

Article

# Synthesis of Silphenylene-Containing Siloxane Resins Exhibiting Strong Hydrophobicity and High Water Vapor Barriers

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**Abstract:** The novel phenylenedisilane, 1,4-bis(dimethoxyphenylsilyl)benzene (BDMPD), was successfully synthesized via the reaction between trimethoxyphenylsilane (TMPS) and a Grignard reagent originating from 1,4-dibromobenzene. In comparison to common Grignard reactions, this process was a facile one-pot method. <sup>1</sup>H NMR spectroscopy, FT-IR measurements, and elemental analysis confirmed the predicted structure of BDMPD. In addition, vinyl-terminated polysiloxanes containing silphenylene units (VPSSP), which were hydrolytically copolymerized from BDMPD, TMPS, and divinyltetramethyldisiloxane, exhibited excellent thermal stabilities ( $T_{10\%}$ : 502 °C,  $R_w\%$ : 76.86 beyond 700 °C) and suitable refractive indices (1.542). Furthermore, water contact angle and water vapor permeability tests confirmed that the fully cured siloxane resins containing VPSSP-based silphenylene units exhibited strong hydrophobicity (water contact angle: 119°) and superior water vapor barrier properties, thereby indicating their potential to serve as strong waterproof coatings for moisture-proof applications or as adhesives for use in immersed equipment.

**Keywords:** 1,4-bis(dimethoxyphenylsilyl)benzene; Grignard reaction; silphenylene; hydrophobicity; water vapor barrier

## 1. Introduction

In the past few decades, the use of polymers in packaging applications or as protective devices has increased considerably due to their low cost, low density, and interesting mechanical properties [1]. Since the transport of gases through food and pharmaceutical packaging [2], the encapsulation of solar cells [2], and the protective coating of water-soluble optical crystals [3,4] are often not desirable due to the potential formation of damaged or spoiled goods, the use of coatings that combine a water vapor barrier [5] with hydrophobicity [6] to repel water and inhibit the permeation of water vapor is of particular interest. However, such materials must possess a high degree of light transmittance [7,8] and a good thermal stability [9]. Due to the challenges associated with such combinations of multiple properties under complex application conditions, the development of eligible materials is not a facile task.

Recently, organic–inorganic hybrid composites [10] have begun to emerge as highly hydrophobic and strong water vapor barrier materials. A series of approaches to prepare such composites have therefore been reported, including the template [11], sol-gel [12], and vapor deposition methods [13], in addition to chemical etching [14]. However, the majority of these methods require expensive raw materials, special equipment, or multistep procedures. Moreover, defects, such as the unfavorable

aggregation of nanoparticles and the weak bonding of nanoparticles onto the substrates, cannot be avoided [6]. However, the layer-by-layer deposition technique is considered to be an effective method for the preparation of an efficient water vapor barrier coating, although phase separation is difficult to avoid within the resulting coatings [15]. In addition, these coatings, and in particular those containing a high resin content [16,17], are susceptible to coating blisters and cracking after penetration of the corrosive medium into the coating.

Polysiloxanes, which are intrinsic and semi-inorganic polymers [18], are comprised of stable hydrophobic Si–O backbones [19], and they possess many outstanding attributes, including a low surface energy, high thermal stability, high gas permeability, low dielectric properties, good insulation properties, and an excellent biocompatibility [20]. As such, polysiloxane-based materials have been recognized as potential long-lasting and wide-ranging coating materials. In addition, silphenylene-siloxane polymers with modified intramolecular backbones are known to exhibit a good thermal stability, corrosion resistance, and irradiation resistance [21], but to date, few studies have been published on their water repellence and water vapor barrier properties. Herein, we report the preparation of a novel phenylenedisilane using a one-pot Grignard reaction. Vinyl-terminated polysiloxanes containing silphenylene units were synthesized based on the phenylenedisilane copolymer component, and the thermal stabilities and refractive indices of the resulting materials were examined, as were the hydrophobicity and water vapor barrier properties.

