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Smectic liquid crystalline polyoxetane with novel mesogenic group

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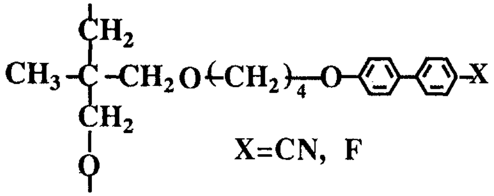
Summary

Polyoxetane was found to be a good main chain for well-developed smectic liquid crystalline state, when cyano substituted biphenyls were used as mesogenic groups attached through four methylene spacer. With this main chain and spacer, fluorine substituted biphenyl was found to be a novel and good mesogenic group for liquid crystalline state.

Introduction

Polysiloxanes, polyacrylates, and polymethacrylates are usually used as main chain components of liquid crystalline polymers(1). There are only few examples in which other main chain structures like polyolefine, poly(vinyl ether), polyphosphazene, or polyisocyanate are used(2-8).

In this communication, we would like to report the first examples in which polyoxetane shown below, and fluorine substituted biphenyl are used as a main chain component, and as a noble mesogenic group for smectic liquid crystalline polymers.



Experimental

General

^{1}H NMR spectra were obtained on a Varian 200 MHz ^{1}H-NMR spectrometer model Gemini 200. Thermal behavior of polymers was evaluated on a SEIKO thermal analysis system model SSC 5500 series with DSC 100. Optical polarization micrographs were taken on a NIKON optical polarization micrograph model OPTIPHOTO-POL equipped with Mettler thermal analysis system model FP800 with a hot stage FP82 controlled by FP 80.

Synthesis of Monomers

The basic synthetic route to the monomers is shown in Scheme 1. Details of the synthesis will be reported later(9).

3-Hydroxymethyl-3-methyloxetane was synthesized from 2-hydroxymethyl-2-methyl-1,3-propanediol(10). Monomers were synthesized through the formation of ether linkage between 3-(4-bromobutoxy)methyl-3-methyloxetane and 4-substituted-4'-hydroxybiphenyl.

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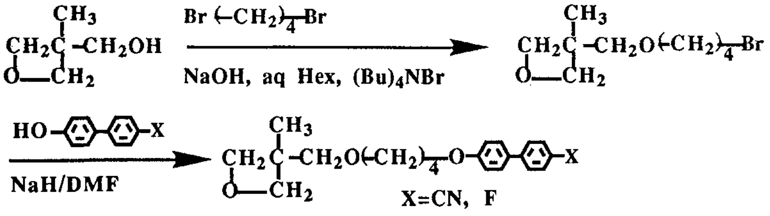
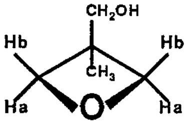


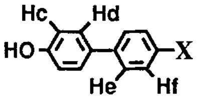
Scheme 1. Synthesis of monomers

3-{4-(4-Cyanobiphenyl-4'-yloxy)butoxymethyl}-3-methyloxetane: (OX-CN4)

To sodium hydride(0.030 g, 1.2 mmol) dispersed in DMF(5 ml), 4-cyano-4'-hydroxybiphenyl(0.18 g, 0.93 mmol) was added portionwise and the reaction system was stirred for 30 min at room temperature and further 10 min at 60°C. To this solution, 3-(4-bromobutoxymethyl)-3-methyloxetane(0.30 g, 1.3 mmol) in DMF(5 ml) was added dropwise during 10 min, and the reaction system was stirred for 3 h at room temperature. After 3 h, DMF was removed under vacuum, and chloroform(50 ml) and water(30 ml) were added to the residual solid. Chloroform layer was separated and washed with aq. sodium carbonate(30 ml). The product was isolated on column chromatography after drying and evaporating the solvent. Rf=0:18(eluent; hexane: ether: chloroform=2: 1: 1). Yield 92.2 %.

Protons of oxetane and biphenyl rings are designated as indicated in next page.





Chemical shifts:1.29(s, 3H, $C\underline{H}_3$), 1.80(m, 4H, $CH_2C\underline{H}_2C\underline{H}_2CH_2$), 3.47(s, 2H, $C(CH_3)$-$C\underline{H}_2$), 3.54(t, 2H, J=6.0 Hz, $CH_2OC\underline{H}_2CH_2$), 4.03(t, 2H, J=6.0 Hz, $OC\underline{H}_2$), 4.34(d, 2H, J=5.8 Hz, Ha), 4.50(d, 2H, J=5.8 Hz, Hb), 6.97(d with fine coupling, 2H, J=8.8 Hz, Hc), 7.51(d with fine coupling, 2H, J=8.8 Hz, Hd), 7.61, 7.68(two d with fine coupling, 4H, J=7.8 Hz, He, Hf).

3-{4-(4-Fluorobiphenyl-4'-yloxy)butoxymethyl}-3-methyloxetane: (OX-F4)

Rf=0.18(eluent; hexane: ether: chloroform=2: 1: 1). Yield 65.3 %.

Chemical shifts: 1.29(s, 3H, $C\underline{H}_3$), 1.82(m, 4H, $CH_2C\underline{H}_2C\underline{H}_2CH_2$), 3.48(s, 2H, $C(CH_3)$-$C\underline{H}_2$), 3.53(t, 2H, J=6.0 Hz, $CH_2OC\underline{H}_2CH_2$), 4.03(t, 2H, J=6.0 Hz, $OC\underline{H}_2$), 4.34(d, 2H, J=5.8 Hz, Ha), 4.50(d, 2H, J=5.8 Hz, Hb), 6.93(d with fine coupling, 2H, J=8.8 Hz, Hc), 7.07(t with fine coupling, 2H, J=8.8 Hz, Hf), 7.44(d with fine coupling, 2H, J=8.8 Hz, Hd), 7.47(q with fine coupling, 2H, J_1=8.8 Hz, J_2=5.4 Hz, He).

