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Liquid-Crystalline State of Cholesterol-Containing Monomers

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A series of cholesterol-containing monomers was synthesized: cholesteryl esters of *N*-acryloyl-ω-aminocarboxylic acids, *N*-methacryloyl-ω-aminocarboxylic acids, ω-acryloyloxycarboxylic acids and ω-methacryloyloxycarboxylic acids. The mesomorphic properties, temperatures and heats of transitions of monomers were investigated in comparison with the cholesteryl alkanoates. The temperature range of cholesteric mesophase of monomers—derivatives of oxycarboxylic acids was shown to be wide. Such monomers can be used in thermographic composites and for synthesis of the liquid-crystalline polymers.

In recent years a new scientific trend covering the synthesis and investigation of polymeric thermotropic liquid crystals (LC) has been developed. Of special interest are polymers containing mesogenic groups as side chains.[1–4] Such polymers are usually synthesized by polymerization of the corresponding low molecular compounds (monomers) containing a polymerizable double bond and a mesogenic group. To understand better the formation of various types of mesophases in polymers, and, consequently, to synthesize LC polymers with desirable properties, it is required to establish the relationship between the structure of monomers and that of polymers. Thus, when studying the structure and properties of LC polymers, one must have information on corresponding monomers. Moreover, in many cases monomers

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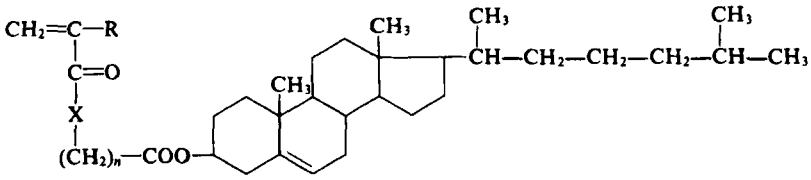
themselves are capable of forming a mesophase and are, therefore, of interest as new LC compounds.

In our earlier publications[5,6] we have presented the results of investigation of some LC polymers with cholesteryl esters as mesogenic side groups. The comparative study of respective cholesterol-containing monomers constitutes the subject of the present article. The monomers under investigation are cholesteryl esters of *N*-acryloyl-ω-aminocarboxylic acids (1), *N*-methacryloyl-ω-aminocarboxylic acids (2), ω-acryloyloxycarboxylic acids (3), and ω-methacryloyloxycarboxylic acids (4).



These compounds will be notated in the article as follows:

Monomer	R	X	Notation
1	H	NH	ChAA-*n*
2	CH_3	NH	ChMA-*n*
3	H	O	ChA-*n*
4	CH_3	O	ChM-*n*

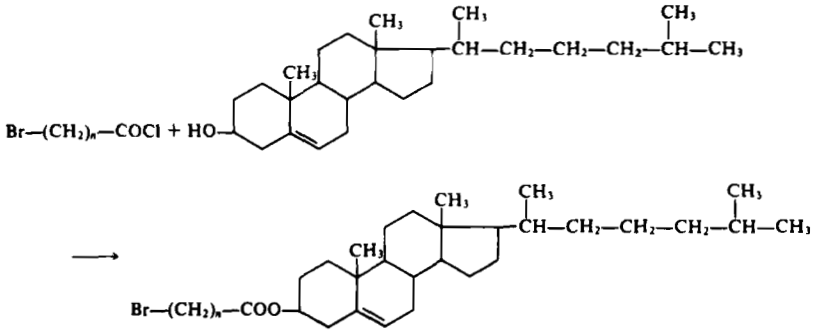
Such choice enabled us, at extensive varying of *n*, R and X, to establish definite correlation between the molecular structure of monomers and the type and thermostability of the mesophase formed. As it is seen from the above formula, the monomers synthesized are actually cholesterylalkanoates with CH_2=C(R)COO— and CH_2=C(R)CONH— groups as substitutes in the ω-position. It was thus also of considerable interest to compare the structure and properties of the compounds obtained with that of cholesterylalkanoates described earlier.[7,9]

