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Specific optical properties of blends of cholesteric copolymers

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The phase behaviour of cholesterol containing liquid crystalline (LC) copolymers of different compositions (copolymers **A** and **B**), and the phase behaviour and optical properties of their blends have been investigated. The phase diagram of the mixture consisting of two fractions **A** and **B** with low molecular masses ($M_W < 10^4$) corresponds to complete solubility of the components over the whole concentration range. The transmittance spectrum of all blends has one minimum, which lies between two peaks corresponding to the wave lengths of the initial samples **A** and **B**. In the case of the cholesteric copolymers with molecular masses above 10^4, the corresponding phase diagram exhibits a lower critical solution temperature (T_{crit}). Below T_{crit} only one peak of the selective reflection of light is observed (SRL). However, above T_{crit} two separate bands of SRL, corresponding to the reflection bands for the individual initial copolymers **A** and **B** are observed. The process of appearance of the single or double bands is reversible and by varying the temperature one can obtain films with bimodal or unimodal curves of SRL.

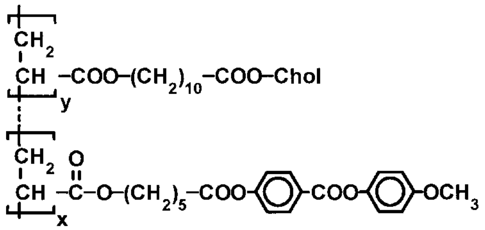
1. Introduction

Recent advances concerning the preparation and characterization of thermotropic liquid crystalline (LC) polymers have been primarily associated with single-component polymeric systems. However, usually, traditional low molecular mass LC materials used commercially are multicomponent systems with a carefully designed composition which provides an optimal combination of their physico-chemical characteristics and offers the best advantages for their particular practical application [1]. Unfortunately, at the present time, almost no investigations concerning binary and, especially, multicomponent LC polymer systems based on main chain and side chain LC polymers are being carried out.

However, some fascinating results have been obtained by studying the introduction of LC additives to various polymer systems. For example, introduction of small amounts of thermotropic LC polymers to amorphous (not liquid crystalline) polymers was shown to decrease the viscosity of the polymers and, hence, to improve their processability [2]. Introduction of low molecular mass liquid crystals to LC polymers [3, 4] was also found to change the rheological, optical, and electro-optical properties of the mixtures prepared [5, 6]. This evidence clearly demonstrates the advantages of using binary and, especially, multicomponent LC polymer systems for the development of advanced LC materials.

To extent our earlier studies on thermotropic LC cholesteric polymers [3, 4, 7–9] and their compositions with low molecular mass liquid crystals, we focused our attention on blends of LC cholesteric materials. Some preliminary and pioneering information concerning these blends was the subject of our reports at various conferences [10–12].

In this work, we have studied systems, very interesting from our viewpoint, which were binary blends of comb-shaped LC cholesteric side group polymers **A** and **B** containing cholesteryl and phenyl benzoate groups in different ratios:



In this work, the phase behaviour and optical properties of blends of the cholesteric copolymers were characterized.

2. Experimental

The acrylate monomers were prepared according to the procedure described in [13]. Copolymers were synthesized by radical polymerization of the corresponding monomers according to the procedure described in [8]. Then, the as-synthesized copolymers in 2% solution in benzene were purified by fractional precipitation with methanol. The blends were prepared by dissolution of the copolymers in chloroform; then the solvent was evaporated and the blends were melted.

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The composition of copolymers was studied by UV-spectroscopy using a Hitachi U-3400 spectrophotometer. Phase transitions were studied by differential scanning calorimetry (DSC) using a Mettler TA-4000 thermal analyser (scanning rate 5°C min^{-1}) and by polarization microscopy using a Polam P-211 microscope. Estimations of molecular masses were made by GPC (Waters 510 GPC pump, 410 differential refractometer, Ultrastirogel columns, THF as eluent). Selective light reflection was studied using a Hitachi U-340 UV-VIS-IR spectrophotometer equipped with a Mettler FP-80 hot stage. The test samples, with a thickness of 20 μm, were sandwiched between flat glass plates. Before each test, the samples were annealed for 40–50 min.

Phase transition temperatures, liquid crystalline phases, and molecular masses of the copolymers are summarized in the table.

