Synthesis and characterization of liquid crystalline polystyrenes with disiloxane linkage in the spacer

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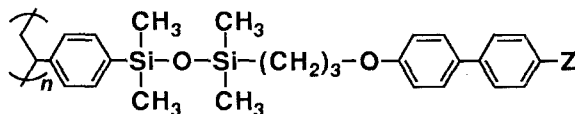
Summary

Novel polystyrenes with mesogenic groups as p-substituents connected through disiloxane-containing spacer are synthesized by anionic and radical polymerization and characterized. Some polymers are found to show smectic phases. Influences of the position of the siloxane linkage in the spacer, molecular weight and molecular weight distribution of the polymer on liquid crystallinity are observed.

Introduction

The temperature range and the mesophase structure of side-chain liquid crystalline polymers are very much dependent on the chemical structure of the polymers, namely, main chain, spacer, and mesogenic groups(1-4). In addition to commonly used main chains like poly(acrylate)s and poly(methacrylate)s, some new examples of hydrocarbon main chain such as polyolefin and poly(vinyl ether) have been recently reported(5-13). It is generally considered that the spacer groups, which act as flexible connecting groups between main chain and mesogenic groups, are playing an essential role in determining the structure and the temperature range of the mesophase. Since polysiloxane is widely used as a flexible main chain component of side-chain liquid crystalline polymers(1-4), the siloxane linkage could be used as a component of the spacer by taking the advantage of its flexibility.

Meanwhile, we reported a new type of side-chain liquid crystalline polydienes in which the main chain is connected to mesogenic groups through the spacer having disiloxane linkages directly attached to the main chain in every four carbons to avoid the steric hindrance(14-16). The polymers showed lower transition temperatures than those connected through the spacer without siloxane linkage. Fontanille also reported a similar polymer(17).

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. Our interest has been paid to the design a kind of semi-rigid, non-polar, and low refractive index liquid crystalline polystyrenes with controlled molecular structure. Molecular weight, polydispersity, and tacticity of the polystyrenes can be controlled by precision polymerization such as living or coordination polymerization. The siloxane segment is introduced in the spacer not only from the point of flexibility but also from its incompatibility with other polymer segments. The structure of the polymers is shown bellow.

$$\left[\!\!\begin{array}{c}\text{}\end{array}\!\!\right]_{n}\!\!-\!\!\left\langle\bigcirc\right\rangle\!\!-\!\!\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}\!\!-\!\!O\!\!-\!\!\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}\!\!-\!\!(CH_2)_3\!\!-\!\!O\!\!-\!\!\left\langle\bigcirc\right\rangle\!\!-\!\!\left\langle\bigcirc\right\rangle\!\!-\!\!Z$$

PS-Z-S6   Z = CN, F, 1(OMe), 4(OBu), 6(OHex)

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Experimental

General ^{1}H and ^{13}C NMR spectra were obtained on a Varian 300MHz ^{1}H NMR (75MHz for ^{13}C) spectrometer Model Gemini 300. The chemical shifts are given in ppm relative to internal CHCl$_3$ (7.26 ppm for ^{1}H) or CDCl$_3$ (77 ppm for ^{13}C). DSC analyses were carried out on a Seiko thermal analysis system Model SSC 5200 equipped with DSC 120 with a heating rate of 3 °C/min. The transition temperature is given at the point where transition starts in the second heating process. Optical polarization micrographs were taken on a Nikon optical polarization micrograph Model MICROPHOT-FXA equipped with a Mettler FP-82 hot stage and FP-90 controller. Pictures were taken at a little lower temperature than the peak in the cooling process at appropriate intervals. GPC analysis was carried out on a JASCO GPC Model 880 equipped with columns of Shodex GPC KF-801 (exclusion molecular weight, polystyrene 1.5×10^3) and GPC KF-804 (exclusion molecular weight, polystyrene 4×10^5), using THF as an eluent at a flow rate of 1 mL/min.

Synthesis

Monomers were synthesized according to Scheme 1.

The polymerizable styrene moiety was introduced by coupling reaction of 4-(dimethylchlorosilyl)styrene(18) and [3-{(4-Z-substitutedbiphenyl-4'-yl)oxy}propyl]-dimethylsilanol(15) in the presence of suitable base. The products were isolated by column chromatography. Abbreviated names of the monomers are given by the combination of S, which indicates styrene, abbreviated name of the mesogen; 1(Z=OCH$_3$), 4(Z=C$_4$H$_9$O), 6(Z=C$_6$H$_{13}$O), and CN(Z=CN), and the abbreviated name of the spacer S6[Si(CH$_3$)$_2$OSi(CH$_3$)$_2$CH$_2$CH$_2$CH$_2$O].

