# Branched Polystyrene with High Reflex Index Synthesized from Selenium-Mediated Polymerization

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**ABSTRACT:** In this article, the polymerization behavior has been investigated utilizing phenyl(4-vinylbenzyl)selane (PVBS) as an inimer under ultraviolet irradiation. Corresponding copolymers and homopolymers were synthesized by copolymerization PVBS with styrene and homopolymerization itself. The branching factors (g') of these branched polymers were characterized along with the polymerization conditions. Moreover, the results showed that the obtained polymers' refractive index (RI) can be enhanced by the introducing of selenium element. The

results also indicated that the RI of obtained polymers could be adjusted extendedly by changing selenium content in them. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2014**, *52*, 504–510

**KEYWORDS**: branched; high refractive index; hyperbranched; iniferter; living radical polymerization (LRP); optics; refractive index; selenium mediated

**INTRODUCTION** Polymeric materials with high refractive index (n) and high Abbe's number (v) have attracted much interest due to their potential applications in many areas, such as coatings for light-emitting diodes (LEDs),<sup>1,2</sup> microlens com-ponents for charge coupled devices (CCD)<sup>3</sup> or volume holo-graphic recording materials,<sup>4</sup> and so on.<sup>5,6</sup> According to the Lorentz-Lorenz equation, the introduction of substituents with high molar refractions and low-molar volume groups have become the common approaches for most researchers to increase the refractive index of polymers.<sup>7</sup> Traditional methods usually be adopted were (1) incorporating organic groups or consisting of highly conjugated structures, such as aromatic groups;<sup>8</sup> (2) incorporation of halogen atoms, sulfur atoms and silicon atoms with high molar refractions into the backbone or side chain of polymers;9-11 (3) synthesizing polymers with enwrapped inorganic nanoparticles.<sup>12</sup> Table 1 showed the molar refractions of common atoms or groups. As shown in the right column of Table  $1^{13}$  the molar refraction ( $R_{\rm M}$ ) of alkyl selenides was higher than that of sulfides, which implied that insertion of selenium atoms in polymer materials maybe a more efficient way to improve the refractive index than incorporation of sulfur atoms. And as far as we know, few relevant literatures have been reported.<sup>14</sup>

The selenium can be incorporated into polymer chain through the polymerization of selenium containing mono-

mer<sup>15,16</sup> or the reaction between selenium agent with polymer.<sup>17–19</sup> However, in these approaches, the amount of incorporated selenium in final polymer was difficult to adjust, which would evidently limit the variable RI range. Recently, our group has reported the controlled radical polymerization, or reversible-deactivation radical polymerization defined by IUPAC, using novel selenium compounds as the mediator.<sup>20-24</sup> In such way, the amount of the selenium concentration in polymer can be adjusted by molecular weight. However, in these cases the selenium was attached at the end of polymer chain, which made it difficult to incorporate more than two selenium-containing groups into one polymer chain. Thus, increasing the amount of polymer chain ends would be the efficient way to increasing the concentration of selenium among the polymer chain with controlled manner. As it well known that hyperbranched polymer contained highly branched structure with high concentration of chain ends. Apart from this, hyperbranched polymers have been of particular interest in polymer science for many years.<sup>25-27</sup> Because the unique globular and highly branched structure can increase their compactness compared to linear ones. And then low viscosities, many functional end-groups and low viscosities<sup>28</sup> are also their proper features, which makes them widely used as targeted drug delivery,29 viscosity modifiers,<sup>30</sup> supports for catalysts,<sup>31</sup> and other materials.<sup>32,33</sup> Yuki<sup>34,35</sup> has briefly reported the synthesis of hyperbranched

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Group	R <sub>M</sub>	Group	$R_{\rm M}$
Н	1.100	Phenyl ( $C_6H_5$ )	25.463
С	2.418	Naphthyl (C <sub>10</sub> H <sub>7</sub> )	43.000
C=C	1.733	1	13.900
C≡C	2.398	C=S	7.970
C=0	2.211	—SH	7.690
0—Н	1.525	-SeR (R=alkyl)	11.170

<sup>a</sup> Data were cited from ref. 13.

polystyrene using selenium containing compounds. However, the detailed polymerization behavior and properties of the polymer were still worth of investigation.

