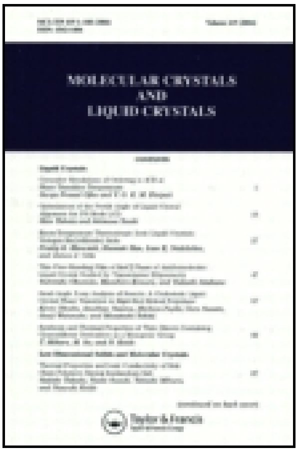

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Structural, Pyro- and Piezoelectric Study of Some New Smectic C* Side Chain Polymers

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STRUCTURAL, PYRO- AND PIEZOELECTRIC STUDY OF SOME NEW SMECTIC C* SIDE CHAIN POLYMERS

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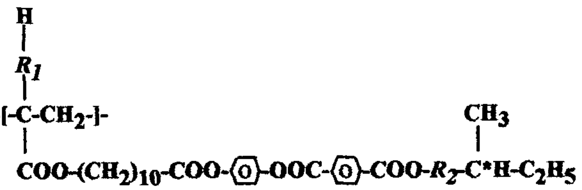
Abstract Effect of minor changes in chemical structure of main chain and mesogenic side chain on phase behaviour and spontaneous polarization, P_S, of the polymer has been studied. Measurements of pyro- and piezoelectric effects and their relaxation are reported.

INTRODUCTION

Since their invention in 1984[1] the ferroelectric liquid crystalline polymers (FLCPs) are of great scientific and technological interest, mainly due to fast switching capability combined with promising advantages in processing of polymer materials[2-7]. To study the correlation between chemical structure of a side chain polymer, on the one side, and its phase behaviour including temperatures of phase transitions and types of mesophases formed as well as the value of spontaneous polarization, on the other side, we have synthesized three new FLCPs with the chemical structure derived from the known polymer P5*M[1,8] by exclusion of a methylene group from polymer main chain and/or in the terminal chiral group:



$$\begin{array}{l}
\mathrm{H}\\
|\\
R_1\\
|\\
-[\mathrm{C}\text{-}\mathrm{CH_2}]-\\
|\\
\mathrm{COO{-}(CH_2)_{10}{-}COO{-}}\bigcirc\mathrm{{-}OOC{-}}\bigcirc\mathrm{{-}COO{-}}R_2\mathrm{{-}}\overset{\overset{\mathrm{CH_3}}{|}}{\mathrm{C^*}}\mathrm{H{-}C_2H_5}
\end{array}$$

Polymer	R_1	R_2
P5*M	$-CH_2-$	$-CH_2-$
P5*A	-	$-CH_2-$
P4*M	$-CH_2-$	-
P4*A	-	-

This paper presents comparative study of the structure, phase behaviour and ferroelectric properties of the four polymers including spontaneous polarization, pyro- and, for the polymer P4*M, piezoelectric effect and corresponding relaxation processes.

EXPERIMENTAL

Chemical procedures

The monomers were prepared using the standard scheme[8,9] (phase transitions are listed below). Chemical structure of the monomers has been confirmed by IR and ^{1}H NMR spectroscopy and chemical purity proved by thin layer chromatography. Table 1 presents the phase transition temperatures for the monomers.

TABLE 1 Phase transitions of the monomers

Monomer corresponding to the polymer	Phase transitions
P4*A	K (~20 Ch) 37 I†
P4*M	K 51 Ch 54 I
P5*A	K 35 S_X 41 I
P5*M	K (< 10 S^*_C 15 S_A) 21 I

† The transition from cholesteric to crystal phase at 20°C takes about three hours.

All the polymers have been synthesized by radical polymerization of corresponding monomers in toluene solution using the 2,2′-azobis-2-methylpropionitrile as the initiator. Molar masses of the polymers measured by gel permeation chromatography using a PMMA standard are within the range $M_w \sim (3\div6)\cdot10^5$ with the ratio $M_w/M_n \sim 2.5\div4$.

