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유연격자에 키랄성 3-메틸아디프산 잔기를 갖는 콜레스테릭 폴리에스테르

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Main Chain Cholesteric Copolyesters Containing Chiral 3-Methyladipoyl Moiety in the Spacers

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Abstract: Two new series of thermotropic, cholesteric copolymers were synthesized, and their thermal properties and cholesteric characteristics were studied by differential scanning calorimetry, by use of a hot-stage on a polarizing microscope, and by visual observation of the melts on a Fisher-Johns melting point apparatus. The copolymers prepared had either a combination of aromatic ester dyad and triad or a triad containing central trans-1,4-cyclohexylene unit and mixed spacers consisting of (+)-3-methyl adipoyl structure and either a polymethylene or 1,3-bis (carboxypropyl) tetramethyl disiloxane moiety. The change in the iridescent colors of the cholesteric polymers could be explained, at least, qualitatively based on the dependence of pitch on the two variables: composition and temperature. A couple of cholesteric polymers reported in the study has particularly low melting points about 50°C and showed visible iridescent colors upon melting.

INTRODUCTION

Many studies have been reported recently on the effect of the structural variations of mesogenic groups and the flexible spacers on the mesomorphic properties of main chain thermotropic polymers containing mesogenic units separated by flexible spacers[1-3]. In one of our recent articles was thoroughly reviewed the dependence of mesomorphic properties on the parameters such as structure and length of mesogenic groups and spacers[4,5].

One of the important molecular parameters is the inclusion of chiral centers into a nematic composition resulting in induction of cholesteric mesophase. We[6] recently reported the synthesis and properties of a series of thermotropic cholesteric copolyesters containing (+)-3-methyladipoly or (+)-3-methylhexylene moieties as chiral spacers. We observed that the pitch of the polymers increased with temperature. It could also be increased by increasing the content of nonchiral spacers. Other main chain as well as side chain cholesteric polymers were reported by other investigators[7,8]. Some of the polymers have pitch distance of such a range that they selectively reflect light of the visible region and show visible iridescent colors in melt or quenched states. As a continuation of our effort to attain a better understanding of the structure-property relationship of thermotropic polyesters, and also as an effort to develop cholesteric

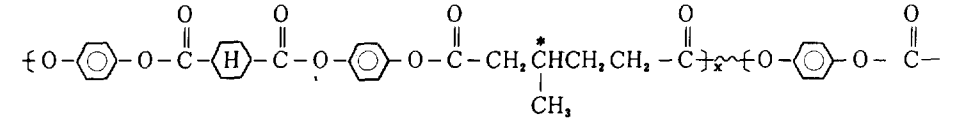
polymers with relatively low melting points (T_m), but with wide mesophase temperature range, we have prepared and characterized two types of copolyesters shown below; The designation of each polymers is shown in the table 1 below: The thermal transitions and the characteristics of the mesophases formed were studied by differential scanning calorimetry (DSC), microscopy on the hot-stage of a polarizing microscope, and by visual observation of the mesophase on a Fisher-Johns melting point apparatus.

Table 1. Designation of Polymers

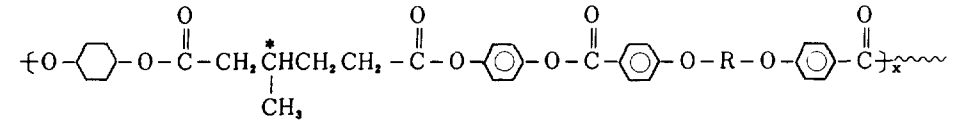
Designation	n	x	Designation	x
I_a	4	1.0	II_a	1.0
I_b	4	0.75	II_b	0.75
I_c	4	0.50	II_c	0.50
I_d	4	0.25	II_d	0.25
I_e	4	0.0	II_e	0.0
I_f	8	0.50		

