The Effect of the Applied Temperature on the Maximum Reflective Wavelength in Chiral Liquid Crystal Polymers

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Abstract. The liquid crystals (LCs) monomers 4-(Undecenoic-1-yloxybenzoyloxy)-4’-cyanobenzene e M1 and 5-{4-[4-(4-undecyloxy) biphenyl] -oxycarbonyl} pentanoic acid cholesteryl ester M2 are synthesized. The liquid crystals polymer was synthesized by nematic and chiral LC monomers. The property of the LC materials are detected by POM and DSC. The bandgaps of the LC polymer are influenced by the change of temperature. The effect of temperature on the reflective wavelength is decreased from 513nm to 394nm with temperature increased. The chiral LC polymer is a one dimension photonic materials. The optical and thermal property of the CLCs polymer is controlled by the out field, and widely used for display, smart windows and chiral liquid crystal laser etc.

1. Introduce

The permittivity and permeability of materials are period arranged, which is called Photonic crystal (PC). The PC materials are divided into one, two- or three-dimensions structure [1-2]. The period structure is made from the helical director of sticklike molecules in chiral liquid crystal (CLCs). The property of the CLCs have been widely discussed as PC based on one-dimension helix period structure. The helix pitch P which the distant of the director of polarity group twists one period is a significant factor for CLCs. The circularly polarized (CP) light which is reflected with the same twisted direction. The wavelength of the circularly polarized light is equal to the optical pitch [3-7]:

\[ \lambda_p = nP \cos \theta \]  

The factor \( n \) is the average refractive index of CLCs from the two different refractive index which contains extraordinary and ordinary indices. The \( \theta \) is incidence angle from the direction of light to axis of CLCs. The width of bandgaps is proportional to the difference of refractive indices \( \Delta n = n_e - n_o \) in conventional CLCs. The wavelength of the circularly polarized light of CLCs can be influenced by outfield, for example, temperature field, ultraviolet lights, electric field and magnetic field etc. in practice.

The effect of the temperature on the bandgaps of the CLCs polymer is characterized in this paper. The bandgap of CLCs polymer is tuned with the changed temperature. As the results of the experiment
which the reflective lights are detected, the PBG was continuously reduced in 117 nanometer with 
accelerating temperature.

2. Experiment

2.1. Materials and method
Poly (methylhydrogeno) siloxane is supplied by Jilin Petrochemical Company. P-hydroxybiphenol, 
p-hydroxybenzoic acid, 4-methoxy-Phenol, undecylenic acid, Sulfuryl chloride, 4-Hydroxybenzonitrile, 
cholesterine and hexan edioic acid were purchased from Sinopharm Chemical Reagent Co., Ltd. 
Pyridine, tetramethylene oxide, ethyl alcohol, trichloromethane, methylbenzene and methyl alcohol 
were supplied from Shenyang Chemical Co.

The products were detected by infrared spectrometer according the KBr method in IR spectra. 
Thermal properties were detected by differential scanning calorimeter (DSC) under nitrogen 
atmosphere by increasing and decreasing the temperature at rates of 10°C/min⁻¹. The optical textures 
and the changed phase are detected by polarized optical microscope which equipped with a hot stage. 
The temperature is controlled by hot stage in 0.01°C.

2.2. Synthesis liquid crystal monomers and polymer

2.2.1. Synthesis LC monomer M1. The solution was composited by 4-Cyanophenol (14.28g, 0.12mol), 
pyridine (10mL) and 100mL dry Tetrahydrofuran by stirred into uniform. The 4-Undec-10-enoyloxy- 
4'-hydroxyphenyl chloride (24g) was added the upper solution. The reaction was completed by stirring 
at ambient temperature for 32h, and then the solvent is distilled out partly under reduced pressure. The 
product was added into cold water when the solution was cooled to room temperature. The precipitates 
were isolated by filtration, washed by hot water and dried in a vacuum oven.

2.2.2. Synthesis LC monomer M2. Jianshe Hu etc. have shown the synthesis of monomer M2 [8]. The 
solution was stirred and composited by 4-undecenoyloxy-4-hydroxybiphenyl (21.6g, 0.06mol), 
pyridine (20mL) and chloroform (200mL). 6-Cholesteryloxy-6-oxohexanoyl chloride (26.6g, 
0.05mol) was mixed to the upper solution. The reaction mixture was refluxed for 48h after stirring at 
room temperature for 2h. After the liquid is distilled out, and the product is cooled and added into 
ethanol at room temperature. The product is filtered off by brinell funnel with filter paper. The dry 
products are dissolved in acetone and washed by acetone several times to remove the impurity. The 
product which we obtained in the liquid crystal monomer.

