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Syntheses and characterizations of side-chain liquid crystalline poly(glycidyl ether)s with biphenyl mesogenic group

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Summary

Four three-armed poly(glycidyl ether)s with biphenyl mesogenic group and various lengths of spacer, new side-chain liquid crystalline polymers, were synthesized by cationic ring-opening polymerization of the corresponding monomers in the presence of 2,2-dihydroxymethylbutanol and $BF_3{\cdot}OEt_2$ as initiator. The structures of the obtained poly(glycidyl ether)s were verified by ^1H and ^{13}C NMR spectroscopy, and their liquid crystalline behaviors were studied by differential. scanning calorimetry (DSC and optical polarizing microscopy (OPM).

Introduction

It is well known that liquid crystal behaviors of side-chain liquid crystalline polymers (SCLCPs) depend upon the structures of polymer backbone, mesogenic unit and flexible spacer connecting the mesogenic group to a polymer backbone. Many reports indicated that although a spacer helps to decouple the mesogenic groups from the main chain, and that decoupling becomes more effective with increasing spacer length, decoupling is nevertheless incomplete. Therefore, the effects of the polymer backbone on phase transitions have been observed (1). Polysiloxanes and poly(meth)acrylates have generally been used as the main chain of SCLCPs (1). Other main chain structures, like poly(vinyl ether)s, poly(phosphazene)s, poly(styrene), poly(olefine)s and poly(isocyanate)s were less reported (2-10). Recently, SCLCPs with oxyethylene or oxypropylene units, such as poly(glycidyl ether) (2, 11-13) and poly(oxetane) (14-16) were synthesized and their LC behaviors were studied. In all these reports, the polyethers were linear. It should be interesting to study the LC behaviors of three-armed polyethers. In this paper, we reported the syntheses and characterizations of three-armed poly(glycidyl ethers) with various lengths of spacer and biphenyl group as mesogenic unit. Their LC behaviors were studied by means of optical polarizing microscopy (OPM), and differential scanning calorimetry (DSC).

Experimental

Materials:

Toluene, epichlorohydrin and chloroform were treated with CaH_2, then distilled prior to use. Methylene chloride was washed with concentrated H_2SO_4, then distilled prior to use. Other solvents and reagents were analytical grade and were used without further purification. The monomers used in this study were synthesized according to scheme 1 (17, 18).

