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Liquid Crystals

Publication details, including instructions for authors and subscription information:
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To cite this Article Skuridin, S. , Badaev, N. , Dembo, A. , Lortkipanidze, G. and Yevdokimov, Yu.(1988) 'Two types of temperature induced transitions of poly(I) · poly(C) liquid crystals', Liquid Crystals, 3: 1, 51 — 62

To link to this Article: DOI: 10.1080/02678298808086349

URL: http://dx.doi.org/10.1080/02678298808086349

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LIQUID CRYSTALS, 1988, VOL. 3, NO. 1, 51–62

Two types of temperature induced transitions of poly(I) · poly(C) liquid crystals

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(*Received 18 March 1987; accepted 2 July 1987*)

Small-angle X-ray scattering curves, C.D. spectra and textures of the liquid-crystalline phase formed from poly(I) · poly(C) in water-salt solutions containing poly(ethyleneglycol) have been obtained at different temperatures. It was found that heating the poly(I) · poly(C) liquid-crystalline phase is accompanied by two types of transitions, the first being cholesteric → compensated structure → cholesteric and the second being cholesteric → isotropic state transition. The latter transition takes place at a temperature which corresponds to that of separation of chains of a double-stranded poly(I) · poly(C) molecule. The temperature dependence of the abnormally high optical activity of poly(I) · poly(C) liquid crystals allows us to estimate the order parameter of poly(I) · poly(C) molecules in both the liquid-crystalline phase and the liquid-crystalline microphases.

1. Introduction

The possibility to obtain the liquid-crystalline state of DNA molecules (or segments of the DNA molecule) in biological systems attracts the attention of both experimentalists and theoreticians [1, 2]. Because of the complex structure of biological objects, modelling seems to be the most convenient tool for investigation, for instance, the formation of liquid crystals from natural and synthetic nucleic acids, *in vitro*. The properties of nucleic acids have been studied using two relatively simple model systems, one of them being concentrated water-salt solutions of nucleic acids, the other is composed of particles of a dispersed phase (microphases) which are formed during the intermolecular condensation of nucleic acid molecules of low molecular mass ($< 1 \times 10^6$) in water-salt solutions containing poly(ethyleneglycol).

For concentrated water-salt solutions of DNA, there has been elaborated a method for the preparation of thin layers of these solutions, the textures of which prove directly not only the liquid-crystalline nature of DNA phases but also the existence of twisted (cholesteric) liquid crystals of DNA [3]. As to the microphases formed via the condensation of DNA molecules in poly(ethyleneglycol) containing water-salt solutions, the speculation concerning their liquid-crystalline nature is based on the appearance of an abnormally intense band in the C.D. spectrum in the absorption region of chromophores incorporated in these microphases [4], that of the small-angle reflections in the X-ray diagrams [5] and specific textures of phases obtained after sedimentation of the DNA microphases [1].

It is also been shown that molecules of double-stranded polyribonucleotide poly(I) · poly(C), like low molecular mass DNA molecules, form a dispersed phase when condensed in water-salt solutions containing poly(ethyleneglycol) [6]. According to the results reported in [6] the formation of the poly(I) · poly(C) dispersed phase is accompanied by the appearance of an intense band in the C.D. spectrum, this band being located in the absorption region of nitrogen bases ($\lambda \sim 260$ nm). This has been interpreted as an indication of the liquid-crystalline nature of the particles of the poly(I) · poly(C) dispersed phase, and the term 'liquid-crystalline microphases of poly(I) · poly(C)' has been introduced to denote them. Heating poly(I) · poly(C) microphases formed under definite conditions leads to a reversal of the sign of the intense band in the C.D. spectrum from negative to positive [5]; at some temperature the amplitude of the band is equal to zero [5]. One of the possible reasons for the absence of high optical activity at a definite temperature is supposed to be the formation of a compensated structure of poly(I) · poly(C) microphases. According to the supposition of [5], the properties of this structure are similar to those of synthetic polymeric nematic liquid crystals. Since this speculation is based only on the disappearance of the intense band in the C.D. spectrum of the liquid-crystalline microphases of poly(I) · poly(C), it is necessary to obtain more direct evidence, based on standard techniques used for the study of polymeric liquid crystals, as this phenomenon cannot be interpreted unequivocally [7].

