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Cholesteric Liquid Crystalline Polyesters. 1. Cholesteric Liquid Crystalline Copolyesters Based on Poly(chloro-1,4-phenylene *trans*-1,4-cyclohexanedicarboxylate)

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ABSTRACT: Thermotropic copolyesters exhibiting cholesteric mesophases were prepared by introducing chiral (*R*)-3-methyladipate units into rigid poly(chloro-1,4-phenylene *trans*-1,4-cyclohexanedicarboxylate), and a morphology study of the solid cholesterics was examined by using a transmission electron microscopy method. The transmission electron micrographs showed a series of dark and bright striation lines which were attributed to the periodic structure of the cholesteric helix. Defects or imperfections such as disclinations and edge dislocations of the cholesteric layer texture were elucidated from the micrographs. These cholesteric copolyesters were also characterized by DSC, spectroscopic, and optical microscopic methods. The inverse cholesteric pitch (or the twisting power) increased in direct proportion to the molar content of chiral units. For a given copolyester, the inverse pitch decreased with increasing temperature. It was significantly affected also by the molecular weight of the polymer; high molecular weight polymers exhibited a smaller twisted angle which may be associated with a larger order parameter.

Introduction

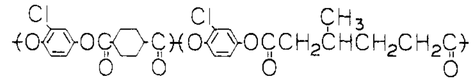
Main-chain liquid crystalline (LC) polymers have been the subject of numerous studies in recent years to understand polymeric effects on the thermotropic liquid crystalline properties. The structure of this type of polymers can be controlled so that flexible and rigid mesogenic segments are incorporated in an alternative fashion along the main chain. Alternation of the repeating units may affect the molecular packing of LC polymers. Such packing alters the properties of the mesophase from those of low-molar-mass mesogen, since mesogenic groups are closely coupled through the flexible part in such alternate structure that a polymeric molecule must adopt a peculiar conformation or molecular packing. Polyesters are some of the typical main-chain LC polymers, and numerous examples have been reported to clarify the peculiar mesogenic properties of LC polymers.[1,2] Since almost all cholesteric polyesters have the alternative–fashion structure in their flexible and rigid mesogenic segments, it is also of interest to investigate how the properties of the cholesteric mesophase would be affected by introducing flexible chiral units into a rigid-rod copolyester in a random fashion.

Apart from the fundamental studies, the main-chain LC polymers are of special interest in the search of industrial materials possessing superior mechanical properties. Rigid polyesters and polyesteramides are such suitable materials with their proven superior mechanical properties in fibers and plaques and with their ease of melt processing in liquid crystalline phases. So far, nematic liquid crystalline polymers have been utilized to prepare ultrahigh modulus fibers, since the uniaxial alignment characteristic of nematic phases offers a narrow distribution of polymer molecules along the fiber axis.[3] In the case of films in which biaxial orientation, with every molecule lying parallel to a film plane, must be required, however, the nematic uniaxial alignment is not adequate. In recent years, thus, cholesteric LC polyesters have been considered as an ideal material for high strength and high modulus films.[4-6] Thin cholesteric mesophases would attain a Grandjean planar texture having all of the helix axes perpendicular to the film surface, since the long rigid or semirigid molecules lie preferentially parallel to the film surface. If this structure could be retained during solidification, the resultant film should exhibit optimum mechanical properties when tested along any arbitrarily selected direction in the film plane. This concept has interested us to investigate cholesteric mesophases of aromatic polyesters.[5-10]

With the objectives mentioned above, we prepared cholesteric liquid crystalline copolyesters by introducing chiral (*R*)-3-methyladipate units into poly(chloro-1,4-phenylene *trans*-1,4-cyclohexanedicarboxylate). The latter rigid homopolyester is well-known to exhibit nematic mesophases, and its fibers obtained by melt processing have yielded superior mechanical properties.[11,12] The cholesteric mesophase properties of the copolyesters were described by examining the dependence of pitch on the content of chiral units, temperature, and molecular weight. Morphology studies for solid cholesterics were also made by transmission and scanning electron microscopy methods which allowed direct observations of cholesteric domain texture.

