Helix elastic modulus in a ferroelectric liquid crystal with varying helical pitch

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Method for determination of the helix elastic modulus (K_h) in ferroelectric liquid crystals (FLCs) from dielectric spectra is proposed. According to the method, temperature dependencies of the dielectric strength of the Goldstone mode and the Goldstone frequency as well as main ferroelectric parameters were measured for the induced FLC mixtures with helical pitch (p_0) known from the selective light reflection measurements. From these data, the helix elastic modulus was calculated using an existing theoretical approach. It appears that, near the SmA^*–SmC^* phase transition, there is remarkable dependence of the helix elastic modulus on the helical pitch; more specifically, the stiffness of helix decreases with p_0. However, at lower temperatures the K_h dependence on p_0 tends to weaken. From these results, it is concluded that, well away from the SmA^*–SmC^* phase transition, the K_h obtained for FLCs with known p_0 can be used as the constant for determination of p_0 which cannot be determined from the selective light reflection. It is also shown that mechanism of the dielectric relaxation in the studied FLC mixtures is not of Debye type and there are several characteristic relaxation times in a FLC cell.

Keywords: ferroelectric liquid crystals, the Goldstone mode, helix elastic modulus, helical pitch.

Модуль пружності гелікоїда у сегнетоелектричному рідкому кристалі зі змінним кроком спіралі. *К.Попова, В.Михайленко, В.Семиноженко, О.Кривошей, О.Федоряко*

Запропоновано метод визначення модуля пружності спіралі (K_h) у сегнетоелектричних рідких кристалах (СРК) за діелектричними спектрами. За цією методикою виміряно температурні залежності амплітуди дисперсії діелектричної проникности та частоти Голдстоунівської моди, основні сегнетоелектричні параметри для індукованих СЖК сумішей із кроком спіралі (p_0), відомим з вимірювань селективного відображення світла. Виявлено, що поблизу фазового переходу SmA^*–SmC^* спостерігається помітна залежність модуля пружності гелікоїда від кроку спіралі, зокрема, жорсткість спіралі зменшується зі зменшенням p_0. Однак при нижчих температурах залежність K_h від p_0 має тенденцію до поменшання. З цих результатів можна зробити висновок, що далеко від фазового переходу SmA^*–SmC^* значення K_h, отримане для СЖК з відомим p_0, можна використовувати як константу для визначення p_0, яке не може бути визначено з селективного відображення світла. Також показано, що механізм діелектричної релаксації у СРК сумішах, що досліджено, не є дебаєвським та у СРК комірці існує декілька характерних часів релаксації.

Предложен метод определения модуля упругости спирали (K_h) в сегнетоэлектрических жидких кристаллах (СЖК) по диэлектрическим спектрам. В соответствии с этим методом измерены температурные зависимости амплитуды дисперсии диэлектрической проницаемости и частоты Голдстоуновской моды, основные сегнетоэлектрические пара-

метры для индуцированных СЖК смесей с шагом спирали (p_0), известным из измерений селективного отражения света. По этим данным рассчитан модуль упругости спирали с использованием существующей теоретической модели. Обнаружено, что вблизи фазового перехода SmA*–SmC* наблюдается заметная зависимость модуля упругости геликоида от шага спирали, а именно, жесткость спирали уменьшается с уменьшением p_0. Однако при более низких температурах зависимость K_h от p_0 имеет тенденцию к ослаблению. На основе этих результатов можно сделать вывод, что вдали от фазового перехода SmA*–SmC* значение K_h, полученное для СЖК с известным p_0, можно использовать в качестве константы для определения p_0, которое не может быть определено из селективного отражения света. Также показано, что механизм диэлектрической релаксации в исследуемых смесях СЖК не является дебаевским и в ячейке СЖК существует несколько характерных времен релаксации.

