Cell thickness dependence of dielectric properties of ferroelectric liquid crystal (CS-1022)

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Dielectric dispersion of the ferroelectric liquid crystal (CS-1022) around the S_C^*–S_A transition and temperature dependence of the spontaneous polarization were measured by varying the cell thickness. Behaviour of the dielectric constant is well described by a formula including the contribution of the soft mode, the Goldstone mode and the ionic conduction. Temperature dependence of the spontaneous polarization is expressed by a formula $P_0(T_C - T)^x$.

1. Introduction

Since the discovery of optical bistability in the surface stabilized ferroelectric liquid crystals (SSFLC) [1], ferroelectric liquid crystals have attracted considerable attention from the view points of both fundamental physical interest and optical display applications. The dielectric properties of ferroelectric liquid crystals (FLC) around the S_C^*–S_A phase transition have been investigated both experimentally [2–7] and theoretically [8–10]. Cell thickness is one of the important parameters which specifies the dielectric properties of the FLC cell because it affects the helical structure in the cell, the transition temperature [11, 12] and the magnitude of spontaneous polarization [13]. The dielectric response of FLCs depends on the cell thickness especially in the S_C^* phase. The dielectric response in the S_C^* phase is mainly due to the contribution of the Goldstone mode. The Goldstone mode is defined as the fluctuation of the azimuthal angle of the molecules around the layer normal. For the specimens in the SSFLC state, the molecules are constrained at the cell surfaces and the helical structure will not be expected even in the S_C^* phase. It has been reported that in the specimens whose cell thickness is less than the helical pitch, the helical structure is completely unwound [1]. The dielectric response of the SSFLC may be somewhat different from that of the specimens with helical structures: the dielectric responses due to the ideal Goldstone mode cannot be expected to have the same meaning as in the thick cell because there is no helical structure in the SSFLC. Though measurements of dielectric properties have been performed on various ferroelectric liquid crystals, less attention was paid to their cell thickness dependence. Systematic

investigation of the cell thickness dependence of the dielectric properties will be expected to clarify the effect of intersurface interaction between the cell surfaces and the molecules on the dielectric properties.

In order to investigate the dynamics of the molecules under the influence of the interface interaction, the dielectric dispersion properties of the ferroelectric liquid crystal (CS-1022) were investigated in the frequency range 1 Hz to 10 MHz with varying cell thickness. The cell thickness dependence of the transition temperatures and the magnitude of the spontaneous polarizations were also investigated.

2. Experimental

The ferroelectric liquid crystal CS-1022 (Chisso Petrochemical Co. Ltd) undergoes the phase transition sequence: $Cr \rightarrow S_C^* \rightarrow S_A \rightarrow N^* \rightarrow I$ at $-11°C$, $60°C$, $72°C$, and $85°C$, respectively. The spontaneous polarization is $34\cdot7\,nC\,cm^{-2}$ and the helical pitch in the S_C^* phase is $14\,\mu m$ at 25°C. The cells with thickness 2, 3, 8, 20, 50 and $100\,\mu m$ were prepared in the following way. Polyimide was spin-coated on ITO (indium–tin oxide) coated glass plates and dried at 100°C. The coated surfaces were cloth rubbed to get homogeneous alignment of the molecules. The cell was made by sandwiching two glass plates with appropriate spacers and the liquid crystal was filled in the cell in an oven kept at 100°C. The specimen was placed in a hot stage made from copper to improve uniformity in temperature at the specimen site. The temperature was monitored with an alumel–chromel thermocouple. Dielectric measurements were performed using an impedance analyser (Schlunberge 1260) controlled through a GP-IB interface by a personal computer (PC9801 Vm). The real and imaginary parts of the dielectric constants, ε' and ε'', in

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the frequency range 1 Hz to 10 MHz (1000 points in a logarithmic scale) were measured while the temperature was kept constant. Measurements were performed in a heating process from 25 to 65°C in 0·2°C to 0·5°C increments. The measuring field was 0·1 V_{pp} and no bias field was applied. The effect of the polymer films on the measured dielectric constant was neglected. The temperature was controlled by a temperature control unit (Chino KP 1150) through a RS232C interface by a personal computer (PC9801 Vm). The accuracy in temperature control was to within ±0·05°C.

The temperature dependence of the spontaneous polarization was measured by using a triangular wave method [14]. The triangular signal from the function generator (Iwatsu Electric Co. Ltd FG-350) through a power amplifier (NF electronic Instrument 4005) was applied to the cell with series resistance (38 kΩ). The voltage on the resistance was monitored by a digital oscilloscope (Kikusui 7061) and transferred to a personal computer (PC 9801VX) through a GP-IB interface.

