

Synthesis and Properties of Cross-Linkable Polysiloxane Using a Super base Catalyst

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Abstract- *Cross-linkable Poly(methyl vinyl)siloxane and Poly(dimethylsiloxane-co-methyl-vinylsiloxane) were synthesized via ring-opening polymerization which was initiated by a superbase 1-tertButyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)-phosphoranylideneamino]-2A5,4A5-catenadi(phosphazene). The cyclic oligosiloxane monomers used in the preparation of the polysiloxanes were 2, 4, 6, 8-tetramethyl-2, 4, 6, 8-tetravinylcyclo-tetrasiloxane (DV₄) and octamethyl-cyclotetrasiloxane (D₄), while 1, 3-divinyl tetramethyl-disiloxane was used as the end-capping reagent. Fourier transform infrared spectroscopy, ²⁹Si and ¹H nuclear magnetic resonance spectroscopy, gel permeation chromatography, and traditional viscometry were employed to characterized the synthesized polysiloxanes. It was found that the synthesized polymers possessed a narrow molecular weight distribution with their polydispersity values less than 2, and the synthesized copolymers had a random microstructure formed by random combination of Si-dimethyl unit from D₄ and Si-methylvinyl unit from DV₄.*

Indexed Terms- *Anionic Ring-opening Polymerization, Cross-linkable, Polysiloxane, Superbase Catalyst*

I. INTRODUCTION

Polysiloxanes are widely used as encapsulation materials for semiconductor and photovoltaic devices. They have excellent electrical insulation characteristics and high transparency for solar radiation. Because of the strong Si-O backbone, they show good chemical inertness and thermal stability with a large range of operating temperature. They also have good weatherability[1]. When applied as encapsulation materials, they offer an important advantage of inflicting lower thermal stress due to

their low modulus of elasticity and thus be beneficial to prevention of packaging failures related to metal shift or passivation cracking [2]. They are very hydrophobic and thus can prevent the encapsulated devices from moisture-related corrosion. However, polysiloxanes have relatively low glass transition temperature. To meet the requirement of superior mechanical properties and to maintain structural integrity at high temperatures, linear polysiloxane molecules must be able to be crosslinked when processing [3].

There are 3 methods for crosslinking polysiloxane: crosslinking by radical reactions, crosslinking by condensation reactions and crosslinking by hydrosilylation[4]. Since crosslinking by condensation or hydrosilylation is accompanied by the formation of a side product that could lead to corrosion of the encapsulated devices, we choose to synthesize a polysiloxane copolymer which can be crosslinked by radical reactions. Ring opening polymerization of cyclic oligosiloxane method was employed here to synthesized a linear unsaturated siloxane copolymer. The main component of the cyclic oligosiloxane was octamethyl-cyclotetrasiloxane (D₄). And the unsaturation was introduced using a cyclic oligosiloxane 2, 4, 6, 8-tetramethyl-2, 4, 6, 8-tetravinylcyclotetrasiloxane (DV₄).

To polymerize these moieties, initiation begins with the opening of one of the rings. When ring-opening is achieved by using a radical initiator such as benzoic peroxide, the reaction is called free radical polymerization. When ring-opening is achieved by using a nucleophilic reagent such as sulfuric acid as an initiator, the reaction is called cationic ring-opening polymerization. When ring-opening is achieved by using an electrophilic reagent such as 1-tertButyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)-phosphoranylideneamino]-

2Λ⁵,4Λ⁵-catenadi(phosphazene) (P₄-t-Bu) as an initiator, the reaction is called anionic ring-opening reaction[5]. In this work, a superbases P₄-t-Bu was used as an anionic polymerization initiator. It has the advantage of high yield of polymerization over other initiators. D₄ was copolymerized with DV₄ to obtain cross-linkable linear polysiloxanes with specific amounts of unsaturation.

II. EXPERIMENTALS

2, 4, 6, 8-tetramethyl-2, 4, 6, 8-tetravinylcyclo-tetrasiloxane (DV₄), 1, 3-divinyl tetramethyl-disiloxane (MV₂) were purchased from United Chemical Technologies. Octamethylcyclo-tetrasiloxane (D₄) was purchased from Gelest Chemicals. 1-tertButyl-4, 4, 4-tris (dimethylamino)-2, 2-bis [tris (dimethyl-amino)-phosphoranylideneamino] -2Λ⁵, 4Λ⁵-catenadi (phosphazene) (P₄-t-Bu) was purchased from Fluka Chemicals. Reagents were used as obtained without purification. All reactions were run under nitrogen.

