

Novel Tin-Coupled Star-Shaped Medium Vinyl Butadiene Rubber. II. Vinyl Content, Molecular Weight, and their Effects on Properties

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ABSTRACT: On the basis of our earlier work, extensive experiments were conducted to further investigate the regulating means of vinyl content, molecular weight, molecular weight distribution, and their effects on overall performance of star-shaped medium vinyl butadiene rubber (S-MVBR), which was prepared by “core-first” method with novel multifunctional organolithium as initiator, tetrahydrofuran (THF) as structure regulator, and raffinate oil as solvent. The results showed that vinyl content and molecular weight for one arm were easily regulated from 30 to 55%, 6–10 ten thousand, respectively. The tensile strength and elongation at break increased with increasing vinyl content and the dynamic heating was the lowest at vinyl content of 43%.

S-MVBR had a relatively wide and symmetrical monomodal distribution, which was in favor of good processing properties. S-MVBR containing Sn atom, with arm number of 3.8, molecular weight for one arm of eight 10,000, vinyl content of 50%, and distribution of molecular weight of 1.54, had optimal overall properties. When compared with *cis*-BR and linear MVBR, S-MVBR had low rolling energy loss, high wet grip, good mechanical and processing properties. It was an ideal rubber for high performance tire tread. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 3924–3930, 2007

Key words: polybutadiene; rubber; star polymers; synthesis; property

INTRODUCTION

In the previous article, star-shaped medium vinyl butadiene rubber (S-MVBR) was successfully prepared by “core-first” method with novel multifunctional organolithium initiator.^{1,2} The regulating means of arm number and its effect on the properties of S-MVBR were studied in detail. However, apart from this, the properties may closely be related to other structure such as vinyl content (Bv%), molecular weight, and its distribution.

1,2-Polybutadiene rubber with different Bv% possesses obviously diverse properties. Increasing Bv% can elevate glass transition temperature linearly to influence mechanical and processing properties.³ And the extent of segment motion related to vinyl group influence dynamic properties including heat accumulation and wet grip.^{4–6} In addition, vulcanization become uneasy with high Bv%. Favorable properties can be attained partially by controlling Bv% with many means.⁷

In addition to Bv% mentioned earlier, high molecular weight is beneficial to improving mechanical

properties and decreasing rolling resistance whereas high viscosity causes processing difficult.^{8,9} However, a properly wide distribution can improve the processing properties.¹⁰ Thus, molecular weight and its distribution should be decided stoichiometrically by anionic living polymerization.

Up to now, there are only a few literatures on properties of S-MVBR prepared by “arm-first” method.^{5,6,8} Reports on S-MVBR prepared by “star-first” method have not been mentioned. To obtain overall balance of all properties, S-MVBR with different Bv%, molecular weight, and distribution was prepared. This article was devoted to studies of the regulating means of above structure factor and relationship between structure and properties including mechanical properties, dynamic properties, rheological properties, and processing properties. And a favorable structure of S-MVBR with optimal performance was achieved.

EXPERIMENT

Materials

Butadiene, platformate raffinate oil, and *cis*-BR (BR-9000) were provided by Yanshan Petrochemical (China). Raffinate oil was rectified and the cut fraction of 65–70°C was dried over Na wire under nitrogen.

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Tetrahydrofuran (THF) was refluxed over CaH₂ for overnight and distilled under nitrogen. It was finally distilled from its sodium naphthalenide solution on the vacuum line. Butyl lithium was prepared by usual procedure. The multifunctional organolithium was synthesized according to our procedures previously reported.¹

Synthesis

A 2-L stainless steel reactor was charged with butadiene-Raffinate oil solution and THF after it was purged with nitrogen gas, and washed with living polystyryl-lithium solution. The polymerization was initiated upon the addition of multifunctional organolithium, which had been prepared.¹ The temperature of reactor was kept at 50°C for 2–4 h. Then, the reaction was terminated by adding small amount of methanol and 2,6-di-*tert*-butyl *para*-cresol. The star-shaped polymer was purified by precipitation with technical alcohol. Linear MVBR was prepared in the similar manner with butyl lithium as an initiator.

