# Synthesis and Characterization of Poly(dimethyl siloxane) Containing Poly(vinyl pyrrolidinone) Block Copolymers

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**ABSTRACT:** ABA-type block copolymers containing segments of poly(dimethyl siloxane) and poly(vinyl pyrrolidinone) were synthesized. Dihydroxyl-terminated poly(dimethyl siloxane) was reacted with isophorone diisocyanate and then with *t*-butyl hydroperoxide to obtain macroinitiators having siloxane units. The peroxidic diradical macroinitiators were used to polymerize vinyl pyrrolidinone monomer to synthesize ABA-type block copolymers. By use of physicochemical methods, the structure was confirmed, and its characterization was accomplished. Mechanical and thermal characterizations of copolymers were made by stress-strain tests and differential scanning calorimetric measurements. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1915–1922, 1999

Key words: block copolymers; poly(dimethyl siloxane); poly(vinyl pyrrolidinone)

## **INTRODUCTION**

Siloxanes are widely used in industry; and the synthesis of siloxane containing multiphases, as block, segmented, or graft copolymers, have been studied for  $\sim 30$  years.<sup>1</sup> Since then, siloxane copolymers are used in various applications, such as surface-modifying agents in paints, coating, and textile fiber mainly because of their high surface activities. Synthesis and characterization of a series of ABA-type siloxane block copolymers are made and reported in our earlier studies.<sup>2–4</sup>

In this study, new block copolymers containing poly(dimethyl siloxane) (PDMS) with water-soluble poly(vinyl pyrrolidinone) (PVP) were synthesized with the purpose of obtaining a new watersoluble siloxane copolymer. This was achieved by using a commercial reactive PDMS as the starting material in the copolymerization,<sup>5</sup> and the reaction was accomplished by using a stepwise procedure.<sup>6</sup> The hydroxyl-terminated PDMS was used to synthesize the macroinitiator (MI) having siloxane units. This diradical MI was used in the free radical polymerization of vinyl pyrrolidinone (VP) to obtain ABA-type (A = PVP; B = PDMS) block copolymers. The structures of copolymers were characterized by using spectroscopic and viscometric methods. Thermal and mechanical characteristics were examined.

## **EXPERIMENTAL**

#### Materials

 $\alpha,\omega$ -PDMS was the product of Gold Schmidt Chemical Corporation (USA). Tegomer H-Si 2311, with a molecular weight of 2500 ± 250 was dried at 30°C in a vacuum for > 48 h before use.

Isophorone diisocyanate was a product of Fluka AG (Switzerland) and used without purification. The purity determined by isocyanate analysis was 95.1%.

The *t*-butyl hydroperoxide (*t*-BHP) used was also a product of Fluka AG. It was distilled under reduced pressure. The peroxide content was 93.3%. It was used after drying over anhydrous magnesium sulfate.

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MI No.	$\begin{array}{c} \text{Mol of} \\ \text{PDMS} \\ (\times \ 10^3) \end{array}$	$\frac{[-\text{NCO}]}{[\text{PDMS}]}$ At the Beginning	Chain Extension Period $(\tau)$ (h)	Added mol of IPDI at the End of $\tau$	Total Reaction Time (1st Step) (h)	$M_n  imes 10^{-3} \ ({ m g mol}^{-1})$	$M_w   imes  10^{- 3} \ ({ m g \ mol}^{-1})$
I	8.60	3/1			96 71	$3.0^{a}$	
II III	$6.16 \\ 4.65$	1/1 1/1	47 69	12.3 9.3	71 93	$\frac{29.6}{29.8^{\mathrm{b}}}$	$34.2^{\circ}$ $74.3^{ m b}$

 Table I
 Preparation Conditions and Characterization of the MIs

<sup>a</sup> Calculated from end-group analysis by a standard iodometric method.<sup>8</sup>

<sup>b</sup> Found by GPC.

Dibutyltin dilaurate (T-12) was a product of Fluka AG. It was used as a catalyst without purification.

*N*-VP (a product of Fluka AG) was washed with 10% aqueous NaOH solution, dried over  $CaCl_2$ , and distilled at 1–2 mmHg at 55°C.

All solvents used during synthesis reactions were products of Merck AG (Germany). They were carefully dried over molecular sieves (Linde type SA), followed by fractional distillation.

#### Analyses

Infrared (IR) spectra were recorded on an A.T.I. UNICAM Mattson 1000 Series Fourier Transform Infrared Spectrometer.

<sup>1</sup>H NMR and <sup>13</sup>C NMR was obtained for  $CDCl_3$  solution without trimethylsilane on a Bruker Avance PPX-400 (400 MHz).

