

PREPARATION OF MULTIFUNCTIONAL ORGANOLITHIUM INITIATOR IN CYCLOHEXANE SOLUTIONS*

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Abstract Multifunctional organolithium initiator was prepared in cyclohexane solvent. The process started with adding the cyclohexane solution of butadiene to naphthalene-lithium in batches to produce butadiene oligomer dilithium with 4–8 butadiene repeating units. In the first feeding, the maximum loading of cyclohexane and the minimum concentration of butadiene cyclohexane solution must be controlled under $V_{\text{cyclohexane}} \leq 1.33V_{\text{THF}}$ and $\rho \geq 40.6c_{\text{N}}$. Then, SnCl_4 was added and eventually the multifunctional organolithium initiator containing Sn atom was synthesized through coupling reaction. Experiment results showed that adding the cyclohexane solution in batches was effective in overcoming some difficulties, such as insolubility of naphthalene-lithium in cyclohexane, low efficiency of naphthalene-lithium in initiating butadiene. In practice, benzene can be replaced by cyclohexane completely, which can not only reduce environmental pollution from benzene, but also overcome the difficulty of solvent recovery caused by similar boiling point between benzene and cyclohexane. Prepared with multifunctional organolithium containing Sn atom as initiator, the star-shaped solution polymerized styrene-butadiene rubber (star S-SBR) with better vulcanization performances, lower rolling resistance and higher wet-skid resistance was obtained.

Keywords: Multifunctional organolithium initiator; Anionic polymerization; Cyclohexane; Star S-SBR.

INTRODUCTION

The synthesis of star-shape polymers from sequential living anionic polymerization can be performed in two different ways: arm-first and core-first^[1]. The arm-first method is to synthesize a linear polymer first and then a multifunction coupling agent is added for the coupling reaction. Due to the high viscosity of polymers, the coupling efficiency of this method is low and the degree of coupling is limited. The core-first method is to synthesize a multifunctional organic alkalimetal initiator, which is then used to initiate the monomers. Generally, the multifunctional organic alkalimetal initiator is obtained through reaction of naphthalene-sodium or naphthalene-potassium, especially alkylolithium with multivinyl compounds such as DVB, PEB, *etc*^[2–7]. Comparing with the arm-first method, this method has higher coupling efficiency. However the main disadvantages are the inaccessibility of raw materials, difficulty in controlling the structure of the multifunctional initiator, and formation of gel during the reaction. In order to solve the above problem, a novel multifunctional initiator from naphthalene-lithium was invented by Zhang *et al*^[8]. The first step of the process was to obtain the dilithium initiator, which was a diene oligomer made from the reaction of the naphthalene-lithium and dienes. Then, the coupling agent SnCl_4 was added to the dilithium initiator to get the multifunctional organolithium initiator. This method has some advantages such as higher coupling efficiency, controlled

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functionality of initiator, readily available raw material source and no gel formation in the final products. Using the multifunctional organolithium initiator, novel structure rubbers were synthesized, including energy-saving star-shape styrene-butadiene rubber^[9], star-shape medium vinyl butadiene rubber^[10, 11] and star-shape block copolymer of styrene and butadiene^[12, 13], etc. But the biggest disadvantage of this method was that naphthalene-lithium could only be dissolved in the polar solvent (for example THF) and the aromatic solvent (for example, benzene and toluene). In the anionic polymerization, THF acts as a molecular structure regulator, while toluene is a chain transfer agent, they are unsuitable as the solvent. Thus the solvent for preparation of the dilithium initiator is limited to benzene, which leads to two obstacles in the industrialized production. One is the environmental pollution owing to high toxicity of benzene. The other is the difficulties in separation and recycling of the solvents, because the boiling point of benzene (80.1°C) is similar to that of cyclohexane (80.7°C) usually used as solvent in anionic polymerization. It will be favorable if cyclohexane is used as solvent to replace benzene for the core-first method to prepare the star-shaped copolymer. The main issue for this approach is try to solve the insolubilization of naphthalene-lithium in cyclohexane solution in the reaction system.

In this work, the preparing process of multifunctional organolithium initiator by naphthalene-lithium was studied, and the reason of the naphthalene lithium insolubilization in cyclohexane was investigated. Based on the analysis of the multifunctional organolithium initiator preparing process, a new reaction route was designed, which was to add the butadiene-cyclohexane solution in batches to the naphthalene lithium, and the loading of cyclohexane in every stage was deliberately controlled. This method would hold the homogeneous reaction between butadiene and naphthalene-lithium, and the multifunctional organolithium initiator was prepared by further coupling with SnCl_4 . Star-shaped solution polymerized styrene-butadiene rubber (star S-SBR) was successfully obtained using the multifunctional organolithium as initiator in a 200 L (minimum industrial scale) reactor.

