

# Synthesis of Rosinimide Modified with Polyphenylpyridinylsiloxane and Its Characteristics

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**Abstract:** Rosin maleic anhydride adduct (RMA)-bisester was prepared by the esterification of chlorinated RMA with hydroquinone. Phenylpyridinylcyclotrisiloxane ( $D_3^{\text{Ph,Py}}$ ) was synthesized from phenylpyridinylchlorosilane in the presence of zinc oxide catalyst, and amino group terminated polyphenylpyridinylsiloxane prepolymer was prepared by equilibrium polymerization of  $D_3^{\text{Ph,Py}}$  with 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane. Rosinimide (PSMR) was prepared from the imidization of RMA-bisester with polyphenylpyridinylsiloxane prepolymer at 120°C for 7 h using  $\gamma$ -butyrolactone/pyridine. It showed that PSMR had better thermal stability than rosinimide modified with polydimethylsiloxane.

**Keywords:** Rosinimide, Polyorganosiloxane, Thermal property

## Introduction

Rosin obtained from pine trees is one of the most important natural resins and produced approximately  $9 \times 10^5$  metric tons annually in the United States, China, Russia, and India. Many studies have been carried out to modify rosin having high functional characteristics and to use in various industrial applications. In general, rosin belongs to an organic unsaturated carboxylic acid consisting various acid compounds with a terpenene group, which has many isomers according to the location of double bond in its molecule. It is well known that rosin isomers can be converted into levopimaric acid by aging them above 100°C [1,2]. But rosin is easily oxidized due to double bond in molecule. Choi reported the preparation method and thermal properties of rosinamideimide, which was synthesized by the reaction of RMA and amine compounds [3,4]. Ogata *et al.* prepared rosinimide compounds and characterized their properties [5-7]. On the other side, polymers containing pyridinyl group are known to have high thermal stability and electrophilic characteristics [8,9]. In this work, amino group terminated polyphenylpyridinylsiloxane prepolymer (APPS) was prepared by equilibrium polymerization of  $D_3^{\text{Ph,Py}}$  with 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane, which has good thermal-oxidative stability, ozone and UV resistance, high permeability to gases, excellent biocompatibility, and electrical properties. PSMR was prepared by imidization of RMA-bisester and APPS, and thermal characteristics were measured.

## Experimental

### Materials and reagents

Rosin and phenyltrichlorosilane were purchased from

Aldrich Co., 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane and tetramethyl ammoniumhydroxide (TMAH) from United Chemical Technology and Fluka were used without further purification. Reagent grade ZnO was finely powered after drying in a vacuum oven. All other chemicals and solvents including ethyl acetate,  $\gamma$ -butyrolactone were reagent grade and further purified by standard procedures.

### Synthesis of RMA-bisester

RMA was synthesized by the reaction of rosin and maleic anhydride (MA) with reference to Maiti's method [10], and was chlorinated with 150 ml of thionyl chloride at 75°C for 3 h. 0.1 mol of hydroquinone and 0.2 mol of RMA-Cl were added into 4 necked-flask reactor and dissolved by slowly adding 350 ml of pyridine at -10°C, reacted for 1 h. After reaction, reactant was poured into excess distilled water. The precipitated viscous product was filtered, and dried under vacuum for 48 h (Yield: 75%).

### Synthesis of $D_3^{\text{Ph,Py}}$

0.3 mol of phenylpyridinylchlorosilane prepared by reacting phenyltrichlorosilane with pyridine and n-BuLi in 250 ml ethyl acetate was slowly added to a shaking flask with 0.3 mol of ZnO in 120 ml ethyl acetate under vigorous stirring. After addition of phenylpyridinylchlorosilane for 1 h, the solution mixture was vigorously stirred at 40°C for 24 h. The ZnO was filtered off by glass filter and the resulting solution was washed three times with excess distilled water to remove ZnCl<sub>2</sub>. White powder mixed with small amount of oily liquid, a mixture of cyclic trimer and other cyclic oligomers, was precipitated. The cyclic trimer was separated by recrystallization from ethyl acetate and dried under high vacuum at 60°C for 24 h (Yield: 55%).

