Effects of Substituting Polyisoprenyl Carbanions for Ethoxyl Groups of Bis-[3-(triethoxysilyl)propyl] Tetrasulfide on the Properties of Carbon Black and Silica-Reinforced NR/SSBR

Cheng-Yang Yeh, Cheng-Yu Kuo, Kuan-Hung Li, Raymond Chien-Chao Tsiang, and Jen-Ray Chang*

Cite This: ACS Omega 2021, 6, 2800–2812

ABSTRACT: The coupling agent TESPT (bis-[3-(triethoxysilyl)propyl] tetrasulfide) was modified by substituting polyisoprenyl (PI) carbanions for the ethoxyl groups on silicon for increasing the interaction of rubber with its fillers. The modification was carried out by the reaction of TESPT with polyisoprenyllithium, which had been previously prepared by anionic polymerization of isoprene using butyllithium. The success of the substitution was confirmed by Fourier-transform infrared spectroscopy, and the molecular weight of the modified TESPT (PI-TESPT) was determined from gel permeation chromatography measurements. The effects of tethered PI, as well as of its chain length, on the mechanical and dynamic properties of rubber compounds were examined using a universal testing machine and dynamic mechanical analysis (DMA). In rubber sample preparation, the amount of PI₃-TESPT (PI of 2900 g/mol) used in rubber compounding is equal to that of the reference sample with TESPT. For PI₆-TESPT samples, the amounts of PI₆-TESPT (PI of 5500 g/mol) and PI₁₄-TESPT (PI of 13,700 g/mol) used were calculated as molar ethoxyl groups which are nearly equivalent to those of PI₃-TESPT. At the same wt % (parts per hundred, phr) of elemental sulfur in rubber compounds, despite the order of cross-linking density being S₆-TESPT > S₁₄-TESPT > S₁₄-TESPT, the exhibited tensile strength is of the order of S₆-TESPT > S₁₄-TESPT > S₁₄-TESPT. The better mechanical properties of S₆-TESPT, as opposed to those of S₁₄-TESPT, could be attributed to the extra reinforcement from the PI–rubber chain linkage and better silica dispersion, as suggested by the mixing torque and Payne effect (ΔG′) measurements. While the dynamic properties of S₆-TESPT are inferior to those of S₁₄-TESPT, these properties can be improved by adding more elemental sulfur to increase the cross-linking density.

1. INTRODUCTION

According to the International Energy Agency, about 27% of the world’s energy consumption is from passenger vehicles, and rolling resistance amounts to 10–13% of the vehicle’s fuel consumption.¹,² To reduce rolling resistance means increasing the fuel efficiency, and therefore, lowering the fuel consumption and CO₂ emission.³ However, besides the rolling resistance, wet grip efficiency is also crucial as it is directly related to driving safety. Hence, developing ways to reduce rolling resistance without sacrificing the grip efficiency has gained much attention during the last three decades both in academics and in the tire industry.⁴,⁵

The rolling resistance, tread wear, and wet grip forming the so-called “magic triangle” of tire properties is a tire technology principle.⁶ Before the invention of the silica–silane system, carbon black (CB) has been widely used as the main reinforcing filler in tire-tread compounding. It offers excellent processability compared to that of untreated silica, whereas the improvement of all three properties at the same time is impossible due to the conflict of the requirements.⁶

In the past two decades, the advancement in the silica–silane technology and the replacement of emulsion-polymerized styrene-butadiene rubbers (ESBRs) with solution styrene-butadiene rubbers (SSBRs) have brought a significant improvement in reducing the rolling resistance without compromising the wet grip properties.⁶ Nowadays, the research of bifunctional organosilanes in silica–silane systems has become popular.⁷

Bifunctional silanes, which greatly enhance the silica–rubber interaction and silica dispersion, are generally made up of three structural units: (a) a silica reactive moiety that reacts with the silanol group on the silica surface during the rubber compounding; (b) an organic spacer function that increases the hydrophobicity of the polar silica surface; and (c) a rubber
active unit, typical of polysulfides, that enables silica to bond chemically to rubber during vulcanization.\(^7,8\)

Among polysulfide-containing coupling agents, bis-[3-(triethoxysilyl)propyl] tetrasulfide (abbreviated as TESPT) is the most widely used one. It plays an indispensable role in the compatibilization of silica with rubber.\(^9\) However, ethanol, which formed from the reaction of ethoxysilyl group with Si–OH groups, competes with silane for adsorption onto the silica surface, leading to decreased silanization efficiency. Furthermore, ethanol condensation may also reduce the mixing efficiency caused by the slipping of compounds on a mixing chamber wall.\(^10\) The drawbacks of ethanol formation for TESPT may be remedied by substituting polyisoprenyl (PI) carbanions for the ethoxyl groups on silicon, thereby reducing ethanol formation and providing different cross-linking sites. The modified TESPT was denoted PI-TESPT, \[((C_2H_5O)_3Si-(CH_2)_3-S-(CH_2)_3-Si-(OC_3H_7)_3)-(PI)\].

It has been reported that triethoxysilyl-terminated 1,4-polyisoprene can be prepared by the reaction of “living” PI anions with a functional trialkoxysilane.\(^11,12\) Analogously, our PI-TESPT was prepared by the synthesis of polyisoprenyllithium via anionic polymerization (Scheme 1), followed by the reaction of polyisoprenyllithium with TESPT (Scheme 2).

**Scheme 1. Synthesis of Polyisoprenyllithium**

\[
\text{Scheme 2. Synthesis of PI-TESPT by a Reaction between Polyisoprenyllithium and TESPT}
\]

Silica aggregates formed from filler–filler interactions restrict the elastomers’ mobility, leading to an increase of mixing torque. A silane coupling agent of higher efficiency is expected to have a lower mixing torque.\(^13\) A homemade mixer, with a mechanical design similar to that of Mooney viscometer, was built for the in situ measurement of torque generated in the mixing process to evaluate PI-TESPT efficiency. The mechanical properties of vulcanizates were determined using a universal tensile/testing machine (UTM). Tan \(\delta\) (ratio of loss modulus to storage modulus) at about 60 and 10 °C, respectively, values were measured to assess the rolling resistance and wet grip efficiency of rubber samples.\(^5,14,15\)

Various PI-TESPT samples of different PI molecular weights were synthesized and compared against TESPT in rubber compounding to study the PI substitution effects. The effects of elemental sulfur on vulcanization characteristics and the corresponding rubber properties were investigated using PI\(_1\)-TESPT with two different sulfur doses.

**2. RESULTS AND DISCUSSION**

It has been reported that tetra-alkoxysilane can undergo nucleophilic substitution with PI carbanions, leading to the formation of mono- to tetra-PI-substituted silanes, and the number of PI substitutions is inversely proportional to the PI chain length.\(^11,12\) TESPT has two electrophilic centers, Si, which could be attacked by polyisoprenyllithium, leading to a substitution of ethoxyl groups by PI [Scheme 2]. In this study, PI-TESPT was characterized by the complementary \(^1\)H NMR, Fourier-transform infrared (FT-IR) spectroscopy, and gel permeation chromatography (GPC) analyses to confirm the successful synthesis of PI-TESPT by the nucleophilic substitution reaction.

Excess of TESPT (mole ratio: TESPT/PI-Li = 1.2) was added to a reaction system to ensure the completeness of the PI-Li’s reaction. To avoid the interference of unreacted TESPT and impurities in structure identification, repetition of dissolution of PI-TESPT in tetrahydrofuran (THF), followed by precipitation of PI-TESPT in methanol, was performed. The unreacted TESPT and impurity were expected to be dissolved in methanol and separated from the precipitated PI-TESPT.

