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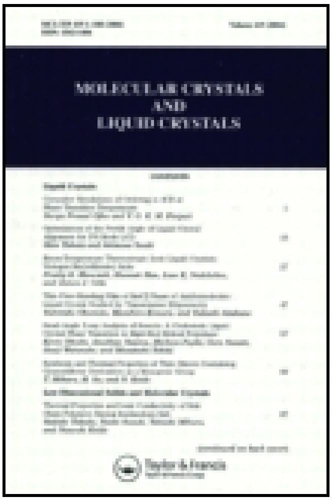

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Synthesis of Amide-Type Smectic A Side-Chain Polysiloxane Liquid Crystal

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Synthesis of Amide-Type Smectic A Side-Chain Polysiloxane Liquid Crystal

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In this paper, monomer N-(4-hydroxyphenyl-1) 4-alkyloxybenzamide was obtained by the Williamson reaction, acylation, and aminolysis. Side-chain polysiloxane liquid crystal was then successfully synthesized by a grafting reaction of the monomer. The monomer and liquid crystal were characterized by Fourier-transform infrared spectroscopy, ^{1}H nuclear magnetic resonance spectroscopy, differential scanning calorimetry, and polarization microscopy. The results showed that both monomer and polymer exhibited thermotropic smectic A behavior, and they were very stable within the studied temperature range. They may be very sensitive to both electric and magnetic fields because of their liquid crystalline properties.

Keywords Amide linkage; liquid crystal; polymers; smectic A

Introduction

Side-chain liquid crystalline polymers have been extensively studied over the last decades [1–5] because of their novel properties, such as light absorption, electric, magnetic, and separation characteristics. Side-chain liquid crystals have potential uses in many applications, such as optoelectronic display, recording, storage, modulation, membrane separation, biological materials, etc.

In recent years, significant progress has been made in the synthesis and application of liquid crystal molecules containing amide linkages [6–10]. Aharoni [11] has synthesized a polymer liquid crystal with an amide linkage and an isolated benzene ring. Kumar et al. [12] have synthesized triphenylene discotic liquid crystalline compounds containing an amide linkage. However, the synthesis of polysiloxane liquid crystals with amide linkages is rarely reported. In this paper, the thermotropic liquid crystalline polysiloxane with an amide linkage was synthesized successfully. The obtained monomer and liquid crystal polymer had good stabilities within the studied temperature range.

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Experimental

Synthesis of 4-Allyloxybenzoyl Acid (Compound 1) and 4-Allyloxybenzoyl Chloride (Compound 2)

4-Allyloxybenzoyl acid was synthesized according to a previous report [13]. The obtained compound 1 (14 g, 80 mmol) was reacted with thionyl chloride (12 mL, 165 mmol) containing a few drops of N,N-dimethylformamide (DMF) at 60°C for 5 h. Then, 4-allyloxybenzoyl chloride (compound 2) was purified by reduced pressure distillation.

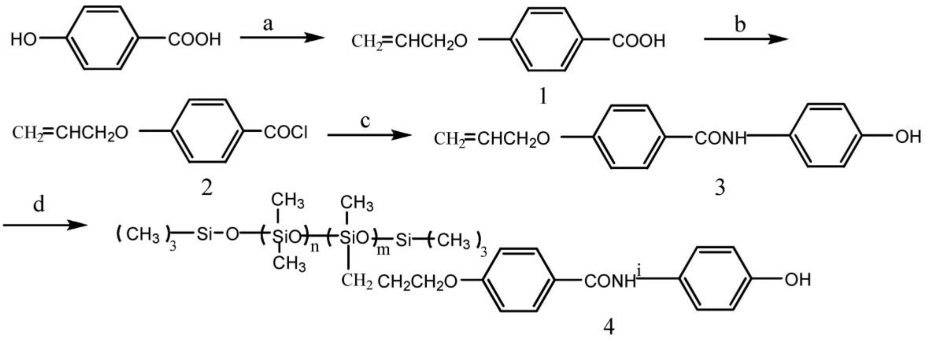
Synthesis of Monomer (Compound 3)

