Mesomorphic and luminescence properties of side chain cholesteric liquid crystalline polymers containing Eu(III) and Tb(III) ions

Wen-Zhi Zhao, Yue-Hua Cong, Bao-Yan Zhang*, Tian-Hao Zhang and Bing Yao

Centre for Molecular Science and Engineering, Northeastern University, Shenyang, P. R. China

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Luminescent cholesteric liquid crystalline polymers consisting of the lanthanide ions covalently attached to cholesteric polysiloxanes are prepared. Cholesteric liquid crystalline monomer and 4-(allyloxy)benzoic acid grafted to poly(methylhydrogenosiloxane) is used as one of the precursors for the preparation of the lanthanide-containing cholesteric liquid crystalline polymers. The chemical structures of the monomers are characterised by Fourier transform infrared, 1H NMR and elemental analyses. The mesomorphic properties and phase behaviour are investigated by differential scanning calorimetry, thermogravimetric analysis, polarising optical microscopy and X-ray diffraction. The polymers containing <3 mol% of the lanthanide ions reveal reversible mesomorphic phase transition, wide mesophase temperature ranges and high thermal stability. The introductions of the lanthanide ions do not change the liquid crystalline state of polymer systems; on the contrary, the polymers are enabled with the significant luminescent properties. With the lanthanide ions contents ranging between 1 and 3 mol%, luminescent intensity and luminescent lifetimes of polymers gradually increased. The temperature dependence of luminescent intensity was studied in the liquid crystalline phase.

Keywords: graft copolymers; fluorescence; luminescence; liquid crystalline polymers (LCP); thermal properties

1. Introduction

Recently, luminescent lanthanide-containing materials have gained more and more attention due to their especially efficient strong narrow-width emission band in the visible region[1,2] and hold large potential applications in many aspects such as light-emitting diodes,[3] fluorescent probes[4] and medical magnetic resonance imaging.[5] However, the unworkability, low thermal stability and low mechanical resistance are major drawbacks that hamper the practical applications of these materials.[6,7] Some methods have been put forward to overcome these problems such as by incorporating lanthanide complexes or lanthanide ion into inert host matrices such as sol-gel glasses,[8–10] polymers,[11–15] liquid crystal (LC) materials[16–20] or organic–inorganic hybrid materials.[21] Among these matrices, LC materials have great advantages. In recent years, LC materials with anisotropic properties have expanded rapidly[22–28] and LC materials with luminescent property are of considerable interest over recent years due to processing performance, thermal stability and their potential applications in the fields of anisotropic light emitters,[29,30] photoconductors,[31] LC display technology[32] and so forth. Cholesteric liquid crystalline polymers (CLCP) are a kind of LC materials exhibiting a marvellous variety of LC phases, including the cholesteric phase and the blue phases, etc. CLCP have attracted considerable interest because of the outstanding optical properties such as selective reflection and transmission of light, circular dichroism and thermochromism.[33–35] In addition, heat resistance, good elasticity and film-forming properties increase the potential application of CLCP, such as flat-panel displays, organic pigments and full-colour thermal imaging.

However, few luminescent lanthanide-containing CLCP have been described so far; as regards the compared studies on polymers with different lanthanide ions, even fewer have been described. So it is necessary and significant to synthesise various kinds of lanthanide-containing CLCP to explore their properties and to be applied in effect. In this paper, luminescent CLCP consisting of europium (Eu) and terbium (Tb) ions covalently attached to cholesteric polysiloxane polymers are prepared. The LC properties were characterised with differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), polarising optical microscopy (POM) and X-ray diffraction (XRD); the luminescent properties were measured by fluorescence spectrophotometer. The influence of the concentration of lanthanide ions on phase behaviour and optical properties was discussed, and the temperature dependence of luminescent intensity was studied in the LC phase.

