Synthesis and Characterization of Chiral azo LCPs

Xuesong Zhang¹, Yuejiao Huang¹ and Xiaozhi He¹²

¹Department of Science, Northeastern University, NO. 3-11, Wenhua Road, Heping District, Shenyang, P. R. China
²corresponding author: E-mail: hexiaozhi@mail.neu.edu.cn

Abstract. Precursor polymer MP series were synthesized by 4-allyloxybenzoic acid cholesteryl ester (M) and 4- hydroxyphenyl 4- (propionyloxy) benzoate (P). We obtained novel thermotropic side-chain liquid crystal polymer MP series by esterification between MP series and 4-((4-ethoxyphenyl) diazenyl) benzoic acid (Z). Differential scanning calorimetry (DSC) was used to measure the thermal properties of those polymers, and the mesogenic properties were characterized by polarized optical micrograph (POM), DSC and X-Ray. MP series exhibited yellow, green, blue and purple Grandjean textures. MPZ series also showed colorful Grandjean textures. They exhibited thermotropic liquid crystal properties in a broad mesogenic region.

1. Introduction

In recent years, much attention has been paid to the irreversible photochromic chiral liquid crystal polymers for optical applications, such as data storage and display devices. There has been a growing interest in developing materials exhibiting liquid crystal properties and photochromism[1-7]. Recently, many researchers have paid more attention to thermotropic liquid crystal polymers containing azobenzene for their unique properties and use them for reversible polymer systems. It is well known that siloxane polymers are materials of significant technological value. The siloxane bond offers a highly flexible structure unit, polymer chains with low glass temperature (Tg) and surface tensions, and as well as unique physical and chemical properties. The properties, textures and the further determination of azo liquid crystal polymers are explored in detail[8].

Here we synthesised a series of novel chiral azo liquid crystal polymers. M is a liquid crystal monomer with a cholesteryl and P is a monomer containing a hydroxyl group. The precursor polymer MP series were synthesized by copolymerization between the liquid crystal monomer M with a cholesteryl and the monomer P containing a hydroxyl group. The azo liquid crystal polymer MPZ series were synthesized by esterification between MP series and azo liquid crystal monomer Z.

2. Experimental

The synthetic route of polymers is outlined in Scheme 1. The monomer 4-allyloxybenzoic acid cholesterylester (M) and the monomer 4-undecenoxybenzoic acid p-benzene monophenolate (P) reacted with Si-H of polymethylhydrosiloxane (PMHS) to form polymers under the catalyst of hexachloroplatinic acid (Pt/THF = 5/103 g/mL). All polymers synthesized are listed in Table 1. The monomers M, P and PMHS was dissolved in dried, freshly distilled toluene. After complete dissolution, 4 mL of catalyst hexachloroplatinic acid was added. The mixtures were heated to 70°C, and continue to react for 24 h. The hydrosilylation reaction, followed the track of the Si-H stretch intensity by FTIR, was completed when the stretch vibrate of Si-H disappeared. The polymers were obtained from methanol after distilled off the solvent toluene. The crude product is repeatedly washed with a 1:1 ethanol acetone solution at 60 °C for several times, and then dried at room temperature.
The polymer MP and the heptyloxyazobenzoic acid chloride (Z) to form polymers after the addition of DMAP. Details of the polymerisation reaction are represented in Table 1. The heptyloxyazobenzoic acid chloride which was added into 10 mL of dichloromethane and the polymers MP which was dissolved in 20 mL of dichloromethane were mixed. And then 0.05 g of DMAP was added and dissolved. The mixtures heated to 65 °C, and refluxed for 15 h. The crude product was purified by recrystallisation from ethanol.