The present work was undertaken in order to investigate the thermal transitions of poly(I) · poly(C) liquid crystals. X-ray diagrams, textures and C.D. spectra of the liquid-crystalline phases of poly(I) · poly(C) were taken at different temperatures. The data obtained were compared with the C.D. spectra of poly(I) · poly(C) liquid-crystalline microphases, and the order parameter of poly(I) · poly(C) molecules upon transition from the liquid crystal to the isotropic state was estimated.

2. Materials and methods

Poly(I) · poly(C) (Calbiochem, U.S.A.; molecular mass $(0{\cdot}3\text{–}0{\cdot}8) \times 10^6$) and poly(ethyleneglycol) (Loba Chemie, Austria; molecular mass 4000) were used without additional purification. The concentration of poly(I) · poly(C) in the water-salt solutions was determined from the optical density, using the known absorption coefficient ($\varepsilon_{\lambda=260\,\mathrm{nm}} = 5{\cdot}300$).

The poly(I) · poly(C) liquid-crystalline phases were prepared following a two-stage scheme [1]. At the first stage, mixing equal volumes of poly(I) · poly(C) water-salt solution with water-salt poly(ethyleneglycol) solution yielded a dispersed phase of poly(I) · poly(C) which consisted of separate particles (microphases) of poly(I) · poly(C). After about 20 hours following the mixing, the absorption spectra and the C.D. spectra of the particles of the poly(I) · poly(C) dispersed phase were taken on a Specord M 40 spectrophotometer and a Roussel–Jouan CD-185 dichrograph. Having estimated the optical properties for particles of the poly(I) · poly(C) dispersed phase, at the second stage a macroscopic phase of poly(I) · poly(C) was prepared. The particles of the dispersed phase formed in a poly(ethyleneglycol) containing solution from poly(I) · poly(C) molecules were centrifuged (5000 rev/min for 40 min). The precipitate resulting from the low-speed centrifuging was a phase of poly(I) · poly(C).

The properties of the poly(I) · poly(C) phase at various temperatures were determined using X-ray scattering [5] and polarization microscopy [1]; the C.D. spectra for the phase of poly(I) · poly(C) and the microphase of poly(I) · poly(C) were compared.

From the temperature dependence of the amplitude of the intense band in the C.D. spectrum and using the methods described in [8] we determined the value of an effective order parameter, S, for the poly(I) · poly(C) molecules in the liquid-crystalline phase and the microphase.

3. Results and discussion

3.1. *X-ray scattering study of poly(I) · poly(C) liquid-crystalline phases*

Figure 1 shows the scattering curves (1–4) taken at different temperatures for the poly(I) · poly(C) phase prepared in a poly(ethyleneglycol) containing solution of high ionic strength. The presence of a small-angle reflection in the X-ray diagrams indicates an ordered arrangement of poly(I) · poly(C) molecules in the phase formed (it may reflect one-dimensional ordering of molecules forming the liquid crystal). Heating the poly(I) · poly(C) phase within the temperature range from 20°C to 75°C is accompanied by an increase of the d value, i.e. by a greater average distance between the axes of adjacent poly(I) · poly(C) molecules (see the inset in figure 1). A similar increase has been detected earlier [5] upon heating the liquid-crystalline phases formed from molecules of other double-stranded polynucleotides, namely, DNA. Interestingly, at a temperature of approximately 80°C, when according to literature data the separation of polynucleotide chains of poly(I) · poly(C) molecules takes place [9], the small-angle reflection in the X-ray pattern disappears (cf. curve 5 of figure 1).

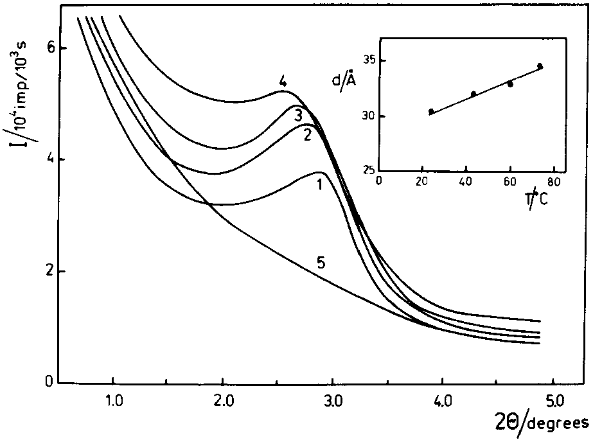

Figure 1. Small-angle X-ray scattering curves for poly(I) · poly(C) phase at different temperatures (C_{PEG} = 190 mg/ml; 1·3 M NaCl + 10^{-2} M phosphate buffer): 1, 24°C; 2, 44°C; 3, 60°C; 4, 74°C; 5, 80°C. In the inset: temperature dependence of d.