Experimental Section

Materials. *trans*-1,4-Cyclohexanedicarboxylic acid (mp 312 °C) and (R)-3-methyladipic acid (mp 89 °C), obtained from Aldrich Chemical Co., were purified before use. Chlorohydroquinone diacetate (mp 68 °C) was prepared by the conventional acetylation of chlorohydroquinone with acetic anhydride and recrystallized from an ethanol–water mixture. Polyesters presented by the following formula were prepared by melt condensation (transesterification).



$$\mathrm{-\!\!\left(O\text{-}C_6H_3Cl\text{-}OC(=O)\text{-}C_6H_{10}\text{-}C(=O)\right)\!\left(O\text{-}C_6H_3Cl\text{-}OC(=O)CH_2CH(CH_3)CH_2CH_2C(=O)\right)\!\!-}$$

Transesterification was performed by placing equimolar amounts (0.01 mol each) of chlorohydroquinone diacetate and dibasic acid, along with 0.025 g of sodium acetate, in a glass flask equipped with a stirrer and short heads provided with nitrogen inlet and outlet. The nitrogen outlet was connected to a glass distillation column, which led to a receiver provided with a vacuum pump. After being evacuated and being purged with nitrogen, the flask was maintained at 150 °C for 1 h and at 200 °C for additional 1 h in a nitrogen atmosphere. Then a flow of nitrogen stream

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Table I
Characterization of Cholesteric Copolyesters

monomer composition (mol %)							
CP[a]	CH[a]	MA[a]	IV, dL/g	T_2,[b] °C	λ_m,[c] nm	cholesteric color	remarks
50	50	0	2.63	314		colorless	nematic
50	40	10	0.23	246	531	green	cholesteric
50[d]	40[d]	10[d]	0.88	243	660	red	cholesteric
50	40	10	1.61	263	685	red	cholesteric
50	40	10	1.91	250	712	red	cholesteric
50	35	15(R&S)	0.37	245		colorless	nematic
50	35	15	0.27	240	396	violet	cholesteric
50[e]	35[e]	15[e]	0.87	239	435	green	cholesteric
50	35	15	1.06	239	456	green	cholesteric
50	35	15	1.30	246	490	green	cholesteric
50	35	15	1.48	245	508	green	cholesteric
50	30	20	0.81	244	390	violet	cholesteric
50	30	20	1.02	228	370	violet	cholesteric

[a] Abbreviations: CP, chloro-1,4-phenylene; CH, *trans*-1,4-cyclohexanedicarboxylate; MA, (*R*)-3-methyladipate. [b] Determined by DSC. [c] λ_ms were measured at 280 °C for copolyesters having 10 mol % MA, 270 °C for those having 15 mol % MA, and 260 °C for those having 20 mol % MA. [d] From proton NMR analysis, the copolyester was composed of 50.8 mol % of CP unit, 39.0 mol % of CH unit, and 10.2 mol % of MA unit. [e] From proton NMR analysis, the copolyester was composed of 49.8 mol % of CP unit, 35.8 mol % of CH unit, and 14.4 mol % of MA unit.

was started and maintained at 200 °C for 0.5 h and at 220 °C for 1.5 h to slowly distill off the acetic acid formed. Finally, the reaction was performed at 270 °C under a reduced pressure (less than 30 Pa). These conditions were maintained for 0.5–2 h, depending on the degree of polymerization desired.

Methods. Inherent viscosities (IV or η_{inh}) were measured at 30 °C by using 0.5 g/dL solutions in a 60/40 mixture by weight of phenol and tetrachloroethane. Melting points were determined with a differential scanning calorimeter, DSC (Du Pont Instruments Model 910) at a scanning rate of 10 °C/min under a flow of dry nitrogen. Proton NMR analysis was used to determine the compositions of the copolyesters. Solutions for NMR analyses were prepared by dissolving 0.04 g of the copolyesters in 1 mL of trifluoroacetic acid. A JEOL Model GX-400 (400 MHz) spectrometer operated at ambient temperature was used. Texture observations were examined with an Olympus BH-2 polarizing microscope equipped with a Mettler FP82 hot stage. The domain texture was also examined by a scanning electron microscope, SEM (JEOL Model JSM-35CF), and by a transmission electron microscope, TEM (Philips Model EM420). Films (about 50 µm thick) for these examinations were prepared by quenching the liquid crystalline phases in ice water so that the original organization and regularity of the cholesteric structure present before quenching were preserved. They were subsequently fractured in liquid nitrogen, and the exposed surface was coated with Au for SEM observation. For TEM observation, the films were buried in an epoxy resin, and then thin microtomed specimens were cut perpendicularly to the film surface at ambient temperature from the hardened resin blocks. The examination using the TEM method was carried out in such a way that the microtomed sections about 100 nm thick were exposed to 100 kV of electron beam without any coating. Circular dichroism spectra were measured to determine the cholesteric pitch by utilizing an automatic recording spectropolarimeter (JASCO Model J-20) in the wavelength range from 300 to 700 nm. Reflection spectra were also detected with a spectrophotometer (Hitachi Model 330) equipped with an integral sphere to collect reflection light in the wavelength range from 350 to 1500 nm.