Ferroelectric liquid crystals (FLCs) are considered as promising materials for various display and photonic applications because of their inherently fast (in µs range) electrooptical response [1–4]. One concept of the practical use of FLC materials is based on deformed helix FLC (DHFLC) [5]. The characteristic relaxation time of perturbations of the helix structure (τ_{off}) in the DHF effect in the case of small helix deformation (well below critical field) is described by the equation (1):

$$\tau_{off} = \frac{\gamma_\varphi p_0^2}{2\pi K_h \sin^2\theta}. \qquad (1)$$

where γ_φ is rotational viscosity, K_h is helix elastic modulus, and θ is tilt angle [6]. Additionally, to secure the high optical contrast for the DHFLC cell it is important to avoid the Bragg diffraction due to the FLC helix [7]. According to [8], the critical pitch below which no diffraction appears in the visible range is ≈ 240 nm, for the normal light incidence, and ≈ 130 nm for the oblique incidence.

Knowledge of all terms from the equation (1) is important from both fundamental and practical point of view. Actually, τ_{off} and θ can be measured [8], γ_φ can be estimated by different approaches [8, 9], and p_0 can be calculated from selective light reflection (λ_{max}) data [8, 10, 11]. However, when p_0 is well below 130 nm it cannot be either measured or estimated from λ_{max} measurements reliably. Thus, in order to calculate p_0 using equation (1), knowledge of the helix elastic modulus (K_h) is needed. At the same time K_h, was only estimated in [12] indirectly from dependences of electrically-controlled birefringence on applied electric field for a FLC material with the helical pitch of single value (330 nm). Further, it was assumed that K_h is almost independent of helical pitch [13]. However, experimental

studies on K_h as function of p_0 were not conducted.

From the other hand, due to change in symmetry of the SmC phase when it becomes ferroelectric SmC*, dispersion occurs in the dielectric spectrum of a FLC that is referred as the Goldstone mode [14]. There is a theory which gives a relationship between the Goldstone mode (GM) and FLC parameters [15, 16]. According to the theory, FLC parameters are related to the dielectric spectrum by the following equation:

$$f_G = \frac{K_h p_0^2}{8\pi^3 \gamma_G}, \qquad (2)$$

where γ_G is viscosity given by:

$$\gamma_G = \frac{P_S^2}{4\pi\varepsilon_0 \theta^2 \Delta\varepsilon_G f_G}, \qquad (3)$$

where $\Delta\varepsilon_G$ is the dielectric strength of the GM which is known from the dispersion amplitudes of real part of complex dielectric permittivity, and f_G is the Goldstone frequency which can also be estimated from the dielectric spectra. And thus, K_h can be obtained from dielectric studies on the Goldstone mode provided that all other pa-
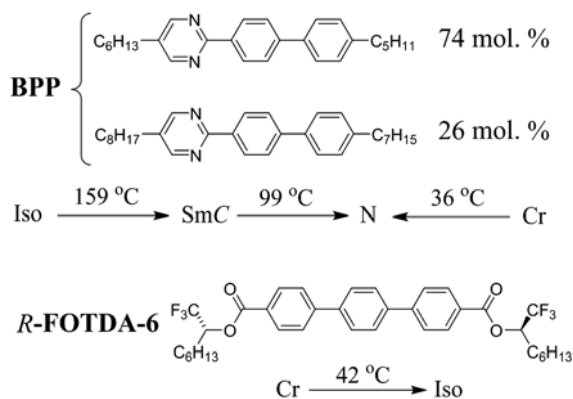