A. Synthesis of Poly(methyl vinyl)siloxane (PMVS) via anionic polymerization

The entire synthesis process was under N₂ atmosphere at 30°C. DV₄ (50 g) and MV₂ (0.5408 g) were placed in a 500 mL four-necked flask. The mixture was stirred with a PTFE magnetic stirrer for 10 min at 30°C. 50 g of diethyl ether was then added and the mixture was allowed to stir for another 10 min to assure a complete mixing. P₄-t-Bu (0.04 mL, 500 ppm) was then added as a catalyst to the stirring mixture and the reaction was allowed to proceed for 6 h. To stop the reaction, the nitrogen flow was switched to a pure CO₂ flow for another 1 h. The resulting poly (methyl vinyl) siloxane was precipitated/washed by adding ethanol to the reacted product, followed by complete evaporation of the volatile solvents under reduced pressure. The washing/evaporation process was repeated 3 times. PMVS's with different molar ratios of DV₄/MV₂ were prepared by using the same procedure. The sample codes and the molar ratio values are listed in Table 1.

B. Synthesis of Poly(dimethylsiloxane-co-methyl-vinylsiloxane) (PDMS-co-PMVS) via anionic polymerization

PDMS-co-PMVS was prepared by a similar procedure as described above. The entire synthesis process was

under N₂ atmosphere. DV₄ (27 g), D₄ (23.22 g) and MV₂ (0.15 g) were placed in a 500 mL

Table 1. Sample code and monomer molar ratio.

Code	DV ₄ (g)	MV ₂ (g)	Molar ratio (DV ₄ /MV ₂)
PMVS-a	50.0	0.541	50/1
PMVS-b	50.0	0.361	75/1
PMVS-c	50.0	0.270	100/1
PMVS-d	50.0	0.135	200/1
Code	D ₄ (g)	DV ₄ (g)	Molar ratio (D ₄ /DV ₄)
D4-co-DV4-a	23.2	27.0	1/1
D4-co-DV4-b	31.0	18.0	2/1
D4-co-DV4-c	37.9	11.0	4/1

four-necked flask. The mixture was stirred with a PTFE magnetic stirrer for 10 min at 30°C. 50 g of diethyl ether was then added and the mixture was allowed to stir for another 10 min to assure a complete mixing. P₄-t-Bu (0.08 mL, 1000 ppm) was then added as a catalyst to the stirring mixture and the reaction was allowed to proceed for 3 h at 38°C. To stop the reaction, the nitrogen flow was switched to a pure CO₂ flow for another 1 h. The resulting PDMS-co-PMVS was precipitated/washed by adding ethanol to the reacted product, followed by complete evaporation of the volatile solvents under reduced pressure. The washing/evaporation process was repeated 3 times. PDMS-co-PMVS's with different molar ratios of D₄/DV₄ were prepared by the same procedure and with the same amount of MV₂. The sample codes and the molar ratio values are also listed in Table 1.

C. Characterization

²⁹Si and ¹H nuclear magnetic resonance (NMR) spectra of 10% w/v polysiloxane/CDCl₃ solutions were obtained on a Varian Unity Inova 500 instrument. Fourier transform infrared (FT-IR) spectra of neat polysiloxane films on NaCl plate were recorded using a Nicolet Magna IR 560 spectrometer. The molecular weight characteristics was analyzed using a Viscotek Model 200 gel permeation chromatography (GPC) system and a Cannon Ubbelohde viscometer.

III. RESULTS AND DISCUSSION

Fig. 1 shows a comparison of the FTIR spectra of PMVS, PDMS and PMVS-co-PDMS. In comparison

to the PDMS spectrum, the PMVS spectrum displays characteristic vinyl peaks at 958 cm⁻¹ (=CH rocking vibration), 1,408 cm⁻¹ (=CH₂ scissoring vibration),

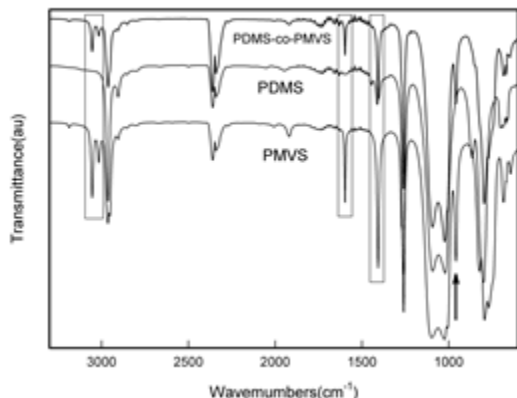


Fig. 1 FTIR spectra of PMVS, PDMS and PMVS-co-PDMS.