Here, through the route shown in Scheme 1, we have investigated the synthesis of hyperbranched polystyrene utilizing phenyl(4-vinylbenzyl)selenide (PVBS)<sup>36</sup> as an inimer under ultraviolet (UV) irradiation. Copolymers and homopolymers have been synthesized by its copolymerization with styrene and homopolymerization itself via self-condensing vinyl polymerization (SCVP).<sup>37–39</sup> The results showed that the polymers showed higher RI than polystyrene. Moreover, the RI of the polymer can be adjusted by the concentration of selenium in polymer.

#### EXPERIMENTAL

#### Materials

Diphenyl diselenide (98%) and tetrabutylammonium hexafluorophosphate were purchased from J & K Scientific). All other reagents (analytical grade) used in this study were purchased from Shanghai Chemical Reagents (China). Styrene was washed with an aqueous solution of sodium hydroxide (5 wt %) three times and then with deionized water until neutralization. After being dried with anhydrous magnesium sulfate, styrene was distilled under reduced pressure and kept in refrigerator under 0 °C. Tetrabutylammonium hexafluorophosphate was recrystallized after dissolving in ethyl acetate. 4-Vinylbenzyl chloride was purified by neutral alumina column.

#### Synthesis of Phenyl(4-vinylbenzyl)selane

Diphenyldiselenide (1.25 g, 4.0 mmol) was dissolved in 10 mL of anhydrous THF, and then 10 mL of an aqueous solution of 0.30 g (8.0 mmol) of sodium borohydride was added. The reaction was finished in a few minutes, and a colorless sodium phenylselenide (PhSeNa) solution was obtained. The obtained PhSeNa solution was immediately injected into 20 mL of a THF solution of 1.22 g (8.0 mmol) of 4-vinylbenzyl chloride, and the reaction was performed at 50 °C for 12 h under argon flow. Then, the product was extracted with diethyl ether and was purified by column chromatography with *n*-hexaneas the eluent. The pure product showed as white powder was obtained with yield of 71%.

<sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ , ppm)  $\delta$  4.09 (s, CH<sub>2</sub>, 2H), 5.20 (d, trans-CH<sub>2</sub>—, 1H), 5.70 (d, cis-CH<sub>2</sub>=, 1H), 6.66 (dd, =CH, 1H), and



**SCHEME 1** Synthesis of selenium-containing hyperbranched polystyrene with PVBS as inimer. [Color figure can be viewed in the online issue, which is available at wileyonline library.com.]

7.16–7.45 (m, C<sub>6</sub>H<sub>4</sub> and C<sub>6</sub>H<sub>5</sub>, 9H). <sup>77</sup>Se NMR (CDCl<sub>3</sub>,  $\delta$ , ppm)  $\delta$  384.5 (s, PhSe-, 1Se). EA: calculated for C<sub>15</sub>H<sub>14</sub>Se: C, 65.94%; H, 5.16%. Found: C, 65.38%; H, 5.09%.

#### Photopolymerization of PVBS with Styrene

A typical polymerization procedure was as follows: St (0.453 g, 4.3 mmol) and PVBS (0.119 g, 0.43 mmol) were added to a dried ampoule with 0.6 mL anhydrous toluene. The content was deoxygenated by bubbling argon for 15 min, and then the ampoule was flame sealed. Afterward, the ampoule was placed in the irradiation of ultraviolet lamp with 150-W high-pressure mercury lamp in the distance of 20 cm at 30 °C. After the desired reaction time, the ampoule was opened and the products were dissolved in THF, precipitated into cold methanol. The polymer was separated via filtration and was dried under vacuum until constant weight at room temperature. The conversion of monomer was determined by gravimetrical method.