*Corresponding author. Email: byzhang2005@126.com

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2. Experimental

2.1. Instrumentation

Fourier transform infrared (FTIR) spectra were measured on a Nicolet 510 FTIR spectrometer (Nicolet Instruments, Madison, USA). 1H NMR were measured by Varian WH-90PFT NMR Spectrometer (Varian Associates, Palo Alto, CA). Element analyses (EA) were measured by Elementar Vario ELIII (Elementar, Germany). DSC and TGA measurements were carried out with a NETZSCH TGA 209C thermo gravimetric analyser, and a NETZSCH instruments DSC 204 (Netzsch, Wittelsbacherstrasse, Germany) at a scanning rate of 10°C min⁻¹ under a flow of dry nitrogen. POM study was performed using a Leica DMRX (Leica, Wetzlar, Germany) equipped with a Linkam THMSE-600 (Linkam, Surrey, England) heating stage. XRD measurements were performed with a nickel-filtered Cu-Kα radiation with a DMAX-3A Rigaku powder diffractometer. The fluorescence excitation and emission spectra were recorded on a HORIBA Jobin Yvon FL3-TCSFC fluorescence spectrophotometer equipped with a 450-W xenon lamp as the excitation source. Luminescence lifetimes were obtained with an Edinburgh Instruments FLS 920 phosphorimeter with a 450-W xenon lamp as the excitation source. Luminescent lifetimes were measured by Varian WH-90PFT NMR Spectrometer (Varian Associates, Palo Alto, CA).

2.2. Materials

Poly(methylhydrogenosiloxane (PMHS, Mn = 582) was purchased from Jilin Chemical Industry Company (China). Bromopropene, 4-hydroxybenzoic acid, biphenyl-4,4'-diol, 4-fluorobenzoic acid, adipic acid, 2-propanol, N,N-dicyclohexyl carbodiimide (DCC), 4-(N,N-dimethylamino)pyridine (DMAP) and isopropoxide were purchased from Shenyang Chemical Co. (China). Isosorbide was purchased from Henan Xiyai Medical Co. (China). Eu₂O₃ and Tb₂O₃ were purchased from Beijing Fuxing Chemical Industry Co. (China). Toluene was used in the hydroisylation reaction over sodium and distilled under nitrogen. All other solvents were purified by standard methods.

2.3. Monomers synthesis

The synthetic route to the olefinic monomers is shown in Figure 1.

4'-((4-(Allyloxy)benzoyloxy)biphenyl-4-yl-6-hydroxyhexahydrofuro[3,2-b]furan-3-yl adipate (M₁) was synthesised according to a previous report.[36] 4-Allyloxybenzoic acid (M₁) was prepared in our laboratory, yield: 77%, IR (KBr): 3054 (=C=H), 2927–2853 (–CH₃, –CH₂–), 2645, 2547 (–COOH), 1745, 1681 (C = O), 1642 (C = C), 1560, 1450 (Ar–), 1250 (C–O). Anal. calcd for C₂₉H₂₈O₂: C 71.65, H 5.66, O 22.69; found: C 71.72, H 5.60, O 22.65. 1H NMR (600 MHz, CDCl₃, δ): 12.60 (s, 1H, –COOH), 7.90–7.02 (m, 4H, Ar–H), 6.10–6.00 (m, 1H, CH₂ = CH–), 5.44–5.27 (t, 2H, CH₂ = CH–), 4.68–4.64 (s, 2H, –OCH₂–).

2.3.1. 4'-((4-(Allyloxy)benzoyloxy)biphenyl-4-yl-6-(4-fluorobenzoxyloxy)hexahydrofuro[3,2-b]furan-3-yl adipate (M₂)