Characterization

Number-average molecular weight (\overline{M}_n) was determined by Knauer 1.00 membrane permeameter at 37°C, with toluene as solvent. Molecular weight distribution ($\overline{M}_w/\overline{M}_n$) was determined by Waters150-C gel permeation chromatography (GPC) equipped with 410 differential refractometer as detector. A set of three Styragel columns (HT3, HT4, and HT5) was used and the calibration curve was obtained by PS standards. The mobile phase was THF (analytical grade), the flow rate was 1 mL/min, and the temperature was 25°C. The ¹H NMR spectra of S-MVBR diluted in CDCl₃ were recorded on an AC-80 spectroscopy (Bruker, 80 MHz).

Formulation and performance test of vulcanizates

The crude S-MVBR was first milled by XK-160 mixing roll produced by Zhanjiang Rubber Machine Factory (China). Then, half carbon black, aids, another half carbon black, and sulfur were added in turn to mix. The formulation was given in Table I. The roll temperature was 40–60°C and the clearance was 0.5–1 mm. After milling for 3 min, the slabs were taken out. One day later, the compounds were cured at 145°C for 20 min by 25T compression molder produced by Shanghai Rubber Machine Factory (China). The pressure was 150 kgf/cm².

Hardness (Shore A), 300% modulus, tensile strength, elongation at break, resilience, tear strength, and tensile permanent set were determined, respectively, according to China state standards: GB/T531-

TABLE I
Formulation for S-MVBR Compounds

Composition	phr
Polymer	100
Carbon black (N220)	50
ZnO	4
Stearic acid	2
Accelerator DM (dibenzothiazyl disulfide)	1.2
Accelerator D (diphenyl guanidine)	0.4
Antioxidant 4010 (Bisphenol A (2,2'-bis(4-hydroxyphenol)))	1
Antioxidant RD (polymerized 2,2,4-trimethyl-1,2-dihydroquinoline)	1
Paraffin wax	4
Sulfur	1.7

92, GB/T528-92, GB/T528-92, GB/T528-92, GB/T1681-91, GB/T529-92, and GB/T528-92.

The temperature rise (ΔT) in compression fatigue was determined by a YS-25 Goodrich Compression Fatigue Machine. The room temperature was 50°C, the load was 1.01 MPa, and the stroke was 6 mm.

The dynamic mechanical properties were measured by DDV-11-EA viscoelastometer produced in Japan. The temperatures were –50–100°C, the frequency was 11 Hz, and the deformation amplitude was 0.7%.

The rheological properties were measured by Monsanto Rubber Tester. The temperature was 100°C, the ratio of length to diameter of capillary was 20, and descending rates were 0.51, 5.08, 15.2, and 50.8 mm/min, respectively. The cross section diameter of extrudate was determined by reading microscope. The ratio of the diameter to that of capillary was die-swell ratio.

RESULTS AND DISCUSSION

Vinyl content

Structure control

The ¹H NMR spectra of S-MVBR were shown in Figure 1. The peaks at 2.02 and 5.36 ppm represented proton of –CH₂– and =CH– of 1,4-unit. The peaks at 1.24 and 5.01–4.79 ppm represented proton of –CH₂– and =CH₂ of 1,2-unit. Vinyl content (Bv%) could be calculated according to the following equation:¹¹

$$\text{Bv}\% = \frac{2I_{(5.01-4.79)}}{2I_{5.36} + I_{(5.01-4.79)}} \times 100\%$$

Vinyl content (Bv%) was influenced by regulator kind, content, and temperature according to the anionic polymerization mechanism of polybutadiene suggested by Jin.⁷ THF with medium polarity was selected as a regulator and the results were shown in Figure 2. It is shown that Bv% increases with the

