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Synthesis of Ferroelectric Liquid Crystalline Polyoxiranes and Polyoxetanes By Ring Opening Polymerization.

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The synthesis of two series of liquid crystalline polyoxiranes and polyoxetanes containing 4-(4-hydroxybiphenyl-4'-carbonyloxy)-phenyl (2S,3S)-2-chloro-3-methylvalerate side groups is presented. Differential scanning calorimetry, polarizing optical microscopy and X-ray diffraction measurements reveal liquid crystalline phases for all obtained polymers. A majority of the prepared polyoxiranes present cholesteric, smectic A, chiral smectic C and an undefined smectic phases. Most of the prepared polyoxetanes reveal only a chiral smectic C phase. Effect of polymer backbone and spacer length on the mesomorphic properties of the obtained polymers is discussed. Although the polyoxirane and polyoxetane backbone are more flexible than the polymethacrylate backbone, side-chain crystallization does not occur in any of the synthesized polymers.

Keywords : ferroelectric liquid crystalline polymers; polyoxirane; polyoxetane

INTRODUCTION

Side-chain crystalline polymers (LCPs) are of theoretical and practical interest because they combine the anisotropic properties of liquid crystals with the polymeric properties and are highly promising for some novel applications^[1]. So far, most of the side-chain LCPs have been prepared

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mainly by radical polymerization of (meth)acrylates and by the hydrosilation of poly(methylhydrosiloxane) backbones with mesogenic olefins. In recent years an increasing amount of research has been directed at synthesizing new well-defined side-chain LCPs by living cationic polymerization,^[2] ring-opening polymerization^[3-7] and living ring-opening metathesis polymerization^[8-10]. Recently, Kawakami et al. reported on the first example of side-chain LC polyoxetanes by cationic ring-opening polymerization^[5-7].

Ferroelectric liquid crystals (FLCs) have attracted growing interest over recent years owing to their bistability in displays and their short switching times^[11-12]. In addition to low molar mass FLCs, ferroelectric LC polymers^[13-20] have also been thoroughly investigated. Ferroelectric LC polymer possesses a response time in the range of mini-second with a weak electric field. These polymers also exhibit a bistability that is comparable to low-molar-mass FLCs. In addition, such polymer materials are highly attractive for display applications owing to their applicability as flexible devices.

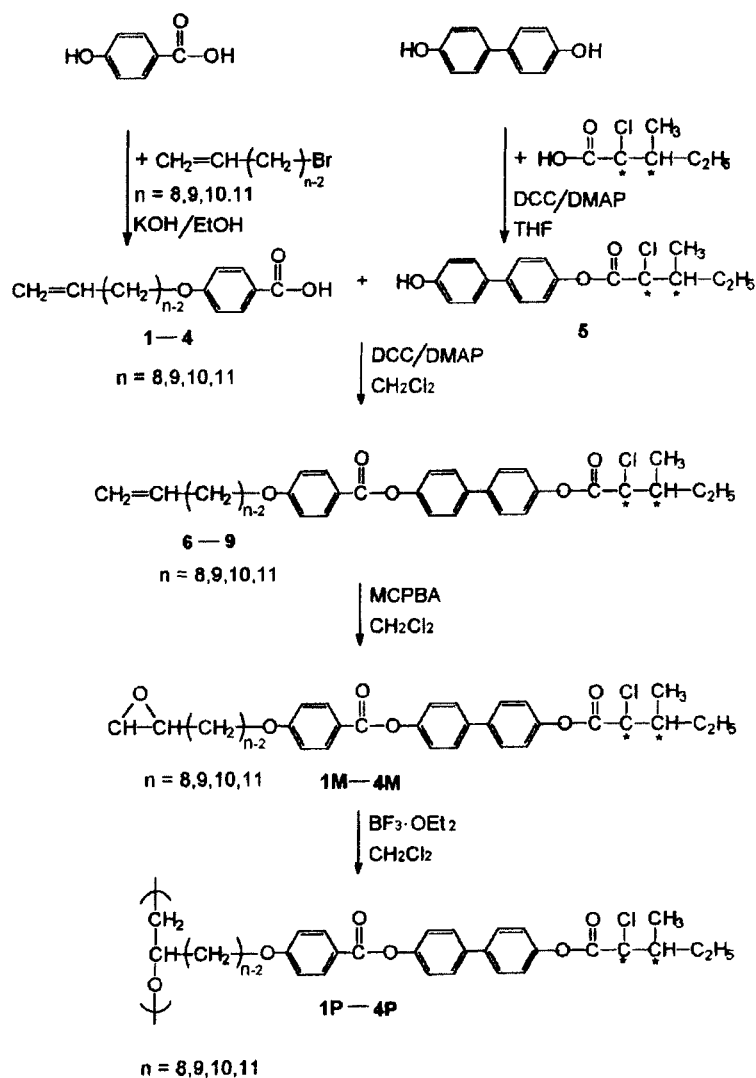
In this study, we synthesize two series of liquid crystalline polyoxiranes and polyoxetanes containing 4-(4-hydroxybiphenyl-4'-carbonyloxy)phenyl (2S,3S)-2-chloro-3-methylvalerate side groups. Differential scanning calorimetry, optical polarizing microscopy and X-ray diffraction are performed to characterize their liquid crystalline properties.

