

# Redox Initiation System of Ceric Salt and $\alpha,\omega$ -Dihydroxy Poly(dimethylsiloxane)s for Vinyl Polymerization

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**ABSTRACT:** The redox system of ceric salt and  $\alpha,\omega$ -dihydroxy poly(dimethylsiloxane) is used to polymerize vinyl monomers such as acrylonitrile and styrene to produce block copolymers. The concentration and type of  $\alpha,\omega$ -dihydroxy poly(dimethylsiloxane) affects the yield and the molecular weight of the copolymers. The copolymers have about 20°C lower glass-transition temperatures and much higher contact

angle values than of the corresponding homopolymer of vinyl monomers, although the weight percent of  $\alpha,\omega$ -dihydroxy poly(dimethylsiloxane) of the copolymers is in the range of 1–2%. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 2112–2116, 2006

**Key words:** silicones; block copolymers; initiators; radical polymerization

## INTRODUCTION

Poly(dimethylsiloxane)-*block*-polystyrene copolymers (PDMS-*b*-PS) have been recently studied for their potential technological importance as thermoplastic elastomers and for their unusual properties. Di-, tri-, and multiblock siloxane containing copolymers have been prepared by different synthetic methods. Sequential anionic polymerization of styrene with hexamethyl cyclotrisiloxane (D<sub>3</sub>) using an alkyl lithium initiator has been described previously.<sup>1</sup> In general, anionic polymerization has some limitations. Moreover, the reaction conditions call for the strict exclusion of impurities such as moisture, O<sub>2</sub>, and CO<sub>2</sub> and the use of highly purified solvents and monomers. Alternative methods such as nitroxide-mediated radical polymerization,<sup>2</sup> polyaddition of  $\alpha,\omega$ -dihydroxy terminated polysiloxane to  $\alpha,\omega$ -divinyl terminated polymers,<sup>3</sup> and cationic polymerization systems<sup>4</sup> have been used to produce block copolymers of PDMS.

We previously studied the polymerization of vinyl monomers with a redox initiation system of ceric (Ce<sup>+4</sup>) salt and various reducing agents. The reducing agents were ketonic resins,<sup>5</sup> cellulose derivatives,<sup>6</sup> amino methylene phosphonic acids,<sup>7</sup> ethoxylated nonyl phenols,<sup>8</sup> and poly(ethylene glycol).<sup>9</sup> The produced polymers had chain ends of reducing agent moieties that impart the physical properties of the polymers. For example, polyacrylonitriles (PANs) with ethoxylated nonyl phenol chain ends have much better water absorption than PAN.<sup>8</sup>

The redox reaction between Ce<sup>+4</sup> salt and the reducing agent produces a radical center that initiates the polymerization of vinyl monomer. Water is the preferred media for this redox polymerization system, and the strict purification of the monomers and the exclusion of impurities are not desired. This method has also been used to produce soluble conductive copolymers of ketonic resin–polypyrrole<sup>10</sup> and PDMS-*block*-polypyrrole copolymers.<sup>11</sup>

In this work, the redox initiation system of Ce<sup>+4</sup> salt and  $\alpha,\omega$ -dihydroxy poly(dimethylsiloxane) [PDMS] was used to polymerize vinyl monomers such as acrylonitrile and styrene to produce PDMS-*block*-PAN (PDMS-*b*-PAN) and PDMS-*b*-PS copolymers, respectively.

## EXPERIMENTAL

### Materials

Ceric ammonium nitrate (BDH) was oven dried at 105°C for 1 h and stored in a desiccator. A calculated amount was dissolved in 1M HNO<sub>3</sub> solution to prepare a 0.2M stock solution that was stored in a refrigerator. Acrylonitrile was used as received. Styrene was freed from inhibitors by shaking with a 10% NaOH solution.  $\alpha,\omega$ -Dihydroxy poly(dimethylsiloxane)s [PDMS]: (tegomers H-Si 2111 and H-Si 2311) were the products of Goldschmidt Chemical Corporation. The molecular weights of the H-Si 2111 and H-Si 2311 tegomers are 950 ± 80 and 2500 ± 250, respectively.