Compound 5 (12.04 g, 0.02 mol), DCC (4.12 g, 0.02 mol) and DMAP (0.21 g, 1.69 mmol) were dissolved in 250 ml of tetrahydrofuran (THF) at 30°C. 4-Fluorobenzoic acid (2.80 g, 0.02 mol) was dissolved in 30 ml of THF at 30°C, and then added to the solution. The reaction mixture was stirred for 2 days at 30°C. The resulting solution was filtered and poured into 1000 ml of cold water. The precipitated crude product was filtered and recrystallised in alcohol and THF (3:1), isolated by filtration and dried overnight at 65°C under vacuum to obtain white crystals. Yield: 73%, IR (KBr): 3083 (=C=H), 2937–2862 (–CH₃, –CH₂–), 1748–1735 (C = O), 1641 (C = C), 1608, 1498 (Ar–), 1257 (C–O), 1170 (C–F). Anal. calcd for C₃₄H₂₄F₂O₁₁: C 67.95, H 5.15, O 24.07; found C 67.90, H 5.08, O 24.07. 1H NMR (600 MHz, CDCl₃, δ): 8.17–7.00 (m, 16H, Ar–H), 6.11–6.04 (m, 1H, CH₂ = CH–), 5.47–5.33 (t, 2H, CH₂ = CH–), 5.23–3.81(m, 8H, –CH₂–O– and –CH₂–O– in isosorbide group), 4.64–4.63 (d, J = 4.8 Hz, 2H, –OCH₂–), 2.63–2.40 (m, 4H, –OOCCH₂(CH₂)₃CH₂COO–), 1.84–1.50 (m, 4H, –OOCCH₂(CH₂)₃CH₂COO–).

2.4. Synthesis of the cholesteric polysiloxane polymers

The polysiloxane polymers were synthesised by a one-step hydroisylation reaction between Si–H groups of PMHS and olefinic C=C of monomers in toluene. The polymerisation experiments are summarised in Table 1. The synthesis of P₁ is presented as an example. Monomers M₁ (0.0093 g, 0.0525 mmol) and M₂ (1.229 g, 1.1897 mmol) was dissolved in 60 ml of dry distilled toluene. To the stirred solution, PMHS (0.145 g, 0.25 mmol) and 1.5 ml of H₂PtCl₆ in 20 ml THF were added; the mixture was heated under nitrogen and anhydrous conditions at 90°C for 48 h. Then the solution was cooled and poured into 200 ml methanol; after
filtration, the product was washed with hot ethanol (three times) and dried at 60°C under vacuum for 12 h to obtain polymer P₁.

### Table 1. Polymerisation and yield.

| Polymer | PMHS (mmol) | M₁ (mmol) | M₂ (mmol) | Ln₂O₃ (mmol) | M₁ (mol%) | Ln³⁺ (mol%) | Yield (%) |
|---------|-------------|-----------|-----------|-------------|-----------|------------|----------|
| P₁      | 0.25        | 0.0525    | 1.6975    | –           | 3         | –          | –        |
| P₂      | 0.25        | 0.1050    | 1.6450    | –           | 6         | –          | –        |
| P₃      | 0.25        | 0.1575    | 1.5925    | –           | 9         | –          | –        |
| Eu-P₁   | 0.25        | 0.0525    | 1.6975    | 0.0088      | 3         | 1          | 73       |
| Eu-P₂   | 0.25        | 0.1050    | 1.6450    | 0.0175      | 6         | 2          | 69       |
| Eu-P₃   | 0.25        | 0.1575    | 1.5925    | 0.0263      | 9         | 3          | 73       |
| Tb-P₁   | 0.25        | 0.0525    | 1.6975    | 0.0088      | 3         | 1          | 77       |
| Tb-P₂   | 0.25        | 0.1050    | 1.6450    | 0.0175      | 6         | 2          | 77       |
| Tb-P₃   | 0.25        | 0.1575    | 1.5925    | 0.0263      | 9         | 3          | 81       |

