Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 26 Apr 2007.

To cite this article: Edward J. Poziomek, Thaddeus J. Novak & Raymond A. Mackay (1972): Transparency Characteristics of Several Cholesteryl Esters, Molecular Crystals and Liquid Crystals, 15:4, 283-295

To link to this article: http://dx.doi.org/10.1080/15421407208083566

Molecular Crystals and Liquid Crystals. 1972. Vol. 15, pp. 283–295

Printed in Great Britain

Transparency Characteristics of Several Cholesteryl Esters

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Received November 23, 1970; *in revised form April* 15, 1971

Abstract—Transparency characteristics are reported for cholesteryl myristate, decanoate, and nonanoate from the solid to the isotropic liquid phases. The procedure involves heating a sample between calcium fluoride plates in a brass holder in a Cary 14 spectrophotometer. Changes in transmittance at fixed wavelengths (3000, 4000, 5000, 7000, and 25,000 A) were recorded continuously as the temperature was allowed to change slowly. The transparency characteristics of cholesteryl nonanoate while being cooled from the liquid phase are also described. All transitions which occur are observed. By comparison with other techniques this method compares very favorably with regard to the detection of transitions and dichroic scattering. The shapes of the transparency curves vary markedly between compounds; the degree of light scattering varies as a function of the incident light wavelength. However, the temperature ranges over which the transitions occur for a particular compound are reproducible irrespective of the light wavelength.

1. Introduction

There is considerable interest in the light scattering properties of mesomorphic materials especially cholesteryl esters. Fergason⁽¹⁾ studied various optical properties of a mixture of cholesteryl benzoate, acetate, and palmitate. He also has described the discovery that absorption or solution of gases, liquids and solids in the cholesteric liquid crystal can temporarily or permanently change optical properties.⁽²⁾ We have been interested in the effects of bulk and surface impurities on the transparency of mesomorphic materials to various light wavelengths versus temperature.

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Surprisingly, little data is available on the transparency of the mesomorphic materials themselves. In 1938, an infrared study was performed with several cinnamates at various temperatures.(3) Changes in the transmission of incandescent light were used to determine phase transition temperatures of alkali metal stearates.(4) In 1963, Chistyakov(5) studied visible light transparency of cholesteryl caprylate, caprate, caproate, stearate, formate, acetate, and palmitate as a function of temperature. A review on light scattering in cholesteryl esters and some illustrations of the application of the photographic light scattering technique to the study of cholesteryl myristate were published in 1968.(6) A helium-neon gas laser has been used to determine depolarization factors as a function of temperature and scattering angle for cholesteryl nonanoate, *p*-[N-(*p*-methoxybenzylidene)amino]phenyl acetate, and cholesteryl myristate.(7) Light scattering studies of orientation correlations in cholesteryl esters have been performed.(8)

Recently, we reported a simple technique of measuring the transparency of materials at any specific wavelength from the ultraviolet to the near infrared versus temperature.(9) It incorporates the sophistication inherent in the capabilities of the Cary 14 spectrophotometer. In the present paper we report using the technique to study the transparency of cholesteryl myristate, decanoate, and nonanoate, from the solid phase to the isotropic liquid. The light wavelengths used were 3000, 4000, 5000, 7000, and 25,000 A. The transparency characteristics of cholesteryl nonanoate being cooled from the liquid phase are also described. These particular liquid crystals were chosen because thermal studies and optical observations (by means of a microscope) concerning their phase transformation have been reported in detail.

2. Materials

The cholesteryl esters were obtained from Distillation Products Industries in a " white label " grade. They were each recrystallized three times from ethanol prior to use. Cholesteryl nonanoate was also recrystallized three times from acetone and hexane in order to check whether any transparency differences arise because of the solvent of recrystallization. The experimental technique chosen for the purification was essentially that described by Vogel(10) for solid organic compounds. In each case the cholesteryl ester was dissolved in the solvent at or near its boiling point. The hot solution was filtered from particles of insoluble material and dust. The solution was allowed to cool to room temperature by swirling the flask under tap water. This caused the ester to crystallize out. (The hexane solution, however, had to be placed in a freezer in order to cause the crystallization.) The solid was collected by filtration; the entire procedure was performed three times. The resulting material was dried in a vacuum dessicator at room temperature and <0.1 mm for a minimum of 15 hr.