Fig. 1. Chemical structures and phase transition temperatures of the FLC components.
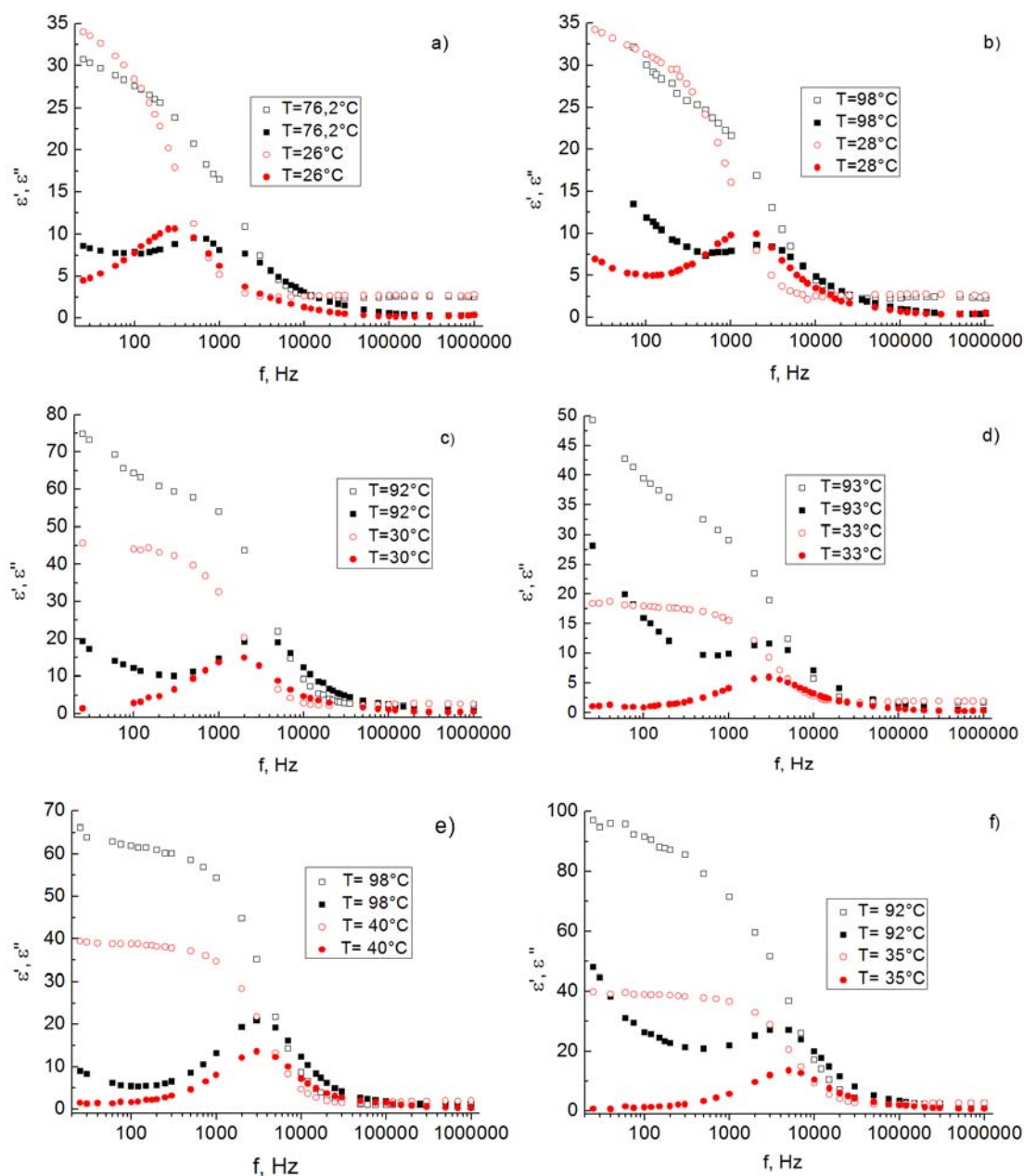
Fig. 2. Typical dependences of real (ε', $\square$, $\bigcirc$) and imaginary (ε'', $\blacksquare$, $\bullet$) parts of dielectric permittivity on frequency (f) at different temperatures for the mixtures of (a) 5.0, (b) 9.7, (c) 12.6, (d) 14.8, (e) 17.8, (f) 23.9 mol. % *R*-**FOTDA-6** in **BPP**.

rameters (p_0, P_S, θ) are known. To this end, for an induced SmC* material obtained by doping non-chiral SmC host with a chiral component (CC) [17], p_0 values can be varied simply by changing concentration of a CC.

Thus, aims of this work are (i) to elucidate type of the dependence of the helix elastic modulus on helical pitch from dielectric spectral data on the Goldstone mode using FLC mixtures with known helical pitch, and (ii) to judge on correctness of

using the helix elastic modulus for estimations of helical pitch values that cannot be reliably measured or estimated from the selective light reflection.