Investigation methods

The DSC curves were taken mostly with Du Pont 990 Thermal Analyzer.

Microscopic observations have been carried out using a Leitz polarizing microscope provided with a Mettler-FP82/FP800 programmable heating stage and a video-recording system.

X-ray curves were measured by a diffractometer with a linear position sensitive detector using CuK$_\alpha$ radiation filtered by Ni film[10]. Resolution limit for the correlation length value, $\xi_{||}$, was about 900 Å.

The spontaneous polarization, P_s, was studied using a pyroelectric technique[11] The pyroelectric coefficient, $\gamma \equiv dP_s/dT$, was measured from the pyroelectric response of a 15 μm thick FLCP sample to standard heat pulses from a Nd YAG laser. The measurements were repeated for increasing values of external (untwisting) d.c. voltage applied until saturation of the measured pyroelectric response (achieved at ~ 12 V/μm). The P_s value was calculated by integrating the curve γ(T).

The piezoelectric effect has been measured by an acoustoelectric method[12]. The piezovoltage response in the FLCP sample was excited by a 80 Hz sound wave, and the piezoelectric signal was detected at the same frequency by a tuned amplifier.

RESULTS AND DISCUSSION

Structure and Phase Behaviour

Table 2 summarizes phase transition temperatures, structural data and maximum P_S values for the polymers. All the four polymers form two enantiotropic LC phases. The clearing point of the polyacrylates is about 10°C higher than of corresponding polymethacrylates; furthermore, the type of the main chain affects drastically the phase sequence of an FLCP: the polymethacrylates tend to form a low temperature Sm C* phase which can be frozen in a glassy state, while the polyacrylates form a high temperature Sm C* phase, which transforms by heating to the isotropic liquid. As an illustration, Fig. 1 shows the interlayer distance, ***d***, versus temperature for an acrylate (P4*A) and a methacrylate (new precise measurements for P5*M, cf. previous data[8]). The Sm C* phase appears to be monolayer for all the polymers. The P4*M show monotropic (in cooling) formation of another phase (probably cholesteric blue) in a narrow temperature region close to the clearing point simultaneously with the formation of Sm C* phase, as observed under the microscope.

TABLE 2. Phase behaviour, X-ray data and maximum P_S values of the polymers.

Polymer	Phase transitions	Phase	***d***, Å	$\xi_{\|\|}$, Å	Tilt angle, $\theta°_{max}$	P_S max, nC/cm^2
P4*A	Sm B 54-60 Sm C*	Sm B	33.7	250÷600	15.5	4.0
	84-88 I	Sm C*	32.7÷33.5	resol. lim.		
P4*M	Sm C* 76-78 I[†]	Sm C*	31.9÷34.7	150÷750	25.7	16.5
P5*A	Sm F* 77 Sm C*	Sm F*	33.5÷34.2	750	21.0	(~1.5)[‡]
	97 I	Sm C*	33.5÷35.4	resol.lim.		
P5*M	Sm C* 74 Sm A	Sm C*	32.0÷34.7	450÷700	25.7	0.9
	85 I	Sm A	34.8	resol.lim.		

[†] A blue phase has been also observed under microscope within ~2°C below the clearing point
[‡] Rough estimation .

The low temperature mesophase of the polyacrylates was referred to Sm B type for P4*A but to Sm F* type for P5*A, since the former one shows a prominent change in the ***d*** value back to the value observed close to the clearing point, while for P5*A it