RESULTS AND DISCUSSION

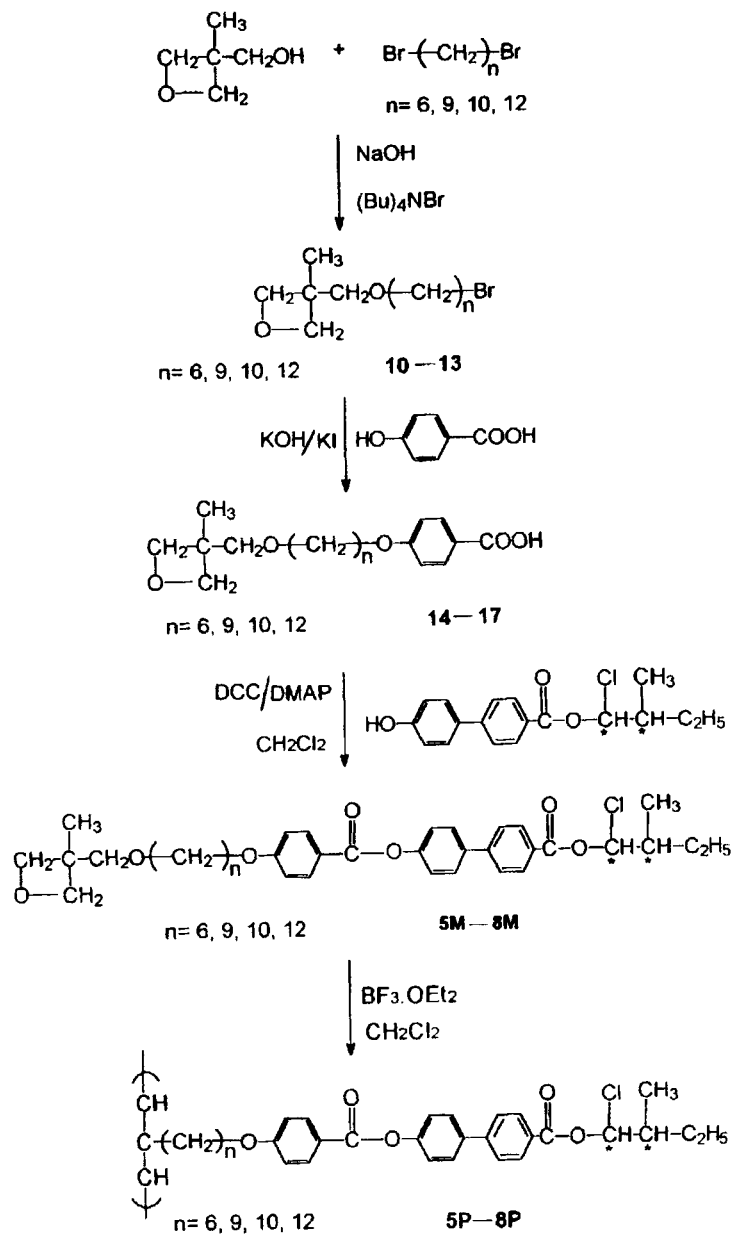
The synthetic routes used for the preparation of oxirane monomers 1M - 4M and oxetane monomers 5M - 8M are outlined in Schemes 1 and 2.

