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Synthesis and characterization of in-chain silyl-hydride functional SBR and self-crosslinking elastomer

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Abstract

Functional in-chain silyl-hydride (Si-H) SBR copolymers of 4-vinyiphenyldimethylsilanol (VPDMS) and butadiene were synthesized by living anionic polymerization, in which active group Si-H was not lost and its content was controllable. Corresponding self-crosslinking elastomers were obtained by hydrosilation of Si-H group with vinyl bonds in chain. The copolymers and elastomers were characterized by ^{1}H NMR, size exclusion chromatography (SEC), Fourier transform infrared (FTIR) spectroscopy, differential scanning calorimetry (DSC), and thermogravimetry analysis (TGA) techniques.

Keywords: 4-Vinyiphenyldimethylsilanol; Functional in-chain sily-hydride copolymer; Self-crosslinking elastomers

Styrene copolymers with butadiene have made a great contribution to many industries because of their excellent flex resistance, crack-initiation resistance, abrasion resistance, relatively low cost, and availability [1,2]. Pure SBR is seldom used in practical applications, often being compounded with varieties of fillers, for example carbon black, silica-based compounds, titania and so on. However, SBR is a non-polar synthetic rubber which lacks the miscibility with organic or inorganic fillers. Therefore great attention has been paid to the modification of SBR with chemically functional groups [1,3,4]. But a few studies have been reported in the literature about the functional SBR polymerized by functional monomer. In our previous work [5], Si-H functional SBS copolymer of VPDMS and butadiene was synthesized by anionic polymerization using high vacuum technique. Nevertheless, high vacuum technique is complicated to operate. In this study, Si-H functional SBR copolymers were prepared under Schlenk conditions by anionic polymerization, and silicon atoms in the polymer chains were advantageous to interact with silicon based fillers [6]. Hydrosilation reaction had advantages of mild reaction conditions, simple operation and high purity of the product [7]. The copolymers of VPDMS and butadiene have a great deal of vinyl bonds as well as Si-H group, which can be cross-linked by hydrosilation. That can avoid the use of sulfurizing agent and the energy consumption, high pollution during vulcanization. So, this work is significant to the theoretical research and practical applications.

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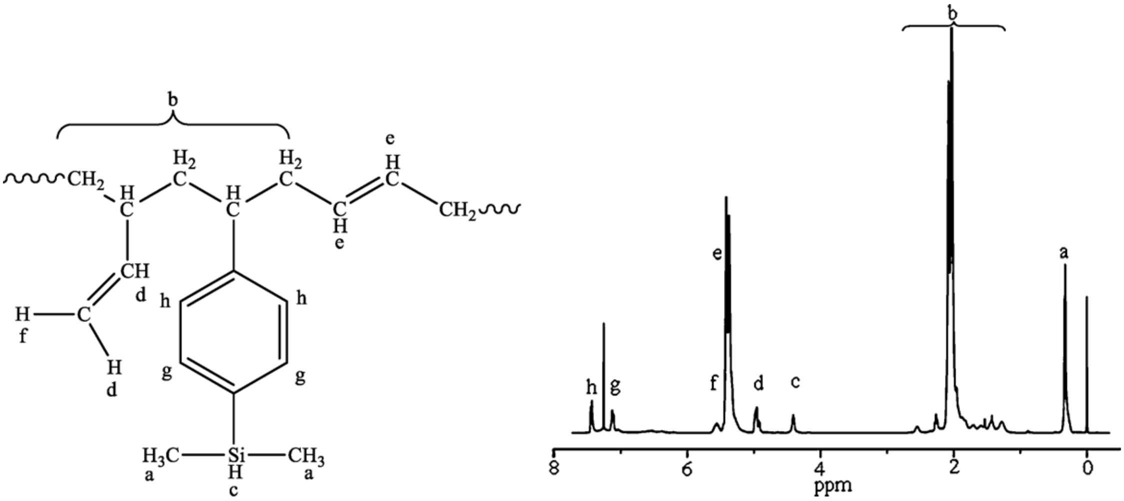


Fig. 1. ^{1}H NMR spectra of R1.

Table 1
Composition, microstructures and SEC results of copolymers.

