Stereoselective Feature in Anionic Ring-Opening Polymerization of 2-(1-Naphthyl)-2-phenyl-5,5-dimethyl-1-oxa-2,5-disilacyclopentane and Influence of Tacticity on the Thermal Property of Polymers

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ABSTRACT: The stereoselective feature in the anionic ring-opening polymerization of racemic 2-(1-naphthyl)-2-phenyl-5,5-dimethyl-1-oxa-2,5-disilacyclopentane was investigated by ^{13}C NMR analysis of the dyad sequence of the resulting polymer. The influences of initiators, polymerization temperature, and solvents on the tacticity of the polymer were discussed. It was found that the polymerization using PhLi as an initiator could afford a polymer rich in syndiotacticity (r/m = 65/35 at −20 °C). The stereoregulation was tentatively considered due to the different stability or reactivity of the diastereomeric intermediates comprised of the propagating chain end, monomer, and countercation. The isotactic polymer prepared from the optically active monomer showed a similar T_g to that of the syndiotactically rich polymer prepared from the racemic monomer, but the former exhibited significantly better thermal stability than the latter.

Introduction

Stereoregularity is one of the most important structural parameters to control the physical properties of polymers. Although the stereoregular polymers have been generally approached either by polymerizing optically active monomers or by the stereoselective (or stereospecific) polymerization of prochiral or racemic monomers, the latter is a more economically attractive route. This has been successful in the polymerization of propylene in the presence of Ziegler−Natta catalysts to produce the highly isotactic polypropylene,[1] the preparation of iso- or syndiotactic poly(methyl methacrylate)s by using organolithium initiators or Grignard reagents at a low temperature,[2] and the ring-opening polymerization (ROP) of propylene oxide in the presence of $Zn(OR)_2$ or ZnR_2/MeOH to give a mixture of isotactic (R)- and (S)-poly(propylene oxide).[3] On the other hand, little knowledge concerning the stereoselective polymerization of organosilicon compounds has been obtained yet, probably due to the unavailability of appropriate organosilicon monomers, the lack of efficient synthetic methods suitable for the stereoselective polymerization, and the difficulties in the evaluation of the stereoregularity of the resulting polymers. Several attempts have been made on the stereochemical control of polycondensation of organosilicon compounds, such as the modified Wurtz-type alkali metal coupling reaction of dichlorosilanes[4−8] and the transition-metal-catalyzed dehydrogenative polymerization of organosilanes.[9,10] Some tacticity variations were observed in these cases, but the stereoselectivity of polymerizations was difficult to be properly judged due to the inconclusive stereochemical assignment[6] and the complexity of the NMR spectra.[9] Some efforts have also been made for the ROP of racemic or prochiral cyclic organosilicon compounds to prepare stereoregular polysiloxanes,[11] polysilanes,[12] etc., but most of them failed to produce stereoregular polymers. The only successful stereospecific ROP of organosilicon compounds was reported recently by Manners et al.,[13] employing a solid polymerization of prochiral ferrocenylmethylphenylsilane ($Fe(\eta\text{-}C_5H_4)_2SiMePh$). The actual tacticity (isotactic or syndiotactic) of the polymer, however, is still not determined.

In our previous report, the ROP of optically active (S)-2-(1-naphthyl)-2-phenyl-5,5-dimethyl-1-oxa-2,5-disilacyclopentane ((S)-**1**) to afford an isotactic and optically active poly[{(1S)-1-(1-naphthyl)-1-phenyl-3,3-dimethyldisiloxan-1,3-diyl}ethylene] was discussed (Scheme 1).[14] The achiral $Si(CH_3)_2$ unit in this polymer can probe different configurations of both neighboring asymmetric silicon atoms to reflect the dyad sequences of the polymer.[14,15] The facile judgment of the tacticity of this polymer by ^{13}C NMR inspired us to investigate the stereoselective feature of the ROP of racemic 2-(1-naphthyl)-2-phenyl-5,5-dimethyl-1-oxa-2,5-disilacyclopentane ((rac)-**1**). Here we report our observations of the influences of initiators, polymerization temperature, and solvents on the stereoselectivity of the polymerization. The thermal properties of poly[{(1-naphthyl)-1-phenyl-3,3-dimethyldisiloxan-1,3-diyl}ethylene] prepared from (S)-**1** and that from (rac)-**1** are also discussed on the basis of the DSC and TGA results.