3. Results and discussion

Before considering the experimental results obtained for the blends of copolymers, let us first discuss the optical properties of the initial copolymers **A** and **B**, which are characterized by their different contents of chiral units.

3.1. *Optical properties of individual copolymers*

All copolymers studied form cholesteric mesophases. They are capable of easy orientation under shear stress in the cholesteric phase and produce the planar texture, which is characterized by the selective reflection of light.

Figure 1 shows the temperature dependences of the selective light reflection wavelength $\lambda_{\max}$ for each pair of copolymers. Copolymers of type **A** are monochromic ($\lambda_{\max}$ is independent of temperature). However, in the case of the copolymers of type **B**, with a greater fractional content of chiral units (table), $\lambda_{\max}$ shows a pronounced temperature dependence. This behaviour may be explained by the fact that, although no transition to a SmA phase occurs on cooling, smectic fluctuations occur and untwisting of the cholesteric helix is observed [3]. For this type of copolymer, invariability of $\lambda_{\max}$ at temperatures below 70°C is associated with the lower mobility of the mesogenic groups, which are able to preserve the cholesteric helix down to temperatures approaching the glass transition temperature. Note that, even after prolonged annealing (for 5 h) at temperatures of 40–65°C, no marked changes in $\lambda_{\max}$ were identified.

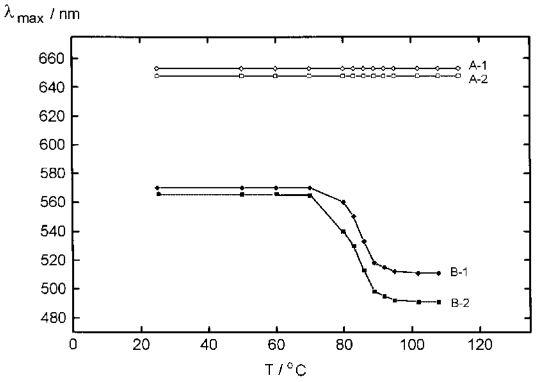


Figure 1. Temperature dependence of the maximum of selective light reflection for individual copolymers **A** and **B**.

It is a far more difficult task to understand the effect of molecular mass on $\lambda_{\max}$ for the individual fractions of the copolymers studied (see figure 1). As can be seen from figure 1, for copolymers of type **A** and **B**, the difference between the corresponding values of $\lambda_{\max}$ is rather small and is equal to 10–20 nm. In this case, with decreasing molecular mass, there is an evident tendency to a shift of $\lambda_{\max}$ towards lower wavelengths. In our opinion, this phenomenon may be explained by the fact that fractionation of the copolymers prepared by radical copolymerization proceeds with respect not only to their molecular masses, but also to their composition. However it must be noted that, as estimated by UV spectroscopy, the composition of the copolymers of each pair remains unchanged (within an accuracy of ±2 mol %).

3.2. *Phase behaviour and optical properties of copolymer blends*

For polymer blends, problems relating to compatibility are crucial. Most pairs of polymers are

Table 1. Molecular masses and transition temperatures of cholesteric copolymers.

Copolymer	Concentration of cholesterol units/ mol %	$\bar{M}_w$	T_g†/°C	$T_{\text{Ch-I}}$‡/°C
$\mathbf{A}_1$	23	$5{\cdot}6\times10^4$	28	116
$\mathbf{A}_2$	23	$4{\cdot}1\times10^3$	25	114
$\mathbf{B}_1$	38	$4{\cdot}3\times10^4$	26	109
$\mathbf{B}_2$	38	$8{\cdot}5\times10^3$	26	108

† T_g = glass transition temperature.
‡ $T_{\text{Ch-I}}$ = cholesteric–isotropic melt transition.

thermodynamically incompatible [14]. In this connection, we studied phase separation in the blends of the cholesteric LC copolymers which are characterized by different molecular masses, but contain similar mesogenic groups taken in different ratios. The most comprehensive information concerning compatibility between the components is provided by examination of their phase diagrams.

Let us start with the phase diagrams corresponding to the lowest molecular mass fractions of copolymers **A**$_2$ and **B**$_2$. As follows from figure 2, for this particular pair of copolymers, the phase diagram suggests the formation of solid solutions, the components of which are infinitely soluble. This behaviour of polymer blends was described in [15] for two chiral comb-shaped isomers, as well as in [16] for cholesteric main chain polymers with molecular masses not exceeding 20 000.