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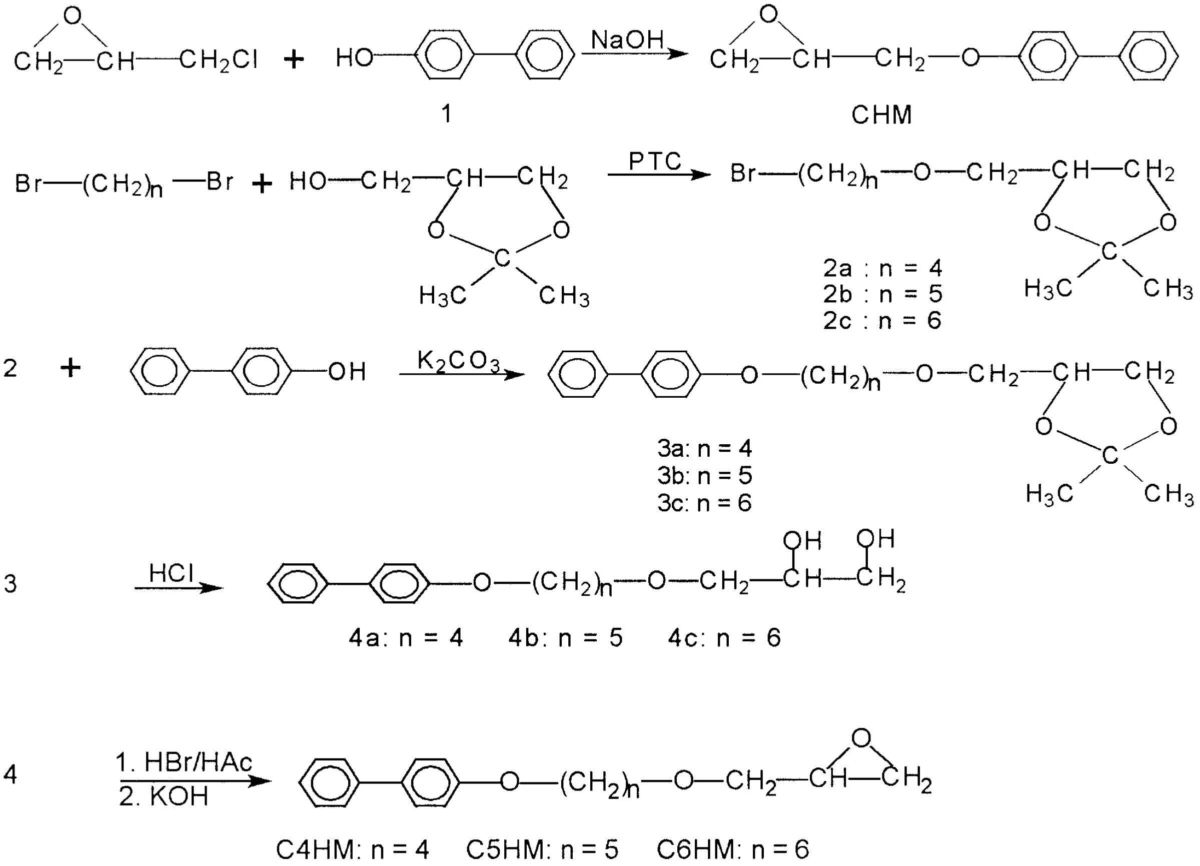
Synthesis of CHM

CHM was prepared by the reaction of epichlorohydrin with biphenyl-4-ol (12). The crude product was purified by column chromatography on silica gel with CH_2Cl_2 as eluent. A white solid was obtained: m.p. 89-91 °C, yield: 73 %.

^1H NMR ($CDCl_3$, ppm): δ2.7-3.3 (m, 3H, epoxy protons), 4.0-4.3 (m, 2H, $-CH_2O$), 7.0-7.6 (m, 9H, aromatic H).

Scheme 1:



Synthesis of 2

The procedure of preparing 2 was according to literature 17. They were purified by distillation. For 2a, b.p. 74-77°C/15pa, yield: 77%; for 2b, b.p. 84-86°C/15pa, yield: 81%; for 2c, b.p. 100-106 °C/2 pa, yield: 89%.

^1H NMR (CCl_4, ppm) for 2a: δ1.3 (d, 6H, $C(CH_3)_2$), 1.5-2.2 (m, 4H, $-CCH_2CH_2C-$), 3.3-4.3 (m, 9H, $-OCH_2CHCH_2OCH_2-$, $-CH_2Br$).

For 2b: δ1.3 (d, 6H, $C(CH_3)_2$), 1.5-2.2 (m, 6H, $-CCH_2CH_2CH_2C-$), 3.3-4.2 (m, 9H, $-OCH_2CHCH_2OCH_2-$, $-CH_2Br$).

For 2c: δ1.3 (d, 6H, $C(CH_3)_2$), 1.4-2.1 (m, 8H, $-CCH_2CH_2CH_2CH_2C-$), 3.3-4.2 (m, 9H, $-OCH_2CHCH_2OCH_2-$, $-CH_2Br$).

Synthesis of 3

They were prepared by the reaction of 2 with biphenyl-4-ol (17). Liquid products were obtained. For 3a, yield: 73%; for 3b, yield: 76%, for 3c, yield: 73%.

^1H NMR (CCl_4, ppm) for 3a: δ1.3 (d, 6H, $C(CH_3)_2$), 1.5-2.0 (m, 4H, $-CCH_2CH_2C-$), 3.3-4.2 (m, 9H, $-OCH_2CHCH_2OCH_2-$, $-CH_2O$-ph), 6.6-7.5 (m, 9H, aromatic H).