The analysis of the peculiarities in X-ray scattering curves was performed as suggested in [10] and demonstrated that heating the poly(I) · poly(C) phase is accompanied by a change of all the parameters (cf. the table) that may be used to characterize different modes of ordering of molecules in polymeric phases. We can see that the radius of interaction, r_m, of poly(I) · poly(C) molecules in a phase (or the size of crystallites, L) becomes smaller and the parameter of disorder, $\Delta/\bar{a}$, of poly(I) · poly(C) molecules greater. From the data summarized in the table we can

Some X-ray parameters of the poly(I) • poly(C) liquid-crystalline phase at different temperatures

Number	T°C	$\bar{a}$/Å	β_s/rad	L/Å	$\Delta/\bar{a}$	r_m/Å
1	24°	30·43	0·0136	113·30	0·165	178·81
2	44°	31·95	0·0154	100·04	0·180	157·91
3	60°	33·05	0·0154	100·04	0·183	157·91
4	74°	34·38	0·0157	98·13	0·188	154·90

Where T denotes temperature, $\bar{a} = d = \lambda/(2\sin\theta)$ is the average distance between axes of adjacent poly(I) • poly(C) molecules, λ is the X-ray wavelength (in our case $\lambda = 1{\cdot}54$ Å), θ is half of the angle for the scattered X-ray, β_s is the integral half-width of the maximum, $L = (\lambda/\cos\theta)\beta_s$ is the size of the ordered regions (crystallites), $\Delta/\bar{a} = (1/\pi)\,(\beta_s\bar{a}/\lambda)^{-1/2}$ is the parameter of disordering (Δ is the semiquadratic deviation from $\bar{a}$) and $r_m = (\pi/2{\cdot}5)^2(\lambda/\beta_s)$ is the interaction radius.

conclude that the degree of ordering of neighbouring poly(I) • poly(C) molecules diminishes with the increase in temperature from 20° to 70°C, while the general mode of ordering of poly(I) • poly(C) molecules in the phase is preserved. A similar conclusion applies to liquid-crystalline phases prepared from DNA molecules. The set of data shown in the table allows us to use the term liquid-crystalline phase to denote the phase formed from poly(I) • poly(C) in poly(ethyleneglycol) containing solutions.

To determine the parameters of the secondary structure of poly(I) • poly(C) forming liquid-crystalline phases at 20°C under moderate (0·3 M NaCl) and high (1·3 M NaCl) ionic strengths of poly(ethyleneglycol) containing solutions, the X-ray scattering curves within angles $2{\cdot}5° < 2\theta < 20°$ were measured (cf. figure 2). Comparison of experimental curves (1 and 2) with the scattering curve that was predicted theoretically for the A′ form of double-stranded polyribonucleotides (curve 3) [11] shows that, irrespective of the conditions of formation of poly(I) • poly(C) liquid-crystalline phases, the parameters of the secondary structure of poly(I) • poly(C)

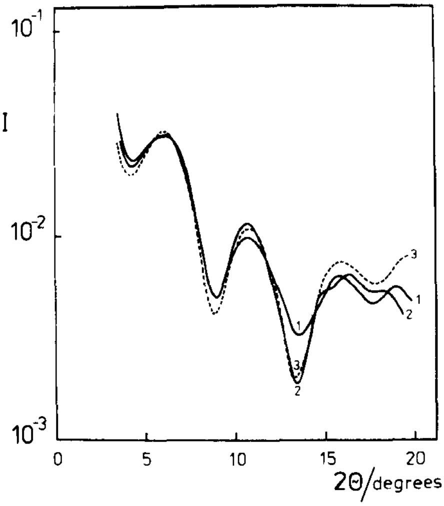

Figure 2. X-ray scattering curves at wide angles for poly(I) • poly(C) phases ($T = 20$°C): Curve 1, $C_{\mathrm{PEG}} = 190$ mg/ml; 0·3 M NaCl + 10^{-2} M phosphate buffer. Curve 2, $C_{\mathrm{PEG}} = 190$ mg/ml; 1·3 M NaCl + 10^{-2} M phosphate buffer. Curve 3, the theoretical X-ray scattering curve for the A′ form of double-stranded polyribonucleotides.

molecules do not change and are close to those for the A′ form. According to the results of preliminary studies, the parameters characteristic of the A′ form are also preserved upon heating of poly(I) · poly(C) liquid-crystalline phases.