The ethyl alcohol was U.S.P. 200 proof from Publiker Industries, Inc. The acetone was Reagent A.C.S. Code 1004 from Allied Chemical, Specialty Chemicals Division. The *n*-hexane was Certified A.C.S. Spectranalyzed® from Fisher Scientific Co.

3. Cell Technique

The cell sample preparation described previously for transparency studies of phenyl benzoate and the nematic liquid crystal, butyl *p*-(*p*-ethoxyphenoxycarbonyl)phenyl carbonate,(9) was used also for this study. Essentially, the procedure involved heating a sample held in a 0.075 mm lead spacer between calcium fluoride plates (25.2 × 5 mm) in a brass holder placed in a Cary 14 spectrophotometer. As mentioned previously,(9) it was necessary to *premelt* the material in the spacer cavity in order to obtain a uniform thickness of the sample in the spacer. (Also, this could allow trapped solvent of recrystallization to boil off.) The second CaF_2 plate was then dropped gently onto the spacer. A surface thermistor probe was mounted permanently in the face of one of the CaF_2 plates. A digital thermistor thermometer (accuracy ± 0.15 °C [10–90 °C]) was used as a visual indication of sample temperature. Further details concerning the technique are available.(9)

Changes in transmittance at a fixed wavelength were recorded continuously as the temperature was allowed to change at approximately 0.5 °C per min. Generally, the same sample was used for repeated runs with different wavelengths of incident light. The longer wavelengths were utilized first in such series of runs. The same sample was never stored in the cell longer than five days. Between runs with different samples the CaF_2 plates were cleaned with CCl_4 (Reagent A.C.S. Code 1554, Allied Chemical, Specialty Chemicals Division) and allowed to dry in air.

4. Transparency Changes with Heating

The appearance of the heating curves obtained with cholesteryl myristate, decanoate and nonanoate (for example see Figs. 1–3) differs considerably between compounds as well as from that of a curve obtained previously(9) with a nematic liquid crystal.

Listed in Table 1 are temperatures corresponding to major features of each transparency curve. Salient features of the transparency curves can be described by maxima, minima, slope changes and shoulders with sharpness and intensity depending on the particular compound and the incident wavelength.

Assignments in Table 1 of the major transitions are based on values reported by others who used differential thermal analysis,

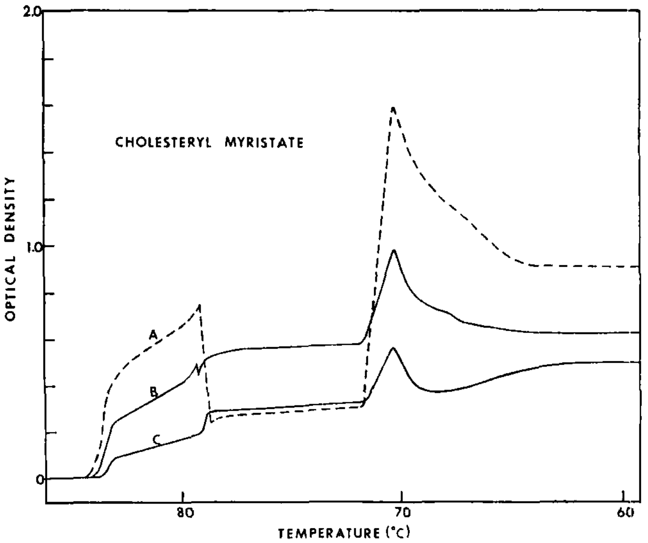

Figure 1. Transparency of cholesteryl myristate to light wavelengths of 3000 A (curve A), 7000 A (curve B), and 25,000 A (curve C) versus increasing temperature.