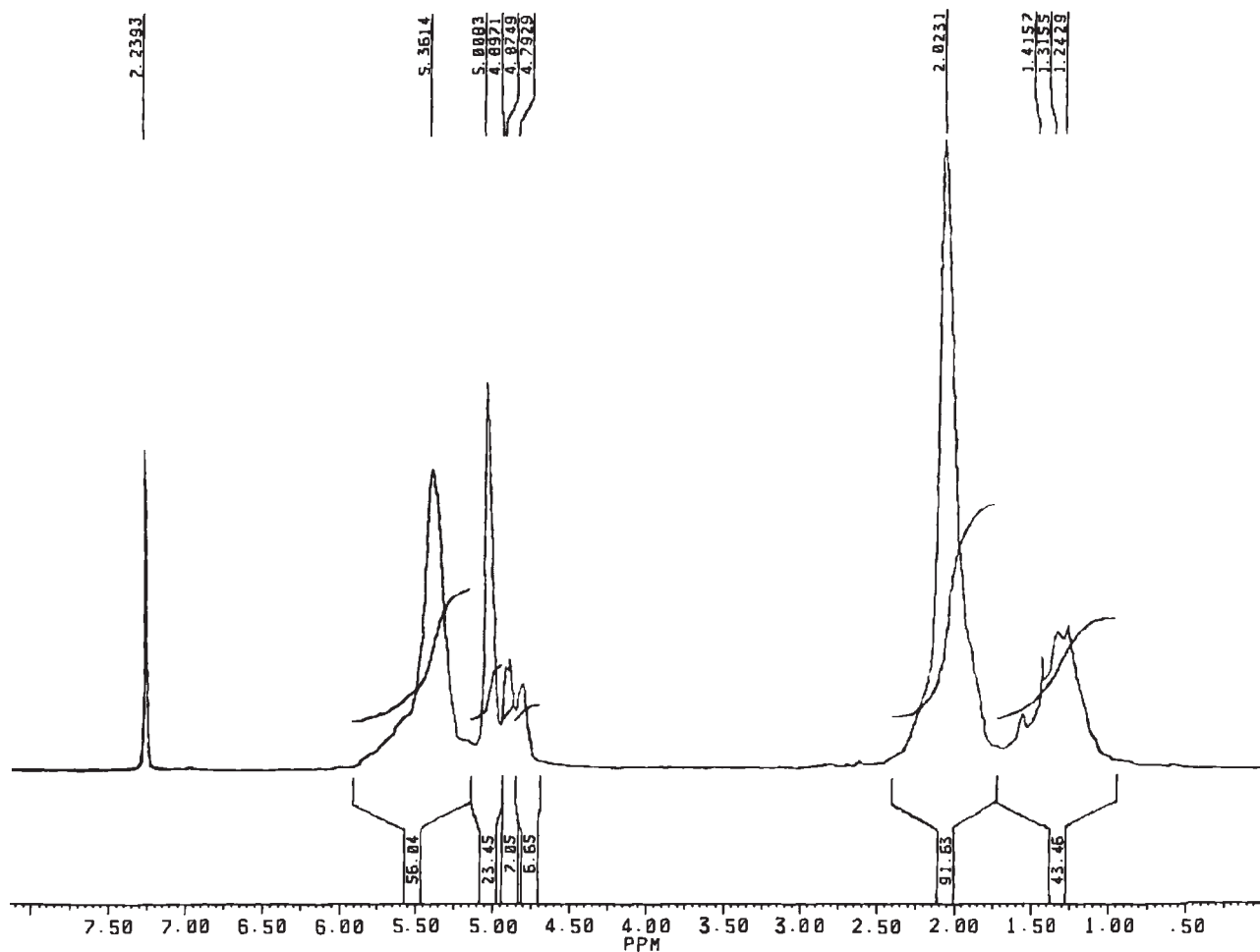


Figure 1 ^1H NMR spectra of S-MVBR.

increase in THF content R (expressed in mole ratio of THF to active lithium of multifunctional organolithium initiator). When R was above 50, Bv% increased slightly. This indicated that Bv% could be regulated from 30 to 55% by controlling THF content.

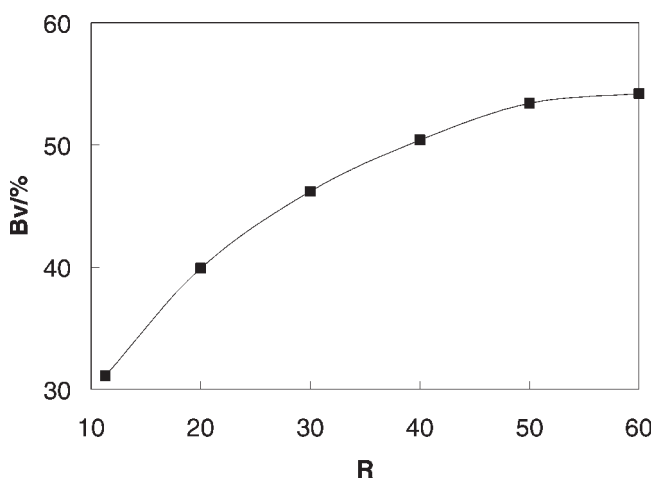


Figure 2 Relation of THF content to Bv% (MW/arm = 8×10^4 ; temperature = 50°C).