(2S, 3S)-2-chloro-3-methylvaleric acid was prepared from L-isoleucine by a Sandmeyer reaction. The reaction was performed with retention of

configuration^[21]. The esterification of (2S, 3S)-2-chloro-3-methylvaleric acid with 4,4'-biphenol and subsequent reactions were also achieved with retention of its configuration. The prepared monomers were characterized by differential scanning calorimetry and polarizing optical microscopy.



SCHEME 1 Synthesis of polyoxiranes 1P - 4P.



SCHEME 2. Synthesis of polyoxetanes 5P - 8P

Table I summarizes the thermal transitions of monomers 1M - 8M. Both monomers 1M and 2M present the enantiotropic cholesteric and smectic A phases and a monotropic smectic B phase, while both monomers 3M and 4M show only the enantiotropic cholesteric and smectic A phases. Monomers 5M - 8M reveal an enantiotropic cholesteric phase and a monotropic chiral smectic C phase. Fig. 1 depicts the representative DSC thermogram of monomer 3M.

TABLE I Phase transitions of monomers 1M-8M			
Monomer	n ^a	Phase transitions, °C	Heating ^b
			Cooling
1M	8	K 102.3 S _A 129.1 N* 155.5 I	
		I 151.1 N* 125.8 S _A 64.7 S _B 58.7 K	
2M	9	K 101.1 S _A 133.8 N* 158.0 I	
		I 154.1 N* 130.0 S _A 73.1 S _B 51.6 K	
3M	10	K 96.0 S _A 131.6 N* 152.4 I	
		I 150.9 N* 130.0 S _A 77.9 K	
4M	11	K 96.6 S _A 129.9 N* 144.4 I	
		I 140.0 N* 124.4 S _A 75.6 K	
5M	6	K 80.3 N* 95 I	
		I 81 N* 59.3 S _C * -18.2 K	
6M	9	K 63 N* 88 I	
		I 67.3 N* 17.5 S _C * 1.6 K	
7M	10	K 47.6 N* 75.1 I	
		I 67 N* 16 S _C * 0.6 K	
8M	12	K 59.5 N* 84 I	
		I 73.1 N* 21.8 S _C * 2.7 K	

a) n according to Schemes 1 and 2.

b) K = crystalline, S_A = smectic A, S_C* = chiral smectic C, S_B = smectic B, N* = chiral nematic, I = isotropic.

Fig. 2 displays the typical cholesteric and smectic A textures exhibited by monomer 3M.

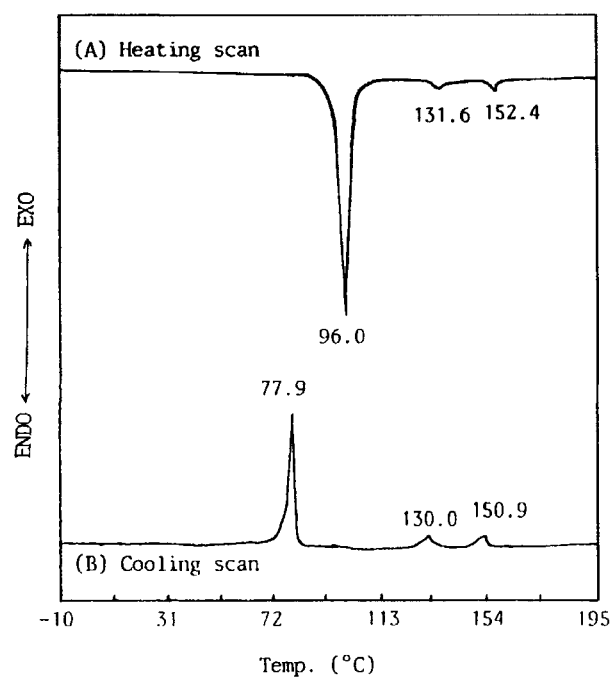


FIGURE 1 DSC thermograms (10°C/min) of monomer 3M.