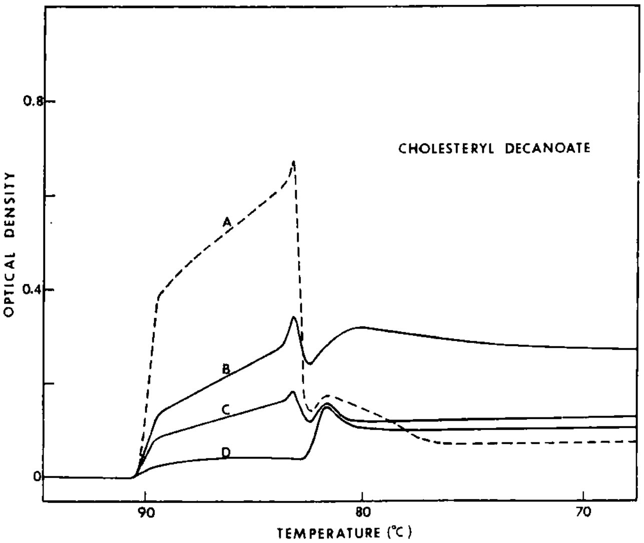

Figure 2. Transparency of cholesteryl decanoate to light wavelengths of 3000A (curve A), 4000A (curve B), 7000A (curve C), and 25,000A (curve D) versus increasing temperature.

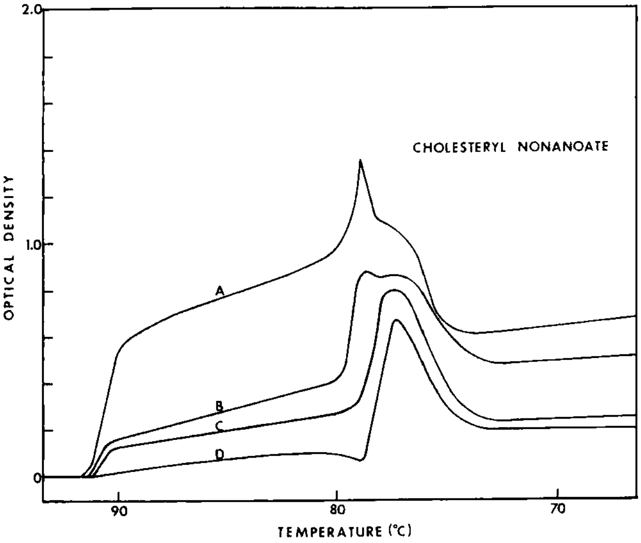

Figure 3. Transparency of cholesteryl nonanoate to light wavelengths of 3000A (curve A), 5000A (curve B), 7000A (curve C), and 25,000A (curve D) versus increasing temperature.

Table 1 Temperatures Corresponding to Transparency Curve Features

Curve feature	Temperature (°C) Incident Wavelength (A) 3000	4000	5000	7000	25,000	Interpretation	
Cholesteryl Myristate						(Average)	
min or slope change	65.1	62.6	63.8	67.5	69.1	(65.6 ± 2.3)	solid–solid
min or shoulder	69.5	69.6	69.6	69.6	69.1	(69.4 ± 0.2)	solid–solid
max	70.3	70.4	70.3	70.4	70.4	(70.4)	solid–smectic
min or slope change	71.0	71.0	71.0	71.1	70.9	(71.0)	
max or slope change	77.9	77.9	78.2	78.0	78.1	(78.0 ± 0.1)	smectic–cholesteric
min	78.0	78.7	78.7	78.7	78.5	(78.5 ± 0.2)	
max	78.6	78.8	78.9	78.8	—	(78.8 ± 0.1)	
slope change	83.0	83.3	83.4	83.3	82.9	(83.2 ± 0.3)	cholesteric–isotropic liquid
isotropic melt	84.0	84.0	83.7	83.7	83.2	(83.7 ± 0.2)	
Cholesteryl Decanoate							
max	81.6	80.3	76.4	82.1	81.9	(80.5 ± 1.8)	solid–solid
min	82.5	82.7	82.9	82.7	82.8	(82.7 ± 0.1)	solid–cholesteric
max	83.3	83.2	83.4	83.2	—	(83.3 ± 0.1)	
slope change	83.5	83.6	83.8	83.4	—	(83.6 ± 0.1)	
slope change	89.6	90.0	90.2	90.1	89.5	(89.9 ± 0.3)	cholesteric–isotropic liquid
isotropic melt	90.4	90.9	90.7	90.5	90.4	(90.6 ± 0.2)	
Cholesteryl Nonanoate							
min or slope change	74.8	75.1	74.9	74.9	75.1	(75.0 ± 0.1)	solid–solid
shoulder or max	77.4	77.3	77.4	77.4	77.8	(77.5 ± 0.2)	solid–cholesteric overlapped with dichroic peak
shoulder or max	78.6	78.5	78.5	78.4	78.6	(78.5 ± 0.1)	
min or slope change[a]	78.9	81.0	78.9	78.9	—	(79.4 ± 0.8)	
slope change	91.0	91.1	91.2	90.9	90.6	(91.0 ± 0.2)	cholesteric–isotropic liquid
isotropic melt	92.0	92.0	91.6	91.5	91.0	(91.6 ± 0.3)	