### 2.5. Synthesis of the lanthanide-containing polymers

The synthetic route to the lanthanide-containing polymers is shown in Figure 2; the polymerisation
experiments are summarised in Table 1. The synthesis of Eu-P₁ is presented as an example. Anhydrous europium chloride (0.0045 g, 0.0175 mmol), which was prepared from Eu₂O₃, ammonium chloride and hydrochloric acid,[37] was dissolved in benzene and anhydrous 2-propanol (1:1). The mixture was heated to 50°C for 12 h under N₂, and then this stirred solution was added to a solution of sodium isopropoxide (0.0043 g, 0.0525 mmol) in 2-propanol. The mixture was refluxed for 4 h to synthesise europium isopropoxide and a solution of P₁ in toluene was added dropwise. The reactive mixture was refluxed for 10 h. After cooling to room temperature, the mixture was filtered to obtain the filtrate, after which the filtrate was poured into 200 ml methanol; after filtration, the product was washed with hot ethanol (three times) and washed with cyclohexane (three times), and dried at 60°C under vacuum for 12 h to obtain polymer Eu-P₁.

3. Results and discussion
3.1. Thermal properties
The thermal properties of M₂ and the lanthanide-containing polymers were determined by DSC, POM and TGA. Thermal properties determined by DSC were consistent with POM observation results. Typical DSC curve of M₂ is shown in Figure 3, and representative DSC thermograms of the polymers are displayed in Figure 4. DSC heating thermograms of M₂ showed a melting transition at 157.1°C and a cholesteric to isotropic phase transition at 242.8°C; the cooling thermogram of M₂ showed an isotropic to cholesteric phase transition at 217.8°C and crystallisation temperature at 126.6°C.

All polysiloxane polymers and lanthanide-containing polymers showed a glass transition at low temperatures and an LC phase to isotropic transition at high temperature. Low temperatures induced vitrification rather than crystallisation[38] due the
intrinsic disordered and atactic systems of the side chains of the siloxane-containing LC. For all the lanthanide-containing polymers, reversible mesomorphic phase transitions were observed due to sufficient LC molecular motion and orientation suggesting that complex units did not change the LC state of polymer systems. The effect of lanthanide ions on phase transition temperature of the polymers is shown in Figure 5. As seen from the data of Table 2 and Figure 5, the glass transition temperature \((T_g)\) values of lanthanide-containing polymers are higher than that of polysiloxane polymers in the same feed ratio. This result indicated that complexation imposes additional constraints on the segment motion of polymer chains and might be expected to raise the glass transition temperature. In addition, the tested range of the lanthanide ions concentrations in polymers \(\text{Eu-P}_1–\text{Eu-P}_3\) and \(\text{Tb-P}_1–\text{Tb-P}_3\) did not significantly affect the glass transition of polymers on heating.

![Figure 3. DSC thermograms of \(M_2\).](image)

![Figure 4. DSC thermograms of the polymers on the second heating.](image)

![Figure 5. Effect of the lanthanide ion content on phase transition temperatures.](image)

### Table 2. DSC, POM and TG results of the polymers.

| Sample | \(T_g\) (°C) | \(T_i\) (°C) | \(\Delta H\) (J g\(^{-1}\)) | \(\Delta T^a\) | \(T_{i1}\)\(^b\) (°C) | \(T_{i2}\)\(^c\) (°C) | \(T_{0.5\%}\)\(^d\) (°C) |
|--------|--------------|--------------|----------------------------|------------|----------------|----------------|----------------|
| \(\text{P}_1\) | 45.7 | 188.0 | 1.97 | 142.3 | 194.4 | 187.5 | 297.4 |
| \(\text{P}_2\) | 44.3 | 182.3 | 0.93 | 138.0 | 188.1 | 181.7 | 295.2 |
| \(\text{P}_3\) | 43.8 | 175.7 | 0.62 | 131.9 | 180.8 | 174.1 | 294.3 |
| \(\text{Eu-P}_1\) | 46.9 | 192.0 | 2.11 | 145.1 | 199.1 | 191.5 | 301.8 |
| \(\text{Eu-P}_2\) | 47.3 | 187.2 | 1.13 | 139.9 | 193.7 | 186.1 | 307.4 |
| \(\text{Eu-P}_3\) | 48.1 | 179.5 | 0.79 | 131.4 | 185.7 | 177.5 | 317.8 |
| \(\text{Tb-P}_1\) | 46.6 | 191.3 | 2.04 | 144.7 | 198.5 | 192.4 | 302.4 |
| \(\text{Tb-P}_2\) | 47.5 | 185.9 | 1.07 | 138.4 | 190.7 | 185.1 | 308.1 |
| \(\text{Tb-P}_3\) | 48.3 | 178.9 | 0.81 | 130.6 | 183.3 | 177.9 | 318.3 |