S-Z-S6
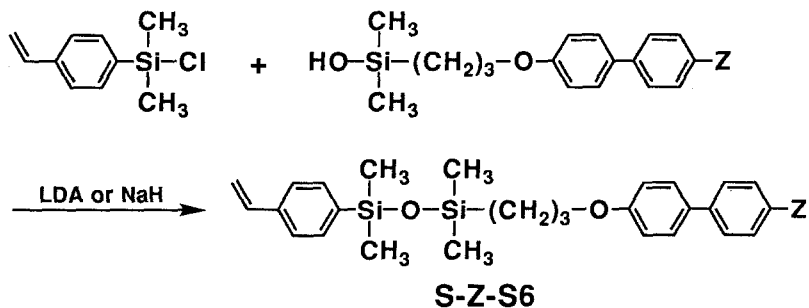
Scheme 1. Synthetic Route to Monomers

Model compounds shown in Table 1 were synthesized similarly to monomers. The protons of the monomer are indicated as shown below.
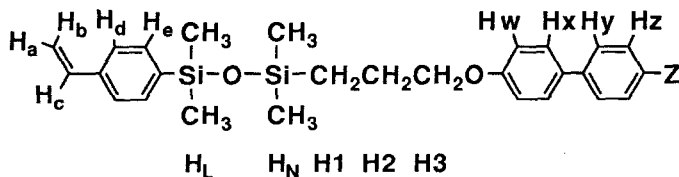
4-[3-{3-[(4-Butoxybiphenyl-4'-yl)oxy]propyl}tetramethyldisiloxanyl]styrene(S-4-S6) To a reaction product from [3-{(4-butoxybiphenyl-4'-yl)oxy}propyl]dimethylsilanol (directly used after the hydrolysis of the product of the hydrosilylation reaction)(6.0 g, 16.6 mmole) and LDA(16.6 mmole) in THF (100 mL) at 0°C for 1 h, 4-(dimethylchlorosilanyl)styrene (3.3 g, 16.6 mmole) was added, and the mixture was allowed to warm up to room temperature and to react for 12 h at the temperature. The reaction was stopped by pouring into methanol, and the product was isolated by column chromatography after evaporation of the solvent. Rf = 0.68 (hexane: ethyl acetate = 5:1). Yield: 88 %.

^{1}H-NMR chemical shifts: δ 0.12(s, 6H, H_N), 0.34(s, 6H, H_L), 0.66(m, 2H, , $H1$), 0.99(t, 3H,

J=7.4, OCH₂CH₂CH₂C*H*₃), 1.52(m, 2H, OCH₂CH₂C*H*₂CH₃), 1.81(m, 4H, OCH₂C*H*₂CH₂CH₃, *H*2), 3.92(t, 2H, J=6.8Hz, *H*3), 3.99(t, 2H, J=6.4, OC*H*₂CH₂CH₂CH₃), 5.26(d, 1H, J=10.9Hz, *H*a), 5.78(d, 1H, J=17.6Hz, *H*b), 6.71(dd, 1H, J₁=10.9Hz, J₂=17.6Hz,*H*c), 6.94(m, 4H, *H*w, *H*z), 7.39-7.53(m, 8H, *H*x, *H*y, *H*d, *H*e).

Other monomers S-CN-S6, S-1-S6, and S-6-S6 were similarly synthesized.

Polymerization

Radical polymerizations were carried out using AIBN as an initiator. Formed polymers were recovered by precipitation into methanol from THF solution, and purified by repeated reprecipitation. The weight average molecular weight of polymers was estimated by GPC using polystyrene standards. Anionic polymerizations of S-4-S6 were carried out using *n*-butyllithium as an initiator in THF. The names of the polymers are given by adding P to the abbreviated name of the monomer, as PS-4-S6.

The characterization data of the polymer by NMR are shown.

PS-4-S6

^{1}H-NMR chemical shifts: δ 0.01(broad, 6H, *H*ₙ), 0.26(broad, 6H, *H*ₗ), 0.61(broad, 2H, *H*1), 0.95(broad, 3H, OCH₂CH₂CH₂C*H*₃), 1.40-1.60(broad, main chain protons and OCH₂CH₂C*H*₂CH₃), 1.73(broad, 4H, OCH₂C*H*₂CH₂CH₃, *H*2), 3.79-4.00(broad, 4H, *H*3, OC*H*₂CH₂CH₂CH₃), 6.85(broad, 4H, *H*w, *H*z), 7.34-7.47(broad, 8H, *H*x, *H*y, *H*d, *H*e).

