

## **Synthesis of polysiloxane-polyoxazoline graft copolymer by hydrosilylation reaction**

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### Summary

Polysiloxane-poly(N-acetyleneimine) graft copolymer of well-defined structure and composition was prepared by means of hydrosilylation reaction. Allyl-terminated poly(N-acetyleneimine) was synthesized by ring-opening polymerization of 2-methyl-2-oxazoline with an initiator of allyl tosylate. Si-H containing polysiloxane was prepared by equilibrium ring-opening polymerization of cyclic siloxane oligomers catalyzed by trifluoroacetic acid. The hydrosilylation reaction between these two polymers produced tailor-made graft copolymer, which showed the characteristic solubilities in organic solvents.

### Introduction

We have studied the ring-opening polymerization of 2-methyl-2-oxazoline for these several years (1). The resulting poly(N-acetyleneimine) (PAEI) can be regarded as a polymer homologue of N,N-dimethylacetamide (DMAc). It is well known that DMAc shows unique characteristics of high hydrophilicity and solubilizing organic polymers. Thus, PAEI showed strongly hydrophilic and well compatible with organic commodity polymers such as poly(vinyl chloride). By using these properties, PAEI was employed as a hydrophilic component of nonionic surfactants (2) or anti-electrostatic agent (3).

On the other hand, polysiloxanes and their copolymers have characteristic properties such as elastomeric behavior (4), gas permeability (5), bio-compatibility (6), thermal-, UV- and oxidative stabilities, low surface energy, good weatherability and electrical properties.

The combination between these two contrastive polymers may produce a new polymeric material. As to block copolymers of these two polymer segments, Imai et al. recently reported the polymerization of 2-methyl-2-oxazoline initiated by polysiloxane tosylate (7).

Previously, we have reported the synthesis of polysiloxane-poly(methyl methacrylate) and polysiloxane-polystyrene graft copolymers of well-defined structure and composition by means of hydrosilylation reactions (8). This hydrosilylation method can be used for various combinations of backbones and branches in graft copolymers of polysiloxanes. Here we wish to report the synthesis of graft copolymers consisting of polysiloxane and PAEI by using hydrosilylation reaction between Si-H containing polysiloxane and allyl-terminated PAEI.

### Experimental

#### Materials and instruments

Allyl tosylate (1) was prepared according to the method reported

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previously (9). Octamethylcyclotetrasiloxane ( $D_4$ ), 1,3,5,7-tetramethylcyclotetrasiloxane ( $H_4$ ) and hexamethyldisiloxane (HMDS) are commercial products, which were used without further purification. 2-Methyl-2-oxazoline (2), trifluoroacetic acid and all solvents were dried and distilled under nitrogen atmosphere.

IR and  $^1H$ -NMR spectra were obtained with a Hitachi 260-50, and a Hitachi R-600 (60 MHz), respectively. GPC was carried out on a JASCO Trirotor (Shodex AC-803) after calibration with standard polystyrene samples. Molecular weight by VPO was determined in chloroform using a Corona-117 instrument.

#### Allyl tosylate (1)

To a mixture of allyl alcohol (14.7 g, 0.25 mol) and tosyl chloride (27.1 g, 0.14 mol) in a 300 ml three-necked flask equipped with a reflux condenser and a dropping funnel, 5N aqueous NaOH (80 ml) was added below 15 °C under nitrogen atmosphere. Additional tosyl chloride (27.2 g, 0.14 mol) and 5N NaOHaq (80 ml) were added consecutively to the reaction mixture to produce a white precipitate after 1 hour stirring. An organic layer was extracted with petroleum ether, washed by 10% NaOHaq and then dried over  $K_2CO_3$ . Evaporation of solvent produced liquid allyl tosylate (1). The purity of 1 was higher than 95% by  $^1H$ -NMR analysis.  $^1H$ -NMR( $CDCl_3$ ),  $\delta$  ppm 7.51 (4H), 5.63 (1H), 5.34 (1H), 5.12 (1H), 4.51 (2H), 2.41 (s, 3H). 1 is pure enough for the following ring-opening polymerization of 2 as an initiator.