Notes: \(^a\)Mesophase temperature ranges \((T_i-T_g)\); \(^b\)temperature at which the birefringence disappeared completely; \(^c\)temperature at which the mesophase occurred; and \(^d\)temperature at which 5% weight loss occurred.
cycles. The glass transition temperature \((T_g)\) may be considered as a measure of the backbone flexibility. For polymers with a low content of lanthanide ions, the glass transition temperature was not significantly affected, indicating that the backbone flexibility did not change significantly.

Unlike \(T_g\), the lanthanide ions obviously influence the clearing point \((T_c)\). In the same feed ratio, the \(T_c\) value of lanthanide-containing polymers is higher than that of polysiloxane polymers. However, for the lanthanide-containing polymers, chemical cross-linking could prevent the motion and orientation of the mesogenic molecule and was not in favour of the mesogenic orientation in the polymers with increasing the content of the lanthanide ions. It can be seen that the \(T_c\) value was reduced with the increasing content of the lanthanide ions. When the concentration of the lanthanide ions increased from 1 to 3\%, the \(T_c\) value of Eu-P\(_1\)-Eu-P\(_3\) and Tb-P\(_1\)-Tb-P\(_3\) decreased from 192.0 to 179.5\(^\circ\)C and 191.3 to 178.9\(^\circ\)C, respectively. At the same time, it can be seen from Table 3 that Eu-P\(_1\)–Eu-P\(_3\) and Tb-P\(_1\)–Tb-P\(_3\) displayed wide meso-phase temperature ranges \((\Delta T)\). \(\Delta T\) values of Eu-P\(_1\)–Eu-P\(_3\) and Tb-P\(_1\)–Tb-P\(_3\) decreased with increasing the content of the lanthanide ions.

For non-coordinated polymers, the decomposition temperature for 5 wt\% loss was in the order of Eu-P\(_3\) > Eu-P\(_2\) > Eu-P\(_1\) > P\(_1\)-P\(_3\) and Tb-P\(_3\) > Tb-P\(_2\) > Tb-P\(_1\) > P\(_1\)-P\(_3\), respectively, indicating that there was an increase with the introduction of the lanthanide ions. Temperature for 5 wt\% loss has often been used as a degradation temperature \((T_d)\) to estimate the thermal stability of a synthetic polymer. The 5\% weight loss of all the lanthanide-containing polymers took place at temperatures above 300\(^\circ\)C, showing good thermal stability.

### 3.2. Optical texture

Optical textures of the samples were studied by POM with hot stage. POM results showed that M\(_2\) exhibited enantiotropic oily-streak texture and focal–conic texture of the cholesteric phase during the heating and cooling cycles. The oily streak texture of M\(_2\) is shown in Figure 6(a). All of the polysiloxane polymers and lanthanide-containing polymers showed similar cholesteric phase textures in the heating and cooling cycles. When Eu-P\(_1\), used as an example here, was heated to 50\(^\circ\)C, the cholesteric texture gradually appeared; the texture disappeared at 199.1\(^\circ\)C. Similarly, when the isotropic state was cooled to 191.5\(^\circ\)C, a similar cholesteric texture gradually appeared. Photomicrographs of P\(_1\), Tb-P\(_1\) and Eu-P\(_1\) are shown in Figure 6(b–d).