#### **Homopolymerization of PVBS**

A typical polymerization procedure was as follows: PVBS (1 g, 3.65 mmol) with anhydrous toluene (1.6 mL) was added to a dried ampoule. The content was deoxygenated by bubbling argon for 15 min, and then the ampoule was flame





**FIGURE 1**  $\ln([M]_0/[M])$  versus time for the polymerization of styrene in the presence of PVBS in bulk under UV irradiation with the molar ratio of  $[St]_0:[PVBS]_0=50/30/10:1$ , temperature= 30 °C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

sealed. Afterward, the ampoule was placed in the irradiation of ultraviolet lamp. Postprocessing method is the same as above.

#### Characterization

The number-average molecular weight  $(M_n)$  and molecular weight distribution  $(M_w/M_n)$  of the resulting polymers were determined using an Agilent PL-50gel permeation chromatograph (GPC) equipped with triple detectors (refractive-index detector, two angles light scattering detector and viscosity detector), using PL Mixed gel C (5- $\mu$ m beads size) columns with molecular weights ranging from 200 to  $2 \times 10^6$  g/mol. THF was used as the eluent at a flow rate of 1.0 mL/min and 40 °C. GPC samples were injected using a PL-AS RT autosampler and calibrated with PS standards purchased from PL. The <sup>1</sup>H NMR spectrum of the polymer was recorded on an INOVA 400-MHz nuclear magnetic resonance instrument using CDCl<sub>3</sub> as the solvent and tetramethylsilane (TMS) as an internal standard. The <sup>77</sup>SeNMR spectrum of the polymer was recorded on a Varian 400 MHz instrument using CDCl<sub>3</sub> as the solvent (CH<sub>3</sub>SeCH<sub>3</sub> as an external standard). Thermogravimetric analysis (TGA) was carried out on a 2960 SDT TA instruments with a heating rate of 10 °C/min from the room temperature to 800 °C under the nitrogen atmosphere. Atomic absorption spectroscopy of polymer was measured on Varian 220DuO instrument. The refractive index of the polymer was determined on J. A. Woollam Alpha-SE ellipsometer.

#### **RESULTS AND DISCUSSION**

## Photopolymerization Behavior of St in the Presence of PVBS

Here, first, the polymerization kinetic of styrene was investigated using PVBS as inimer in different feeding ratio of monomer to inimer. The result was showed in Figure 1. As shown in Figure 1, the polymerization rate of styrene was



**FIGURE 2** Relationships between  $M_n$ ,  $M_w/M_n$  and conversion in the polymerization of St at various concentrations of PVBS. [St]<sub>0</sub>:[PVBS]<sub>0</sub>= 50/30/10:1, temperature= 30 °C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

increased with the increasing of the inimer concentration. As showed in Scheme 1, the PVBS decomposed to one carbon centered radical and one selenium centered radical under the irradiation of UV. The carbon centered radical initiated the polymerization of styrene and selenium centered radical served as the dorment radical to recombinating with propagation radical through iniferter way.<sup>34,35</sup> Thus, increasing the inimer concentration would result in the increasing of initiation radical, which enhanced the polymerization rate. Figure 2 indicated the relationship between number-average molecular weight  $(M_n)$  and the molecular weight distribution  $(M_w/M_n)$  to the monomer conversion with different feeding ratios. The molecular weight increased almost linearly with the monomer conversion in all cases of polymerizations. The molecular weights were determined by GPC with RI detector due to the low polymer molecular weight (<8000 g/mol), which cannot be measured precisely by LS detector. The obtained polymers showed broad molecular weight distribution  $(M_w/M_n > 1.8)$ , which was normally found in hyperbranched polymers. The molecular weight distribution of the resulting polymers was ever broadening as the polymerization proceeds because of the chain branching reaction, which has been predicated<sup>40</sup> and reported<sup>41</sup> previously. Meanwhile, the  $M_w/M_n$  value increased with the monomer conversion, which was consistent with iniferter polymerization characteristic. The GPC traces of these polymers were showed in Figure 3. It showed significant shoulders, tailings, or even multiple distributions appeared in GPC traces, suggesting the possible partial loss of CTA functionality and different branching generations. Yuki et al. have demonstrated that diphenyl diselenide (DPDSe) formed in the polymerization process.<sup>34,35</sup> As the result, the broad  $M_w/M_n$  and multicomponent may also partially caused by the "side" polymerization initiated by the generated DPDSe, which lead to little linear polymers mixed in the hyperbranched polymers.