For 3b: δ1.3 (d, 6H, $C(CH_3)_2$), 1.4-2.0 (m, 6H, $-CCH_2CH_2CH_2C-$), 3.3-4.2 (m, 9H, $-OCH_2CHCH_2OCH_2-$, $-CH_2O$-ph), 6.6-7.5 (m, 9H, aromatic H).

For 3c: δ1.3 (d, 6H, $C(CH_3)_2$); 1.4-1.8 (m, 8H, $-C(CH_2)_4C-$); 3.3-4.2 (m, 9H, $-OCH_2CHCH_2OCH_2-$, $-CH_2O$-Ph); 6.6-7.5 (m, 9H, aromatic H)

Synthesis of 4

Hydrolysis of 3 in hydrogen chloride gave 4 (17). The crude product was crystallized from acetonitrile. For 4a, yield: 67%; for 4b, yield: 70%; for 4c, yield: 73%.

^{1}H NMR ($CDCl_3$, ppm) for 4a: δ1.5-2.0 (m, 4H, $-CCH_2CH_2C-$), 2.6 (s, 2H, 2-OH), 3.4-4.2 (m, 9H, $-OCH_2CHCH_2OCH_2-$, $-CH_2O$-ph), 6.7-7.6 (m, 9H, aromatic H).

For 4b: δ1.4-2.0(m, 6H, $-CCH_2CH_2CH_2C-$), 2.7(s, 2H, 2-OH), 3.3-4.2(m, 9H, $-OCH_2CHCH_2OCH_2-$, $-CH_2O$-ph), 6.8-7.8 (m, 9H, aromatic H).

For 4c: δ1.4-2.0 (m, 8H, $-CCH_2CH_2CH_2CH_2C-$), 2.6(s, 2H, 2-OH), 3.3-4.2 (m, 9H, $-OCH_2CHCH_2OCH_2-$, $-CH_2O$-ph), 6.7-7.6 (m, 9H, aromatic H).

Syntheses of C4HM, C5HM and C6HM

Dehydration of 4 was carried out in acetic acid solution of HBr, and the crude product was purified by column chromatography on silica gel with CH_2Cl_2 as eluent. For C4HM, m.p. 81-83°C, yield: 83%; for C5HM, m.p. 66°C, yield: 80 %; for C6HM, m.p: 56°C, yield: 80 %.

^{1}H NMR ($CDCl_3$, ppm) for C4HM: 1.5-1.8 (m, 4H, $-CCH_2CH_2C-$), 2.6-2.8, 4.41(3H, epoxy protons), 3.4-4.0 (m, 6H, $3-CH_2O-$), 7.0-7.6 (m, 9H, aromatic H).

For C5HM: 1.5-1.9 (m, 6H, $-CCH_2CH_2CH_2C-$), 2.6-2.8, 4.41(3H, epoxy protons), 3.4-4.0 (m, 6H, $3-CH_2O-$), 7.0-7.9 (m, 9H, aromatic H).

For C6HM: 1.5-1.8 (m, 8H, $-CCH_2CH_2CH_2CH_2C-$), 2.6-2.8, 4.41(3H, epoxy protons), 3.4-4.0 (m, 6H, $3-CH_2O-$), 6.9-7.6 (m, 9H, aromatic H).

Cationic polymerization:

The distilled $BF_3\cdot OEt_2$ (0.0063 ml, 0.05 mmol) was injected into a solution (2 ml) of CHM (0.22 g, 1 mmol) and 2,2-dihydroxymethylbutanol (DHMB) (8 mg, 0.06 mmol) in chloroform (2 ml). Polymerization was carried out at room temperature (20-25 °C) under N_2 atmosphere for 48 h. The reaction mixture was poured into methanol, white precipitate was isolated and purified further by reprecipitation in methanol to gave 0.18 g poly-CHM, yield 82%. For C5HM and C6HM, yields were 80 % and 35 % respectively.