## 2. Materials and Methods

### 2.1. Materials

1,4-Dibromobenzene (DBB, >99.5%) was obtained from Sain Chemical Technology Co., Ltd. (Shanghai, China), and magnesium powder (100–200 mesh, >99%) was obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Trifluoromethanesulfonic acid (TFMSA, >99.5%), superdry tetrahydrofuran (STHF, >99.5%), and Pt catalyst (Karstedt's platinum catalyst  $\text{Pt}_2(\text{H}_2\text{C}=\text{CHSiMe}_2\text{OSiMe}_2\text{CH}=\text{CH}_2)_3$ ) were purchased from J&K Scientific Ltd. (Beijing, China). KOH (>99%) and  $\text{NaHCO}_3$  (>99%) were supplied by Tianjin Fuchen Chemical Reagent Factory (Tianjin, China). Divinyltetramethyldisiloxane ( $^{\text{V}}\text{MM}^{\text{V}}$ , >99%) and trimethoxyphenylsilane (TMPS, >99%,  $n_{\text{D}}$ : 1.473) were provided by Guangzhou ShuangTao Fine Chemical Co., Ltd. (Guangzhou, China). Two types of commercially available siloxane resin (i.e., polymethylsiloxane resin, PMSR and polyphenylsiloxane resin, PPSR) were provided by Guangdong Wanmu New Material Technology Co., Ltd. (Jiangmen, China).

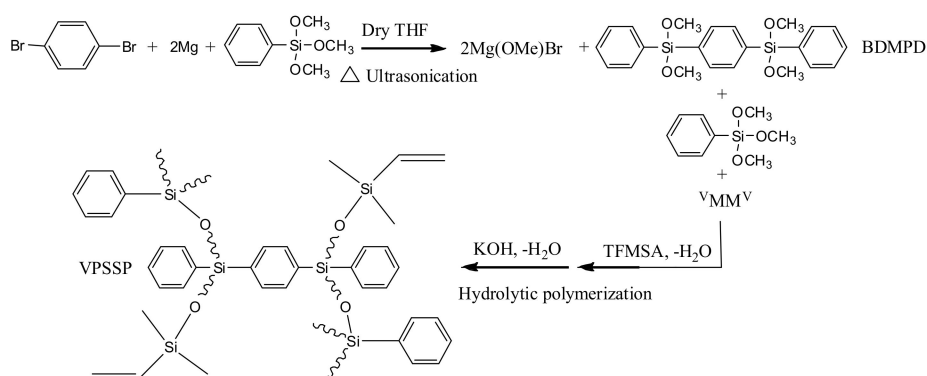
### 2.2. Synthesis of the 1,4-Bis(Dimethoxyphenylsilyl)Benzene (BDMPD)

TMPS (33.6 g, 169.6 mmol), excess magnesium powder (6 g), and STHF (60 mL) were added to a 250 mL three-necked flask under nitrogen. The contents of the flask were warmed to 45 °C and the mixture was subjected to ultrasonication under stirring. After dissolving DBB (20 g, 84.8 mmol) in STHF (40 mL), an aliquot (4 mL) of the DBB solution was added dropwise to the three-necked flask. Following initiation of the Grignard reaction, the remaining DBB solution was then added dropwise to the flask over 1 h using a syringe pump, and the reaction was allowed to proceed for 50 min after the addition was complete. Following centrifugation, column chromatography (silica gel (80–120 mesh) as chromatography column, tetrahydrofuran as eluent), and distillation to remove the solvent under vacuum, BDMPD was obtained as a transparent product (yield 70.61%). Elemental analysis: Calculated for BDMPD: C, 64.35%; H, 6.38%. Found: C, 63.51%; H, 6.32%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.66 (s, 4H,  $-\text{C}_6\text{H}_4-$ ), 7.43–7.38 (t, 5H,  $-\text{C}_6\text{H}_5$ ), 3.63–3.60 (d, 12H,  $-\text{OCH}_3$ ).

### 2.3. Synthesis of the Vinyl-Terminated Polysiloxanes Containing Silphenylene Units (VPSSP) via the Hydrolytic Polymerization of BDMPD, TMPS, and <sup>V</sup>MM<sup>V</sup>

