Novel Tin-Coupled Star-Shaped Medium Vinyl Butadiene Rubber. I. Arm Number and Its Effect on Properties

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ABSTRACT: To achieve low rolling resistance, high wet grip, and favorable overall performance, star-shaped medium vinyl butadiene rubber (S-MVBR) was designed and prepared by ''core-first'' method, where novel multifunctional organolithium containing Sn atom as initiator, THF as structure regulator, and carbon–hydrogen compound as solvent. The results showed that coupling reaction between $SnCl_4$ and dilithium is stoichiometrical, and this method has much higher efficiency than the ''arm-first'' method. When dilithium is composed of 4–10 repeating units, the average arm number of S-MVBR is conveniently controlled between 3 and 5 by initiator functionality, which can be easily regulated by the mole ratio of active lithium of dilithium short chain to Cl^- in $SnCl_4$. As Sn coupling decreases numbers of noncrosslinking free ends, S-MVBR has lower rolling resistance, dynamic heating and higher wet grip than linear MVBR. Meanwhile, mechanical properties and processing properties are improved. And the formation of multiarm structure has little effect on viscosity. S-MVBR with arm number of 3.8 has optimal overall performance. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 3917–3923, 2007

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

INTRODUCTION

Medium vinyl butadiene rubber (MVBR) is a kind of polybutadiene rubber with vinyl content (Bv%) of 35–55% and is mostly synthesized with alkyl lithium initiators. It exhibits some excellent properties as *cis*-BR and improved wet grip performance as well as thermal aging resistance, but simultaneously has some unfavorable performance, such as slightly high heat accumulation and rolling resistance, poor mechanical property, poor processing property, and serious cold flow resistance.[1] With higher requirement for high performance tire tread in recent years, a rise in wet grip is asked to be contemporaneous with a decrease in rolling resistance[2] and therefore we should improve them and balance other properties. This can be achieved by macromolecular design instead of traditional method.

Rolling resistance is incompatible with wet grip performance. Both of them are related to side group and noncrosslinking long chain end after vulcanization. Long chain end can motion freely and lead to hysteresis, which is the key factor contributing poor rolling resistance and heat accumulation,[3] thus low long chain end concentration is favorable[4] and can be achieved by decreasing numbers of noncrosslinking free ends[5] or increasing number-average molecular weight.[6] As to butadiene rubber, side group, that is, vinyl group have little effect on rolling resistance whereas obvious effect on wet grip performance.[7] Fall of wet grip performance due to decreasing long chain end concentration accordingly can be offset so much as enhanced by increasing vinyl content.

Processing properties are related to intermolecular force and molecular weight. The vinyl groups of MVBR increase free volume, decreasing intermolecular force and cohesive force, leading to poor processing properties. Narrow distribution of molecular weight of MVBR is another reason, which contributes bad cold flow resistance at the same time. While satisfied mechanical properties are attributed to high molecular weight and narrow distribution of molecular weight, which make processing difficult.

According to above analysis, MVBR with multiarms, high number-average molecular weight, properly wide distribution, and vinyl content are expected to posses overall balance of good mechanical properties, good processing properties, low rolling resistance, and high wet grip. Star-shaped MVBR (S-MVBR) should be introduced by anionic polymerization.

In general, the synthesis of star-shaped polymers by sequential anionic living copolymerization can be performed in two different ways, ''arm-first'' and

"core-first" method.[8] The "Arm-first" method comprises in first synthesizing the linear polymer and then adding a multifunctional coupling agent to carry out the coupling reaction; since it is complex and has low coupling efficiency due to high viscosity of polymerizing compound and there exist many limitations: not sufficiently improved performances, larger energy consumption and big investment. The "core-first" method comprises in first synthesizing multifunctional organic alkali metal initiator and then initiating the monomers. Multifunctional organic alkali metal initiator can be obtained upon reaction of sodium or potassium naphthalene,[9,10] especially alkyllithium with multivinyl compounds. The multivinyl compounds include: (a) divinylbenzene (DVB)[11,12]; (b) other compounds containing several double-linkages[13–15]; (c) oligomer containing several double-linkages.[16] The multifunctional initiator can also be prepared by reaction of low molecular weight living polymer with DVB,[17–20] etc. In comparison with the "arm-first" method, the "core-first" method has high coupling efficiency whereas has other problems, such as inaccessibility starting materials, functionality being neither easily controlled nor regulated thus tending to form gel.