As activation energy of 1.2-addition was lower than 1.4-addition in polar regulator, Bv% decreased from 31 to 20% (R was 11) when temperature changed from 50 to 80°C . The result accorded with the relationship between Bv% and temperature.⁷

The influences of number-average molecular weight for one arm (MW/arm) and arm number on Bv% are listed in Tables II and III, respectively. Table II showed that with increasing MW/arm, Bv% increased a little. Table III showed that with increasing arm number, Bv% decreased slightly. This could be explained by initial steric hindrance. At the beginning of polymerization, active chain was short; the formation of π allyl active center took much more steric hindrance than σ -allyl active center, and so the formation of vinyl group was restricted. With increas-

TABLE II
Effect of MW/arm on Bv%

MW/arm ($\times 10^4$)	6.08	8	9.68
Bv%	49.8	49.3	47.0

R: 28, temperature: 50°C , arm number: 3.8.

TABLE III
Effect of Arm Number on Bv%

Arm number	3.4	3.8	4.1	4.4
Bv%	47.8	49.3	45.4	43.8

R: 28, Temperature: 50°C, MW/arm: 8×10^4 .

ing arm number, chain entanglement became serious, the steric hindrance of vinyl group formation became large, and Bv% decreased.

It was concluded that the influence factors on Bv% in sequence were THF content, temperature, and SnCl_4 content. As THF content was the main influence factor, Bv% was easily controlled by means of controlling THF content.

Mechanical properties

The influence of Bv% on mechanical properties of S-MVBR was shown in Figures 3 and 4. Figures 3 and 4 show that with an increasing of Bv%, the tensile strength (T_s) and elongation at break increased to the maximum value of 49.7% at Bv%, the hardness, and 300% modulus first increased and later decreased slightly, and the tear strength and resilience decreased. S-MVBR with Bv% of 49.7 exhibited optimal mechanical properties.

Dynamic properties

Figure 5 show the influence of Bv% on Goodrich compression heat accumulation (ΔT) and tensile permanent set (H%). On one hand, increasing of Bv% increased the resistance of chain movement and friction loss; on the other hand, increasing of Bv%

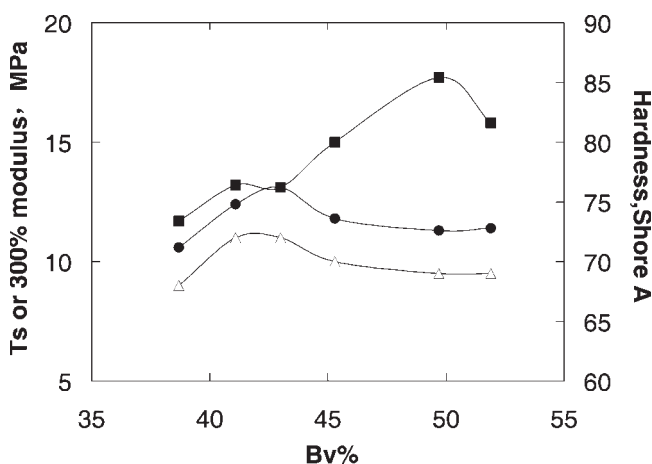


Figure 3 Effect of Bv% on the mechanical properties of S-MVBR (arm number = 3.8, MW/arm = 8×10^4): ● - 300% modulus, ■ - tensile strength (T_s), and Δ - hardness, shore A.