**FIGURE 3** Evolution of GPC traces for the copolymerization of St with PVBS in toluene under UV irradiation.  $[St]_0 = 7.2 \text{ mol/L}$ . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The structure of obtained polymer was investigated utilizing <sup>77</sup>Se NMR spectrum. Due to the low abundance of <sup>77</sup>Se, the homopolymer of PVBS, poly(phenyl(4-vinylbenzyl)selane) (PPVBS), was synthesized by the UV-irradiated polymerization (Scheme 1). The results were showed in Figure 4. The observation of <sup>77</sup>Se resonance in both of the spectra before and after the polymerization indicated that selenium can be successfully incorporated into polymer through polymerization. The resonance of <sup>77</sup>Se shifted from 384.5 to 276.3 ppm



**FIGURE 4** <sup>77</sup>Se NMR spectra of PVBS and PPVBS ( $M_n = 13,400$ ,  $M_w/M_n = 15.18$ ) in CDCl<sub>3</sub>. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

after polymerization, indicating that the chemical environment of selenium has changed after polymerization, which was consisted with the polymerization reaction showed in Scheme 1. Furthermore, only single peak were detected in each spectra, which illustrated that the synthesized PVBS has high purity and the selenium components in hyperbranched PPVBS have similar structures.

# The Branching factor (g') and Selenium Content of Hyperbranched Polymers

The branching factor (q') was used to investigate the degree of branching of the hyperbranched polymers on a side-note. Usually g' defined by Zimm and Stockmayer with equation:  $g' = [\eta]_{\rm b}/[\eta]_{\rm b}$  where  $[\eta]_{\rm b}$  and  $[\eta]_{\rm l}$  are intrinsic viscosities of branched and linear polymers with same molecular weight, respectively. Table 2 showed the results of photocopolymerization of St with PVBS in different feeding ratios along with the values of g'. The g' values increased from 0.17 to 0.74 when the St-to-PVBS feeding ratio increased from 10 to 50, which indicated that branching factor becomes smaller with an increase of the PVBS concentration. Thus, the homopolymer of PVBS showed the lowest g' value of 0.13 as shown in Table 2. These results indicated that the homopolymer has more branching structure than that of copolymers. Meanwhile, the selenium content in polymers has been measured via atom absorption spectroscopy (AAS). The value of selenium content was also listed in Table 2. The values decreased from 8.1 to 3.0% when the St-to-PVBS feeding ratio increased from 10 to 50. And the AAS determined selenium content values were closed to the theoretical ones (assumed that all the PVBS has participated in the reaction). In the case of homopolymerization, the highest selenium content was 28.9%, which was approximate to the value in PVBS. The branching factors for copolymers obtained by SCVP of St and PVBS at constant comonomer ratios were also investigated. The results were listed in Table 3. It showed that the branching structure was increased with the increasing of conversion, which was consisted with the SCVP process.<sup>42,43</sup>

#### The Thermostabilities of Hyperbranched Polymers

Figure 5 presented the thermogravimetric analysis (TGA) results for hyperbranched polymers incorporated with



TABLE 2 Branching	Factor for Copo	ymers Obtained by S	SCVP of St and PVBS a	t Different Feeding Rati	ios
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No.	Feeding Ratio <sup>a</sup>	Conv.% <sup>b</sup>	<i>M</i> <sub>n</sub> <sup>c</sup>	$M_n^d$	$M_{\rm w}/M_{\rm n}^{\rm d}$	g′ <sup>e</sup>	Se% <sup>f</sup>	Se <sub>th</sub> % <sup>g</sup>
P-1	50	51.7	4300	5150	4.03	0.74	3.0	2.8
P-2	30	58.8	4500	6370	2.12	0.54	5.6	4.0
P-3	10	73.3	7000	12900	6.49	0.17	8.1	8.3
P-4*	0	60.2	7100	13400	15.18	0.13	28.9	29.2