2.1. \(^1\)H NMR Characterization of PI\(_1\)-TESPT. PI\(_1\) was prepared by the deactivation of “living” polyisoprenyllithium of molecular weight of about 3000 g/mol with methanol. The presence of peaks around 5.1, 4.7, 2.1, 1.7, 1.6, and 1.5 ppm for the \(^1\)H NMR spectrum of PI\(_1\) [Figure 2a], which were assigned to olefinic (\(=\text{CH}=\)) (H3), terminal alkene (=\(\text{CH}_2\)) (H1), methylene (–CH\(_2\)–) (H2), methyl (=\(\text{CH}_3\)) (H5, H6), and methylene (=\(\text{CH}–\text{Bu}–\text{s}\)) protons (H4), respectively, suggests the successful preparation of polyisoprenyllithium via 3,4- and 1,4-addition reactions.\(^16\) The peaks at about 3.75 and 1.85 ppm were assigned as trace THF present in PI\(_1\).\(^17,18\)

Figure 2b shows the \(^1\)H NMR spectrum of TESPT with proton assignments. The peaks at about 3.85 and 1.25 ppm were assigned to the methylene (–CH\(_2\)–) proton (Ha) and the methyl (–\(\text{CH}_3\)) proton (Hd) of the ethoxyl (O\(\text{CH}_2\text{CH}_3\)) group, respectively. The peaks at about 1.80 and 0.75 ppm were assigned to the methylene (–\(\text{CH}–\)) proton adjacent to \(\beta\) (Hc) and to \(\alpha\) (He) carbons of silicon, respectively. The peaks between 2.6 and 3.1 ppm correspond to CH\(_2\)=SX protons (Hb) in the area of TESPT. The presence of at least three triplets suggested the existence of at least three different polysulfides.

As the \(^1\)H NMR peaks for PI\(_1\)-TESPT are mainly contributed by the long-chain PI group, the chemical shifts of prominent peaks of \(^1\)H NMR spectrum of PI\(_1\)-TESPT are almost identical to those of PI\(_1\). However, the presence of small peaks at about 0.75 (e), 1.25 (d), 1.80 (c), 2.6 (b), and 3.85 (a) ppm for PI\(_1\)-TESPT [Figure 2iii] suggests a linkage of TESPT with PI\(_1\).\(^17,19\)

These small peaks were not assigned as the characteristic peaks of unreacted TESPT because repetitive precipitate/re-precipitate procedures were performed for PI\(_1\)-TESPT purification; by this, the unreacted TESPT was expected to be dissolved in methanol and was separated from PI\(_1\)-TESPT.

It has been reported that \(\delta_{\text{THF}} = 1.6\) ppm is the characteristic peak of methylene protons of PI chain in the \(\alpha\)-position to the silicon atom of PI-substituted alkoxyamines.\(^20\) The relatively small peak at 1.6 ppm [Figure 2iii] could be the characteristic peak of methylene protons of PI chain in the \(\alpha\)-position to the silicon atom of PI-substituted alkoxyamines.\(^20\)
Hence, the FT-IR peak intensity characterizing Si–C–C stretching vibrations of 1,4 and 3,4 units, respectively. The appearance of these peaks suggested that both 3,4- and 1,4-addition products were formed in the polymerization reaction. The peaks at about 1450 and 1375 cm\(^{-1}\) were assigned to the bending vibration of C–H in the \(-\text{CH}_2\) group and the scissoring vibration of CH\(_3\), respectively.\(^{20}\)

For TESPT, the characteristic peaks for the ethoxyl group bonded to Si of TESPT were located at about 1160, 1100, 1086, and 960 cm\(^{-1}\), which were assigned to the C–H rocking of CH\(_3\), C–O asymmetric stretching, C–O symmetric stretching, and C–C stretching of CH\(_3\)CH\(_2\)O–, respectively.\(^{21,22}\) The shoulder at 803 cm\(^{-1}\) could be the characteristic peak of SiO\(_4\) asymmetric stretching in TESPT.\(^{22}\) The shoulder and the small peak located at about 1040 and 1000 cm\(^{-1}\), respectively, could be the characteristic peaks of impurity formed in TESPT production or from the hydrolysis and condensation of TESPT.\(^{23−25}\)

A comparison of FT-IR spectra of PI\(_3\) + TESPT and PI\(_3\)-TESPT in the stretching range of CH\(_3\)CH\(_2\)O– of TESPT and in the vinyl group range of PI\(_3\) is shown in Figure 3b. The figure shows that the band intensities characterizing the vinyl group (890 and 840 cm\(^{-1}\)) of PI\(_3\)-TESPT and PI\(_3\) + TESPT are almost the same. In contrast, the peak intensities at 1160, 1100, 1086, 960, and 803 cm\(^{-1}\) of PI\(_3\)-TESPT are lower than those of PI\(_3\) + TESPT. The results indicated that some of the ethoxyl groups bonded to the silicon center of TESPT are detached, confirming the substitution of PI for the ethoxyl group.

For Si–CHO\((\text{CH}_2)\_3\)CH\(_3\) with a long alkyl chain, the characteristic peak of methylene protons bonded to silicon (Si–CH\(_2\)-) is located at 1190–1170 cm\(^{-1}\).\(^{25}\) The peak appearing at about 1196 cm\(^{-1}\) could be assigned to the characteristic peak of Si–CH\(_2\).

### 2.3. GPC Characterization of PI-TESPT

The molecular weight (\(M_n\)) of PI-TESPT was analyzed by GPC and its chromatogram was compared to that of the unfunctionalized PI originating from the deactivation of the same “living” PI-Li with methanol (Figure 4). All PI-TESPT GPC chromatograms present the main peak with a small shoulder. Relative to the peak of the chromatograms for PI, the main peak of PI-TESPT shifting to a lower elution time points to an increase of molecular weight after the reaction of PI-Li with TESPT. These results are consistent with the substitution of ethoxyl groups with PI, as evidenced by FT-IR spectroscopy. The presence of an additional shoulder at a lower elution time suggests the occurrence of a second substitution.

The molecular weights of PI and PI-TESPT were determined by GPC. After deconvolution, GPC chromatograms for the PI\(_3\)-TESPT sample present two distinct deconvoluted peaks: peaks 1 and 2. The corresponding molecular weight of these peaks was determined via an \(M_n\) calibration curve. The molecular weight for the right deconvoluted peak (peak 1) of PI\(_3\)-TESPT is 2863, 401 g/mol greater than that of PI\(_3\) (Table S2b) and almost equal to the molecular weight of TESPT eliminating one ethoxyl group. This peak was thus suggested to be the characteristic peak of monosubstituted PI\(_3\)-TESPT. As the molecular weight difference between peaks 1 and 2 is about 3000 g/mol (Figure 4, Table S2a), the peak at the lower elution time (peak 2) was suggested to be the peak characterizing disubstitution. Moreover, no significant peak appears at the molecular weight of the methylene protons of PI\(_3\) bonded to silicon (Hf).\(^{12}\)

However, this peak is too small to be conclusive evidence for the success of substitution of PI for the ethoxyl group. Hence, FT-IR and GPC analyses were used for further confirmation of the substitution reaction.

### 2.2. FT-IR Characterization of PI\(_3\)-TESPT

After PI substitution, C\(_2\)H\(_4\)OLi formed in the reaction (Scheme 2) was dissolved in methanol and was separated from PI\(_3\)-TESPT. Hence, the FT-IR peak intensity characterizing Si–O–C and –OC\(_2\)H\(_5\) of PI\(_3\)-TESPT (product) should be lower than those of PI\(_3\) + TESPT (a mixture of PI\(_3\) and TESPT reactants).