TMPS (37 g), BDMPD (15.34 g, BDMPD/TMPS: 20 mol %), <sup>V</sup>MM<sup>V</sup> (16 g), and TFMSA (0.14 mL, 1.58 mmol, 15 mmol/L) were added to a 250 mL three-necked flask equipped with a stirrer. An aqueous solution of ethanol (ethanol: 3.3 mL, H<sub>2</sub>O: 30 mL) was then added dropwise to the above mixture at 50 °C over 30 min. After the addition of the ethanol solution was complete, the polymerization reaction was allowed to proceed under reflux at 60 °C over 2 h. After this time, the water and alcohol were removed by distillation at atmospheric pressure until the temperature of the liquid in the flask reached 110 °C. Excess NaHCO<sub>3</sub> (2 g) was then added to neutralize the TFMSA, and the precipitated salt was removed by filtration after the addition of toluene (47 mL). KOH (0.05 g, 0.053 mmol) was subsequently added, and the polymerization reaction allowed to continue in refluxing toluene with the removal of water over 2–3 h until no water remained. After this time, the solution in the flask was washed several times with deionized water to remove the base. Finally, the copolymer (VPSSP) was obtained after vacuum distillation to remove the solvent at 150 °C. The obtained VPSSP was found to have a vinyl content of 0.17 mol% as determined by titration (see Supplementary Materials). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.56 (s, 4H, -C<sub>6</sub>H<sub>4</sub>-), 7.37 (s, 5H, -C<sub>6</sub>H<sub>5</sub>), 6.08–5.71 (t, 3H, -CH=CH<sub>2</sub>), 0.17 (s, 9H, -SiCH<sub>3</sub>). <sup>29</sup>Si NMR (79 MHz, CDCl<sub>3</sub>): δ -1.51--2.51, -7767, -79.56.

The Synthesis of Both the BDMPD and the VPSSP is Shown in Scheme 1.



**Scheme 1.** Syntheses of 1,4-bis(dimethoxyphenylsilyl)benzene (BDMPD) and vinyl-terminated polysiloxanes containing silphenylene units (VPSSP). Note: The actual morphology of the VPSSP is not as symmetrical and uniform as shown; a simplified model with the essential structures is shown for clarity.

### 2.4. Preparation of the Fully Cured Siloxane Resins Containing Silphenylene Units (SRS)

VPSSP (12.1 g, vinyl content: 0.17 mol %), hydrogen-terminated polysiloxanes (7.9 g, Si-H content: 0.26 mol %), and the Pt catalyst (0.03 g, 5000 ppm) were mixed and stirred uniformly at 50 °C for 30 min. The molar ratio of Si-H groups to vinyl groups was set to 1:1. The resulting mixture was then poured into a mold and heated to 90 °C for 30 min, followed by curing at 150 °C over 2 h.

PMSR and PPSR were fully cured via the same process as described for SRS. PMSR was cured with hydrogen-terminated trifunctional polymethylsiloxanes and vinyl-terminated trifunctional polymethylsiloxanes, whose viscosity before curing was 3500 cP, while PPSR was cured with hydrogen-terminated trifunctional polyphenylsiloxanes and vinyl-terminated trifunctional polyphenylsiloxanes, whose viscosity before curing was 8500 cP.

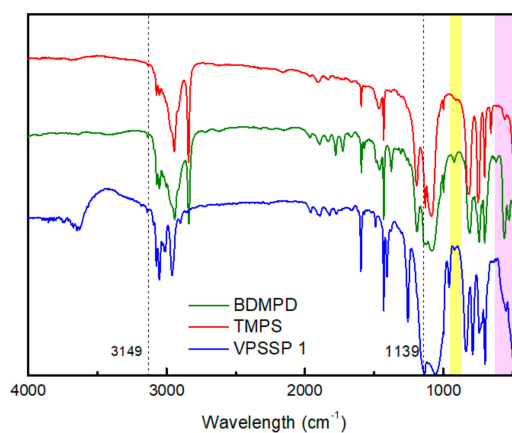
### 2.5. Measurements

Fourier transform infrared (FT-IR) measurements were conducted on a Spectrum 100 infrared spectrometer (Perkin-Elmer, Fremont, CA, USA) at room temperature (25 °C) at 4000–450 cm<sup>-1</sup>. The refractive indices were measured using a WZS-1 refractometer (Shanghai Optical Instrument Factory,