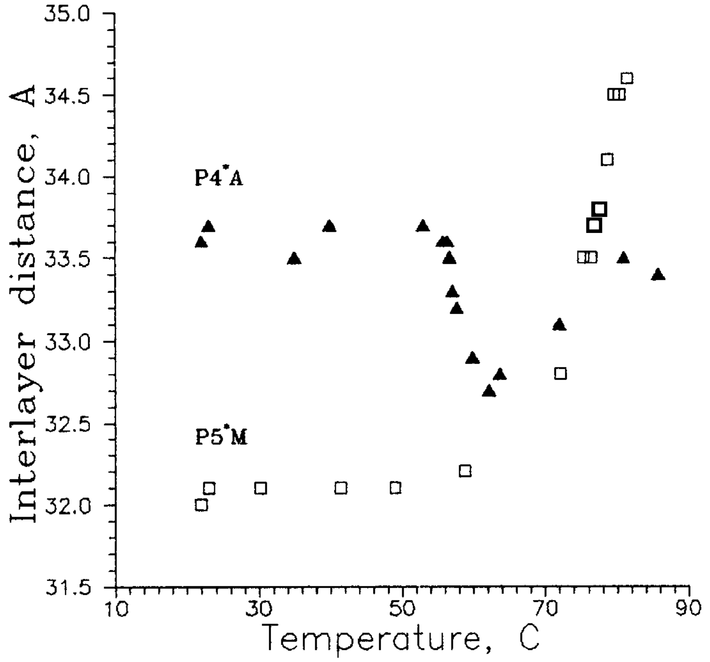


FIGURE 1 Smectic layer thickness versus temperature for P4*A and P5*M

remains almost constant under the smectic-smectic phase transition. All the polymers show a good ordering in smectic phases at room temperature (second order peak and also high enough $\xi_{||}$ values which indicate conservation of the ordering over 10-20 smectic layers).

For the polymer P4*A, an unusual dependence of the clearing point in heating on voltage applied has been observed (Fig.2). Some theoretical considerations for the phenomena are discussed elsewhere[13]

Pyroelectric measurements

All the four polymers form Sm C* phase and should have therefore ferroelectric properties. Fig. 3 shows the pyroelectric coefficient, γ, versus temperature for the polymethacrylates P4*M and P5*M (a) and for the polyacrylate P4*A (b). The maximum values of spontaneous polarization, P_S, at room temperature are given in Table 2. It should be noted that we failed to measure the $\gamma(T)$ curve for P5*A, since even at low values (3 V/μm) of the d.c. voltage applied to the FLCP in a pyroelectric cell broke down when approaching the clearing point. The value given in Table 2 is a rough

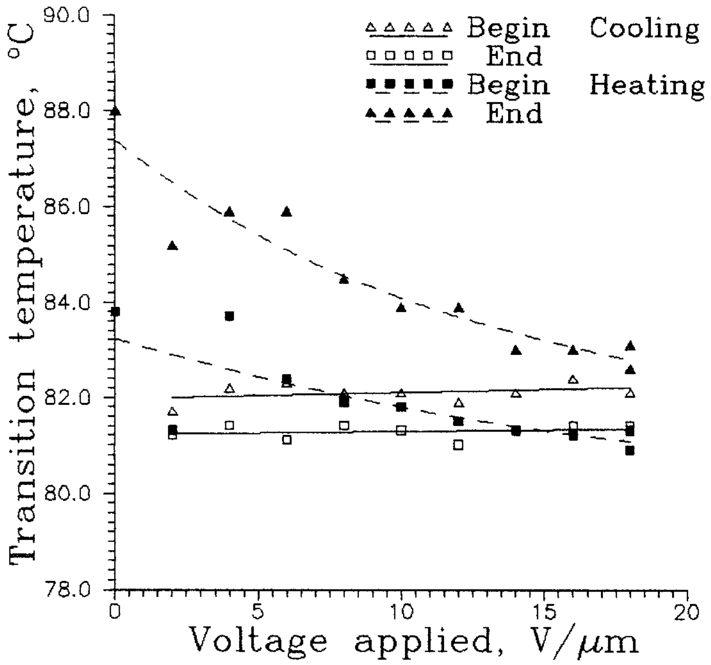


FIGURE 2 Temperature range of the clearing phase transition for P4*A in heating and cooling versus applied voltage

estimation from the value of the pyroelectric response at lower temperatures (peak at 78 °C) as compared with the data for the P4*A measured under the same conditions.

