

Poly(*N*-Acylethylenimine) Copolymers Containing Pendant Pentamethyldisiloxanyl Groups. I. Synthesis

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SYNOPSIS

10-(Pentamethyl disiloxanyl) decyl oxazoline (**Si**) was synthesized. It was copolymerized with either undecyl (**U**) or nonyl (**N**) oxazolines using methyl 4-nitrobenzenesulfonate as initiator. Two series of random poly(*N*-acylethylenimine) copolymers, **U/Si** and **N/Si**, were synthesized over the whole composition range of **Si** monomer with a total degree of polymerization of about 100. Narrow molecular weight distributions were obtained. At a monomer to initiator ratio of about 1060, the final degree of polymerization was 374 with a polydispersity index of 1.93. This shows the effect of chain transfer in this system.

Keywords: copolymers • oxazolines, poly(*N*-acylethylenimines) • polydispersity • siloxane

INTRODUCTION

Polymers containing siloxane groups offer a wide range of specialty applications in many diverse fields because of their unique combination of properties such as surface activity, physiological inertness (biocompatibility), high oxygen permeability, hydrophobicity, low temperature flexibility, etc.¹ Most siloxane containing polymers studied have been those with siloxane in the polymer backbones. We were interested in the synthesis and study of polymers with siloxane groups in side chains. In earlier studies, a series of undecyl oxazoline homopolymers [also called poly(*N*-dodecanyl ethyleneimine)s] and phenyl/undecyl oxazoline block copolymers, which were characterized as adhesive materials, were developed.²⁻⁴ In these polymers, the undecyl block is highly crystalline.^{3,5} When the undecyl homopolymers were coated on substrates, the films had the polymer backbones parallel to the surface with the undecyl tails oriented toward the surface.⁴ The addition of bulky siloxane groups at the tails of the highly crystallizable oxazoline polymers with long alkyl side chain might generate a new class of siloxane-containing polymers with interesting properties such as low critical surface energy, high oxygen

permeability, etc. Since the siloxane groups are flexible and should not be able to crystallize, they could possibly form amorphous domains between the highly crystalline amide backbone/hydrocarbon tail regions and generate a sandwich-like crystalline structure.

We therefore decided to synthesize poly(*N*-acylethylenimine)s with pentamethyldisiloxanyl pendant groups attached to the terminal methylene of the alkyl side chain. We chose 10-(pentamethyl disiloxanyl) decyl oxazoline (**Si**) which can polymerize to generate a polymer with a highly crystallizable $-(CH_2)_{10}-$ attached to its backbone, followed by a bulky, flexible $-Si(CH_3)_2-O-Si(CH_3)_3$ tail. In order to study the effect of varying the concentration of the pendant siloxane groups on the polymer surface properties, thermal and crystallization behaviors, etc., we made a series of random copolymers (**U/Si**) by copolymerizing **Si** with undecyl oxazoline (**U**) over the whole composition range. Because the **U** monomer unit has one more methylene group in its side chain than the **Si** monomer unit, the pentamethyl disiloxane group may interfere with the crystallization of the polymethylene tails. To avoid this possible interference, we made a second series of random copolymers (**N/Si**) by copolymerizing **Si** with nonyl oxazoline (**N**) which has one less methylene group in its side chain than **Si**. The synthesis of the two series of random copolymers is given in this paper. Their thermal behaviors, wide

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angle X-ray diffraction study, and polymer crystalline structures are given in Part II⁶ of this series, and their surface properties are given in Part III.⁷

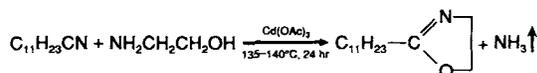
EXPERIMENTAL

Materials

Methyl 4-nitrobenzenesulfonate (MeONs, Aldrich, 99%) was purified by recrystallization from acetone/hexane. Toluene was refluxed with CaH₂ for 4 h before distillation. *o*-Dichlorobenzene (ODCB) was purified by drying over P₂O₅ for 24 h with stirring, distilled under vacuum using a spinning band column, and stored under N₂. Undecyl cyanide (Aldrich, 99%), undecylenic acid (Aldrich, 99%), decanoic acid (Aldrich, 99%), ethanolamine (Aldrich, 99%), pentamethyldisiloxane (Petrach Systems), hydrogen hexachloroplatinate(IV) (Alfa, H₂PtCl₆ · 6H₂O, 39.12% Pt), ferrous chloride (FeCl₂ · 4H₂O, Fisher), and basic alumina (Fisher, Brocknan Activity I, 80–200 Mesh) were used as received.