Experimental Section

The preparation of monomers, polymerization procedure, and analytical methods were similar to those described previously,[14] except for the ^{13}C NMR spectra which were obtained in $CDCl_3$ on a 500 MHz Unity INOVA spectrometer. The differential scanning calorimetry (DSC) analysis and the thermogravimetric analysis (TGA) were performed on a Seiko SSC/5200H instrument at a heating rate of 10 °C/min (DSC) and 5 °C/min (TGA) under a nitrogen atmosphere (50 mL/min), respectively. The polymerization conditions and the results are shown in Table 1.

Results and Discussion

In the ROP of (S)-(1-naphthyl)-2-phenyl-5,5-dimethyl-1-oxa-2,5-disilacyclopentane ((S)-**1**) using PhLi as an initiator, the nucleophilic attack of the propagating chain end $-Si(NpPh)O^-$ was found to occur regioselec-

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Scheme 1

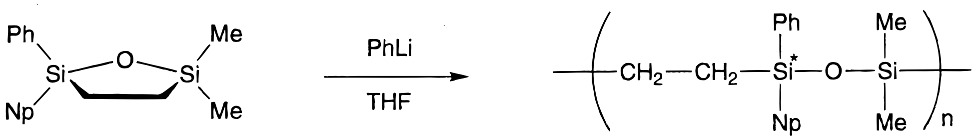


Table 1. Stereoselective Feature in Ring-Opening Polymerization of Monomer 1[a]

run	polymer	initiator	T, °C	time, h	conv, %[b]	M_n[b]	M_w/M_n[b]	r/m[c]
1	**2a**	PhLi	0	67	93	11300	1.12	<1/99
2	**2a′**		0	24	87	5900	1.15	<1/99
3	**2b**		−20	77	77	3800	1.15	65/35 (63/37)
4	**2c**		0	24	93	4600	1.13	64/36 (62/38)
5	**2d**		20	15	92	6800	1.19	64/36 (62/38)
6	**2e**		50	15	93	9200	1.31	62/38 (59/41)
7	**2f**		20	1	47	3100	1.24	60/40 (58/42)
				2	71	4700	1.18	58/42 (56/44)
				3.5	81	5800	1.17	55/45 (53/47)
				12	94	6800	1.17	54/46 (51/49)
8	**2g**[d]		20	144	36	2700[e]	1.06	(59)/41)
9	**2h**	MeONa	20	15	89	4700	1.20	57/43 (54/46)
10	**2i**	*t*-BuOK	20	0.17	81	10800	2.60	57/43 (54/46)
11	**2j**	*n*-Bu_4NOH	20	89	53	2400	1.74	(52/48)
12	**2k**	MeOH/Sp[f]	80	72	78	2600	1.15	(57/43)
13	**2l**	PhLi/Sp[f]	20	24	94	2400	1.24	(61/39)

[a] Monomer: (*S*)-**1** (>98.2% ee for **2a** and **2a′** and 39.3% e.e. for **2f**) and (*rac*)-**1** (others); [M]/[I] = 60 (**2a** and **2e**), 45 (**2f**), and 30 (others). [b] Estimated by SEC with polystyrene standards. [c] *r*/*m*: *racemo* and *meso* dyad ratio calculated according to the integrals of dyad splitting signals of $Si(CH_3)_2$ in ^{13}C NMR spectra. r/m = [peak area at −0.377 ppm]/2 × [peak area at −0.445 ppm]. Values in the parentheses are apparent r/m = ([peak area at −0.377]/([peak area at −0.308] + [peak area at −0.445]). [d] In benzene. [e] Isolated yield: 19%. [f] Sp: (−)-sparteine, [I]/[Sp] = 0.5.