As seen from Fig. 3, the shape of the $\gamma(T)$ curve for both polymethacrylates is quite similar despite the 15 time difference in the absolute value: a typical growth of pyroelectric response at the high temperature boundary of Sm C* phase and slowly descending low temperature section, as it has been reported for other FLCPs[8,14]. On the other hand, the polyacrylate P4*A shows another type of the $\gamma(T)$ dependence with two maxima at two phase transitions. Such a temperature dependence is first reported for an FLCP but has been observed for low molar mass ferroelectric liquid crystals having a Sm C* phase between two other LC phases[10].

As it could be expected, the maximum spontaneous polarization value, P_S, grows with the elimination of an extra methylene group between chiral carbon atom and rigid mesogenic core. However the growth is much better developed for the methacrylates (P4*M/P5*M) than for acrylates (P4*A/P5*A). The lower maximum γ and P_S values for the P4*A as compared with P4*M can be explained by the lower θ angle.

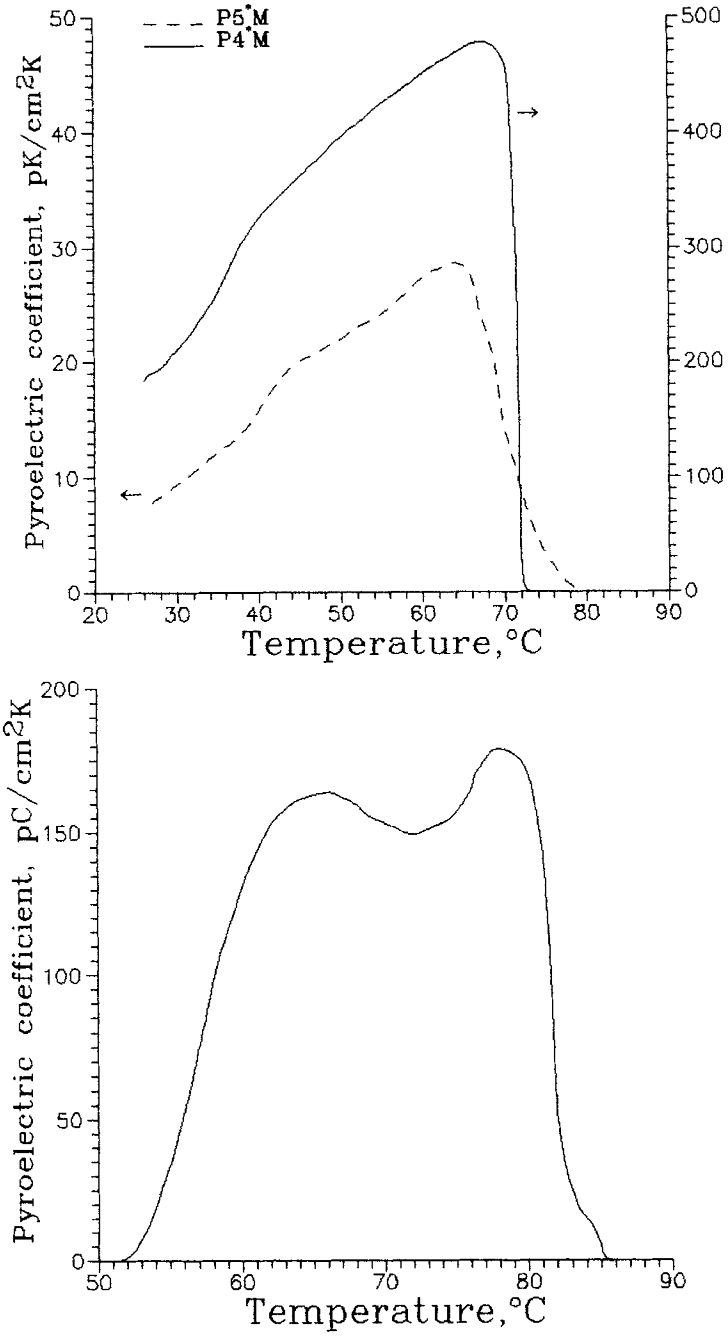


FIGURE 3 Pyroelectric coefficient, γ, versus temperature for the polymethacrylates P4*M and P5*M (a) and for the polyacrylate P4*A (b)