To find the method for solving the above-indicated problems, a deep going research was conducted by our lab and a novel multifunctional organolithium initiator containing Sn atom[21] was accomplished to prepared star-shaped polymer, such as star-shaped SIBR,[22] star-shaped S-SBR,[23,24] star-shaped HVBR,[25] star-shaped LCBR[26] which features high coupling efficiency, easily regulated functionality, properly wide distribution, lower cost, simple technology and better product performances. On the basis of the initiator and above analysis, a specially designed S-MVBR was prepared, which posses well-defined structure in terms of arm number (AN), vinyl content (Bv%), molecular weight, molecular weight distribution. The regulating means of structure factor and relationship between structure and properties, such as mechanical properties, dynamic properties, rheological properties, processing properties were studied. In this article, we mainly focus on the regulation of arm number and its effect on properties and other structure will be discussed latter.

EXPERIMENT

Synthesis

The synthesis of star-shaped medium vinyl butadiene rubber (MVBR) was prepared using the "core-first" method with novel multifunctional organolithium as initiator. The basic anionic polymeriza-
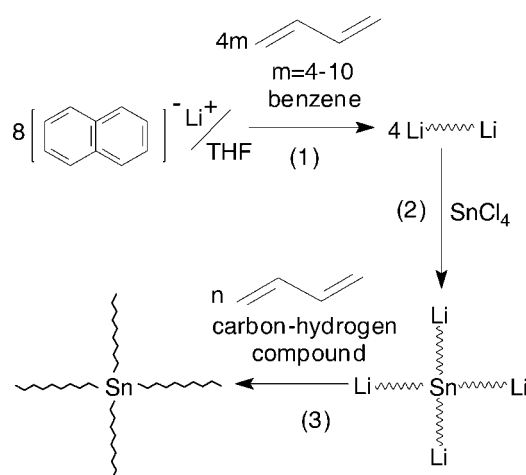
Scheme 1　Synthesis of star-shaped medium vinyl polybutadiene.

tion reactions are presented in the reaction Scheme 1. At first the multifunctional organolithium is synthesized in two steps: (a) the ready-made naphthalene-lithium initiate a small quantity of butadiene to form dilithium short chain with repeating unit of m, the reaction is carried out for 0.5 h at 50°C in benzene (reaction 1), subsequently, (b) SnCl$_4$ is added and the reaction further continues for 0.5 h at 50°C (reaction 2). Then multifunctional organolithium is introduced into a 2 L stainless steel reactor which has been charged with butadiene-carbon-hydrogen compound having 9 g monomers in 100 g solution and tetrahydrofuran (THF) after it is purged with nitrogen gas and washed with living polystyryllithium solution. The temperature of reactor was kept at 50°C for 2–4 h (reaction 3). Then the reaction was terminated by adding small amount of methanol and 2,6-di-*tert*-butyl paracresol. The star-shaped polymer was purified by precipitation with technical alcohol. Linear MVBR was prepared with butyl lithium as initiator by the same method. And *Cis*-BR (BR-9000) was provided by the Beijing Yanshan Synthetic Rubber Factory in China.