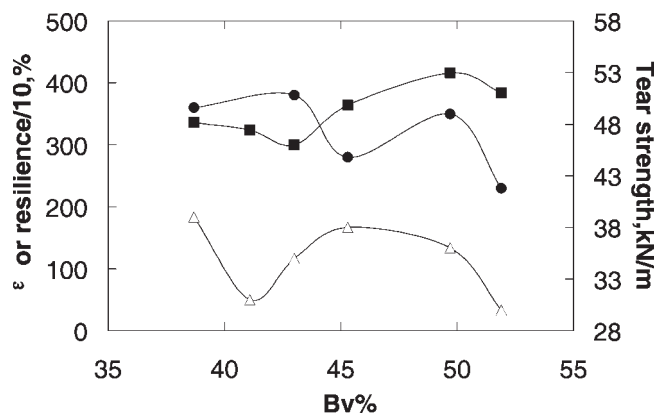


Figure 4 Effect of Bv% on the mechanical properties of S-MVBR (arm number = 3.8, MW/arm = 8×10^4): ● - resilience/10, ■ - elongation at break (ϵ), and Δ - tear strength.

increased the resistance of chain deformation. The actions of two factors made ΔT and H% change differently. ΔT first increased and later decreased, and the corresponding Bv% at lowest ΔT was 43%. H% increased and the tendency is obvious especially at Bv% above 45%. In addition, rolling resistance changed slightly while wet grip improved evidently with increasing Bv%,¹ which accorded with the relationship between wet grip and Bv% of star-shaped S-SBR.¹²

Processing properties

As vulcanization reactivity of double bond of the backbone was higher than that of side chain, with an increasing of Bv%, vulcanization was in retard and incipient scorch time increased, which was shown in Figure 6. Thus, a higher temperature could be introduced to cut vulcanization cycle.

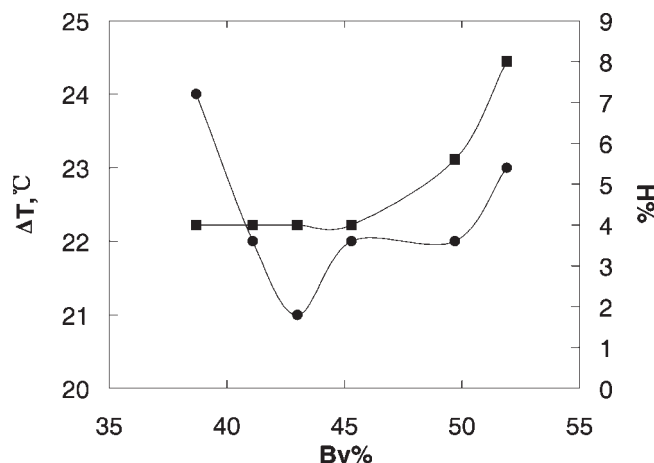


Figure 5 Effect of Bv% on ΔT and H% of S-MVBR (arm number = 3.8, MW/arm = 8×10^4): ● - dynamic heating (ΔT) and ■ - tensile permanent set (H%).

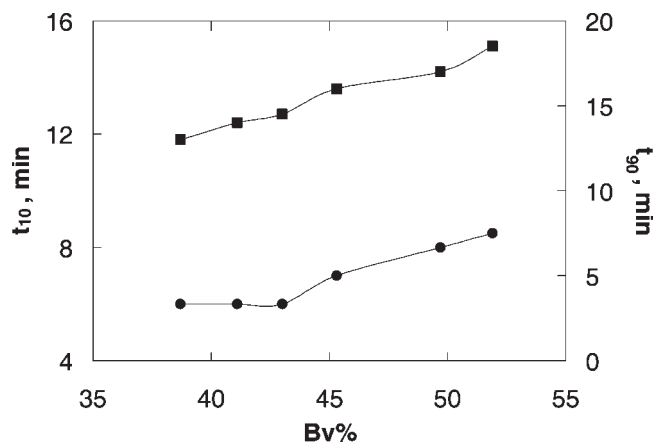


Figure 6 Effect of Bv% on incipient scorch time of S-MVBR (arm number = 3.8, MW/arm = 8×10^4): ● – t_{10} and ■ – t_{90} .

Molecular weight for one arm

Structure control

The relation of butadiene content to MW/arm was listed in Table IV. The results showed that the experimental value accorded basically with calculated value and MW/arm could be controlled by means of controlling butadiene content. The synthesis of S-MVBR initiated by multifunctional organolithium could be realized by anionic living stoichiometric polymerization.