2. Experimental

As induced FLCs with varying helical pitch, we used binary mixture **BPP** of biphenylpyrimidines as a wide-range non-chiral LC host and non-mesogenic high-twisting compound *R*-**FOTDA-6** as the CC at different concentrations (from 5.0 to
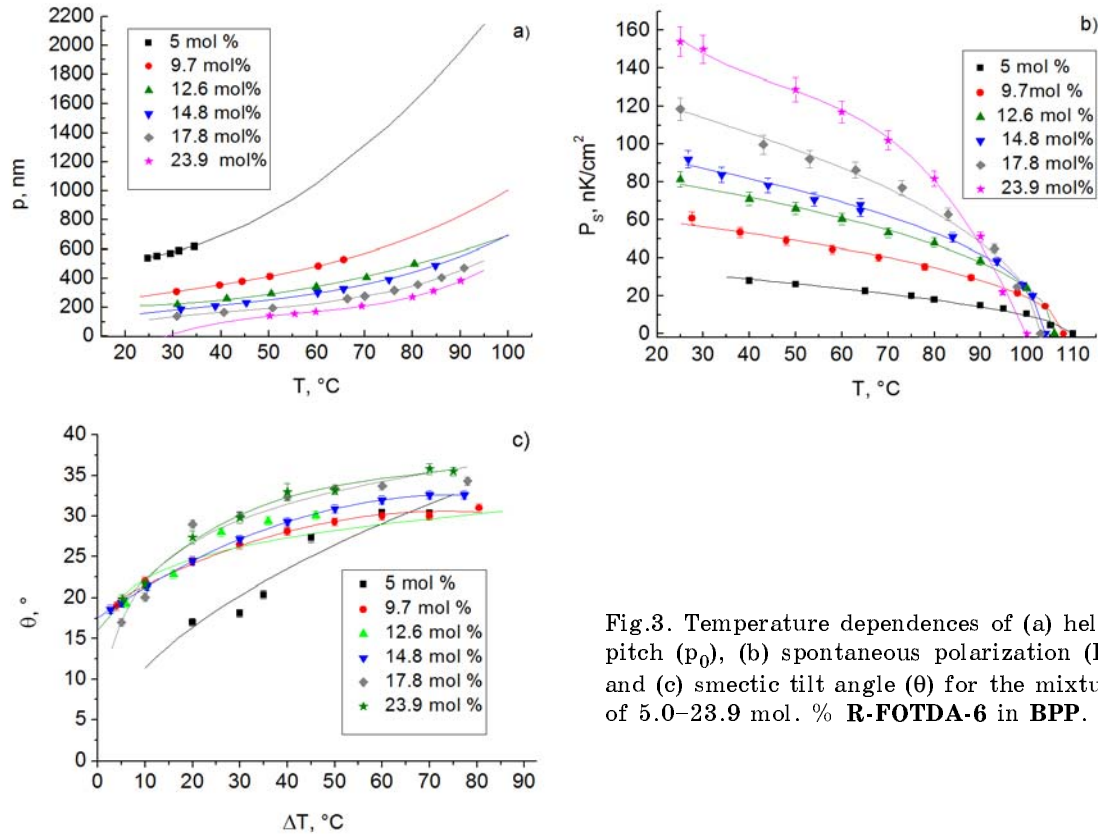
Fig.3. Temperature dependences of (a) helical pitch (p_0), (b) spontaneous polarization (P_S), and (c) smectic tilt angle (θ) for the mixtures of 5.0–23.9 mol. % **R-FOTDA-6** in **BPP**.

23.9 mol. %)) in the **BPP** with (Fig. 1) [8]. The phase transition temperatures and helical pitch values of the FLCs were measured as described in [8].

Electro-optical measurements were made using commercially available LC2-5.0 cells (INSTEC, thickness of 5 μm, an electrode area of 25 mm^2, planar boundary conditions) and using cells self-fabricated by known technique [18]. The P_S values of SmC* mixtures were measured using the polarization reversal current method [19, 20]. The θ measurements were performed according to the known method [21]. Dielectric studies were done with the use a E7-20 immittance meter ("MNIPI" Public Joint Stock Company, Republic of Belarus) 25–10^6 Hz.