 $M_n$  and  $M_w$  values of samples were calculated from gel permeation chromatography (GPC) chromatograms according to standard polystyrene calibration using a Waters instrument, and tetrahydrofuran served as eluent at 25°C. The flow rate was 1 mL min<sup>-1</sup>.

An inductively coupled plasma (ICP) spectroscope (Atomscan 25, U.S.A. Thermo Jarrell Ask Argon) was used during silicon content determination of the copolymers.

Thermal characterization of the samples was done by using Perkin-Elmer DSC-6 Model apparatus with a heating rate of  $10^{\circ}$ C min<sup>-1</sup>.

Stress-strain tests were performed on a Tensilon (Toyo Measuring Instruments Co., Ltd.) UTM II tester at room temperature with a crosshead speed of 5 mm min<sup>-1</sup>.

## Procedure

## Preparation of Capped Siloxane Tegomers

The diisocyanate-terminated polysiloxanes were prepared in two different types. In the first, the

		Initial (wt %)				$M_{v}~ imes$		
Cop. No.	MI No.	MI	VP	Yield (%)	$[\eta] (dl g^{-1})$	$10^{-4}$ (g mol <sup>-1</sup> )	$T_g$ (°C)	$T_m$ (°C)
I-1		7	93	93	1.07	70.1	42	83
I-2		15	85	95	0.97	60.2	40	80
I-3	Ι	22	78	86	0.90	53.6	42	80
I-4		30	70	71	0.86	49.9	41	76
II-1		7	93	51	1.16	79.6	40	82
II-2	II	30	70	71	1.50	119.0	42	74
III-1		14	86	48	0.84	48.0	36	63
III-2	III	29	71	54	0.97	60.2	39	77
Homo-PVP			100		0.54	23.9	54	86
H-Si 2311							$-125.6^{\rm a}$	
MI-I							$-120.7^{\mathrm{a}}$	

Table II Preparation Conditions and Some Physical and Thermal Characteristics of Copolymers



**Figure 1** FTIR spectrum of: (a) urethane-I, (b) urethane-II, (c) MI-I, (d) MI-II, (e) Cop. No. I-3, and (f) Cop. No. II-2.

original PDMS was used, while in the second type the chain extension was made and higher molecular weight diisocyanate-terminated siloxanes were obtained.

The hydroxyl-terminated prepolymers (Tegomer H-Si 2311) were dried, and they were reacted with the aliphatic diisocyanate (isophorone diisocyanate) at 60°C in dichloroethane under a blanket of dry nitrogen for 96 h to obtain the first group of samples. The molar ratio of diisocyanate to prepolymer was taken as three to prevent chain extension.

For chain extension, the molar ratio of the diisocyanate to Tegomer H-Si 2311 was taken as an equivalent (1/1) at the same reaction conditions as described for 30 h, then two equivalents of diisocyanate were added to the reaction mixture to cut the chain extension reaction and to obtain diisocyanate-terminated chain-extended polysiloxane.

The resulting products (urethanes) obtained were either of the first type (urethane-I) or chain extended (urethane-II/urethane-III), were extracted with acetonitrile at least twice, isolated by decantation, and dried in a vacuum at room temperature. The isocyanate content of the endcapped products were determined by end group titration of isocyanates, and the molecular weights of the urethanes were calculated.<sup>7</sup>

HO—R<sub>1</sub>—OH + 
$$p$$
 OCN—R'—NCO  $\rightarrow$   
( $p \ge 1$ )

if p>2 OCN—R'—NH—(CO)O—R<sub>1</sub>—O(CO) —NH—R'—NCO

#### urethane-I

if p=1 OCN—R'—NH—(CO)[OR<sub>1</sub>—O(CO) —NH—R'—NH—(CO)—]<sub>y</sub>···NCO

y depends on the chain extension time

#### urethane-II/III

where



## **Preparation of MIs**

In the second step, the diisocyanate-terminated siloxane was reacted with t-BHP in methylene chloride. A few drops of dibutyltin dilaurate catalyst was then added to the reaction mixture. This procedure was conducted under a nitrogen blanket at room temperature, in darkness, for 100 h. In the system, the molar ratio of t-BHP to isocyanate (—OOH/—NCO) was always kept at a



**Figure 2** <sup>1</sup>H NMR spectrum of: (a) Cop. No. I-3 and (b) Cop. No. II-2.

value that is higher than three to prevent chain extension.