Figure 3a shows the comparison of the FT-IR spectra of TESPT, PI\(_3\), PI\(_3\) + TESPT, and PI\(_3\)-TESPT. For PI\(_3\) (ii), the peak at 750 cm\(^{-1}\) was assigned to the alkene sp\(^2\) band, while the shoulder at 585 cm\(^{-1}\) to the twisting vibration of the CCC group in the trans 1,4 unit.\(^{20}\) The peaks at 890 and 840 cm\(^{-1}\) were assigned to the out-of-plane bending vibrations of CH\(_2\) in the –C––CH\(_2\) of the 3,4-unit and C–H in the –CH=C–H group of the 1,4 unit, respectively. These two peaks are characteristic of the trans structure of PI\(_3\). The smaller peaks at 1665 and 1645 cm\(^{-1}\) were the characteristic of cis structure and were assigned to the C=C stretching vibrations of 1,4 and 3,4 units, respectively.\(^{20}\)

The shoulder at 803 cm\(^{-1}\) could be the characteristic peak of SiO\(_4\) asymmetric stretching in TESPT.\(^{22}\) The peak at 750 cm\(^{-1}\) was assigned to the out-of-plane bending vibrations of CH\(_2\) in the trans 1,4 unit.\(^{20}\) The peaks at 890 and 840 cm\(^{-1}\) were assigned to the out-of-plane bending vibrations of CH\(_2\) in the –C––CH\(_2\) of the 3,4-unit and C–H in the –CH=C–H group of the 1,4 unit, respectively. These two peaks are characteristic of the trans structure of PI\(_3\). The smaller peaks at 1665 and 1645 cm\(^{-1}\) were the characteristic of cis structure and were assigned to the C=C stretching vibrations of 1,4 and 3,4 units, respectively.\(^{20}\)}
corresponding to PI₃, confirming the completeness of the reaction of PI-Li.

GPC analysis for PI₆-TESPT and PI₁₄-TESPT is similar to that for PI₃-TESPT. After deconvolution, two peaks appear for both samples. The corresponding molecular weights of these two samples and the difference in the molecular weight between PI and PI-TESPT are summarized in Table S1a,b, respectively.

As reported by Derouet et al., the reaction of n-butyl carbanion on functional trialkoxysilanes always leads to the preferential formation of higher n-butyl-substituted products. However, for polyisoprenyllithium (PI-Li), due to steric hindrance effects, the substitution of a second reactive PI-Li for the ethoxyl group of [(C₂H₅O)₂PI−Si−] previously formed is unfavorable.

Our GPC results are consistent with the hindrance of the second substitution by the PI first substituted, [(C₂H₅O)₂(PI)−Si−(CH₂)₃−S₄−(CH₂)₃−Si−(OC₂H₅)₃]. Moreover, GPC indicated that the second substitution, [(C₂H₅O)₂(PI)−Si−(CH₂)₃−S₄−(CH₂)₃−Si−(OC₂H₅)₃], is less than 10%. As at most two ethoxyl groups of TESPT were substituted, grafting PI-TESPT onto SiO₂ can be accomplished via the reaction of at least four to five unsubstituted ethoxyl groups with the silanol groups of silica.

2.4. Influence of PI Chain Length of PI-TESPT on Mixing Torque. For silica-filled rubber compounds, the aggregation of silica and rubber trapped inside the silica network (occluded rubber) restricts elastomer mobility, leading to an increase of the mixing torque. The mixing torque can, however, be reduced by the use of silica coupling agents. During mixing, coupling agents are anchored onto silica and form silane-grafted silica (SiO₂−Sln) by the ethoxy groups’ reaction with silanol groups of silica. The formation of SiO₂−Sln increases the hydrophobicity of the SiO₂ filler surface that suppresses silica aggregation and leads to a decrease of the mixing torque.

In this study’s first mixing stage, viscosity induced by rubber flow initiates the torque’s onset. After dumping all ingredients except vulcanization agents into the mixer, an entanglement of rubber chains caused by molecular interactions is resistant to flow. Without rubber processing oil, the rubber may flow at a higher temperature under high pressure, but it may deteriorate the rubber properties. Hence, at this stage, two-thirds of rubber processing oil used was added to reduce the rubber’s molecular entanglement, thereby making rubber molecules easier to

Figure 2. ¹H NMR spectra of (a) PI₃, (b) TESPT, and (c) PI₃-TESPT.
The time elapsed before the onset of torque was defined as the induction period of mixing, \( t_{\text{mix}} \), and that for \( S_{\text{PI}14-\text{TESPT}} \), \( S_{\text{PI}6-\text{TESPT}} \), \( S_{\text{PI}3-\text{TESPT}} \), and \( S_{\text{TESPT}} \) is about 20, 20, 60, and 110 s, respectively (Table 2, Figure 5). As PI has a high degree of unsaturation, it is very compatible with high aromatics containing (30%) rubber processing oil, SN150 (group I base oil, viscosity index = 95–100, kinematic viscosity at 40 °C = 28–32). In comparison with \( S_{\text{TESPT}} \), the lower \( t_{\text{mix}} \) for \( S_{\text{PI}3-\text{TESPT}} \) could be due to the dissolution of PI-TESPT in the rubber processing oil; the dissolved PI-TESPT plays a role like a plasticizer that converts rigid rubber to a soft elastic material. The longest \( t_{\text{mix}} \) for \( S_{\text{PI}14-\text{TESPT}} \) among the three \( S_{\text{PI}-\text{TESPT}} \) could be due to its long PI chain that is less compatible with SN150 than the other two \( S_{\text{PI}-\text{TESPT}} \).

After the mixing reached a plateau, the mixing torque was in the following order: \( S_{\text{PI}14-\text{TESPT}} > S_{\text{PI}6-\text{TESPT}} > S_{\text{TESPT}} > S_{\text{PI}3-\text{TESPT}} \). Notwithstanding the fact that the molar ethoxyl group in \( S_{\text{TESPT}} \) is about 7 times that in \( S_{\text{PI}3-\text{TESPT}} \), the mixing torque for \( S_{\text{PI}3-\text{TESPT}} \) is lower. The lower mixing torque (better processability) for \( S_{\text{PI}3-\text{TESPT}} \) may mostly be caused by reducing the unwanted hydrolysis condensation reaction in the silanization reaction.\(^{10,29,30}\) The shielding effects could also cause a decrease in the mixing torque.\(^{30}\) As it was reported by Sengloyluan et al.,\(^{13}\) long alkoxyl chains, such as tridecane-1-oxyl in VP Si-369, grafted on the silica surface shields silica against flocculation, and thus, decrease the mixing torque.

However, the adsorption of PI-TESPT on CB due to increasing hydrophobic property of PI with a longer length and the viscosity build-up due to tangling of long PI chains may decrease the amount of PI-TESPT transported to the silica surface for the silanization reaction. Both factors led to an increase in silica flocculation. As shown in Figure 5 and Table 2, the increasing mixing torque rate (torque(mix)/\( dt \)) as well as the mixing torque at the plateau, increased with the PI length.

2.5. Influence of PI Chain Length on Vulcanization Isotherms and the Payne Effect. Vulcanization with elemental sulfur is used to cross-link rubbers, such as NR and SSBR, to a three-dimensional network of interconnected chains. Vulcanization accelerators and coupling agents can activate sulfur for the cross-linking reaction. Double bonds in rubber molecular act as reactive sites in vulcanization. The allylic hydrogen atoms adjacent to the C=C bond are also
very active. During vulcanization, sulfur reacts with these double bonds to form C–S–S–C that links the rubber molecules, and some C–H bonds may be broken and replaced by C–S bonds to link with another polymer chain.32

During the vulcanization process, the sulfur moiety (polysulfide groups) of TESPT and PI-TESPT act primarily as acceptors activated by the elemental sulfur to form a polysulfide link to the rubber.1,3,28 The sulfur moiety may also liberate reactive sulfur at the vulcanization temperature to cross-link rubber.7,28 However, this reaction may lead to premature scorch at too high temperatures.