Instrumentation

The reaction extent and the purity of the compounds were checked by GC, a Perkin-Elmer 8500 Gas Chromatograph equipped with a OV-17 phenyl silicone type column, usually running from 100 to 320°C at 30°C/min heating rate. The molecular weight distribution was measured by gel permeation chromatography (GPC); and the polymerization progress was also followed by GPC, as described in a previous paper.² The uncorrected number and weight average molecular weights were calculated using $\bar{M}_n = \sum H_i / (\sum H_i / M_i)$ and $\bar{M}_w = \sum H_i M_i / \sum H_i$, where H_i is the height of ΔRI trace, measured at every 0.1 ml interval, and M_i is the molecular weight obtained from the polystyrene calibration curve. Infrared spectra were recorded on a Michelson 110 FT-IR spectrophotometer from KBr pellet samples. Proton NMR spectra were taken in CDCl₃ solutions on an XL-200, 200 MHz FT-NMR spectrometer. TMS or CHCl₃ (δ 7.24 ppm, for siloxane-containing monomer and polymers) was used as internal standard.



Scheme 1. Synthesis of undecyl oxazoline (U).

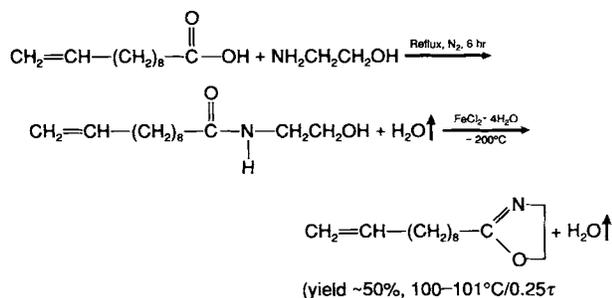
Synthesis of Undecyl Oxazoline (U)

Undecyl oxazoline was synthesized from undecyl cyanide (Scheme 1).^{8,9} Into a 1000 mL three-necked round bottom flask were added cadmium acetate (Cd(OAc)₂, 10.0 g, 0.045 mol) and undecyl cyanide (400 g, 2.21 mol). The solution was heated to 132–135°C. Ethanolamine (201.6 g, 3.30 mol) was added with stirring. A mole ratio (1.5 : 1.0) of ethanolamine to undecyl cyanide was used to get high conversion of the cyanide to the oxazoline. The reaction mixture was refluxed under N₂ at 135–140°C for 24 h. GC analysis showed that more than 95% of undecyl cyanide was transformed to undecyl oxazoline after 24 h while very little ethanolamine was left. The reaction mixture was poured into cyclohexane; a phase containing the unreacted ethanolamine and other colored impurities separated. A clear cyclohexane solution was obtained after decanting from the colored ethanolamine phase. More monomer was extracted from the ethanolamine phase by cyclohexane (2 × 100 mL). After combining the cyclohexane solutions, the cyclohexane was removed by a rotary evaporator and the crude oxazoline was purified by spinning band distillation at 128°C/0.9 τ , lit.,¹⁰ bp = 114°C/0.5 τ . The oxazoline was distilled into a flask with stopcock. After the distillation, the receiving flask was filled with dry N₂ and sealed by closing the stopcock. 344.0 g of undecyl oxazoline was obtained, yield 70.5%. GC analysis indicated that the purity of the monomer was greater than 99.5%; the main impurity was unreacted undecyl cyanide.

¹H-NMR (TMS as internal standard): δ 4.20 (t, 2H, , δ 3.80 (t, 2H, , δ 2.25 (t, 2H, , δ 1.58 (p, 2H, , δ 1.30 (br, 16H, $-(\text{CH}_2)_8-$), δ 0.80 (t, 3H, $-\text{CH}_3$).

Synthesis of Decenyl Oxazoline (D)

The general procedure of References 11 and 12 was followed for the synthesis of decenyl oxazoline (Scheme 2). 91.62 g (1.5 mol) of ethanolamine was mixed with 92.2 g (0.5 mol) of undecylenic acid in a flask connected to a spinning band distillation column. The mixture was refluxed for 6 h at a pot temperature at about 180°C. 9.17 g water (theory: 9.00 g) and 61.57 g of excess ethanolamine (theory: 61.08



Scheme 2. Synthesis of decenyl oxazoline (**D**).

g) were distilled through the spinning band column. To the resulting yellowish hydroxy amide melt, 4.01 g (3.5 wt %) of ferrous chloride hydrate was added. The mixture was heated under reduced pressure (about 10 mm Hg). The reaction mixture temperature was raised to $\sim 200^\circ\text{C}$, and the distillate, which is a mixture of water and **D**, was collected as rapidly as possible.

The distillate was extracted five times with 100 mL portions of cyclohexane. The cyclohexane solution was stirred with anhydrous Na_2CO_3 and the cyclohexane was removed by rotary evaporator. 52.3 g (yield, 50.0%) of clear and colorless **D** with 99.0% purity (checked by GC) was obtained. To the above product, 3 g anhydrous Na_2CO_3 was added. Decenyl oxazoline was distilled at $100\text{--}101^\circ\text{C}/0.25 \tau$, lit.,¹⁰ bp = $89^\circ\text{C}/0.1 \tau$ through a spinning band distillation column.