Therefore, within the temperature range studied the poly(I) · poly(C) molecules forming the liquid-crystalline phase retain the A′ conformation. Separation of polynucleotide chains of poly(I) · poly(C) molecules accompanied by the change of flexibility of poly(I) · poly(C) chains leads to a disappearance of the ordering of poly(I) · poly(C) molecules in the phase so formed.

3.2. *Textures of the poly(I) · poly(C) liquid-crystalline phase at different temperatures*

Figure 3 illustrates the textures of thin layers of the poly(I) · poly(C) liquid-crystalline phase observed at various temperatures using polarized light and crossed nicols. The texture (cf. figure 3 (*a*)) resembles a crystallized polycrystalline mass. Similar textures of concentrated water-salt solutions of DNA and those of synthetic polynucleotides have also been obtained by other investigators [12]. The texture seen with polarized light is determined by the anisotropy in the optical properties of the phase, which is connected with the mode of arrangement of the poly(I) · poly(C) molecules. This texture as well as the one dimensional ordering of poly(I) · poly(C) molecules prove once again the liquid-crystalline nature of the phases. It should be noted that the texture (figure 3 (*a*)) observed is termed a non-specific texture [13]; at room temperature the texture does not allow us to idetify the structural organization of the liquid-crystalline phases of poly(I) · poly(C).

Attention is drawn to the texture that appears at a temperature of about 70°C (cf. figure 3 (*b*)). This texture, unlike those shown in figure 3 (*a*) and (*c*), is presented as a system of black bended lines [14]. In accord with [14], such a texture is typical of nematic liquid crystals formed by polymers. A similar texture has been observed for nematic liquid-crystalline phases formed by low molecular mass double-stranded DNA molecules [1]. The appearance of this texture together with the one dimensional ordering of poly(I) · poly(C) molecules in liquid-crystalline phase at a given temperature (cf. figure 1, curve 3) allows us to describe this poly(I) · poly(C) phase as nematic.

At a temperature of about 80°C (cf. figure 3 (*d*)) the optical texture is not observed with polarized light, that is, the anisotropy of the system disappears. This observation correlates with our data on the disappearance, at a given temperature, of the one dimensional ordering in the molecular arrangement of poly(I) · poly(C) (cf. figure 1, curve 5).

A question arises as to what type of liquid-crystalline phases does poly(I) · poly(C) exist in at temperatures above and below 70°C. The following observations should be accounted for.

(1) The molecular structure of double-stranded poly(I) · poly(C) as well as that of double-stranded RNA and DNA correspond to a right-handed helix.

(2) The poly(I) · poly(C) as well as RNA and DNA are intrinsically optically active.

(3) Poly(I) · poly(C) forms liquid-crystalline phases under the same conditions as RNA and DNA [6].

(4) The chromophores of poly(I) · poly(C) are nitrogen bases which absorb at about 260 nm; their position about the axis of the poly(I) · poly(C) molecules is not changed on formation of the liquid-crystalline phases (cf. figure 2).

(5) As shown in [1], optically active DNA molecules form either cholesterics or nematics depending on the solvent properties.