^{13}C-NMR chemical shifts: δ 0.34, 0.99, 13.9, 19.2, 23.3, 31.4, 70.4, 114.7, 127.5, 132.7, 133.2, 158.1.

NMR spectra of other polymers, PS-CN-S6, PS-1-S6, PS-6-S6 showed signals at reasonable positions.

Results and Discussion

Although it was shown that disiloxane linkage could act as flexible spacer for polydiene main chain(14-16), it is not clear if it can act also as an effective spacer for polystyrene since the mesogenic branches are introduced in every other carbon along the main chain in contrast to polydiene in which they are introduced in every four carbons. In order to study the effects of the position of the siloxane linkage on the liquid crystalline behavior, some model compounds containing the siloxane linkage were synthesized.

Table1. The Effect of the Position of the Disiloxane Linkage on Liquid Crystallity

Compound	Z	Transition Temperature (°C)[a]	Texture
[structure] ⬡–Si–O–Si–CH₂CH₂CH₂O–⬡–⬡–Z	OBu	2.5; 35.5	batonnet, fan
	OMe	59.1	batonnet
[structure] ⬡–OCH₂CH₂CH₂–Si–O–Si–⬡–⬡–Z	OMe	-33.1[b];13.1; 23.0	—[c]

a) Determined by DSC on second heating. b) Exothermic. c) Texture was not developed.

It was found siloxane linkage should be introduced as apart from the mesogenic group as possible. Based on this result the structure of monomers was proposed.

The yield of the monomers are not always high. It is well known that condensation of silanols easily occurs under basic or acidic condition. In order to obtain reproducible yield in the synthesis by Scheme 1, the kind of the bases and order of the addition of the reagent, terminating agent, and separation procedure were studied. Although lithium diisopropylamide is preferred, some other bases such as triethylamine, pyridine, sodium hydride sometimes gave good results. However reproducible yield could not be obtained. The order of the addition of the reagents also sometimes altered the yield. Finally, we found that the terminating agent is very important to obtain clean reaction product. Use of methanol as the terminating agent gave reasonable and reproducible yield in the synthesis. This is considered to be

656

because unreacted 4-(dimethylchlorosilyl)styrene is converted to easily separable 4-(dimethylmethoxysilyl)styrene by methanol instead of 1,3-bis(4-vinylphenyl)-1,1,3,3-tetramethyldisiloxane produced by water, which is only separable with difficulty. High and reproducible yield could be obtained by this procedure. Yield and thermal transition of monomers are shown in Table 2.

Table 2. Thermal Transition of S-Z-S6

Z	Transition temperature (°C)[a]	Texture (°C)[b]
OMe	44.5; 75.6	batonnet, fan (70.0)
OBu	48.0; 78.5	fan (67.5)
OHex	28.6; 49.6	fan (44.8)
CN	-49.3; -36.7	-

a) Determined by DSC.
b)Values in the parenthesis are annealing temperature.

Table 3. Polymerization of S-Z-S6 by AIBN

Z	AIBN (mol%)	Mn [a]	Mw / Mn [a]
OMe	10	3900	1.7
OBu	10	4700	1.4
	3	23300	2.3
OHex	10	5500	1.6
CN	3	22000	2.4

a) Estimated by GPC using standard polystyrene.

Monomers basically showed enatiotropic smectic mesophase. Chemical structure of the spacer is an important factor to determine the liquid crystalline state as studied by model compounds.

Radical polymerization of the monomers gave reasonable results as shown in Table 3.

PS-4-S6 with molecular weight 23,300 showed smectic phase with a batonnet texture. However, clear mesophase could not be observed for other polymers even in case of PS-CN-S6 having a polar mesogenic group.

Siloxane linkage introduced apart from mesogenic group was reported to be effective for the formation of liquid crystalline phase by polymers(19, 20). We also reported that the transition temperatures of the polymers having siloxane-containing spacer is much lower compared with that with alkylene spacer. The reason for the formation of the well-developed smectic structure by PS-4-S6 is considered to be the good balance of the properties among the tail group, flexible spacer, and the main chain structure.

Interested in the effects of the molecular weight and molecular weight distribution on the mesomorphic behavior of the polymers, anionic polymerization of S-4-S6 was attempted, and the results are shown in Table 4.