Shanghai, China) at 25 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , TMS) and  $^{29}\text{Si}$  NMR (79 MHz,  $\text{CDCl}_3$ ) spectra were recorded using a Bruker AVANCE AV 400 MHz spectrometer (Bruker Co., Karlsruhe, Germany) at room temperature. Gel permeation chromatography (GPC) was carried out on a Waters 1525/2414 chromatograph (Waters Co., Milford, MA, USA) in a linear column eluted with tetrahydrofuran at a flow rate of 1.0 mL/min. Differential scanning calorimetry (DSC) was performed on a DSC214 instrument (Netzsch Co., Selb, Germany) under a nitrogen atmosphere. Thermal gravimetric analysis (TGA) was carried out on a TGA 2 thermogravimetric analyzer (Mettler-Toledo AG Co., Columbus, OH, USA) under a nitrogen atmosphere from 40 to 700 °C at a heating rate of 10 °C/min. Elemental analysis was performed on an Elementar Vario EL Cube machine (Elementar Co., Langenselbold, Hesse, Germany). Contact angle measurements were performed using an automatic contact angle meter (Theta, Biolin Scientific Ltd., Espoo, Finland). The water vapor permeability (WVP) values of the films were measured using a water vapor transmittance tester (W3/030, Labthink Ltd., Jinan, China) at 38 °C with a gradient of 90%–0% relative humidity across the film.

### 3. Results and Discussion

As shown in Figure 1, the spectra of trimethoxyphenylsilane, BDMPD, and VPSSP clearly exhibited three key absorptions. More specifically, the signal at  $1139\text{ cm}^{-1}$  was attributed to the Si– $\text{C}_6\text{H}_4$ –Si group [22,23], while the weak signal at  $3149\text{ cm}^{-1}$  originated from vibrations of the phenylene C–H moieties [21], and the signals at  $1000$ – $650\text{ cm}^{-1}$  corresponded to the aromatic C–H deformation vibration region, where a new signal and a shift in the signal (emphasized by colored bands) were observed. This was likely due to the difficulty in accurately controlling the Grignard reaction during synthesis, and so small amounts of silicon monomers containing more than one phenylene unit were simultaneously formed. However, the observed spectra confirm the successful incorporation of silphenylene units into the main chains of BDMPD and VPSSP.



**Figure 1.** Fourier transform infrared (FT-IR) spectra of the silicone and siloxane resins.

As shown in Figure 2, the  $^1\text{H}$  NMR spectra of phenylenedisilane exhibited signals corresponding to the  $-\text{OCH}_3$  (3.63–3.60 ppm),  $-\text{C}_6\text{H}_5$  (7.43–7.38 ppm), and  $-\text{C}_6\text{H}_4-$  (7.66 ppm) moieties [24], confirming that the main chain and side groups of the silane structure were as predicted. In addition, elemental analysis of the silane gave C and H mass ratios of 63.51% and 6.32%, respectively, in addition to a sum of 30.17% for the remaining Si and O. As the theoretical mass ratios of C, H, and other elements are 64.35%, 6.38%, and 29.27%, respectively, it was apparent that phenylenedisilane had been successfully prepared. The slight deviation corresponds to the previously discussed FT-IR result, where a small amount of monomers appeared to not strictly obey the configuration of the designed phenylenedisilane.

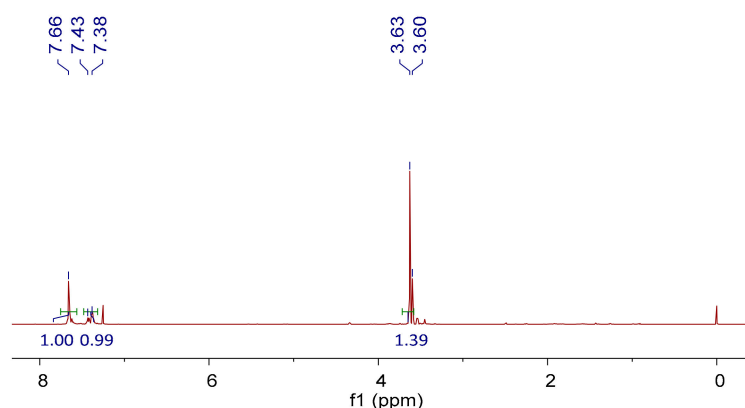


Figure 2.  $^1\text{H}$  NMR spectrum of BDMPD.