Mechanical properties

The influence of MW/arm on mechanical properties of S-MVBR was listed in Table V. Increasing MW/arm enhanced the space resistance of molecular chain movement and decreased ultimate deformation, as a result, 300% modulus and hardness increased, whereas the elongation at break decreased. Meanwhile, longer chain decreased internal friction resistance, and resilience increased. The tear strength and tensile strength changed slightly.

Dynamic properties

Table V shows that with an increasing of MW/arm, Goodrich compression heat accumulation (ΔT) and tensile permanent set (H%) decreased. From this, it

TABLE IV
Effect of Butadiene Content on MW/arm

Bd content (g)	98	130	162
$\overline{M}_n \times 10^5$ (deter.)	2.31	3.04	3.68
MW/arm ($\times 10^4$) (deter.)	6.08	8	9.68
$\overline{M}_n \times 10^5$ (calc.)	2.4	3.2	4.0

Arm number = 3.8.

TABLE V
Effect of MW/Arm on Mechanical, Dynamic, and Processing Property of S-MVBR

MW/arm ($\times 10^4$) (deter.)	6.08	8	9.68
Hardness (shore A)	66	69	68
300% modulus (MPa)	9.9	11.3	10.5
Tensile strength (MPa)	17.5	17.7	17.5
Elongation at break (%)	428	416	408
Resilience (%)	31	35	37
Tear strength (kN/m)	40	36	38
Dynamic heating ($^{\circ}\text{C}$)	24	22	22
Tensile permanent set (%)	8	5.6	4
Incipient scorch Time			
t_{10} (min)	8	8	7
t_{90} (min)	17.5	17	15

Bv%: 49%, arm number: 3.8.

could be concluded that large MW/arm made S-MVBR lose internal friction resistance produced by molecular end groups and relax quickly. In the range of MW/arm tested, MW/arm did not influence rolling resistance and wet grip.

Rheological properties

Apparent viscosity of S-MVBR carbon black compounds with different MW/arm was shown in Figure 7. Figure 7 shows that S-MVBR had characteristic of non-Newtonian pseudoplastic fluid. With an increasing of MW/arm, compounds viscosity increased because of enhancement of long-chain entanglement.

The effects of MW/arm on elastic memory of S-MVBR were shown in Figure 8. Figure 8 shows that with an increasing of shear rate, die-swell ratio increased. At the same low shear rate, the bigger the MW/arm, the higher the die-swell ratio. This was due to longer relaxation time of S-MVBR with bigger

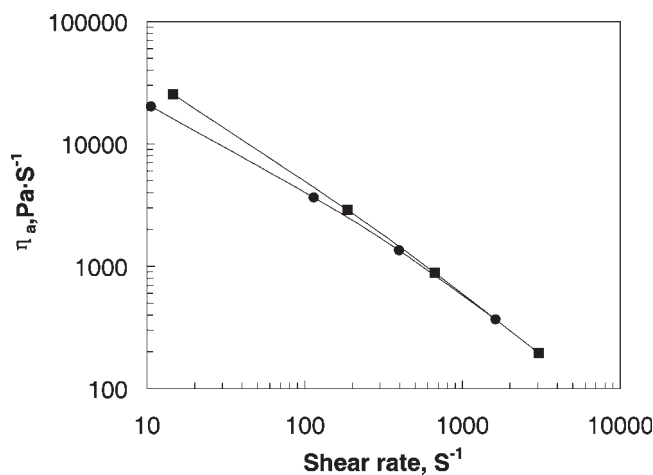


Figure 7 Effect of MW/arm on flow property of S-MVBR: ● – MW/arm = 6.1×10^4 , Bv% = 49%, arm number = 3.8, and ■ – MW/arm = 9.68×10^4 , Bv% = 47%, arm number = 3.8.