RESULTS AND DISCUSSION

Polymers of Series I The polymers I_a through I_e contain varying amount of chiral center, while I_f has octamethylene unit instead of tetramethylene spacer of I_c. The polymers were prepared at room temperature in 1,1,2,2-tetrachloroethane (TCE) by reacting binary mixtures of bisphenols, 1,4-bis (4-hydroxyphenoxycarbonyl)-(+)-2-methylbutane and 1,4-bis(4-hydroxyphenoxycarbonyl)butane or the similar 1,8-octanylene derivative, with dichloride of 1,4-trans-cyclohexanedicarboxylic acid. Pyridine was employed as an HCl acceptor. All of the polymers of this series were obtained as white powders. Elemental analyses confirmed that compositions of the obtained copolymers were the same as those of feed. These polymers were insoluble in the reaction medium and precipitated out during polymerization as they were formed. They were soluble in 4:1 (w/w) TCE : phenol mixture and in p-chlorophenol. The general properties of the polymers are presented in table 2. The melting temperature, T_m, of this series with tetramethylene i.e., n=4, spacer steadily containing the chiral branched spacer, x, was decreased. The presence of methyl side group in the spacer certainly causes depression in T_m of polymers. For the polymer with x = 1 (I_a), the melting transition peak could not be observed on DSC analysis, indicating the amorphous nature or a very low degree of crystallinity of the composition. This is in contrast with the fact that the similar polymer having terephthaloyl moie-



(I)



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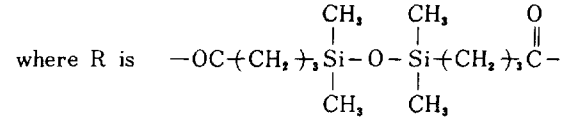


ty in the center of mesogenic unit is crystalline (T_m = 233°C) as reported earlier by us[6]. The polymer I_f with n = 8 was included in this study to examine the effect of the length of polymethylene spacer on the properties of polymers. The melting point of polymer I_f is unexpectedly, slightly higher than that of polymer I_c with shorter polymethylene spacer of n = 4. This seems to have been resulted from the significantly higher molecular weight of the former.

Differently from what observed for T_m's of the polymers, the isotropization temperature, T_i, decreased slightly in the order of $I_a > I_b > I_c > I_d > I_e$. In order words, the presence of methyl side group in the spacer appears to enhance the thermal stability of the mesophase, although the degree of enhancement is not too much. Similar phenomenon was observed for a similar series of polymers reported previously by us. Further study is required to clarity whether the so-called interlocking effect[9] of the methyl side group causes such an increase in mesophase thermal stability. The cholesteric polymers I_a, I_c and I_f exhibited clear oily streak type optical textures[10] when their melts were observed on a hot-stage attached to a cross-polarizing microscope. However the optical texture of the polymer I_d was very poorly organized, probably due to the low concentration of chiral centers along the back-bone. The melt of the polymer I_e which did not contain any chiral center showed a typical nematic, schlieren optical texture[11].

The melts of I_b, I_c and I_f showed visible iridescent colors which depended on the composition of polymers and observation temperature (Table 3). It is well known that cholesteric compositions selectively reflect light whose wave length (λ) has the relation with pitch distance (p) and average refractive index ($\bar{n}$) of the melt[12]: $\lambda = \bar{n} \cdot p$. The cholesteric melt of I_a did not show any reflection of visible light indicating its short pitch compared with those of I_b, I_c and I_f. I_d was expected that the melt of I_d would show iridescent colors of longer wavelength than those of I_b and I_c. However, no iridescent color was observed. This could be most probably due to the extremely low intensity of reflected light caused by its low concentration of chiral centers. The observation summarized in Table 3 point out to us the following: 1) The reduction in the concentration of chiral centers increases the pitch (compare the wave lengths of reflected lights by I_b and I_c), 2) lengthening of the polymethylene spacer increases the pitch (compare the wave lengths of iridescent colors by I_c and I_f) and 3) pitch increases with temperature (observe the increase in the wave length of reflected lights with temperature). These observation are in complete accord with those reported earlier by us for a similar series of copolymers.