¹H-NMR (TMS as internal standard): δ 5.88–5.65 (m, 1H, $\text{CH}_2=\text{CH}-$), δ 5.05–4.82 (m, 2H, $\text{CH}_2=\text{CH}-$), δ 4.20 (t, 2H, $-\text{C} \begin{array}{l} \diagup \text{N}-\text{CH}_2 \\ \diagdown \text{O}-\text{CH}_2 \end{array}$), δ 3.80 (t, 2H, $-\text{C} \begin{array}{l} \diagup \text{N}-\text{CH}_2 \\ \diagdown \text{O}-\text{CH}_2 \end{array}$), δ 2.25 (t, 2H, $-\text{CH}_2-\text{C} \begin{array}{l} \diagup \text{N} \\ \diagdown \text{O} \end{array}$), δ 2.10–1.85 (m, 2H, $\text{CH}_2=\text{CH}-\text{CH}_2-$), δ 1.58 (p, 2H, $-\text{CH}_2-\text{CH}-\text{C} \begin{array}{l} \diagup \text{N} \\ \diagdown \text{O} \end{array}$), δ 1.30 (br, 10H, $-(\text{CH}_2)_8-$).

ANAL. Calcd for $\text{C}_{13}\text{H}_{23}\text{NO}$: C 74.6%, H 11.0%, N 6.7%. Found: C 74.0%, H 10.0%, N 7.0%.

Synthesis of Nonyl Oxazoline (**N**)

Nonyl oxazoline (**N**, bp $106\text{--}107^\circ\text{C}/1.15 \tau$, lit.,¹³ bp = $77^\circ\text{C}/0.35 \tau$) was synthesized from 172.3 g of decanoic acid similarly using a cyclization temperature of $180\text{--}200^\circ\text{C}$, 139.5 g (yield, 70.8%).

¹H-NMR (TMS as internal standard): δ 4.20 (t, 2H, $-\text{C} \begin{array}{l} \diagup \text{N}-\text{CH}_2 \\ \diagdown \text{O}-\text{CH}_2 \end{array}$), δ 3.80 (t, 2H, $-\text{C} \begin{array}{l} \diagup \text{N}-\text{CH}_2 \\ \diagdown \text{O}-\text{CH}_2 \end{array}$), δ 2.24 (t, 2H, $-\text{CH}_2-\text{C} \begin{array}{l} \diagup \text{N} \\ \diagdown \text{O} \end{array}$), δ 1.55 (p, 2H, $-\text{CH}_2-\text{CH}_2-\text{C} \begin{array}{l} \diagup \text{N} \\ \diagdown \text{O} \end{array}$), δ 1.30 (br, 12H, $-(\text{CH}_2)_8-$), δ 0.85 (t, 3H, $-\text{CH}_3$).

Synthesis of 10-(Pentamethyl Disiloxanyl) Decyl Oxazoline (**Si**)

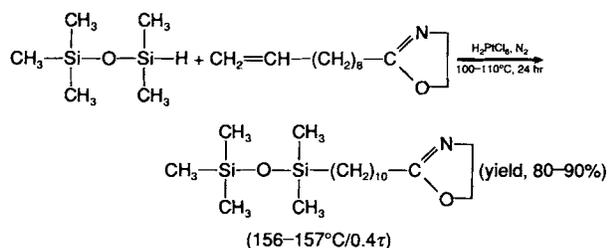
22.68 g (0.153 mol) of pentamethyldisiloxane was mixed with 21.29 g (0.102 mol) of decenyl oxazoline (**D**) in a three-necked flask (Scheme 3). 0.0500 g (0.102 mmol) of chloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) was dissolved in 2 mL of anhydrous ethanol and injected into the reaction mixture. It was refluxed ($100\text{--}110^\circ\text{C}$) under dry nitrogen for 24 h. The resulting solution was passed through a basic alumina (20 g) column with toluene as eluent. Slightly yellow product was obtained after removing toluene by rotary evaporator. It was then distilled from anhydrous Na_2CO_3 through a spinning band column at $156\text{--}157^\circ\text{C}/0.4 \tau$. 29.6 g of **Si** was obtained, yield, 81.3%.

¹H-NMR (CHCl_3 as internal standard): δ 4.22 (t, 2H, $-\text{C} \begin{array}{l} \diagup \text{N}-\text{CH}_2 \\ \diagdown \text{O}-\text{CH}_2 \end{array}$), δ 3.82 (t, 2H, $-\text{C} \begin{array}{l} \diagup \text{N}-\text{CH}_2 \\ \diagdown \text{O}-\text{CH}_2 \end{array}$), δ 2.27 (t, 2H, $-\text{CH}_2-\text{C} \begin{array}{l} \diagup \text{N} \\ \diagdown \text{O} \end{array}$), δ 1.65 (p, 2H, $-\text{CH}_2-\text{CH}_2-\text{C} \begin{array}{l} \diagup \text{N} \\ \diagdown \text{O} \end{array}$), δ 1.28 (br, 14H, $-(\text{CH}_2)_8-$), δ 0.50 (m, 2H, $-\text{O}-\text{Si}-\text{CH}_2-$), δ 0.07 (s, 6H, $-\text{O}-\text{Si}-\text{CH}_2-$), δ 0.04 (s, 9H, $-\text{O}-\text{Si}-\text{CH}_3$).