#### Allyl-terminated PAEI (3)

In a typical procedure, a mixture of 2-methyl-2-oxazoline (2) (2.25 g, 26.4 mmol), allyl tosylate (1) (1.24 g, 5.85 mmol) and acetonitrile (10 ml) was placed in a 50 ml flask with a reflux condenser, and heated at 60 °C for 5.5 hours under nitrogen atmosphere. The resulting allyl-terminated PAEI (2) was isolated by precipitation in diethyl ether, and purified by reprecipitation and drying *in vacuo*. Yield: 2.52 g (72%). The degree of polymerization was 4.5 by  $^1H$ -NMR analysis.

#### Si-H containing polysiloxane (4)

A mixture of  $D_4$  (20.1 g, 67.6 mmol),  $H_4$  (1.30 g, 5.41 mmol), HMDS (0.38 g, 2.41 mmol) and trifluoroacetic acid (1.60 g, 16.3 mmol) was placed in a 100 ml flask with a reflux condenser, and heated at 70 °C for 35 hours. The resulting viscous liquid was dissolved in dichloromethane (50 ml) and washed with distilled water repeatedly to remove the acid catalyst. Volatile cyclic siloxane oligomers were removed by washing with methanol followed by evaporation under reduced pressure. The yield of viscous colorless liquid (4) was 16.4 g (75%).

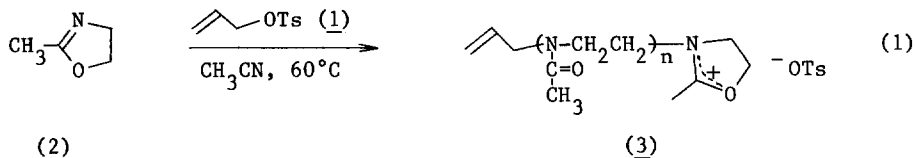
The titration of Si-H bonds in 4 was carried out as follows (10). 4 was reacted with mercuric acetate in  $CHCl_3/MeOH$  (1/1 by vol.). The evolved acetic acid was titrated with a MeOH solution of KOH by using phenolphthalein as an indicator.

#### Graft copolymer (5)

In a 50 ml flask equipped with a reflux condenser and a dropping funnel, 3 (degree of polymerization by  $^1H$ -NMR; 4.5, 0.51 g, 0.85 mmol) in dichloromethane (3 ml) and chloroplatinic acid catalyst ( $4.05 \times 10^{-4}$  mmol) were stirred at room temperature for 1 hour under nitrogen atmosphere. Then, 4 ( $M_n$  by VPO; 9430, Si-H (wt %);  $9.5 \times 10^{-2}$ , 1.02 g) in dichloromethane (4 ml) was added slowly from a dropping funnel over a period of 1.5 hours. After complete addition, the reaction mixture was refluxed for

12.5 hours. The graft copolymer (5) was obtained by evaporating the solvent and extracting with diethyl ether and purified by reprecipitation from methanol into water.

### Results and Discussion



Poly(N-acetylethylenimine) (PAEI) bearing an allyl group at one end was prepared according to eq (1). Allyl tosylate (1) was prepared from allyl alcohol and tosyl chloride. Without distillation, the obtained 1 has enough purity as the initiator for ring-opening polymerization of 2-methyl-2-oxazoline. Figure 1 shows  $^1\text{H-NMR}$  spectrum of allyl-terminated PAEI (3). From the integral ratio of vinyl protons ( $\delta$  5.26 and 5.61 ppm, 3H) to methyl protons ( $\delta$  2.09, 2.37 and 2.47 ppm,  $(3n+3+3)\text{H}$ ), the molecular weight of 3 can be calculated. This value was close to that calculated from feed ratio of the initiator (1) to the monomer (2). In other words, allyl group was effectively introduced at one end of the resulting polymer (3). In Figure 1, the peaks due to oxazolinium tosylate ( $\delta$  2.37, 2.47, 4.00, 4.43 and 7.45 ppm) at the propagating end were also observed. The integral ratio of vinyl protons to aromatic protons of tosylate anion ( $\delta$  7.45 ppm, 4H) was nearly 3 to 4. This result strongly indicates the