tively at the achiral silicon atom $Si(CH_3)_2$ in the monomer to produce a highly isotactic and optically active polymer **2a**.[14] To calculate the areas of peaks in the ^{13}C NMR spectra accurately, and therefore estimate the tacticity of polymers, a 500 MHz NMR instrument was employed by taking long enough pulse waiting time and enough integrating time for each sample.[16] The125.8 MHz ^{13}C NMR spectrum of **2a** clearly showed two equivalently separated peaks at −0.308 and −0.445 ppm, respectively, which represent carbon atoms of $Si(CH_3)_2$ in the *S*−*S* *meso* dyad sequence of the polymer (Figure 1). On the other hand, the polymerization of racemic 2-(1-naphthyl)-2-phenyl-5,5-dimethyl-1-oxa-2,5-disilacyclopentane ((*rac*)-**1**) gave a polymer **2d** with three peaks at −0.308, −0.377, and −0.445 ppm in the $Si(CH_3)_2$ region of ^{13}C NMR spectrum, due to the *S*−*S* (or *R*−*R*) *meso* and *S*−*R* (or *R*−*S*) *racemo* dyad splitting. That the central peak (representing the *racemo* dyads) is broader than the two side peaks (representing the *meso* dyads) might reflect the slightly different environments of the $Si(CH_3)_2$ groups in the *S*−*R* dyad and in the *R*−*S* dyad.[15] It was also shown that the peak at −0.445 is a true singlet, but that at −0.308 contained a minor peak in the spectrum of **2d**. The shoulder peaks of **2j** may be due to the polymer ends or to the cyclic oligomers. Although the molecular weights of the polymers are not high enough to be treated statistically, nor is peak separation good in the case of low molecular weight samples (**2g**, **2j**, **2*k***, **2l**), the *r*/*m* ratio was calculated as *r*/*m* = [area at −0.377]/2 × [area at −0.445]. Interestingly, the calculated integral ratio of *racemo* and *meso* dyads (*r*/*m*) of polymer **2d** was found to be 64/36 (Table 1), which apparently varied from that of a random sequence distribution (*r*/*m* = 50/50), suggesting the rich syndiotacticity of this polymer. The tacticity variation of the polymer formed was also observed during the polymerization. When a mixture of (*S*)-**1** and (*rac*)-**1** was used (run 7 in Table 1), the *r*/*m* ratio of the resultant polymer **2f** decreased from 60/40 at the early stage (conversion: 47%) to 54/46 at the later stage (conversion: 94%), indicating the faster *racemo* dyad formation over the *meso* dyad formation. The changes of the optical purity of the remaining monomer during the polymerization further confirmed this tendency (Figure 2). As polymerization proceeded, the optical purity of the remaining monomer increased

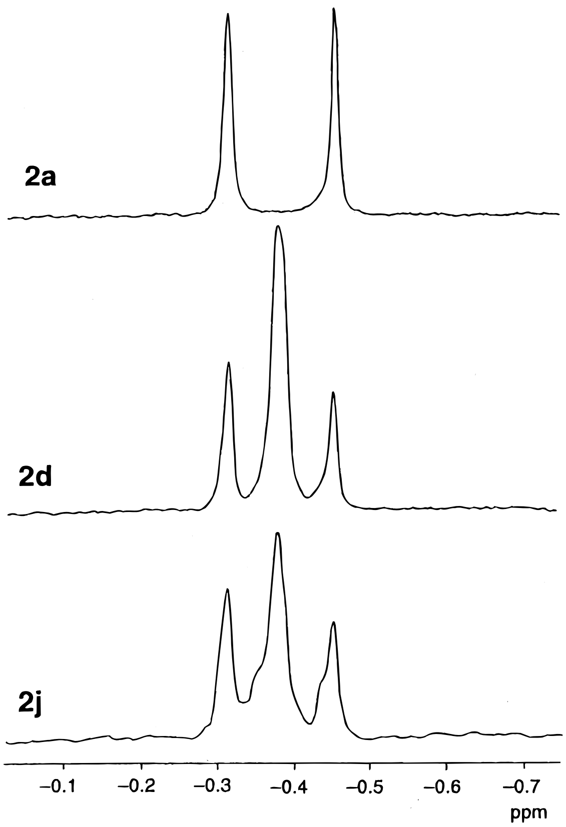


Figure 1. The 125.8 MHz ^{13}C NMR spectra of the $Si(CH_3)_2$ region of polymers **2a**, **2d**, and **2j**.