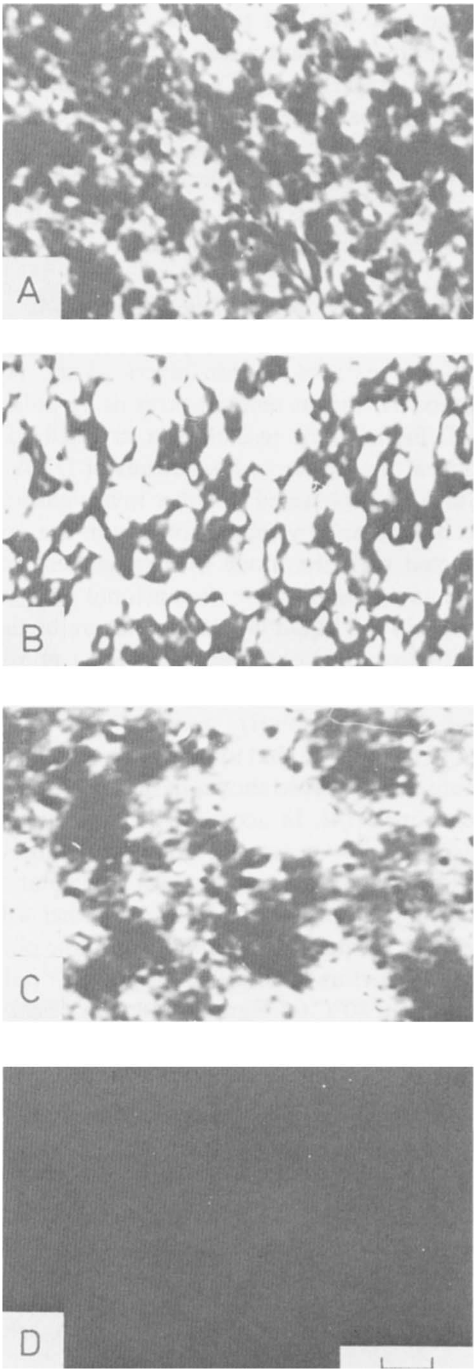

Figure 3. Thin layer textures of the poly(I) • poly(C) liquid-crystalline phase at different temperatures ($C_{\mathrm{PEG}} = 170\,\mathrm{mg/ml}$; 1·3 M NaCl + 10^{-2} M phosphate buffer; polarized light, crossed nicols): (*a*) 20°C $\leqslant T <$ 70°C; (*b*) $T \sim$ 70°C; (*c*) 70°C $< T <$ 80°C; (*d*) $T \geqslant$ 80°C. ●—● Bar, 10 μm.

Formation of cholesterics is accompanied by the appearance of a fingerprint texture whereas the formation of nematics is characterized by the black bent line texture. However, there are cases [1] when under conditions of formation of cholesterics from DNA, non-specific textures are observed [12] (cf. figures 3 (*a*) and (*c*)). Both cases of the formation of cholesterics from DNA are accompanied by an intense band in the C.D. spectrum which is located in the absorption region of the nitrogen bases. Despite the complex nature of the band induced in the C.D. spectra, analysis of this phenomenon [4] demonstrated that for liquid crystals formed from double-stranded polynucleotides the nitrogen bases play the role of chromophores incorporated into the liquid-crystalline phase [7]. The intense band induced in the C.D. spectrum for this case is predetermined because these polymers form lyotropic cholesteric liquid crystals. Formation of nematic liquid crystals from optically active DNA molecules [1] does not induce an intense band in the C.D. spectrum. It is typical that the change of properties of DNA molecules or those of the solvent results in two types of cholesterics with similar fingerprint textures but different signs of the intense bands in the C.D. spectrum.

Considering these observations, it can be supposed that optically active poly(I) · poly(C) as well as DNA are able to form cholesteric liquid crystals. If this is the case, the intense band should appear in the C.D. spectra in the absorption region of nitrogen bases. Taking into account that formation of nematics for poly(I) · poly(C) takes place at about 70°C, it can be expected that the intense band in the C.D. spectra would be observed at all temperatures except 70°C. Moreover, it can be supposed that the signs of the bands in the C.D. spectra would differ if a cholesteric-I → nematic → cholesteric-II transition occurs for poly(I) · poly(C) liquid crystals, since cholesterics I and II arising at particular temperatures differ only in the handedness of the helix.

3.3. *C.D. spectra of the poly(I) · poly(C) liquid-crystalline phase at different temperatures*

Figure 4 shows typical C.D. spectra of the poly(I) · poly(C) liquid-crystalline phase taken at different temperatures. It can be seen that the formation of the liquid-crystalline phase is accompanied by the appearance of an intense band in the C.D. spectrum (cf. curve 1); its amplitude is significantly larger than that in the C.D. spectrum for the original poly(I) · poly(C). We note that on heating the liquid-crystalline phase of poly(I) · poly(C) the position of the maximum of the band in the C.D. spectrum is not changed. This implies that the intense band in the C.D. spectrum of the poly(I) · poly(C) mesophase is not the selective reflection band directly connected with the P value. If this were the case, then the increase in temperature would be followed by a shift of the maximum of the selective reflection band [7]. The appearance of the intense band cannot be explained as originating from the optical properties of the isolated chromophores (nitrogen bases) of poly(I) · poly(C). For the appearance of this band not only is the formation of an ordered liquid-crystalline phase of poly(I) · poly(C) necessary but also the long-range helical order of nitrogen bases.