Polymerization

Polymerizations were carried out in dichloromethane at 0°C. Monomers were dried under vacuum at 60°C for 24 h after the purification on column chromatography. Freshly distilled boron trifluoride ether complex was used as an initiator.

Results and Discussion

The results of polymerization by $BF_3 \cdot OEt_2$ as an initiator are shown in the Table.

Table **Polymerization of Mesogenic Monomers**[a] **by Boron Trifluoride Ether Complex**

Monomer	Conc. (mol/l)	$BF_3 \cdot OEt_2$ (mol%)	Yield (%)	Mw[b] $x10^3$	Mn $x10^3$	Mw/Mn
OX-CN4	2.7	1.20	18.4	85.2	38.5	2.2
OX-F4	1.0	1.00	99.3	45.6	26.6	1.7

a) Solvent: CH_2Cl_2, Temp: 0 °C, Time: 20~28 h.

b) Estimated by GPC correlating to standard polystyrene.

Although cyano substituted monomer gave rather poor yield, excellent yield could be obtained for fluoro substituted monomer. Molecular weight and molecular weight distribution of polymers are reasonably high and narrow. Proper choice of an initiator may give better-defined polymers.

Monomers showed only one thermal transition temperature in DSC, and did not showed mesophase.

DSC curves of poly[3-{4-(4-cyanobiphenyl-4'-yloxy)butoxymethyl}-3-methyloxetane](POX-CN4) and poly[3-{4-(4-fluorobiphenyl-4'-yloxy)butoxymethyl}-3-methyloxetane](POX-F4) are shown in Figure 1.

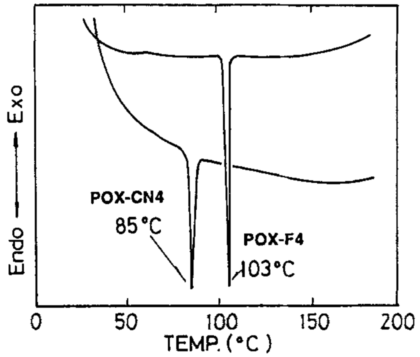


Fig 1. DSC Curves of POX-CN4 and POX-F4

Only one thermal transition was observed in DSC for both polymers. POX-CN4 and POX-F4 showed discrete transition at 85°C and 103°C, respectively, and showed discrete mesophase structure in both cooling and heating process. Typical structure shown in optical polarization micrograph are shown in Figures 2 and 3.

Batonett structure seen in 30 min by annealing the sample at a little lower temperature than the transition temperature changed into well-developed fan like focal conic structure under further standing. Well developed smectic phase was considered to be taken by both polymers.

In such polymers, the main chain polyoxetane polyether is considerably flexible compared with polymethacrylate or polyacrylate, which makes it easy to organize mesogenic side chains. Compared with the fact that 6 methylene and ester function are needed even for polyacrylate to take nematic phase[1)], shorter spacer, namely four methylene and ether function, is long enough for polyoxetane with cyano or fluoro substituted biphenyl as a mesogenic group to take more ordered smectic phase.

Structure of mesogenic group is one of the important factor which determine the mesophase structure. Polar and less bulky cyano susbstituted biphenyl seems to be a good mesogenic group. Polar interaction between cyano susbstituted biphenyls makes it easy for the mesogenic groups to organize.

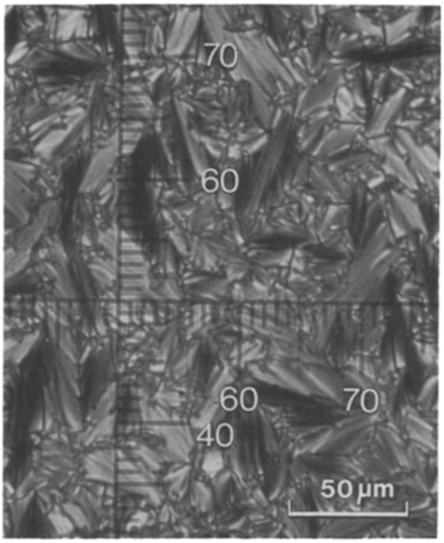


Fig 2. Optical Polarization Micrograph of POX-CN4 Annealed at 82.5°C for 48 h.

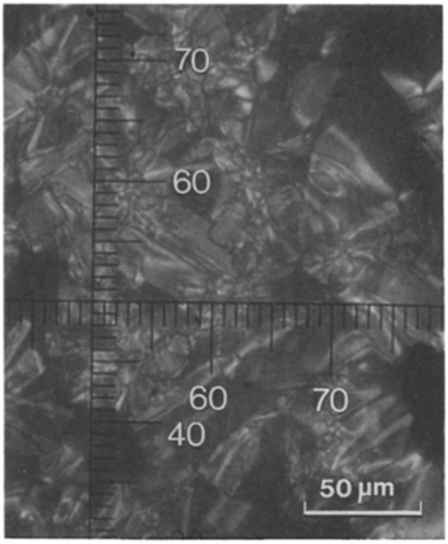


Fig 3. Optical Polarization Micrograph of POX -F4 Annealed at 102 °C for 48 h.

Related to this, fluoro substituted biphenyl was of interest as a possible mesogenic group. This is the first example in which fluorine atom is used as a tail group in liquid crystalline polymer.

Acknowledgments

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