The resulting products were precipitated with acetonitrile and dried in vacuum at room temperature. The peroxide content of MI-I obtained from urethane-I, determined by iodometric titration, was identical with the theoretically expected value.<sup>8</sup>

The molecular weights of MI-II and MI-III obtained from urethane-II and urethane-III, respectively, were calculated by using GPC results. The structural formula of a MI expected is as follows:

$$\begin{array}{ccccc} CH_3 & CH_3 & I \\ I & I \\ H_3C - C - OO - C - N - R - N - C - OO - C - CH_3 \\ I & II & I & I & I \\ CH_3 & O & H & H & O & CH_3 \end{array}$$

where R depends on the type of urethanes.

### Synthesis and Characterization of the Copolymers

During the polymerization of VP, the diradical MIs were used. The copolymers were synthesized



Figure 3 <sup>13</sup>C NMR (partial) spectrum of: (a) Cop. No. I-3 and (b) Cop. No. II-2.

in dichloromethane or in ethanol solutions. Weighed amounts of MI were dissolved in predetermined amounts of VP, then the polymerization solvent was added to the mixture. The mixture was degassed, and the solution was distributed into borosilicate tubes through the vacuum line. All tubes were immersed into thermostatically controlled oil baths at 60°C, and polymerization was conducted for 100 h. The solid product was then dissolved in ethanol, precipitated in benzene, filtered, and dried *in vacuo* at 30°C for 48 h.

Specific viscosity of copolymers was measured at 25°C in chloroform. The following viscosity molecular weight relationship was used<sup>9</sup>:

$$[\eta] = 1.94 \times 10^{-4} \times M_v^{0.64} \qquad (dL g^{-1})$$

The viscosity-average molecular weight calculated by use of this relationship is expected to be an approximate value, because the preceding relation was forwarded for pure PVP. Solubilities of copolymers in water were also examined as follows: 20 mg of solid sample in 2 mL of water were mixed in a test tube at room temperature and shaken.

The intermediates and products were also characterized by Fourier transform IR spectroscopy (FTIR), <sup>1</sup>H NMR, <sup>13</sup>C NMR, and ICP methods, as well as by thermal and mechanical tests, as previously outlined in the "Analyses" section. Polymeric films used in these tests were prepared from a solution by use of a 50 : 50 (vol %) mixture of dichloromethane and ethanol.

## **RESULTS AND DISCUSSION**

In this study, two new chain-extended MI and one standard MIs were prepared and characterized. These MIs were used as the starting material for the synthesis of ABA-type 8 new block copolymers of PVP-PDMS-PVP. Experimental data on the



**Figure 4** DSC thermograms of: (a) homo-PVP, (b) Cop. No. I-1, (c) Cop. No. I-3, (d) Cop. No. II-2, and (e) Cop. No. III-1.

preparation of the MIs and copolymers were given in Tables I and II, respectively.

In these series of studies, a PVP homopolymer prepared earlier was also used for comparison purposes.<sup>3</sup>

Intermediates and products obtained were characterized by IR spectroscopy (Fig. 1). In the FTIR spectra of dihydroxy-terminated PDMS, the peaks at 3520 and 3590 cm<sup>-1</sup> are due to the H—bonded OH groups. These OH absorption peaks disappeared at the end of the capping reaction with diisocyanate to obtain diisocyanateterminated PDMSs, because it can be seen from Figures 1(a,b). The peak at 2280 cm<sup>-1</sup> is due to the stretching vibration of —NCO, and it is the principal absorption peak for the isocyanate group. If we compare Figure 1(a,b) the relative peak intensity of stretching vibration of -C=0 in the -NH-CO- group is higher in Figure 1(b), because of the chain extension in MI-II.

In the second reaction step, disappearance of the stretching vibration of —NCO peaks certainly indicate the formation of MIs, which were illustrated in Figure 1(c,d).

In the FTIR spectra of copolymers [Fig. 1(e,f)], urethane peaks  $\sim 3440 \text{ cm}^{-1}$  were observed in all copolymer samples. This absorption is due to the —NH stretching in the —NH—CO— group of all the MIs. These main absorption peaks shown in the spectra prove the incorporation of MIs into the structure; hence, these also provide a definite evidence for the formation of block copolymers.

In the <sup>1</sup>H NMR spectra of Cop. No. I-3 and Cop. No. II-2 [Fig. 2(a,b)], it was observed that the signals of dimethylsiloxy protons in siloxane segments were between 0.09-0.12 ppm. Signals appearing at 4.57 ppm may be due to the ---NH group existing in the structures. Other signals are the characteristic signals of the MIs and PVP.<sup>2,3</sup> <sup>1</sup>H NMR spectra were also used to determine the chain extension value of urethane-II by calculating the ratio of the peak areas of these NMR spectra. The chain extension value so calculated was found to be 11. This result was compared with the molecular weights of MI-II obtained by GPC as  $M_n = 29.6 \times 10^3$  g mol<sup>-1</sup> and  $M_w = 34.2 \times 10^3$  g mol<sup>-1</sup>. The chain extension value was calculated as 10.7, and it is approximated to 11.