2.2.3. Synthesis CLCs polymer
The synthesized CLCs polymer were employed poly (methylhydrogeno) siloxane, the NLC monomer 
M1, and CLC monomer M2 according to hydrosilication method. The composites of the different 
polymer are listed in Tab. 1. The synthesized polymer is characterized as follow. The NLC M1, CLC 
M2 and PMHS are dissolved in toluene (100ml) by stirring. 1.5ml of 0.5% hexa-chloroplatinic (THF 
solution) were formulated and added under nitrogen conditions at 68°C for 72h to upper solution. The 
finished reaction is determined by the spectrum of FTIR according the diminished bond of Si-H 
(2166cm⁻¹). After reaction, the mixture was cooled and added into methanol with stirring 1h. The 
precipitated product is filtered and dried under vacuum in 24h. The liquid crystal monomer is removed 
by excess ethanol for several times. The swollen LC polymer was placed in vacuum oven for 24h. The 
synthesized rout is shown in Fig. 1.
3. Results and discussion

3.1. Structure of $M_1$, $M_2$ and CLCs polymers by FTIR

The synthesized LC monomers were as discussed in part 2.2. The groups of LC were described according to the FTIR spectrum. The structure of $M_1$ and $M_2$ were shown by $C=C$ at 1644 cm$^{-1}$, $C=O$ bond at 1705 cm$^{-1}$, $-CN$ bond at 2236 cm$^{-1}$ for $M_1$, 1744 and 1779 cm$^{-1}$ for $M_2$, respectively.

The synthesized CLCs polymers were employed the method of hydrosilylation reaction. The Si-C-C bond was formed according the reaction of the group Si-H and C=C. After finished the reaction, the position of the $C=C$ group is disappeared in the FTIR spectra of polymers P1-P7. The Si-H vibrating band (2160 cm$^{-1}$) and C=C vibrating band (1645 cm$^{-1}$) are dispersed in the CLCs polymer P1-P7. A new stretched bands Si-O-Si are appeared at 1200-1000 cm$^{-1}$. The CLCs polymers is characterized by the formed Si-O-Si stretching bands as shown in Fig. 2. In Fig. 2, the absorption bands of ester $C=O$ (1705-1739 cm$^{-1}$) and aromatic (1607-1507 cm$^{-1}$) were unchanged. The polysiloxane chains were substituted by the two different LC monomers for all the polymers as illustrated by the position of the characteristics band. The FT-IR spectrum is obtained by Potassium bromide method.

| sample | PMHS (mmol) | $M_1$ (mmol) | $M_2$ (mmol) | $M_2$ (mol%) |
|--------|-------------|-------------|-------------|-------------|
| P1     | 0.500       | 3.500       | 0.000       | 0.00        |
| P2     | 0.500       | 3.000       | 0.500       | 12.5        |
| P3     | 0.500       | 2.500       | 1.000       | 25.0        |
| P4     | 0.500       | 2.000       | 1.500       | 37.5        |
| P5     | 0.500       | 1.500       | 2.000       | 50.0        |
| P6     | 0.500       | 1.000       | 2.500       | 62.5        |
| P7     | 0.500       | 0.000       | 3.500       | 87.5        |

Figure 1. The synthesized CLCs Polymer P1-P7
3.2. Analysis of thermal property

The thermograms of polymer P1-P7 are shown by DSC in Fig. 3. The melting temperature (Tm) is detected and shown by different curves of DSC in polymer P1-P7. As shown in the different curves, the value of Tm is increased with the content of LC monomer M2 is increased from polymer P1-P7. With comparing the curves and photos of POM measurement, a Tm and an isotropic temperature (Ti) were detected in polymer. The phase of polymers transients from nematic to chiral cholesteric phase with adding M2 content as shown in the photos of POM. The polymer P1 shows nematic phase which is characterized by treads texture. The cholesteric phase is determined by planar texture which is characterized cholesteric phase in P2-P7. Two Tm is shown in the curves of thermograms. The first Tm is same as the melting temperature in CLC polymers, and the second Ti is called clearing point which is the liquid anisotropy phase changed to isotropic phase as shown on the DSC curves. The texture which detected by the POM in LC monomers and CLC polymers are shown in Fig 4. The phase of monomers and polymers are illustrated by textures.
Figure 4. The textures of the M₁, M₂ and P₅.

Figure 5. The shifted wavelength with changing temperature in the polymers P₅.
3.3. Dynamic change of band gap by temperature
The helix twist power (HTP) of the polymer is depended on the temperature\textsuperscript{[9]}. The helix pitch is originated the HTP, then, the pitch is determined by the temperature. As shown in formula (1), the selective reflection wavelengths are changed with the applied temperature. The pitch of polymer is decreased with the temperature which is heated on the CLCs polymer in the range of the liquid crystals. When the polymer is melted, the viscosity is decreased and the HTP is increased in the CLCs polymer. The director of the LCs is easily twisted by the HTP which is decreased in the liquid phase. The shortened pitch is discovered at lower viscosity in the CLCs polymer. As shown in Fig.5, The bandgaps of the P\textsubscript{3} is changed with the applied temperature from ambient temperature 32\textdegree C to 120\textdegree C in the interval at 5 and 10\textdegree C, respectively. The bandgaps is changed from 513nm to 394nm with increased temperature. The maximum reflective wavelength is linear shifted with heating temperature as shown in Fig.6. As the heated temperature, the bandgaps are shifted in 119nm.

4. Conclusions
The synthesis, characterization and property of a series of CLCs polymers are described containing cyano and chiral group. The thermal property of polymer is detected by DSC. The texture and optical property of polymer are characterized by POM and UV/vis/IR spectrum. The structure of monomer and polymer is illustrated by FTIR. The property and the structure are defined based on the detected data. The bandgaps of polymer is shifted for the effect of the temperature in range of 32\textdegree C to 120\textdegree C. The bandgaps is decreased from 513nm to 394nm with applied temperature. As the practical applications, the CLCs polymer maby applied in displays, reflective films, smart windows and CLCs laser.

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