ANAL. Calcd for $\text{C}_{18}\text{H}_{39}\text{NO}_2\text{Si}_2$: C 60.5%, H 10.9%, N 3.9%, Si 15.7%. Found: C 59.4%, H 10.8%, N 3.9%, Si 16.0%.

General Procedure for Polymerization

Since all the polymerizations were carried out using the same procedure, only the copolymerization of U



Scheme 3. Synthesis of 10-(pentamethyl disiloxanyl) decyl oxazoline (**Si**).

and **Si** is described here as an example. The copolymerization was carried out in *o*-dichlorobenzene (ODCB) at 120°C with methyl *p*-nitrobenzenesulfonate (MeONs) as initiator (Table I). Four copolymers, **USi**(85/9), **USi**(74/20), **USi**(59/57) and **USi**(27/74), with nearly the same total degree of polymerization, 100, and different monomer ratios were synthesized. The numbers in parentheses show the calculated number of each of the monomer units in the copolymers. Freshly distilled **U** and **Si** with the weights and mole ratios shown in Table I were mixed with 5.0 mL ODCB in long necked 25 mL

flasks under dry nitrogen and capped with rubber septa. After the monomer solutions were heated to 120°C, 2.0 mL of freshly prepared ODCB/MeONs solutions were injected. The polymerization progress was followed by GPC. Both **U** and **Si** were consumed after 2 h. The polymerization was terminated by pouring the resulting viscous solutions into ethyl ether [for **USi**(85/9)], or ether/methanol mixture [for **USi**(74/20) and **USi**(59/57)], or methanol [for **USi**(27/74)]. After cooling, **USi**(85/9), **USi**(74/20), and **USi**(59/57) crystallized and formed gels. They were washed with methanol (4 × 20 mL) four times to remove ODCB. For **USi**(27/74), most of the solvent was removed by rotary evaporator (80–95°C). All the polymers were further dried in a vacuum oven (80–100°C/0.1 τ) for 24 h. The copolymers of **N** and **Si** and homopolymers of **U**, **N**, and **Si** were synthesized similarly. In the preparation of **USi**(543/521), which has the same composition as **USi**(59/57) but higher monomer to initiator ratio, much more dilute initiator solution (3.612×10^{-5} mol/g ODCB) was used; the polymerization was complete at 120–130°C after 7 h. All the purified polymers obtained were characterized by GPC, FT-IR, and ¹H-NMR.

Table I. Polymerization Conditions of Undecyl (**U**), Nonyl (**N**), and 10-(Pentamethyl disiloxanyl) Decyl (**Si**) Oxazolines

Polymer ^a	Initiator (mg)	ODCB (mL)	Monomer (g)		Moles per Initiator		Temperature (°C)	Time (h)
			U or N	Si	U or N	Si		
U (99)	109.00	10.0	11.10	0	98.8	0	120–130	3.5
USi (82/9)	65.10	7.0	5.54	1.20	82.0	9.4	120	2
USi (74/20)	73.30	7.0	5.47	2.32	73.6	19.7	120	2
USi (59/57)	60.00	7.0	3.60	5.48	59.2	56.9	120	2
USi (27/74)	66.70	7.0	1.79	7.89	26.5	73.7	120	2
USi (543/521)	7.84	3.5	4.24	6.72	542.6	521.0	120–130	7
Si (92)	43.40	7.0	0	6.59	0	92.3	120	2
N (100)	86.8	8.0	7.88	0.00	100	0	110–120	2
NSi (95/5)	86.8	8.0	7.49	0.71	95	5	110–120	2
NSi (90/10)	86.8	8.0	7.09	1.42	90	10	110–120	2
NSi (80/20)	86.8	8.0	6.31	2.86	80	20	110–120	2
NSi (70/30)	43.4	5.0	2.76	2.14	70	30	110–120	2
NSi (50/50)	43.4	5.0	1.97	3.57	50	50	110–120	2
NSi (35/65)	43.4	5.0	1.38	4.64	35	65	110–120	2
NSi (20/80)	43.4	5.0	0.79	5.71	20	80	110–120	2
NSi (8/83)	43.4	5.0	0.32	5.94	8	83	110–120	2

^a The names of **USi** (*m/n*) and **NSi** (*m/n*) are used to represent the **U/Si** and **N/Si** random copolymers, where *m* and *n* are the calculated numbers of monomers **U** or **N** and **Si** in the final polymers, respectively.

RESULTS AND DISCUSSION

Synthesis of Monomers

In the preparation of undecyl oxazoline, if a mole ratio of ethanolamine to undecyl cyanide was 1.1 : 1.0, after 1 day's refluxing all the ethanolamine was consumed or removed in the nitrogen gas stream, while more than 15% of undecyl cyanide remained unreacted. When the mole ratio was increased to 1.5 : 1.0, almost all the cyanide was transformed to undecyl oxazoline.

