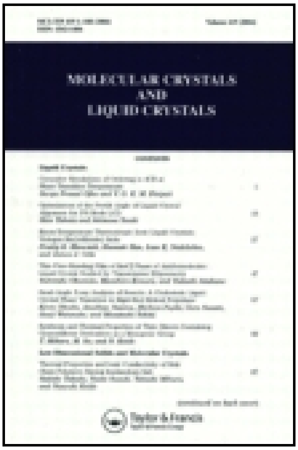

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Side-Chain Liquid Crystalline Silicon-Containing Polymers

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Side-Chain Liquid Crystalline Silicon-Containing Polymers

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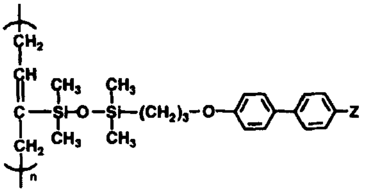
Synthesis and properties of side-chain liquid crystalline polymers containing disiloxane linkage were shown. Stereochemical control of the silicon atoms in the main chain was also studied.

Keywords: optically active silicon compounds; disiloxane; poly(oxetane); poly(diene); stereoregularity; poly(carbosilane); poly(carbosiloxane); liquid crystal

INTRODUCTION Finkelmann started a systematic research on side-chain liquid crystalline polymers[1,2]. Mesogens are usually introduced to poly(siloxane) main chain through methylene spacer of suitable length by taking advantage of the low energy barrier of the rotation of the Si-O bond. It has been recognized that structure of main chain, mesogenic and tail groups, and structure and length of the spacer, and spacing of the mesogenic groups along the main chain are the principal factors for determining the liquid crystalline phase. Although there have been extensive reports on the effects of the length of the methylene groups as spacer on liquid crystalline phase, relatively few studies have pointed out the importance of the chemical structure of the main chain, and the structure and spacing of mesogenic groups along the main chain. Poly(siloxane)s, poly(acrylate)s, and poly(methacrylate)s are usually used as main chain components and alkoxy- or cyano-substituted biphenyls as mesogenic groups[3]. Liquid crystalline polymers having poly(olefin), poly(vinyl ether), poly(phosphazene), or poly(isocyanate) main chain were reported[4-12]. We reported a novel side-chain smectic poly(oxetane) with cyano- or fluoro-substituted biphenyl as mesogenic group, and pointed out the importance of the flexibility of the main chain, and the structure of the mesogen on the liquid crystalline structure[13-15].

As can be seen that poly(siloxane) is used as a flexible main chain component in side-chain liquid crystalline polymers, the siloxane linkage might be considered as a flexible component in the spacer by taking advantage of its low energy barrier of rotation. However, there were only few examples where siloxane linkage was used as a spacer component[16,17]. In these studies, the siloxane linkage was used in the middle of the alkylene spacer group to avoid the steric requirements of dimethyl substituted siloxane linkage, which restricts the aggregation of mesogenic group to form mesophase.

We reported side-chain liquid crystalline poly(diene)s with siloxane linkage directly attached to main chain as a flexible component of the spacer.



PB-Z-S6 (Z = CN, F, OMe, OHex)

The weight average molecular weight of polymers estimated by GPC using polystyrene standards ranges from 2.7×10^4 to 12.0×10^4 ($M_w/M_n \sim 1.4$). ^{1}H NMR spectrum of PB-CN-S6 is shown.

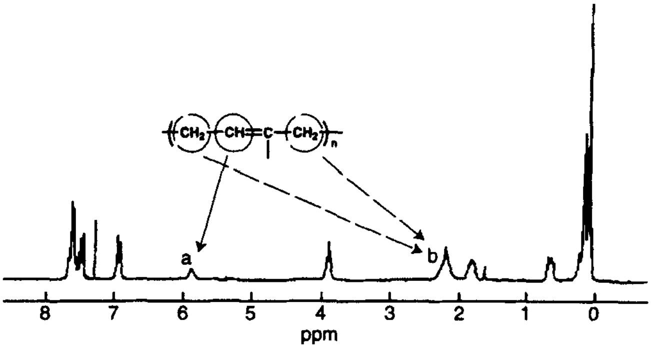


Figure 1. ^{1}H NMR Spectrum of PB-CN-S6 (200 MHz, r.t., in $CDCl_3$)

The area of the proton **a**, which is assigned to olefin proton, is one-fourth of that of proton **b** which is assigned to methylene protons of the main chain. This fact excludes the possibility that polymers were formed through 3,4- or 1,2-opening of the diene functions. It is of interest to point out that the double bonds takes one predominant stereochemistry, 1,4-E concerning the main chain, as elucidated by NOE analysis. This may be because that the bulky mesogen-containing substituent tends to be incorporated at *trans* position to polymer main chain (E form) in the repeating monomer unit.