3. Results and discussion

For the FLC mixtures, dielectic spectra ($\varepsilon'(f)$, $\varepsilon''(f)$) and ferroelectric parameters (P_S, θ) were measured (Fig. 2 and 3 respectively).

Dielectric strength ($\Delta\varepsilon_G$) can be determined from the $\varepsilon'(f)$ dependence (Fig. 4) [22].

It is seen from Fig. 4 that the $\Delta\varepsilon_G$ increases with temperature especially at higher CC concentrations. According to the generalized Landau model [23], the dispersion amplitude is given by:

$$\varepsilon_0\varepsilon_G(T) = \lim\frac{<P_i>}{E}, \qquad (4)$$

where $<P_i>$ is average induced polarization, ε_0 is permittivity of free space, and E is the magnitude of applied static electric field. Specifically, the dispersion amplitude is given as follows [23]:

$$\varepsilon_0\varepsilon_G(T) = \left(\frac{1}{2K_h}\right)\left(\frac{p_0 P_S}{2\pi\theta}\right)^2. \qquad (5)$$

Since, according to the theory [23], K_h does not depend on temperature, and θ has weak temperature dependence for all studied mixtures (see Fig. 3), variations of $\Delta\varepsilon_G$ with temperature are determined mainly by variations of p_0 and P_S.

Goldstone frequencies (f_G) were determined from maxima of $\varepsilon''(f)$ dependences (see Fig. 4) [22]. It is seen that f_G initially increases with temperature but decreases again when approaching to the SmC*–SmA* phase transition. It seems that such behaviour is related to an effect of the so-called soft mode (i.e. tilt angle fluctuations [14]). Complex dielectric permittivity $\varepsilon^*(f,T)$ can be written as:
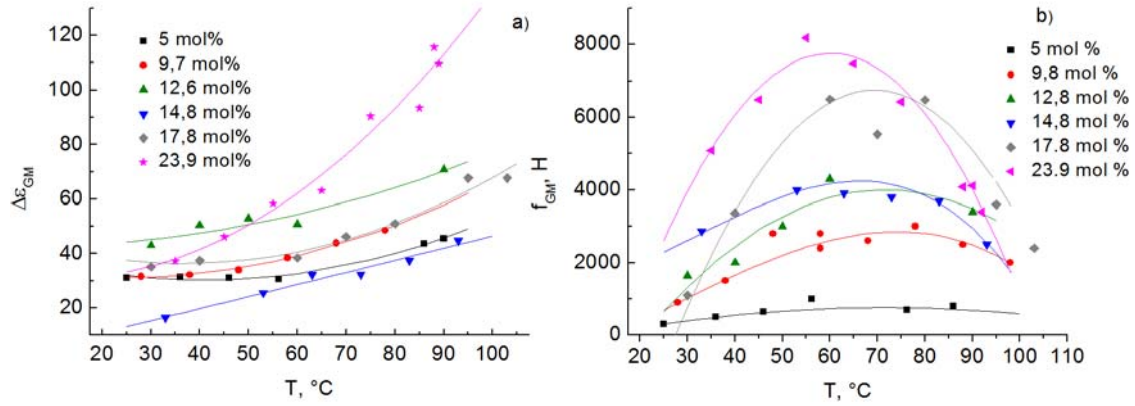
Fig. 4. Temperature dependences of (a) dispersion amplitude of dielectric permittivity ($\Delta\varepsilon_G$), and (b) the Goldstone frequency (f_G) for the mixtures of 5.0–23.9 mol. % *R*-**FOTDA-6** in **BPP**.

$$\varepsilon^*(\omega,T) = \left(\frac{\Delta\varepsilon_G(T)}{1 + i\omega t_G}\right) + \left(\frac{\Delta\varepsilon_S(T)}{1 + i\omega t_S}\right)^2, \quad (6)$$

where t_G, t_S are characteristic relaxation times of the Goldstone mode and the soft mode, respectively. Depending on temperature, the soft mode relaxation frequency changes in the range of 10^3–10^7 Hz and it decreases on approaching to the SmC*–SmA* phase transition [24]. At the same time, the Goldstone frequency changes in the range of 10–10^4 Hz [24]. In such a way, near the phase transition these two modes have comparable frequencies. This fact is thought to be a condition of interaction between these modes.