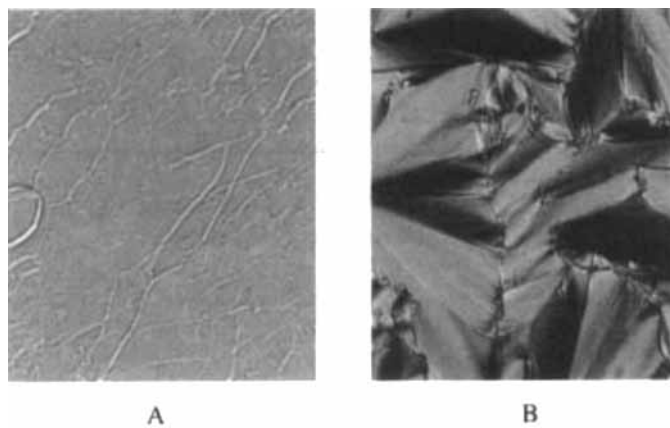


FIGURE 2 Optical polarizing micrographs displayed by monomer 3M: (A) Cholesteric texture obtained at 134°C; (B) S_A texture obtained at 98°C. (See Color Plate I).

Table II lists the thermal transitions of polymers 1P - 8P. All polymers reveal liquid crystalline phases. The phase assignment was conducted by both optical polarizing microscopy and X-ray diffraction measurements. Polymer 1P which contains eight methylene units in the spacers, shows the enantiotropic cholesteric, chiral smectic C and an undefined smectic phases. Mean while polymers 2P and 3P which contain respectively nine and ten methylene units in the spacers, reveal the enantiotropic cholesteric, smectic A, chiral smectic C and an undefined smectic phases.

TABLE II Phase transition of polymers		XIIP—XVIP.
Polymer	n ^a	Phase transitions, °C
		Heating ^b Cooling
1P	8	<u>G 38.3 Sx^b 87.2 Sc[*] 176.8 N[*] 200.6 I</u> I 198.0 N [*] 169.8 Sc [*] 80.9 Sx 33.9 G
2P	9	<u>G 38.7 Sx 100.3 Sc[*] 192.1 SA 198.5 N[*] 212.5 I</u> I 200.7 N [*] 195.3 SA 187.6 Sc [*] 91.9 Sx 33.3 G
3P	10	<u>G 36.1 Sx 96.5 Sc[*] 182.9 SA 189.3 N[*] 201.2 I</u> I 195.6 N [*] 185.1 SA 187.0 Sc [*] 93.2 Sx 27.0 G
4P	11	<u>G 37.5 Sx 95.7 Sc[*] 195.0 SA 206.8 I</u> I 200.6 SA 193.6 Sc [*] 88.9 Sx 36.5 G
5P	6	<u>G 2.3 Sc[*] 165 SA 173 I</u> I 168.2 SA 160.9 Sc [*] -7.6 G
6P	9	<u>G 16.8 Sc[*] 157 I</u> I 153.9 Sc [*] 1.4 G
7P	10	<u>G 16.9 Sc[*] 198.4 I</u> I 190 Sc [*] 7.7 G
8P	12	<u>G 21.1 Sc[*] 205.3 I</u> I 201.2 Sc [*] 10.5 G

a) n according to Schemes 1 and 2.

b) G = glassy phase, N* = cholestric phase,
SA = smectic A phase, Sc* = chiral smectic C phase,
Sx = undefined smectic phase, I = isotropic phase.

Polymers 4P which contains eleven methylene units in the spacer, displays the enantiotropic smectic A, chiral smectic C and an undefined smectic phases. Above experimental results demonstrate that the nature of mesophases heavily depends on the spacer length. Those polymers containing a shorter spacer length incline to form a cholesteric phase.

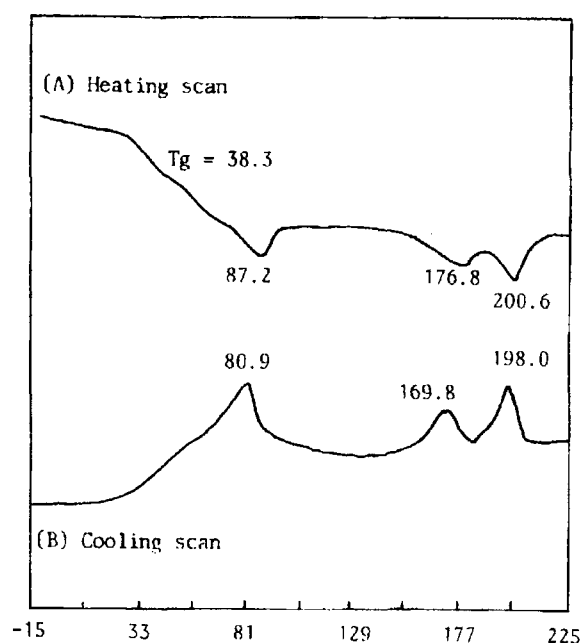


FIGURE 3 DSC thermograms (10 °C / min) of polymer 1P.