Characterization

Molecular weight was determined by Knauer 1.00 membrane permeameter at 37°C, with toluene as solvent. Molecular weight distribution was determined by Waters150-C gel permeation chromatography at 25°C, with THF as solvent. The insoluble gel was determined by filtration of S-MVBR-toluene solution of 2.5 mg/mL, with glass sintered funnel of 0.04–0.08 mm pore diameter. The gel percentage was expressed by the ratio of weight of unfiltered parts to the total weight of S-MVBR. Vinyl content (Bv%) was determined by AC-80 ^{1}H NMR spectroscopy

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

(Bruker, 80 MHz) and calculated according to the following equation: [27]

$$Bv\% = \frac{2I_{(5.02\sim4.82)}}{2I_{5.35} + I_{(5.02\sim4.82)}} \times 100\% \qquad (1)$$

where I is the peak area of H at $\delta = 5.35$ and $\delta = 5.02$–4.82, respectively.

Formulation and performance test of vulcanizates

S-MVBR was compounded according to the formulation given in Table I. The compounds were then cured at 145°C for 20 min.

The mechanical properties of the vulcanizates were measured according to the state standards in China. They include: hardness (Shore A), 300% modulus, tensile strength, elongation at break, resilience, tear strength, and tensile permanent set.

The temperature rise (ΔT) in compression fatigue was determined by a YS-25 Goodrich compression fatigue machine produced in China. 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 to 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, 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 gives the die swell ratio.

RESULTS AND DISCUSSION

Regulation of arm number

As the intermolecular coupling reaction (3) between dilithium and SnCl₄ can be done stoichiometrically,

initiator functionality can be regulated by means of changing the ratios between them, therefore, the arm number (AN) of macromolecule is conveniently controlled. If we express the ratio of reactant in the mole ratio of active lithium of dilithium short chain to Cl^- in coupling agent $SnCl_4$ ($[Li^+]/[Cl^-]$) and it equals to 2, AN can be 4 theoretically.

On the premise that Cl^- in coupling agent $SnCl_4$ react entirely with Li^+ of dilithium short chain and the coupling is uniform, the actual functionality of polymer can be calculated by the following equation:

$$AN = \frac{N_1 V_1 - 4N_2 V_2}{\dfrac{W_m}{\overline{M}_n}} \qquad (2)$$

where N_1, N_2 are the mol concentration of naphthalene–lithium and $SnCl_4$, respectively, V_1, V_2 are the volume of naphthalene-lithium and $SnCl_4$, respectively, W_m is the mass of feeding monomer, and $\overline{M}_n$ is the determined number-average molecular weight. The results are listed in Table II. The results show that the actual arm number is a little smaller than the theoretical one. When $[Li^+]/[Cl^-] > 2$, AN is higher than 4, it shows all macromolecular chains almost link to Sn atom and coupling efficiency of the novel initiator is much higher than that of ''arm-first'' method.

In fact, formation of initiator with 4 arms is a ideal reaction according to reaction statistics, there are little initiator molecule with 5–6 arm and uncoupling dilithium short chain and initiator molecule can exist in the form of different arm shown in Figure 1. When $[Li^+]/[Cl^-]$ is 2.2, Li^+ is excessive, there are uncoupling dilithium short chain, initiator molecule mainly exist in the form of A and C. When $[Li^+]/[Cl^-]$ is 2, half Li^+ just reacts with Cl^-, initiator molecule mainly exist in the form of C. As actual arm number is less than 4, it follows that a small quantity of molecule exists in the form of A and B. When $[Li^+]/[Cl^-]$ is 1.8, excessive Cl^- connecting to one Sn atom reacts with lithium connecting to another one, the amount of D and E increases. When $[Li^+]/[Cl^-]$ is 1.6, excessive Cl^- increase coupling probability between two Sn atom, the amount of C decreases

TABLE II
The Effect of $[Li^+]/[Cl^-]$ on Arm Number

$[Li^+]/[Cl^-]$ (mole ratio)	$\overline{M}_n \times 10^5$ (deter.)	AN (deter.)
2.2	2.68	3.4
2	3.04	3.8
1.8	3.24	4.1
1.6	3.55	4.4