3. Results

The temperature dependences of real (ε') and imaginary (ε'') parts of the dielectric constants of the FLC with a 2 μm cell thickness (thin cell) at 10 Hz, 100 Hz, 1 kHz, 10 kHz, 100 kHz and 1 MHz are shown in figure 1 (a) and (b). The magnitude of ε' was in the order of the cell thickness and inversely proportional to the frequencies in both the S_C^* and S_A phases. The dielectric constants ε' at 10 Hz, 100 Hz and 1 kHz were almost independent of temperature in the S_C^* phase and exhibited rather abrupt decreases in the region just below the S_C^*–S_A transition. The dielectric constant ε' measured at 10 kHz exhibited a tiny peak at the S_C^*–S_A transition. The imaginary part ε'' at 1 kHz showed the largest value at room temperature. The ε'' measured at 10 Hz increased with increasing the temperature and exceeded that measured at 1 kHz. The ε'' measured at 100 kHz exhibited a tiny peak at the S_C^*–S_A transition.

The temperature dependences of the dielectric constants of the FLC with a cell thickness of 50 μm (thick cell) at 10 Hz, 100 Hz, 1 kHz, 10 kHz, 100 kHz and 1 MHz are shown in figure 2 (a) and (b). The magnitude of the dielectric constants ε' were more than ten times larger than those of the thin cell specimen. Though the magnitude of the dielectric constants of thick cells were larger in comparison with those of the thin cell specimens, the temperature dependence was almost the same as that of the thin cell specimen. The ε'' did not show a remarkable temperature dependence in the S_C^* phase and showed a rather abrupt decrease just below the S_C^*–S_A transition temperature. The Cole–Cole plots for the thin and thick cell specimens are shown in figure 3 (a) and (b).

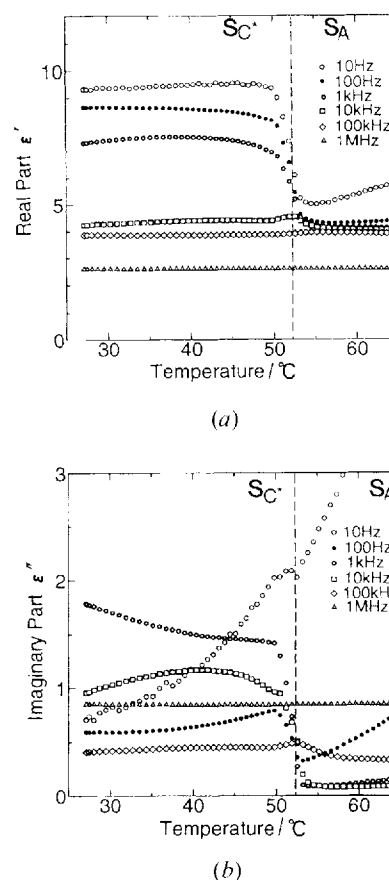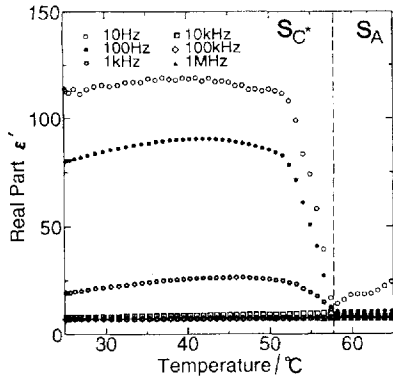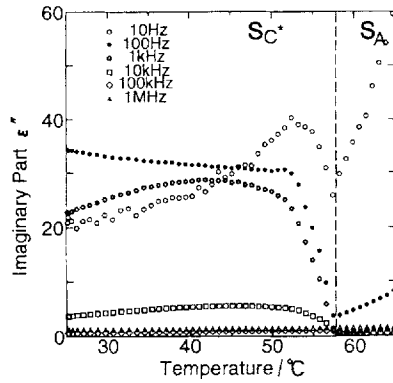The cell thickness dependence of the dielectric con-

Figure 1. Temperature dependences of (a) the real part ε' and (b) the imaginary part ε'' of the complex dielectric constants at 10, 100, 1 k, 10 k, 100 k and 1 MHz for CS-1022. The cell thickness is 2 μm.

stants of the FLC was systematically measured at 10 Hz. The temperature dependences of the dielectric constants ε' at 10 Hz for the specimens with a thickness of 2, 3, 8, 20, 50 and 100 μm are shown in figure 4. The magnitude of the dielectric constants ε' was proportional to the cell thickness and the transition temperature decreased with diminishing the cell thickness. The cell thickness dependence of the S_C^*–S_A transition temperature is shown in figure 5. The transition temperatures for those of the bulk specimen are almost independent of the cell thickness but for the SSFLC rapidly decrease with further decrease of the cell thickness as shown in figure 5.