(a) Dichroic peak.

differential scanning calorimetry, and microscopy (Table 2). In all cases transparency curve features changed markedly at or near the reported transition temperatures. The curves reflect the *temperature ranges over which the transitions occur within the sample volume exposed to the spectrophotometer light beam.* Light scattering changes during the transition reflect nucleation phenomena, growing of the new phase, and disappearance of the previous phase. The degree of light scattering at any particular point depends on a number of factors including the size of the domains present, their relative orientations,

TABLE 2 Reported Transition Temperatures

Cholesteryl Ester	Technique (ref)	Transition Temperatures (°C)				
		monotropic metastable$^{(c)}$	solid–smectic	solid–cholesteric	smectic–cholesteric	cholesteric–isotropic liquid
Myristate	DTA (11)		73.6		79.7	85.5
	Microscopy (12)		71		81	86.5
	DTA (13)$^{(a)}$		70.8		78.8	84.2
	DTA (13)$^{(b)}$		69.5		78.4	83.5
	DSC (14)		73.6		79.7	85.5
	DSC (15)		70.2		77.6	82.4
Decanoate	DTA (11)			85.7		91.2
	Microscopy (12)	81.5		85.5		92.5
	DSC (14)			87.5		91.2
	DSC (16)	79.5		84		91.5
Nonanoate	DTA (11)		74.0		80.8	93.0
	Microscopy (12)	77.5		80.5		92
	DSC (14)		74.0		80.8	93.0
	DSC (16)	76.5		79.5		92.5
	DSC (17)			77.0$^{(d)}$		90.5$^{(d)}$
		74.8$^{(e)}$		77.8$^{(e)}$		91.7$^{(e)}$

(a) Recrystallization solvent, acetone-benzene. (b) Recrystallization solvent, ethanol. (c) Observed on cooling. (d) As received from Eastman Chemicals (no purification). (e) Recrystallization solvent, *n*-pentanol.

and also film thickness. In the present study the sample was contained within a 0.075 mm spacer. Secondary scattering and birefringence can also affect the " apparent " transmission, thus causing increases or decreases in the observed optical density. Furthermore, a cholesteric phase can reduce transmitted light as a result of a dichroic effect. Such an effect was noted with cholesteryl nonanoate. The dichroic peak appears to overlap the light scattering change caused by the solid to cholesteric phase transition. Fundamental information on light scattering by liquid crystals is available.(6–8)

High intensity light scattering is shown in the curves by low transmittance, i.e., high apparent absorbance. As expected it was found that the shorter wavelengths generally scattered more than the higher ones. The one exception was noted in the smectic phase of cholesteryl myristate. In this instance the light scattering by 3000 A and 25,000 A were nearly the same. In general, the wavelength affected the degree of light scattering. However, it did not influence the position (temperature) at which curve features changed.

Dichroic properties of the cholesteric phase of cholesteryl nonanoate are evident in the series of curves in Fig. 3. The intensity of reflected light due to dichroism is much more pronounced with the lower wavelengths. No dichroic peak was evident with the 25,000 A light. However, it may be merged with the solid–cholesteric transition scattering peak. With 7000 A light a shoulder appears on the phase transition scattering peak. With 3000 A the dichroic effect produces a maximum while the solid–cholesteric transition scattering is observed as a shoulder. The shape of the dichroic peak varies somewhat from sample to sample. Different heating rates produce marked effects.