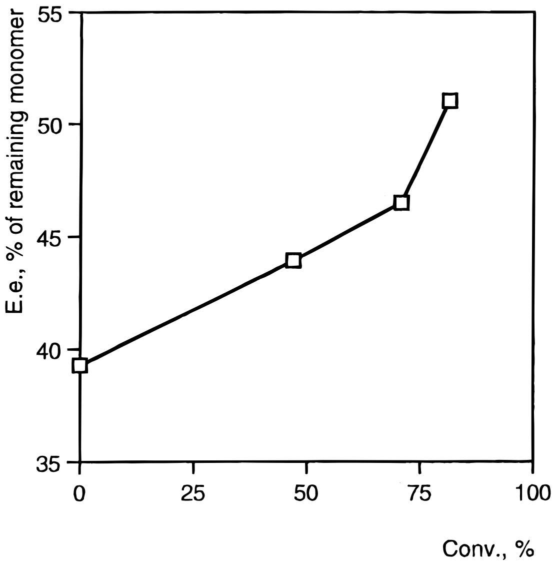


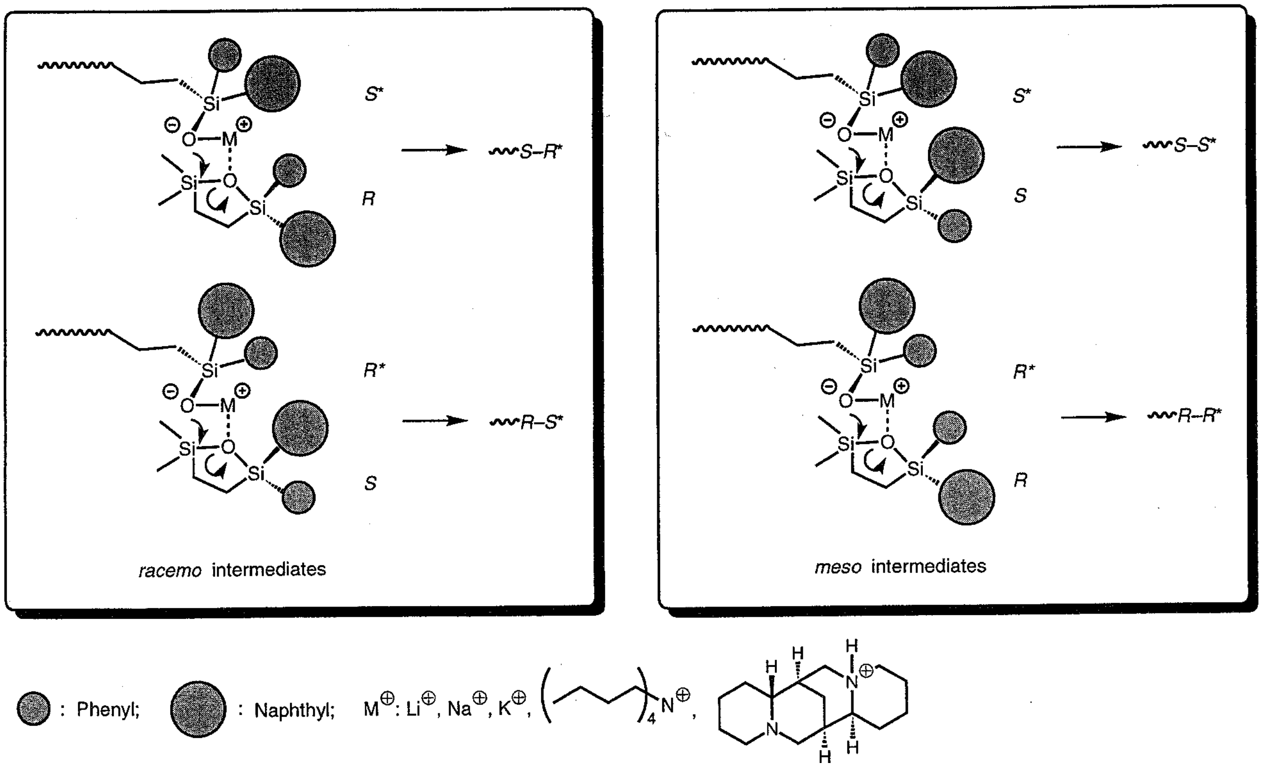
Figure 2. Enantiomeric excess (e.e.)[17] of the remaining monomer **1** versus the conversion of polymerization (run 7 in Table 1).