Results and Discussion

Characterization of Polymers. Copolyesters with molar contents of (*R*)-3-methyladipate unit varying from 0 to 20 mol % were synthesized, and several samples varying over a range of inherent viscosities were prepared for each polymer. They are listed in Table I. Proton NMR analysis was used to determine the compositions of the copolyesters; the calculated compositions were identical with the mole fraction of each monomer unit as listed in Table I.

Column 5 of Table I lists the transition temperatures of the polymers measured by DSC heating thermograms. The basic homopolyester, poly(chloro-1,4-phenylene *trans*-1,4-cyclohexanedicarboxylate), was characterized by the presence of two first-order reversible transitions: a major one at T_1 (197 °C) which involves a crystal–crystal transition and the second at T_2 (314 °C) which represents the melting of the crystal into a nematic liquid crystal. No transition of liquid crystal to isotropic melt was detected before thermal decomposition. These data for the homopolyester are in good agreement with those previously reported.[11,12] The introduction of flexible (*R*)-3-methyladipate units into this rigid-rod homopolyester reduced both transition temperatures remarkably.

The introduction of chiral units also caused the conversion of nematic liquid crystal to cholesteric (chiral nematic). This was easily recognized during the polymerization process because bright iridescent colors attributable to a cholesteric helical structure appeared on the wall of the glass flask. These colors are listed in column 7 of Table I. Further confirmation of cholesterics was made by microscopic observation of the liquid–crystal texture. Figure 1a shows a photomicrograph of the liquid–crystal phases attained at 245 °C in the copolyester having 15 mol % of (*R*)-3-methyladipate unit and η_{inh} = 0.27 dL/g. Here, the thin sample was prepared by applying shear stress to the melt placed between glass plates. It displays oily streaks in the fluid Grandjean texture, which is the decisive characteristic of cholesteric mesophases. By contrast, Figure 1c shows a photomicrograph of the nematic schlieren texture exhibited by the nematic mesophases of the copolyester with the same content of racemic 3-methyladipate unit. It should be noted here that such an appearance of a typical Grandjean texture is limited to the cholesterics of low molecular weight copolyesters. High molecular weight copolyesters exhibited an obscure polydomain texture composed of a great number of small birefringent regions which were never transformed into a Grandjean texture even after a period of more than 30 min. Their high viscosities might have interrupted the development of a well-defined texture. The example can be seen in Figure 1b for the copolyester with a chiral content of 15 mol % and with η_{inh} of 0.87 dL/g.

The cholesteric mesophase structure of a polymer system can be retained in a solid film.[5,13,14] The high viscosity of the liquid crystalline phases is responsible for ease of solidification. In the present study, the films retaining the cholesterics were prepared by melt pressing according to the following procedure. Copolyester powders were placed