### Synthesis of APPS

APPS was prepared by the equilibrium polymerization.

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For example,  $D_3^{\text{Ph,Py}}$  and 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane with 5 to 1 mol ratio were reacted at 90°C for 24 h in the presence of 0.02 wt% of TMAH, and then heated to 120°C, maintained for 1 h to decompose TMAH. The reaction mixture was subjected to vacuum stripping to remove cyclic species and then viscous APPS was obtained (Yield: 61%).

### Synthesis of PSMR

1 mol of RMA-bisester and 1 mol of APPS were added to the reactor containing 250 ml of  $\gamma$ -butyrolactone/pyridine cosolvents (volume ratio, 8:2) and then reacted with stirring at 70°C for 4 h to obtain poly(amic acid) solution. PSMR was prepared by imidization of poly(amic acid) in the presence of triethylamine at 120°C for 3 h. The reaction mixture was poured into excess acetone, and then solid product was dried under high vacuum for 24 h (Yield: 92%).

### Characterization

FT-IR spectra were obtained from KBr pellets of samples using an FT-IR spectrometer (Shimadzu DR-8011). NMR spectra were obtained from samples containing tetramethylsilane 0.01% in  $\text{CDCl}_3$  solution using a NMR spectrometer (Varian EM-360A). The melting temperature ( $T_m$ ) and glass transition temperature ( $T_g$ ) were determined calorimetrically using a Mettler Model 30 Thermal Analyzer/Differential Scanning Calorimeter in air at the heating rate of 10°C/min. Residual weight ( $W_r$ ) was determined using a Mettler TG 50 thermogravimetric system at the heating rate of 10°C/min.

## Results and Discussion

### Synthesis of RMA-bisester

RMA-bisester was synthesized by the condensation of 2 mol of RMA-Cl and 1 mol of hydroquinone at -10°C for 1 h. Various solvents such as 1,4-dioxane, *N*-methyl-2-pyrrolidone, and pyridine, were used. In case of using pyridine as a solvent, the greatest yield (75%) was obtained. The structure of RMA-bisester was confirmed by FT-IR. In FT-IR spectrum of RMA-bisester, the absorption peaks due to carbonyl group of RMA at 1775 and 1884  $\text{cm}^{-1}$ , and ester group at 1750  $\text{cm}^{-1}$  appeared. And also, in  $^{13}\text{C}$ -NMR spectrum of RMA-bisester, the carbonyl group peak of RMA newly appeared at 170 ppm.

### Synthesis of $D_3^{\text{Ph,Py}}$ and APPS

$D_3^{\text{Ph,Py}}$  was prepared by ring formation of phenylpyridinyldichlorosilane in the presence of ZnO catalyst with reference to Takiguchi's method[11]. The structure was confirmed by FT-IR. The absorption peak due to Si-O-Si appeared broadly at 1020~1100  $\text{cm}^{-1}$ , Si-Ph absorption peak at 1824, 1892, 1961  $\text{cm}^{-1}$ , Si-Py absorption peak at 1594  $\text{cm}^{-1}$ , respectively. APPS+ was prepared by the equilibrium

polymerization of  $D_3^{\text{Ph,Py}}$  and 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane in the presence of TMAH catalyst with reference to McGrath's method[12]. The structure was confirmed by FT-IR and  $^1\text{H}$ -NMR. Figure 1 is the FT-IR spectrum of APPS. The absorption peak due to primary amino group of APPS appeared newly at 3360  $\text{cm}^{-1}$ . Figure 2 is the  $^1\text{H}$ -NMR spectrum of APPS. The peaks due to  $\alpha$ -,  $\beta$ -,  $\gamma$ -methylene protons of propyl groups appeared at 0.7, 2.1, 2.8 ppm and the peaks due to Si-Ph, Si-Me, Si-Py appeared at 7.2~7.8, 0.2~0.6, 8.0~8.3 ppm, respectively.