MW/arm $= 8 \times 10^4$.
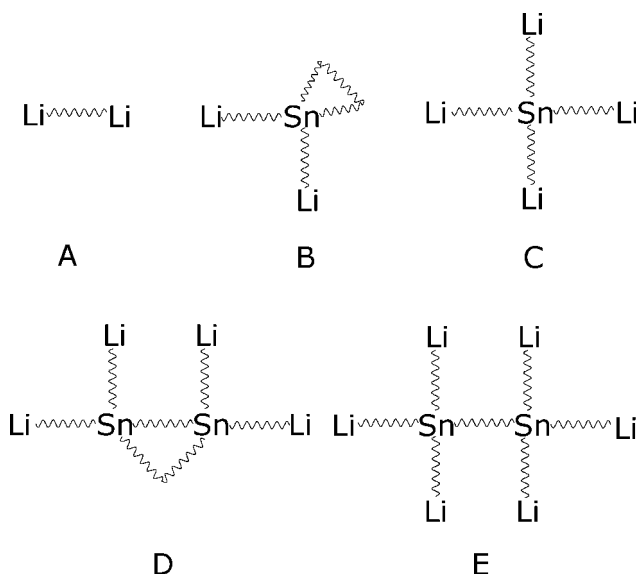
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Figure 1 Possible forms of multifunctional organolithium.

and the amount of D and E increases more. When $[Li^+]/[Cl^-]$ is 1.4,

$$\bar{f} = \frac{8}{1 + 2 \times [Li^+]/[Cl^-]} = 2.1 \quad (3)$$

gel come into being. Thus average arm number of S-MVBR is greatly controlled by means of controlling $[Li^+]/[Cl^-]$.

In addition to $SnCl_4$ content, the chain length of dilithium, that is, repeating unit of m has effect on the coupling reaction. If the chain length is too long, the chain that have linked to Sn atom will prevent unlinking dilithium chain to attack residue Cl atom and its residue Li will react to the residue Cl atom, the form of B consequently come into being. On the contrary, too short chain means not enough feeding of butadiene and can't assure thorough conversion of naphthalene–lithium to dilithium short chain. The experiments show that the proper chain length that is, m is 4–10. And temperature has slightly effect on arm number.

In general, a great deal gel is easy to form when star-shaped polymer are prepared by ''core-first'' method, especially coupling with DVB.[11,12] The gel percentage of star-shaped MVBR is determined and

TABLE III
The Effect of $[Li^+]/[Cl^-]$ on Gel Percentage

$[Li^+]/[Cl^-]$ (mole ratio)	Gel percentage (%)
2.2	0.30
2	0.29
1.8	0.34
1.6	0.92

MW/arm $= 8 \times 10^4$.

Journal of Applied Polymer Science DOI 10.1002/app

TABLE IV
The Effect of MW/arm on Gel Percentage

MW/arm (10^4)	Gel percentage (%)
6.08	0.30
8	0.29
9.68	0.34

$[Li^+]/[Cl^-] = 2$.

the results are listed in Tables III and IV. It indicates the gel percentage of star-shaped MVBR is low. Gel tends to form with increasing $[Li^+]/[Cl^-]$ and molecular weight per one arm (MW/arm) has no effect on gel percentage.