Representative DSC traces of polymer 1P is depicted in Fig. 3. The heating scan (curve A) in this figure reveals a glass transition temperature (Tg) at 38.3 °C and an undefined smectic to chiral smectic C phase transition at 87.2 °C, a chiral smectic C to cholesteric phase transition at 176.8 °C and a cholesteric to isotropic phase transition at 200.6 °C. The cooling scan (curve B) closely resembles the heating scan, except that an extremely small supercooling (less than 7 °C) is observed for three exothermic transitions.

Fig. 4 displays the typical cholesteric and chiral smectic C textures exhibited by polymer 1P. Fig. 5 presents the temperature-dependent X-ray diffraction diagrams obtained from the powder sample of polymer 1P at 190, 165, 135, 105 and 70 °C. Curve A shows only a diffuse reflection at 4.72 Å that corresponds to the lateral spacing of mesogenic side groups. Both X-ray diffraction results and optical microscopic texture (Fig. 4A) observation are consistent with a cholesteric structure. When the measuring temperature is lowered from 190 to 165 °C, it (curve B) shows a diffuse reflection at 4.62 Å and a sharp reflection at 26.67 Å which corresponds to the d-spacing of a smectic layer. When the measuring temperature is further lowered from 165 °C to 105 °C, the d-spacing of a smectic layer gradually decreases from 26.67 Å to 25.57 Å. This finding strongly suggests for the formation of the tilted chiral smectic C phase. This result is also in agreement with the optical microscopic observation which reveals a broken fan texture (Fig. 4B). When the measuring temperature has been further cooled to 70 °C, the d-spacing of a smectic layer maintains nearly the same value; in addition the wide angle diffraction peak becomes very sharp (curve E). The texture obtained at this temperature closely resembles that of Fig. 4B. Experimental results confirm the formation of a tilted smectic phase, probably a smectic G phase. X-ray diffraction of an aligned monodomain sample should be performed to examine the detailed structure of this smectic phase.

According to Table II, among polymers 5P - 7P containing the polyoxetane backbone, polymer 5P reveal the enantiotropic smectic A and chiral smectic C phases while polymers 6P - 8P presents only an enantiotropic chiral smectic C phase, respectively. Our experimental results again demonstrate that the spacer length prominently influences in the type of mesophases formed. Comparing these results with those

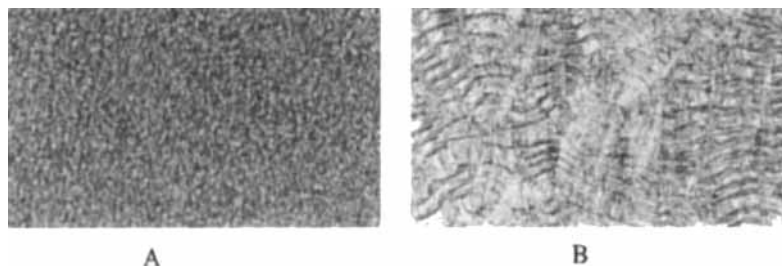


FIGURE 4. Optical polarizing micrographs displayed by polymer 1P: (A) Cholesteric texture obtained at 191 °C; (B) S_C^* texture obtained at 157 °C. (See Color Plate II).