Investigation of the Piezoelectric Effect

Fig. 4 shows the acoustically induced piezoelectric response from the P4*M sample in terms of the apparent piezoelectric coefficient, d_{31}^*, versus temperature. The curve was taken in heating with no external d.c. field after polarization of the sample by 9 V/μm voltage above T_c and cooling to room temperature with the voltage applied. It should be noted, that the measured d_{31}^* value corresponds quantitatively to the true d_{31} value only below the glass temperature; above the temperature it represents an apparent value only but gives a qualitative presentation of its temperature dependence. As seen from the Fig., shape of the both curves $d_{31}^*(T)$ and $\gamma(T)$ is quite similar, as it has been reported for other methacrylic FLC polymers[8,15]; while the d_{33} component of the piezoelectric tensor shows another temperature dependence[16].

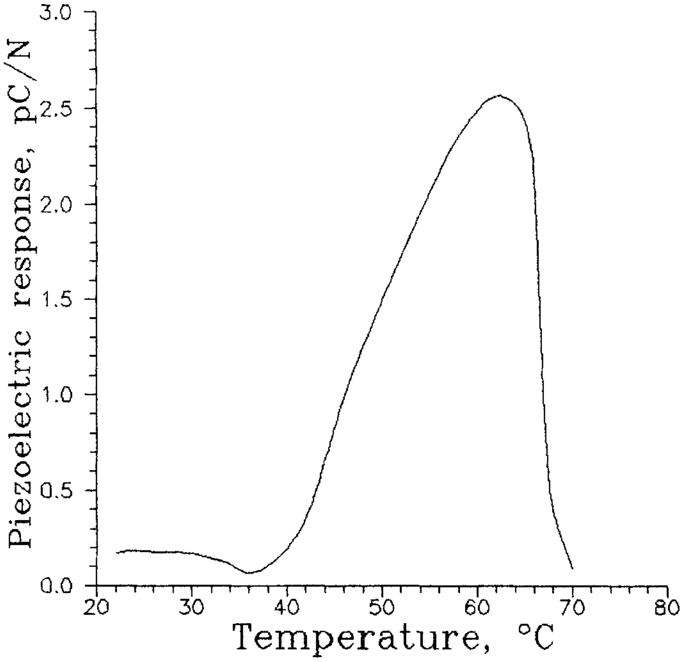


FIGURE 4 Piezoelectric response, d^*_{31}, versus temperature for the polyacrylate P4*A (b)

The phase delay of the piezoelectric response relative to the affecting acoustic wave (Fig. 5) is sensitive to the glass transition, showing a pronounced threshold within the temperature range 32-45°C (the transition can be observed also as a point of inflection for the descending section of the $\gamma(T)$ curve, Fig. 3, at 40-45°C).

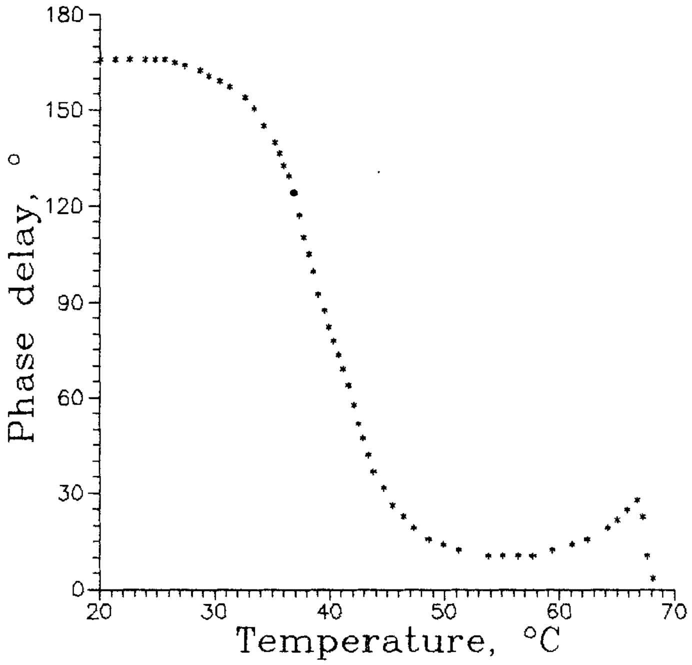


FIGURE 5 Phase delay of the piezoelectric response from P4*M to the inducing acoustic wave versus temperature.