The cholesteric mesophase of the polymers was also confirmed by XRD. XRD studies were carried out to obtain more detailed information on the LC phase structure. All polymers displayed broad peaks at wide angles around 2\(\theta\) = 18–20\(^\circ\) in the wide-angle region of XRD measurement and a sharp peak associated with the smectic layers did not appear in the small-angle region of XRD measurement. Therefore, the cholesteric phase structure of polymers was confirmed by XRD, which was consistent with DSC and POM results. Figure 7 shows the representative XRD diagrams of the polymers at 120\(^\circ\)C.

### 3.3. Luminescent properties

By quick freezing the obtained polymers in the LC phase in liquid nitrogen, vitrified mesophase solids

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**Table 3. Luminescent property data of the Eu-containing polymers.**

| Sample  | Excitation bands (nm) | Emission bands (nm) | Relative intensities a | \(\tau\) (ms) |
|---------|-----------------------|---------------------|------------------------|--------------|
| Eu-P\(_1\) | 380 | 580, 592, 616, 650, 703 | 38.4, 66.0, 171.6, 15.8, 16.0 | 0.421 |
| Eu-P\(_2\) | 380 | 579, 592, 616, 653, 702 | 59.3, 136.4, 398.0, 16.5, 16.7 | 0.433 |
| Eu-P\(_3\) | 380 | 579, 591, 615, 653, 702 | 89.4, 169.7, 514.9, 29.2, 27.4 | 0.439 |

Notes: a: Relative intensities were obtained by the calculation of the integral area of the same emission bands; b for the \(^{5}\)D\(_{0}\)→\(^{5}\)F\(_{2}\) transition of Eu\(^{3+}\).
were obtained and the luminescent properties of the LC states were examined. Representative photoluminescence spectra of the polymers are given in Figures 8 and 9, and the detailed luminescent data are shown in Tables 3 and 4.

There are narrow-width red emissions of the Eu-containing polymers. The narrow–wide green emissions were observed in the Tb-containing polymers. Figure 8 illustrates the typical photoluminescence spectra of the Eu-containing polymers. The luminescence spectra were measured with 380 nm as the excitation wavelength. In the emission spectra, the red $^5D_0 \rightarrow ^7F_j$ ($J = 0, 1, 2, 3, 4$) transitions were clearly observed. The band near 579 nm was assigned to the $^5D_0 \rightarrow ^7F_0$ transition; the band near 592 nm was assigned to the $^5D_0 \rightarrow ^7F_1$ transition; the band near 612 nm was assigned to the $^5D_0 \rightarrow ^7F_2$ transition; the band near 653 nm was assigned to the $^5D_0 \rightarrow ^7F_3$ transition; and the band near 702 nm was assigned to the $^5D_0 \rightarrow ^7F_4$ transition. The maxima of these bands were sourced from $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ transitions, respectively. It is common knowledge that the $^5D_0 \rightarrow ^7F_0$ transition of Eu$^{3+}$ was strictly prohibited in a symmetric field, so the existence of this band indicates that Eu$^{3+}$ in polymers was in low symmetry and did not have an inversion centre. The $^5D_0 \rightarrow ^7F_1$ transition was a magnetic dipolar transition; its intensity hardly changes with the local structural environment. On the other hand, the $^5D_0 \rightarrow ^7F_2$ transition was an electric dipole transition and was sensitive to the coordination environment of the Eu$^{3+}$.

The intensity (the integration of the luminescent band) ratio of the $^5D_0 \rightarrow ^7F_2$ transition to the $^5D_0 \rightarrow ^7F_1$ transition has been widely used as an indicator of Eu$^{3+}$ site symmetry. In these Eu polymers, from Eu-P$_1$ to Eu-P$_3$, this was confirmed by the values of the intensity ratios of the $^5D_0 \rightarrow ^7F_2$ to $^5D_0 \rightarrow ^7F_1$ transitions, which were 2.60, 2.92 and 3.03 respectively. These ratio values are only possible when the Eu$^{3+}$ ions did not occupy a site with inversion symmetry.[39,40] Figure 9 illustrates typical photoluminescence spectra of the Tb-containing polymers. The luminescence spectra were measured with 286 nm as the excitation wavelength. The narrow peaks observed in the emission spectra were transitions between the excited $^5D_4$ level and the different
J-levels of the $^7F$ term. The band near 490 nm was assigned to the $^5D_4$→$^7F_6$ transition; the band near 545 nm was assigned to the $^5D_4$→$^7F_5$ transition; the band near 585 nm was assigned to the $^5D_4$→$^7F_4$ transition; and the band near 621 nm was assigned to the $^5D_4$→$^7F_3$ transition.