gradually from 39.4% e.e. (the starting monomer rich in (*S*)-isomer) to 51.0% e.e. (at conversion of 81%),[17] elucidating that the formation of *S*−*S* dyad sequence was slower than the formation of *S*−*R* and *R*−*S* dyads. Slight increases in the syndiotacticity were observed when the reaction temperature was lowered ($r/m = 62/38$ (50 °C, **2e**), 64/36 (20 °C, **2d**), 64/36 (0 °C, **2c**), and 65/35 (−20 °C, **2b**)). When the polymerization was conducted in benzene instead of THF, the polymer **2g** formed had a similar apparent dyad ratio to that obtained in THF (**2d**). Polymerization using MeONa and *t*-BuOK as initiators also showed a preference to form the syndiotactic sequence in the polymers, but the *r*/*m* ratios (**2h**: 57/43; **2i**: 57/43) were lower than that of the polymer obtained by PhLi (**2d**).

Tetra-*n*-butylammonium hydroxide (n-Bu$_4$NOH) could also initiate this polymerization, but the rate was quite slow. The polymer (**2j**) obtained had an apparent *r*/*m* ratio of 52/48 (Figure 1), close to that of the random structure, indicating that there was almost no stereoregulation by this initiator. On the other hand, the polymerization using MeOH/(−)-sparteine as an initiator favored the formation of the syndiotactic structure (**2*k***: apparent $r/m = 60/40$). When (−)-sparteine was used as an additive in the polymerization using PhLi, there was almost no change in tacticity of the resulting polymer **2l** compared to that of **2d**.

The mechanism for the tacticity variation observed above is still not well understood. However, from the fact that there was little influence of the polarity of the solvents on the tacticity of the resulting polymers (**2d** and **2g**), it is tentatively considered that the chiral propagating chain ends may participate in the stereoregulation. As proposed in Scheme 2, the propagating chain ends and the approaching monomers possibly form diastereomeric intermediates via the interaction of cations and oxygen atoms. Such cation−monomer interaction was theoretically considered[18] and discussed.[19,20] Differences in the size, association ability, chirality, etc., of the countercations might result in the differences in the stability or reactivity of four diasteromeric intermediates shown in Scheme 2, which in turn lead to the different outcomes with respect to the stereoregulation of the polymerization. For instance, the formation of *S*−*S** diastereomeric intermediate seems kinetically or thermodynamically unfavorable in the case of PhLi (run 7 in Table 1) which resulted in the richer *racemo* dyads of the polymer **2f** at the early stage and the excess (*S*)-isomer of the remaining monomer at the later stage of the polymerization. In the case of MeOH/(−)-sparteine, the chirality of countercation may exert some effect on the stereoselection.

Scheme 2



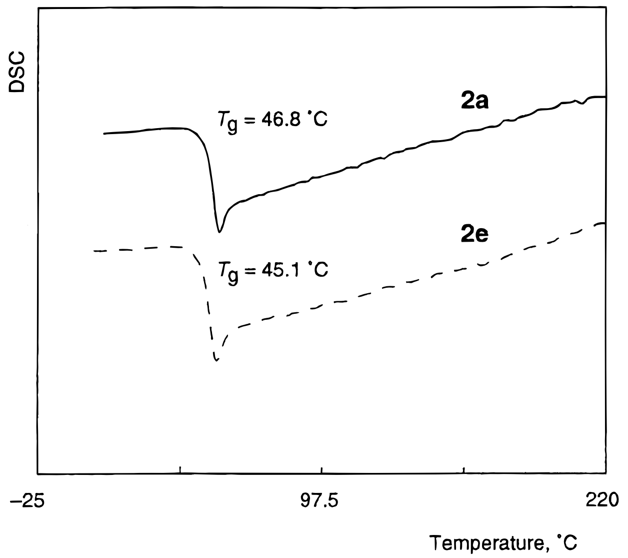


Figure 3. DSC curves (second heating) of polymers **2a** and **2e** at a heating rate of 10 °C/min under a nitrogen flow (50 mL/min).