According to above discussion, star-shaped MVBR can be synthesized with novel multifunctional organolithium as initiator. The average arm number is conveniently controlled between 3 and 5 by initiator functionality, which can be easily regulated by $[Li^+]/[Cl^-]$.
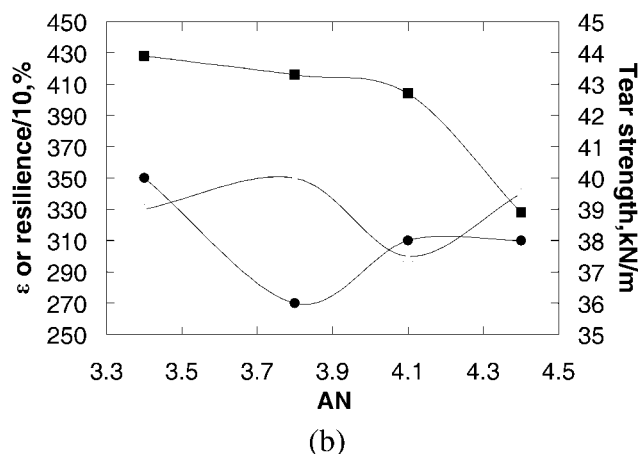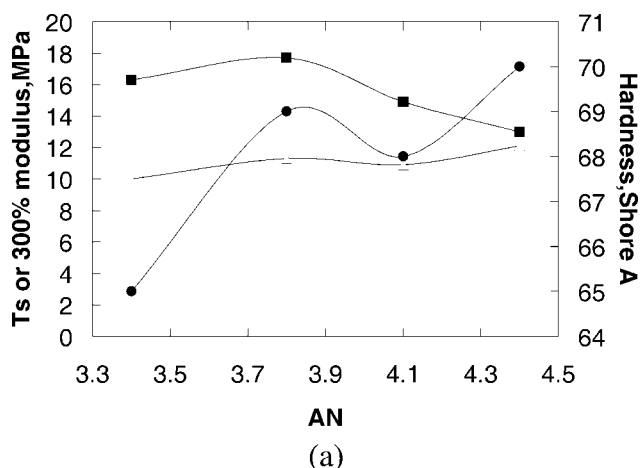

(a)

(b)

Figure 2 Effect of arm number on the mechanical properties of S-MVBR (Bv% = 49%, MW/arm = 8×10^4). (a) △-300% Modulus, ■-Tensile strength (Ts), ●-Hardness, Shore A. (b) △-Resilience/10, ■-Elongation at break (ε), ●-Tear strength.

TABLE V
Properties of Three Kinds of Tread Rubber

Properties	Star-MVBR[a]	MVBR (linear)	cis-BR (BR-9000)
Hardness, Shore A	69	66	62
300% Modulus (MPa)	11.3	10.5	10.3
Tensile strength (MPa)	17.7	16.9	16.5
Elongation at break (%)	416	428	432
Resilience (%)	35	31	37
Tear strength (kN/m)	36	38	39
Dynamic heating (°C)	22	26	21
Tensile permanent set (%)	5.6	8	4
Incipient scorch time			
t_{10} (min)	8	9	6.5
t_{90} (min)	17	19	12
Loss factor, tg δ, 11 Hz			
−25°C	0.278	0.126	0.094
0°C	0.100	0.088	0.085
50°C	0.065	0.089	0.084

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

The effect of arm number on properties

Mechanical properties

As S-MVBR with AN of 5–6 shows bad processing properties according to previous experiences, mechanical properties of S-MVBR with arm number of 3.4–4.4 have been examined and the influence of AN is shown in Figure 2. Figure 2 shows that with an increasing of AN, the hardness and 300% Modulus increase, the elongation at break and tear strength decrease, and the tensile strength (T_s) and resilience first increase and later decrease. This is because increasing the arm number of S-MVBR makes the space resistance of molecular chain movement increase and ultimate deformation decrease, and then 300% Modulus increase, the elongation at break decrease. At the same time, coupling decreases the numbers of noncrosslinking free ends, internal friction resistance produced by molecular end groups decreases. The changes of the two resistance cause together tear strength to increase slightly. The results show that star-MVBR with AN of 3.8 exhibits higher mechanical properties than star-MVBR with other AN. Comparing with linear MVBR and cis-BR (Table V),[28] mechanical properties of star-MVBR is improved. The results prove that the method of coupling linear macromolecule with Sn by "core-first" method can improve its mechanical properties.