### Synthesis of PSMR

PSMR was synthesized by the reaction of RMA-bisester and APPS ( $\overline{M}_n$ : 2,200) prepared by the equilibrium polymerization of  $D_3^{\text{Ph,Py}}$  and 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane in the presence of TMAH catalyst. The reaction mechanism of PSMR is briefly shown in Scheme 1. The reaction conditions, yield, and inherent viscosity ( $\eta_{\text{inh}}$ ) of PSMR prepared from RMA-bisester and APPS are shown in Table 1. In the case of using cosolvent ( $\gamma$ -butyrolactone/pyridine, 8:2) and reacting for 7 h at 120°C, the greatest yield, 92% was obtained. But, not using pyridine as cosolvent, the yield was dropped to 52%. While  $\eta_{\text{inh}}$  of PSMR-5 was 0.58 dl/g, that of PSMR-1 was only 0.15 dl/g.

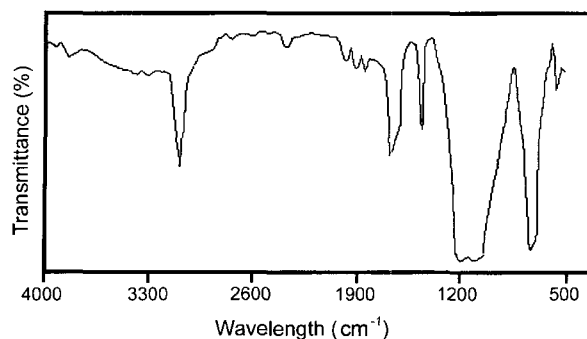


Figure 1. FT-IR spectrum of APPS.

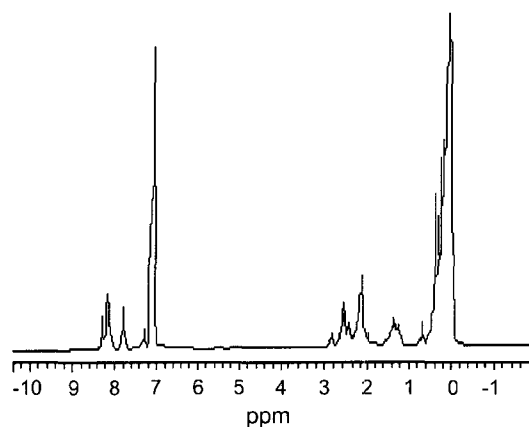
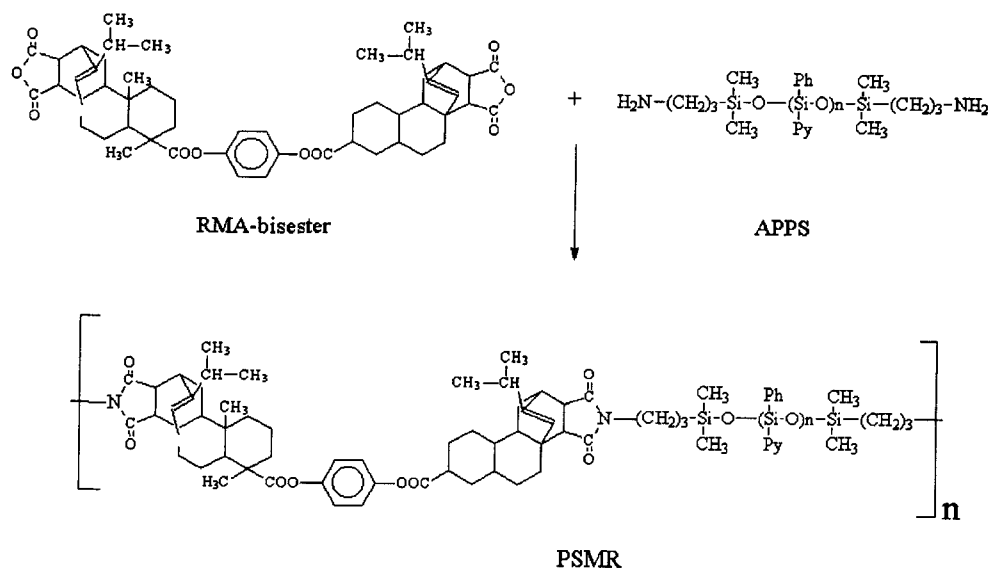


Figure 2.  $^1\text{H}$ -NMR spectrum of APPS.



