tough materials. However, the fastest response times are not found for the lowest substitution rate (17 per cent) but for 30 per cent polymers near the S_C^* transition (at about 70°C). This is

due to the fact that the transition temperatures are much higher in the latter compounds and the higher the temperature, the faster the response time. So, 30 per cent polymers certainly combine rather small viscosities with sufficiently high transition temperatures. This could explain their faster response times. Then, the obtention of a very broad S_C^* temperature range up to 60°C including room temperature, with a high polarization and fast switching times is achieved with a 30 per cent substitution rate.

5.2.3. Influence of the chiral end-group

Measurements were only carried out on the A and B series which have very polar chiral end-groups. Their measured polarization values are similar to those found for analogous low molecular weight liquid crystals [29–32]. They are among the highest for ferroelectric liquid crystal polymers (100 nC/cm^2 or more). For the C-type series, polarization measurements could not be achieved on our polymers because the C chiral end-group has a low polarization [32, 43] and, in our case, a sufficient polarization

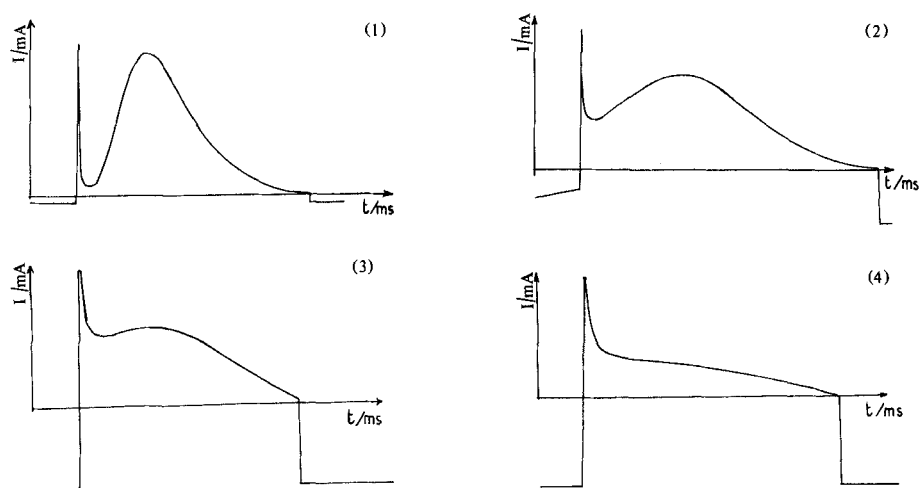


Figure 14. Evolution of the polarization bump with frequency (polymer II.8.30%.A). (1) 50°C ; 30 V; 5 Hz. (2) 50°C 30 V 25 Hz. (3) 50°C 30 V 50 Hz. (4) 50°C 30 V 75 Hz.

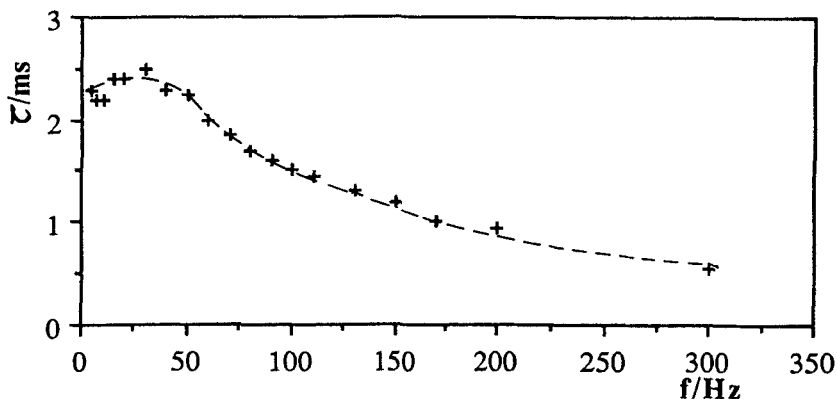


Figure 15. Response time versus frequency for II.11.30%.A at 65°C under 25 V.

