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Fixation of a cholesteric helical structure by the photopolymerization of a cholesteryl derived monomer

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A cholesteryl derived monomer was synthesized according to a conventional synthetic route; it exhibits a cholesteric phase above 129°C, and shows a red colour due to selective reflection in the cholesteric phase. Photopolymerization of the monomer was carried out at 135°C in the cholesteric phase. The helical structure of the cholesteric phase of the monomer was frozen by photopolymerization. A peak based on the selective reflection of the cholesteric phase was detected at 615 nm in the transmittance UV-Vis spectrum. Mixtures of the monomer with a binaphthyl derivative were prepared to control the selective reflection wavelength; they all also exhibited a cholesteric phase. The selective reflection wavelength of the mixture was dependent upon the ratio of the binaphthyl derivative in the mixture. This wavelength became shorter with increasing ratio of the binaphthyl derivative. The polymer films obtained by photopolymerization displayed almost the same selective reflection wavelength as the corresponding mixtures before photopolymerization. The selective reflection wavelength of the polymer films did not change up to about 250°C.

1. Introduction

There are in the main four liquid crystalline (LC) phases, namely, nematic, smectic, cholesteric and discotic phases. A cholesteric phase is usually exhibited by cholesteryl derivatives, chiral calamitic molecules and mixtures of calamitic compounds with chiral compounds [1]. A cholesteric phase has a helical structure and shows unique optical properties such as a large optical rotation, and selective reflection based on the pitch of the helical structure [2]. The selective reflection wavelength (λ_R), is given by,

$$\lambda_R = n_{avg} P \cos\theta$$

where n_{avg} and θ indicate the average refractive index and the incident angle, respectively, and P is the helical pitch length of the cholesteric phase. The cholesteric pitch length can be altered by an external influence such as temperature, an electric field, or pressure. Furthermore, the amount of the chiral additive also affects the helical pitch length of a cholesteric phase.

Selective reflection of cholesteric materials has application potential in passive optical components such as reflectors, polarizers, and band-pass and notch filters. Many researchers have investigated the thermal and optical properties of side-chain cholesteric polymers, because the polymeric materials show good processability compared with low molar mass cholesteric materials, and exhibit long term stability of the cholesteric mesogenic order at temperatures below the glass transition temperature. A cholesteric phase is usually exhibited by mesogenic homopolymers with a chiral moiety, copolymers composed of a mesogenic monomer and a chiral mesogenic monomer or a non-mesogenic chiral monomer [3–12]. In general, however, it is not easy to prepare polymeric materials with selective reflection in the visible light region using conventional solution polymerization. The pitch length of cholesteric polymers is dependent upon many factors such as molecular weight, molecular weight distribution, viscosity, the chemical structure of the chiral moiety, copolymer composition and so on.

In order to obtain cholesteric materials with selective reflection in the visible light region, and long term stability of mesogenic alignment, Shi and Chen have been actively investigating glass-forming cholesteric materials [13–15]. On the other hand, Broer *et al.* reported that polymer films exhibiting cholesteric liquid crystal order can be prepared by *in situ* photopolymerization of a mixture of a mesogenic monomer and a chiral monomer [16, 17].

Hoyle *et al.* investigated the photopolymerization of a liquid crystalline methacrylate monomer containing a cholesterol moiety in the crystalline, smectic, cholesteric, and isotropic phases. They found that the cholesteric phase seemed to provide the optimum balance between monomer order and translational mobility resulting in a maximum polymerization rate [18].