Scheme 1. Reaction mechanism of PSMR.

Table 1. Reaction condition and inherent viscosity ( $\eta_{inh}$ ) of PSMR

Samples	Imidization Conditions		Color	Yield (%)	$\eta_{inh}^{**}$ (dl/g)
	Vol ratio of cosolvent*	Temp.(°C)/Time(h)			
PSMR-1	10/0	100/7	Light Yellow	52	0.15
PSMR-2	8/2	100/7	Yellow	85	0.47
PSMR-3	6/4	100/7	Yellow	79	0.39
PSMR-4	10/0	120/7	Light Brown	61	0.27
PSMR-5	8/2	120/7	Light Brown	92	0.58
PSMR-6	6/4	120/7	Light Brown	83	0.45

\*( $\gamma$ -butyrolactone/pyridine).

\*\*Measured at a concentration of 0.5 g/dl in  $\gamma$ -butyrolactone at 30°C.

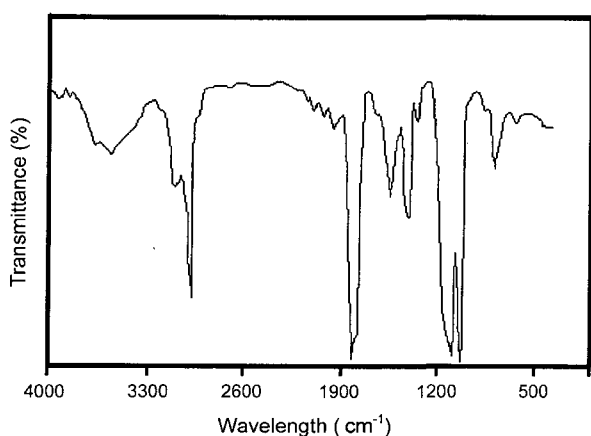


Figure 3. FT-IR spectrum of PSMR.

The structure of PSMR was confirmed by FT-IR and  $^{13}C$ -NMR. Figures 3 and 4 are FT-IR and  $^{13}C$ -NMR spectra of PSMR. In Figure 3, the absorption peak appeared at 1775, 1745  $cm^{-1}$  due to imide group, Si-O-Si absorption peak at

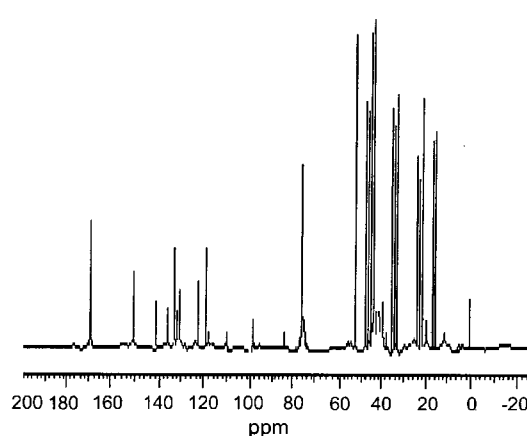


Figure 4.  $^{13}C$ -NMR spectrum of PSMR.

1020~1100  $cm^{-1}$ , Si-Ph absorption peak at 1824, 1892, 1961  $cm^{-1}$ , Si-Py absorption peak at 1593  $cm^{-1}$ . In Figure 4, the peak due to carbonyl group of imide in PSMR appeared at 170 ppm.