The Cole-Cole diagrams were used in order to clarify the mechanism of the dielectric relaxation. Complex dielectric permittivity $\varepsilon^*(f, T)$ described by the Cole-Cole distribution can be written as:

$$\varepsilon^* - \varepsilon(\infty) = \frac{\varepsilon_G}{1 + (jf/f_G)^{1-\alpha_G}} + \frac{\varepsilon_S}{1 + (jf/f_S)^{1-\alpha_S}} \quad (7)$$

where $\varepsilon(\infty)$ is dielectric permittivity limit at high frequencies, f_G and f_S are relaxation frequencies of the Goldstone mode and the soft mode respectively, α_G, α_S are respective distribution parameters, and ε_G, ε_S are dielectric strengths of the Goldstone mode and the soft mode, respectively [14]. The Cole-Cole diagrams $\varepsilon''(\varepsilon')$ were plotted (Fig. 5).

As it follows from the Fig. 5, Cole-Cole index is about 0.3 for all studied concentrations whereas it is expected to be 1.0 for the Debye relaxation mechanism [14]. Consequently, there are several characteristic relaxation times in a cell. It is thought that

this effect is related to the presence of near-electrode areas where helix is additionally deformed by cell plates [25]. As a result, the additionally deformed helix has different characteristic relaxation time.

Using the experimental data and equations (2) and (3), the dependences of the K_h on the CC concentration (i.e. on the helical pitch) at different temperatures were obtained (Fig. 6).

According to the theory [15, 16], there is a restriction that the equations (2) and (3) hold true only near the SmA*–SmC* phase transition (where tilt angle does not exceed ~ 20°). Under these circumstances, the K_h should not depend on temperature. However, in the present case, the SmC* temperature range is essentially wider than 20°C, and tilt angle reaches values essentially higher than 20° (see Fig. 3c). Therefore, the K_h may depend on temperature. Indeed, near and far from the SmA*–SmC* phase transition, the behaviour of the K_h is different. At high temperatures, pronounced dependence of the K_h is seen at relatively low concentrations of the CC (i.e. for long pitches, see Fig. 3a and 6), and as the pitch becomes shorter the dependence weakens. However, well away from the SmA*–SmC* phase transition, the helix elastic modulus does not depend strongly on the helical pitch in wide range of p_0 values, and therefore it can be used as the constant for confident estimations of p_0 by the equation (1).