EXPERIMENTAL

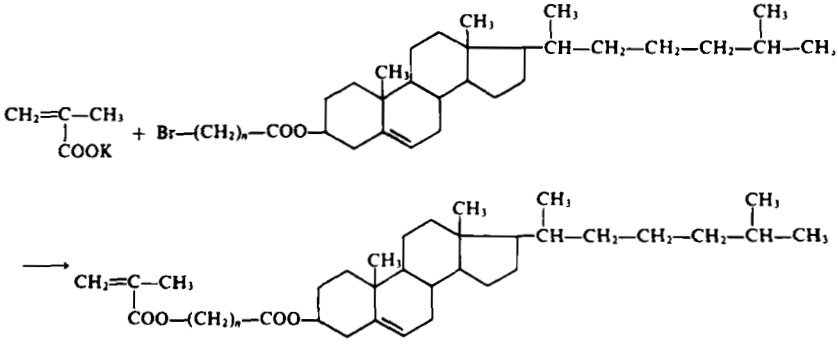
The syntheses of cholesterol esters of *N*-acryloyl-ω-aminocarboxylic acids (ChAA-*n*), of cholesterol esters of *N*-methacryloyl-ω-aminocarboxylic acids (ChMA-*n*) and of cholesterol esters of ω-oxypentadecane carboxylic acid (ChM-14) were described elsewhere.[5,6]

Cholesterol esters of ω-acryloyloxycarboxylic acids and of ω-methacryloyloxycarboxylic acids were synthesized by following steps:

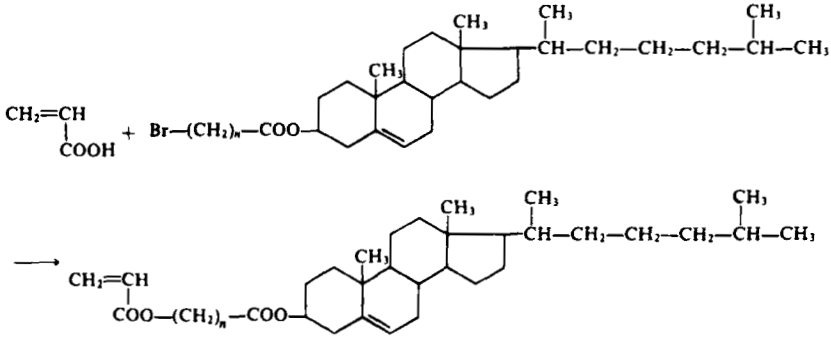
1. Synthesis of cholesterol esters of ω-bromocarboxylic acids (ChBrAc-*n*)



2. Synthesis of cholesterol esters of ω-methacryloyloxycarboxylic acids (ChM-*n*)



3. Synthesis of cholesterol esters of ω-acryloyloxycarboxylic acids (ChA-*n*)



1. Cholesterol esters of ω-bromocarboxylic acids

Distilled triethylamine (0.04 moles) was added to 0.03 moles of cholesterol dissolved in 150 ml of absolute benzene, after which acylchloride of the corresponding ω-bromocarboxylic acid (0.04 moles) was slowly added. The solution was vigorously mixed at room temperature for two hours. Benzene was then evaporated; the resulting precipitate was dissolved in ether, washed with water and dried over fused $MgSO_4$. Then ether was partly evaporated and ChBrAc-*n* was precipitated with methanol. The precipitate was filtered and purified by column chromatography (silica gel, benzene). ChBrAc-5: M.p. = 123°C, yield = 90%. ChBrAc-10: M.p. = 105°C, yield = 75%.

2. Cholesterol esters of ω-methacryloyloxycarboxylic acids (ChM-5 and ChM-10)

0.013 moles of ChBrAc-*n*, 0.025 moles of potassium methacrylate and 0.4 g of hydroquinone were dissolved in 60 ml of distilled DMF under the constant flow of argon. The reaction mixture was then heated to 115°C and kept at this temperature for 8 hours, with periodic agitation. After cooling to room temperature the solution was diluted with a 5-fold amount of ether and thoroughly washed with water. The solution was dried over fused $MgSO_4$, the solvent was entirely evaporated and the reaction products were chromatographically separated on a silica gel column with benzene used simultaneously as a solvent and eluent. Yield of ChM-5 = 62%, of ChM-10—64%.