The frequency dependence of the real and imaginary parts of the dielectric constants at room temperature was measured with varying the frequencies from 1 Hz to 1 MHz for the specimens with cell thicknesses of 2, 3, 8, 20 and 50 μm. The results are shown in figure 6 (a) and (b). These results show that there exists a typical Debye-type relaxation around several hundred Hz. The relaxation frequencies shifted to the higher frequency side with diminishing the cell thickness.
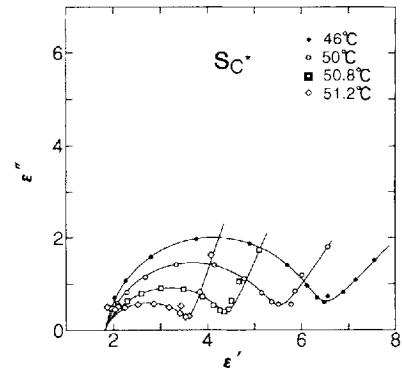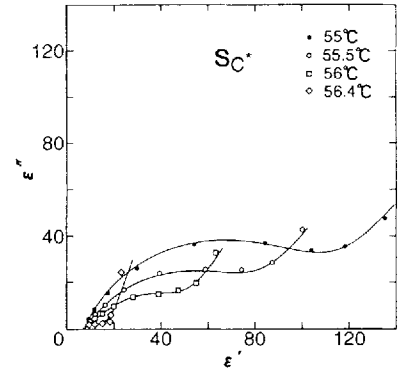
Figure 2. Temperature dependences of (a) the real part ε' and (b) the imaginary part ε'' of the complex dielectric constant at 10, 100, 1 k, 10 k, 100 k and 1 MHz for CS-1022. The cell thickness is 100 μm.

The temperature dependences of the spontaneous polarizations for the specimens with a cell thickness of 3, 8, 20 and 50 μm were measured by using the triangular wave method. The results are shown in figure 7. The amplitudes of the applied triangular waves were 48, 96, 60 and 160 V_{pp} for the specimens with cell-thicknesses of 3, 8, 20 and 50 μm, respectively. The amplitude of the applied voltage to achieve saturation of the spontaneous polarization in the specimens with a cell thickness of 3 and 8 μm (thin cell) was 3 or 4 times larger than those of the specimens with 20 and 50 μm (thick cell). The temperature dependence was almost the same for the specimens with a cell thickness of 20 and 50 μm. The magnitudes of the spontaneous polarization of the thin cell specimens were smaller than those of thick cell specimens. The specimen with a 3 μm cell thickness exhibited a trace of the switching current even after passing through the S_C^*–S_A transition. The solid lines represent the results of the least-squares fitting of the data to the formula $P_0(T_C - T)^\alpha$ [13], where T_C and α

Figure 3. Cole–Cole plots: (a) 2 μm thickness cell and (b) 50 μm thickness cell in the S_C^* phase around the S_C^*–S_A phase transition.
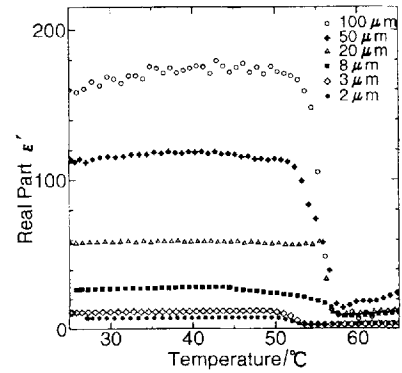

Figure 4. Temperature dependences of the real part ε' of the complex dielectric constant at 10 Hz for various cell thicknesses.

represent the transition temperature and the index of critical exponent.