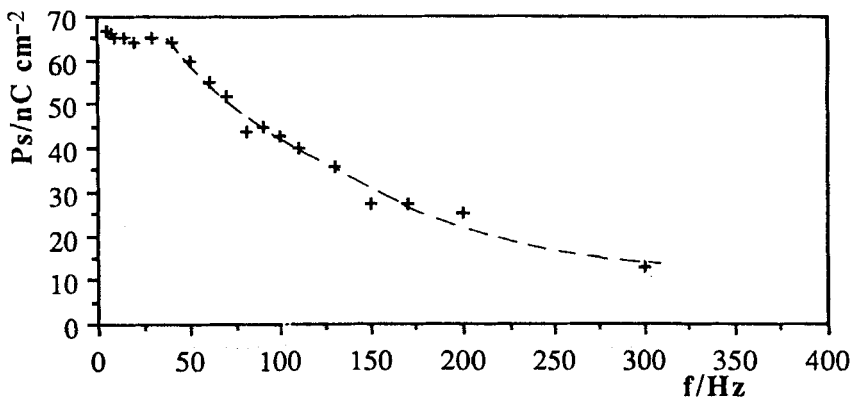


Figure 16. Polarization versus frequency for II.11.30%.A at 65°C under 25 V.

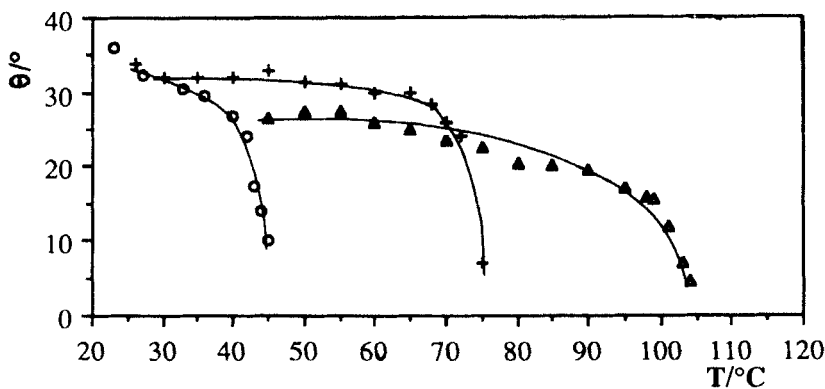


Figure 17. Tilt angle versus temperature for polymers of the II.11.x%.A series. \circ , II.11.17%.A; +, II.11.30%.A; \triangle , II.11.100%.A.

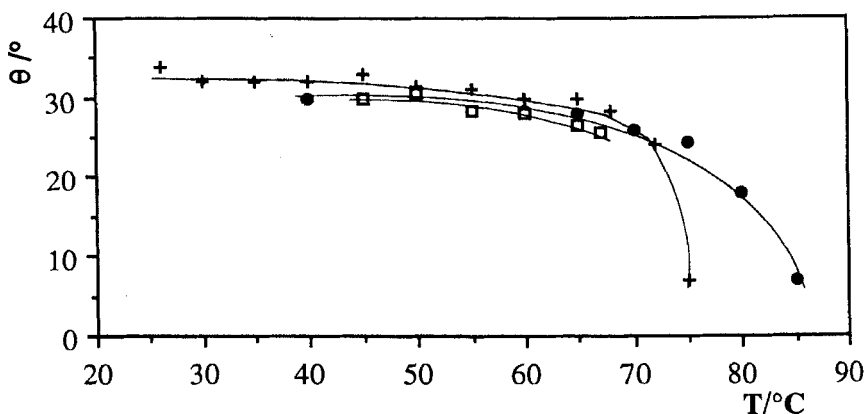


Figure 18. Tilt angle versus temperature for polymers II.11.30%.R*. R* = A, B and C. +, II.11.30%.A; \bullet , II.11.30%.B; \square , II.11.30%.C.