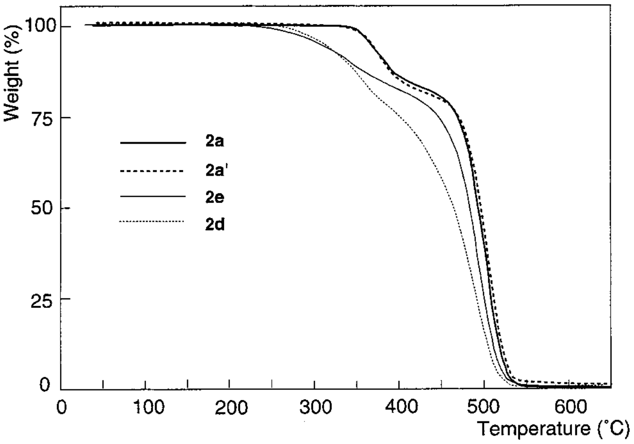


Figure 4. TGA of polymers prepared from (*S*)-**1** (**2a** and **2a′**) and (*rac*)-**1** (**2d** and **2e**) at a heating rate of 5 °C/min under a nitrogen flow (50 mL/min).

Polymers with different tacticities usually show dramatic differences in their properties; e.g., a high tacticity often leads to a high melting point and/or a high glass transition temperature of the polymer.[21] Isotactic polymer **2a** (r/m < 1/99) prepared form (*S*)-**1** and syndiotactically rich polymer **2e** (r/m = 62/38) prepared from (*rac*)-**1** were chosen for the DSC analysis. These polymers did not show any first-order transition, indicating no crystalline phase in the polymer, and these two polymers showed nearly the same glass transition temperatures (T_g = 46.8 °C (**2a**) and 45.1 °C (**2e**)). No other transition temperatures were observed for both polymers on DSC curves (Figure 3). On the other hand, the TGA analysis clearly revealed their significantly different thermal decomposition behavior. As shown in Figure 4, isotactic polymer **2a** showed apparently a two-step decomposition profile. A first onset T_d (decomposition temperature) at about 350 °C was considered due to the partial cleavage of Si–C bonds in the main chain, and a second onset T_d at 480 °C was probably originating from the main chain Si–O bond cleavage to give back monomers. In the sharp contrast, polymer **2e** showed a first onset T_d at 270 °C and a second onset T_d at about 465 °C, 80 and 15 °C lower than those of polymer **2a**, respectively. Furthermore, the two decomposition steps of polymer **2e** were not clearly separated as in the case of polymer **2a**, also indicating their different decomposition profiles. Higher syndiotactic configuration of **2a** might make the bonds difficult to be cleaved compared with those of random configuration. Polymers **2a′** (r/m < 1/99, M_n = 5900) and **2d** (r/m = 64/36, M_n = 6800) with the similar tacticity but different M_n from those of **2a** and **2e** showed a similar tendency (Figure 4). The different decomposition behavior of polymers prepared from (*S*)-**1** and (*rac*)-**1** may be due to the different assembly of their side chains and/or main chains in the melting state, which intrinsically is caused by their different tactic placements.

Conclusion

As a summary, this study revealed the stereoselective feature in the anionic ROP of (*rac*)-**1**. Syndiotactically rich polymers were obtained using PhLi as an initiator in THF (r/m = 65/35 at −20 °C). Although the mechanism for the stereoselectivity is still not clear, it is tentatively considered that the propagating chain end and approaching monomer may form diastereomeric intermediates via the countercation. The stability or reactivity of the intermediates probably contributes to the stereoregulation observed in this polymerization. The isotactic polymer prepared from (*S*)-**1** exhibited apparently better thermal stability than that of the syndiotactically rich polymer prepared from (*rac*)-**1**.

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(16) Conditions: d1 (first delay) = 9 s, dm (decoupler mode for first decoupler) = “nny”, np (number of data points) = 94 272, repetitions = 15 000−20 000.

(17) The optical purity of the remaining monomer was estimated by HPLC analysis (performed on an optically active stationary phase) of 1-(1-naphthyl)phenylsilyl-2-dimethylsilylethane which was obtained by reduction of monomer **1** with $LiAlH_4$ in ether (described in ref 14).

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