4. Discussion

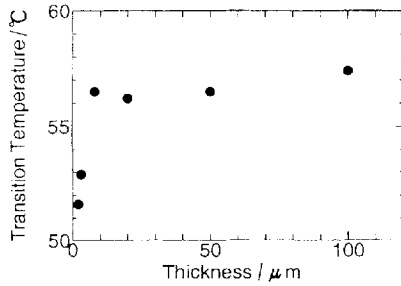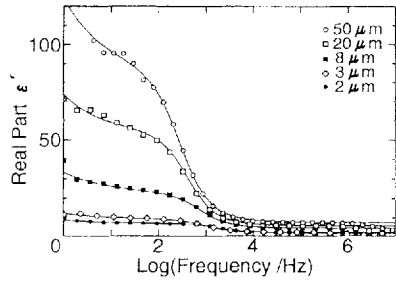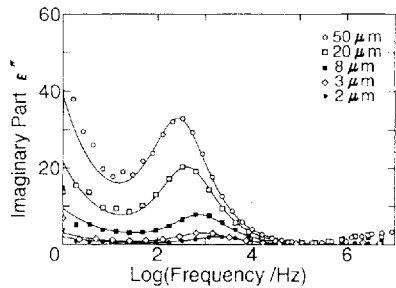The dielectric properties of the FLC around the S_C^*–S_A transition were investigated with varying the cell-

Figure 5. Cell thickness dependence of the S_C^*–S_A phase transition temperature.

(a)

(b)

Figure 6. Frequency dependences of (a) ε' and (b) ε'' for specimens with various cell thicknesses.
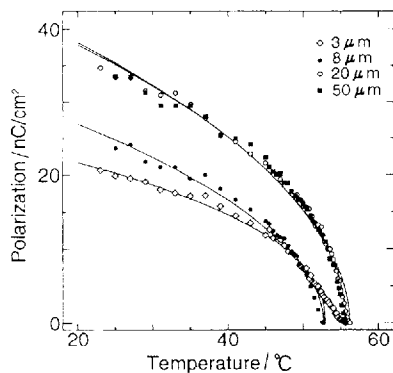

Figure 7. Temperature dependence of the magnitude of spontaneous polarization for specimens with various cell thicknesses. The solid line represents the fitting to the $P = P_0(T_C - T)^x$.

thickness. The temperature dependence of the dielectric constants ε' and ε'' for the thin cell (2 μm) and thick cell (50 μm) specimens was measured. The magnitude of the dielectric constants ε' in the S_C^* phase measured above 1 kHz was almost the same for both specimens but that measured below 1 kHz exhibited a large difference as seen in figures 1 and 2. The dielectric response in the S_C^* phase is supposed to be mainly due to the contribution of the Goldstone mode. The experimental results indicate that the relaxational frequency of the Goldstone mode is around 1 kHz and the contribution of the Goldstone mode is suppressed for the thin cell specimen. The Cole–Cole diagrams for the specimens with a cell thickness of 2 and 50 μm as shown in figure 3 indicate that the radius of the semicircle for the thin specimen is much smaller than that of thick specimen and the shape of the semicircle is deformed for the thick specimen. The dielectric constants of the specimens with cell thicknesses of 2, 3, and 8 μm, which are less than the helical pitch in the S_C^* phase are much smaller than those of the specimens with a thicker cell thickness as shown in figure 4. The transition temperature depends on the cell thickness as shown in figure 5 and this agrees qualitatively with the result of Pikin and Yoshino [12]. The result indicates that the effect of surface anchoring cannot be neglected for the thin cell [11].

The temperature and frequency dependences of the dielectric constants for the specimens with cell thicknesses of 2, 8 and 50 μm were analysed by fitting them to a modified Debye-type relaxational expression. The complex dielectric constant ε for fitting was assumed to be

$$\varepsilon - \varepsilon_\infty = \frac{\Delta\varepsilon_S}{1 + (j\omega\tau_S)^{\beta_S}} + \frac{\Delta\varepsilon_G}{1 + (j\omega\tau_G)^{\beta_G}} + \frac{1}{(j\omega\tau_C)^\gamma} \quad (1)$$

where the first and the second terms on the right-hand side indicate the contributions from the soft mode and the Goldstone mode, respectively, and the third term represents the complex conductivity [3,8,9]. Since the contribution from the soft mode can be neglected in the S_C^* phase except for close to the transition, the experimental data were analysed in the S_C^* phase and the fitting to the expression was carried out with varying the parameters τ_G, τ_C, β_G and γ.