Table 2. Properties of Polymers of Series I

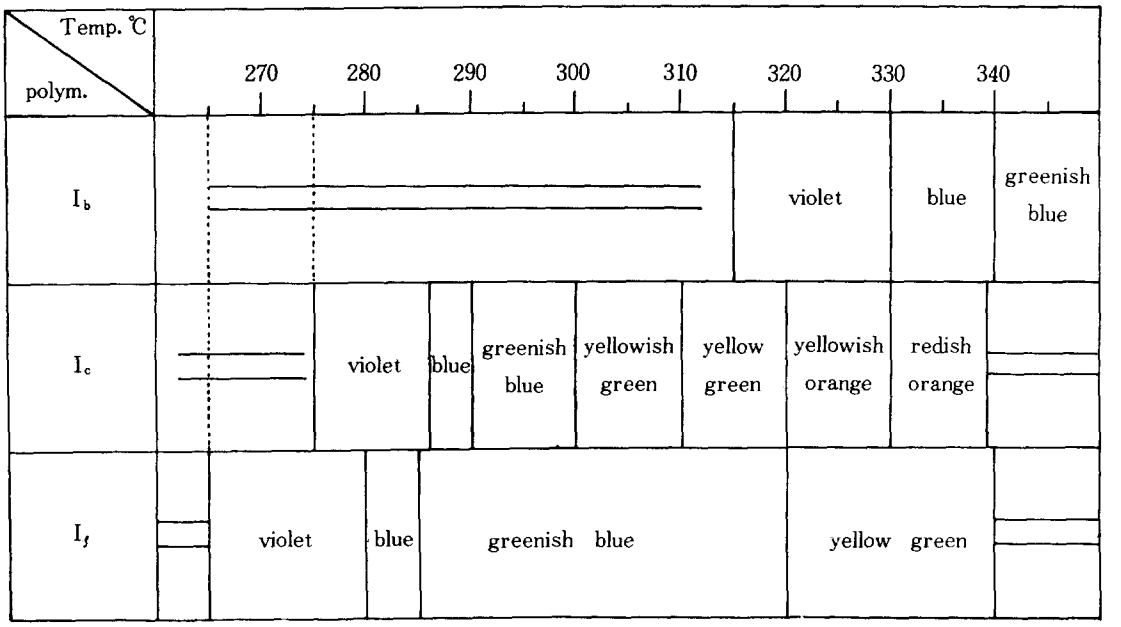
Designation	Yield, wt. %	η_{inh}[a]	T_m, °C	T_i^o, °C	L.C. Phase
I_a	89	0.52	—	350	Chol
I_b	92	0.41	195	348	Chol
I_c	91	0.47	234	342	Chol
I_d	94	0.64	259	335	Chol
I_e	87	0.37	275	335	N
I_f	86	0.52	240	340	Chol

[a] Measured on a 0.5g/dl solution in TCE and phonol mixture (4:1 by wt.) at 30°C.

[b] Obtained on a Fisher-John's melting point apparatus.

Polymers of Series II The polymers of Series II are copolyesters containing varying concentration of chiral, (=)-3-methyladipoyl unit and 1,3-bis (3-carboxypropyl) tetramethyl disiloxane moieties as spacers. The polymers were prepared at room temperature by reacting a mixture of hydroquinone and (+)-bis(4-hydroxyphenyl)-3-methyladipate with 1,3-bis[3-(p-carboxyphenoxycarbonyl)propyl]tetramethyl disiloxane in 1,2-dichloroethane. Pyridine was employed as an HCl acceptor. Elemental analyses confirmed that compositions of the copolymers were the same as those of feeds. The properties of the polymers are presented in table 4. The polymers were insoluble in reaction medium and precipitated out during polymerization as they were formed. They were soluble in phenolic solvent such as p-chlorophenol and pentafluorophenol. The molecular weights of the polymers seem to be rela-

Table 3. Dependence of Iridescent Colors[a] of Cholesteric Polymers of Series I on Temperature



tively low as indicator by their solution viscosities in table 4. A couple of copolymers have fairly low melting temperatures, about 50°C. Their glass transition temperature, T_g, was below room temperature (see Table 4). The isotropization transition of II_c could not be observed on DSC analysis. However, the transition could be detected clearly when the disappearance of birefringence of the melts were examined on the hot-stage of a cross-polarizing microscope. Differently from the melts of polymers of Series I, the melts of the compositions containing chiral centers did not show well organized cholesteric optical textures, although some of the polymers such as II_b and II_c exhbited definite iridescent colors when visually observed (Table 5). No iridescent color was observed for the melt of II_a probably due to its short pitch distance. A threaded schlieren texture, typical to nematics, was observed for the melt of II_e which did not contain any chiral center. The melt of II_d, which was expected to reflect visible light of longest wave length compared with those of other compositions, did not show iridescent colors. This could be due to the

Table 4. Properties of Polymers of Series II

Designation	Yield, wt. %	η_{inh}[a]	T_g, °C	T_m, °C	T_i, °C	L.C. Phase
II_a	86	0.16	—	186	215	Chol
II_b	91	0.20	22	57	216	Chol
II_c	81	0.17	16	50	150[b]	Chol
II_d	79	0.15	—	100	200	Chol
II_e	67	0.23	—	86	160	N

[a]Measured on a 0.5g/dl solution in p-chlorophenol at 45°C.
[b]Determined microscopically on the hot-stage of a polarizing microscope.