The fact that the fractions of copolymers **A**$_2$ and **B**$_2$ produce ‘an LC solution’ is supported by optical observations. Figure 3 shows the transmission spectra of the initial components of both fractions of copolymers **A**$_2$ and **B**$_2$, as well as of the **A**$_2$/**B**$_2$ (50 : 50 wt %) blend. As shown in figure 3, in the latter case, the corresponding transmission spectrum shows only one peak of selective light reflection. Note that the transmission spectrum of the **A**$_2$/**B**$_2$ blend lies between the corresponding spectra of the initial copolymers.

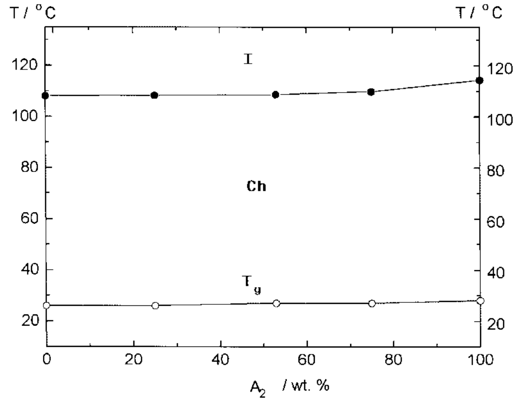


Figure 2. Phase diagram of copolymer blends **A**$_2$ and **B**$_2$.

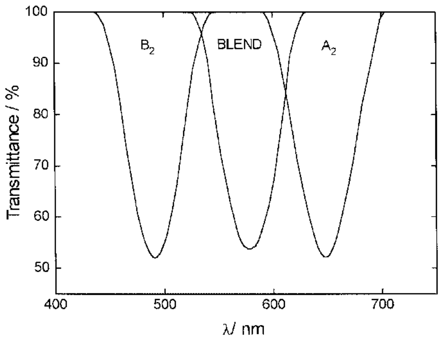


Figure 3. Transmittance spectrum of copolymers **A**$_2$ and **B**$_2$ and their blend (50 : 50 wt %) at temperature $T = 0{\cdot}9\ T_{cl}$.

Let us also note that for the **A**$_2$/**B**$_2$ blends the values of λ_{max} are almost independent of temperature (except for the blends containing 80 wt % and more of component **B**$_2$). Figure 4 shows the temperature dependence of λ_{max} for the **A**$_2$/**B**$_2$ (50 : 50 wt %) blend. Over the entire interval of existence of the mesophase, the system remains ‘monochromic’, even though one of the components (**B**$_2$) is characterized by a pronounced temperature dependence of λ_{max}. This behaviour is probably explained by a decrease in the mean concentration of cholesteryl units in the blend down to 29 mol % through the dilution of copolymer **B** by copolymer **A**; as a result, the content of cholesterol units in the LC solution decreases. This evidence agrees well with earlier results [8] which showed that the temperature dependence of the wavelength of selective light reflection was characteristic for copolymers containing more than 30 mol % of cholesterol units.

Note that this type of phase diagram (complete compatibility) is observed for the binary blends of the copolymers in which the molecular mass of at least one component is lower than 10^4:(**A**$_1$ + **B**$_2$) and (**A**$_2$ + **B**$_1$) blends.

A somewhat different situation is observed for the blends of copolymers **A**$_1$ and **B**$_1$, in which both components are characterized by rather high molecular masses (see the table). In this case, the phase diagram (figure 5) is similar to that of systems with a lower critical solution temperature (LCST), and this temperature is observed at about 66°C. Below this temperature, in the **A**$_1$/**B**$_1$ blends, a single cholesteric mesophase (denoted as Ch) is produced. With increasing temperature above 66°C, the system undergoes separation into two cholesteric mesophases, which are characterized by their own helical pitch values.

As follows from figure 5, at low content of each of the

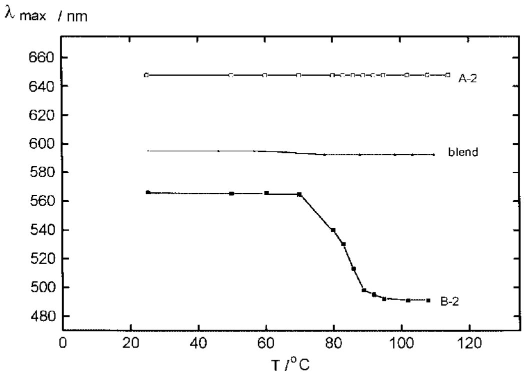


Figure 4. Temperature dependence of the maximum of selective light reflection for copolymers **A**$_2$ and **B**$_2$ and their blend (**A**$_2$:**B**$_2$ = 50 : 50 wt %).