Polymer	Feed		Calculate[a]		1,2-PB[a]	1,4-PB[a]	Blockiness VPDMS[b] ($f_{VPDMS-B}$)	Mn[c] ($\times 10^{-4}$)	M_w/M_n [c]
	VPDMS	Bu	VPDMS	Bu					
R1	7	93	7.4	92.6	7.1	85.5	85.5	7.62	1.15
R3	26	74	26.2	73.8	6.3	67.5	67.5	7.66	1.12
R5	52	48	53.7	47.3	4.5	42.8	42.8	7.36	1.18

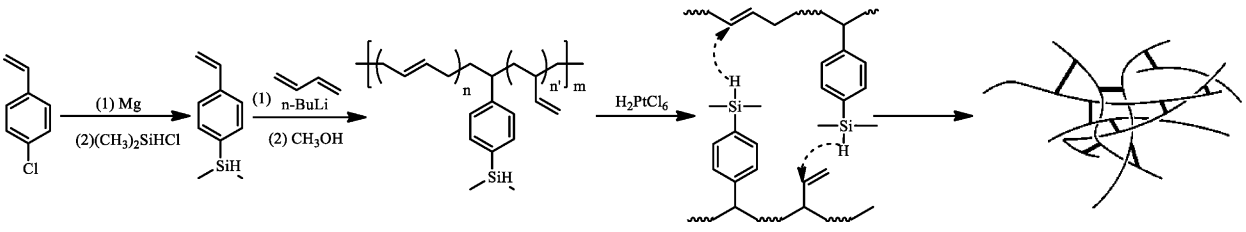
[a] Calculated by ^{1}H NMR, percentage of mole.

[b] The calculation of the blockiness VPDMS contents is similar to that of Ref. [9], but the equations is: $4M_1 + 2M_2 = A_{7.5\text{–}6.9}$; $2M_2 = A_{6.8\text{–}6.1}$; $f_{VPDMS\text{-}B} = M_2/(M_1 + M_2)$. Because there are four phenyl protons on VPDMS. Where, M_1 is the relative number of moles of non-block VPDMS, M_2 is the relative number of moles of block VPDMS, $f_{VPDMS\text{-}B}$ is the mole content of block VPDMS in VPDMS.

[c] Calculated by SEC.

The synthesis of VPDMS was presented in Ref. [8]. The polymerizations were carried out under argon atmosphere in ampoules equipped with latex tube and glass plug at 50 °C with *n*-BuLi as the initiator in cyclohexane. After 4 h, the reaction mixture was deactivated by a few drop of degassed 2-propanol. The copolymers were precipitated by adding a large excess of ethanol and freeze-dried. The copolymer composition and microstructures are calculated by ^{1}H NMR spectra. The peak areas $A_{7.45\text{–}6.22}$:$A_{4.4}$:$A_{0.33} \approx 4{:}1{:}6$ show that Si-H group is stable at the polymerization condition. Molecular weights and molecular weight distributions of copolymers were monitored by SEC. The ^{1}H NMR spectra of R1 are shown in Fig. 1 as an example. These results are summarized in Table 1.

0.5 g copolymer was dissolved in 30 mL toluene, to which 3–4 drops of H_2PtCl_6 were added. The temperature of the mixture was slowly raised to 60 °C, and the reaction was allowed to proceed for 24 h. The elastomer was precipitated by adding a large excess of ethanol (Scheme 1). Product was dried in vacuum oven until constant weight



Scheme 1. Synthetic route of silyl-hydride functional SBR and self-crosslinking elastomer.

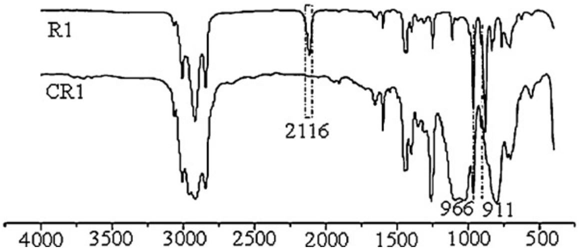


Fig. 2. FTIR spectrum of copolymer R1 and self-crosslinking elastomer CR1.

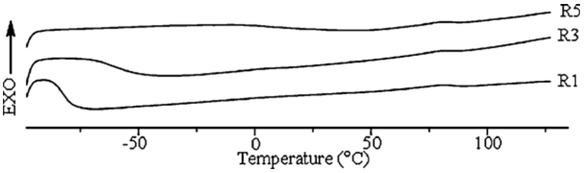


Fig. 3. DSC traces of copolymers.