### Instruments

The <sup>1</sup>H-NMR spectra of PDMS-*b*-PS and PDMS-*b*-PAN copolymers were obtained from their respective CCl<sub>4</sub> and dimethylformamide (DMF) solutions by using a

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Bruker AC spectrometer (200 MHz). Tetramethylsilane was not added to the solutions. The IR spectra were recorded on a Jasco FTIR 5300 Fourier transform IR (FTIR) spectrometer. The glass-transition temperatures ( $T_g$ ) of the copolymers were determined with a DSC-6 under a nitrogen atmosphere. The heating and cooling rates were 10°C/min. Samples were heated from 30 to 140°C and then cooled to 30°C. This cycle was repeated 3 times and the  $T_g$  was determined from the last cycle.

### Contact angle measurements

The contact angle measurements of the copolymer films were carried out on a Kernco model GIII contact angle meter at room temperature using distilled water. The measurements were made immediately at the beginning, after 10 s, and finally after 3 min for water droplets on the films prepared by casting from a 1% (w/v) polymer solution in the appropriate solvent (DMF for PDMS-*b*-PAN and toluene for PDMS-*b*-PS copolymers).

### Polymerization procedures

#### Preparation of PDMS-*b*-PAN

$\alpha,\omega$ -Dihydroxy poly(dimethylsiloxane) and acrylonitrile were added to water with stirring. The contents of the flask were flushed with oxygen-free nitrogen. The ceric ammonium nitrate stock solution was then added dropwise to the reaction mixture in about 20 min while stirring under a nitrogen atmosphere at 20°C. Water-insoluble copolymer precipitated during the polymerization. After about 2 h the powdery product was filtered, washed several times with water, washed with methanol, and dried under a vacuum at 60°C. The copolymer was freed from any residual  $\alpha,\omega$ -dihydroxy poly(dimethylsiloxane) by extracting with 2-butanone in a Soxhlet extractor.

#### Preparation of PDMS-*b*-PS

$\alpha,\omega$ -Dihydroxy poly(dimethylsiloxane), styrene, and a drop of sodium dodecyl benzene sulfonate were added to water with stirring, and an emulsion was formed. The contents of the flask were flushed with oxygen-free nitrogen. The cerium ammonium nitrate stock solution was then added dropwise to the emulsified reaction mixture over about 20 min while stirring under a nitrogen atmosphere at 20°C. The copolymer was recovered and purified by dissolving in 2-butanone and precipitating into methanol.

### Blank experiments

In the absence of  $\alpha,\omega$ -dihydroxy poly(dimethylsiloxane), no polymer was formed in 2 h at 20°C by carrying out similar experiments under comparable conditions using the vinyl monomers and  $Ce^{+4}$  salt.

### Molecular weight

The solution viscosities ( $[\eta]$ ) of PDMS-*b*-PAN copolymers in DMF at 25°C and PDMS-*b*-PS copolymers in toluene at 30°C were measured using a Cannon-Fenske capillary viscometer. Their molecular weights were calculated from single-point values using the following equations<sup>12-14</sup>:

$$[\eta] = (\eta_{sp}/c)/(1 + 0.28 \times \eta_{sp})$$

$$[\eta] = 2.43 \times 10^{-4} \times M_v^{0.75}$$

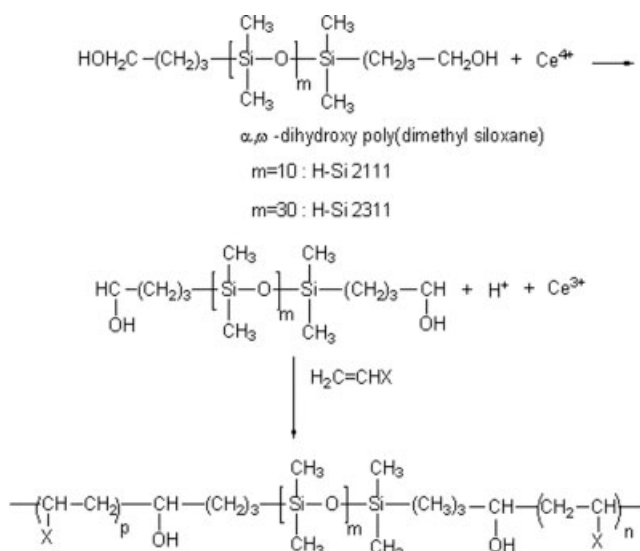
for PDMS-*b*-PAN

$$[\eta] = 1.1 \times 10^{-4} \times M_n^{0.725}$$

for PDMS-*b*-PS, where  $M_v$  and  $M_n$  are the viscosity-average and number-average molecular weights, respectively. The  $M_v$  values of these copolymers are obviously approximate values because the preceding relations were given for pure PAN and PS.