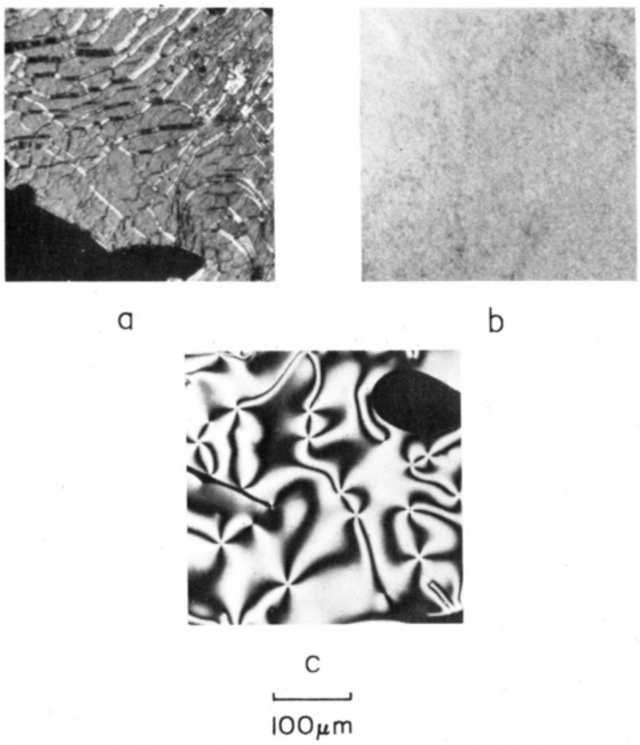


Figure 1. Photomicrographs of (a) the cholesteric mesophases of copolyester (η_{inh} = 0.27dL/g) with 15 mol % of (*R*)-3-methyladipate unit taken at 245 °C, (b) the cholesteric mesophases of copolyester (η_{inh} = 0.87 dL/g) with 15 mol % of (*R*)-3-methyladipate unit taken at 270 °C, and (c) the nematic mesophases of copolyester (η_{inh} = 0.37 dL/g) with 15 mol % of racemic 3-methyladipate unit taken at 240 °C.

between two polyimide films, in which a metal shim was inserted to adjust the film thickness, and heated at the temperature at which an anisotropic melt would form. Then, the melt was made to flow by using a hydraulic press, and, after a period of less than 1 min, quenched in ice water to form a thin film of about 50 μm. It should be noted here that low molecular weight copolyesters, which displayed a typical Grandjean texture in the melt, were too weak to form a solid film.

We believe that this freezing process has completely preserved the original cholesteric structure before quenching, since both the cholesteric colors and shape of reflection spectra remained unchanged except for a slight blue-shift of the wavelength of the maximum reflection. The blue-shift can be explained by the appearance of a thermal shrinkage of the distance between neighboring cholesteric layers.

Factors Affecting Cholesteric Pitch. Circular dichroism (CD) and reflection spectra were observed for solid cholesteric films to determine their cholesteric pitches. The typical CD and reflection spectra are shown in Figure 2 for the copolyester having 10 mol % of chiral unit. The positive CD spectrum indicates that the sense of cholesteric helix is left-handed. The same sense has been observed in other copolyesters with the same chiral unit.[5,6] The rather broad spectra suggest wide distributions for both pitch lengths and orientations of the cholesteric helical axes.[15]

From the wavelengths of maximum reflectivity of the spectra, the cholesteric pitch (*P*) can be calculated from the following equation[16]

$$\lambda_m = nP \qquad (1)$$

where λ_m is the wavelength of maximum reflectivity and n is the average refractive index of a film which is assumed

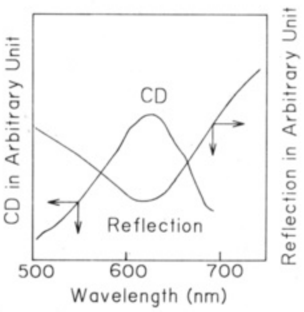


Figure 2. CD and reflection spectra observed for the solid cholesteric film of copolyester (η_{inh} = 0.88 dL/g) having 10 mol % of chiral unit.

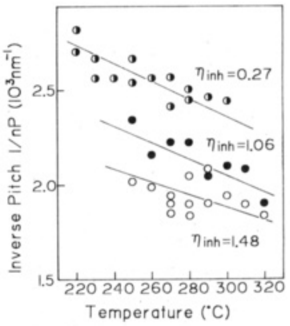


Figure 3. Temperature dependence of inverse optical pitch for three copolyesters having 15 mol % of chiral unit and different inherent viscosities. Inherent viscosities are shown in the figure.

to be 1.5. In using this equation, cholesteric planes should be perpendicular to the incident light.[16] This is qualitatively satisfactory in the present system when the light is aimed perpendicularly at the film surface, since the cholesteric layers are distributed nearly parallel to the film surface as shown in Figure 7a. As found in Figure 2, the wavelengths of maximum reflectivity of both CD and reflection spectra were completely coincident; so, hereafter, the reflection spectra were utilized for the determination of pitch lengths.