Characterization

^{1}H and ^{13}C NMR spectra were performed on DMX 500 instrument with D-chloroform as solvent, TMS as standard. The molecular weight and distribution were measured by WATERS-120C gel-permeation chromatography (GPC), using tetrahydrofuran (THF) as eluent, standard polystyrene was used for calibration. Thermal properties of the polymers were measured on METTLER differential scanning calorimetry (DSC) at a scanning rate of 20°C / min. The textures of liquid crystalline polymers were observed by OLYMPUS BH-2 optical polarizing microscope (OPM) equipped with a Mettler FP-52 hotstage.

Results and discussion

Syntheses and characterization of three-armed polyethers

The results in our previous paper (19) demonstrated that when the cationic ring-opening polymerization of cycloether was carried out in the presence of polyhydroxy alcohol compounds, such as glycol, and using CF_3SO_3H or $BF_3\cdot OEt_2$ as catalyst, in addition to active chain end mechanism, intermolecular chain transfer of chain propagation center with polyhydroxy alcohol took place, then propagation occurred via active monomer mechanism. and a polyether capped with hydroxy group was formed, Therefore, we tried to prepared three-armed SCLCPs, poly(glycidyl ether)s by the cationic ring-opening polymerization of CHM, C4HM, C5HM and C6HM in the presence of DHMB, using $BF_3\cdot OEt_2$ as catalyst. The conditions and results are lasted in Table 1. As the mole ratio of [M]/[DHMB] increased, the average number molecular weight (Mn) also increased (see Table 1).

Table 1. Polymerization of CHM, C4HM, C5HM and C6HM with $BF_3{\cdot}OEt_2$ as initiator

monomer	$[M]_0^b$ (mol/l)	[M]/[DHMB] (mole ratio)	[M]/[Cat] (mole ratio)	yield (wt-%)	$(Mn)_{th}^c$	M_n^d	M_n^e	M_w/M_n^e (GPC)
CHM	0.44	29.6	20	85	5830	6330	3020	1.14
C4HM	0.37	24.7	20	80	6000	5900	3560	1.15
C5HM	0.35	26.2	20	72	5990	5410	3840	1.12
C6HM	0.27	17.2	20	75	4210	4210	3330	1.24

a) Polymerization conditions: temperature 20-25℃; time 48 h. b) Initial monomer concentration. c) Calculated based on the assumption : the each polymer molecule contains only one molecule of DHMB. d) Calculated based on the integral values of methyl protons of DHMB and biphenyl protons in ^1H NMR spectra. e). Measured by GPC, standard polystyrene was used for calibration.

Fig. 1 is the proton NMR spectra of the poly(glycidyl ether)s obtained. The complete disappearance of the peaks of epoxy protons at δ2.5-3.3 ppm, the appearance of new peaks at 3.5-4.3 ppm corresponding to methylene and methine protons next to oxygen, and 5/9 of the integral value ratio of the peak at δ3.5-4.3 ppm to that at 7.0-7.8 ppm in Fig. 1a indicate the ring-opening polymerization of CHM to give a polyether. For cationic ring-opening polymerization of C4HM, C5HM and C6HM, the same results could be obtained when analyzing their proton NMR spectra of poly-C4HM (Fig. 2a), poly-C5HM (Fig. 1b) and poly-C6HM (Fig. 1c). The peaks at around 1.5-2.0 ppm in Fig.2a, 1b and 1c correspond methylene protons in the middle of spacer (-O-C-$(CH_2)_n$-C-O-). The results were confirmed by their ^{13}C NMR spectra. For example, in the ^{13}C NMR spectrum of poly-C4HM (see Fig. 1), the peaks at 44.2 and 50.8 ppm, corresponding to methylene and methine carbons of epoxy group respectively, were shifted to 69.4 and 74.6 ppm, indicating that the cationic ring-opening polymerization occurred. In Fig. 1, the peaks at around δ0.82 and 1.23 ppm are ascribed to methyl and methylene protons of DHMB respectively. This was the result of transfer reaction of active cationic species with DHMB. Therefore, the polymerization mechanism of CHM, C4HM, C5HM and C6HM was proposed as shown in Scheme 2.