The molecular weights of the copolymers cannot be measured by using GPC, because the samples are water-soluble, and they are insoluble in tetrahydrofuran. For comparison of molecular weights of the copolymers, the intrinsic viscosities were measured in chloroform, and their approximate molecular weight were calculated by using the viscosity measurements. These results of two samples (Cop. No. I-3 and Cop. No. II-2) were compared with the results obtained from ICP. The ICP studies of the block copolymers have resulted in 18.3 ppm Si in the sample No. I-3 (C = 0.5826 g/100 ml), which yields 0.31% Si in the sample. Because 31 mol of Si are known to exist in the sample, from this the molecular weight of the copolymer can be estimated as  $2.81 \times 10^5$  g  $mol^{-1}$ . In the ICP studies of Cop. No. II-2, 27.1 ppm Si were found in the sample (C = 0.4816g/100 ml), which yields 0.56% Si in the sample. With the GPC of MI-II and <sup>1</sup>H NMR results of the



**Figure 5** Stress–strain curves of: (a) Cop. No. I-1, (b) Cop. No. I-2, (c) Cop. No. I-3, (d) Cop. No. I-4, (e) Cop. No. II-1, (f) Cop. No. II-2, (g) Cop. No. III-1, (h) Cop. No. III-2, and (i) homo-PVP.

copolymers, combined with the ICP results, the molecular weight of the Cop. No. II-2 was calculated as  $1.71 \times 10^6$  g mol<sup>-1</sup>. If they were compared with the approximate  $M_v$  results, the molecular weights found by ICP were higher than viscosity-averaged molecular weights of these samples.

<sup>13</sup>C NMR spectra of Cop. No. I-3 and Cop. No. II-2 [Fig. 3(a,b)] supported the structure.<sup>3</sup>

The solubility investigation of copolymers showed that all samples dissolved in water at room temperature.

Glass transition temperatures of samples were determined from differential scanning calorimetric thermograms (Fig. 4), and they were given in Table II. PDMS segments had very low  $T_g$  values as expected, and the values of  $T_g$  and  $T_m$ 's given in Table II were due to the PVP segments in the block copolymers. PDMS blocks in the copolymer apparently were effecting as plasticizer, because  $T_g$  and  $T_m$  values of homo-PVP were much higher than those of the copolymers obtained.

Results of static mechanical tests for the block copolymers and homo-PVP films were presented in the form of stress-strain curves (Fig. 5) and in Table III. As seen from the latter, copolymers containing chain-extended MIs have higher ultimate tensile elongations because of the high si-

Cop. No.	UTE <sup>a</sup> (%)	$\begin{array}{c} \text{Tensile Strength} \\ (\text{MN } \text{m}^{-2}) \end{array}$	UTS (MN m <sup>-2</sup> )	Young's Modulus $(GN m^{-2})$
I-1	3.2	_	24	1.7
I-2	3.4	_	18	1.6
I-3	3.8	21	18	1.5
I-4	2.6	_	14	1.4
II-1	5.3	19	18	1.2
II-2	7.3	19	17	1.1
III-1	4.6	_	25	1.4
III-2	5.2	_	19	1.3
$Homo\text{-}PVP^{\mathrm{b}}$	10.5	33.2	20.4	0.75

 Table III
 Mechanical Characteristics of Copolymers

<sup>a</sup> UTE, ultimate tensile elongation.

<sup>b</sup> Ref. 3.

loxane content in the MIs. However, they have lower Young's Moduli values than those of copolymers containing MI-I, although all copolymers synthesized have ultimate tensile strength values as high as homo-PVP.

## CONCLUSIONS

From the results presented herein, the following conclusions can be drawn:

- 1. The ABA-type PVP-PDMS-PVP block copolymers can be synthesized by using PDMS containing new chain-extended peroxidic MIs.
- 2. All copolymers (with or without chain-extended MI) are water-soluble, which means that all samples are PDMS containing water-soluble polymers.
- 3. Thermal characteristics of the copolymers are not so much different than those of homo-PVP.
- 4. According to the mechanical properties, the ultimate tensile strength of the copol-

ymers are as high as PVP's and their Young's Moduli values are higher than PVP's.

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