EXPERIMENTAL

Materials

Naphthalene (AR) was purchased from Beijing Chemical Reagents Company. Metal lithium and 1, 3-butadiene (Industrial Grade) were provided by the Synthetic Rubber Plant of Yanshan Chemical Co., Ltd. Cyclohexane (AR) was purchased from Beijing Chemical Reagents Company, it was rectified and the cut fraction of 80–81°C was dried over Na wire under nitrogen. Tetrahydrofuran (THF, AR) was purchased from Beijing Chemical Reagents Company and refluxed over CaH_2 for overnight. It was finally distilled from its sodium naphthalene solution. Tin(IV) chloride ($\geq 99\%$) was produced by Acros Organics. Nitrogen ($\geq 99.999\%$) was provided by Beijing Shun An Qi Te Gas Company.

Solution polymerized styrene-butadiene rubber (S-SBR): SL552 was purchased from Synthetic Rubber Company of Japan. 2305 was supplied by the synthetic Rubber Plant of Yanshan Chemical Co., Ltd. Star S-SBR was prepared using the multifunctional organolithium initiator in a 200 L reactor in Synthetic Rubber Plant of Yanshan Chemical Co., Ltd. Other common additives were produced in China.

Synthesis of Multifunctional Organolithium Initiator

Naphthalene-lithium was first made^[14]. Then the ready-made naphthalene-lithium initiated a small quantity of butadiene at 30°C for 30 min. Subsequently, the residual cyclohexane solution of butadiene was added and the reaction further continued for 30 min to form butadiene oligomer dilithium. Finally, cyclohexane solution of SnCl_4 ($c = 0.7 \text{ mol/L}$) was added slowly and the reaction continued for 1 h.

Characterization

The mol concentration of naphthalene-lithium (c_N) was determined according to the literature^[15].

Polymerization degree of butadiene could be calculated by the following equation because it was prepared by living anionic polymerization:

$$\overline{X}_n = \frac{m}{M_0 \times n_{\text{Li}^+}} \times 2 \quad (1)$$

where m is the mass of butadiene monomer; M_0 is the molecular weight of butadiene, $M_0 = 54$; n_{Li^+} is the mole of active lithium, which is equal to the mole of naphthalene-lithium.

The functionality of multifunctional organolithium initiator was determined as follows: First, butadiene-styrene copolymer was prepared using the ready-made multifunctional organolithium initiator. The arm number (AN) of the copolymer was calculated by the following equation:

$$\text{AN} = \frac{n_{\text{Li}^+} - n_{\text{Cl}^-}}{m/M_n} \quad (2)$$

where n_{Li^+} is the mole of the active Li^+ in dilithium initiator; n_{Cl^-} is the mole of Cl^- in coupling agent SnCl_4 ; m is the mass of feeding monomer (butadiene and styrene), M_n of copolymer is determined by Knauer 1.00 membrane permeameter at 37°C with toluene as solvent. So the functionality of initiator is equal to the arm number (AN) of the copolymer.

M_n , M_w and M_n/M_w of S-SBR were measured by gel permeation chromatography (GPC) (Waters-150C, American). THF was used as the eluent at a flow rate of 1.0 mL/min at 40°C.

The mechanical properties of the vulcanizates were measured according to the state standards in China (e.g., GB/T 531-92 for Shore A hardness, GB/T 528-98 for tensile strength and elongation, GB1681-82 for rebound, GB 530-81 for tear strength).

Temperature rise at dynamic compression fatigue was determined with a YS-25 compression fatigue tester made in China (GB/T 1687-93). The preheating time was 20 min, the compression time was 25 min, the compression frequency was 30 Hz, the stroke was 4.45 mm, and the load was 1 MPa.

Loss tangent ($\tan\delta$) was determined by DDV-11-EA dynamic viscoelastometer produced in Japan. The temperature range was -100°C to 100°C , the frequency was 10 Hz, and the deformation amplitude was 0.5%.