Dynamic properties

Figure 3 shows the influence of AN on Goodrich compression heat accumulation (ΔT) and tensile permanent set (H%). The curve shows that with an increasing of AN, the ΔT, and H% decrease. This is because increasing AN makes the space resistance of macromolecular chain deformation increase and the

ultimate deformation decrease, simultaneously, internal friction resistance produced by macromolecular end groups decrease and relax quickly. As for S-MVBR with AN of 4.4 has slightly higher dynamic heating, the reason is large value of distribution of molecular weight ($\overline{M}_n/\overline{M}_n = 5.77$). In a word, dynamic heating and tensile permanent set are lower than those of linear MVBR. The value of the lowest dynamic heating of vulcanizate even approaches to that of cis-BR (Table V).[28]

Many studies have shown that loss factor (tg δ) in different temperature could reflect on rolling resistance and wet and ice grip performance, that is, the large values of tg δ in the temperature range from −50 to 0°C can be correlated to high wet and ice grip, and small values of tg δ in the temperature range from 50 to 60°C correlatives to low rolling resistance.[2,29] The relationships between temperature and tg δ of S-MVBR, linear MVBR and cis-BR are shown in Figure 4. Figure 4 shows tg δ of linear MVBR at −50 to 0°C are higher than those of cis-BR and tg δ of linear MVBR at 50–100°C are higher than those of cis-BR. This indicates that wet grip is improved but rolling resistance becomes unfavorable because of large amount of vinyl. After Sn coupling, AN of macromolecular chain increases from 2 to 3.8 (the "arm number" of linear MVBR can be regarded as 2), tg δ of star-MVBR with AN of 3.8 at −50 to 0°C are higher than those of linear MVBR and cis-BR, and tg δ of star-MVBR with AN of 3.8 at 50–100°C are lower than those of linear MVBR and cis-BR. The results are expected and indicate that star model formed by Sn coupling makes molecular chain relaxation slow and wet grip increase, simultaneously, space resistance and internal friction loss among molecular chains decrease due to decreasing numbers of noncrosslinking free ends, rolling resistance, and dynamic heating decrease. The conflict is
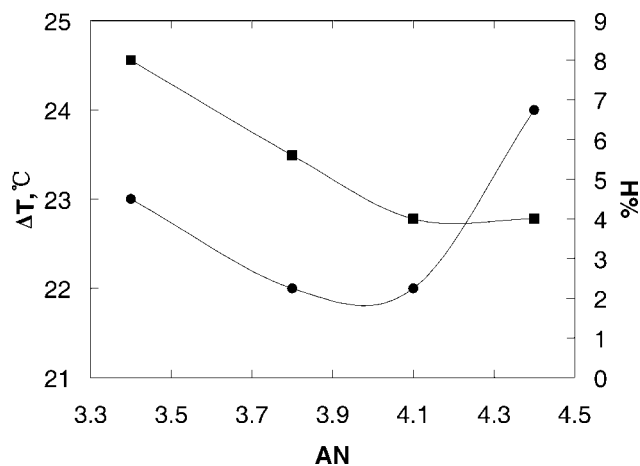