**Table 1.** Polymerisation of MP series and MPZ series

| MP series | Feed | M (mmol) | P (mmol) | M:P | MPZ series | Feed | M (g) | P (g) | MP:Z |
|-----------|------|----------|----------|------|------------|------|-------|-------|-------|
| MP1       | 0.30 | 4.4103   | 0.0909   | 98:2 | MPZ1       | 0.3  | 0.00399 | 1:1.2 |
| MP2       | 0.30 | 4.275    | 0.225    | 95:5 | MPZ2       | 0.3  | 0.01014 | 1:1.2 |
| MP3       | 0.30 | 4.14     | 0.36     | 92:8 | MPZ3       | 0.3  | 0.01619 | 1:1.2 |
| MP4       | 0.30 | 4.05     | 0.45     | 90:10| MPZ4       | 0.3  | 0.02034 | 1:1.2 |
| MP5       | 0.30 | 3.9597   | 0.5404   | 88:12| MPZ5       | 0.3  | 0.02453 | 1:1.2 |
| MP6       | 0.30 | 3.825    | 0.675    | 85:15| MPZ6       | 0.3  | 0.03089 | 1:1.2 |

**Scheme 1.** The synthetic route of polymers MP series and MPZ series

3. Results and Discussion

3.1. LC Texture Studies

The POM results showed that the polymers of MP series and MPZ series exhibited cholesteric phase on the heating and cooling cycle. When MP4 was heated to 151°C, a typical Grandjean blue texture
appeared. When MP4 was heated to 176°C, it displayed a Grandjean yellow-blue texture. When MPZ1 was heated to 156°C, it exhibited a Grandjean green-red texture. With the temperature rising, the red colour became deeper and deeper, which indirectly proved that azo group had been introduced successfully. The textures of precursor LCPs (MP series) and azo LCPs (MPZ series) are presented in Figure 1. For MP series, MP1–MP6 all exhibited blue Grandjean textures on heating and cooling cycles. For MPZ series, they exhibited more obvious red Grandjean textures with the increase of azo content.

Figure 1. Textures of MP series and MPZ series (200×): (a) MP4 heating to 151°C; (b) MP4 heating to 176°C; (c) MPZ1 heating to 156°C; (d) MPZ4 heating to 217°C.

3.2. Thermal Characterization

Many researches need to measure the phase transition temperatures of polymers. The DSC measurement is an appropriate choice. The DSC diagram measured on the second heating cycle (20°C/min) are shown in Table 2 and Figure 2. It is evident that $T_i$ of MPZ series increased from 224°C to 241°C for MPZ1 to MPZ6, while $T_i$ of MP series increased firstly from MP1 to MP2, then decreased from MP2 to MP3, and increased from MP3 to MP6.

There are many factors that affect $T_g$ and $T_i$ of LCPs, such as molecular weight, flexibility of chain, change of substituents and copolymerized components. As the content of P increased, the $T_g$ of MP series showed a trend of decrease, which was result from the interaction between flexible spacers and intermolecular hydrogen bonds. The interaction between the flexible spacer group and hydroxyl group lead to the increase of $T_i$. For MPZ, after the introduction of the monomer Z with azo mesogenic units, the rigid part and the soft part counterbalanced with each other. $T_g$ showed a decreasing trend while $T_i$ showed an increasing trend.

Table 2. Thermal properties of MP series and MPZ series.

| MP series | $T_g$ | $T_i$ | $\Delta T$ | MPZ series | $T_g$ | $T_i$ | $\Delta T$ |
|-----------|-------|-------|------------|------------|-------|-------|------------|
| MP1       | 60.76 | 146.57| 85.81      | MPZ1       | 67.59 | 224.23| 156.64     |
| MP2       | 56.05 | 151.92| 95.87      | MPZ2       | 66.70 | 225.87| 159.17     |
| MP3       | 55.62 | 139.38| 83.76      | MPZ3       | 65.51 | 237.02| 171.51     |
| MP4       | 53.91 | 157.43| 103.5      | MPZ4       | 63.39 | 237.54| 174.15     |
| MP5       | 53.34 | 179.07| 125.7      | MPZ5       | 62.72 | 240.49| 177.77     |
| MP6       | 54.51 | 169.12| 114.6      | MPZ6       | 62.26 | 241.95| 179.69     |