In order to study the structure of the end group of the polyether obtained, trifluoroacetic anhydride (TFA) was added into the solution of the polyether in $CDCl_3$ before measurement. Fig. 2 is the proton NMR spectra of poly-C4HM before (a) and after (b) treated with $(CF_3CO)_2O$. No peaks at δ4.3-4.4 ppm representative of methylne protons, which comes from epoxy group and /or DHMB, were found in Fig. 2b, and only a new peak at δ5.32 ppm, which is ascribed to methine group next to secondary hydroxy group (see Fig. 2b) demonstrate that propagation occurred almost exclusively at the less sterically hindered carbon of active epoxy ring. Therefore, predominant head to tail structure was formed, and only CH(R)OH stood at one end of polyether. The integral values of the peaks at δ5.32 and 0.82 ppm are almost equal, that is, each macromolecule contained one molecule of DHMB, which will be discussed later, and three ending methine protons. Thus it could be concluded that the polyether with three arms was formed as shown in scheme 2. Based on the assumption that each polyether molecule contains one molecule of DHMB. Theoretical number-average molecular weight [$\overline{(Mn)}_{th}$] can be calculated according to equation 1.

$$\overline{(Mn)}_{th} = \frac{W_m \times C \times 134}{W_{DHMB}} + 134 \qquad (1)$$

where W_m and W_{DHMB} are the weight of monomer and DHMB respectively, M is molecular weight of the monomer, C is conversion and 134 is the molecular weight of DHMB.

With the same assumption and based on proton NMR spectra, $\overline{(Mn)}_{NMR}$ could be also calculated according to equation 2.

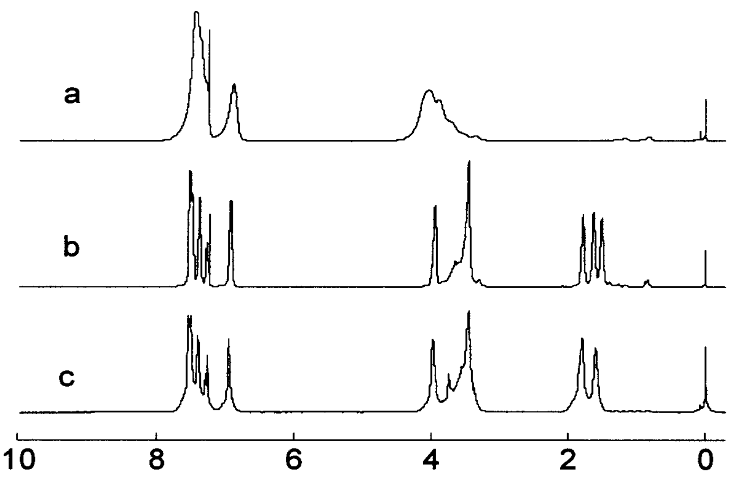


Fig. 1 ^{1}H NMR spectra of poly-CHM (a), poly-C5HM (b) and poly-C6HM (c)

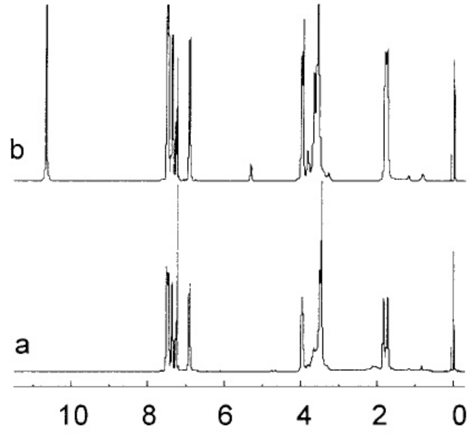


Fig. 2 ^{1}H NMR spectra of poly-C4HM (a) and poly-C4HM treated with $(CF_3CO)_2O$ (b)