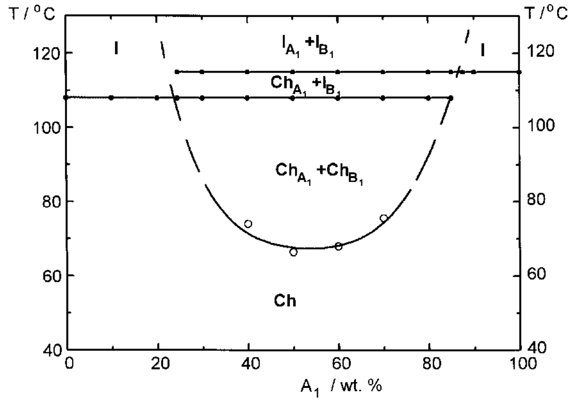


Figure 5. Phase diagram of copolymer blends **A1** and **B1**.

components of the **A1**/**B1** blends (for example about 15–20 wt % of **A1** or **B1**), only one transition temperature is observed, and this temperature corresponds to isotropization of the cholesteric mesophases of the initial copolymers **A1** and **B1**. On the other hand, for the **A1**/**B1** blends, with increasing content of component **B1** from 20 to 80 wt %, the phase diagram shows a pronounced two phase region at temperatures above LCST.

Figure 6 shows the dependence of the light transmission on wavelength for the blend of copolymers **A1** and **B1** at temperatures above (dashed lines) and below LCST (solid line). It follows from figure 6 that at temperatures below LCST, one peak of selective light reflection is observed, and this peak suggests that, in the **A1**/**B1** blend prepared by mixing, a single cholesteric helix is produced. At temperatures above LCST, two peaks of selective light reflection are evident, and this suggests the formation of two different supermolecular cholesteric helices.

As supported by the data from DSC and polarization microscopy, further heating is accompanied by the development of two phase regions (Ch + I). Note that the isotropic melt which is then formed is not homogeneous (the region of the existence of two isotropic melts in the corresponding phase diagram, figure 5), and this conclusion is supported by direct microscopic observations.

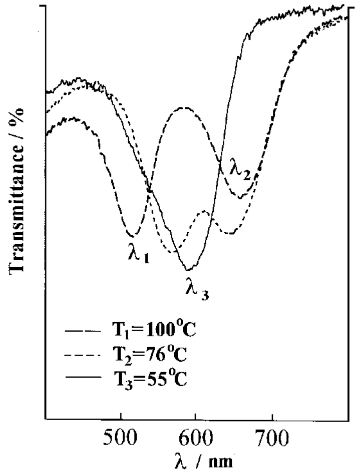


Figure 6. Transmittance spectra of a blend of copolymers **A1** and **B1** of equal composition at different temperatures.

Considering the phase diagram shown in figure 5, there is an open question concerning the origin of the peak of selective light reflection observed at temperatures below the critical solution temperature. This single peak may be associated with the fact that both components produce a common cholesteric helix and suggests a complete miscibility of the components of the **A1**/**B1** blend within this temperature interval. According to an alternative explanation, this peak is a result of overlapping of the two peaks corresponding to the initial components, which come closer due to the temperature dependence of λ_{max} of copolymer **B1**.

Usually, mutual solubility of two components is estimated by measuring the glass transition temperatures of the related blends: when the blend studied is characterized by two glass transition temperatures, the components are insoluble [17]. As seen in figure 7, all blends studied are characterized by one glass transition temperature. However, taking into account the fact that the values of the glass transition temperatures of the initial components are quite similar and differ only by 2°C, this approach seems to be invalid.