As shown in Figure 3, the NMR spectrum of VPSSP 1 revealed the presence of all expected structures. More specifically, the hydrogen atoms on the silphenylene units were represented by a signal at 7.56 ppm, while the signal corresponding to the hydrogen atoms on the pendant benzene ring shifted to 7.37 ppm. In addition, the hydrogen atoms on the  $-\text{SiCH}_3$  moiety were clearly observed at 0.17 ppm [25], while the vinyl protons appeared at 6.08, 5.94, and 5.71 ppm, likely due to their bonding to Si centers of different functionalities. Furthermore, the strong signals observed between  $-1$  and  $-2$  ppm corresponded to the silphenylene units of the silphenylene-siloxane resin, as confirmed by literature studies [26,27]. Moreover, the  $\text{T}_3$  structure of the silphenylene-silicone resin was clearly revealed in the low phase signal groups ( $-77.67$  and  $-79.56$  ppm) in the  $^{29}\text{Si}$  spectrum. The obtained NMR results therefore confirm that VPSSP can be successfully prepared via the described hydrolytic polymerization process.

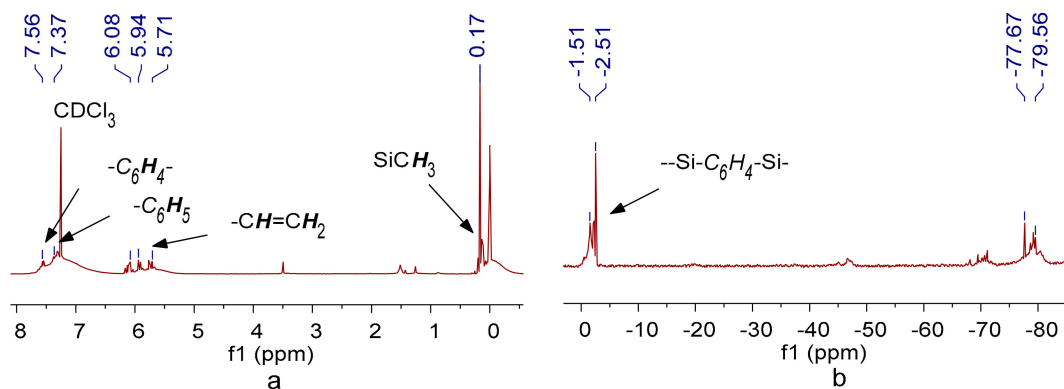


Figure 3. (a)  $^1\text{H}$  NMR and (b)  $^{29}\text{Si}$  NMR spectra of VPSSP 1.

As outlined in Table 1, upon increasing the degree of silphenylene unit introduction, the refractive index of the copolymer tended to increase, giving a maximum value of 1.542 (c.f., 1.473 for TMPS). As the refractive index is a key parameter in light-emitting diode (LED) encapsulators, with higher values being favored [28], silphenylene-siloxane resins are of particular importance in the field of LED packaging. Furthermore, the incorporation of rigid structures, such as silphenylene units, into the silicone backbone limits the flexibility of the siloxane framework, thereby increasing the glass transition temperature [21]. In this case, the copolymer with the largest silphenylene content was VPSSP 1, which exhibited a glass transition temperature  $10.8^\circ\text{C}$  higher than that of VPSSP 4, which contained the lowest silphenylene content. In addition, analysis by GPC showed that the molecular weight distributions of VPSSP 2–4 were relatively concentrated, and their  $M_w$ s values were low. In contrast, the  $M_w$  of VPSSP 1 was significantly higher by one order of magnitude, as was the molecular weight distribution. These results do, however, indicate that the introduction of high numbers of silphenylene

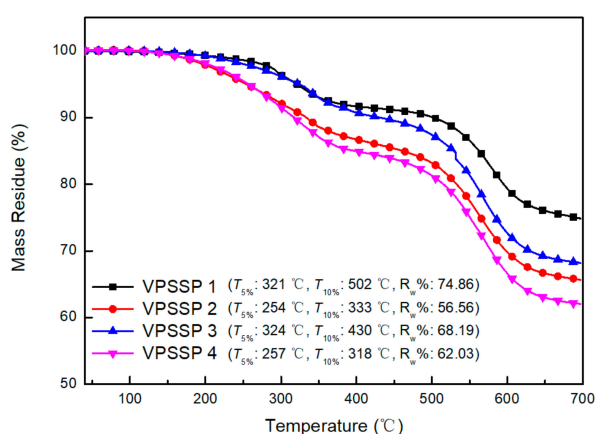
units is not easily controlled during the hydrolytic polymerization process. Unexpectedly, the GPC results (see Supplementary Materials) showed that the molecular weight distribution of VPSSP 1 was mostly concentrated in the macromolecular region, and did not contain smaller molecules, which could be inferred to be qualified polymers.