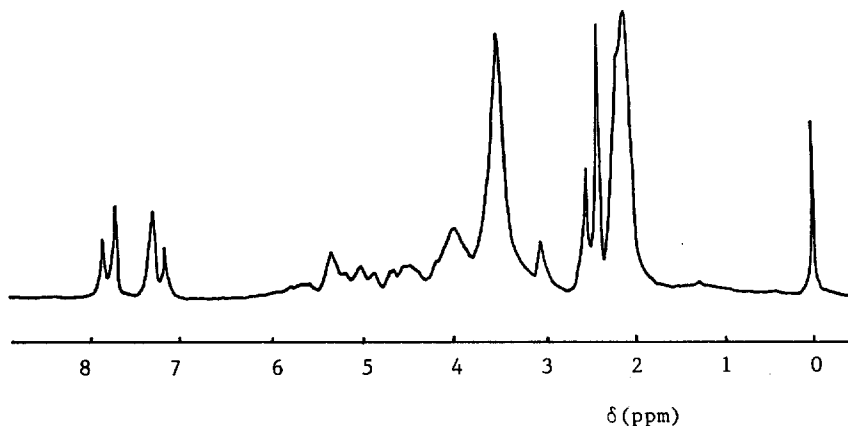


Figure 1.  $^1\text{H-NMR}$  spectrum of allyl-terminated PAEI (3, Run 3 in Table I) in  $\text{CDCl}_3$ .

polymerization proceeds in living mechanism and the active propagating species (oxazolinium) were remained at  $\omega$ -position even after the isolation of 3. The results of preparation of 3 are summarized in Table I. In every case, the conversion of 2 was almost 100 %. The molecular weights of 3 were easily controlled by the feed ratio of 1 to 2.

Table I. Preparation of allyl-terminated PAEI (3)

Run	$\frac{[2]}{[1]}$ a)	Time (h)	Temp (°C)	<u>3</u>		
				Yield (%) <sup>b</sup>	D.P. <sup>c</sup>	$\bar{M}_n$ <sup>d</sup>
1	5.1	4.5	60	70	4.9	630
2	4.7	5.0	60	72	5.1	650
3	4.5	5.5	60	72	4.5	590
4	4.6	9.5	80	74	4.3	570
5	10.0	5.0	70	72	9.3	1000
6	2.9	5.5	60	74	3.5	510

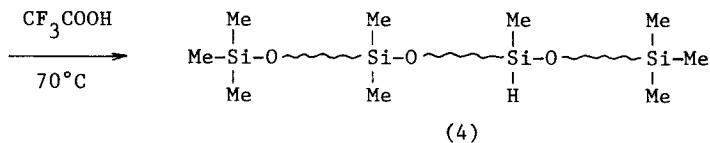
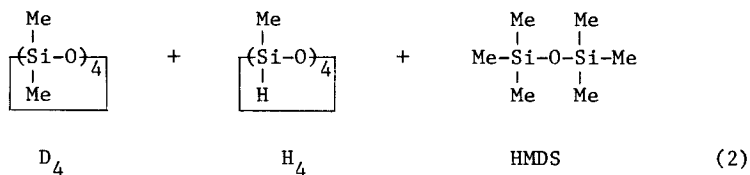
a) Feed ratio of 2 to 1.

b) Isolated yield after reprecipitation.

c) Degree of polymerization was determined by  $^1\text{H-NMR}$  analysis.

d) Calculated from  $^1\text{H-NMR}$ .