Relaxation of pyro- and piezoelectric effects in P4*M

The pyroelectric pulse technique enables measurements of relaxation time for helix twisting, τ^t, and untwisting, τ^u, observed as decrease (increase) of the magnitude of pyroelectric response to laser heat pulses after switching off (on) the applied d.c. voltage. Those values correspond to the restoration of equilibrium azimuthal angle of helical structure in the Sm C* phase and are referred to the Goldstone mode[5,8]. Fig. 6 presents the times τ^t and τ^u for P4*M measured at various temperatures. As seen, growth in both values can be interpreted in terms of Arrhenius' law with corresponding values of the activation energy $E_A{}^t = 82 \pm 17$ kJ/mol and $E_A{}^u = 115 \pm 3$ kJ/mol correspondingly, the values being within the range reported for another side chain FLC polymers[5].

The acoustically induced piezoelectric technique is also applicable to study the similar decrease in the magnitude of piezoelectric response and to measure corresponding relaxation times. Fig. 7 shows the falldown of the piezoelectric response, $d_{31}{}^*$, after switching off the external voltage for different values of the voltage applied, at a fixed temperature (T = 60°C) and a fixed polarization time (Δt = 10 min). The falldown can be approximated by biexponential decay as

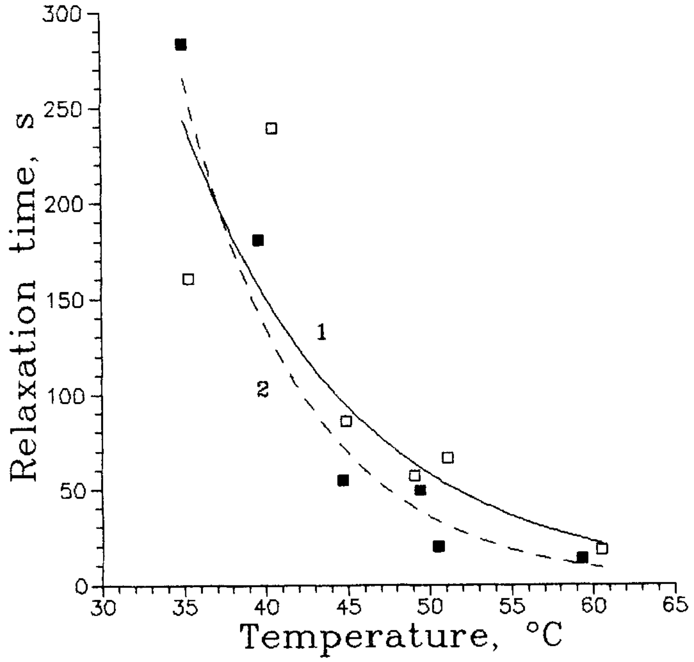


FIGURE 6 Relaxation times for helix twisting, τ^t (□, 1) and untwisting, τ^u (■, 2), versus temperature