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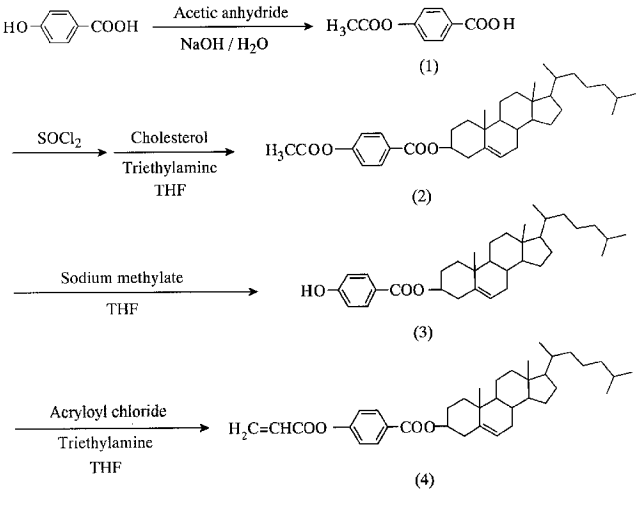
Shannon reported the photopolymerization of a mixture of two cholesteryl-based monomers in the cholesteric phase [19]. The monomers had a flexible spacer of different length between the polymerizable and the cholesteryl groups. Monomers with a short alkyl chain (ethyl or propyl) reflected only infrared light, whereas monomers with a long alkyl chain (decyl) displayed a colour due to the selective reflection of visible light in a very short temperature range. Therefore the author prepared mixtures of the cholesteryl monomers having long and short alkyl chains to obtain cholesteric materials with a wider cholesteric temperature range compared with the monomer with a long alkyl chain, and prepared the cholesteric polymer film with cholesteric mesogenic order by *in situ* photopolymerization.

Cholesteryl derivatives are one class of materials that exhibit cholesteric phases. Saeki *et al.* reported that a cholesteryl-based monomer exhibited selective reflection of the blue colour in the cholesteric phase [20]. In contrast, cholesteryl-based polymers mainly exhibit smectic behaviour [3]. Therefore, in order to freeze the cholesteric phase of the monomer, the cholesteric polymer film should be prepared by *in situ* photopolymerization of the monomer in the cholesteric phase.



Scheme 1. Synthesis of cholesteryl monomer.

In this study, we synthesized the cholesteryl derived monomer without a flexible spacer to obtain a polymer film with cholesteric mesogenic order. Furthermore we prepared a binaphthyl derivative as a chiral dopant. The chiral dopant was used to control the selective reflection wavelength. We investigated the fixation of the cholesteric helical structure by the *in situ* photopolymerization of the cholesteryl monomer and of mixtures of the monomer and the chiral dopant in the cholesteric phase. Selective reflection of the resulting polymer films was examined by UV-Vis spectroscopy. We also investigated the thermal properties of the cholesteryl-based polymers prepared by radical polymerization using AIBN as an initiator, to compare with the thermal properties of the polymer prepared by *in situ* photopolymerization.

2. Experimental

2.1. *Synthesis*

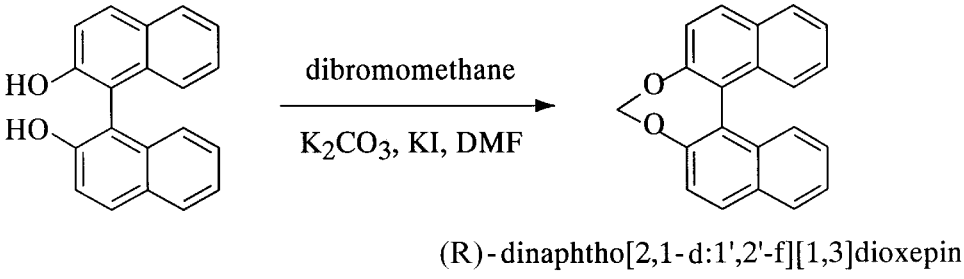
The monomer and the chiral dopant, (*R*)-dinaphtho-[2, 1-d : 1′,2′-f][1, 3]dioxepin, were prepared according to schemes 1 and 2, respectively [21, 22].

2.1.1. *4-Acetoxybenzoic acid (**1**)*

4-Hydroxybenzoic acid (125 g, 1.02 mol) was dissolved in aqueous NaOH (2l, 123 g, 3.08 mol). Acetic anhydride (209 g, 2.05 mol) was then added dropwise with cooling in an ice bath; the reaction mixture was stirred for 1 h. Aqueous HCl was added to the reaction mixture, which was then stirred for 1 h. The precipitate obtained was washed with water until a neutral solution was obtained. The crude product was purified by recrystallization from methanol; yield 70% (129.3 g). IR (nujol) ν cm^{-1}: 2551, 2676 (OH, carboxylic acid), 1753 (C=O, ester), 1682 (C=O, carboxylic acid), 1605 and 1508 (aromatic group).