Figures 8 and 9 show that when the lanthanide ion content increases, the luminescent intensity of the polymers gradually increases accordingly. At Ln$^{3+}$ (mol %) = 3%, the lanthanide-containing polymers still did not show fluorescence quenching, possibly due to the introduction of PMHS. With the introduction of PMHS, the lanthanide ions can be evenly distributed in the polymers, thus preventing the lanthanide ions from approaching and aggregating. In addition, the typical decay curves of the lanthanide ions in polymers were measured, and the resulting lifetimes of the lanthanide-containing polymers are included in Tables 3 and 4. When the lanthanide ion content increases, the luminescent lifetimes of the polymers are extended slightly. This indicated that the content of the lanthanide ions in polymers had a small influence on the lifetime of the lanthanide-containing polymers.

To study the thermal stability of luminescence in the LC phase, the temperature dependence of luminescent intensity was measured. Figures 10 and 11 display the emission spectra of Eu-P$_3$ and Tb-P$_3$ at different temperatures. It is obvious that the luminescent intensity of Eu-P$_3$ and Tb-P$_3$ decreased monotonically with the increasing temperature in the studied range. The intensity as a function of temperature can be well fitted by the well-known thermal activation function[41]

$$I(T) = I_0/[1 + \alpha \exp(-E_A/K_BT)]$$

where $I_0$ is the emission intensity at 0 K, $\alpha$ is the proportional coefficient, $E_A$ is the thermal activation energy, $K_B$ is Boltzmann’s constant and $T$ is the absolute temperature. In the same polymer, the value of $E_A$ is the same.

4. Conclusions
In this paper, monomer $M_2$ exhibited cholesteric oily-streak texture and focal-conic texture. The TGA results showed that 5% weight loss temperatures were >300°C for all the lanthanide-containing polymers. With an increase of the lanthanide ions in the polymers, the glass transition temperature ($T_g$) does not change significantly; the isotropic temperature ($T_i$) and mesophase temperature range ($\Delta T$) decreased. All the polymers showed similar cholesteric textures when heated and cooled, which were confirmed by XRD. With the lanthanide ion content

### Table 4. Luminescent property data of the Tb-containing polymers.

| Sample | Excitation bands (nm) | Emission bands (nm) | Relative intensities$^a$ | $\tau^b$ (ms) |
|--------|-----------------------|---------------------|--------------------------|--------------|
| Tb-P$_1$ | 286                   | 490, 545, 585, 621  | 127.8, 321.3, 20.5, 8.6  | 0.842        |
| Tb-P$_2$ | 286                   | 491, 546, 585, 622  | 180.3, 437.0, 34.6, 11.1 | 0.851        |
| Tb-P$_3$ | 286                   | 490, 546, 586, 622  | 279.1, 643.5, 42.8, 15.2 | 0.865        |

Notes: $^a$Relative intensities were obtained by the calculation of the integral area of the same emission bands; $^b$for the $^5D_4$→$^7F_5$ transition of Tb$^{3+}$.
ranging between 1 and 3 mol%, luminescent lifetimes of polymers gradually increased. These results indicated that the introduction of the lanthanide ions did not change the LC state of the polymer systems, while the polymers were enabled with significant luminescent properties. The luminescent intensity of polymers decreased monotonically with the increasing temperature in the LC phase.

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**Supplemental data**

Supplemental data for this article can be accessed here.

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