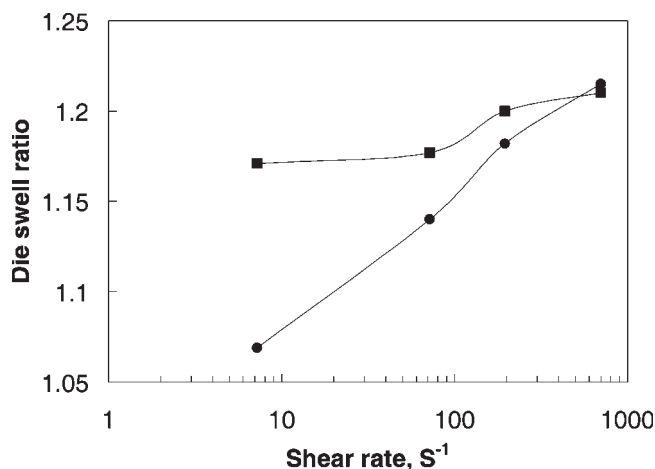


Figure 8 Effect of MW/arm on elastic memory of S-MVBR: ● – MW/arm = 6.1×10^4 , Bv% = 49%, arm number = 3.8 and ■ – MW/arm = 9.68×10^4 , Bv% = 47%, arm number = 3.8.

MW/arm. However, the difference of value was reduced at high shear rate.

Processing properties

Table V shows that with an increasing of MW/arm, vulcanization time decreased slightly. The bigger the MW/arm was, the more difficult the processing became, and so a suitable MW/arm to offer favorable performance was eight 10,000.

Distribution of molecular weight

Linear MVBR was mostly synthesized with alkyl lithium initiators, so its distribution of molecular weight ($\overline{M}_w/\overline{M}_n$) was narrow and it exhibited poor process-

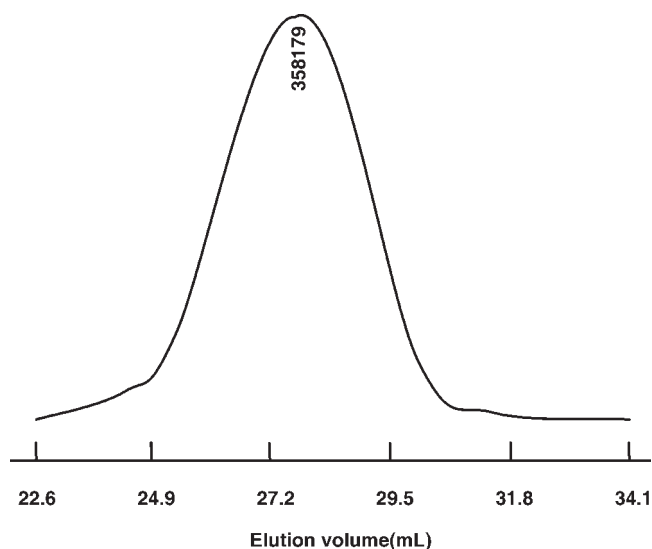


Figure 9 GPC trace of star-shaped MVPB sample (arm number = 3.8, MW/arm = 8×10^4 , $\overline{M}_w/\overline{M}_n$ = 1.54).

TABLE VI
Effect of $[\text{Li}^+]/[\text{Cl}^-]$ on $\overline{M}_w/\overline{M}_n$

$[\text{Li}^+]/[\text{Cl}^-]$ (mole ratio)	2.2	2	1.8	1.6	MVBR ^a (linear)
$\overline{M}_w/\overline{M}_n$	1.94	1.54	2.16	5.77	1.29

MW/arm: 80,000, Bv%: 47–50.

^a \overline{M}_n : 160,000, Bv%: 41.

ing property. Figure 9 showed a GPC trace of S-MVBR sample via one-step polymerization with multifunctional organolithium as initiator, which exhibited a relatively wide and symmetrical mono-modal distribution. On one hand, the initiator existed in the form of different arms and distribution of functionality was not uniform¹; so, $\overline{M}_w/\overline{M}_n$ was widened and star-shaped MVBR showed better processing properties than linear MVBR, that is, fast carbon black bound, lubricous slabs, and no fracture. On the other hand, the most form was four arms. It meant that the coupling degree could be close to 100% and there was basically not much linear macromolecule. In contrast, the star-shaped products via “arm-first” method usually exhibits low coupling degree and give rise to a bimodal or multimodal distribution, thus the overall performances are affected.²

The influence of $[\text{Li}^+]/[\text{Cl}^-]$ on $\overline{M}_w/\overline{M}_n$ was listed in Table VI. When $[\text{Li}^+]/[\text{Cl}^-]$ was two, the distribution was the narrowest. This was because initiator molecule mainly exists in the form of four arms.¹ When $[\text{Li}^+]/[\text{Cl}^-]$ was above and below two, initiator molecule existed in multifunctional, and the distribution was widened. Table VII shows MW/arm and Bv% had little effect on $\overline{M}_w/\overline{M}_n$. It was concluded that $\overline{M}_w/\overline{M}_n$ could be regulated by $[\text{Li}^+]/[\text{Cl}^-]$, that is, SnCl_4 content.