2.1.2. *Cholesteryl-4-acetoxybenzoate (**2**)*

Thionyl chloride (150 ml) and a small amount of dimethylformamide were added to 4-acetoxybenzoic acid (13 g, 72.2 mmol) in a dry vessel; the reaction mixture was stirred at 50°C for 5 h. Excess thionyl chloride was evaporated under reduced pressure, and the residue was



Scheme 2. Synthesis of binaphthyl derivative.

dissolved in dry tetrahydrofuran (THF) (100 ml). The THF solution was added dropwise to a THF solution (200 ml) of cholesterol (17.1 g, 44.2 mmol) and triethylamine (14.6 g, 144 mmol) cooled in an ice bath. The reaction mixture was stirred at room temperature for 24 h and THF evaporated off under reduced pressure. The residue was washed with water and then with methanol. The product was purified by recrystallization from acetone and was obtained in a 48% yield (11.7 g). IR (nujol) ν cm^{-1}: 1753 (C=O, acetyl group), 1716 (C=O, ester), 1603 and 1504 (aromatic group). ^1H NMR ($CDCl_3$) δ ppm: 0.7 (s, 3H, cholesterol), 0.8–2.1 (m, 38H, cholesterol), 2.4 (s, 3H, CH_3), 2.5 (d, 2H, cholesterol), 4.85 (m, 1H, cholesterol), 5.45 (s, 1H, cholesterol), 7.15 (d, 2H, Ar–H), 8.05 (d, 2H, Ar–H).

2.1.3. *Cholesteryl-4-hydroxybenzoate (**3**)*

A methanol solution of sodium methylate (1.0 g, 18.5 mmol) was added dropwise to a THF solution (30 ml) of the intermediate **2** (8.9 g, 16.2 mmol). The reaction mixture was stirred for 3 min and then poured into 10% aqueous HCl (500 ml). The precipitate was washed with water and then methanol. The product was purified by recrystallization from chloroform and was obtained in a 93% yield (7.7 g). IR (nujol) ν cm^{-1}: 3309 (OH, phenol), 1672 (C=O, ester), 1608 (aromatic group).

2.1.4. *Cholesteryl-4-acryloylbenzoate (**4**)*

Acryloyl chloride (1.1 g, 12.2 mmol) was added dropwise to a THF solution of the intermediate **3** (5.0 g, 9.9 mmol) and triethylamine (3.0 g, 29.6 mmol), cooled using an ice bath. The reaction mixture was stirred for 12 h. After removing the THF under reduced pressure, the residue was extracted with chloroform, and the extract dried over magnesium sulfate. The chloroform solution was evaporated to dryness under reduced pressure, giving a crude product which was washed with methanol. The product was purified by recrystallization from acetone and was obtained in a 43% yield (2.4 g). IR (nujol) ν cm^{-1}: 1739 (C=O, acrylate ester), 1706 (C=O, ester), 1606 and 1506 (aromatic group). ^1H NMR ($CDCl_3$) δ ppm: 0.7 (s, 3H, cholesterol), 0.8–2.1 (m, 38H, cholesterol), 2.45 (d, 2H, cholesterol), 4.9 (m, 1H, cholesterol), 5.45 (s, 1H, cholesterol), 6.05 (d, 1H, acryl group), 6.35 (q, 1H, acryl group), 6.60 (d, 1H, acryl group), 7.2 (d, 2H, Ar–H), 8.05 (d, 2H, Ar–H).

2.1.5. *(R)-Dinaphtho[2, 1-d:1′, 2′-f][1, 3]dioxepin*

Potassium carbonate (6.1 g, 44.1 mmol) and a small amount of potassium iodide were added to a dimethylformamide solution (50 ml) of (*R*)-(+)-1, 1′-bi-2-naphthol (2.1 g, 7.3 mmol). After the mixture was heated at 80°C for 1 h, a dimethylformamide solution of dibromomethane (1.27 g, 7.3 mmol) was added dropwise to the mixture over 30 min. The reaction mixture was then heated at 80°C for 24 h. After the resulting precipitate was removed, chloroform (300 ml) was added to the dimethylformamide solution, which was then washed twice with 2% aqueous KOH and three times with water. The chloroform solution was dried over magnesium sulfate; it was then evaporated to dryness under reduced pressure, and residue purified by recrystallization from acetone. The white yellow product was obtained in an 18% yield (0.4 g). $[\alpha]_{25}^{D}$ −762.7° (c 0.216, $CHCl_3$). IR (nujol) ν cm^{-1}: 1618 and 1506 (aromatic group). ^1H NMR ($CDCl_3$) δ ppm: 570 (s, 2H, CH_2), 7.20–7.31 (m, 2H, Ar–H), 7.40–7.55 (m, 6H, Ar–H), 7.90–8.00 (m, 4H, Ar–H).