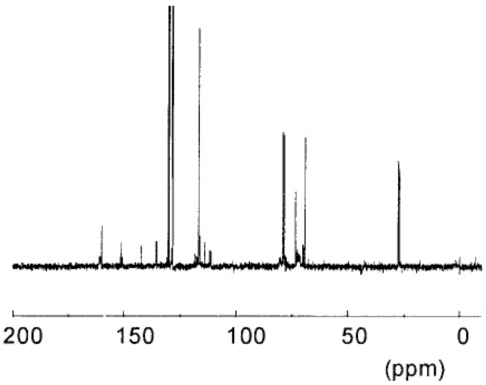
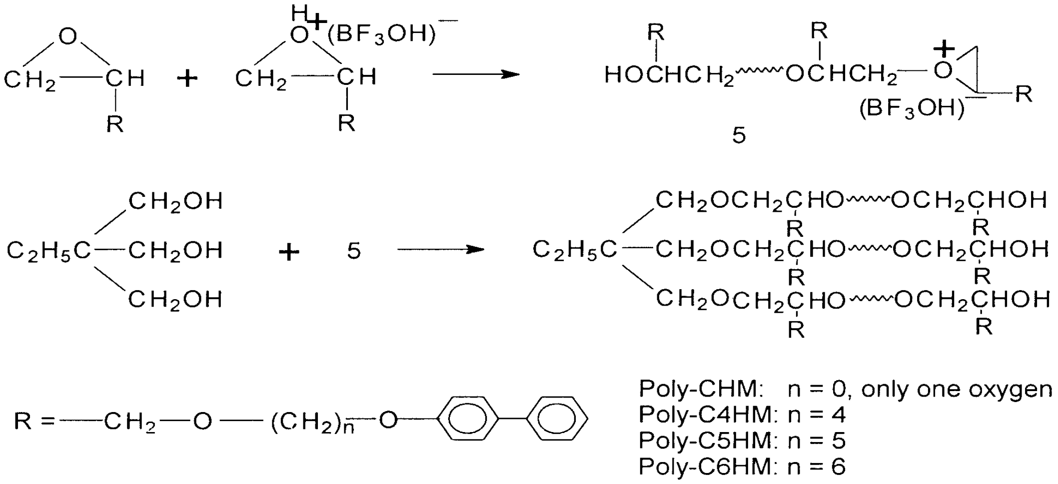


Fig. 3 ^{13}C NMR of poly-C4HM

Scheme 2:



Poly-CHM: n = 0, only one oxygen
Poly-C4HM: n = 4
Poly-C5HM: n = 5
Poly-C6HM: n = 6

$$\overline{(\mathrm{Mn})}_{\mathrm{NMR}} = \frac{I_{7.0} \times M}{3I_{0.82}} + 134 \qquad (2)$$

where $I_{7.0}$ and $I_{0.82}$ are the integral values of the peaks at δ6.7-7.6 and 0.82 ppm, which are respectively representative of biphenyl protons in the monomer and methyl protons in DHMB, M is the molecular weight of the monomers. The agreement of $\overline{(Mn)}_{th}$ and $\overline{(Mn)}_{NMR}$listed in Table 1 further verifies the assumption and polymerization mechanism proposed in scheme 2.

Thermal behavior study

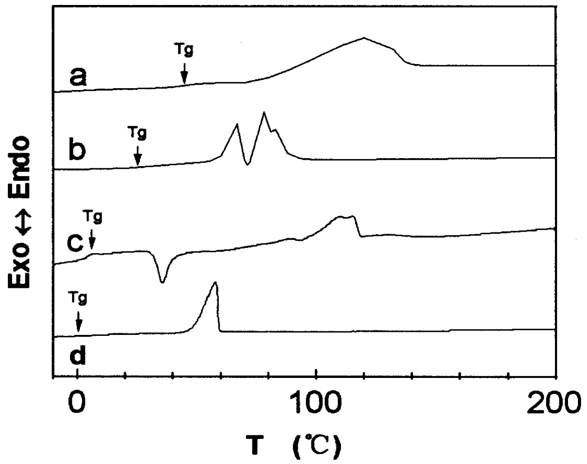


Fig. 4 DSC curves of polyoxiranes (second heating)
a. poly-CHM; b. poly-C4HM; c. poly-C5HM;
d. poly-C6HM.