Figure 3 Effect of arm number on ΔT and H% of S-MVBR (Bv% = 49%, MW/arm = 8×10^4). ●-Dynamic heating (ΔT), ■-Tensile permanent set (H%).
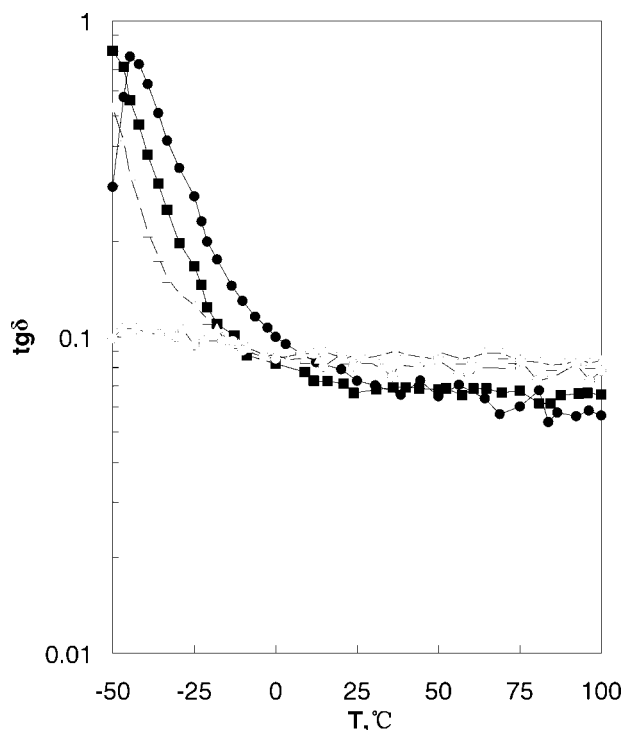
Figure 4 The effect of arm number on rolling resistance and wet grip of S-MVBR. ●-AN = 3.8, Bv% = 49.7%, MW/arm = 8 × 10⁴, ■-AN = 4.4, Bv% = 44%, MW/arm = 8 × 10⁴, △-linear MVBR, Bv% = 41%, MW/arm = 1.6 × 10⁵, ○-cis-BR.

solved by molecular design of macromolecular. When AN of S-MVBR increases to 4.4, wet grip decreases slightly and rolling resistance increases slightly because of wide distribution of molecular weight and low vinyl content, but the performances are still more favorable than linear MVBR and cis-BR. The optimal AN of star-MVBR is 3.8.

Rheological properties

Apparent viscosity of S-MVBR carbon black compounds with different AN are shown in Figure 5. Figure 5 shows that with an increasing of AN, the apparent viscosity increase slightly. This indicates that increasing average arm number makes structure of compound complicated, but only increases flow resistance slightly. Proper coupling structure doesn't influence flowability of star-MVBR. As for the value of linear MVBR is little higher than that of S-MVBR, the reason is that linear MVBR has more noncrosslinking free ends than coupled S-MVBR, and the probability of chain end movement to entanglement of linear MVBR is higher than S-MVBR. That is, linear molecular chain is in favor of entanglement than coupled chain.

The effects of AN on elastic memory of star-MVBR are shown in Figure 6. Figure 6 shows that at low shear rate die swell ratios of linear MVBR are
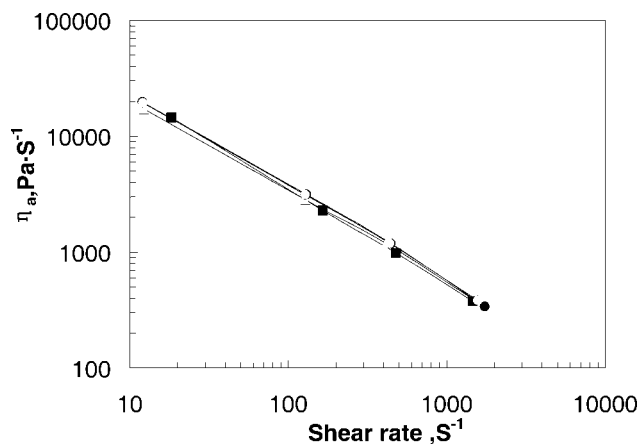

Figure 5 Effect of arm number on flow property of S-MVBR. (S-MVBR: Bv% = 49%, MW/arm = 8 × 10⁴; linear MVBR: Bv% = 41%, MW/arm = 1.6 × 10⁵). △-AN = 3.4, ■-AN = 3.8, ●-AN = 4.1, ○-linear MVBR.

smaller than those of star-MVBR. This indicates linear molecular chain is in favor of entanglement, but relaxes quickly. At high shear rate die swell ratio of linear MVBR is slightly smaller than that of star-MVBR with AN of 4.1. This indicates although coupling weakens entanglement and cut the relaxation time, chain deformation harmony prolongs the relaxation time. The result is that with increasing AN, total relaxation time and die swell ratio increase.