2.1.6. *Photopolymerization*

Cholesteryl-4-acryloylbenzoate (0.1 g, 0.18 mmol), 2,2-dimethoxy-2-phenylacetophenone (5 wt %) and *p*-methoxyphenol (200 ppm) were dissolved in chloroform. The chloroform solution was evaporated to dryness under reduced pressure, and the residue dried *in vacuo*. The mixture was used to fill a cell fabricated from rubbed quartz; the cell gap was 12 μm. The sample in the quartz cell was irradiated with UV light at 135°C for 10 min (1.19 mW cm^{-2} at 365 nm).

The NMR and IR data for the photopolymerized polymer after purification are provided. IR (film) ν cm^{-1}: 2947 and 2868 (CH, methylene), 1753 (C=O, ester, –COO–Ar), 1714 (C=O, ester, Ar–COO–cholesterol), 1605 and 1504 (aromatic group). ^1H NMR ($CDCl_3$) δ ppm: 0.7 (s, 3H, cholesterol), 0.8–2.1 (m, 38H, cholesterol), 2.44 (m, 2H, cholesterol), 2.98 (m, 1H, CH–COO–, polymer backbone), 4.78 (m, 1H, cholesterol), 5.39 (s, 1H, cholesterol), 6.8–7.1 (m, 2H, Ar–H), 7.7–8.0 (m, 2H, Ar–H).

2.1.7. *Radical polymerization*

The polymer was prepared by radical polymerization in a sealed ampoule with 1.0 mol % of α, α′-azobisisobutyronitrile in anhydrous tetrahydrofuran at 60°C for 24 h. The polymer was obtained by precipitation with methanol and then dissolved in chloroform and reprecipitated with acetone three times. The polymer was dried at 40°C under vacuum and obtained in a 61% yield ($\overline{M_n} = 2100$, $\overline{M_w}/\overline{M_n} = 1.1$). IR (KBr) ν cm^{-1}: 2951 and 2868 (CH, methylene), 1759 (C=O, ester, –COO–Ar), 1720 (C=O, ester, Ar–COO–cholesterol), 1605 and 1504 (aromatic group). ^1H NMR ($CDCl_3$) δ ppm: 0.7 (s, 3H, cholesterol), 0.8–2.1 (m, 38H, cholesterol), 2.43 (m, 2H, cholesterol), 2.98 (m, 1H, CH–COO–, polymer backbone), 4.77 (m, 1H, cholesterol), 5.39 (s, 1H, cholesterol), 6.8–7.1 (m, 2H, Ar–H), 7.7–8.0 (m, 2H, Ar–H).

2.2. *Characterization*

^{1}H NMR spectroscopy was carried out using a JEOL JNM-LA 400 spectrometer with $CDCl_3$ as the solvent. Infrared spectra were recorded on a JEOL JIR 7000 spectrometer, and collected at 4 cm^{-1} resolution. DSC measurements were conducted with a Mettler DSC821^e differential scanning calorimeter. Optical microscopy was performed on a Nikon polarizing optical microscope, OPTIPHOTO-POL, equipped with a Mettler FP80 controller and FP82 hot stage. Gel permeation chromatography (GPC) was carried out with a Tosoh HLC-8020 instrument using chloroform as the eluent, equipped with four columns (TSK gel $G4000H_{HR}$, $G3000H_{HR}$, $G2000H_{HR}$ and $G2000H_{HR}$). The rate of the elution was 1.0 ml min^{-1}; the instrument was calibrated with a polystyrene standard. UV-Vis spectroscopy measurements were carried out with a HITACHI U-3410 spectrophotometer. X-ray diffraction patterns were recorded with a RIGAKU RINT2500 series with Ni-filtered CuK_α radiation. The sample in a quartz capillary (diameter 1 mm) was held in a temperature-controlled cell (RIGAKU LC high-temperature controller).

3. Results and discussion

The chemical structure of the cholesteryl monomer is shown in scheme 1. An oily streak texture characteristic of a cholesteric phase was observed for the cholesteryl monomer above 129.8°C on heating. The DSC curve of the cholesteryl monomer is shown in figure 1. Thermal polymerization of the cholesteryl monomer took place at about 235°C, before the monomer became isotropic. A red colour based on selective reflection was observed for the cholesteryl monomer.