and 1597 cm⁻¹ (C=C stretching vibration), 3016 cm⁻¹ (=CH stretching vibration) and 3055 cm⁻¹(=CH stretching vibration). These vinyl group characteristic peaks are also seen in the PDMS-co-PMVS spectrum. Fig. 2 shows the ¹H NMR spectra of PDMS and PMVS. The peaks in the range from 0.03 to 0.11 ppm in the PDMS spectrum represents the Si-CH₃ protons. In comparison, one sees in the PMVS spectrum three packets of peaks, with the peaks in the range from 0.11 to 0.20 ppm representing the Si-CH₃ protons (designated as the a protons), the peaks from 5.74 to 5.82 ppm representing the Si-(C=)-H protons (designated as the b protons) and the peaks in the range from 5.88 to 6.03 ppm representing the Si-(C-) =H₂ protons (designated as the c protons). The ratio of the integrated areas under the three packets of peaks of a, b, c protons is 3.01:1.05:2.11, which is very close to 3:1:2. The molecular weight distribution of the synthesized PMVS was further characterized using GPC and a viscometer. Table 2 shows the values of the number-averaged molecular weight (M_n), the weight-averaged molecular weight

Table 2. Molecular weights and distributions of the synthesized PMVS

	M _n [*]	M _n [†]	M _w [†]	M _w /M _n [†]	Intrins
PMVS	(kg/mol)	(kg/mol)	(kg/mol)		ic

					viscosity (dl/g)
PMVS-a	17.4	17.4	27.2	1.57	0.17
PMVS-b	26.0	22.5	38.3	1.70	0.20
PMVS-c	34.7	32.3	51.6	1.60	0.26
PMVS-d	69.1	54.9	79.4	1.46	0.55

* Theoretical molecular weight calculated from DV₄/MV₂ ratio.

† Experimental values

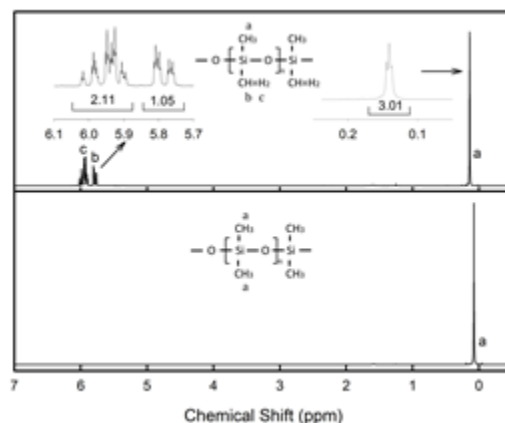


Fig. 2 ¹H NMR spectra of PDMS and PMVS.

(M_w), and the intrinsic viscosity of PMVS of different DV₄/MV₂ molar ratios. As one can see from the table, molecular weight, molecular weight of PMVS can be easily controlled by varying the molar ratio of monomer and end-capping molecule and theoretically, one mole of polymer is obtained for one mole of the end-capping agent. The polydispersity values are smaller than 2, indicating that the molecular weight distributions are relatively uniform. The intrinsic viscosity increases with increasing DV₄/MV₂ ratio which is consistent with the GPC measurements.

It is important to investigate the microstructure of PDMS-co-PMVS synthesized with different molar ratios of DV₄/D₄. ²⁹Si NMR spectroscopy was employed to study the sequence arrangement of the two repeating units and to determine whether the resulting copolymer type was block, alternating or

random. Fig. 3 shows the ^{29}Si NMR spectra of PDMS, PMVS and PDMS-co-PMVS with D_4/DV_4 ratios of 1/1 and 4/1. Both the spectra of PDMS and PMVS exhibit a single sharp peak, at -21.6 ppm for PDMS and at -34.86 ppm for PMVS, respectively. Let M denote the Si-dimethyl unit from D_4 and V denote the Si-methylvinyl unit from DV_4 . In the two copolymer spectra, the ratios obtained by integration of the signals due to the M units and to the V units for the copolymers are approximately the same as their starting monomer ratios. The M/V signal ratio is 4.1/4.0 for PDMS-co-PMVS with a D_4/DV_4 ratio of 1/1, and the M/V signal ratio is 100.9/24.9 for PDMS-co-PMVS with a D_4/DV_4 ratio of 4/1. Both the signals due to the M units and to the V units are split into three major triads: MMM, MMV and VMV