<sup>a</sup> Feeding ratio: [St]<sub>0</sub>:[Inimer]<sub>0</sub>. Polymerization conditions:  $\lambda_{UV}$  =365 nm, in toluene at 30 °C. [St]<sub>0</sub>=4.35 mol/L,\* [Inimer]<sub>0</sub>=2.3 mol/L.

<sup>b</sup> The conversion of monomer was determined by a gravimetrical method.

<sup>c</sup> Determined by GPC with RI detectors.

<sup>d</sup> Determined by GPC with triple detectors(RI, LS, and Viscosity).

<sup>e</sup>  $g' = [g]_b/[g]_l$ , where,  $[g]_b$  is intrinsic viscosity of branched polymers,  $[g]_l$  is intrinsic viscosity of linear polymers.

Determined by atomic absorption spectrophotometer.

<sup>g</sup> Calculated by formula:  $80m_{PVBS}/[274 \times Con.\% \times (m_{PVBS} + m_{St})]$ .

TABLE 3 Branching Factor for Copolymers Obtained by SCVP of St and PVBS at Constant Comonomer Ratios

No.	Feeding Ratio <sup>a</sup>	<i>t</i> (h)	Conv.%	<i>M</i> <sub>n</sub> <sup>b</sup>	<i>M</i> <sub>n</sub> <sup>c</sup>	M <sub>w</sub>	$M_{\rm w}/M_{\rm n}$	g'
P-5	10	24	42.0	2,200	4,360	7,540	1.73	0.58
P-6	10	40	61.5	3,300	5,600	15,800	2.83	0.51
P-7	10	50	68.0	4,000	8,160	27,900	3.42	0.45
P-8	10	65	70.0	4,800	10,000	38,600	3.85	0.33

<sup>a</sup> Feeding ratio: [St]<sub>0</sub>:[Inimer]<sub>0</sub>. Polymerization conditions:  $\lambda_{UV} = 365$  nm, in toluene at 30 °C. [St]<sub>0</sub> = 7.26 mol/L.

<sup>b</sup> Determined by GPC with RI detectors.

<sup>c</sup> Determined by GPC with triple detectors (RI, LS, and Viscosity).

different contents of selenium atoms. In generally, polystyrene showed decomposition temperature of 300–400 °C. As showed in Figure 5, the copolymer P-1, P-2, and P-3 showed similar decomposition behavior in the range of 350–360 °C. The increasing of selenium concentration resulted in the decreasing of thermostability. The homopolymer of PVSB (P-4) with selenium content of 28.9% started decomposing at 275 °C. The reason may attribute to the fact that C—Se bonds were existed abundantly and the bond energy of C-Se bond (243 KJ/mol) was lower than that of C—C bond (347



**FIGURE 5** TGA curves of hyperbranched polymers under constant nitrogen flow of 20 mL/min and heating rate of 10  $^{\circ}$ C/ min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

kJ/mol).<sup>44</sup> Additionally, at 450 °C, all polymers were decomposed completely. The decline of weight above 450 °C was mainly due to the evaporation of selenium. Then, the last platform of every curve also indicated the difference of the selenium content in these polymers. The amount measured in TGA was in good accordance with the measured values by AAS.

### The Optical Properties of Hyperbranched Polymers

Figure 6 showed UV-vis absorption spectra of the studied polymers (P-1, P-2, P-3, and P-4) in  $CH_2Cl_2$ . All the samples showed no absorption in the visible and infrared region (>350 nm). And absorption around 240–325 nm becomes larger in the order of P1 < P2 < P3 << P4, which probably contributed from the stronger absorption capacity of -SePh groups.