3. Cholesterol esters of ω-acryloyloxycarboxylic acids (ChA-5 and ChA-10)

0.012 moles of ChBrAc-*n*, 0.4 g of hydroquinone, 0.028 moles of acrylic acid and 0.028 moles of distilled triethylamine were dissolved in 60 ml of distilled DMF. The subsequent procedure was as in the syntheses of ChM-5 and -10. Yield of ChA-10 = 70%, of ChA-5—44%.

The structure of monomers was confirmed by IR-spectra and elemental analysis (Table I); their purity was checked by TLC on "Silufol" plates. Optical studies were conducted in the crossed polarizers with a MIN-8 polarizing microscope equipped with a hot stage. Pictures were taken with Zenit-3M camera mounted on a microscope tube by means of a microphotographic attachment. Temperatures and heats of phase transitions were measured on a differential scanning microcalorimeter DSM-2. X-ray patterns were obtained on URS-55 apparatus with a flat cassette chamber (irradiation with CuK_α). Selective light reflection measurements of cholesteric mesophase were carried out by means of SF-18 specrophotometer.

TABLE I

Elemental analyses of monomers

Monomer	Found (%)		Calculated (%)	
	C	H	C	H
ChA-5	78.2	10.8	78.0	10.5
ChM-5	78.4	10.7	78.2	10.6
ChA-10	78.7	10.9	78.7	10.9
ChM-10	79.3	10.8	79.0	11.0

RESULTS AND DISCUSSION

Cholesterol esters of *N*-acryloyl- and *N*-methacryloyl-ω-aminocarboxylic acids (ChAA-*n* and ChMA-*n*)

All ChAA-*n* and ChMA-*n* monomers are crystalline; some of them (ChAA-11, ChMA-8 and ChMA-11) form even two crystalline modifications (Table II).

Crystalline modification I of ChAA-11, ChMA-8 and of ChMA-11 is formed upon crystallization from solutions. On heating, it transforms to modification II (at 85°C for ChMA-5 and 84°C for ChMA-11) ChAA-11 displays at 84°C a cholesteric LC phase which is, however, unstable and undergoes rapid transformation to crystalline modification II. On fusion, all monomers (except for ChAA-2) yield isotropic melts whose cooling leads to the formation of a monotropic cholesteric

TABLE II

Basic interplanar distances and melting points of ChAA-*n* and ChMA-*n* monomers

Monomer	M.p., °C	Interplanar distances, nm				
		d_1	d_2	d_3	d_4	d_5
ChAA-2	125	0.600	0.741	1.041	1.420	2.1
ChMA-2	123	0.385	0.472	0.588	0.958	4.1
ChMA-5	108	0.384	0.405	0.442	0.600	2.5
ChMA-6	98	0.413	0.550	0.848	1.250	3.0
ChMA-8 (mod.I)	85	0.381	0.413	0.503	0.600	2.5
ChMA-8 (mod.II)	120	0.366	0.493	—	1.590	2.5
ChMA-10	84	0.381	0.413	0.503	0.600	2.6
ChAA-11 (mod.I)	84	0.459	1.041	1.341	1.706	2.7
ChAA-11 (mod.II)	104	0.459	0.543	0.612	0.776	1.1
ChMA-11 (mod.I)	84	0.467	0.510	0.595	0.770	2.6
ChMA-11 (mod.II)	102	0.372	0.490	0.530	0.770	3.6

mesophase which rapidly is transformed to crystalline (ChMA-8, ChAA-11 and ChMA-11 form modification II).

ChAA-2 monomer forms a cholesteric LC phase upon melting at 125°C which polymerizes rapidly and therefore, one cannot observe the melting of pure monomers mesophase.