4. Conclusions

In summary, for the short-pitch induced ferroelectric liquid crystal, we have shown that, near the SmA*–SmC* phase transition, there is remarkable dependence of the helix elastic modulus on the helical pitch; more
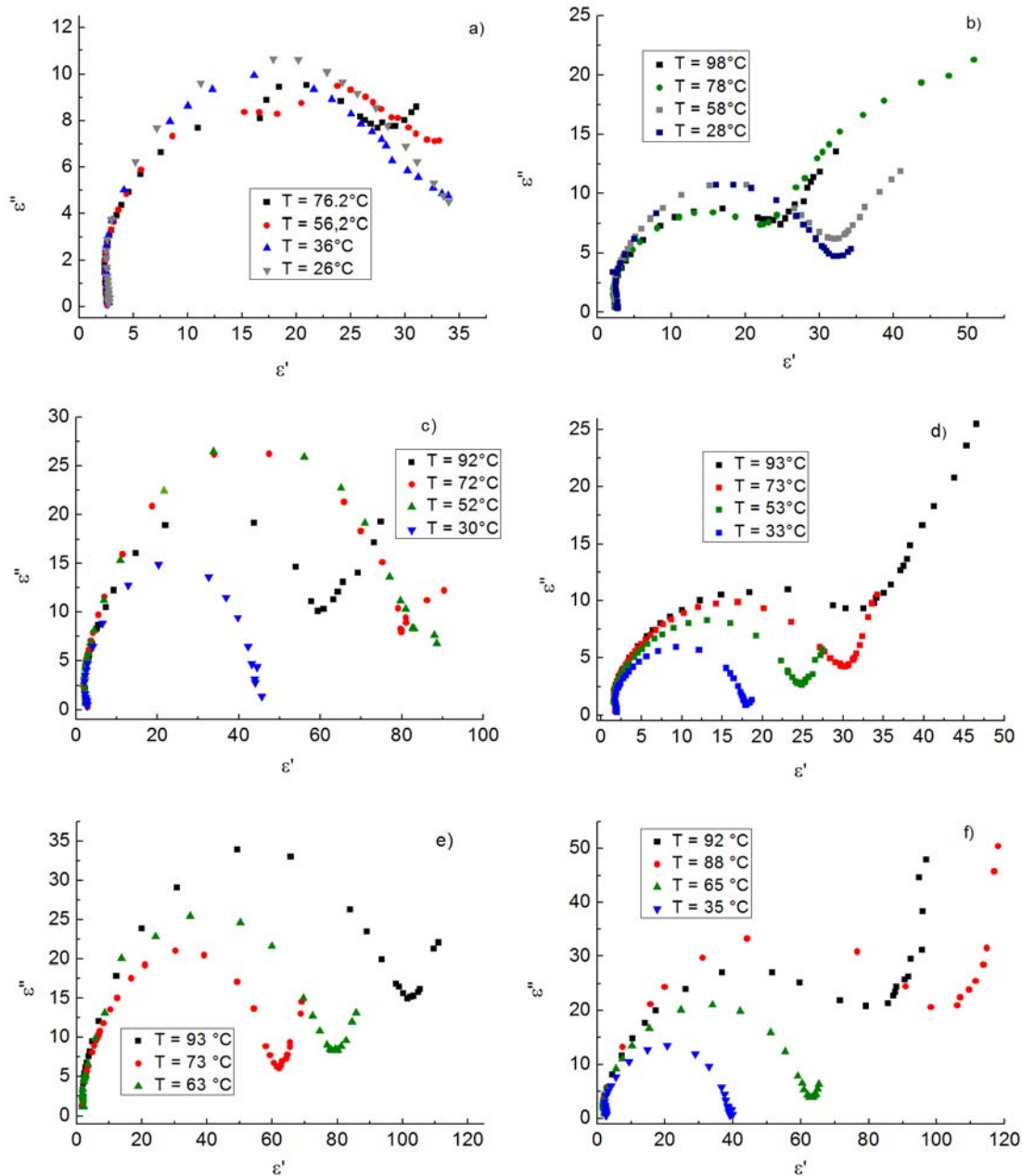
Fig. 5. Cole-Cole diagrams at different temperatures for the mixtures of (a) 5.0, (b) 9.7, (c) 12.6, (d) 14.8, (e) 17.8, (f) 23.9 mol. % *R*-**FOTDA-6** in **BPP**.

specifically, the stiffness of helix decreases with p_0. However, at lower temperatures the K_h dependence on p_0 tends to weaken. From these results we conclude that, well away from the SmA^*–SmC^* phase transition, the K_h obtained for FLCs with known p_0 can be used as the constant for determination of p_0 which cannot be determined from the selective light reflection. We have also shown that mechanism of the dielectric relaxation in the studied FLC mixtures is not of Debye type and there are several characteristic relaxation times in a FLC cell.

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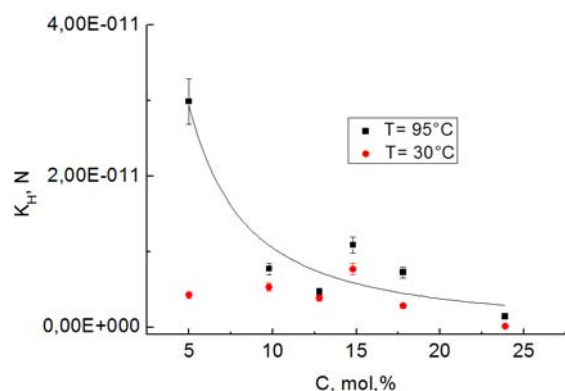
Fig. 6. Dependence of the helix elastic modulus on concentration of *R*-**FOTDA-6** in **BPP** at different temperatures.

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