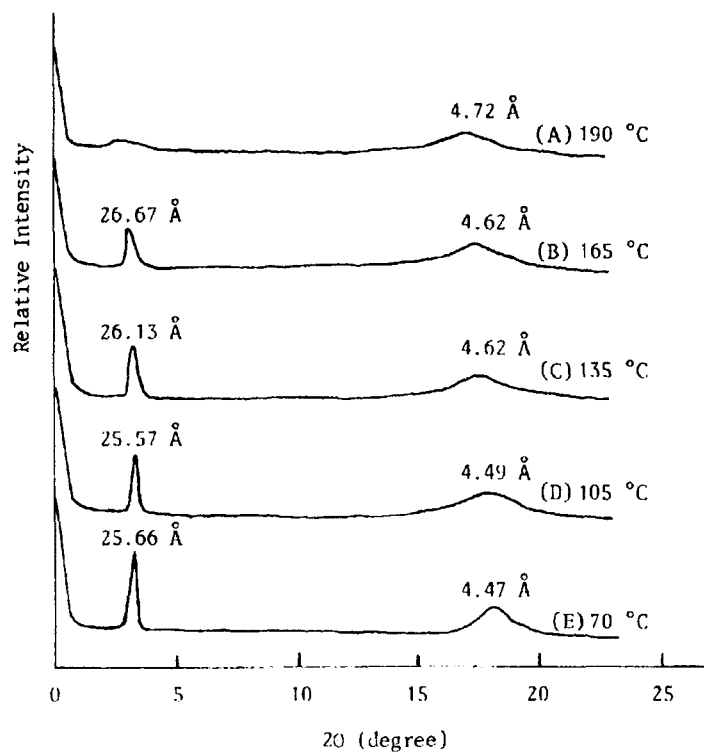


FIGURE 5. Temperature -dependent X-ray measurements for polymer 1P at (A) 190, (B) 165, (C) 135, (D) 105, and 70 °C.

presented by polymers 1P - 4P that contain the polyoxirane backbone, reveals that polymers 5P - 8P possess less mesophases. The experimental results demonstrate that the polymer backbone also profoundly influences the type of mesophases formed.

In conclusion, two series of side-chain liquid crystalline polyoxiranes and polyoxetanes containing 4-(4-hydroxy-biphenyl-4'-carbonyloxy)phenyl (2S,3S)-2-chloro-3-methylvalerate side groups were synthesized and characterized. Both series of polymers show liquid crystalline phases including the chiral smectic C phase. Both the spacer length and polymer backbone profoundly influence on the nature of mesophases formed. Although the polyoxirane and polyoxetane backbones are expected to be more flexible than the polymethacrylate backbone, all the obtained polymers do not undergo side-chain crystallization.

EXPERIMENTAL

Materials

3-(Hydroxymethyl)-3-methyloxetane, biphenyl, L-isoleucine and all other reagents were obtained from Aldrich and used as received. Boron trifluoride ether complex was purchased from Tokyo Kasei Inc. and was distilled before use. Dichloromethane used in the ring-opening polymerization was refluxed over calcium hydride and then distilled under nitrogen.

Techniques

^1H NMR spectra (300 MHz) were recorded on a Varian VXR-300 spectrometer. FT-IR spectra were measured on a Nicolet 520 FT-IR spectrometer. Polymer samples were casted film onto a KBr tablet for the

IR measurements. Thermal transitions and thermodynamic parameters were determined by using a Seiko SSC/5200 differential scanning calorimeter equipped with a liquid-nitrogen cooling accessory. Heating and cooling rates were 10 °C/min. Thermal transitions reported were collected during the second heating and cooling scans. A Carl-Zeiss Axiophot optical polarized microscope equipped with a Mettler FP 82 hot stage and an FP 80 central processor was used to observe the thermal transitions and to analyze the anisotropic textures. Preparative gel permeation chromatography (GPC) was run on a Waters 510 LC instrument equipped with a 410 differential refractometer and a preparative GPC column (22.5 mm × 60 cm) supplied by American Polymer Standard Co. X-ray diffraction measurements were performed with nickel-filtered Cu K α radiation with a Rigaku powder diffractometer. Optical rotations were measured at 25 °C on a Jasco DIP-140 polarimeter with chloroform as solvent for all compounds.

Synthesis of Monomers 1M - 8M

Schemes 1 and 2 outline the synthesis of monomers 1M - 8M.

4-(Alkenyloxy)benzoic acids (1 - 4)

All four compounds were prepared by the etherification of alkenyl bromide with 4-hydroxybenzoic acid according to a literature procedure^[18].