Radical polymerization of the cholesteryl monomer was carried out to compare its thermal properties with those of the polymer prepared by photopolymerization.

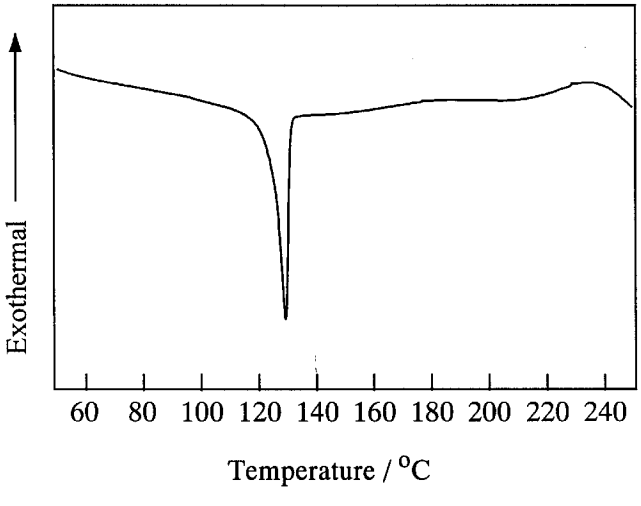


Figure 1. DSC curve of the cholesteryl monomer.

The number-average molecular mass of the polymer was 2100, as detected by GPC. A focal-conic texture was observed on cooling the product prepared by radical polymerization as shown in figure 2. It is well known that a focal-conic texture is observed when the helical axis of the cholesteric structure aligns randomly. We tried to induce a planar texture by shear strain imposed by shifting the glass substrates to confirm the assignment of a cholesteric phase. After shearing the glass substrates, however, the focal-conic texture still remained. Therefore we concluded that the phase was smectic.

In addition, to confirm that the polymer prepared by radical polymerization exhibited a smectic phase, X-ray measurements were carried out. A small peak in the small angle region and a broad peak in the wide angle region were detected. A *d*-spacing estimated from the peak in the small angle region was 21.8 Å. The calculated length of the side chain was 22.9 Á. Therefore the phase structure shown by the polymer obtained by radical polymerization was a smectic A_1 phase. The glass transition temperature of the polymer prepared by radical polymerization was 92.4°C, as measured from the DSC curve on heating. Thermal decomposition of the polymer took place at about 300°C and before the polymer became isotropic. We concluded that the polymer exhibited a smectic A_1 phase in the temperature range from 92.4°C to about 300°C.

Figure 3 shows a GPC curve of the polymer prepared by *in situ* photopolymerization in the cholesteric phase. The number-average molecular mass of the photopolymerized polymer without the chiral dopant was 24 000 (see the table). The peak near 33 min corresponds to a molecular weight of 560, which is that of the cholesteryl monomer. The polymerization yield calculated from the peak area ratio of the peak near 23 min and all other peaks were above 90%. This result was supported by NMR measurements. The amount of monomer remaining

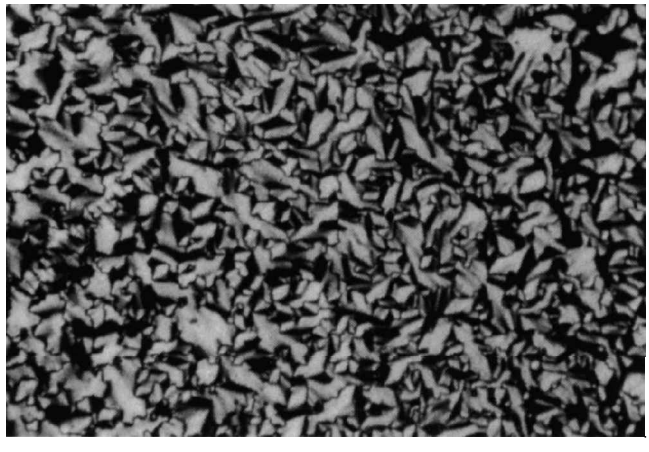


Figure 2. Optical texture of the polymer prepared by radical polymerization at 209°C on heating.