Solid–solid transparency curve features were generally not reproducible from sample to sample and in repeated runs with the same sample. Changes in solid state transparency are due undoubtedly to effects caused by impurities or products from sample decomposition. For example, cholesteryl nonanoate recrystallized from ethanol usually exhibited a slight minimum in the transparency curve near 75 °C when 5000 A light was employed. A sample freshly recrystallized from acetone did not show this; the scattering simply increased at that point. However, after the heating and cooling cycle was repeated five times the minimum did develop. The effect of recrystallization solvent on transition temperatures is discussed later in this paper.

As shown in Table 1, the temperature ranges over which transitions occur for a particular compound agree closely irrespective of the wavelength. Widest variations from the average are evident with the ultraviolet and infrared wavelengths. Very close agreement was found between the three visible wavelengths. Also, temperatures agreed within 0.1 °C in three runs at 5000 A with the same sample of cholesteryl nonanoate at three slightly different heating rates (0.25, 0.4 and 0.75 °C/min). Checks at several wavelengths with the three esters showed that agreement within 0.3 °C of the values shown in Table 1 was obtained with new samples from different batches of compound.

Though the cell was not designed originally for use with a microscope, it was convenient to find that the apparatus fitted easily on the stage of a Bausch and Lomb PBV–5B microscope with the 10X objective in place. The reported assignments through microscopy(12) of cholesteryl nonanoate were confirmed by visually following the heating events through crossed polarizers. Repeated runs indicated clearly that the solid–cholesteric transition occurs between 78.4 to 78.7. Dichroic scattering did not interfere with the visual observation of the transition. The cholesteric–isotropic liquid transition was observed occurring between 91.1 to 91.3 °C in repeated runs.

5. Transparency Changes with Cooling

Cooling curves were obtained with each of the compounds. All of the curves exhibited characteristics which could be attributed to supercooling phenomena. An example with cholesteryl nonanoate is given in Fig. 4. The scattering of 5000 A light is shown for a complete heating and cooling cycle. An interpretation of the curve obtained during the heating was given previously in Table 1. In the cooling step, several " peaks " are immediately evident in the cholesteric portion of the curve. These were not reproducible from run to run. It is not clear at this time what these are due to. Obser-

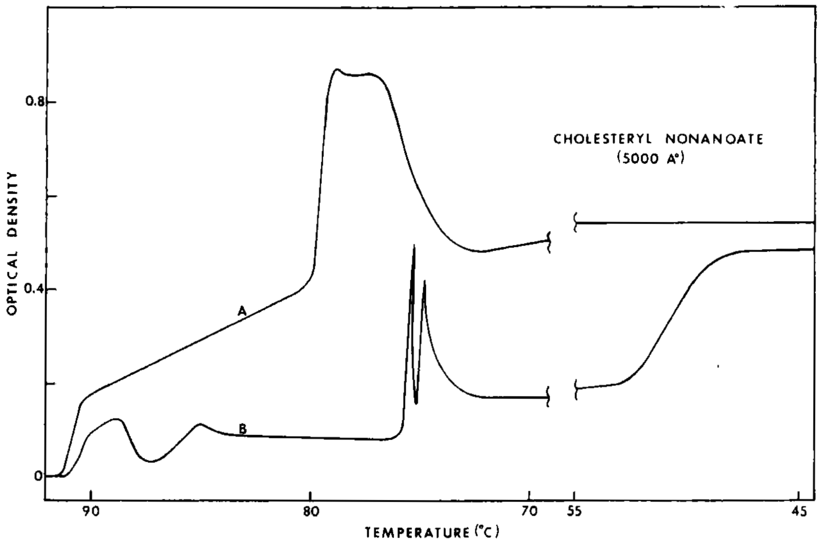

Figure 4. A comparison of the transparency to 5000 A light of cholesteryl nonanoate while being heated from the solid state (curve A) and being cooled from the isotropic liquid state (curve B). (Heating rate, 0.35 °C/min; cooling rate, 0.8 °C/min).

vations using a polarizing microscope showed that the transition from isotropic liquid to the cholesteric phase takes place over a wide range. In several instances some liquid phase could be seen near the temperature of the dichroic scattering.

In general, through all phases and transitions, cholesteryl nonanoate scattered less light on being cooled from isotropic liquid than on being heated from the solid state. Two sharp maxima are evident in the cooling curve shown in Fig. 4. The temperatures corresponding to these curve features are given in Table 3 as a function of wavelength.