Processing properties

The processing of S-MVBR with AN of 3.4–4.1 is easier than linear MVBR (Table V), that is, fast carbon black bound, lubricous slabs, no bagging. This reason is that Sn—C bond contained in coupled Star-shaped MVBR breaks easily under shear action, and
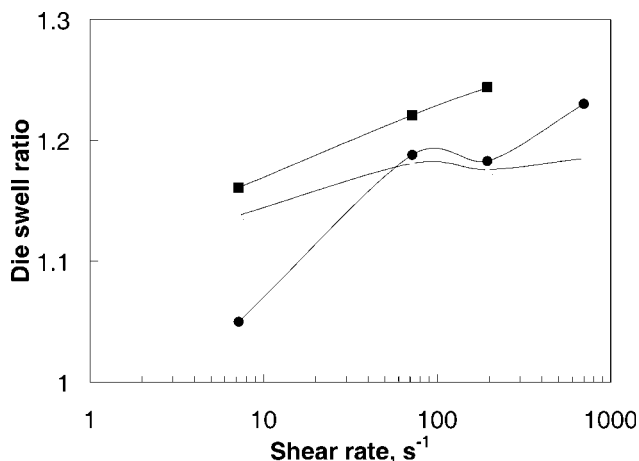

Figure 6 Effect of arm number on elastic memory of S-MVBR. (S-MVBR: Bv% = 49%, MW/arm = 8 × 10⁴; linear MVBR: Bv% = 41%, MW/arm = 1.6 × 10⁵). △-AN = 3.8, ■-AN = 4.1, ●-linear MVBR.
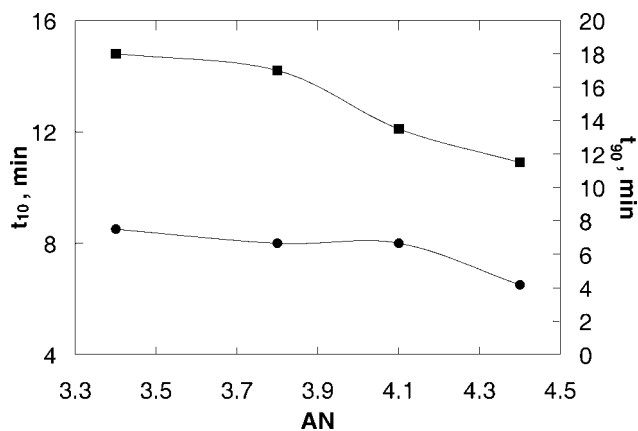
Figure 7 The effect of arm number on incipient scorch time of S-MVBR. (Bv% = 49%, MW/arm = 8×10^4). ●-t_{10}, ■-t_{90}.

the free group produced bonds immediately to an active group on the surface of the carbon black particle.[23] Thus carbon gel produce and there appear better carbon black absorption and dispersion. But processing of S-MVBR with AN of 4.4 greatly becomes complicated. Figure 7 shows that with an increasing of AN, incipient scorch time cuts. This is because increasing AN requires more $SnCl_4$ which can promote vulcanization.

CONCLUSIONS

Tin coupled star-shaped MVBR can be prepared by ''core-first'' method with novel multifunctional organolithium as initiator. The coupling reaction is uniform, stoichiometrical, and highly efficient. The average arm number of star-shaped MVBR is conveniently controlled between 3 and 5 by initiator functionality that can be easily regulated by $[Li^+]$/$[Cl^-]$. As Sn coupling decreases numbers of noncrosslinking free ends, star-shaped MVBR has lower rolling resistance, dynamic heating and higher wet grip than linear MVBR. Meanwhile, mechanical properties and processing properties are improved. And the formation of multiarm structure has little effect

on viscosity. Star-shaped MVBR with arm number of 3.8 has optimal overall performance.

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