Figure 3 illustrates temperature dependence of the inverse optical pitch, $1/nP$, for copolyesters containing 15 mol % of chiral unit and having different inherent viscosities. The inverse pitch, which is proportional to the twist angle, decreases with increasing temperature. The temperature dependence appears to be independent of chiral contents and of inherent viscosities, giving the average value of $\mathrm{d}\ln P/\mathrm{d}T = 1.9 \times 10^{-3}\ \mathrm{K}^{-1}$ or $\mathrm{d}(1/nP)/\mathrm{d}T = -4.1 \times 10^{-4}\ \mathrm{nm}^{-1}\ \mathrm{K}^{-1}$. This value exceeds, to a large extent, the thermal expansion of molecular spacing, *D*, with an expansion factor, $\mathrm{d}\ln D/\mathrm{d}T$, of the order of $10^{-4}\ \mathrm{K}^{-1}$; thus, one can attribute the value mainly for decreasing the twisted angle. This dependence is of interest when it is compared to that observed in copolyesters with flexible and rigid mesogenic segments incorporated in an alternative fashion.[5,6,10] Krigbaum and Watanabe[5,6] reported a reverse tendency in which inverse optical pitches increased with increasing temperature (an average value of $\mathrm{d}(1/nP)/\mathrm{d}T = 1.0 \times 10^{-5}\ \mathrm{nm}^{-1}\ \mathrm{K}^{-1}$). On the other hand, the same tendency with negative values of $\mathrm{d}(1/nP)/\mathrm{d}T$ was observed in the cholesteric copolyesters prepared by Lenz.[10] Further accumulation of data concerning the temperature dependence of inverse optical pitch would be necessary for clarification of the phenomenon.

Figure 3 also shows that optical pitches are significantly affected by inherent viscosities (or molecular weight) of the polymers. This can be more clearly observed in Figure 4 where inverse optical pitches are plotted against inherent viscosity. The higher molecular weight polymer indicates

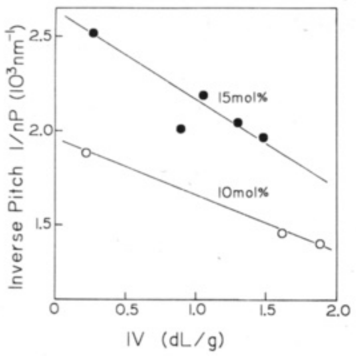


Figure 4. Dependence of inverse optical on the inherent viscosity of copolyester: (○), the data at 280 °C for copolyester with 10 mol % chiral unit; (●), the data at 270 °C for copolyester with 15 mol % chiral unit.

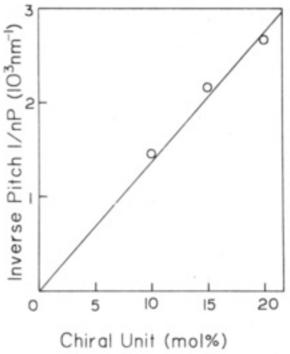


Figure 5. Dependence of inverse optical pitch on the mole fraction of chiral unit. The data were collected at 270 °C for copolyesters with the inherent viscosity of 1.0–1.6 dL/g.

a larger optical pitch, thus a smaller twisting angle. Concerning this point, one recalls previous results that cholesteric phases with higher order parameters have smaller twisting angles.[6] A similar situation, hence, is likely here such that larger order parameters or stronger orientation-dependent interactions, expected for high molecular weight polymers, may cause a decrease in the twisting power. We, however, also recall that different variations on molecular weight dependence of pitch in the lyotropic cholesteric polymer liquid crystals have been observed.[14,17–19] Such observations point to other factors affecting the dependence which may not be simple.

At some given temperature (270 °C) and inherent viscosity (1.0–1.6 dL/g), the inverse optical pitch is plotted against the molar content of chiral unit in Figure 5 where a linear relationship is observed between both parameters, at least in this limited region of chiral content from 0 to 20 mol %, exhibiting the arising of the twisting power as a direct result of the introduction of chiral units.

Domain Texture of Cholesteric Films. Characteristics of a cholesteric layer texture are generally examined by optical microscopic methods based on the observation of defects or imperfections of the layer texture. Three types of cholesteric textures can be defined in terms of the kinds of defects which they contain: planar textures with dislocations only; polygonal textures with dislocations and focal conics; fan textures with dislocations, disclinations, and focal conics.[20–22] In the present system, however, optical microscopy is not suitable to define a cholesteric structure, since no well-developed textures were observed with middle and high molecular weight cholesteric copolyesters. Moreover, it has a resolution of only about 1 μm which makes it difficult to decide whether the iterative filling of the cholesteric layers is complete or not.