Cholesterol esters of ω-acryloyl- and ω-methacryloyloxycarboxylic acids (ChA-*n* and ChM-*n*)

Structural parameters of ChA-*n* and ChM-*n* in a crystalline state are listed in Table III.

Phase transitions of ChA-*n* and ChM-*n* monomers are summarized in Table IV. Figures above the arrows correspond to the temperatures (°C), and figures below them to the heats (cal/g) of phase transitions.

As is seen from Table IV, all ChA-*n* and ChM-*n* compounds form enantiotropic cholesteric phase and all of them, but ChA-5, form enantiotropic smectic phase as well.

Figure 1 illustrates optical microphotographs of smectic and cholesteric mesophases of ChM-5. Focal conic texture of a smectic mesophase and cholesteric texture with oily streaks are common for conventional low molecular liquid crystalls.[8]

X-ray studies at different temperatures have shown that at wide angles cholesteric and smectic mesophases as well as isotropic melt, display single diffuse halo (0.55 nm), while at small angles X-ray patterns for these three states are significantly different (Table V).

The presence, at small angles, of 3 reflections for smectic phase of ChM-5 indicates the perfect layer packing of its molecules. Intensive small angle signal displayed by cholesteric phase corresponds to interplanar distance of 2.9 nm, which actually coincides with the length of the molecules calculated on the basis of molecular model (2.8 nm).

TABLE III

Basic interplanar distances for ChA-*n* and ChM-*n* monomers

Monomer	Interplanar distances, nm						
	d_1	d_2	d_3	d_4	d_5	d_6	d_7
ChA-5	0.364	0.466	0.519	0.653	1.56	—	—
ChM-5	0.376	0.454	0.532	0.699	1.29	2.8	—
ChA-10 (mod.I)	0.389	0.454	0.516	0.636	1.27	3.2	—
ChA-10 (mod.II)	0.364	0.458	0.509	0.591	1.25	2.7	—
ChM-10	0.389	0.454	0.522	—	1.28	2.9	4.1
ChM-14	0.380	0.469	0.559	—	1.06	2.6	—

TABLE IV

Temperatures and heats of phase transitions of ChA- and ChM-*n* monomers

Monomer	Temperatures (T, °C) and heats (ΔH, cal/g) of phase transitions
ChA-5	$K \xrightarrow[10.4]{44} Ch \xrightarrow[0.13]{70} I$
ChM-5	$K \xrightarrow[11.0]{37} S \xrightarrow[0.08]{48} Ch \xrightarrow[0.13]{59} I$
ChA-10	$K_I \xrightarrow[1.4]{28} K_{II} \xrightarrow[7.7]{42} S \xrightarrow[0.13]{67} Ch \xrightarrow[0.15]{78} I$
ChM-10	$K \xrightarrow[11.3]{55} S \xrightarrow[0.23]{58} Ch \xrightarrow[0.17]{62} I$
ChM-14	$K \xrightarrow[12.8]{59} S \xrightarrow[0.21]{61} Ch \xrightarrow[0.24]{64} I$

Cholesteric mesophase of all ChA-*n* and ChM-*n* monomers selectively reflects light, the color of the monomers changing, when heated, from red to violet, which is common for most cholesterics. Figure 2 shows, as an example, the temperature dependence of the wavelength of selectively reflected light for ChA-5 and ChM-5.

The comparison of transition temperatures of ChA-*n* and ChM-*n* (Figure 3) reveals that the existence region of cholesteric mesophase is wider for ChA-*n*, than for corresponding ChM-*n*, and decreases with increasing length of an alkyl substituent for both series of compounds. Melting points of cholesteric phase of ChA-*n* are higher than of ChM-*n*. Replacement in the monomer molecules of ester COO— group for amide CONH—, leads to a substantial rise of melting points due to the intermolecular hydrogen bonding. This actually levels the difference in properties of acrylic and methacrylic compounds. Mesophase melting points, which are determined by interaction of cholesterol fragments, are less dependent on the presence of amide groups in aliphatic chains, and must thus be close to the melting points of the corresponding monomers with COO— groups, i.e. around 60–80°C. These values are lower than the melting points of crystalline phase. It is, apparently, the reason why ChAA-*n* and ChMA-*n* form monotropic phase only.