## RESULTS AND DISCUSSION

Polysiloxanes have high surface activity and low solubility parameters. These properties lead to the thermodynamic incompatibility of polysiloxanes with most organic polymers. Siloxane containing copolymers are



**Scheme 1** The redox reaction between  $Ce^{+4}$  salt and the hydroxyl groups of  $\alpha,\omega$ -dihydroxy poly(dimethylsiloxane), and formation of block copolymers.

TABLE I  
Synthesis of PDMS-*b*-PAN and PDMS-*b*-PS Copolymers with Redox System  
of  $\alpha,\omega$ -Dihydroxy Poly(dimethylsiloxane)/Ce<sup>+4</sup> at 20°C for 2 h

No.	Type of PDMS (mmol/IL)	Ce <sup>+4</sup> (mmol/L)	Acrylonitrile (mol/L)	Polymerization solvent	Yield (%)	Mol. wt
1	H-Si 2111 (4.7)	5	0.7	Water	80	595,000
2	H-Si 2111 (1.4)	5.2	0.7	Water	24	376,000
3	H-Si 2111 (8.0)	10	1.2	Acetone/water (8 : 1)	15	90,000
4	H-Si 2111 (4.7)	5	0.7	CH <sub>3</sub> CN	Trace	—
5	H-Si 2311 (0.6)	5.2	0.7	Water	18	260,000
6	H-Si 2311 (5.5)	5.2	0.7	Water	81	142,000
7	H-Si 2311 (0.6)	5.2	(0.7) <sup>a</sup>	Water	30	190,000

<sup>a</sup> Styrene monomer.

important types of multiphase copolymer systems. Because of their multiphase morphology, they display interesting properties of siloxanes in addition to the organic polymers with which they are combined. Polysiloxanes, especially PDMS, have an extremely low  $T_g$  (about  $-130^\circ\text{C}$ ); very high chain flexibility; good oxidative, thermal, and UV stability; hydrophobicity; biocompatibility; high gas permeability; and low surface energy. Despite their many outstanding properties, potential applications of these polymers are hindered by poor mechanical properties.<sup>15-17</sup>

Block copolymers of silicone oligomers–vinyl polymers also have lower surface tension and lower  $T_g$  values than corresponding vinyl homopolymers, even if the silicone oligomer content of the copolymer is low. Low surface tension is explained by silicone blocks arranging themselves in such a way that they are at the surface of the film when a film is prepared from block copolymer solution. We prepared block copolymers from  $\alpha,\omega$ -dihydroxy poly(dimethylsiloxane) by using the peroxy-carbamate method. This method had a number of steps<sup>18</sup> the copolymer yield was rather low, and

strict polymerization conditions were necessary. We applied the redox initiation system of Ce<sup>+4</sup> salt and  $\alpha,\omega$ -dihydroxy poly(dimethylsiloxane) at room temperature for about 2 h and produced a number of block copolymers in this work. The polymerization probably proceeded with a mechanism similar to the Ce<sup>+4</sup>/poly(ethylene glycol) system proposed earlier.<sup>9</sup> A redox reaction between Ce<sup>+4</sup> salt and the hydroxyl groups of  $\alpha,\omega$ -dihydroxy poly(dimethylsiloxane) produces the radicals on the carbon atoms that initiate the polymerization of vinyl monomers as shown in the Scheme 1.

$\alpha,\omega$ -Dihydroxy poly(dimethylsiloxane)s with molecular weights of about 1000 (H-Si 2111) and 2500 (H-Si 2311) were used as reducing agents (Table I) and similar polymerization yields were obtained (nos. 1 and 6). By comparison of polymer 1 with 2 and 5 with 6, one may conclude that with increasing  $\alpha,\omega$ -dihydroxy poly(dimethylsiloxane) concentration up to the value of the Ce<sup>+4</sup> salt concentrations, both the yield and molecular weight increased. Water was the best media (solvent) for the polymerization. Acetonitrile and a mixture of acetone and water were also used as