4-Hydroxybiphenyl-4'-yl

(2S, 3S)-2-chloro-3-methylvalerate (5)

Compound 5 was synthesized by esterification of 4,4'-dihydroxybiphenyl with (2S, 3S)-2-chloro-3-methylvaleric acid according to a literature procedure.^[22]

4-[(4-Alkenyloxyphenyl) carbonyloxy]biphenyl-4'-yl (2S, 3S)-2-chloro-3-methylvalerates (6 - 9)

All four compounds were prepared by esterification of 4-(alkanyloxy)benzoic acid with compound 5. The synthesis of compound 6 is described below.

4-(7-octen-1-yloxy)benzoic acid (1.06 g, 4.28 mmol), compound 5 (1.50 g, 4.71 mmol), N, N-dicyclohexyl-carbodiimide (1.06 g, 4.71 mmol) and 4-(dimethylamino)pyridine (0.2 g) in 50 mL of CH_2Cl_2 was stirred at room temperature until esterification was completed. The solution was filtered, washed three times with water and dried over anhydrous MgSO_4 . The solvent was removed in a rotary evaporator and the obtained crude product was purified by column chromatography (Silica gel, ethyl acetate : n-hexane = 1 : 1 as eluent) to yield 1.69 g (72 %) of white crystals. ^1H NMR (CDCl_3 , TMS, ppm) : δ 1.06 (t, 3, $\text{H}-\text{CH}_2-\text{CH}_3$), 1.18 [d, 3H, $-\text{CH}(\text{CH}_3)-$], 1.21-1.95 [m, $-\text{CH}_2-\text{CH}_3$ and $-(\text{CH}_2)_4-$], 2.19-2.31 [m, 1H, $-\text{CH}(\text{CH}_3)-$], 4.00 (t, 2H, $-\text{OCH}_2-$) 4.38 [d, 1H, $-\text{CH}(\text{Cl})-$], 4.08-5.00 (m, 2H, $\text{CH}_2=$) 5.70-5.90 (m, 1H, $=\text{CH}-$), 6.80-8.20 (m, 12 aromatic protons).

Synthesis of monomers 1M - 4M

The monomers 1M - 4M were synthesized by epoxidation of corresponding compounds 6 - 9 with 3-chloroperoxybenzoic acid. The synthesis of monomer 1M is described as follows.

Compound 6 (1.75 g, 3.19 mmol) was dissolved in 20 mL of CH_2Cl_2 at 0 °C, and 3-chloroperoxybenzoic acid (0.83 g, 4.79 mmol) in 10 mL of CH_2Cl_2 was added dropwise under N_2 atmosphere. The subsequent solution was stirred at room temperature overnight, washed with 5 % NaHCO_3 solution and water, and dried over anhydrous MgSO_4 . The solvent was removed in

a rotary evaporater and the crude product was purified by column chromatography (silica gel, n-hexane : CH_2Cl_2 = 1 : 3 as eluent) to yield 1.01 g (56 %) of white crystals.

^1H NMR (CDCl_3 , TMS, ppm) δ 1.05 (t, 3H, $-\text{CH}_2\text{CH}_3$), 1.17 (d, 3H, $-\text{CH}(\text{CH}_3)$), 1.30-1.95 [m, 10H, $(\text{CH}_2)_5$], 2.20-2.30 [m, 1H, $-\text{CH}(\text{CH}_2)$], 2.40-3.00 (m, 3 protons in the oxirane ring), 4.05 (t, 2H, $-\text{CH}_2-\text{OPh}-$), 4.43 [d, 1H, $-\text{CH}(\text{Cl})-$] 6.80-8.20 (m, 12 aromatic protons).

3-[(bromoalkanyloxy)methyl]-3-methyloxetanes (10 - 13)

All four compounds were prepared by a phase transfer catalyzed reaction of dibromoalkane and 3-(hydroxymethyl)-3-methyloxetane according to a literature procedure.^[22]

4-[[w-(3-methyloxetan-3-yl)methoxy]alkanyloxy]benzoic acids (14 - 17)

Compounds **14** - **17** were prepared by etherification of compounds **10** - **13** with 4-hydroxybenzoic acid. The synthesis of compound **14** is described below. 4-Hydroxybenzoic acid (0.98 g, 7.1 mmol), KOH (0.96 g, 17.1 mmol) and KI (0.2 g) were dissolved in 150 mL of ethanol. The obtained solution was heated to reflux temperature for 1 hr. 3-[(5-bromohexyloxy)methyl]-3-methyloxetane (2.25 g, 8.5 mmol) was added dropwise. The subsequent solution was heated to reflux temperature overnight, and cooled to room temperature. The salt was removed by filtration, and ethanol was removed in a rotary evaporater. The obtained solid was washed three time with water, and then dried over anhydrous MgSO_4 . The obtained crude product was recrystallized from acetic acid to yield 1.65 g (72 %) of white crystals.