To understand the problems concerning complete miscibility of components **A1** and **B1** at temperatures below LCST, the following experiments were carried out. At temperatures below the critical temperature, the transmission spectrum of the blend of components **A1** and **B1** taken in a ratio of 1 : 1 (wt %) was compared with that of a 'sandwiched' sample composed of *two* films of the initial copolymers, through which the optical beam passed. As seen in figure 8, in the case of the **A1**/**B1** blend, the pattern is quite similar to that shown in figure 6—that is, only one peak of selective light

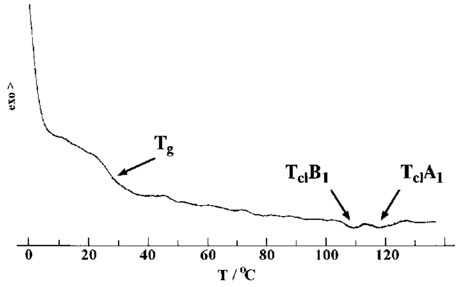


Figure 7. DSC-curve of copolymer blend **A1** and **B1** (50 : 50 wt %). T_g = glass transition; $T_{cl}B_1$ and $T_{cl}A_1$ = cholesteric–isotropic clearing transition for copolymers **B1** and **A1**, respectively.

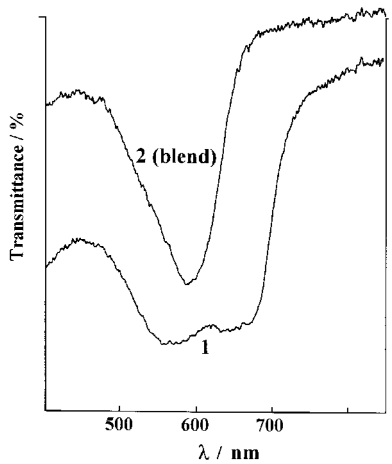


Figure 8. Transmittance spectra of a sandwich of two films of copolymers **A**$_1$ and **B**$_1$ (curve 1) and their blend (1 : 1 wt %) (curve 2) at temperatures below 60°C.

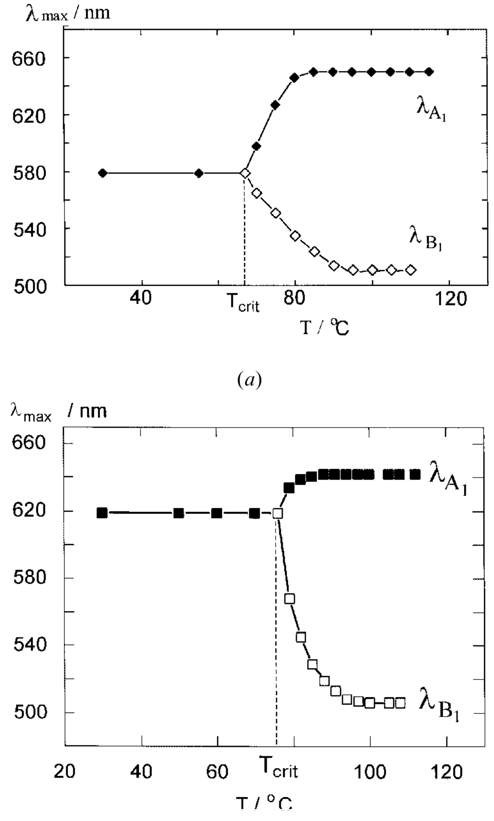
reflection is observed. However, in the case of the sandwiched sample, two different maxima of selective light reflection are identified. This evidence unequivocally suggests a mutual miscibility of two initial components in their blend.

Let us especially emphasize the reversible character of the microphase separation, which allows one to obtain unimodal or bimodal profiles of selective light reflection curves at temperatures below or above LCST, respectively. In this work, this phenomenon is described for the first time for blends of cholesteric copolymers.

3.3. *Temperature dependence of the selective light reflection wavelength for the blends of the cholesteric copolymers*

Interesting information may be obtained from examining the temperature dependences of the helical pitch or λ_{max} for various blends of copolymers **A**$_1$ and **B**$_1$ (figure 9).

At temperatures below LCST, the initial components show complete phase compatibility: the chiral composition is averaged, and in the case of the blends in which the content of **B**$_1$ is not very high, λ_{max} is independent of temperature.



(*a*)

(*b*)

Figure 9. Temperature dependence of the maximum of selective light reflection for blends of copolymers **A**$_1$ and **B**$_1$ of different composition (wt %): (*a*) **A**$_1$:**B**$_1$ = 50 : 50; (*b*) **A**$_1$:**B**$_1$ = 70 : 30.