As a result, freeze–fracture electron microscopy, which was useful to examine such defect structures as disclinations, edge dislocations, and confocal domains,[23,24] was used here. In Figure 6 are shown SEM micrographs which were observed for the fractured surface of a cholesteric film having 15 mol % chiral unit and exhibiting an obscure polydomain texture. Here, the film of about 50 μm was fractured so that the fractured surface was perpendicular to the film plane. No obvious layer texture was detected in these photographs although the fractured surface was completely different from that of a nematic film which exhibited a fibrous structure. In contrast, the TEM micrographs obtained from microtomed specimens cut out of the same film showed a series of dark and bright lines (see Figure 7). Since no lines are observed for microtomed nematic films, these lines can be attributed to the periodic structure of cholesteric helix. This attribution is also supported by the fact that minimum distances between parallel bright or dark lines well correspond to a half of the pitch lengths determined by the spectroscopic methods listed in Table II.

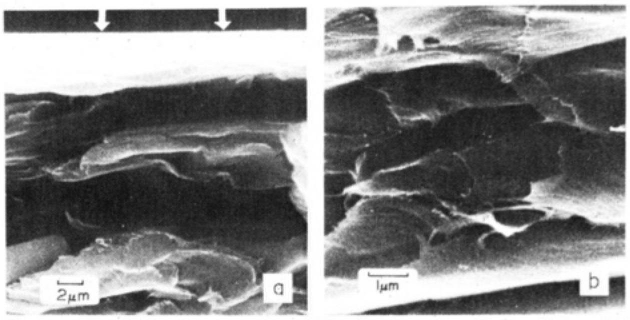


Figure 6. SEM micrographs of the fractured surface of the solid cholesteric film (around 50 μm) for copolyester (η_{inh} = 0/87 dL/g) having 15 mol % of chiral unit. The micrographs (a) and (b) were taken with different magnifications for the same fractured surface. Arrows indicate the film surface.

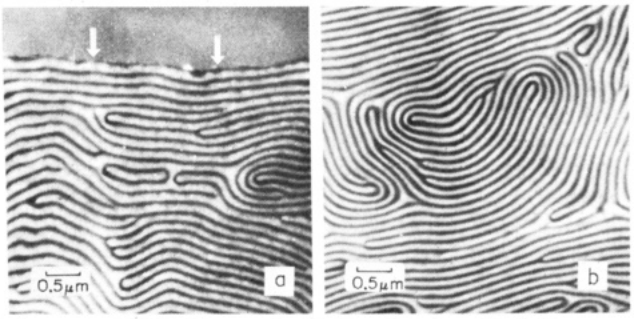


Figure 7. TEM micrographs of the microtomed specimens cut out of the same film as in Figure 6. Arrows on the micrograph (a) indicate the film surface, and the micragraph (b) shows the deep section of the film.

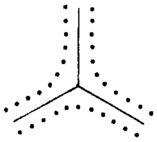
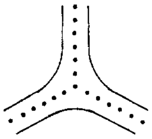
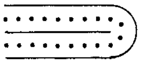
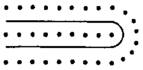
Table II
Pitch Lengths Estimated by Spectroscopic and TEM Methods

chiral unit content, mol %	spectroscopic method (nm)	TEM method (nm)
15[a]	280	290
10[b]	440	440

[a] The data were collected for the copolyester film with the inherent viscosity of 0.87 dL/g. [b] The data were collected for the copolyester film with the inherent viscosity of 0.88 dL/g.

The TEM photographs thus give useful information on cholesteric morphology retained in a film. First, one can readily see that striation lines are, to some extent, distributed parallel to the film surface such that the spectroscopic determination of cholesteric pitch can be made by using eq 1. In more precise observation, one knows that