The obtained compound 2 (3.4 g, 20 mmol) was dissolved in 20 ml of acetone, and a mixture of 2.18 g of aminophenol, 12 mL of acetone, and 2 mL of DMF was slowly added to the reaction vessel. The reaction was carried out at 0°C for 30 min. Thereafter, the product was cooled and placed in a refrigerator overnight. After the filtrate was concentrated, the product was precipitated by adding water to the residue. Compound 3 was obtained by filtration and recrystallization from dichloromethane (yield: 76.8%; mp: 199–200°C).

Synthesis of Side-Chain Polysiloxane Liquid Crystal (Compound 4)

About 2.2 g (25 mmol) of compound 3, 1.6 g of polysiloxane, 100 μg of potassium chloroplatinate, and 17 ml of toluene were poured into a 100-mL three-neck round-bottom flask equipped with a reflux condenser and magnetic stirrer. The mixture was refluxed under nitrogen atmosphere at 110°C for 24 h. After two times of recrystallization in dichloromethane, compound 4 was dried in a vacuum oven at 110°C for 24 h (yield: 51.1%).

The preparation is shown in Scheme 1.



Reagents: (a) allyl bromide, potassium hydroxide, potassium iodide, and ethanol; (b) thionyl chloride and DMF; (c) p-aminophenol, triethylamine, and toluene; (d) polysiloxane (n=10, Mr=2000), potassium chloroplatinate, and toluene.

Scheme 1. Preparation of target molecules.

Results and Discussion

Figure 1 shows the Fourier transform infrared (FT-IR) spectra of (a) polysiloxane, (b) monomer (compound 3), and (c) side-chain polysiloxane liquid crystal (compound 4). Clearly, (a) the Si-H stretching bond at 2162 cm^{-1} and (b) the C=C bond at 1653 cm^{-1} were

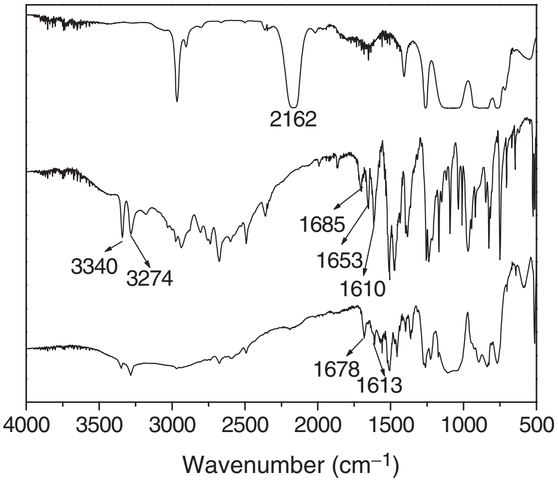


Figure 1. FT-IR spectra of (a) poly(methylsiloxane), (b) compound 3, and (c) side-chain polysiloxane liquid crystal compound 4.

not present in the (c) resultant compound 4. The characteristic Si–O–Si stretching bond appeared at 1000–1300 cm^{-1}, whereas the absorption bands of amide C=O (at 1678 cm^{-1}) and aromatic band (at 1613 cm^{-1}) still existed in compound 4. Thus, the appearance of the characteristic absorption bands of corresponding compound 3 indicated the successful incorporation of monomers into the polysiloxane chains for all liquid crystal polysiloxanes [14].

Figure 2 shows the ^{1}H NMR (400 MHz, DMSO, ppm) spectra of compound 4: δ = 0.01033 (a), 1.30881 (b), 3.15539 (c), 3.40765 (d), 6.86120 (e), 7.1894 (f), 7.71279 (g), 8.11688 (h), 9.65872 (i), and 9.95479 (j). In addition, δ = 4.74 (Si-H) was not detected by ^{1}H-NMR, suggesting the successful incorporation of monomers into the polysiloxane chains. The result of the analysis was the same as that of FT-IR spectroscopy. δ = 2.90476 was the result of the α or β grafting reaction of compound 3.