The polymers show following transition temperatures. PB-CN-S6: 57.4°C (smectic → isotropic; ΔH= 2.8 mJ/mg); PB-F-S6: 51.9, 73.4 °C (smectic → isotropic; ΔH= 6.1 mJ/mg); PB-OMe-S6: 116.3 °C (smectic → isotropic; ΔH= 16.9 mJ/mg) with tail at lower temperature; PB-OHex-S6:

110.9 °C (smectic → isotropic; $\Delta H = 2.0$ mJ/mg) with shoulder at 107.5 °C (only in heating process). The transition was enantiotropic. The monomers did not show any mesophase. PB-CN-S6 shows a well organized smectic phase, which is in agreement with other side-chain liquid crystalline polymers having polar cyanobiphenyl mesogenic group[1]. PB-F-S6 shows similar smectic phase with focal conic fan structure. The reason for the formation of the well-developed smectic structure of these polymers is considered not only because of the polar tail group but also because of the flexibility of the poly(diene) main chain, and the very mobile disiloxane in the spacer which also spaces the mesogenic groups apart from each other along the polymer main chain, compared with ordinary vinyl polymers. PB-OMe-S6 immediately formed similar fine structure on cooling near the transition temperature.

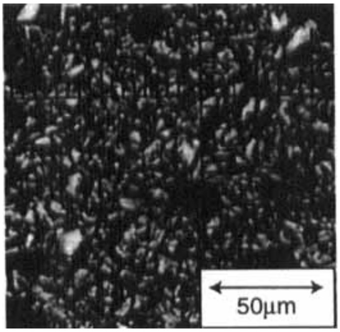


Figure 2. Optical Polarization Micrograph of PB-CN-S6.

The polymer, with cyano-substituted mesogenic group connected to the main chain without siloxane linkage, (poly[2-{6-[(4-cyanobiphenyl-4'-yl)oxy]hexyl}-1,3-butadiene] showed the transition temperature at 144.9 °C, and formed fan structure on cooling a little below the temperature.

Supposing that a side-chain liquid crystalline polymer finds an application as optical materials like optical shutter or display, optical properties, for example low refractive index of main chain polymer, are important factors. Polystyrene is a candidate of transparent and low refractive index main chain[21].

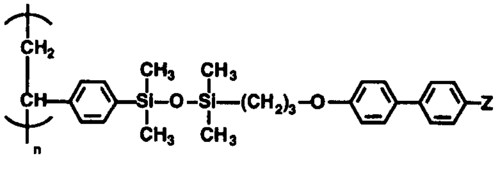


Figure 3. Structure of Polystyrene Containing Disiloxane.

It was also shown that the liquid crystalline temperature range became wider by the introduction of siloxane side chains to liquid crystalline poly(oxetane)[22].

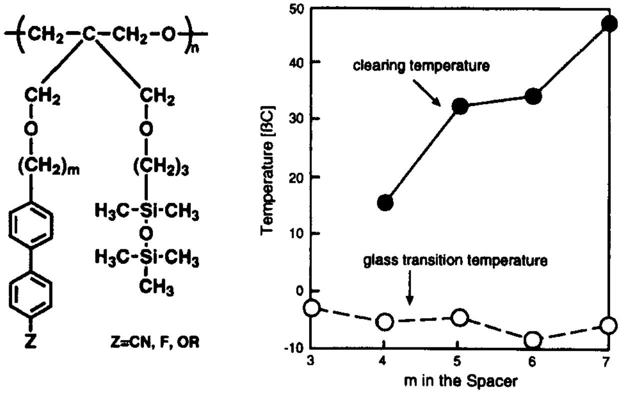


Figure 4. Side-chain Liquid Crystalline Poly(oxetane) with Siloxane Side Chain

Recently, investigations focussing on liquid crystalline behavior of poly(carbosilane) have been published[23]. We reported liquid crystalline poly(carbosilane) with directly attached siloxane linkage. These polymers exhibited well developed liquid crystalline phase because of the presence of flexible disiloxane linkage in the structure[24]. The siloxane segments of these polymers are introduced in the spacer not only from the point of flexibility but also from its incompatibility with other polymer segments.