very low intensity of reflected light owing to the low concentration of chiral centers or to the long pitch causing the reflection of light beyond visible region. Table 5 shows how the iridescent colors of the melts of II_b and II_c changed as temperature was increased. Examination of the data in Table 4 lead us to the conclusion same as made for polymers of series I about the dependence of the wave lenth of reflected light by, or the iridescent colors of the melts of cholesteric polymers on composition and temperature. Especially, we seem to be very close

Table 5. Dependence of Iridescent Colors[a] of Polymers II_b and II_c on Temperature

Temp. ℃ / Polym.	50	100	150	200	250	300
II_b		T_m violet		T_i blue		
II_c	T_m violet	blue	greenish blue	yellowish green	T_i yellow green	

[a] Observed on a Fisher-John's melting point apparatus.

to the possibility of synthesizing cholesteric polymers which would show visible iridescent colors even at room temperature.

CONCLUSION

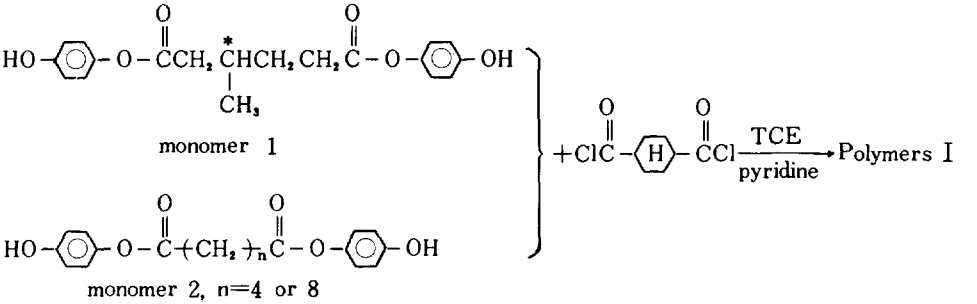
The following conclusion can be drown from the present investigation:

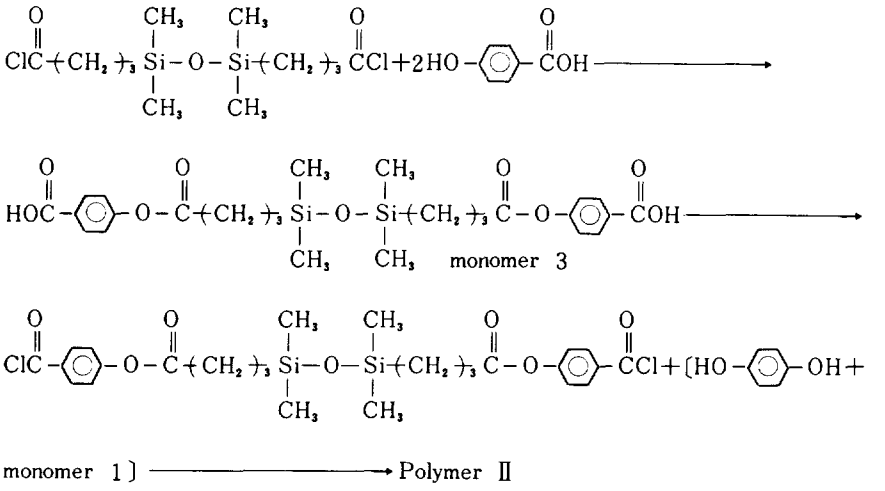
1. All of the polymers reported in this study were thermotropic and the ones containing chiral centers were cholesterics.
2. A couple of the cholesteric copolymers containing disiloxyl spacer unit revealed relatively low melting temperatures of about 50°C. Their T_g's were below room temperature.
3. Some of the cholesteric compositions reflected visible light and showed iridescent colors.
4. Cholesteric pitch increased with the length of spacers and with the reduction in the concentration of chiral centers in the spacers. The pitch also increased as temperature was increased.

EXPERIMENTAL

Preparation of Polymers I The two bisphenol monomers, bis-4-hydroxyphenyl esters of (+)-2-methyl adipic acid (1) and adipic acid (2) or 1,8-octanedioic acid are known compounds and they were synthesized following the literature methods[6]. 1,4-Trans-cyclohexane dicarboxylic acid (Aldrich Chemical Co.) was used as received in the preparation of corresponding dichloride by reacting with thionyl chloride. All of the solvents used were purified prior to us by usual method.