The thermal phase transition behaviors of the side-chain liquid crystalline poly(glycidyl ether)s were studied by DSC and OPM. The DSC curves of poly-CHM, poly-C4HM, poly-C5HM and poly-C6HM are shown in Fig. 4. The phase transition temperatures and enthalpy values are listed in Table 2. It estimated from the DSC curves that poly-CHM and poly-C6HM showed one liquid-crystalline state, poly-C4HM showed three, and poly-C5HM showed one crystalline peak at 36°C, one liquid crystalline state and three melting processes of crystals at 89°C, 109°C and 114°C respectively. The glass transition temperature of the three-armed polyethers decreased with the increase of spacer length. However, the isotropization temperature clearly showed an odd-even effect. It can be explained based on the placement of the mesogenic groups on relation to the polymer backbone (1). When interconnecting group between the spacer and mesogen is considered as part of the flexible spacer, a spacer containing an even number of atoms places the mesogen essentially perpendicular to the polymer chain, thus it is easy to form higher ordered LC phase. When the spacer contains an odd number atoms, the mesogen is titled in relation to the backbone, resulting lower phase transition temperature (1).

Table 2. Thermal phase transition behaviors of poly(glycidyl ether)s

Polymer	DSC (the second heating)[a]						
	Tg (°C)	T_1 (°C)	ΔH_1 (j.g^{-1})	T_2 (°C)	ΔH_2 (j.g^{-1})	Ti (°C)	ΔHi (j.g^{-1})
CHM	45	—	—	—	—	117.8	29.6
C4HM	25	66.0	6.2	75.9	13.5	81.1	12.0
C5HM	8			—	—	132	
C6HM	0			—	—	57	

a) T_n: the transition temperature, ΔH_n: the enthalpy changes. Ti: isotropic temperature.

By means of optical polarizing microscopy, the textures of four poly(glycidyl ether)s at different temperatures were observed. Although monosubstituted biphenyl unit exhibits very weak mesogenic character and it is directly attached to the backbone of poly-CHM, the three-armed poly-CHM still exhibited a fan-shaped texture of smectic phase at 101°C (see Fig. 5a). This fact indicates that the polyether backbone with high flexibility could be easily distorted from its normal random-coil conformation. For poly-C4HM, only two different textures were observed at 60 °C and 72°C respectively, (see Fig. 5b and 5c), although three phase transition temperatures appeared on DSC curve in Fig. 4. Poly-C5HM exhibited fan-shaped texture, a highly ordered structure as shown in Fig. 5d. When poly-C6HM was annealed at 52 °C for 10 min, a well developed fan-like focal conic structure (Fig. 5d), which is typical smectic phase, was observed. Further characterizations of the liquid crystalline structures of the poly(glycidyl ether)s are in progress.