At temperatures above LCST, a far more intriguing situation is observed (figure 9). In this case, the system is composed of two phases, and the selective light reflection is characterized by two maxima corresponding to the initial supermolecular structures (see the two different branches in the corresponding plots). Let us also mention that, in the vicinity of the critical solution temperature, both branches appear to be temperature dependent. For the lower branch associated with the initial component **B**$_1$, this behaviour seems to be as expected (see figure 1). However, the fact, that the upper branch manifests a violation of 'monochromic' character, appears to be rather unusual. As was shown earlier, all copolymers of type **A** are characterized by an invariant wavelength of selective reflection of light over the whole temperature range of existence of the mesophase (figure 1). Hence, the above behaviour might be expected if the cholesteric helix produced by copolymer **A**$_1$ should have a somewhat different average chemical composition (in this case, the cholesteric helix would be enriched with the chiral component of copolymer **B**$_1$). This condition would be provided only for a partial, not a complete solubility of initial copolymers **A**$_1$ and **B**$_1$.

Furthermore, examination of the temperature dependence of λ_{max} at temperatures above LCST allows one to estimate the temperature at which the system experiences a complete phase separation into two individual components (in the case studied, into two initial copolymers). As follows from figure 9, at temperatures above 80°C, a complete phase separation into two initial cholesteric helical supermolecular structures is observed. This conclusion is demonstrated well by figure 10, which shows

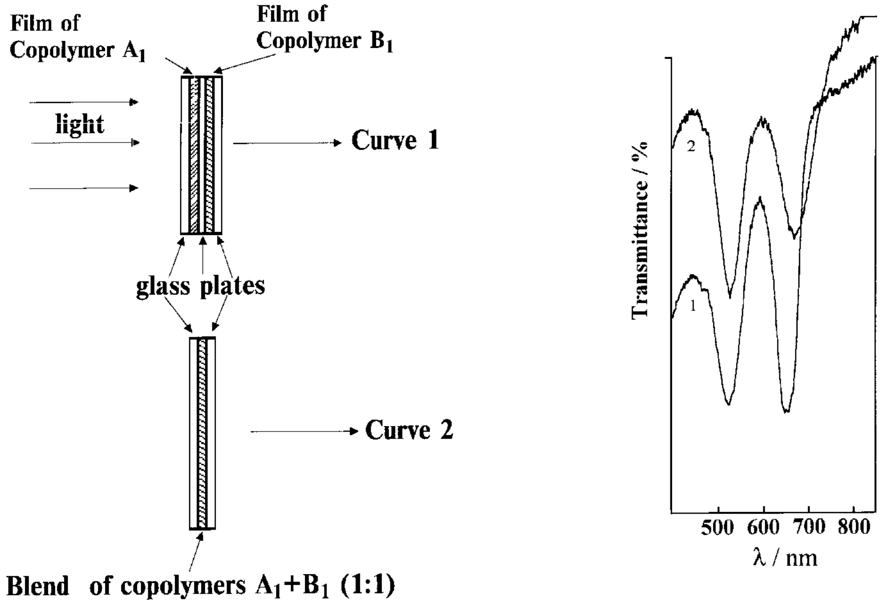


Figure 10. Schematic representation of the optical experiment and the transmittance spectra of (spectrum 1) sandwich of two separate films of copolymer **A**$_1$ and **B**$_1$, and (spectrum 2) the blend of copolymers **A**$_1$/**B**$_1$ (50:50 wt %).

the transmission spectra for the sandwiched sample composed of two films of the initial copolymers and for the blend of the two copolymers at 100°C. As seen in figure 10, the values of $\lambda_{\max}$ (curve 1) corresponding to the two peaks for the initial individual copolymers coincide with the values of $\lambda_{\max}$ (curve 2) corresponding to the two peaks for the different helical structures produced in the system after complete phase separation.

4. Conclusion

The experimental evidence obtained allows one to draw the following conclusions:

(1) Examination of the phase state and optical properties of the comb shaped cholesteric copolymers shows that the polymers of molecular masses not exceeding 10^4 are characterized by complete miscibility over the whole temperature–concentration range.
(2) In the case of the cholesteric copolymers with molecular masses above 10^4, the corresponding phase diagram exhibits a lower critical solution temperature. At temperatures above this critical temperature, the system undergoes complete phase separation.
(3) For the first time, polymeric cholesteric liquid crystals have been shown to undergo a reversible phase separation at a macromolecular level, and this finding allows one to obtain unimodal and bimodal curves of selective light reflection.

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