**Table 1.** Synthetic results and key properties of the VPSSP series.

Sample	BDMPD/TMPS (mol %)	Glass Transition Temperature ( $T_g/^\circ\text{C}$ )	$n$	Yield (%)	$M_w$ (kDa)	$M_z/M_w$
VPSSP 1	20	-23.6	1.542	64.96	65.72	21.03
VPSSP 2	15	-28.2	1.539	76.46	3.309	2.00
VPSSP 3	10	-29.8	1.537	79.15	4.165	2.09
VPSSP 4	5	-34.4	1.532	51.56	2.919	1.87

$M_w$  represents the weight average molecular weight of the polymers.  $M_z/M_w$  represents the expression of the molecular weight distribution of the polymers.  $n$  represents the refractive index.

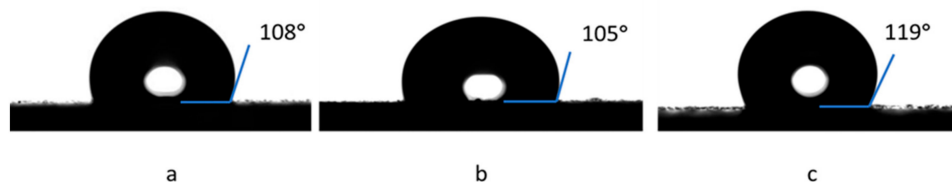
Figure 4 outlines the thermal performances of the prepared VPSSP series. In general, copolymers containing more silphenylene units exhibited superior thermal stabilities. However, the thermal stability of VPSSP 2 was lower than that of VPSSP 3. Its lower molecular weight as determined by GPC confirms the incorporation of 15 mol % silphenylene units, although the  $M_w$  deficiency appeared to result in a lower thermal stability. VPSSP 2 and VPSSP 4, both with a lower molecular weight, began to thermally decompose below 200 °C, most likely due to insufficient polymerization. Of course, uninterrupted matters, such as solvents and small molecular compounds, might also cause this interference. According to their respective  $T_{10\%}$  value and final mass residue, their thermal stabilities are still satisfactory. In addition, the  $T_{5\%}$  values of both VPSSP 1 and VPSSP 3 exceeded 300 °C, and the  $T_{10\%}$  value of VPSSP 1 was 502 °C, while the final mass residue at 700 °C was 74.86%. This directly demonstrates that silphenylene units can provide considerable thermal stability in place of the Si–O–Si backbone, since the Si–C<sub>6</sub>H<sub>4</sub>–Si main chain can prevent the rearrangement or dissociation of pure Si–O bonds at high temperatures [21]. Combined with the GPC results obtained for VPSSP 1, its broad distribution in the high molecular weight region did not negatively affect the thermal stability. As such, the higher thermal stability and refractive index of VPSSP 1 render it potentially suitable for application in heat-resistant packaging materials (such as coatings for microelectronic materials) and luminescent material adhesives (such as LED encapsulators).



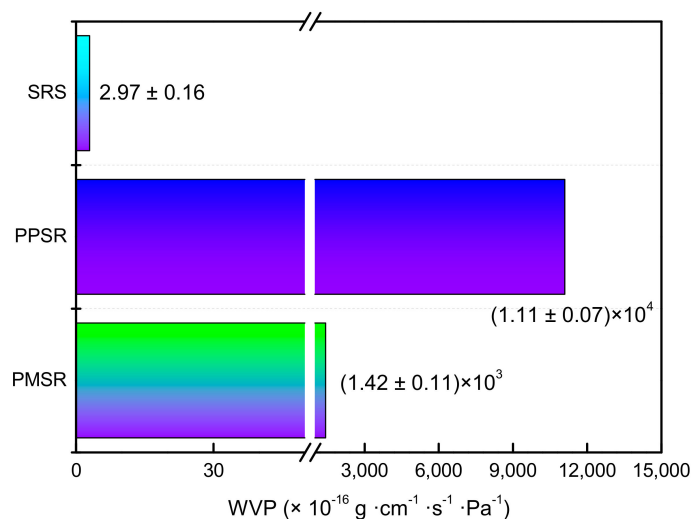
**Figure 4.** Thermal gravimetric analysis (TGA) curves of the VPSSPs.  $T_{5\%}$  represents the 5% thermal decomposition temperature,  $T_{10\%}$  represents the 10% thermal decomposition temperature, and  $R_w\%$  represents the mass residual ratio.