^1H NMR (CDCl_3 , TMS, ppm) δ 1.31 (s, 3H, CH_3-), 1.28-1.77 [m, 8H, $(\text{CH}_2)_4$], 3.43 (m, 4H, $-\text{CH}_2-\text{O}-\text{CH}_2-$), 3.99 (t, 2H, $-\text{CH}_2-\text{OPh}-$), 4.33 and 4.49 (two d,

4H, two-CH₂-in the oxetane ring).

Synthesis of monomers 5M - 8M

Monomers 5M - 8M were prepared by esterification of corresponding compounds **14** - **17** with compound **5**. The synthesis of monomer 5M is described as follows.

A solution of compound **14** (1.21 g, 3.75 mmol) compound **5** (1.14 g, 3.57 mmol), N, N-dicyclohexylcarbodiimide (0.81 g, 3.93 mmol) and 4-(dimethylamino)pyridine (0.044 g, 3.60 mmol) were dissolved in 30 mL of CH₂Cl₂. The resulting solution was stirred at room temperature overnight. The N,N-dicyclohexylurea was filtered. The obtained filtrate was washed three times with water and dried over anhydrous MgSO₄. The solvent was removed in a rotary evaporator and the crude solid product was purified by column chromatography (silica gel, ethyl acetate : n-hexane = 1 : 1 as eluent) to yield 1.69 g (76 %) of white crystals.

¹H NMR (CDCl₃, TMS, ppm) δ 1.05 (t, 3H, -CH₂CH₃), 1.17 (d, 3H, -CH(CH₃)), 1.28-1.95 (m, 11H, (CH₂)₄ and -CH₃ in the oxetane ring), 2.20-2.30 [m, 1H, -CH(CH₃)] 3.42-3.46 (m, 4H, -CH₂-O-CH₂-), 4.05 (t, 2H, -CH₂-OPh-) 4.43 [d, 1H, -CH(Cl)-] 4.34 and 4.50 (two d, two -CH₂-in the oxetane ring), 7.00-8.14 (m, 12 aromatic protons).

Synthesis of polyoxiranes 1P - 4P and polyoxetanes 5P - 8P

The synthesis of polyoxiranes 1P - 4P and polyoxetanes is also outlined in Schemes 1 and 2. All polymers were synthesized by a similar method. The preparation of polymer 1P is described below. Dichloromethane was dried over calcium hydride and was distilled under nitrogen just prior to use. Freshly distilled boron trifluoride ether complex was used as an initiator. A solution of monomer 1M (1.0 g) in 1 mL of CH₂Cl₂ was cooled to 0 under nitrogen and the initiator (2 % mol with respect to monomer 1M) was then

injected with a syringe. The reaction mixture was stirred at 0 °C for 24 hr. After this reaction time, the polymers were separated and purified by several reprecipitations from CH₂Cl₂ solution into methanol. The absence of monomer was checked by ¹H NMR and GPC. The results of ring-opening polymerization of monomers 1M - 8M are summarized in Table III. All monomers gave reasonable yields in the polymerization.

Table III Polymerization of monomers 1M-8M
by boron trifluoride ether complex

monomer	n ^a	yield (%)	\overline{M}_n	\overline{M}_w	$\overline{M}_w / \overline{M}_n$
1M	8	63.8	5104	5352	1.05
2M	9	59.7	5128	5259	1.03
3M	10	62.1	4830	4929	1.03
4M	11	55.3	4910	5008	1.02
5M	6	51.2	5180	10400	1.99
6M	9	60.3	7860	14630	1.86
7M	10	62.1	4600	8210	1.78
8M	12	65.4	11200	17500	1.57

a) n according to Schemes 1 and 2.

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