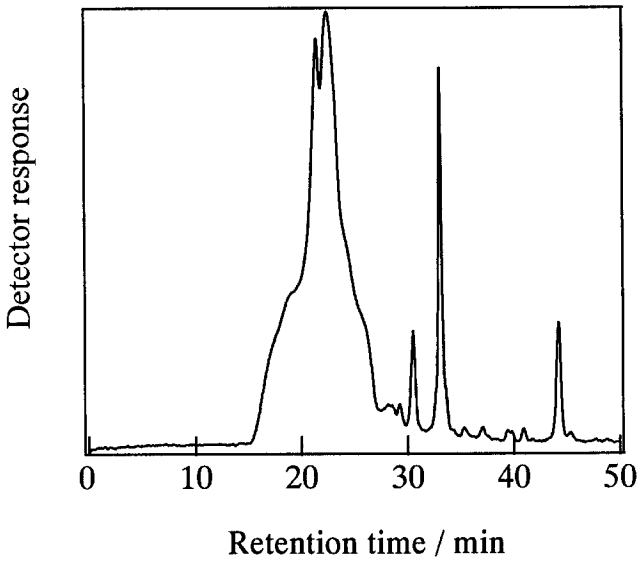


Figure 3. GPC curve of the polymer prepared by photopolymerization.

Table. Selective reflection wavelength and number-average molecular mass of the polymer films prepared by photopolymerization.

Cholesteryl monomer ratio/mol %	Selective reflection wavelength/nm	Number-average molecular mass
100	615	24000
98	558	475000
96	498	26000
94	474	439000
92	405	31000
90	366	31000

was estimated from the integrated ratio of the peaks assigned to the acrylate and phenyl groups. The ratio of the monomer in the polymer film was 8.1%. This result also indicated that the polymerization yield was above 90%.

DSC measurements of the photopolymerized polymer film revealed only a glass transition at 95.4°C. The glass transition temperature of the photopolymerized polymer film was similar to that of the product obtained by radical polymerization. Thermal decomposition of the polymer prepared by photopolymerization took place above 300°C and before the polymer became isotropic.

Glass transition temperatures and clearing points of conventional LC polymers increase until the molecular mass reaches about 10 000. The phase transition temperatures of conventional LC polymers are almost constant when the molecular mass exceeds 10 000. The molecular mass of the product obtained by radical polymerization was very low compared with that of the photopolymerized polymer. However, the thermal transition temperatures of the product obtained by radical polymerization were the same as those of the photopolymerized polymer. We cannot explain these observations at the present time; however, the lower molecular mass polymer can be considered as a polymer, because polymers are defined as giant molecules with molecular mass at least 100 times greater than those of smaller molecules such as water or methanol [23].

The photopolymerized polymer film still exhibited a red colour based on selective reflection. We measured the transmittance spectra of the polymer films, and determined the selective reflection wavelength as 615 nm after photopolymerization at room temperature.

We considered that cholesteric materials with three colours, red, green and blue (RGB), were needed from a standpoint of applications as colour films. Therefore we tried to shorten the helical pitch length using a chiral dopant. Chen *et al.* have controlled the helical pitch length of the cholesteric phase by adding a binaphthyl derivative as a chiral dopant [21]. It is known that binaphthyl derivatives have large twisting powers. We employed a binaphthyl derivative as a chiral dopant for the preparation of mixtures that exhibited two selective reflections, green or blue.

We investigated the selective reflection wavelengths of the mixtures of the cholesteryl monomer and the binaphthyl derivative by UV-Vis spectroscopy. Each mixture exhibited different colours such as green or blue depending upon the helical pitch length, which itself was dependent upon the fraction of the binaphthyl derivative in the mixture. The mixtures were irradiated with UV light under the same conditions as the cholesteryl monomer. We obtained polymer films with different colours by photopolymerization as shown in figure 4.

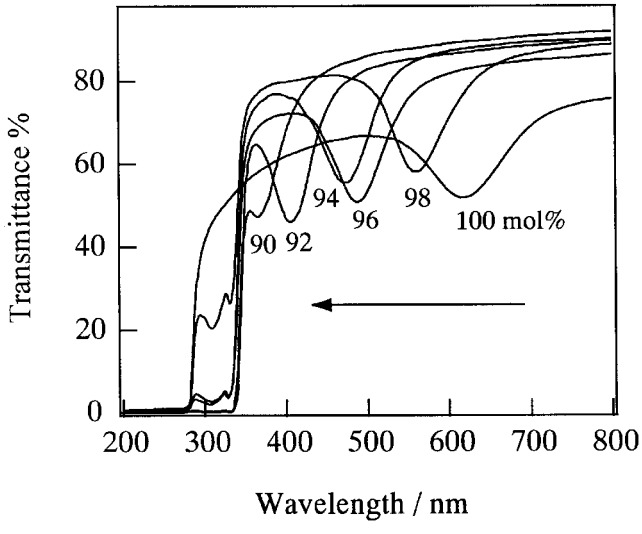


Figure 4. UV-Vis transmittance spectra of polymer films prepared by photopolymerization. Numbers indicate the molar ratio of the cholesteryl monomer in the initial mixture with chiral dopant.