Since the preparation method of the polymers was all the same, only one representative procedure which was used in the preparation of I_c is given below: Trans-1,4-cyclohexane dicarboxylic acid (1.01g; 5.80 mmole) was dissolved in 10ml of thionyl chloride containing 2 drops of N,N-dimethylformamide and the solution was refluxed for 5 hours. The excess thionyl chloride and DMF were removed by vacuum distillation at room tempera-





ture. The solid diacid dichloride was dissolved in 10ml of dry 1,1,2,2-tetrachloroethane (TCE). The solution was added dropwise under a nitrogen atmosphere to the solution of an equimolar mixture of monomer 1(0.998g; 2.90 mmole) and monomer 2(0.957g; 2.90 mmole) dissolved in 10ml of dry pyridine. The mixture was stirred overnight at room temperature, after which 300ml methanol was added. The polymer formed was washed with methanol, distilled water, dilute sodium bicarbonate solution, dilute HCl and distilled water again, and then dried in a vacuum oven.

Preparation of Polymers II The polymers of Series II were prepared at room temperature by reacting a mixture of hydroquinone and the monomer 1 with the dichloride of 4,4′-dicarboxyphenyl ester (monomer 3) of 1,3-bis(3-carboxypropyl) tetramethyl disiloxane (Silar Laboratory) in 1,2-dichloroethane. Since the preparative procedure for the syntheses of the polymers were the same, a representative procedure for the 1:1 copolymer is described below. The monomer 3 was first prepared as follows: 1,3-Bis (3-carboxypropyl)tetramethyl disiloxane (4.99g; 16.3 mmole) was dissolved in 50ml of thionyl chloride containing 2 drops of DMF and the mixture was refluxed for 6 hours. After removing the excess thionyl chloride and DMF by vacuum distillation at room temperature, the dichloride formed was added dropwise with vigorous stirring to a solution of p-hydroxybenzoic acid (7.99g; 57.9 mmole) dissolved in 100ml of dry tetrahydrofuran and 10ml of dry pyridine. The reaction was allowed to proceed for 12 hours at room temperature, after which 500ml of distilled water was added, the precipitate was washed with water, dilute $NaHCO_3$, dilute HCl, and then with distilled water. The product was recrystallized from toluene. The yield was 78% (m.p. 172°C). The results of elemental analyses agreed well with theoretical values. (Found: C, 56.9% and H, 6.4%; Caled.: C, 57.3% and H, 6.3%). The monomer 3 (2.00g; 3.66 mmole) thus prepared was dissolved in 20ml of thionyl chloride containing 2 drops of DMF and the solution was refluxed for 6 hours. The dichloride of monomer, obtained by removing the excess thionyl chloride and DMF by vacuum distillation at room temperature, was dissolved in 10ml of dry 1,2-dichloroethane. The solution was added dropwise to the solution of an 1:1 mixture of hydroquinone (0.201g; 1.83 mmole) and the monomer 1 (0.608g; 1.83 mmole) dissolved in 10ml of dry pyridine. The reaction was allowed to proceed at room temperature for 5 hours under nitrogen atmosphere. The mixture was poured into methanol and the precipitate was washed with distilled water, dilute $NaHCO_3$, dilute HCl and finally with methanol, then dried in a vacuum oven.

Polymer Characterization Inherent solution viscosity numbers were determined using a Cannon-Ubbelohde type viscometer. The thermal pro-

perties of polymers were determined under nitrogen atmosphere using a thermal analyzer of du Pont's DSC 910. DSC temperature readings were calibrated against indium and lead. The reacting and cooling rate used was 10°C/min for all of the samples.

The temperatures where peak maxima appeared were taken as transition temperatures of T_m and T_i. The positions of the first base-line shift, however, was taken as T_g's. Optical textures of, and appearance and disappearance of birefringence by the polymer melt were examined on a hot-stage (Mettler FP-2) attached to a polarizing microscope (Leitz, Orthoplan). Heating rate of the hot-stage was maintained at 2°C/min near transition temperatures. The isotropization temperature (T_i) of polymers I were determined on a Fisher-John's melting point apparatus by observing the temperature where the stir-opalescence of the melts completely ceased to exist. The T_i of II_c was determined on the polarizing microscope by observing the temperature where the birefringence by the melts started to disappear. The colors of reflected light by the cholesteric melts were observed on a Fisher-John's melting point apparatus. Observations were made at a right angle to the cover glasses between which the polymer melts were positioned.

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