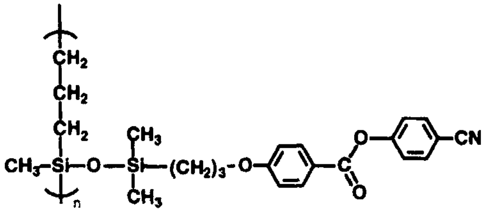
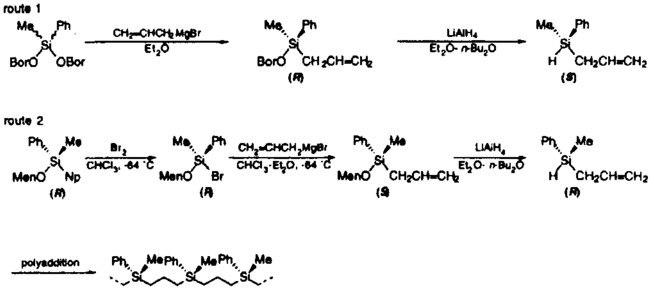


Figure 5. Liquid Crystalline Poly(carbosilane)

It is needless to say the importance of stereoregularity to obtain the desirable properties of the polymers. It is very important to control the stereochemistry of Si atom in the repeating units to correlate precisely liquid crystalline behavior with the primary structure of polymers. We designed a synthesis starting from optically active silane[25,26]. The synthetic scheme for



Bor = bornyl, Men = menthyl, Np = 1-naphthyl

Scheme 1. Synthetic Routes to Stereoregular Poly[(phenylmethylsilylene)(trimethylene)] the preparation of poly[(methyl-phenylsilylene)(trimethylene)] is shown.

Diastereomeric splitting of the signals seen on $SiCH_3$ at 0.35 and 0.36 ppm of allylmethylphenyl-(-)-bornyloxysilane is used to determine the diastereomer excess (d.e.) of allylmethylphenyl-(-)-bornyloxysilane to be 60.8 %. The d.e. of (*S*)-methylphenyl-(+)-menthoxybromosilane is estimated by the splitting of the signal at 0.62 and 0.79 ppm. The d.e. of allylated products: allylmethylphenyl-(-)-menthoxysilane is estimated by the splitting of the signal at 0.60 and 0.63 ppm. Diastereomer excess of 76.5 % is attained from the bromo derivative of d.e. of 78.9 %. The results of the polymerization are summarized in Table 1.

Table 1. Elucidation of Tacticity of Poly[(methylphenylsilylene)(trimethylene)]

run	d.e. of precursor of monomer [%]	$[\alpha]_D^{26}$ of monomer[a] [degree]	(e.e.[b]) ([%])	I : H : S		e.e. of monomer[c] [%]
				calcd.	obs.	
1[d]	---	---	(0)	1.0 : 2.0 : 1.0	1.0 : 2.0 : 1.0	---
2	61	19.6	(62)	3.3 : 2.0 : 1.0	3.5 : 2.0 : 1.0	61
3	76	24.0	(76)	6.6 : 2.0 : 1.0	7.0 : 2.0 : 1.0	77

[a] c 1.00, pentane. [b] calculated value assuming otically pure monomer has the optical rotation of $[\alpha]_D^{26}$=31.4. [c] estimated from triad tacticity. [d] racemic monomer.

Molecular weight and its distribution of the polymer are estimated to be $M_w = 3.2 \times 10^4$, $M_n = 1.1 \times 10^4$, and $M_w/M_n = 2.8$. In the aliphatic region of the spectra, three types of signals assignable to $SiCH_3$ (0.13 ppm), α-CH_2 (0.70 ppm) and β-CH_2 (1.29 ppm) are observed. No signal derived from α-addition is present, which supports the high β-regioselectivity in the hydrosilylation reaction. The spectra of methyl region of atactic and isotactic polymers are shown. The $SiCH_3$ signal is split into three singlets at 0.120, 0.125 and 0.131 ppm reflecting the triad tacticity. It is reasonable to conclude that the signals at 0.120 and 0.131 ppm are assigned to the isotactic and syndiotactic triad, respectively, and that at 0.125 ppm to the heterotactic triad.

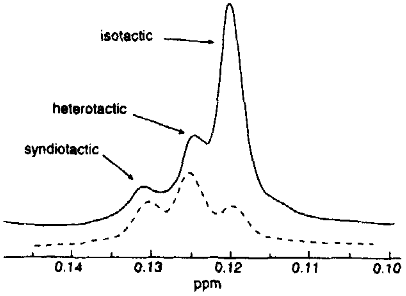
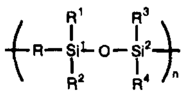


Figure 6. ^1H NMR Spectra of Isotactic Rich (solid line) and Atactic (dashed line) Poly[(phenylmethylsilylene)(trimethylene)].