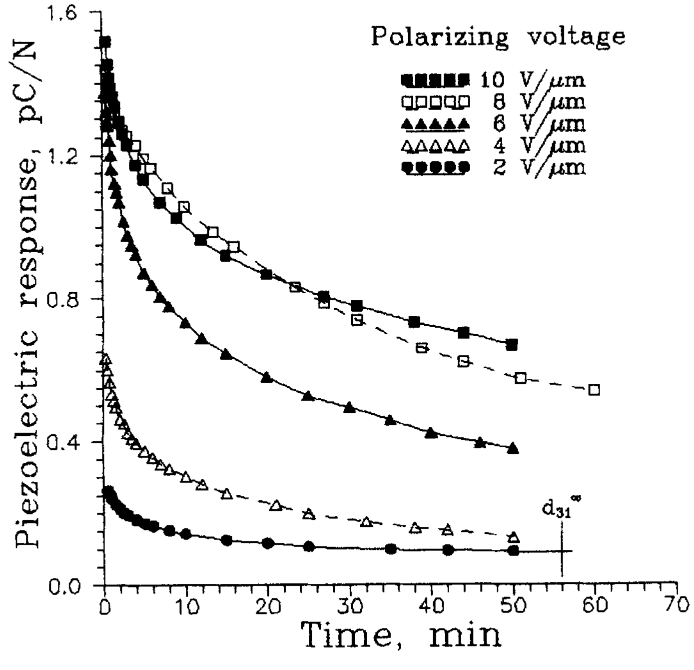


FIGURE 7 Relaxation of the piezoelectric response, d_{31}^*, after voltage switching off for different values of voltage applied

$$d_{31}^* = d_{31}^{*\infty} + A_1\exp(-t/\tau_1) + A_2\exp(-t/\tau_2)$$

Fig. 8 presents the two relaxation times, τ_1 and τ_2, versus the polarization voltage. The shorter relaxation time, τ_1, is independent of the voltage and has the same order of magnitude as the τ^t and τ^u times for the pyroelectric relaxation, thus corresponding probably to the same molecular motion (90 s vs 20 s correspondingly). On the other hand, the longer time, τ_2, depends evidently on the voltage applied (as well as on polarization time) and may correspond to a relaxation of nonequilibrium macroscopic orientation of the sample. A two-stage orientation process in an electric field with reorientation of helix axis followed by helix untwisting has been reported for cholesteric polyacrylates and polymethacrylates[18].

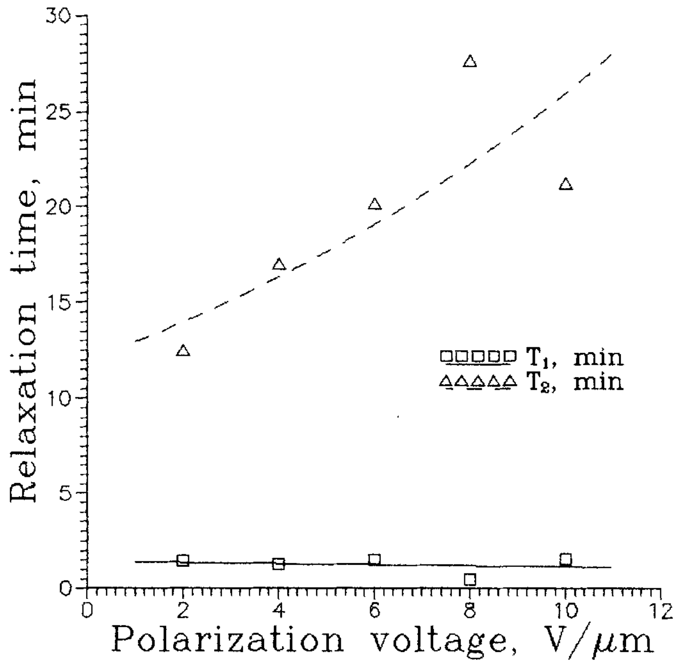


FIGURE 8 Relaxation times of the piezoelectric response, τ_1 and τ_2, versus the polarization voltage

CONCLUSIONS

Eliminating of the methylene group between the chiral centre and the rigid mesogenic core in side chains of an FLCP results mainly in the increase of P_s value, while the change from polymethacrylic main chain to polyacrylic one affects strongly the sequence of LC phases formed.

The acoustoelectric technique is applicapable to study glass transition in FLCPs as well as long-term relaxation processes (~ 10^3 s). The time corresponding to the shorter-term relaxation (~ 10^2 s) correlates with the data obtained by pyroelectric measurements.

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