TABLE 3 Temperatures Corresponding to Maxima in Transparency Curves of Cholesteryl Nonanoate Being Cooled from the Isotropic Liquid State (Cooling rate, 0.8 °C/min)

Wavelength (A)	Temperature (°C) Dichroic effect	Temperature (°C) Cholesteric–smectic
3000	84.4	74.8
4000	76.0	74.7
5000	75.5	74.9
7000	75.0[a]	74.6
25,000	—	72.9

(a) This peak was not always seen. It sometimes appeared as a shoulder on the adjacent peak.

That the maximum which occurs at the higher temperature is actually due to a dichroic effect was confirmed visually in a separate experiment by observing the colored light reflectance. At wavelengths below 5000 A the dichroic band in the transparency curve becomes much broader. At wavelengths above 5000 A the band is more difficult to see because it approaches the adjacent peak. This latter band signifies the monotropic transition from the cholesteric to the smectic phase. This was verified through use of a polarizing microscope. Also, the position of the maximum corresponds closely to the temperature assigned for this transition by others (Table 2). Finally, a smectic–solid state transition occurs over a 5 °C range below 55 °C as verified by microscopic examination of the cell sample.

We found no evidence through microscopy or transparency measurements for the formation of a smectic phase when cholesteryl nonanoate is heated from the solid state.

6. Effect of Recrystallization Solvent

In a recent report on the thermodynamic properties of cholesteryl esters it was pointed out that a significant portion of the recrystallization solvent may remain sorbed or bound in the solid phase.(18) The solvent would act as an impurity in the solid crystals and alter thermal properties. The authors(18) purposely introduced impurities by allowing solutions of the cholesteryl esters to evaporate slowly to dryness. Differences were noted in heats and temperatures of the mesophase transitions with the magnitudes depending on which solvent the test residues were obtained from. Of the solvents studied acetone appeared to give the most pure compounds.

A comparison of transparency curve features from samples of cholesteryl nonanoate recrystallized three times from either ethanol, acetone or hexane, is given in Table 4. All features except for the initial one (attributed to a solid phase transition) correspond closely. In view of recent reports(17,18) concerning effects of recrystallization solvent on transition temperatures and thermal properties of liquid crystals, the agreement of transparency features given in Table 4

TABLE 4 Effect of Recrystallization Solvent on Transparency–Heating Curve Features of Cholesteryl Nonanoate(a)

Curve feature	Temperatures (°C)(b)				
	Recrystallization solvent				
	Ethanol	Acetone(c)	Acetone(c)	Acetone(c)	Hexane
min or slope change	74.9	75.2	75.3	75.5	76.5
shoulder or max	77.4	77.7	77.7	(d)	(d)
shoulder or max(e)	78.5	78.1	78.1	78.1	78.2
min or slope change	78.9	78.8	78.7	78.9	78.9
slope change	91.2	91.0	90.9	91.1	90.9
isotropic melt	91.6	91.4	91.3	91.5	91.4

(a) Incident wavelength 5000 A. For an interpretation of the curve features, see Table 1. (b) Irrespective of the recrystallization solvent, a second run with the same sample gave curve features which agreed within 0.1 °C. (c) Different sample. (d) Appears to be merged with max at 78.1 °C. (e) Dichroic peak.

appears surprising. However, careful recrystallization and premelting the ester during sample preparation (which could allow evaporation of trapped solvent and degassing) resulted in samples similar enough in purity so as not to affect the transition temperature ranges. On the other hand the solid state features are more sensitive to impurities. Of the three solvents tried, hexane gives the least pure material.

7. General Considerations

The technique reported in this paper provides a spectrophotometric method of following transitions which occur from the solid to isotropic liquid phases. It is reliable with regard to the detection of the transition and the accuracy and reproducibility of the temperature range over which the transition occurs. Additionally, this method may be used to obtain intensity vs wavelength curves at a fixed temperature, with or without polarized light.

The events corresponding to transparency curve features can be checked with the sample cell by using a microscope. The sophistication inherent in the use of a spectrophotometer will allow this technique to be used in studying the effect of bulk impurities on the various transitions of mesomorphic materials.

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