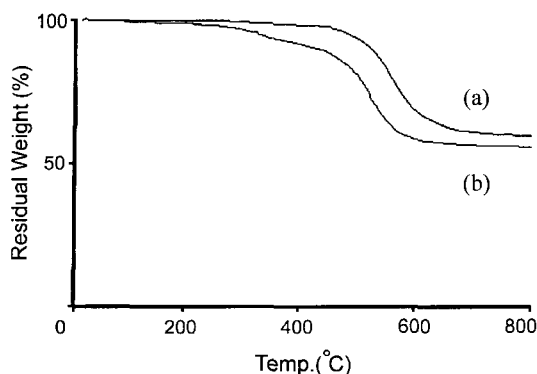


Figure 5. TGA curves of PSMR (a) and  $D_3^{\text{Ph,Py}}$  (b).

Table 2. Physical and thermal Properties of rosinimides modified with cyclotrisiloxanes

Samples	$T_g$ (°C)	$T_m$ (°C)	$W_r^*$ (%) at 800°C
SMR-I	None	None	20
SMR-II	259	None	43
SMR-III	None	None	51
SMR-IV	None	None	55
PSMR	None	None	60

\* $W_r$ : Residual weight.

#### Thermal property of $D_3^{\text{Ph,Py}}$

In the previous paper[13], the thermal property of hexamethylcyclotrisiloxane ( $D_3$ ), methylphenylcyclotrisiloxane ( $D_3^{\text{Me,Ph}}$ ), hexaphenylcyclotrisiloxane ( $D_3^{\text{Ph}}$ ), and phenyl-tolylcyclotrisiloxane ( $D_3^{\text{Ph,Tol}}$ ) were reported.  $T_m$  of  $D_3$ ,  $D_3^{\text{Me,Ph}}$ ,  $D_3^{\text{Ph}}$  and  $D_3^{\text{Ph,Tol}}$  were 59, 105, 190 and 202°C, and residual weights were 2, 30, 35, and 45% at 800°C, respectively. From the DSC result of  $D_3^{\text{Ph,Py}}$ ,  $T_m$  was shown at 230°C, but  $T_g$  was not found. TGA result of  $D_3^{\text{Ph,Py}}$  was shown in Figure 5. In Figure 5, residual weight at 800°C was approximately 54%. Thermal stability of  $D_3^{\text{Ph,Py}}$  was increased with introducing aryl or polar substituents such as pyridine group in cyclotrisiloxane.

#### Thermal property of PSMR

Physical and thermal properties of rosinimides modified with polyarylsiloxane are shown in Table 2. In Table, SMR-I, II, III, IV, and PSMR are rosinimides modified with aminopropyl group terminated siloxane prepolymer prepared by equilibrium polymerization of  $D_3$ ,  $D_3^{\text{Me,Ph}}$ ,  $D_3^{\text{Ph}}$ ,  $D_3^{\text{Ph,Tol}}$ , and  $D_3^{\text{Ph,Py}}$  with 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane, respectively.  $T_g$ ,  $T_m$  and decomposition temperature ( $T_d$ ) for PSMR were measured by a DSC. As the result of DSC,  $T_m$  and  $T_g$  did not appear, but exothermic peak due to thermal decomposition appeared at 400°C. Residual weight for PSMR was also measured by a TGA.

Residual weight at 800°C for PSMR was much increased to 60% than that of SMR-I, which was only 20%. The thermal stability of PSMR was increased with introducing aryl or polar substituents such as pyridine into its molecule.

### Conclusions

PSMR was prepared by the reaction of RMA-bisester and APPS. It had the greatest viscosity (0.58 dl/g) under the reaction condition of cosolvent ( $\gamma$ -butyrolactone/pyridine, 8:2) at 120°C for 7 h and was thermally decomposed near around 400°C. And also residual weight at 800°C was approximately 60%. It's thermal stability was superior to those of the rosinimides modified with  $D_3$ ,  $D_3^{\text{Me,Ph}}$ ,  $D_3^{\text{Ph}}$ ,  $D_3^{\text{Ph,Tol}}$ . Thermal stability of rosinimide was increased with introducing aryl or polar substituent such as pyridine into its molecule.

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