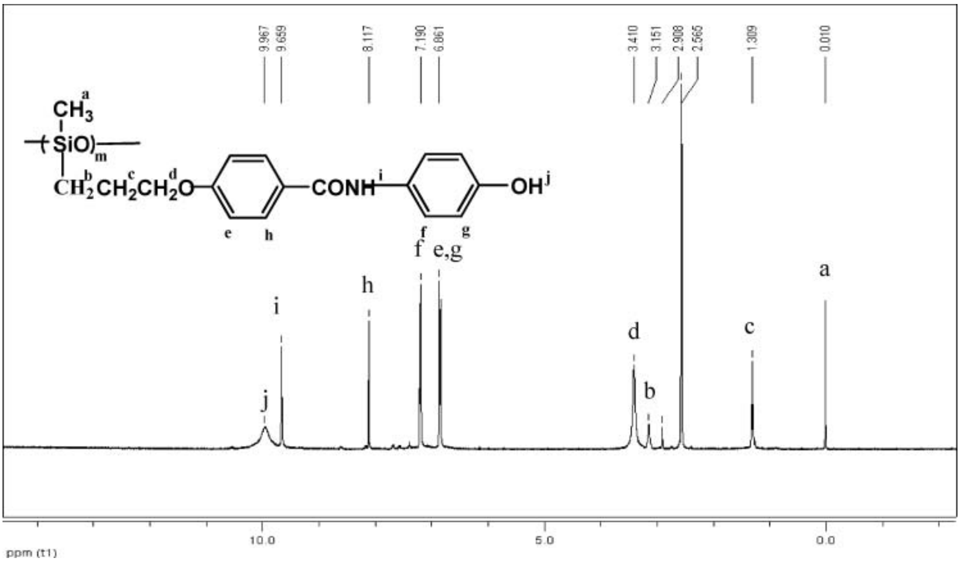


Figure 2. ^{1}H-NMR spectra of the obtained side-chain polysiloxane liquid crystal compound 4.

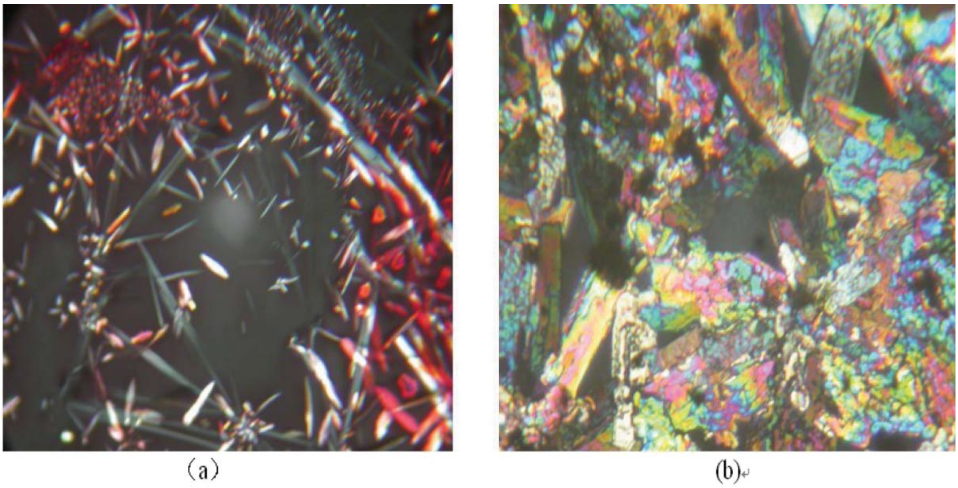


Figure 3. (a) POM photos of compound 3 (200×) at 189°C; (b) POM photos of compound 4 (200×) at 305°C.