Polysiloxanes containing Si-H bonds were prepared by acid-catalyzed equilibrium copolymerization of two cyclic siloxane oligomers ( $\text{D}_4$  and  $\text{H}_4$ ) (eq 2). Hexamethyldisiloxane (HMDS) was used as an end-blocker and trimethylsilyl groups were introduced at both ends ( $\alpha$ - and  $\omega$ -positions) of 4. In this equilibrium reaction, trifluoroacetic acid was used as a catalyst. Base catalyst can not be used because Si-H bonds are relatively sensitive to bases. The resulting Si-H containing polysiloxane (4) is soluble in common organic solvents such as benzene, dichloromethane, chloroform and THF. According to the previous work on the thermodynamic equilibration of



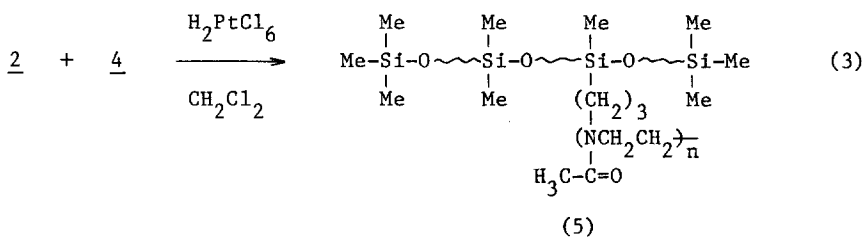
cyclic siloxane oligomers, the "re-distribution" of  $\text{D}_4$  and  $\text{H}_4$  cannot be avoided under the present reaction conditions (12). Thus, the distribution

of Si-H groups might be random in 4. Table II summarizes the results of preparation of 4. Of these two polysiloxanes in Table II, one sample of polymer with the molecular weight 9,430 (Run 1) was used for the following hydrosilylation to produce graft copolymer.

Table II. Preparation of polysiloxane (4)

Run	$[D_4]_o$	$[D_4]_o + [H_4]_o$	Yield (%)	<u>4</u>			
	$[H_4]_o$	$[HMDS]_o$		$\bar{M}_n \times 10^{-3}$		wt%(Si-H) $\times 10^2$	
				calc.	VPO	calc.	tit.
1	12.5	30.3	75	9.03	9.43	10.0	9.5
2	2.4	15.8	65	4.60	3.99	40.6	38.5

The hydrosilylation reaction of 4 (Run 1 in Table II) with 2 was carried out as shown in eq (3). The reaction in dichloromethane proceeded in a homogeneous system. The reaction can be monitored by IR spectroscopy, in which  $\nu$ Si-H absorption at  $2150 \text{ cm}^{-1}$  disappeared completely after the hydrosilylation reaction. The yield of 4 was relatively low (~10%) due to a large loss of graft copolymers during the repeated reprecipitations. The oxazolinium end group of PAEI segment in 5 was allowed to be hydrolyzed to form hydroxyl group during the reprecipitation of the resulting graft copolymer.

Table III. Solubilities of 3, 4 and 5

	<u>3</u>	<u>4</u>	<u>5</u>
n-Hexane	x	○	○
Cyclohexane	x	○	○
Benzene	x	○	○
MeOH	○	x	○

○ : Soluble

x : Insoluble

Table III shows the solubilities of 5 together with those of 3 and 4 for comparison. As a typical sample, the graft copolymer prepared from 3 (Run 3 in Table I) and 4 (Run 1 in Table II) was picked up for the examination of solubility. Compared with the solubilities of homopolymers (3 and 4), 5 was characteristically soluble both in methanol and hydrocarbons such as n-hexane, cyclohexane and benzene.

The studies on the properties and applications of these graft copolymers are now under investigation and will be reported in the new future.

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