The data in figure 4 demonstrate that there exist three temperature regions in which the poly(I) · poly(C) mesophase has a different optical activity. For the range from 20°C to 70°C a negative band in the C.D. spectrum is typical; within the range 70°C to 80°C a positive band is observed; at about 70°C and for temperatures greater than 80°C the intense band in the C.D. spectrum is absent (cf. curves 5 and 8).

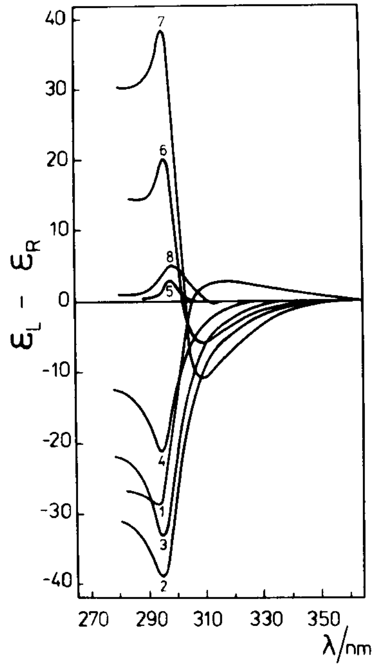

Figure 4. C.D. spectra of a thin layer of the poly(I) • poly(C) liquid-crystalline phase at different temperatures ($C_{\mathrm{PEG}} = 170\,\mathrm{mg/ml}$; 1·3 M NaCl + 10^{-2} M phosphate buffer): 1, 22°C; 2, 41°C; 3, 52°C; 4, 68°C; 5, 73°C; 6, 75°C; 7, 77°C; 8, 83°C.

The existence of one dimensional ordering (cf. figure 1) in combination with the anisotropy of the optical properties revealed by means of polarization microscopy (cf. figures 3 (*a*) and (*c*)) (in spite of the absence of a specific texture) and the presence of intense bands with different signs in the C.D. spectra at temperatures lower or higher than 70°C allow us to suggest that the intense bands in the C.D. spectra reflect the formation of a cholesteric phase for poly(I) • poly(C) that differ in the handedness of the helix.

It should be noted that formation of poly(I) • poly(C) microphases in conditions when the intense band appears in the C.D. spectrum is accompanied by an abnormal O.R.D. spectrum. The reverse of the sign of the band in the C.D. spectrum correlates completely with inversion of the sign of the O.R.D. spectrum.

The texture, which is a system of black bent lines, the absence of the intense band in the C.D. spectrum at a temperature of approximately 70°C and the one dimensional ordering of poly(I) • poly(C) (cf. figure 1, curve 3) demonstrate that under these conditions a compensated structure is being formed; its properties are similar to those of a nematic.

The disappearance of the band in the C.D. spectrum at temperatures ⩾ 80°C is predetermined by the formation of the isotropic phase of poly(I) • poly(C) (the transition of poly(I) • poly(C) from the liquid-crystalline to the isotropic state). This statement is supported by the vanishing of the small-angle reflection (figure 1, curve 5) and the absence of optical anisotropy (figure 3 (*d*)) of the poly(I) • poly(C) phase that is formed at a high temperature.

Thus, the analysis of the C.D. spectra of the liquid-crystalline phases allows us to discriminate between the two types of thermal transitions for the poly(I) • poly(C) liquid crystal on heating. The first transition is cholesteric → compensated structure → cholesteric. (A similar transition has recently been observed upon heating liquid crystals poly-γ-benzyl-L-glutamate prepared in organic solvents [15].) The theoretical description for such a transition for cholesteric liquid crystals is given in [16, 17]. The explanation of this transition is based on the theory [16] generalized in [17]. According to [17], the angle, ϕ, of the helical twist of the director depends not only on correlation of dielectric properties of the media and the polymeric molecules, but also on the temperature. The temperature dependence of ϕ may be expressed by [17]

$$\phi = \frac{2\pi d}{P} = A\,\frac{[\varepsilon_{\mathrm{m}}^2 + \varepsilon_{\mathrm{m}}(\varepsilon_{\parallel} - 3\varepsilon_{\perp}) + \varepsilon_{\parallel}\varepsilon_{\perp}][(2g_{\parallel} - g_{\perp})\varepsilon_{\mathrm{m}} - g_{\perp}\varepsilon_{\perp}]}{\varepsilon_{\mathrm{m}}(\varepsilon_{\mathrm{m}} + \varepsilon_{\perp})^3} - kTB \quad (1)$$