Table 4. Polymerization of S-4-S6 by n-BuLi

Feed		Yield (%)	GPC[a]			
[M](mol /l)	[M] / [I]		DP	Mn	Mw	Mw / Mn
0.1	1.1	70	8	4300	5700	1.3
0.07	3.1	80	11	5600	7000	1.2
0.07	3.1	76	16	8100	9600	1.2
0.07	6.3	62	18	9000	14000	1.6
0.07	10	63	46	23300	36100	1.5

a) Estimated by GPC using standard polystyrene.

Although radical polymerization gave reasonable results, we had a difficulty in anionic polymerization. As seen in Table 4, actual degrees of polymerization by GPC is much higher than those calculated from the feed monomer/initiator ratio. However, it can be also seen that actual molecular weight can be controlled by the ratio of the monomer and initiator. From these data, proper feed ratio was chosen to obtain the polymer of desired molecular weight. Anionic polymerization gave polymers of narrower molecular weight distribution compared

with those by radical polymerization.

The effects of molecular weight and its distribution are shown in Figure 1-a), b).
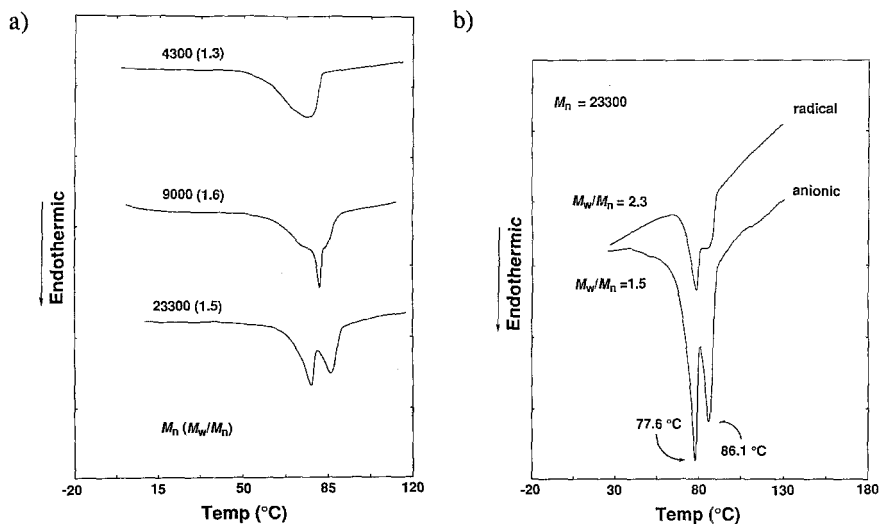

Figure 1. Influence of a) Degree of Polymerization and b) Molecular Weight Distribution on the Thermal Property of PS-4-S6

PS-4-S6's with molecular weight higher than 9,000 showed smectic phase with a batonnet texture. Certain molecular weight seems necessary for the polymers to take liquid crystalline state. Polymers with narrower molecular weight distribution gave sharp transition temperature.

There has been considerable discussions about the molecular weight dependence of thermal property of noncrystallizable side-chain liquid crystalline polymers(1, 21-23). The temperature range of liquid crystalline state of noncrystallizable polymers are determined by Tg and Tc(clearing temperature). Tg is usually lower than Tc, and liquid crystalline state is observed between these temperatures. Both these temperatures become higher with increase in degree of polymerization of the polymer, and the change in Tc is usually bigger than that of Tg. Thus, liquid crystalline state often becomes clear for higher molecular weight polymer.

The two transition temperatures seem to be close to each other for PS-4-S6's with molecular weight lower than 9,000, and clear liquid crystalline state was not observed for these polymers. Difference between these temperatures seems to become bigger for higher molecular weight PS-4-S6's.

The effects of molecular weight distribution on liquid crystalline phase is reported to be not so big for polymers with high enough degree of polymerization. The value of 9,000~23,300(DP=18~46) for PS-4-S6 is a transient molecular weight, and there must be a considerable influence of molecular weight distribution on Tg and Tc of the polymers, and this may be a reason for the difference in thermal behavior between radically and anionically formed polymers.

Conclusion

Synthesis and thermal behavior of novel liquid crystalline polystyrene with siloxane-containing spacer is described. Polystyrene with butoxy tail group in the mesogenic side chain showed smectic liquid crystalline phase. The transition temperature is dependent on the molecular weight and polydispersity of the polymers.

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