If coupling agents act as a sulfur acceptor, besides the rubber–rubber network (R–R) formed from the reaction of elemental sulfur in the curing package, the silica–silane–rubber (SiO2–Sn–R) network is formed from the reaction of the sulfur built-in coupling agent with rubber.7,28 Using PI-TESPT as coupling agents, besides the sulfur moiety, SiO2–Sn–R can also be formed from cross-linking between the vinyl group of PI and rubber via a polysulfide bridge. These reactions, linking rubber to the silica surface, are the preferred reactions for improving rubber’s mechanical properties.

The force generated by the specimen’s deformation resistance in vulcanization is measured as torque S′ (dIN m) and shown in vulcanization isotherms (Figure 6). The difference between the maximum torque (MH) and the minimum torque (ML), ΔM (MH–ML), is proportional to the number of cross-links formed between the elastomer chains.14 The cure characteristics for the samples using TESPT and PI-TESPT are shown in Figure 6 and Table 2. Before scorch time (tsc), the induction period of vulcanization is characterized by a slow chemical reaction between the rubber and the additive.

With the same parts per hundred (phr) of sulfur, scorch times (tsc) for STESPT and SPI-TESPT are almost the same (within 2% experimental error), suggesting that the influence of PI substitution on scorching characteristics is insignificant.

After the induction period, the curing of rubber molecular chains occurs to form network structures. The vulcanization rate can be considered the rate of this stage (Figure 6). Unlike the effect on scorch time, PI’s substitution for ethoxyl groups significantly influences the vulcanization rate and ΔM. The vulcanization rate, for these rubber compounds, was on the order of \( S_{\text{PI-TESPT}} < S_{\text{TESPT}} \approx S_{\text{PI3-TESPT}} < S_{\text{PI6-TESPT}} < S_{\text{PI14-TESPT}} \) while ΔM was on the order of \( S_{\text{PI14-TESPT}} < S_{\text{PI6-TESPT}} < S_{\text{PI3-TESPT}} < S_{\text{TESPT}} \) (Table 2). The results show that the vulcanization rate of \( S_{\text{PI-TESPT}} \) increased with PI length while ΔM decreased.

It has been reported that bound rubber blocks the spatial pathway for the vulcanization reaction due to the continuous filler network mediated by bound rubber.33 Once SiO2–Sn–R is formed, the vulcanization reaction is retarded by these spatial hindrances. Mixing torque measurements show that the SiO2–Sn formation decreased with PI length (Table 1). Hence, due to lower SiO2-bound rubber formed in the mixing stage, the vulcanization rate of \( S_{\text{PI-TESPT}} \) with a longer PI length presents a higher vulcanization rate.

### Table 1. Compositions (in phr) of Rubber Compound Samples

| ingredient | S_{TESPT} | S_{PI-TESPT} | S_{PI3-TESPT} | S_{PI6-TESPT} | S_{PI14-TESPT} |
|------------|-----------|--------------|---------------|---------------|----------------|
| sulfur     | 2         | 2            | 3             | 2             | 2              |
| stearic acid | 0.67      | 0.67         | 0.67          | 0.67          | 0.67           |
| ZnO        | 2         | 2            | 2             | 2             | 2              |
| DM         | 1         | 1            | 1             | 1             | 1              |
| M          | 1         | 1            | 1             | 1             | 1              |
| CZ         | 1         | 1            | 1             | 1             | 1              |
| CB         | 20        | 20           | 20            | 20            | 20             |
| silica     | 20        | 20           | 20            | 20            | 20             |
| SN150      | 6.67      | 6.67         | 6.67          | 6.67          | 6.67           |
| NR/C       | 20        | 20           | 20            | 20            | 20             |
| SSBR       | 80        | 80           | 80            | 80            | 80             |

“phr: All ingredients of the rubber compound samples are based on 100 (g) rubber (SSBR + NR/C*), for example, for rubber processing oil, 6.67 g of SN150 was added to 100 g of rubber. NR/C: 17% CB and 83% natural rubber; CB was premixed with natural rubber by a rubber vendor. *Carbon black: CB N330 added in compounding; total carbon in the rubber sample = N330 + carbon in NR/C; for example, wt % C in S_{TESPT} = (20 × 0.17) + 1.67 \times 100\% = 3.71%.

PI-TESPT in processing oil-containing rubber may adsorb sulfurating complexes (SC) on the polar ethoxyl groups of TESPT, while adsorbing rubber on the hydrophobic PI tail of PI-TESPT facilitates the reaction of rubber with SC, and thus, increases the vulcanization rate.33 However, for PI-TESPT grafting on silica, the facilitation effects are decreased due to the interaction of SC with high polar silica.

PI-TESPT bound on silica decreased with PI length. Based on material balance, the portion of PI-TESPT in the neat processing oil-containing rubber phase increased with the PI length. Hence, facilitated (catalyzed) by the PI-TESPT, the curing rate also increased with the longer tethered PI.

In the rubber industry, CB is mainly used as a pigment and a reinforcing additive in automobile tires. Typical reinforcing
CBs have different functional groups such as hydroxyl, carboxyl, ketone, and aldehyde on the surface. Still, the amount is much less than that of silica, and thus, the surface is more hydrophobic. Although the CB filler used in this study is about one-fourth of silica, PI-TESPT with a long PI chain may be more likely to be adsorbed on less polar CB instead of grafting on silica. PI-TESPT on CB can also facilitate the reaction of rubber with SC.

In this study, to keep the same molar ethoxyl group content, PI-TESPT added in compounding increases with the PI length. The molecular weight of PI-TESPT is much lower than that of rubber. PI-TESPT dissolved in the processing oil softens rigid rubber; due to the plasticizing effects, increasing PI-TESPT dose leads to a reduction of ΔM of the final vulcanizate.

Besides the plasticizing effects, ΔM decrease with PI chain length could also be caused by decreased sulfur-cross-linking efficiency. TESPT may donate some of its sulfur to the compound to implicitly raise the amount of “free sulfur”, and consequently, give extra cross-linking. Instead of cross-linking between SiO₂ and rubber via these free sulfur moieties, the formation of dangling chains due to the cross-linking of long PI chains results in a decrease of ΔM.

Compared with S₁₅TESPT, S₁₅P₁₅TESPT has higher SiO₂−Sln−R network formation but lower ΔM. With the same dose of coupling agent, the sulfur in P₁₅TESPT is about one-sixth that of TESPT. In terms of cross-links, the lower ΔM for S₁₅P₁₅TESPT could be due to the less amount of sulfur donated from the sulfur moiety of PI-TESPT. These cross-links can be increased by adding more elemental sulfur in compounding. As expected, ΔM increased as additional sulfur was added (Figure 6). The ΔM increment is mostly contributed by R−R formation, as was suggested by the increase of vulcanization rate while with decreasing cure time (t₉₀) (Figure 6).

The difference storage modulus (G′) between low strain (0.1%) and high strain (20%) is referred to as the Payne effect. The Payne effect is normally used to evaluate the filler networking originating from filler−filler as well as from filler−rubber interactions. Normally, the lower the Payne effect value (ΔG′), the higher the silica dispersity, and the higher the development of the filler−rubber network. Payne effect measurements of G′ for S₁₅TESPT and S₁₅P₁₅TESPT are shown in Figure 7. Lower ΔG′ for S₁₅P₁₅TESPT, as opposed to S₁₅TESPT, suggested that S₁₅P₁₅TESPT has a higher SiO₂−Sln−R network, consistent with the results inferred from the curing rate of vulcanization isotherms.

Possibly due to the decrease of SiO₂−Sln formation caused by steric hindrance and tangling of long PI chains, leading to flocculation of silica, ΔG′ increased with PI chain length. These results are also consistent with decreasing silica dispersity with PI length, inferred from the mixing torque measurement.