(W_0). Then it was extracted with Soxhlet extraction for 72 h, using acetone as medium, and dried to a constant weight (W_1). The content of gel (G) was calculated by $G = (W_1/W_0) \times 100\%$. $G1$, $G3$ and $G5$ are 88.91%, 92.13% and 87.95%. As shown, all the copolymers cross linked obviously and the content of gel had change a little with increasing VPDMS content. The result indicated that it contributes little to gel content by increasing crosslinking point. Because a sound three dimensional network structure can be shaped even there is only 10% (mol) Si-H group in the copolymer.

As shown in Fig. 2, the FTIR spectrum of the polymer R1 has strong absorptions at 2116, 966, and 911 cm^{-1} corresponding to the Si-H group, 1,4-vinyl bonds and 1,2-vinyl bonds. In the spectrum of self-crosslinking elastomer CR1, the absorption at 2100 cm^{-1} was not observed and the absorption at 911 cm^{-1} still exists. This means that the Si-H group had completely reacted with vinyl bonds and 1,2-vinyl bonds in the polymer were left over. As shown in Table 1, the molar content of Si-H group, 1,2-vinyl bonds and 1,4-vinyl bonds in R1 is 7.4:7.1:85.5. It indicated that Si-H group not only reacted with 1,2-vinyl bonds, but also reacted with 1,4-vinyl bonds in the self-crosslinking reaction, although previous literatures have shown the inertness of the internal double bonds towards chlorosilane [10,11]. Meanwhile, the similar result was obtained in the FTIR spectrums of CR3, and the FTIR spectrum of CR5 shows no peaks at 2116, 966 and 911 cm^{-1} showing that all the silyl hydride units and vinyl bonds had been converted to Si-CH_2 groups in the self-crosslinking reaction.

There are two glass transition temperatures to every copolymer (Fig. 3 and Table 2). The first T_g in low temperature region denotes the glass transition of Bu-VPDMS graded structure in copolymer, and the second T_g denotes that of

Table 2
Glass transition temperature of copolymers.

Polymer	T_g 1 (°C)	T_g 2 (°C)
R1	−82.32	86.23
R3	−63.15	85.49
R5	4.43	85.13

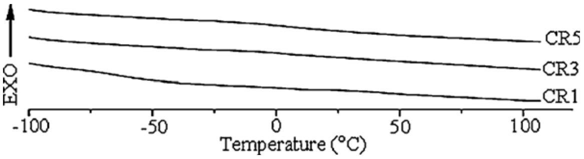


Fig. 4. DSC traces of self-crosslinking elastomers.

Table 3
TGA results of copolymers and self-crosslinking elastomers.

Sample	5% weight loss (°C)
R1	367.5
CR1	400.7
R3	378.2
CR3	412.0
R5	381.9
CR5	415.0

VPDMS block structure, which hovered around 85 °C. T_g 1 goes up with increasing VPDMS content. That is because the probability of VPDMS initiated by Bu anion increased with increase of VPDMS content and decrease of Bu content in the polymerization systems, and the glass transition temperature ascend as the amount of rigid group in the Bu-VPDMS graded structure increased. As shown in Fig. 4, there are no obvious glass transitions in all self-crosslinking elastomers. This is because the movement of chain segment was limited by too much crosslinking points.

The results of thermogravimetric analysis (Table 3) showed that the thermo decomposing temperature of all the self-crosslinking elastomers was much higher than that of corresponding copolymers. It indicated that cross-link is helpful to increasing the thermal stability of copolymer.

In conclusion, a series of in-chain SiH-functionalized copolymers and corresponding self-crosslinking elastomers were synthesized successfully by anionic polymerization and hydrosilation reaction, respectively. Active group Si-H remained stable in the polymerization system, and the quantity of Si-H in the chain can be controlled by reactant ratio. The perfect three dimensional network structure can be shaped even there is only 10% (mol) Si-H group in the copolymer. That is because the Si-H group in VPDMS reacted with not only 1,2-vinyl bonds but also 1,4-vinyl bonds. There are no obvious glass transitions in all self-crosslinking elastomers. However, there are two T_g to all the copolymers. The lower denotes the glass transition of Bu-VPDMS graded structure, which ascends with increase of VPDMS content. The other denotes the T_g of VPDMS block structure, which hovered around 85 °C. The results of TGA showed that the heat stability of copolymers can be improved obviously by cross-link. The mechanical properties of self-crosslinking elastomers will be the subject of future work.

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