The temperature dependence of the dielectric strength $\Delta\varepsilon$, the index β, and the relaxation frequency for the specimens with 2, 8 and 50 μm in the S_C^* phase is shown in figure 8 (a), (b) and (c), respectively. The $\Delta\varepsilon$ is constant in the S_C^* phase except in the vicinity of the S_C^*–S_A transition. The dielectric strength strongly depends on the cell thickness: $\Delta\varepsilon$ decreases remarkably with decreasing cell thickness as shown in figure 8 (a). The index β indicates the degree of deviation from the single Debye-
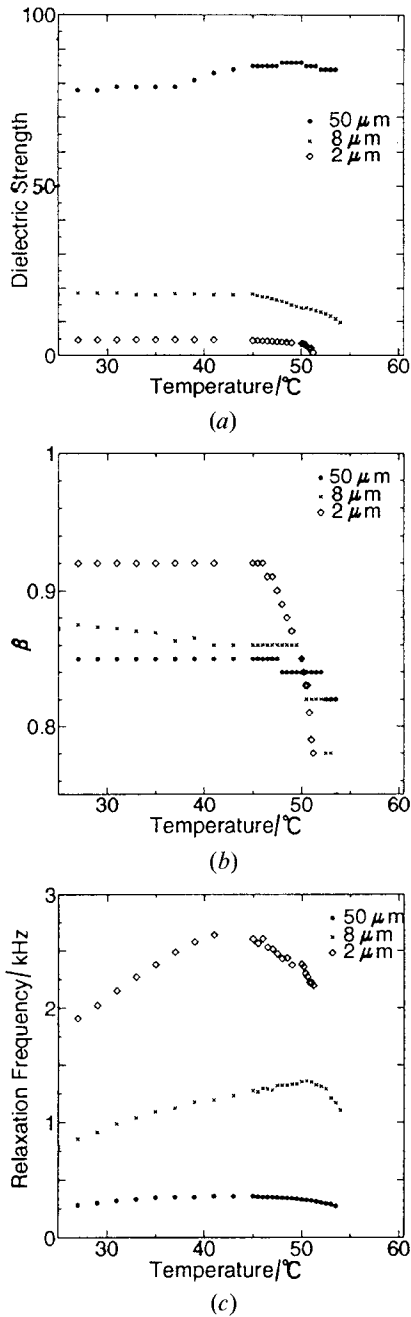
Figure 8. Temperature dependences of (a) the dielectric strength, (b) the index β and (c) the relaxation frequency for the Goldstone mode.

than that of the thin cell specimen. The molecular motion in thin cell may be somewhat restricted due to the surface anchoring.

The cell thickness dependence of the dielectric strength, the index β and the relaxation frequency at room temperature are shown in figure 9 (a), (b) and (c), respectively. The dielectric strength depends on cell thickness: the dielectric strength increases with increasing cell thickness. This indicates that the molecular motion responsible for the dielectric response in the thick cell will be much freer than that of the thin cell specimens. The index β depends slightly on the cell thickness for the specimens of 2, 3 and 8 μm but almost independent for the thicker cell specimens. On the other hand, the

Figure 9. Cell thickness dependences of (a) the dielectric strength, (b) the index β and (c) the relaxation frequency for the Goldstone mode at room temperature.

type relaxation process. The deviation is rather small for the thin cell specimens but becomes slightly larger for the thick cell specimens as shown in figure 8 (b). The relaxation frequency depended significantly on the cell thickness: the relaxation frequency became higher with diminishing the cell thickness. This indicates that the characteristic molecular motion responsible for the fluctuation of the azimuthal angle in the thick cell is slower

relaxation frequencies increased remarkably with diminishing cell thickness in the region below $20\,\mu m$.

The magnitude of the spontaneous polarization depends on the cell thickness as shown figure 7. This implies that in the thin cell whose thickness is much smaller than the helical pitch, the switching of the azimuthal angle of the molecules will be suppressed. A trace of the switching current after passing through the transition as seen in the specimen with a cell thickness of $3\,\mu m$ may be due to the smearing out of the transition temperature because of the biasing field as has been observed for crystalline ferroelectrics with a 2nd order phase transition [15]. The cell thickness dependence of the parameters P_0, α and T_C in the formula $P = P_0(T_C - T)^\alpha$ are shown in figure 10 (a), (b) and (c), respect-

ively. Within experimental error, it can be said that P_0 tends to decrease with diminishing cell thickness. The index α is nearly constant except for the specimen of $3\,\mu m$ cell thickness. The cell thickness dependences of P_0 and the index α are similar to that reported by Patel *et al.* [13]. T_C tends to decrease with diminishing cell thickness. The cell thickness dependence of the transition temperature (T_C) determined from the dielectric measurements (see figure 5) exhibits the same tendency as shown in figure 10 (c).