2.6. Improvement of Mechanical and Dynamic Properties of Rubber Compounds. Figure 8 shows the stress−strain curves for S₁₅TESPT and S₁₅P₁₅TESPT. Considering the non-linearity of these curves, the tangent modulus (dr/dε) at the elongation of 300% (ε = 300) and the tensile stress with mean absolute deviation of three samples at ε = 100, 200, and 300% are tabulated in Table 2. The dr/dε₃₀₀ and ε follow the order: S₁₅P₁₅TESPT ≈ S₁₅TESPT < S₁₅P₁₅TESPT < S₁₅TESPT, while elongation at break σ₉₀₀ are of the order: S₁₅P₁₅TESPT < S₁₅P₁₅TESPT < S₁₅TESPT < S₁₅P₁₅TESPT.

Due to extra cross-linking between PI and rubber and higher SiO₂−Sln formation resulting in a higher SiO₂−Sln−R network, S₁₅P₁₅TESPT having a lower ΔM (cross-links) than that of S₁₅TESPT, higher tensile strength with a more extended elongation at break was observed. For S₁₅P₁₅TESPT, both ΔM (cross-links) and silica dispersity are lower than those of S₁₅TESPT. It could be due to the extra reinforcement from the PI−rubber chain linkage and lower elongation at break, but higher tensile strength was observed in stress−strain curves.

The formation of C−S bonds evidenced the extra reinforcement from PI−rubber chain linkage. To confirm C−S bond formation from PI, PI vulcanize was prepared. X-ray photoelectron spectroscopy (XPS) spectra characterizing the PI vulcanizate is shown in Figure 10a. Based on the assignment of XPS C₁s and S₂p peaks characterizing sulfur-containing polymer reported by Yu et al., the peak at 284.3 eV to the sp²-type C−C bond and the shoulder at 285.9 eV to
the C–S bond. The PI–PI chain linkage can be inferred from the S_2p peak at 162.4 eV characterizing the S–S bond in di or polysulfidic bridges and the shoulder at 163.5 eV characterizing the S–C bond joining PI chains via sulfidic bridges (Figure 10b).

Besides XPS, FT-IR also indicated the formation of sulfidic bridges. Figure S1 shows the FT-IR spectrum of PI vulcanizate. Peaks at 530, 480, and 435 cm\(^{-1}\) were assigned to the characteristic peaks of dicyclopentadiene, tri- to tetra-sulfidic, and polysulfidic bridges, respectively.\(^{40,41}\) The peaks at 890, 840, and 750 cm\(^{-1}\) and the shoulder at 585 cm\(^{-1}\) are PI’s characteristic peaks (Figure 3a).\(^{40}\) The peaks at 720, 705, and 690 cm\(^{-1}\), which do not appear in the PI’s FT-IR spectra, could be the characteristic peak of C–S stretching.

Summarizing the XPS, FT-IR, and UTM results, we suggested that when PI-TESPT was used as the coupling agent, besides the sulfur atoms built in TESPT, the C–C unsaturated bond in PI also participates directly in sulfur vulcanization and link with rubber chains that provide the extra reinforcement. In rubber product manufacturing, changing the coupling agent in compound and re-tuning silica, CB, and vulcanization agent dose to optimal is necessary. However, our current research purposes are the following: to prepare PI-TESPT, demonstrate the merits of using PI-TESPT, as opposed to TESPT, and investigate the effects of PI chain length. The silica dose of 20 phr (Table 1) may not be optimal with respect to PI-TESPT. Tuning silica doses in future studies may further improve the rubber compounds’ mechanical properties.

For tire applications, rubber material’s dynamic mechanical properties, such as wet grip and rolling resistance, are of great importance. Wet grip refers to the breaking ability for tires, and rolling resistance is the amount of energy consumed for the force resisting the motion as a tire rolls and deflects on the surface.\(^{12,43}\) For optimal tire design, rolling resistance should be low to minimize the energy consumption, while wet grip should be high to shorten the car braking distance.

Because of the inherent difficulties in measuring the energy loss of rolling resistance and wet grip in a tire under actual operation, tan δ values at about 0–30 and 40–70 °C are typically used to indicate the wet grip and rolling resistance, respectively.\(^{5,44}\) However, correlating the mechanical loss factor tan δ to rolling and wet skid resistance is entirely empirical, especially for the silica-filled compound.\(^{13,44,45}\) Hence, in this study, the comparison of tan δ values for \(S_{\text{TESPT}}\) and \(S_{\text{PL-TESPT}}\) measured at 10 and 60 °C, respectively, can only be qualitative indicators for dynamic mechanical performance evaluation.

As shown in Table S3, \(S_{\text{TESPT}}\) gives the lowest tan δ at 60 °C (0.062), while the highest (0.285) at 10 °C among the four samples, indicating that this sample has the best dynamic mechanical properties. Since \(S_{\text{PL-TESPT}}\) presents a lower ∆ΔC, as opposed to \(S_{\text{TESPT}}\), the inferior dynamic properties for \(S_{\text{PL-TESPT}}\) could be caused by less reactive sulfur liberated from polysulfides of PI-TESPT; with the same phr of coupling agents, polysulfides in PI-TESPT is about one-sixth of that in TESPT. Hence, in \(S_{\text{PL-TESPT-S}}\) preparation, additional 1.0 phr sulfur was added to compensate for the low reactive sulfur in PI-TESPT (Table 1). As expected, concomitant with the increase of ∆ΔC (Figure 6), dynamic properties were improved. As shown in Table 2, tan δ at 60 °C is decreased from 0.073 to 0.054, while that at 10 °C increased from 0.262 to 0.302. However, this sulfur addition may contribute mostly from R–R cross-links via polysulfide; hence, the elongation at break was decreased (Figure 8).

The height of tan δ maximum is associated with the fraction of free motion rubber chains at \(T_g\). For vulcanizates with the same amount of accelerator, level of processing oil, and volume fraction of fillers, only chain motions restricted by rubber–filler interactions change tan δ maximum significantly; increasing the amount of sulfur in the vulcanization does not have a significant influence on tan δ maximum.\(^{43,45}\) However, increasing the cross-linking density by adding more sulfur in vulcanization may decrease the rubber chains’ segmental mobility, leading to an increase of the glass-transition temperature.\(^{43,46}\) As shown in Figure 9, the glass-transition temperatures for \(S_{\text{PL-TESPT-S}}\), \(S_{\text{TESPT}}\), and \(S_{\text{PI-TESPT}}\) are around −18.6, −20.2, and −20.7 °C, respectively. Hence, higher tan δ at 10 °C for \(S_{\text{PL-TESPT-S}}\) could be caused by the shift of tan δ curves toward higher temperatures.

According to Cichomski and Dierkes,\(^{45}\) the Payne effect can be used to assess the filler–filler interactions only when the