In the preparation of decenyl and nonyl oxazolines from the amides, ferrous chloride was used as the cyclodehydration catalyst.^{11,12} Temperatures above 180°C were needed to make the reaction go. Under such conditions, the oxazolines formed are not stable. Therefore, it is important to remove them as quickly as possible. When the pot temperature was higher than 230°C, the reaction was too fast for the resulting oxazoline to be removed because the evaporation of the water increased the system pressure. Over 70% yield of the oxazoline could be obtained when the temperature was kept below 200°C.

Molecular Weight Distributions

In order to study the effect of composition on the copolymer properties, we synthesized two series of copolymers over the whole composition range: (1) **U** and **Si** and (2) **N** and **Si**, with a total degree of polymerization of about 100. We did not use high vacuum techniques^{14,15} to run the polymerization. Instead, we prepared the reaction mixtures in a dry box filled with dry nitrogen and carefully kept the monomers, initiator, and the solvent away from air and moisture. The resulting polymers had quite narrow molecular weight distributions as demonstrated by their GPC traces (Fig. 1 for **U/Si** series of copolymers) and their polydispersities (Table II) calculated from the GPC traces. Their half widths ranged between 0.58 and 0.69 mL compared with 0.30 mL of ODCB. As we expected, the molecular weight of the copolymers calculated from polystyrene calibration curve were linearly proportional to the mole fraction of **Si** monomer (Table II and Fig. 2).

We also prepared a **U/Si** copolymer, **USi**(543/521), with total monomer to initiator ratio, *M/I*, of 1064. The resulting polymer had a quite broad molecular weight distribution (Fig. 3); its polydispersity index was 1.93. When its peak position is

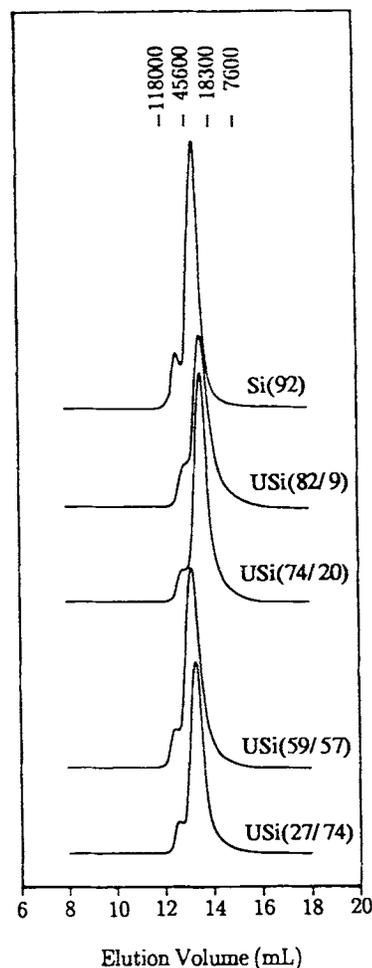


Figure 1. GPC curves of purified homopolymer of 10-(pentamethyl disiloxanyl) decyl oxazoline (**Si**) and a series of **U/Si** copolymers.

compared with that of **USi**(59/57), which has nearly the same composition, this polymer has an estimated degree of polymerization of only 374, much lower than the *M/I* ratio (1064). The reason for the low molecular weight and broad molecular weight distribution is that chain transfer to monomer occurs at high *M/I* ratios.^{16,17}

As we can see from Figure 1, all GPC traces have a small peak at twice the molecular weight of the main peak. We believe that the high molecular weight polymer was generated from the coupling of two lower molecular weight polymers. The mechanism of the coupling reaction is not clear. In fact, there was almost no coupled polymer after a short polymerization time with a monomer conversion of about 80% (curve 1 in Fig. 4). As the polymerization

Table II. Molecular Weights and Polydispersity Indexes of U/Si and N/Si Random Copolymers Based on Polystyrene Calibration

Polymer	Theoretical MW from M/I	\overline{M}_n	\overline{M}_w	M_{peak}	$\overline{M}_w/\overline{M}_n$
U (99)	22200	16400	19700	22300	1.20
USi (82/9)	21810	19700	23100	22800	1.17
USi (74/20)	23610	21200	23500	22800	1.11
USi (59/57)	33630	29500	33600	32600	1.14
USi (543/521)	308000	55300	107000	105000	1.93
USi (27/74)	32270	27300	30300	30000	1.11
Si (92)	32950	28900	31500	30000	1.09
N (100)	19700	18000	20500	19100	1.14
NSi (95/5)	20500	18600	21400	19900	1.14
NSi (90/10)	21300	19900	22900	22200	1.15
NSi (80/20)	22900	19700	22700	21800	1.17
NSi (70/30)	24500	20300	24100	23900	1.19
NSi (50/50)	27700	23400	28100	27400	1.20
NSi (35/65)	30100	25700	29800	28600	1.16
NSi (20/80)	32500	26500	31000	30000	1.17
NSi (8/83)	31210	25400	29200	28100	1.15

proceeded and monomer was consumed, the amount of coupled polymer increased. Even after the polymer was purified, a long heating time (120–140°C

for 24 h) under vacuum generated more coupled polymers as demonstrated by curve 3 in Figure 4.