5. Conclusions

The dielectric dispersion of the ferroelectric liquid crystal (CS-1022) around the S_C^*–S_A transition and the temperature dependence of the spontaneous polarization were investigated by varying the cell thickness. The temperature and frequency dependences of the dielectric constants were analysed by fitting them to the modified Debye-type relaxation formula including the contribution of the soft mode, the Goldstone mode and the ionic conductivity.
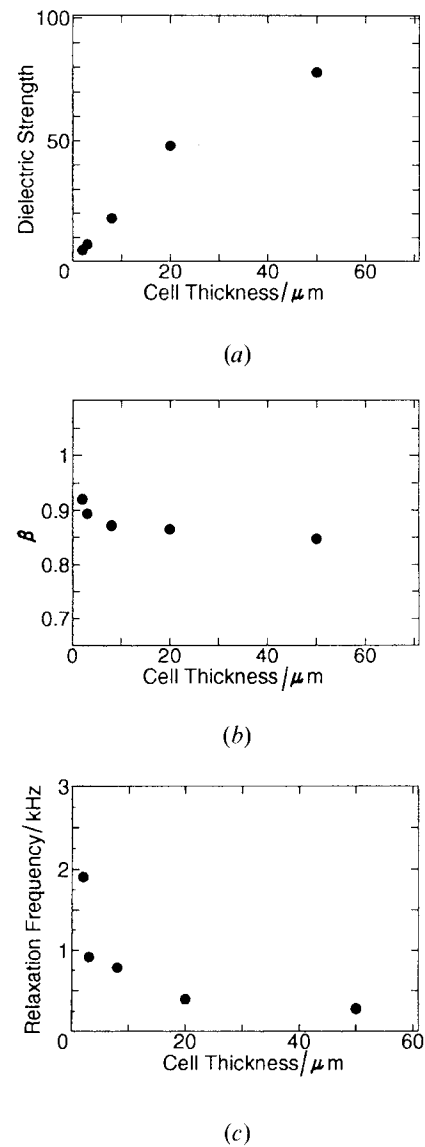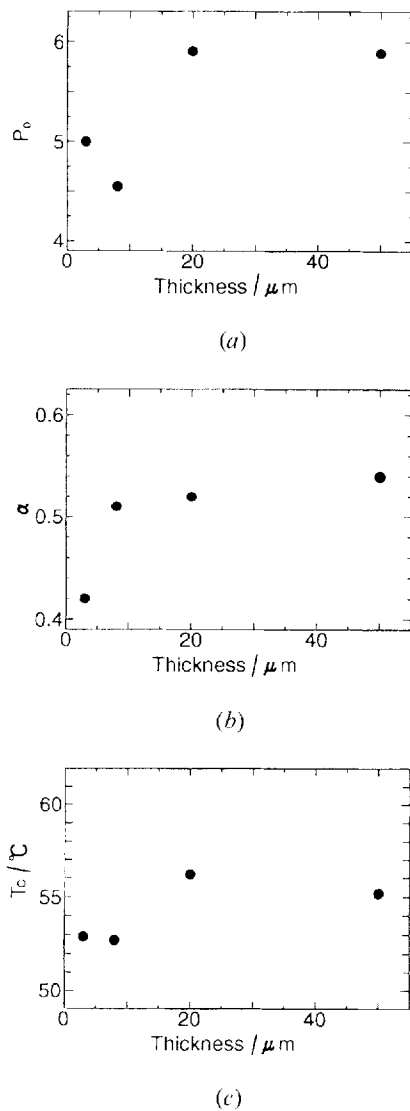
The temperature and cell thickness dependence of the dielectric strength, the index β and the relaxation frequency of the Goldstone mode was determined. The dielectric strength for the Goldstone mode is nearly proportional to the cell thickness. The relaxation frequency and the index β for the Goldstone mode depend on the cell thickness as the helical structure is unwound. The index β approaches unity and the relaxation frequency increases with diminishing the cell thickness. The magnitude of the spontaneous polarization and the transition temperature vary significantly with diminishing cell thickness for the specimen with a cell thickness less than the helical pitch; however, for the specimens with a cell thickness greater than the helical pitch, these values do not depend on cell thickness.

Figure 10. Cell thickness dependence of (a) P_0, (b) β and (c) T_C for the equation $P = P_0(T_C - T)^\alpha$.

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