---

**Table 2. Mixing Characteristics and Mechanical Properties of \(S_{\text{TESPT}}\) and \(S_{\text{PL-TESPT}}\)**

| samples       | \(S_{\text{TESPT}}\) | \(S_{\text{PL-TESPT}}\) | \(S_{\text{PI-TESPT}}\) | \(S_{\text{PI6-TESPT}}\) | \(S_{\text{PL-TESPT-S}}\) |
|--------------|---------------------|------------------------|------------------------|------------------------|------------------------|
| \(t_{\text{mix}}\) (s) | 100                  | 50                     | 20                     | 25                     |                        |
| max. torque(mix) (N m) | 2.82                 | 2.00                   | 3.29                   | 3.78                   |                        |
| torque(mix)/dt (N m/s) | 0.0319               | 0.0263                 | 0.0467                 | 0.0651                 |                        |
| MH (dN m)   | 11.813               | 11.49                  | 10.968                 | 10.688                 | 12.764                 |
| ML (dN m)   | 1.018                | 1.123                  | 0.989                  | 0.984                  | 1.197                  |
| ∆M (dN m)   | 10.795               | 10.367                 | 9.979                  | 9.704                  | 11.567                 |
| \(t_1\) (s) | 139                  | 144                    | 138                    | 136                    | 106                    |
| \(\Delta\)s_\(c,90\) (s) | 313                  | 353                    | 301                    | 291                    | 295                    |
| vulcanization rate, \(\Delta S'/\Delta t'\), (dN/m/s) | 0.0687               | 0.0641                 | 0.0724                 | 0.0756                 | 0.0760                 |
| \(\sigma_{\text{break}}\) (MPa) | 19.0 ± 0.3           | 23.7 ± 0.1             | 17.4 ± 0.1             | 14.8 ± 0.3             | 11.5 ± 0.2             |
| \(\varepsilon_{\text{break}}\) (%) | 578 ± 35             | 623 ± 12               | 523 ± 12               | 498 ± 24               | 371 ± 33               |
| \(\sigma_{\text{200}}\) (MPa) | 0.852 ± 0.007        | 0.946 ± 0.005          | 0.965 ± 0.007          | 0.798 ± 0.012          | 1.119 ± 0.005          |
| \(\sigma_{\text{200}}\) (MPa) | 3.010 ± 0.057        | 3.339 ± 0.022          | 3.300 ± 0.017          | 2.970 ± 0.07           | 3.920 ± 0.04           |
| \(\sigma_{\text{200}}\) (MPa) | 6.41 ± 0.09          | 7.026 ± 0.055          | 6.835 ± 0.051          | 6.342 ± 0.08           | 8.11 ± 0.07            |
| \(\Delta G\) (MPa) | 0.037                | 0.041                  | 0.040                  | 0.038                  | 0.046                  |
| \(\Delta G\) (MPa) | 0.397                | 0.334                  | 0.395                  | 0.482                  | 0.398                  |

\(^{4}>Note: \Delta S'/\Delta t: \text{slope of the tangent line at } t_c, \Delta\)σ/\(\Delta t: \text{slope of tensile stress at } \varepsilon = 300\%.

---

https://dx.doi.org/10.1021/acsomega.0c05133
ACS Omega 2021, 6, 2800–2812
cross-link densities and the polymer–filler interactions are similar. In this study, an increase of elemental sulfur in vulcanization may increase both the overall cross-linking density and polysulfidic cross-links.43,45 As polysulfidic cross-links are easily broken,47 leading to a quick drop in the storage modulus at high strains (Figure 7), higher $\Delta G'$ for S$_{PI3}$-TESPT-S, as opposed to that of S$_{PI3}$-TESPT, is more likely to be caused by increasing the polysulfidic cross-link content, instead of decreasing the silica dispersion in vulcanization.

The relation between mechanical property results and $\Delta M$ (Figures 6, and 8, Table 2) suggested that mechanical properties were influenced by the overall cross-link density and the type of cross-links. The tensile strength for different cross-links decreases on the order of polysulfidic > di- and monosulfidic > carbon–carbon, whereas in comparison with di- and monosulfidic bridges, rubber chains with polysulfidic bridges have a higher possibility of movement, and so, is easier to break.45,48

PI in PI-TESPT provides the extra reinforcement for S$_{PI,TESPT}$ due to C–S linkage. However, FT-IR characterization results (Figure S1 of the Supporting Information) indicate the formation of polysulfidic bridges besides mono- and di-sulfidic bridges when extra elemental sulfur was added. The increase of cross-linking density of S$_{PI,TESPT}$-S as opposed to that of S$_{PI,TESPT}$ due to this extra elemental sulfur addition, increases the tensile strength and $\tan \delta$ at 10 °C. However, possibly due to the formation of polysulfidic cross-links, which have a lower bonding energy and the easier movement of polysulfidic bridges than those of di- and monosulfidic bridges, the elongation at break was decreased.

3. CONCLUSIONS

Bifunctional silanes are used to graft rubber matrices onto fillers, which greatly enhance the silica–rubber compatibility and silica dispersion. Among them, TESPT is the most commonly used in silica–silane-reinforced tire-rubber compounds. The reaction of ethoxyl groups in TESPT with silanol groups of silica during mixing and the coupling reaction between TESPT and rubber during the vulcanization reaction lead to the formation of SiO$_2$–Sln–R. In this study, PI-TESPTs were modified from TESPT to enhance silica dispersion and provide extra reinforcement by linking the PI chain with rubber in sulfur vulcanization.

PI-TESPT was prepared by the reaction of TESPT with polyisoprenyllithium (PI-Li), which was prepared by anionic polymerization of isoprene with butyllithium as an initiator. GPC analysis of PI-TESPT indicated that at most, two of the six ethoxyl groups were substituted (Figure 4 and Table S1). After the first substitution, the substitution of a second reactive PI-Li for the ethoxyl group of [(C$_2$H$_5$O)$_2$PI]$^-$ previously formed is unfavorable. Moreover, the formation of [(C$_2$H$_5$O)$_2$(PI)$^-$Si$^-$(CH$_2$)$_3$-S$_n$-(CH$_2$)$_3$-Si$^-$PI(OC$_2$H$_5$)$_2$] decreased with increasing PI length (Figure 4). Since at least four ethoxyl groups are in PI-TESPT, the grafting functions remain (Table S1). Substituting PI with a moderate chain length, PI of 3000 g/mol, for the ethoxyl groups at silicon suppresses the unwanted condensation reaction and shield the silica surface, thereby increasing silica dispersity. Experimental results confirmed the dispersity improvement, evidenced by a decrease of the mixing torque (Figure 5) and Payne effect value (Figure 7) when PI$_{14}$-TESPT replaced TESPT. However, for PI$_{14}$-TESPT and PI$_{6}$-TESPT, too long PI-chains slow down the transportation of PI-TESPT to the silica surface, leading to silica flocculation.
Besides improving SiO₂ dispersion, the presence of vinyl groups in the PI of PI₃-TESPT offers extra active sites for linking rubber chains onto SiO₂—Sn that increase SiO₂—Sn—R formation, thereby enhancing rubber compounds’ mechanical properties. The existence of a C—S bond formed from PI is essential to confirm that PI offers different active sites besides TESPT, and it was evidenced by XPS spectral characterization of the PI vulcanizate (Figure 10). Hence, with the same phr of coupling agents and elemental sulfur in compounding, notwithstanding the lower cross-linking density due to lower sulfur in PI₁-TESPT, as opposed to TESPT, both tensile strength and elongation at break for Sₚ₃₁−TESPT are higher (Figure 8 and Table 2).

The polysulfdide moiety in both PI₁-TESPT and TESPT release reactive sulfur for linking rubber chains. With the same phr of dosing, inferior dynamic mechanical properties for Sₚ₃₁−TESPT as opposed to Sₚ₃-TESPT could be caused by the less sulfur donated from PI₁-TESPT, as inferred from the lower cross-linking density of Sₚ₃₁−TESPT as inferred from ΔM (Table 2). By adding more elemental sulfur, the dynamic properties of Sₚ₃₁−TESPT were improved; the rolling resistance (tan δ at 60 °C) was improved by increasing the cross-linking density, while shifting the glass-transition temperature to higher temperatures results in an increase of wet grip (tan δ at 10 °C) (Figure 9 and Table S2). However, this sulfur addition may be contributed mostly by R—R cross-links via polysulfdide; hence, elongation at break was decreased.

In rubber product manufacturing, to fulfill specific performance requirements, compounding ingredients should be selected first. Our investigation has demonstrated the merits of using PI-TESPT in improving the mechanical properties of rubber compounds and the potential of PI-TESPT in making tire treads with low rolling resistance and high wet grip. However, further research on adjusting the PI chain length for fitting the compounding ingredients selected, tuning the ingredients, and optimizing the process to satisfy product specifications with minimum cost is warranted.