A high hydrophobicity is required for various applications to prevent the erosion and deterioration caused by water absorption, and so we examined the contact angles of our prepared SRS materials and

two commercially available silicone resins (PMSR and PPSR), as shown in Figure 5. The contact angles of these three materials were all found to be  $>90^\circ$ , but the contact angle obtained for the structure containing alternated SRS moieties in the backbone (Figure 6c) was  $>10^\circ$  higher than those of common siloxanes with pure Si–O backbones (Figure 6a,b). This was attributed to the nonpolar phenyl structures imparting hydrophobicity to the polymers [29–31], although surprisingly, the silphenylene units also appear to contribute unexpectedly to the increase in hydrophobicity.



**Figure 5.** Water contact angles of the resins: (a) polymethylsiloxane resin (PMSR), (b) polyphenylsiloxane resin (PPSR), and (c) siloxane resin containing silphenylene units (SRS).



**Figure 6.** Water vapor permeability (WVP) values for the prepared resins.

The water barrier effect of the polymer is also known to play a significant role in the protection of the covered substance. Thus, Figure 6 clearly shows the significant difference in the water vapor barrier properties of several siloxane resins. More specifically, the WVP value of the SRS is only  $(2.97 \pm 0.16) \times 10^{-16} \text{ g cm}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$ , indicating its excellent water vapor barrier ability when cured with VPSSP 1 containing only 20 mol % silphenylene units. Indeed, the SRS is superior to both common siloxane resins in this context, with water vapor barrier properties of approximately three orders of magnitude larger. To the best of our knowledge, no previous reports have discussed the ability of silphenylene units to enhance the water vapor barrier properties of such polymers. By contrast between the PMSR, PPSR, and SRS, the significant difference is that the SRS contains nonpolar silphenylene backbones. Clearly, the silphenylene backbones with bulkier aromatic rings have greater steric hindrance than the pure Si–O backbones, which may bring about a polymer with a greater barrier.

#### 4. Conclusions

We herein reported the successful preparation of the novel phenylenedisilane, 1,4-bis(dimethoxyphenylsilyl)benzene (BDMPD), via a one-pot Grignard reaction. The copolymer containing silphenylene units copolymerized with BDMPD, trimethoxyphenylsilane (TMPS), and divinyltetramethyldisiloxane ( $^V\text{MM}^V$ ) exhibited a good refractive index and a superior thermal stability, indicating its promise for application in heat-resistant coatings or optical application encapsulators.

Surprisingly, the fully cured siloxane resins containing silphenylene units also exhibited a high hydrophobicity and excellent water vapor barrier properties. This is a previously unrecognized effect of the silphenylene skeleton on polysiloxanes compared to the well-known properties of radiation and UV resistance. It is believed that this research will inspire the development of novel silphenylene-siloxane resins exhibiting an excellent hydrophobicity and strong water vapor barrier properties.

**Supplementary Materials:** The following are available online at <http://www.mdpi.com/2079-6412/9/8/481/s1>, Figure S1: Water contact angle of PMSR, Figure S2: Water contact angle of PPSR, Figure S3: Water contact angle of SRS, Figure S4: The original GPC curve of VPSSP 1, Table S1: GPC data of the VPSSPs, Table S2: WVP data of the prepared resins, Table S3: Elemental analysis results of BDMPD.

**Author Contributions:** Conceptualization, X.C. and M.Y.; Methodology, M.Y.; Software, L.T.; Validation, X.C.; Formal Analysis, M.Y.; Investigation, S.W.; Resources, Y.X.; Data Curation, Z.G.; Writing—Original Draft Preparation, M.Y.; Writing—Review and Editing, M.Y. and X.C.; Visualization, X.C.; Supervision, J.G.; Project Administration, X.C.; Funding Acquisition, G.Y.

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**Conflicts of Interest:** The authors declare no conflicts of interest.

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