or

$$\phi = AJ(\varepsilon_{\parallel}/\varepsilon_{\mathrm{m}};\, \varepsilon_{\perp}/\varepsilon_{\mathrm{m}}) - kTB, \quad (2)$$

where d is the average distance between the axes of the polymer's molecules in a quasi-nematic layer of the cholesteric; P is the pitch of the helical structure; ε_{m} is the dielectric constant of the medium; $\varepsilon_{\perp}$ and $\varepsilon_{\parallel}$ are the transverse and longitudinal components of dielectric constant of the polymeric molecule; $g_{\perp}$ and $g_{\parallel}$ are the transverse and longitudinal tensors for the optical rotation of the polymeric molecule; A and B are constants. It follows from equation (1) that at a definite temperature, which in turn depends on a combination of ε_{m}, $\varepsilon_{\perp}$ and $\varepsilon_{\parallel}$, the angle of twist, ϕ, may vanish. It means that at this temperature a transition from an ordered twisted structure to a compensated one takes place, and at this temperature the abnormal optical activity of the liquid crystal disappears. The second transition which takes place at about 80°C is the known transition cholesteric → isotropic states.

3.4. *Estimation of the order parameter for poly(I) • poly(C) at the cholesteric–isotropic state transition*

The C.D. spectrum of poly(I) • poly(C) (cf. figure 4) which has an intense band at $\lambda \approx 296\,\mathrm{nm}$ is typical for the so-called dyed cholesterics [7]. The presence of the intense band in the C.D. spectrum of liquid crystals is connected with the spatial arrangement of poly(I) • poly(C) molecules combined with the chromophore's (nitrogen bases) orientation about the director. The amplitude of the band in the C.D. spectrum for dyed cholesterics is proportional [7]

$$\Delta\varepsilon \sim (\Delta n)\,(\mathrm{LD})\,[f(P/\lambda)], \quad (3)$$

where Δn and LD are the anisotropy of the refractive index and linear dichroism associated with the director of the cholesteric liquid crystal; P is the cholesteric pitch and λ is the wavelength that corresponds to the maximum of the chromophore's absorption. The two initial parts of equation (3) are associated with values of the order parameter, S, for the molecule that forms a liquid crystal and the chromophore, S_{chr}

$$S = \frac{(3\cos^2\theta_n - 1)}{2}, \quad (4)$$

where θ_n is the angle between the effective long axis of the polymer's (or chromophore's) molecule and the director. However it must be remembered that for molecules as complex as those considered here the long axes is not defined by molecular symmetry but is an operational definition. From equations (3) and (4) it follows that the amplitude of the band in the C.D. spectrum allows the estimation of the value of an order parameter for both the polymer and the chromophore molecules. The temperature dependence of the amplitude of the band in the C.D. spectrum in the absorption region of the chromophore which is introduced in the cholesteric capable of being transformed to the isotropic state underlies the method for estimating the order parameter for the molecules that form the liquid crystal [8].

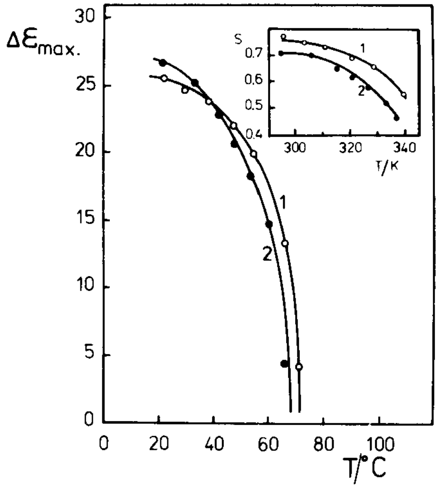

Figure 5. Temperature dependence of the amplitude of the band in the liquid-crystalline phase (curve 1, $\lambda = 296\,\mathrm{nm}$) and solution of the liquid-crystalline microphases (curve 2, $\lambda = 275\,\mathrm{nm}$) of poly(I) • poly(C) ($C_{\mathrm{PEG}} = 120\,\mathrm{mg/ml}$; 0·3 M NaCl + 10^{-2} M phosphate buffer). In the inset: temperature dependence for the order parameter, S, in a liquid-crystalline phase (curve 1) and in the liquid-crystalline microphases (curve 2) of poly(I) • poly(C).