The optical textures of the samples were studied by polarized optical microscopy (POM) with a hot stage. The representative optical textures of monomeric compounds 3 and 4 are shown in Figs. 3(a) and (b).

For compound 3, the images became bright and liquid crystal textures appeared when the temperature was higher than 104°C. The textures became clearly visible as the sample was heated continuously. Ultimately, compound 3 exhibited textures with some small rods, as shown in Fig. 3(a). The bar-like texture of compound 3 disappeared when the temperature was higher than 205°C, and the sample became isotropic. Compared with nematic spherules, the smectic phase formed a small rod called a "batonnet." Therefore, the appearance of the batonnet showed that compound 3 had new high-ordered smectic phase [15]. The POM results revealed that the liquid crystal temperature range of compound 3 was from 104 to 205°C.

The POM also showed that compound 4 had a smectic A texture. The images became bright and liquid crystal textures appeared when the temperature was higher than 247°C. The bar-like texture existed until the temperature of isotropic transition was 310°C. This phenomenon indicated the appearance of smectic textures upon heating compound 4. When compound 4 was cooled from the isotropic state, similar bar-like textures appeared gradually, and a broken fan-shaped texture appeared, as shown in Fig. 2(b). The POM results revealed that the liquid crystal temperature range of compound 4 was from 247 to 310°C.

The transition temperature can be obtained by differential scanning calorimetry (DSC). Compounds 3 and 4 were further characterized by DSC measurements using a DSC 822e instrument (METTLER TOLEDO, Switzerland) under nitrogen flow at a heating rate of 10°C/min. The results are shown in Figs. 4(a) and (b).

The melting point (T_{m}) of compound 3 was observed at 106.13°C, and the smectic-isotropic transition temperature ($T_{\mathrm{S\text{-}I}}$) was 200.22°C. The temperature range and the characterization were consistent with the POM results. However, there was only one endothermic peak in the DSC thermogram of compound 4, i.e., a melting point at 255.27°C. This finding can be attributed to the higher glass transition temperature when the isotropic liquid crystal phase change cannot proceed until the sample decomposed [15]. However, the performance of the liquid crystal was not affected.

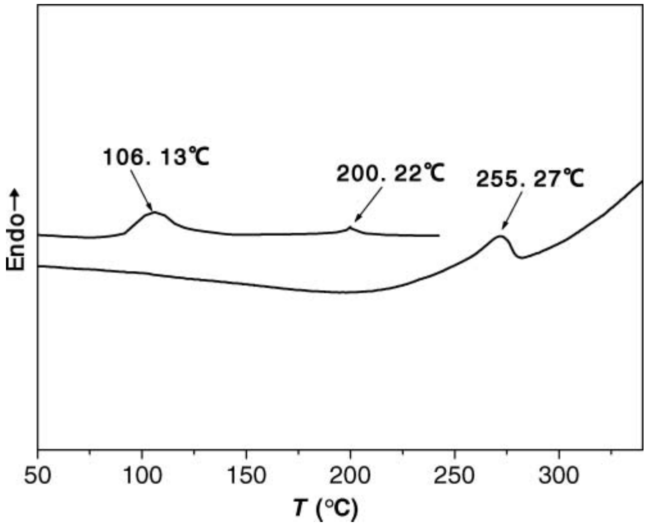


Figure 4. DSC thermograms of (a) monomer compound 3, and (b) side-chain polysiloxane liquid crystal compound 4.

Conclusions

A new amide-type smectic A side-chain polysiloxane liquid crystal was synthesized, and its phase behavior was melting point (Cr) = 255.27°C. Its liquid crystal domain was narrower than that of the monomer. Both side-chain polysiloxane liquid crystal and monomer had good stabilities in wide temperature ranges. They can be applied in optoelectronic displays as well as recording and storage materials.

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