The selective reflection wavelengths and the number-average molecular masses of the resulting polymer films are summarized in the table.

The colour of the polymer films was almost the same as that of the mixtures before photopolymerization. After photopolymerization, the colour of the polymer films remained at room temperature. This indicated that the cholesteric mesogenic order of the monomer was maintained at room temperature after photopolymerization. Thus succeeded in the fixation of the cholesteric phase structure of the mixtures of the cholesteryl monomer and the binaphthyl derivative by photopolymerization. Furthermore we controlled the selective wavelength by adding the binaphthyl derivative as a chiral dopant. Photopolymerized polymer films have maintained the cholesteric mesogenic order for about ten months at room temperature.

It is well known that the helical pitch of a cholesteric phase changes with temperature. The temperature dependence of selective reflection for the polymer films with different colours was investigated by UV-Vis spectroscopy. Figure 5 shows the temperature dependence of the selective reflection wavelength for the polymer films. The selective reflection wavelength of the polymer film without the chiral dopant was shifted to longer wavelengths with increasing temperature. The shift of the wavelength was 54 nm for the polymer film without the chiral dopant. On the other hand, the shift of the selective reflection wavelength became smaller with increasing amount of the chiral dopant. In the case of the polymer film containing 10 mol % of chiral dopant, the shift of the selective reflection wavelength was 26 nm. The colour of all the polymer films obtained did not appear to change with temperature. The helical pitch was stable in the temperature range between 30°C and 250°C.

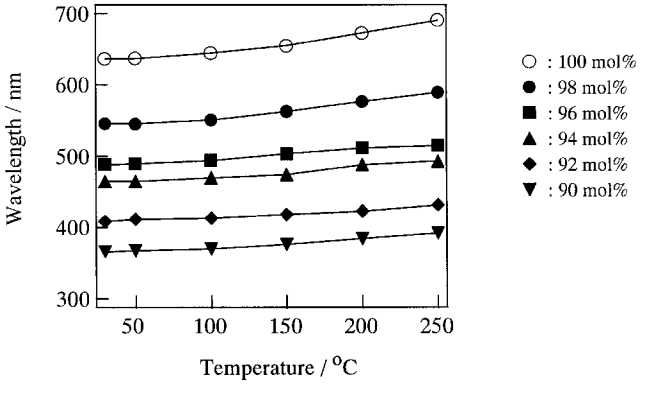


Figure 5. Temperature dependence of selective reflection wavelength for the polymer films prepared by photopolymerization. The legend indicates the cholesteryl monomer ratio in the initial mixture.

As shown in the table, the number-average molecular masses of the polymers containing 98 and 94 mol % of cholesteryl monomer were larger than those of the other polymers. However, there does not appear to be a strong dependence of the optical properties of the polymer films on the number-average molecular mass. Therefore we concluded that the molar ratio of the cholesteryl monomer and the chiral dopant plays an important role in controlling the helical pitch of the cholesteric phase.

4. Conclusion

We obtained a cholesteryl derived monomer which shows a red colour due to selective reflection in the cholesteric phase. The helical structure of the cholesteric phase for the monomer was frozen by photopolymerization. The selective reflection wavelength of the cholesteric phase was 615 nm. Mixtures of the monomer and the binaphthyl derivative were prepared to control the selective reflection wavelength; all the mixtures also exhibited the cholesteric phase. The selective reflection wavelength of the mixtures was dependent upon the ratio of the binaphthyl derivative in the mixture. The polymer films obtained by photopolymerization of the mixtures of the cholesteryl monomer and the binaphthyl derivative displayed almost the same selective reflection wavelength as the corresponding mixtures before photopolymerization. The selective reflection wavelength of the polymer films did not change up to about 250°C.

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