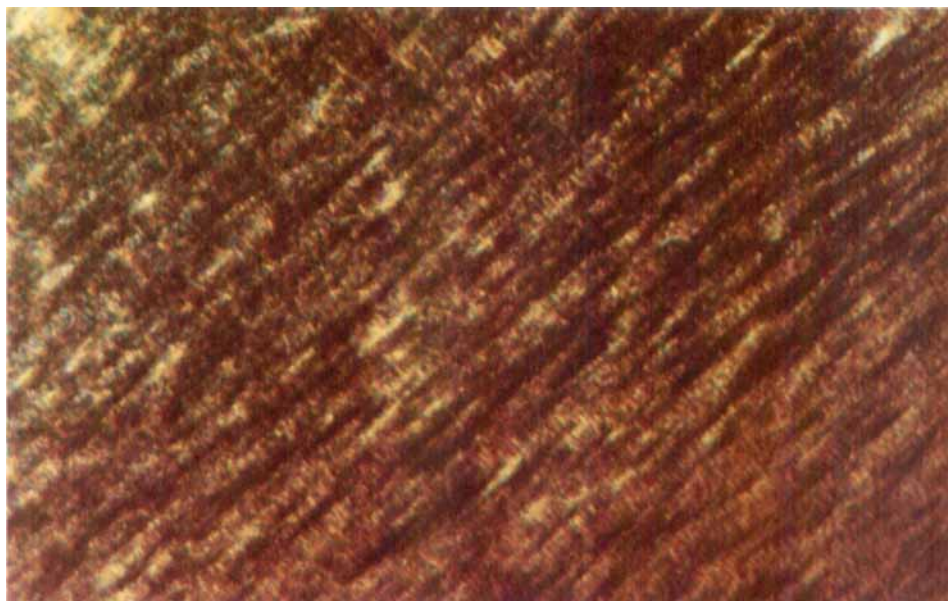


Figure 19. Optical photographs of the two stable states of polymer I.11.30%.A at 60°C.

current was not obtained probably because the alignment was not good enough. Another method, such as pyroelectric coefficient measurements, could be used.

5.2.4. Influence of frequency

At a given temperature and a given voltage, the frequency of the applied rectangular wave voltage is increased from nearly 0 Hz up to a frequency for which no polarization bump is observed (see figure 14). This frequency is a cut-off frequency for the polymer at the voltage and the temperature considered. Figures 15 and 16 represent the response time and the spontaneous polarization versus frequency for polymer II.11.30%.A at 65°C under 25 V, respectively. The response time remains constant over a narrow, low frequency range: from 0 Hz up to about 50 Hz for II.11.30%.A but this range can be narrower (5 Hz for II.8.30%.A at 50°C under 28 V). Then τ quickly falls with frequency but, as is seen in figure 14, the definition of τ becomes quite inaccurate. In the same way, polarization is not frequency dependent over a range whose width depends on the polymer, on voltage and on temperature. Beyond this range, P_s decreases to zero at the cut-off frequency. Then, for each polymer, at a given temperature and voltage, we can define a frequency range in which the ferroelectric properties are constant and can be used. This range usually goes from a few Hz up to 50–100 Hz. In this range, 5 to 10 Hz always seem to be good frequencies for measurements.

Tilt angles were optically measured between the two stable states. Figures 17 and 18 represent the thermal variations of the tilt angle for some polymers. The saturation tilt angles are always found to be about 30° whatever the substitution rate or the chiral end-group.

Figure 19 represents the two stable states for polymer II.11.30%.A and shows the alignment obtained.

6. Conclusion

Several mesogenic groups likely to provide high spontaneous polarizations have been linked to siloxane polymer backbones at variable substitution rates. All synthesized polymers exhibit a S_C^* phase over a wide temperature range including room temperature. The modification of the substitution rate on the polymer backbone leads to copolymers with adaptable properties (transition temperature, polarization, response time, etc.). As for low molecular weight liquid crystals, the chiral mesogenic group derived from the isoleucine provides high polarization values. As a result, a polymer bearing the isoleucine group, at a substitution rate of 30 per cent, exhibits a polarization over 100 nC/cm² and an optimal very fast response time of 300 μ s. In order to improve the switching times, mixtures with low molecular weight molecules are going to be investigated.

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