Si(92), USi(25/74), and NSi(8/83) were sol-

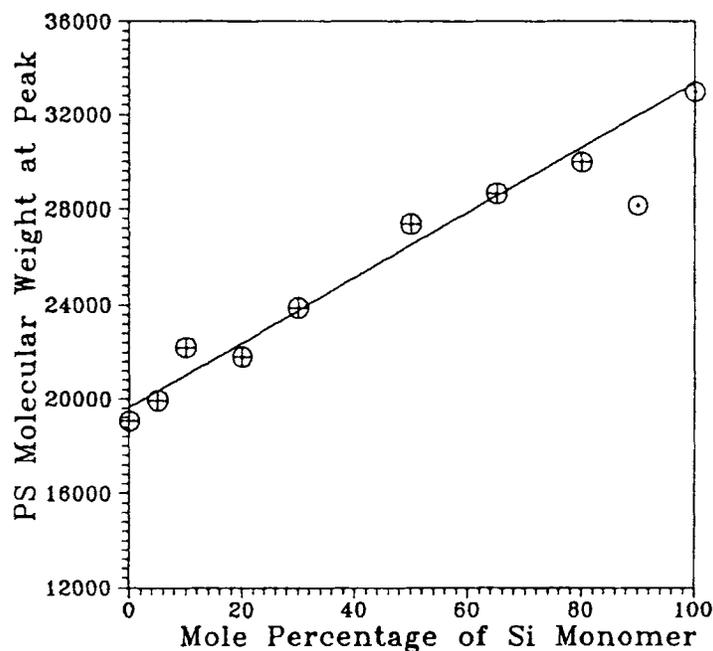


Figure 2. Variation of polystyrene molecular weights with the mole percentage of Si monomer for a series of N/Si copolymers based on their GPC trace peaks: (⊕) polymers with total degree of polymerization of ~ 100 ; (⊙) polymers with total degree of polymerization of ~ 91 .

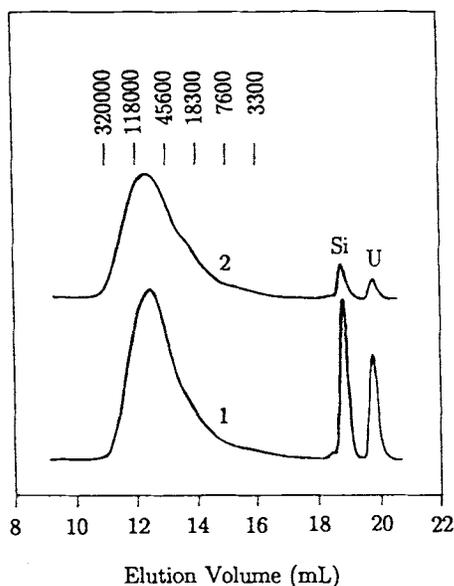


Figure 3. GPC curves of **USi**(543/521) copolymers. Polymerization at 120–130°C for (1) 4 h and (2) 7 h.

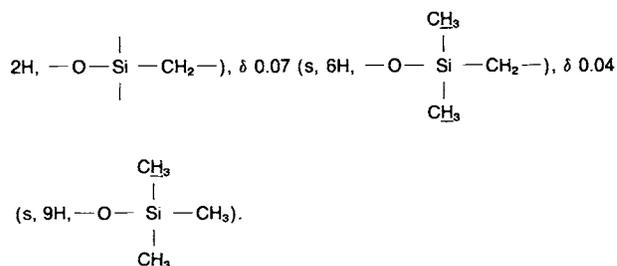
uble in most organic solvents. At low temperature, they precipitated as oils from methanol. It was difficult to remove all the ODCB by washing them with methanol. They were dried at 100–115°C under vacuum (0.1 τ). They are soft and transparent gel-like solids at room temperature. Heating them at 140–150°C for 24 h under vacuum resulted in their cross-linking; they could no longer be dissolved in any solvent. While we are not certain, a possible explanation of the crosslinking could be silyloxy exchange reactions, with the loss of hexamethyldisiloxane and the formation of a —Si—O—Si— crosslink.

Copolymer Composition and Randomness

The polymers were characterized by FT-IR and $^1\text{H-NMR}$. Typical $^1\text{H-NMR}$ [**USi**(74/20)] and FT-IR [**USi**(59/57)] spectra are shown in Figures 5 and 6.