4. EXPERIMENTAL SECTION

4.1. Materials. Isoprene and tetraethylenediamine used for the preparation of polysoprenyllithium were purchased from Sigma-Aldrich and were pretreated with activated alumina (Alcoa Co.) and CaH₂ (Sigma-Aldrich), respectively, for the removal of trace water before their use. sec-Butyllithium was purchased from Acros as 11.0 wt % solution in cyclohexane (600 mL) was introduced into the autoclave. The exclusion of air and moisture. 20 mL of isoprene in 1 mm in diameter and placed in a Soxhlet extractor. Trace additives in the PI vulcanizate were extracted in a toluene/acetone (100/100 mL) solvent at 80 °C. After drying by vacuum evacuation, the sample was characterized by XPS and FT-IR spectroscopy. XPS analyses were performed with a PHI (Hybrid Quantera) using a monochromatic Al Kα (1486.6 eV) X-ray source. The chemical state of sulfur and CB in the PI vulcanize was analyzed with PHI Multipak software.

4.2. PI-TESPT and PI MCV Preparation and Characterization. The preparation of TESPT-terminated 1,4-polyisoprene (PI-TESPT) samples is similar to the synthesis of trialkoxysilyl-terminated 1,4-polyisoprene reported by Derouet et al., and the preparation method is shown in reactions Schemes 1 and 2. Before the polymerization reaction, the cyclohexane solvent and the isoprene reactant were purified through a column filled with molecular sieve pellets and aluminum-oxide-based powder, respectively. The anionic polymerization reaction for the preparation of polysoprenyllithium (PI-Li) was carried out in an autoclave of 1000 mL capacity (cyclone 075, Büchiglas) in a N₂ environment with the exclusion of air and moisture. 20 mL of isoprene in cyclohexane (600 mL) was introduced into the autoclave. The solution was vigorously stirred at 60 °C, and reactions were initiated by the addition of 4.00, 2.00, and 1.00 mL of sec-butyllithium to the reaction system and expected to form PI-Li of about 2500, 5000, and 10,000 g/mol, respectively. After 90 min of polymerization reaction, TEMDA (mole ratio: TEMDA/sec-butyllithium = 0.5) was introduced into the reaction system, followed by the addition of 2.80, 1.50, and 0.65 mL of TESPT, respectively. The stirring was maintained for 60 min and the materials were poured into a flask. After the addition of 600 mL of methanol, PI-TESPT was precipitated; meanwhile, PI samples were prepared by the addition of methanol to PI-Li cyclohexane solution for comparison. THF was added to dissolve the PI-TESPT precipitate, and methanol was added again to re-precipitate PI-TESPT. The precipitate/re-precipitate procedure was repeated several times, and then the residue solvent was removed from the sample by 2 h of vacuum treatment. H NMR, FT-IR, and GPC analysis were used to characterize the resultant light-white solid. The molecular weights of PI and PI-TESPT samples determined by GPC were denoted PI₆₉, PI₆₁₀, and PI₃₁₄-TESPT, PI₆₁₅₁₄-TESPT, and PI₃₁₄-TESPT, respectively.

The C—S bond formed from PI is essential to confirm PI of PI-TESPT, offering different active sites, besides the sulfur moiety, to link rubber chains to silica. As the C—S bond formed from rubber vocalization cannot be differentiated, C—S formed from PI, MCV (model compound vulcanization), was used to confirm PI’s vulcanization roles. 500 mg of PI₁₆ was mixed with 10 mg of elemental sulfur, 10 mg of ZnO, and 5 mg each of vulcanization accelerators M, DM, and CZ, respectively. The vulcanization reaction was then carried out with a stirring rate of 60 rpm at 150 °C under 1 atm pressure for 2 h. The unreacted PI₁₆ was removed by washing with THF. The resulting PI vulcanize was cut into small pieces of about 1 mm in diameter and placed in a Soxhlet extractor. Trace additives in the PI vulcanizate were extracted in a toluene/acetone (100/100 mL) solvent at 80 °C. After drying by vacuum evacuation, the sample was characterized by XPS and FT-IR spectroscopy.
dissolved in 200 mL of THF; the PI₃ + TESPT sample was prepared by mixing PI₃ with TESPT (mole ratio of TESPT/PI = 1.2). About 50 mg of KBr powder was loaded into the DRIFT cell, and the IR spectra were recorded and noted as background spectra. About 0.2 mL of sample solution was added to 50 mg of KBr powder and connected to a vacuum/gas handling manifold. After the removal of THF solvent by evacuation, sample spectra were recorded. For PI vulcanize, after washing with THF, toluene/acetone extraction, and vacuum evacuation drying, samples were mixed with KBr and pulverized into powder. The sample and KBr background spectra were recorded in an air environment.

The ¹H NMR spectra of polymers were taken with a Bruker AMX 400 spectrometer. The NMR spectra were referred to tetramethylsilane and chemical shifts were given in parts per million (ppm). The relative molecular weights and the molecular weight distributions of the synthesized PI-TESPT were determined with a Waters gel permeation chromatograph system equipped with Waters 410 differential RI detectors (GPC-RI). The GPC was operated using four Waters Styragel HR columns (HR3, HR4, and HR5) at a nominal flow rate of 1 mL/min with a sample concentration of 0.1% in THF solvent. Direct methods of calibrating GPC columns have been used to obtain molecular-weight averages. Monodisperse polystyrene standards were purchased from Polymer Laboratories (UK) for instrument calibration. The calibration curve was obtained by plotting elution time (on the linear x-axis) versus the corresponding value (on the logarithmic y-axis) of each standard’s peak molecular weight.

4.3. Preparation and Characterization of Rubber Samples. Silica and CB-reinforced rubber compounds, with the formulations in phr, are given in Table 1. In preparing rubber samples for testing, a commercial laboratory Banbury mixer needs at least 100 g of coupling agent per batch. As we can only prepare 15 g of PI-TESPT coupling agent per batch of reactions, the commercial Banbury mixer is too big for us to prepare rubber samples. Hence, a homemade batch mixer with a mechanical design similar to that of Mooney viscometer (Figure 1) was built for sample preparation. A force transducer was used to determine the relative mixing torque (force detected/maximum force detected for all samples) versus mixing time of the blended rubber compound process.

SSBR/NR lumps were first masticated using a two-roll mill with rollers (hollow metal cylinders) of 55 mm in diameter and 120 mm in length. The roll nip opening was set to 2 mm and the roll temperature was maintained at 60 °C. The rubber lumps were then charged into the open mixing mill gap and squeezed to make a sheet by the roller. The sheet was folded up and squeezed to make a sheet again. The procedure was repeated 20 times to shred the rubber molecules into smaller units; this process takes about 20 min. The sheet was cut into small chips of about 4–5 square mm by scissors after that.

Two mixing steps were used to prepare the rubber samples for testing. In the first step, SSBR/NR chips mixed with two-thirds (about 4.5 phr) of rubber processing oil (SN 150) and all ingredients except for elemental sulfur and vulcanization accelerators (M, DM, and CZ). The main roles of processing oils are reducing the viscosity, increasing the dispersion of fillers, and reducing the power consumption. SN 150 is a base oil categorized as group I. In this study, SN 150 was used because of its low cost, high viscosity index (95–100), and high aromatics containing (about 30%) oil.