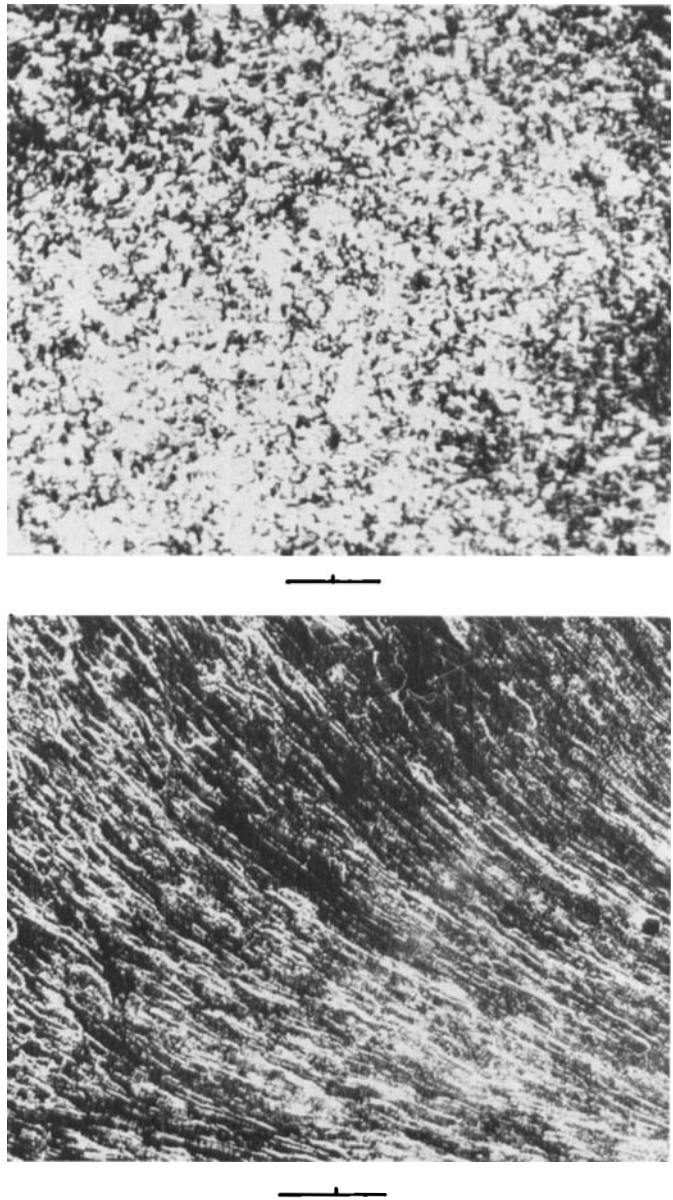


FIGURE 1 Optical microphotographs of monomer ChM-5: smectic mesophase (a); cholesteric mesophase (b).

TABLE V

Data on x-ray scattering by ChA-5 and ChM-5 monomers

Monomer	Interplanar distances, nm		
	Smectic mesophase	Cholesteric mesophase	Isotropic melt
ChA-5	—	2.9 s; 0.55 dif.	0.55 dif.
ChM-5	3.0 s[a]; 2.4 m 1.4 w; 0.55 dif.	2.9 s; 0.55 dif.	0.55 dif.

[a]Notation of reflex intensity: s—strong; m—medium; w—weak; dif.—diffuse.