$^1\text{H-NMR}$ of **USi**(59/57) (CHCl_3 as reference): δ 3.80–3.10 (br, —N—CH₂—CH₂—), δ 3.05 (s, CH₃—N < of Chain head), δ 2.45–2.05

(br, $\begin{array}{c} \text{O} \\ || \\ \text{—C—CH}_2\text{—} \end{array}$), δ 1.75–1.42 (br, $\begin{array}{c} \text{O} \\ || \\ \text{—C—CH}_2\text{—CH}_2\text{—} \end{array}$), δ 1.42–1.02 (br, —(CH₂)_n—), δ 0.85 (t, CH₃—CH₂—), δ 0.50 (m,



FT-IR of **USi**(59/57) (KBr, cm^{-1}): 2958(s), 2924(vs), 2853(s), 1647(vs), 1467(s), 1431(s), 1315(w), 1254(s), 1185(s), 1161(w), 1060(vs), 843(vs), 805(w), 753(w), 721(w), 625(w).

Monomer **Si** and monomers **U** and **N** are all oxazolines with long alkyl tails attached to the 2-carbon of the oxazoline ring. **Si**, however, has a pentamethyl disiloxanyl group at the far end of the polymethylene tail. These monomers should have the same reactivity since their structural differences are ten atoms or more away from the reactive site.

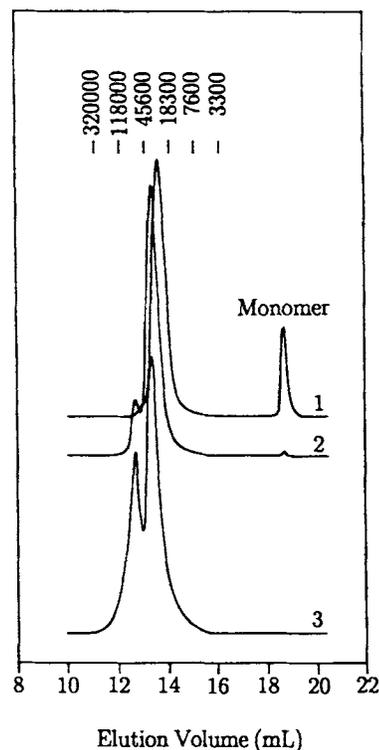


Figure 4. GPC curves of **Si**(92) homopolymers: (1) polymerization at 120°C for 0.5 h, (2) polymerization at 120°C for 1.5 h, (3) purified polymer, dried at 120–140°C for 24 h under vacuum (0.1 τ).

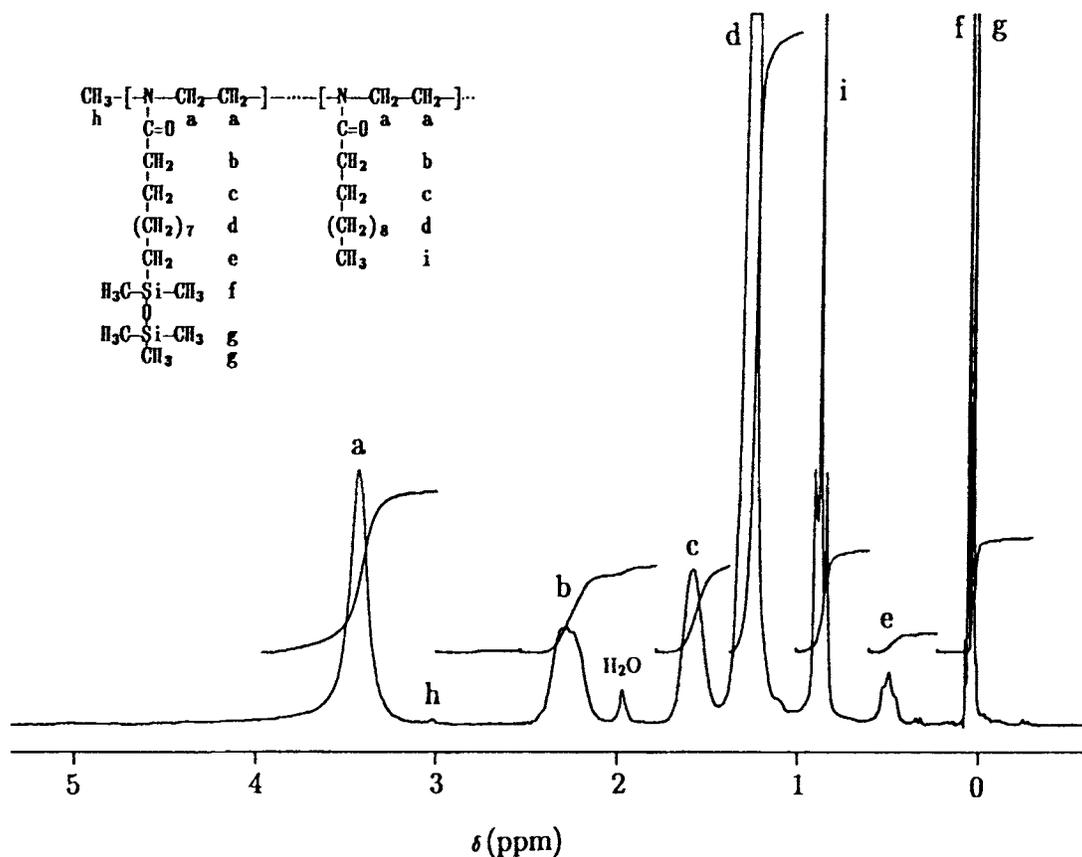


Figure 5. 200 MHz NMR spectrum of USi(74/20) copolymer in CDCl_3 solution with CHCl_3 as internal reference.