$T_g$: glass temperature; $T_i$: isotropic temperature; $\Delta T$: mesophase temperature ranges ($T_i$–$T_g$).
3.3. X-ray Diffraction

XRD analysis allowed for a complementary assessment of the nature of the phases observed by DSC and POM, giving additional information about their structural parameters. Figure 3 shows X-ray scatterings of MP series and MPZ series. The wide-angle X-ray diffraction pattern of the polymer film quenched from the liquid crystal state showed a broad reflection, while no sharp reflections at small angles observed. There is no absorption peak in the small angles, indicated that there was no smectic phase in the polymer structure. Combined with POM, DSC and XRD measurements, both MP and MPZ were cholesteric phases.

Figure 2. DSC thermograms of the representative MP series and MPZ series on the second heating cycle.

Figure 3. XRD curves of the representative MP series and MPZ series.
4. Conclusions
In this study, we synthesized a series of new side-chain chiral azo liquid crystal polymers by esterification reaction between precursor MP and azo liquid crystal monomer Z. Their structures and liquid-crystal properties have been investigated by DSC, POM and XRD, respectively. Both the polymer precursors MP series and the liquid crystal polymer MPZ series all presented impressive colorful Grandjean textures. The melting points and clearing points of the cholesteric liquid crystal polymers MPZ series were higher than that of the polymer precursors MP series. The T_g of MP series and MPZ series showed a downward trend, while the T_i showed an upward trend. A series of novel azo liquid crystal polymers that had been synthesized in this study showed excellent liquid crystal properties and exhibited interesting cholesteric phase textures. All obtained liquid crystal polymers exhibited wide interphase temperature range and typical Grandjean textures. The optical structures and X-ray images of LCPs confirmed that the obtained polymers are of cholesteric azo LCPs. The current work enabled us to better understand the cholesteric azo liquid crystal polymers, which would broaden the application of cholesteric azo LCPs in material science and provide possibilities for the design of the next generation of optical devices.

5. References
[1] Zhi J, Zhang B, Zang B, Shi G 2002 Synthesis and properties of photochromic cholesteric liquid crystalline polysiloxane containing chiral mesogens and azobenzene photochromic groups. *J. Appl. Polym. Sci.* **85**:2155-62.
[2] Chilaya G, Chanishvili A, Petriashvili G, Barberi R, Bartolino R, De Santo MP, Matranga MA, Collings P 2006 Light Control of Cholesteric Liquid Crystals Using Azoxy-Based Host Materials. *MOL CRYST LIQ CRYST*. **453**:123-40.
[3] Meng F-B, Wang Z-Y, Chai G-W, Wang H-G, Chen Y, Zhang B-Y 2010 Synthesis and characterization of fluorine-containing liquid crystalline polysiloxanes bearing cholesteryl cinnamate mesogens and trifluoromethyl-substituted mesogens. *J. Appl. Polym. Sci.* **116**(4): 2384-2395.
[4] Yamamato T, Sano M 2017 Chirality-induced helical self-propulsion of cholesteric liquid crystal droplets. *SOFT MATTER*. **13**(18): 3328-3333.
[5] Bose E 1972 Behaviour of liquid crystal [J]. *J PHYS*. **8**(4): 513-518.
[6] Demus D, Richter L 1972 The texture of liquid crystals [J]. *APPL PHYS LETT*. **13**(1): 91-100.
[7] Pauluth D, Tarumi K 2004 Advanced liquid crystals for television [J]. *J MATER CHEM*, **14**: 1219-1227.
[8] Haiyi Z, Li C, Xiaomin D, et al 2018 Physio-and chemo-dual crosslinking toward thermo-and photo-response of azobenzene-containing liquid crystalline polyester [J]. *SCI CHINA MATER*, **61**(9): 1225-1236.