The calculated concentration of each triad starting from the optically active monomer with 80.0 %e.e. assuming complete retention of Si stereochemistry in the reduction step by lithium aluminum hydride[27] and in the polymerization is S : H : I = 1.0 : 2.0 : 6.6. The actual concentration of each triad evaluated from Figure 6 was 1.0 : 2.0 : 7.0. This fact proves that there is no racemization in allylation and reduction step to synthesize allylmethylphenylsilane. This also proves that the e.e. of allylmethylphenylsilane having $[\alpha]_D^{26}$ = 24.0° is 80.0 %. This value is a little higher than that recently estimated[28].



$-\!\left(R-\overset{R^1}{\underset{R^2}{Si^1}}-O-\overset{R^3}{\underset{R^4}{Si^2}}\right)_n\!-$

Figure 7. Structure of a Poly(carbosiloxane)

When substituents R^1 and R^2 (and/or R^3 and R^4) are different in the Figure, the silicon atom is chiral that would cause the polymer optically active if this silicon atom is of excessive enantiomer. With this concept, optically pure (>99 %e.e.) bifunctional (1*S*)-(1-naphthyl)-1-phenyl-1-vinyl-3,3-dimethyl-3-hydro-1,3-disiloxane was prepared from (*S*)-(1-naphthyl)phenylvinyl-(-)-menthoxysilane and an optically active polymer was synthesized *via*

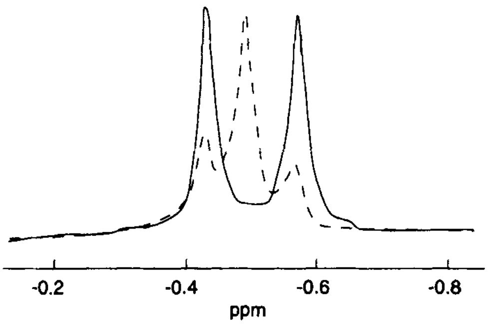


Figure 8. ^{13}C NMR Spectra of Highly Isotactic (solid line) and Atactic (dashed line) of Poly[oxy(dimethylsilylene)ethylene{(1-naphthyl)phenylsilylene}]

hydrosilylation. This polymer is proved to be optically pure (>99 %e.e.) and highly stereoregular (tacticity >99%)[29]. ^{13}C NMR spectra of $Si(CH_3)_2$ in the polymer obtained from racemic and optically active monomers are shown. Atactic polymer showed three peaks (-0.427 ppm, -0.503 ppm and -0.564 ppm), while the polymer from optically active monomer showed mainly two peaks (-0. 427 ppm and -0.564 ppm). Two methyl carbons in *S-S* (or *R-R*) diad are located in quite different environments and therefore have two chemical shifts. In the case of *S-R* (or *R-S*) diad, two methyl groups are in very similar environments, and their carbon resonances will appear at the similar position, *i.e.*, methyl groups of *S-R* and *R-S* diads will appear as one inseparable peak. $Si(CH_3)_2$ in atactic polymer, therefore, would be split into three peaks (the central peak represents the *S-R* and *R-S* diads, two side peaks represent *S-S* and *R-R* diads) in the ^{13}C NMR spectrum, with an intensity of 1 : 2 : 1. While pure isotactic polymer, containing only *S-S* (or *R-R*) diad, would show two peaks of methyl carbons, and pure syndiotactic polymer only one (*S-R* and *R-S* diads). The present polymer showed two distinct peaks of methyl carbons, indicating high isotacticity.

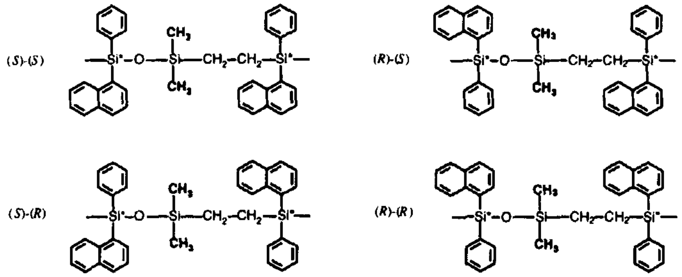


Figure 9. Possible Diads of Poly[oxy(dimethylsilylene)ethylene{(1-naphthyl)phenylsilylene}]

Optically active poly[(methylphenyl-silylene)(propenylene)] was also synthesized[30]. Catalytic synthesis of poly(carbosiloxane)s from silane and water was also developed[31].

Conclusion

The flexibility of disiloxane linkage was taken advantage of to design liquid crystalline polymers. In order to improve the property, stereochemistry of silicon-containing polymers was controlled starting from optically active monomers.

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