Table III
Relative Frequencies of Disclinations

$-\pi$		$+\pi$	
τ^-	λ^-	τ^+	λ^+
			
rare	frequent	rare	frequent

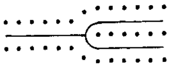
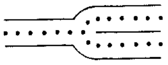
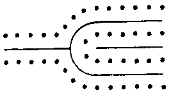
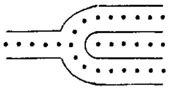
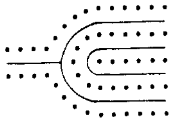
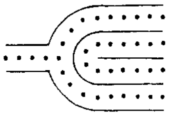
well-paralleled alignment of the lines is limited only in the section near the film surface. In the section deep into the surface (Figure 7b), the alignment is somewhat disturbed to produce a polydomain structure. The disturbed alignment may be associated with the broad appearance of CD and reflection spectra and also with the microscopic observations of a great number of birefringent regions as described previously. Second, one notices that the domains assemble with each other in such a way that the layers match coherently from one domain to another with layer deformations. The same kinds of deformations as those required by special rules of association and established in the cholesteric liquid crystals of low-molar-mass compounds[20,21] containing typical disclinations and translation dislocations are thus observed. Disclinations can be regarded as either triple points corresponding to the junction of three layers ($-\pi$) or as layers which abruptly disappear ($+\pi$). In each case, the core of the defects may be continuous or discontinuous depending on whether the molecules lie parallel (λ) to or normal (τ) to the defect line.

Since the least transmissibility of an electron beam makes a dark line on the TEM micrograph, the molecules on the dark lines presumably lie parallel to the plane of the micrographs (normal to the defect lines). The assumption was verified from the TEM micrographs of laminate films which were fabricated by stacking melt extruded nematic films such that their molecular orientations were arranged nearly at right angles to each other.[26] On the basis of the molecular orientations, $+\pi$ and $-\pi$ disclinations were counted from Figure 7 and from other TEM micrographs. These situations and their occurrences are summarized in Table III where molecules are represented by lines and dots when they are, respectively, parallel to and normal to the plane of the drawing. Both $-\pi$ and $+\pi$ disclinations occur in the micrographs, and the λ-type appears more frequently than the τ-type in each disclination. Their frequencies follow the rule noted by Kleman and Friedel[25] and λ disclinations are more likely to occur since molecular configurations are continuous in their cores.

Translation dislocations arise from the association of two disclinations and are separated according to the molecular orientations in the core and to the number of added layers. These situations and their occurrences are summarized in Table IV. The dislocations arise preferentially with a small Burgers' vector ($P'/2 > P' > 3P'/2 > ...$), and again it is quite reasonable that only $\lambda^-\lambda^+$ configurations are observed for the Burgers' vector of length P'. The rule that $\tau^-\lambda^+$ configurations appear more frequently than those of $\lambda^-\tau^+$ also corresponds to the rule deduced from the lyotropic cholesteric mesophase of polymers reported by Livolant.[22]

On the melt-processing cholesteric films with ideal biaxial orientation, it is most important to discover how to prepare a planar cholesteric texture and freeze it completely into a solid film as mentioned in Introduction. This could be accomplished only by studying details of the cholesteric texture. On this point, the TEM method presented here appears to offer relevant information although a better understanding can be achieved by combining it with the observations made by spectroscopy and optical microscopy methods. In the following papers of this series,[26] we will clarify conditions for developing an ideal planar texture by adjusting several factors such as chiral contents, molecular weight, and conditions of melt processing; and we will also present a relationship between the texture preserved in a film and its mechanical properties.

Table IV
Relative Frequencies of Dislocations

Burgers' vector		
$P'/2$	$\tau^-\lambda^+$  frequent	$\lambda^-\tau^+$  frequent
P'	$\tau^-\tau^+$  absent	$\lambda^-\lambda^+$  frequent
$3P'/2$	$\tau^-\lambda^+$  rare	$\lambda^-\tau^+$  rare

Summary and Conclusions

Copolyesters exhibiting cholesteric mesophases were prepared by introducing chiral (R)-3-methyladipate units into rigid poly(chloro-1,4-phenylene *trans*-1,4-cyclohexanedicarboxylate). The introduction of chiral flexible units decreased the homopolyester's transition temperature of crystal to liquid crystal and, at the same time, altered the nematic mesophase to the cholesteric. Observations of circular dichroism and reflection spectra were performed to determine the cholesteric pitches varying from 200 to 500 nm. The inverse cholesteric pitch (or the twisting power) increased in direct proportion to the molar content of chiral units. For a given copolyester, the inverse pitch decreased with incleasing temperature. The inverse pitch was also affected significantly by the molecular weight of the polymer; high molecular weight polymers exhibited a small-twisted angle, which may be associated with a large-order parameter. The twisted cholesteric structure was conserved by quenching to produce films having a distorted laminate structure at room temperature. Transmission electron microscopy observations of the microtomed specimens cut out of these films were made to examine the domain texture. The fine striation lines, so-called fingerprint pattern, were clearly observed by use of this method, offering useful information about such defects as disclinations and edge dislocations.