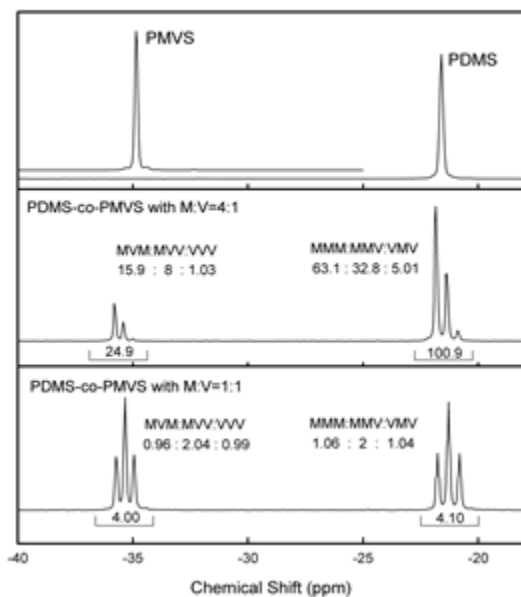


Fig. 3 ^{29}Si NMR spectra of PDMS, PMVS and PDMS-co-PMVS

for the M-centered triads, MVM, MMV and VVV triads for the V-centered triads. If the sequence arrangement of M units and V units is completely statistically random and D_4/DV_4 ratio is 1/1, the expected intensity ratios are $\text{MMM}:\text{MMV}:\text{VMV} = 1:2:1$ for the M-centered triad and $\text{MVM}:\text{MMV}:\text{VVV} = 1:2:1$ for the V-centered triad [6]. The ratios obtained from the ^{29}Si NMR spectrum are $\text{MMM}:\text{MMV}:\text{VMV} = 1.06:2:1.04$ for the M-centered triad and $\text{MVM}:\text{MMV}:\text{VVV} = 0.96:2:0.99$ for the V-

centered triad. The experimental result is in good agreement with the random copolymer expectation. Under the same assumption, the expected ratios for PDMS-co-PMVS with a 4/1 D_4/DV_4 ratio are $\text{MMM}:\text{MMV}:\text{VMV} = 64:32:4$ for the M-centered triad and $\text{MVM}:\text{MMV}:\text{VVV} = 16:8:1$ for the V-centered triad. The ratios obtained from the ^{29}Si NMR spectrum are $\text{MMM}:\text{MMV}:\text{VMV} = 63.1:32.8:5.01$ for the M-centered triad and $\text{MVM}:\text{MMV}:\text{VVV} = 15.9:8:1.03$ for the V-centered triad. The agreement between experimental result and the random copolymer assumption is still very good.

REFERENCES

- [1] J. E. Mark, —Some interesting things about polysiloxanes, *Acc. Chem. Res.* 2004, vol. 37, no. 12, pp. 946-953, Dec. 2004.
- [2] W.F. van den Bogert, D.J. Belton, M.J. Molter, D.S. Soane, and R.W. Biernath, —Thermal stress in semiconductor encapsulating materials, *IEEE Trans. Comp. Hybrids Manuf. Technol.*, vol. 11, no. 3, pp. 245-252, Sept. 1988.
- [3] L. Yang, K. Cao, Y. Huang, G. Chang, F. Zhu, and J. Yang, —Synthesis and properties of cross-linkable polysiloxane via incorporating benzocyclobutene, *High Performance Polymers*, vol. 26, no 4, pp. 463-469, June 2014.
- [4] J.J. Lebrun and H. Porte, —Polysiloxane, in *Comprehensive Polymer Science*, vol. 5: Step Polymerization, G. Allen and J. C. Bevington, Ed. Oxford, England: Pergamon Press, 1989, ch. 34, pp. 593-609.
- [5] O. Nuyken and S. D. Pask, —Ring-opening polymerization—an introductory review, *Polymers*, vol. 5, no. 2, pp. 361-403, April, 2013.
- [6] C. J. Teng and W. P. Weber, —Anionic and cationic ring-opening polymerization of 2,2,4,4,6,6-hexamethyl-8,8-divinylcyclotetrasiloxane, *Macromolecules*, vol. 36, no. 14, pp. 5126-5130, July 2003.