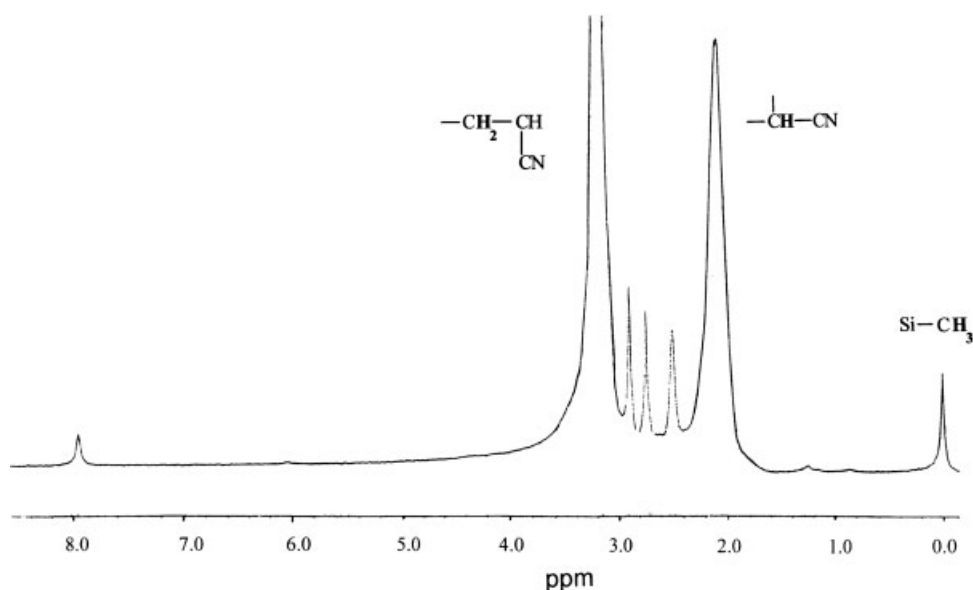


Figure 1 The <sup>1</sup>H-NMR spectrum of PDMS-*b*-PAN (copolymer no. 6).

**TABLE II**  
**Calculated  $\alpha,\omega$ -Dihydroxy Poly(dimethylsiloxane) Content and Contact Angle Values of Block Copolymers**

Copolymer no.	Copolymer type	PDMS content (wt %)		$T_g$ ( $^{\circ}\text{C}$ )	Contact angle
		Mol. wt	NMR		
—	PAN	—	—	65	78
1	PDMS- <i>b</i> -PAN	—	0.16	—	86
2	PDMS- <i>b</i> -PAN	—	0.25	—	90
3	PDMS- <i>b</i> -PAN	—	1.05	—	94
5	PDMS- <i>b</i> -PAN	—	0.96	—	102
6	PDMS- <i>b</i> -PAN	2.5	1.76	45	98
7	PDMS- <i>b</i> -PS	1.3	1.32	80	96
—	PS	—	—	100	78 <sup>a</sup>

<sup>a</sup> According to Baysal et al.<sup>20</sup>

the polymerization solvent in order to dissolve water-insoluble  $\alpha,\omega$ -dihydroxy poly(dimethylsiloxane) during the polymerization. A low copolymerization yield was obtained (nos. 3 and 4). This was expected because the radical polymerization rate constant ( $k_p$ ) of acrylonitrile in water is much higher than in the organic solvents.<sup>19</sup>

#### Spectroscopic properties of copolymers

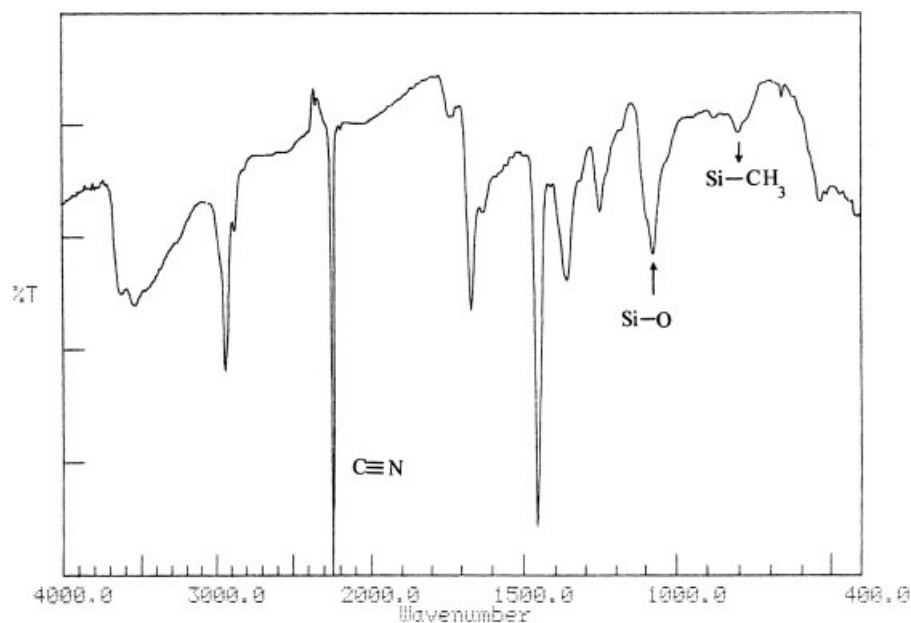
The <sup>1</sup>H-NMR spectrum of PDMS-*b*-PS showed a small signal at about 0.08 ppm due to Si—CH<sub>3</sub> groups of the PDMS segment and signals at 1.4 and 1.8 ppm due to aliphatic protons of PS blocks. Signals attributable to the aromatic protons of PS appeared between 6.4 and 7.5 ppm. The integration ratio of the signals of Si—CH<sub>3</sub> and the aromatic protons is about 0.02. This means that

