Poly(N-Acylethlenimine) 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-acylethlenimine) 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-acylethlenimines) • 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.5 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-acylethlenimine)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 \(-\text{CH}_2\text{O}-(\text{CH}_3)_2\text{SiO}-(\text{CH}_3)_3\) 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
angle X-ray diffraction study, and polymer crystal-line structures are given in Part II 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, Brockman 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 an 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. The uncorrected number and weight average molecular weights were calculated using $M_n = \Sigma H_i / (\Sigma H_i / M_i)$ and $M_w = \Sigma H_i M_i / \Sigma H_i$, where $H_i$ is the height of the RI 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.

\[
\text{C}_{11}\text{H}_{20}\text{CN} + \text{NH}_2\text{CH}_2\text{CH}_2\text{OH} \xrightarrow{\text{C}_{11}\text{H}_{20}\text{CN}} \text{C}_1\text{H}_{25}\text{CO} + \text{NH}_3
\]

Scheme 1. Synthesis of undecyl oxazoline (U).

Synthesis of Undecyl Oxazoline (U)

Undecyl oxazoline was synthesized from undecyl cyanide (Scheme 1). Into a 1000 mL three-necked round bottom flask were added cadmium acetate (Cd(OC(O))), 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 torr. 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.

\[
\delta 4.20 (1H, -C\text{H}_3), \delta 3.80 (1H, -CH_2\text{COSO}_2), \delta 1.30 (br, 16H, -(\text{CH}_2)_n), \delta 0.80 (1H, CH_2)
\]

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 g)
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CH₂=CH-(CH₃)₅-C-OH + NH₂CH₂CH₂OH → \( \text{N-CH₂-} \)

\( \text{CH₃=CH-(CH₅)₅-C} \)OH + H₂O

\( \text{CH₂=CH-(CH₅)₅-C} \)O

(yield ~50%, 100-101°C/0.25 atm)

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

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 (H₂PtCl₆ · 6H₂O) was dissolved in 2 mL of anhydrous ethanol and injected into the reaction mixture. It was refluxed (100-110°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 Na₂CO₃ through a spinning band distillation column at 156-157°C/0.4 atm. 29.6 g of Si was obtained, yield, 81.3%.

\[ \text{H-NMR (CHCl₃ as internal standard): } \delta 4.22 \text{ (t, } 2H, -C\text{=}CH₂), \delta 3.82 \text{ (t, } 2H, -CH₂=CH₂), \delta 2.27 \text{ (t, } 2H, -CH₂=CH₂), \delta 1.28 \text{ (br, } 14H, -(CH₂)₄-), \delta 0.07 \text{ (s, } 6H, -O-Si-CH₃), \delta 0.04 \text{ (s, } 9H, -O-Si-CH₃). \]

ANAL. Caled for C₁₃H₃₉NO₂Si₂: 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...
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 (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 purified polymers obtained were characterized by GPC, FT-IR, and 1H-NMR.

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

| Polymer* | Initiator (mg) | ODCB (mL) | Monomer (g) | Moles per Initiator | Temperature (°C) | Time (h) |
|----------|----------------|-----------|-------------|---------------------|------------------|----------|
| U (99)   | 109.00         | 10.0      | 11.10       | 1.0                 | 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       | 3.69        | 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   |

*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. 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 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 I) 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 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.

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 | $\bar{M}_n$ | $\bar{M}_w$ | $M_{\text{peak}}$ | $M_w/M_n$ |
|--------------------------|-------------------------|-------------|-------------|------------------|-----------|
| 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.

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).

Copolymer Composition and Randomness

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

1H-NMR of USi(59/57) (CHCl₃ 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. -C—CH₂—), δ 1.75–1.42(br, -C—CH₂—CH₂—), δ 1.42–1.02 (br, -(CH₃)₃—), δ 0.85 (t, CH₃—CH₂—), δ 0.50 (m, CH₃)

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.

Poly(N-acylethlenimine) Copolymers. I

Polymerization at 120-130°C for (1) 4 h and (2) 7 h.

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.
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, $A_u/A_{si}$, 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 $^1$H-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.

**Figure 5.** 200 MHz NMR spectrum of USi(74/20) copolymer in CDCl$_3$ solution with CHCl$_3$ as internal reference.

**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 'H-NMR

| Polymer | i (−CH₃) | e (−CH₂−) | f + g (Si−CH₃) | Calcd from i/e | Calcd from i/(f + g) | Theory* |
|---------|----------|-----------|----------------|---------------|---------------------|--------|
| 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 | 80.0/30.6 | 80.0/27.4 | 80.0/30.0 |
| NSi (70/30) | 24.0 | 7.0 | 47.0 | 70.0/48.8 | 50.0/42.5 | 50.0/50.0 |
| NSi (60/50) | 20.0 | 13.0 | 85.0 | 60.0/54.4 | 35.0/54.4 | 35.0/51.0 |
| NSi (50/50) | 14.0 | 14.5 | 102.0 | 50.0/54.4 | 20.0/74.2 | 20.0/80.0 |
| NSi (35/65) | 7.5 | 20.0 | 139.0 | 20.0/80.0 | 20.0/74.2 | 20.0/80.0 |
| NSi (20/80) | 3.2 | 21.0 | 145.0 | 9.0/88.6 | 9.0/81.6 | 9.0/91.0 |

* 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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