Optical transparency of the polymer films was a crucial factor for their use in optical applications. So, in this article, we coated thin sample films on quartz wafer and evaluated the transmittance with a UV-vis spectrometer. Figure 7 shows the UV-vis absorption spectra of selenium-containing hyperbranched polystyrene films with thickness of 1.4  $\mu$ m approximately. As shown in the figure, the optical transmittance spectra of P-1, P-2, P-3, and P-4 were similar to each other. Simultaneously, all the polymer films exhibit relatively low cutoff wavelengths (determined at 50% transmittance) ranged between 283 and 318 nm and excellent transparency with transmittance much higher than 90% after the wavelength over 350 nm, which indicate that the incorporation of selenium atoms have little effect on the transmissivity of the



**FIGURE 6** UV-vis absorption spectra of polymers dissolved in  $CH_2CI_2$ . Polymer concentration: 0.25 mg/mL. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

polymers. These characters were favorable for the polymer been used as optical materials.

In order to investigating the optical properties of the obtained polymer, the refractive indices and Abbe's number of these polymer films were investigated. Table 4 shows the refractive indices of three hyperbranched polymers with different selenium content at 486, 589, and 656 nm. Simultaneously, as shown in Table 4, all the films have a relative high Abbe's number of 36.3, 33.6, and 31.7, respectively, which indicates that these materials were endowed with low-light dispersion. The dates of refractive indices were measured with an ellipsometer by spin-coating samples on silicon wafer. The wavelength dispersion (300–800 nm) of the refractive indices ( $n_{\lambda}$ ) was plotted in Figure 8(a). All the polymers incorporated with selenium element were of high RI values compared to ordinary polystyrene (n = 1.58),



**FIGURE 7** Transmittance UV-vis spectra of the synthesized hyperbranched polymers with film thickness ~1.3  $\mu$ m. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE 4 Optical Properties of the Selenium-Containing Films

Entry	Se%	n <sub>486</sub>	n <sub>589</sub>	n <sub>656</sub>	vD
P-1	3.0	1.629	1.617	1.612	36.3
P-3	8.1	1.651	1.638	1.632	33.6
P-4	28.9	1.713	1.697	1.691	31.7

which suggest that the introduction of a selenium (-Se-) element with high atom refraction and low molecular dispersion was effective to develop high-*n* and high-*v* polymers. And with the increasing of selenium content in polymers from 3.0 to 28.9%, their RI value at 583.9 nm increased from 1.617 to 1.697. Figure 8(b) revealed the wavelength dispersion (300–800 nm) of calculated refractive indices ( $n_{\lambda}$ ) of these three films with a fitted curve using the Cauchy's formula. The calculations well reproduce the experimental refractive indices of polymer films, although the calculated  $n_{\lambda}$  of polymers were slightly overestimated. This because the existence of hyperbranched structure induces additional free volume.<sup>45,46</sup> So, based on the description above, we can



**FIGURE 8** Wavelength dispersion of (a) experimental and (b) calculated refractive indices of three polymer films. The dispersions are fitted by the Cauchy's formula. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

change the selenium content via simply change the feeding ratio to get the materials with the different refractive index, which probably was an effective method to expand the application area of polystyrene.

#### CONCLUSIONS

In summary, the polymerizable iniferter PVBS was designed and synthesized. Hyperbranched PS was synthesized via the combination of SCVP and iniferter polymerization techniques using PVBS as the mediator. The branched nature of the resulting polymers was confirmed by <sup>77</sup>Se NMR spectroscopy and gel permeation chromatograph (GPC). The incorporation of selenium can improve the refractive index of optical materials effectively. And the RI value can be adjusted by simply changing the selenium content in polymers. Simultaneously, these serial selenium-containing materials also have good transparency and relative high Abbe's numbers. So, in consider of the multifaceted functionalities mentioned above and high selenium content analyzed, the synthesized hyperbranched polymers may have potential application in optical area.

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