Properties of five kinds of tread rubber

The properties of five kinds of rubber for tire tread were listed in Table VIII. The hardness, 300% modulus, and tensile strength of star-MVBR were higher than those of linear MVBR and *cis*-BR, elongation at break, resilience, and tear strength of star-MVBR corresponded with the later two, and the main mechanical properties of star-MVBR was lower than S-SBR and E-SBR.¹² The ΔT of star-MVBR was smaller than S-SBR, E-SBR, and linear MVBR, and approached the level of *cis*-BR. The $T_g\delta$ at 0–50°C of star-MVBR was

TABLE VII
Effect of MW/Arm and Bv% on $\overline{M}_w/\overline{M}_n$

Bv%	38.9	43.9	49.7	49.7
MW/arm ($\times 10^4$)	8	8	8	6
$\overline{M}_w/\overline{M}_n$	1.46	1.58	1.54	1.58

$[\text{Li}^+]/[\text{Cl}^-] = 2$.

TABLE VIII
Properties of Five Kinds of Tread Rubber

Properties	S-SBR ¹² (linear)	E-SBR ¹² (SBR-1500)	Star-MVBR ^a	MVBR (linear)	Cis-BR (BR-9000)
St (%)	22.4	23.5	–	–	–
Bv (%)	42.4	–	49.7	41	–
Hardness, (shore A)	67	65	69	66	62
300% modulus (MPa)	12.6	10.6	11.3	10.5	10.3
Tensile strength (MPa)	23.3	25.4	17.7	16.9	16.5
Elongation at break (%)	528	548	416	428	432
Resilience (%)	–	–	35	31	37
Tear strength (kN/m)	49	47	36	38	39
Dynamic heating (°C)	26	25	22	26	21
Tensile permanent set (%)	–	–	5.6	8	4
Incipient scorch time					
<i>t</i> ₁₀ (min)	–	–	8	9	6.5
<i>t</i> ₉₀ (min)	–	–	17	19	12
Loss factor (<i>Tgδ</i> , 11 Hz)					
–25°C	0.363	0.295	0.278	0.126	0.094
0°C	0.154	0.167	0.100	0.088	0.085
50°C	0.139	0.149	0.065	0.089	0.084

^a Star-MVBR, arm number: 3.8, MW/arm: 8×10^4 .

smallest, *Tgδ* at –25–0°C was much higher than linear MVBR and *cis*-BR, and even approached the level of E-SBR. These conclusions indicated that star-MVBR had higher mechanical properties than linear MVBR, same dynamic heating as *cis*-BR, lower rolling resistance than *cis*-BR, and higher wet grip than linear MVBR. Therefore, star-MVBR was an ideal rubber for high performance tire tread.

CONCLUSIONS

A favorable structure of MVBR with optimal performance was achieved by molecular design of macromolecular and star-shaped MVBR was synthesized by “core-first” method with novel multifunctional organolithium as initiator. The Bv% could be controlled in 30%–55% by THF content, MW/arm controlled by butadiene content, and $\overline{M}_w/\overline{M}_n$ regulated by [Li⁺]/[Cl[–]]. As SnCl₄ coupling decreased the number of “free end,” molecular weight and its distribution increased, the mechanical properties, dynamic properties, and processing properties of MVBR were improved in evidence. S-MVBR, with arm number of 3.8, MW/arm of eight 10,000, vinyl content of 50%, and distribution of molecular weight of 1.54, had

optimal overall properties. When compared with *cis*-BR and linear MVBR, S-MVBR has low rolling energy loss, high wet grip, good mechanical, and processing properties. It was an ideal rubber for high performance tire tread.

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