The dependence of the amplitude of the band $\Delta\varepsilon_{\mathrm{max}}$ in the C.D. spectrum of the poly(I) • poly(C) liquid-crystalline phase prepared at a moderate ionic strength (0·3 M NaCl) in a poly(ethyleneglycol) containing solution is presented in figure 5 (curve 1). This dependence is described by

$$\log(\Delta\varepsilon_{\mathrm{max}}) = 2\gamma \log\left(\frac{T_0 - T}{T_0}\right) + K, \qquad (5)$$

where in our case γ is 0·135, the constant K is 1·46 and T_0 equals 71°C; this is the temperature that corresponds to the transition of poly(I) • poly(C) from the cholesteric to the isotropic state. The observed reduction of the amplitude of the band in the C.D. spectrum on heating the poly(I) • poly(C) phase may be connected with the decrease in the ordering of both poly(I) • poly(C) molecules assumed to be rigid polyphosphates and the nitrogen bases (chromophores) in their composition.

For nematics it is established that S is linear in Δn [8]; it is shown that LD is approximately S_{chr} [8]. Taking into account that the nitrogen bases (chromophores) of poly(I) • poly(C) are rigidly bound with the sugar phosphate chain, it can be thought that the value of the order parameter for the chromophores (S_{chr}) would not differ significantly from the value of the order parameter, S, for poly(I) • poly(C),

$S_{chr} \approx S$. In this case it follows from equation (3) that $\Delta\varepsilon \sim S^2$, and from equation (5) that the order parameter for the polymer varies with temperature according to

$$S = S_0\left(1 - \frac{T}{T_0}\right)^{\gamma}. \qquad (6)$$

Following Prokhorov and Kizel' [8] we assume that S_0 equals 1 since $S \rightarrow 1$ as $T \rightarrow 0$. The temperature dependence of the order parameter deduced from equation (6) for poly(I) · poly(C) is shown in the inset to figure 5 (curve 1). Similar temperature dependences of the order parameter have been obtained for other cholesteric liquid crystals [8]. The change of the ordering of poly(I) · poly(C) ensures that $\Delta\varepsilon$ changes with a rise in temperature.

Thus, the value of the order parameter for poly(I) · poly(C) and its temperature dependence support the view that poly(I) · poly(C) forms a cholesteric liquid crystal which is transformed to the isotropic state, similar to cholesterics of other low and high molecular mass compounds.

3.5. *Correlation between the properties of poly(I) · poly(C) liquid-crystalline phases and microphases*

The measured optical properties of poly(I) · poly(C) liquid-crystalline phases are rather close to those of poly(I) · poly(C) microphases, as noted earlier [5, 6]. For liquid-crystalline microphases prepared in poly(ethyleneglycol) containing water-salt solutions, two major states of these microphases can be distinguished. For one of them, the presence of an intense negative or positive band in the C.D. spectrum is typical, while for the other — this band is absent. Based on the existence of cholesteric and nematic phases for poly(I) · poly(C), it can be expected that an abnormal optical activity reflects the presence of a twisted spatial structure of a cholesteric type. Estimation of the order parameter for poly(I) · poly(C) liquid-crystalline microphases from the temperature dependence of the ε_{max} (cf. figure 5, curve 2) performed by this method demonstrates that γ is equal to 0·17; it means that S is equal to 0·71 at $T = 300$ K and is reduced to 0·42 at $T = 340$ K (inset in figure 5, curve 2). The value of the order parameter obtained implies that the spatial organization of poly(I) · poly(C) in the microphases is close to that of phases prepared in water-salt solutions containing poly(ethyleneglycol).

Basing on the concepts concerning the formation of the particles of the disperse phase (microphases) in poly(ethyleneglycol) containing water-salt solutions, the properties of which are determined not only by the properties of the solvent but also by the surface–volume ratio, we suggest that the major difference in the properties of the liquid-crystalline phases and microphases is in the surface energy of the microphases which effects their properties more than for the phases. Taking this into account, it can be expected that the cholesteric → compensated structure transition connected with the alteration of the surface properties of microphases can take place for microphases at a lower temperature comparing it with the temperature of a similar transition for the liquid-crystalline phase. As to the transition from the cholesteric to the isotropic state associated with chain separation of poly(I) · poly(C) molecules, it can take place at nearly the same temperature for both liquid-crystalline phases and microphases. It can be stated that the spatial organization of the liquid-crystalline microphases of other double-stranded polynucleotides should be similar to that of their liquid-crystalline phases.

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