The mixer was preheated to 120 °C at a rate of 10 °C/min. After the addition of rubber and ingredients into the mixer, the blended process was then performed in the batch mixer at a pressure of 0.785 MPa with a stirring rate of 6 rpm for 20 min and then cooled down to room temperature. The stirring rate was set at 6 rpm because the Mooney viscosity increases with the speed (rpm) and reaches a plateau at about 8 rpm.50 After finishing the first step, the rubber mixes were charged to the mill at 60 °C and squeezed to make a sheet. Elemental sulfur with vulcanization accelerators (M, DM, and CZ) was mixed with one-third (about 2.2 phr) rubber processing oil to make a paste. The reason for making sulfur paste first is because it is challenging to mix the sulfur powder with rubber directly in the open two-roll mill without losing any sulfur. The paste was then smeared on the rubber sheets carefully, and the smeared sheets were folded up and squeezed to make a sheet again. This squeeze, followed by a fold-up procedure, was repeated 80 times (about 20 min) to ensure that rubber and all ingredients were mixed well.

After the completion of the mixing process, vulcanization characteristics of the mixing samples were measured at 160 °C (1.67 Hz) on a moving die rheometer (Gotech Testing Machines, M-3000AU). The samples were prepared by treating the rubber mixes at 160 °C for 15 min under 3.93 MPa pressure based on the vulcanization characteristics. The rubber samples were denoted Sᵗᵉˢᵖᵗ and Sᵖⁱ,ᵗᵉˢᵖᵗ. For studying the effects of PI chain length on the grafting functions of PI-TESPT, the amounts of PI₆-TESPT (1.20 phr) and PI₁₅-TESPT (3.47 phr) used in compounding were calculated as molar ethoxyl groups nearly being equivalent to that of PI₃-TESPT (0.67 phr).

The glass-transition temperature of the vulcanized samples was measured by differential scanning calorimeter (DSC). Before DSC measurement, the samples were thoroughly dried by vacuum evacuation. About 15 mg of the test sample was added to a Tzero hermetic aluminum pan and the lid was placed over the pan. The pan and lid were sealed by pressing and the sealed pan was placed in the sample slot of DSC. The same process was repeated with an empty pan to be used as a reference and placed in a reference slot. DSC measurements were performed in a DSC 2910 from TA Instruments with a cooling rate of 10 °C/min, from room temperature down to −150 °C, and then each sample was heated at the rate of 10 °C/min from −130 to +50 °C.

Tensile strength and elongation of the samples were characterized by a UTM (Shimadzu, AG-1) at 50 mm/min. The Payne effect value was measured by dynamic mechanical analysis (DMA) (Thermo Electron Corporation, HAAKE RheoStress 600) using an 8 mm rotor at 70 °C and 0.5 Hz with γ = 0.1–50%, and the loss factor (tan δ) of the DMA was measured at 10°/60 °C and 1 Hz with γ = 2.5%.

ASSOCIATED CONTENT
Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c05133. Molecular weight of PI-TESPTs, as estimated from GPC chromatogram deconvolution; molecular-weight difference between PI-TESPTs and PIs; tan δ at 10 and 60 °C of vulcanizates with PI and PI-TESPT coupling agent, and deconvolution of FT-IR spectra for analyzing polysulfides in the PI vulcanize (PDF)
Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c05133

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS
Support from the Ministry of Science & Technology, R. O. C. (contract no. MOST-108-2221-E-194-037), and Chih Cheng Rubber Factory Co., Ltd., Taiwan is acknowledged.
(33) Song, L.; Li, Z.; Chen, L.; Zhou, H.; Lu, A.; Li, L. The effect of bound rubber on vulcanization kinetics in silica filled silicone rubber. RSC Adv. 2016, 6, 101470–101476.

(34) Mostoni, S.; Milana, P.; Credico, B. D.; D’Arienzo, M.; Scotti, R. Zinc-Based Curing Activators: New Trends for Reducing Zinc Content in Rubber Vulcanization Process. Catalysts 2019, 9, 664–685.

(35) Tang, Z.; Huang, J.; Wu, X.; Guo, B.; Zhang, L.; Liu, F. Interface Engineering toward Promoting Silanization by Ionic Liquid for High-Performance Rubber/Silica Composites. Ind. Eng. Chem. Res. 2015, 54, 10747–10756.

(36) Kim, S. W.; Park, H. Y.; Lim, J. C.; Jeon, I. R.; Seo, K. H. Cure characteristics and physical properties of ground-rubber-filled natural rubber vulcanizates: effects of the curing systems of the ground rubber and rubber matrix. J. Appl. Polym. Sci. 2007, 105, 2396–2406.

(37) Sae-oui, P.; Suchiva, K.; Sirisinha, C.; Intiya, W.; Yodjun, P.; Thepsuwan, U. Effects of Blend Ratio and SBR Type on Properties of Carbon Black-Filled and Silica-Filled SBR/BR Tire Tread Compounds. Adv. Mater. Sci. Eng. 2017, 2017, 2476101.

(38) Sae-oui, P.; Sirisinha, C.; Thepsuwan, U.; Hatthapanit, K. Roles of silane coupling agents on properties of silica-filled polychloroprene. Eur. Polym. J. 2006, 42, 479–486.

(39) Yu, X.-g.; Xie, J.-y.; Yang, J.; Huang, H.-j.; Wang, K.; Wen, Z.-s. Lithium storage in conductive sulfur-containing polymer. J. Electroanal. Chem. 2004, 573, 121–128.

(40) Litvinov, V. M.; De Prajna, P. Spectroscopy of Rubbers and Rubbery Materials; Smithers Rapra Publishing, 2002; pp 222–264.

(41) Trofimov, B. A.; Sinegovskaya, L. M.; Gusarova, N. K. Vibrations of the S–S bond in elemental sulfur and organic polysulfides: a structural guide. J. Sulfur Chem. 2009, 30, 518–554.

(42) Rai, A. K.; Singh, R.; Singh, K. N.; Singh, V. B. FTIR, Raman spectra and ab initio calculations of 2- mercaptobenzothiazole. Spectrochim. Acta, Part A 2006, 63, 483–490.

(43) Cichomski, E. Silica-silane reinforced passenger car tire treads: effect of silica morphology, silica-polymer interface structure and rubber matrix network on tire-performance indicators. Ph.D. Dissertation, University of Twente, Enschede, The Netherlands, 2015.

(44) Cichomski, E.; Dierkes, W. K.; Tolpekina, T. V.; Schultz, S.; Noordermeer, J. W. Influence of physical and chemical-filler bonds on tire wet traction performance indicators for passenger car tire tread materials. Kautsch. Gummi Kunstst. 2014, 67, 50–57.

(45) Cichomski, E.; Dierkes, W. K. Effect of the crosslink density and sulfur-length on wet-traction and rolling resistance performance indicators for passenger car tire tread materials. Presented at the Fall 188th Technical Meeting of Rubber Division, ACS Cleveland, OH October 13–15, 2015, 2015.

(46) Warasitthinon, N.; Robertson, C. G. Interpretation of the tanδ Peak Height for Particle-Filled Rubber and Polymer Nanocomposites with Relevance to Tire Tread Performance Balance. Rubber Chem. Technol. 2018, 91, 577–594.

(47) Mullins, L. Relation between structure and properties. Proceedings of NRPRa Jubilee Conference, Cambridge, 1964.

(48) Ten Brinke, J. W.; Van Swaaij, P. J.; Reuvekamp, L. A. E. M.; Noordermeer, J. W. The influence of silane sulphur rank on processing of a silica-reinforced tyre tread compound. Kautsch. Gummi Kunstst. 2002, 55, 244–254.

(49) Heideman, G.; Datta, R. N.; Noordermeer, J. W. M.; van Baarle, B. Influence of Zinc Oxide during Different Stages of Sulfur Vulcanization. Elucidated by Model Compound Studies. J. Appl. Polym. Sci. 2005, 95, 1388–1404.

(50) Kim, C.; Bonfils, F.; Sainte-Beuve, J.; Morel, M.-H.; Guilbert, S. Importance of the Homogenization Method for Natural Rubber Characterization by Variable Speed Mooney Viscometer. IRRDB International Rubber Conference Siem Reap, Cambodia, 12–13 November 2007, 2007.