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Registry No. (Chlorohydroquinone diacetate)(*trans*-1,4-cyclohexanedicarboxylic acid)((R)-3-methyladipic acid) (copolymer), 111325-19-0.

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Diphenyl (2,3-Dihydro-2-thioxo-3-benzoxazolyl)phosphonate: A New, Reactive Activating Agent for the Synthesis of Amides and Polyamides

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ABSTRACT: A new activating agent for amide condensations, diphenyl (2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonate (**1**), was readily prepared at room temperature by the reaction of 2-benzoxazolethiol (**3**) with diphenyl phosphorochloridate (**2**) in the presence of triethylamine (TEA) in benzene. The reaction of carboxylic acids with amines in the presence of **1** was investigated by two procedures, a two-step and a one-step procedure. Both procedures gave corresponding amides in high yields under mild conditions. The direct polycondensation of dicarboxylic acids with diamines by using the activating agent **1** in the presence of TEA proceeded smoothly at room temperature to produce polyamides with inherent viscosities up to 1.2 dL g^{-1}. Furthermore, the activating agent **1** was used successfully for the chemoselective polyamidation; that is, polyamides from dicarboxylic acids and diamines containing various functional groups were prepared without special protection of the acylation-sensitive groups.

Introduction

Condensation ranks among the most important and fundamental reactions in organic synthesis, and many activating agents for promoting condensations by a two-step or a one-step procedure have been reported. Most such activating agents first react with carboxylic acids to give intermediates, such as acid anhydrides, active esters, or amides, which undergo subsequent nucleophilic attack by amino or hydroxyl groups. Therefore, a primary factor in determining whether or not the activating agents are effective is their ability to activate carboxylic acids.

It is well recognized that increased reactivity of carboxylic acid derivatives toward nucleophiles may be roughly correlated with greater stability of the leaving group anions, that is, the pK_a of the leaving groups. From this point of view, we previously exploited a series of good leaving groups in the synthesis of active esters and amides, demonstrating that the active ester and amide methods are useful in the preparation of high molecular weight polyamides under mild conditions.[1]

Based on the success of those studies, we continued to investigate new activating agents for the synthesis of amides, esters, and polyamides.[2] In the preceding papers, we showed diphenyl 2,3-dihydro-1,3-benzisoxazol-3-yl phosphonate,[3] phenyl bis(2,3-dihydro-2-oxobenzothiazol-3-yl)phosphinate,[4] and diphenyl (2,3-dihydro-2-oxo-3-benzothiazolyl)phosphonate[5] were new activating agents for the synthesis of amides and polyamides.

We now report that amides and polyamides can be easily obtained from carboxylic acids and amines by a two-step and a one-step procedure using the new activating agent diphenyl (2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonate.

Experimental Section

Materials. Solvents, Amines, and Carboxylic Acids. *N*-Methyl-2-pyrrolidone (NMP) (supplied by Idemitsu Kosan Co., Ltd.) and hexamethylphosphoramide (HMPA) were purified by vacuum distillation and stored over 4-Å molecular sieves. 4,4′-oxydianiline (**12a**) (supplied by Mitsui Toatsu Chemical Industries Ltd.) and 4,4′-methylenedianiline (**12b**) (supplied by Mitsubishi Chemical Industries Ltd.) were purified by recrystallization from tetrahydrofuran and benzene, respectively. Isophthalic acid (**9a**), adipic acid (**9b**), sebacic acid (**9c**), 5-hydroxyisophthalic acid (**14**), 5-aminoisophthalic acid (**16**), and 3,5-diaminobenzoic acid (**18**) were purified by recrystallization. Other reagents and solvents were obtained commercially and used as received.

Diphenyl (2,3-Dihydro-2-thioxo-3-benzoxazolyl)phosphonate (1). To a solution of 2-benzoxazolethiol (**3**) (4.53 g, 0.03 mol) and triethylamine (TEA) (4.2 mL, 0.03 mol) in benzene (35 mL) was added dropwise at room temperature with stirring a solution of diphenyl phosphorochloridate (6.2 mL, 0.03 mol) in benzene (10 mL). The addition was completed in 30 min, and stirring was continued at room temperature for an additional 90

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