Let us now consider the effect of acyloxy groups, containing double bonds of the type CH_2=CHOO— and CH_2=C(CH_3)COO— in ChA-*n* and ChM-*n* molecules. For this purpose let us compare thermal behavior of these compounds with that of cholesterol alkanoates. It is a well known fact that cholesterol esters of aliphatic carboxylic acids with alkyl substituents of more than 5 carbon atoms, form a cholesteric mesophase at temperatures over 75°C, its existence interval not exceeding 5°C, as a rule.[7] The introduction of a double bond into an alkyl

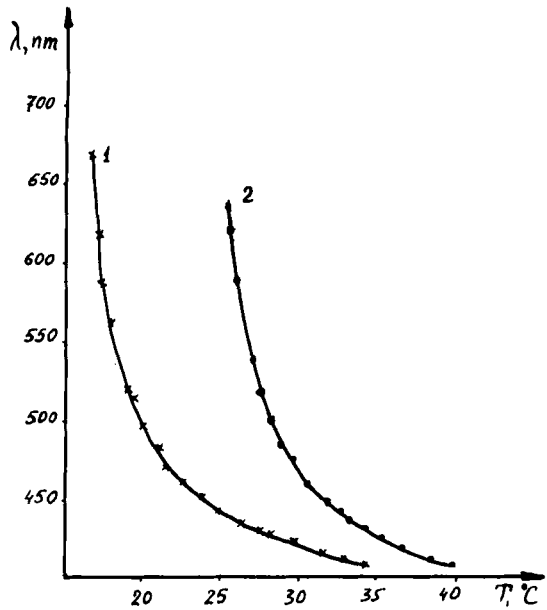


FIGURE 2 Temperature dependence of selective reflection of monomers ChA-5 (1) and ChM-5 (2). (The data were obtained under heating of supercooled samples).

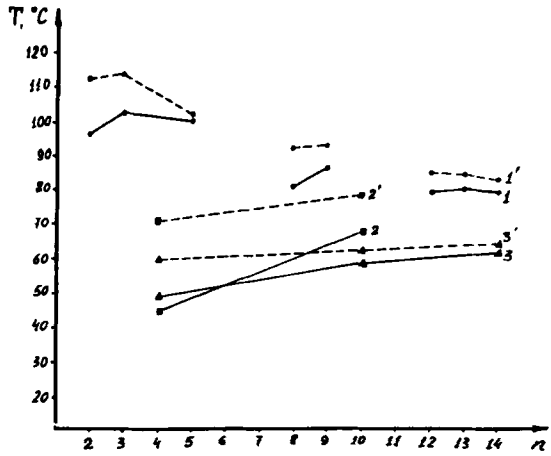


FIGURE 3 Temperatures of formation (1, 2, 3) and melting (1', 2', 3') of cholesteric mesophase as a function of carbon atoms for cholesteryl alkanoates (1, 1'); ChA-*n* (2, 2') and ChM-*n* (3, 3').

substituent leads, in some cases, to the decrease of transition temperatures and to the widening of the existence region of cholesteric mesophase (i.e., elaidic and erucic acid derivatives). Figure 3 illustrates that the presence CH_2=CHCOO— and CH_2=C(CH_3)COO— groups in the structure of alkyl radical also greatly decreases the transition temperatures and increases the existence range of cholesteric mesophase.

The lowering of transition temperatures must probably be attributed to the repulsion of ChA-*n* and ChM-*n* molecules, enhanced by the presence of acyloxy groups at the ends of aliphatic chains of the substituents. As a result, a more "defect" structure is formed both in a crystalline state and in a mesophase. Lower heats of transitions of monomers, as compared to those of low molecular cholesterol esters, are of the same origin.[9] For instance, heats of transitions of ChM-10 differ significantly from the corresponding values of cholesterol lauri-

TABLE VI

Heats of transitions of some cholesterol esters

Cholesterol ester	ΔH, cal/g		
	K → S	S → Ch	Ch → I
ChM-10	11.3	0.23	0.17
Cholesteryl laurinate	13.4	0.40	0.31
Cholesteryl miristate	18.6	0.56	0.41

nate and cholesterol miristate, the length of their molecules being close to that of ChM-10 (Table VI).

Thus, cholesterol esters, that are capable of forming smectic and cholesteric mesophases, are of certain interest from the standpoint of both synthesis of new polymeric liquid crystals and their utilization in thermographic composites.

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