The copolymerization of **U** with **Si** or **N** with **Si** should be random. This hypothesis is confirmed by the fact that both monomers were consumed at the same rate during the copolymerization of **U** and **Si** (Fig. 3). The ratio of the two monomer peaks on GPC traces, $A_{\text{Si}}/A_{\text{U}}$, was 1.57 after 4 h polymerization at 120–130°C, and 1.64 after 7 h. Since the concentration ratio of the two monomers was constant, the polymerization rates of the two monomers were the same, which results in random copolymers.

The relative peak areas of the methyl (i, $\delta = 0.85$) in the undecyl group and the methylenyl (e, $\delta = 0.50$) or methyl (f + g, $\delta = 0.07, 0.04$) in the ^1H -NMR spectra were used to calculate the copolymer compositions. The monomer ratios calculated from the NMR spectra were in reasonably good agreement with the monomer ratios given in Table I (Table III).

The homopolymer of **Si**, **Si(92)**, was analyzed by element analysis, which also confirms the correct element composition of the **Si** monomer.

ANAL. Calcd. for $(\text{C}_{18}\text{H}_{39}\text{NO}_2\text{Si}_2)_{92}$: C 60.5%, H 10.9%, N 3.9%, O 9.0%, Si 15.7%. Found: C 60.3%, H 10.9%, N 3.8%, Si 16.2%.

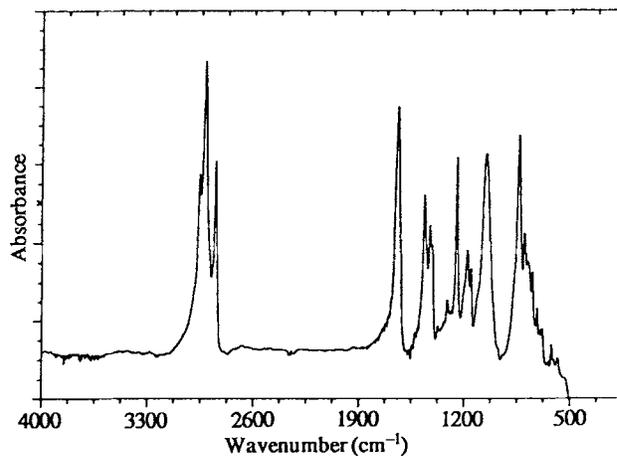


Figure 6. FT-IR spectrum of USi(59/57) copolymer (KBr).

Table III. Monomer Unit Ratios in U/Si and N/Si Random Copolymers Determined by ¹H-NMR

Polymer	Intensity (Unit)			Monomer Unit Ratio (U/Si or N/Si)		
	i (-CH ₃)	e (-CH ₂ -)	f + g (Si-CH ₃)	Calcd from i/e	Calcd from i/(f + g)	Theory ^a
USi (82/9)	35.0	2.7	17.3	82.0/9.5	82.0/8.1	82.0/9.4
USi (74/20)	27.5	4.8	30.6	73.6/19.3	73.6/17.0	73.6/19.7
USi (59/57)	18.0	10.7	73.0	59.2/53.3	59.2/48.3	59.2/56.9
USi (27/74)	13.7	24.0	161.0	26.5/69.4	26.5/62.1	26.5/73.7
NSi (95/5)	34.0	1.4	9.0	95.0/5.9	95.0/5.0	95.0/5.0
NSi (90/10)	32.0	2.8	18.0	90.0/11.8	90.0/10.1	90.0/10.0
NSi (80/20)	29.5	4.5	33.5	80.0/18.3	80.0/18.1	80.0/20.0
NSi (70/30)	24.0	7.0	47.0	70.0/30.6	70.0/27.4	70.0/30.0
NSi (50/50)	20.0	13.0	85.0	50.0/48.8	50.0/42.5	50.0/50.0
NSi (35/65)	14.0	14.5	102.0	35.0/54.4	35.0/54.4	35.0/51.0
NSi (20/80)	7.5	20.0	139.0	20.0/80.0	20.0/74.2	20.0/80.0
NSi (8/83)	3.2	21.0	145.0	9.0/88.6	9.0/81.6	9.0/91.0

^a Values calculated from the monomer ratios in Table I. The number of monomer units of the alkyl monomer, U or N, was assumed to be the calculated value.

SUMMARY AND CONCLUSIONS

10-(Pentamethyl disiloxanyl) decyl oxazoline (Si) was synthesized from decenyl oxazoline and pentamethyldisiloxane. Si copolymerizes randomly with either undecyl (U) or nonyl (N) oxazolines. Two series of random copolymers, U/Si and N/Si, were made with a total degree of polymerization of 100 and narrow molecular weight distribution.

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