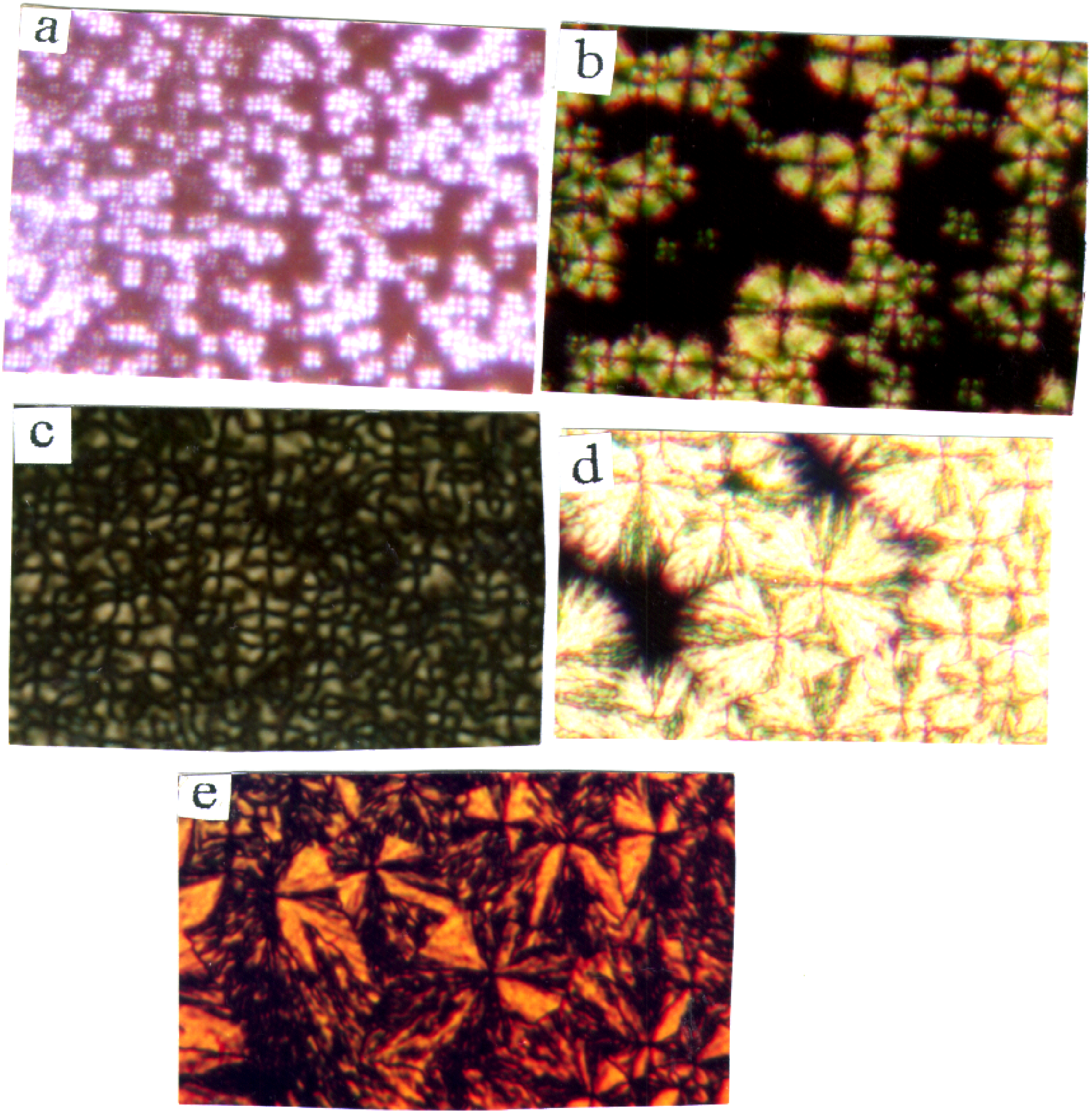


Fig. 5 Optical polarizing micrography of poly(glycidyl ether)s (magnification x 200) on the first cooling. (a) poly-CHM annealed at 101℃; For poly-C4HM: (b) annealed at 60℃ for 10 min; (c) at 72℃ for 10 min; (d) poly-C5HM at 51℃; (e) poly-C6HM at 53℃

Conclusion

Four new glycidyl derivatives with various lengths of spacer and biphenyl group as mesogenic group could undergo cationic ring-opening polymerization in the presence of DHMB, and using $BF_3 \cdot OEt_2$ as initiator, three-armed poly(glycidyl ether)s obtained are the results of the chain transfer reaction of propagate species with DHMB. All of the four poly(glycidyl ether)s exhibited different textures of liquid crystalline, even poly-CHM, in which the biphenyl group directly attached to the backbone of the polyethers. Comparison with the SCLCPs with other types of backbone and the same mesogenic moiety, these poly(glycidyl ether)s show relatively low Tg and a wide of temperature range of the mesophase, and are easier to form highly ordered structure, it may be related to their three-armed structure. As spacer length increases, Tg decreases, but the isotropization temperature clearly shows an odd-even effect. It could be explained based on the placement of the mesogenic groups in relation to the polymer backbone.

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