the number of styrene units of PS segments ( $n + p$ ) is about 1800 (Scheme 1).

The <sup>1</sup>H-NMR measurement of PDMS-*b*-PAN (no. 6) showed that the integration ratio of the signals of Si—CH<sub>3</sub> (at about 0.05 ppm) and —CH<sub>2</sub>— protons of PAN blocks (at about 2 ppm) is about 0.05. The total value of ( $n + p$ ) was calculated to be about 1800 by NMR analysis (Fig. 1).

The PDMS content of the copolymers could be calculated approximately from their NMR spectrum and their molecular weight values, assuming that each copolymer chain contains only one PDMS block. As seen in Table II, the results of both methods are similar and the block copolymers contain only a small amount (1–2.5%) of PDMS.

The FTIR spectra of PDMS-*b*-PAN copolymers showed the characteristic PAN spectrum including a small peak at 802 cm<sup>-1</sup> that is due to Si—O bonds of the PDMS blocks (Fig. 2). This was expected because



**Figure 2** The FTIR spectrum of PDMS-*b*-PAN.

the block copolymers contain only a small amount of PDMS. Peaks appeared at about 1250 and 1070  $\text{cm}^{-1}$  that were attributable to both the PDMS and PAN blocks of PDMS-*b*-PAN.

### Glass-transition temperature

The  $T_g$  values of the copolymers were measured with a DSC-6 instrument at a heating rate of 10°C/min under a nitrogen atmosphere starting from room temperature. The  $T_g$  values of PDMS-*b*-PS and PDMS-*b*-PAN copolymers are about 20°C lower than their corresponding PS and PAN homopolymers, even if the size of the PDMS segment is much smaller than the vinyl polymer segments (Table II).

Only one PDMS-*b*-PS copolymer  $T_g$  was observed at about 80°C. This single  $T_g$  value is good agreement with the single  $T_g$  value of triblock PS-PDMS-PS copolymer (T90) reported earlier.<sup>4</sup> Triblock PS-PDMS-PS type copolymers produced from  $\alpha,\omega$ -dihydroxy poly(dimethylsiloxane) by the multistep peroxy carbamate method were reported to have a  $T_g$  of 70°C.<sup>20</sup> The  $T_g$  of PDMS-*b*-PAN copolymer was about 45°C, which was 20°C lower than of PAN homopolymer measured under similar conditions. These values suggest that polymers 6 and 7 are probably triblock copolymers.

### Contact angle measurements

Contact angle measurements were made on the films of the PDMS-*b*-PAN and PDMS-*b*-PS copolymers prepared by casting from DMF and toluene solutions, respectively, on the glass slides. The results are given in the Table II. The high contact angle values of the copolymers with rather low silicone content is explained by the fact that the PDMS segments migrate to the air-polymer surface, probably because of the high surface energy and low solubility parameter of PDMS during the drying process of their solutions on the glass slides.

## CONCLUSION

PDMS-*b*-PAN and PDMS-*b*-PS copolymers were easily produced in one step with the redox system of  $\alpha,\omega$ -

dihydroxy poly(dimethylsiloxane)/ceric ammonium nitrate at ambient temperature in water. The molecular weight of the copolymers could be regulated by the concentration ratios of PDMS/monomer/Ce<sup>+4</sup> salt.

The copolymer products had much higher contact angle values than corresponding homopolymers, although their silicone content was as low as 1–2%. This method may be useful to produce PDMS-*b*-vinyl polymers with higher contact angle values. In addition, these block copolymers may act as compatibilizers in the blending application of vinyl polymers with polysiloxanes as well as existing applications of the block copolymers of PDMS and vinyl polymers.

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