RESULTS AND DISCUSSION

Design of Reaction Process

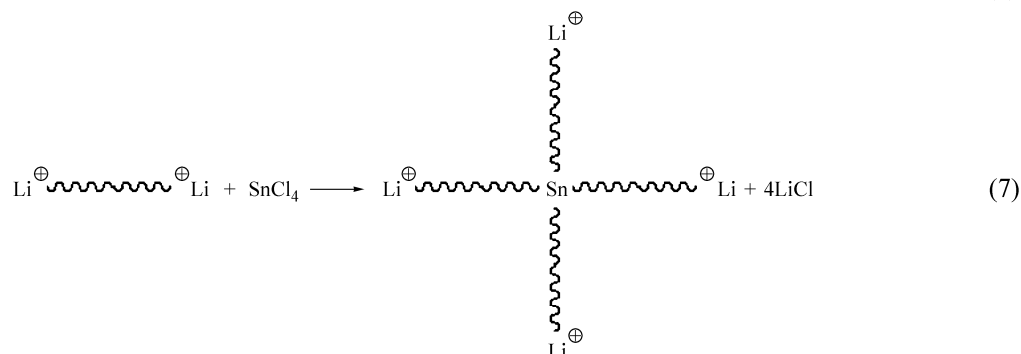
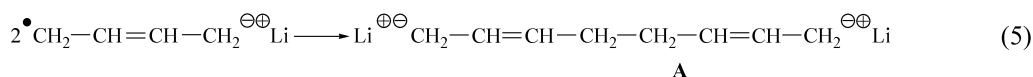
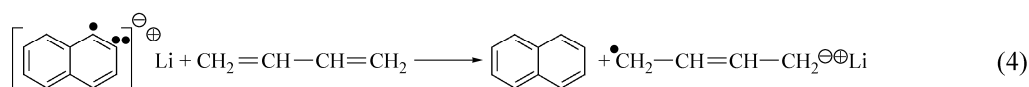
The multifunctional organolithium initiator was synthesized through the following reaction steps:

Equation (3) is the reaction of naphthalene and lithium in THF solvent to produce naphthalene-lithium. In this reaction, one outer electron of lithium is transferred to the lowest empty orbit of naphthalene, turning it into naphthalene anionic free radical, which forms ionic pair with Li^+ . This is a reversible reaction. As the unshared electron of oxygen atom of THF bands together with Li^+ to form a complex compound, the reaction is favourable to the formation of naphthalene-lithium. If benzene is used as solvent, the reaction is more likely in the other direction. Then naphthalene is dissolved in benzene, and Li remains in the system in a highly active and scattering status^[16].

Equations (4)–(6) are the reactions to synthesize polybutadiene dilithium in solution. To maintain homogenous condition for the reactions, the solvent needs to have good solubility to naphthalene-lithium, butadiene and polybutadiene dilithium. As mentioned before, benzene is a good solvent for such purposes, however it has certain limitations for industrialized production, whereas THF and toluene are also not ideal solvents. Therefore cyclohexane, which is used as solvent in anionic polymerization, was considered as the ideal solvent.

The experiment demonstrated that when high loading of butadiene cyclohexane solution was mixed with small amount of naphthalene-lithium THF solution, the naphthalene-lithium precipitated from the solution promptly and deposited at the bottom of the reactor due to the insolubility of naphthalene-lithium in the non-polar solvent cyclohexane. Thus the reaction between butadiene and naphthalene-lithium could not be conducted in homogenous phase. However, if a small amount of butadiene cyclohexane solution was added into naphthalene-

lithium THF solution, as the cyclohexane concentration is low in the mixture, dissolution of the naphthalene-lithium was not affected and thus the homogeneous condition was achieved. Free radical butadiene anion was formed (Eq. 4), which was then converted to butadiene dianion through further coupling (Eq. 5). Consequently, the rest of the butadiene cyclohexane solution was gradually added, and the butadiene dianion continued to initiate butadiene to form polybutadiene dilithium (Eq. 6). With the active center being transferred to polybutadiene dilithium from naphthalene-lithium, increasing the cyclohexane loading in reaction system would no longer affect the homogeneous phase of the reaction. In the end, coupling agent SnCl_4 was added and reacted with polybutadiene dilithium to form multifunctional organolithium initiator (Eq. 7).



In reaction Eqs. (4)–(6), the maximum loading of cyclohexane can be calculated by the solubility parameter of the solvent mixture. According to the principle of “similar solubility parameter”^[17], if the difference in solubility parameter of two solvents is less than 2, they are considered to be soluble to each other^[15]. Therefore the maximum volume ratio of cyclohexane to THF in the solvent mixture can be calculated, at which the naphthalene-lithium can be dissolved as follows.

The solubility parameter for cyclohexane, THF, and naphthalene are 16.8, 20.3 and 20.3 $(\text{J}/\text{cm}^3)^{0.5}$ respectively^[15], thus the solubility parameter for the mixed solvent which can dissolve naphthalene should be greater than 18.3 $(20.3-2)$ $(\text{J}/\text{cm}^3)^{0.5}$. Assume the volume ratio of cyclohexane to THF is x , according to the equation for mixed solvent solubility parameter^[17],

$$\delta_{\text{mix}} = \delta_1\varphi_1 + \delta_2\varphi_2$$

then

$$(20.3 + 16.8x)/(1+x) \geq 18.3$$

$$x \leq 1.33$$

i.e.

$$V_{\text{cyclohexane}} \leq 1.33V_{\text{THF}} \quad (8)$$

In reaction Eq. (4), the cyclohexane and naphthalene-lithium should also be in equivalent amount. Therefore the mass concentration of the butadiene cyclohexane solution is also an important parameter. Assume the concentration of naphthalene-lithium is c_N , and the volume is V_N (it is the same as V_{THF} since naphthalene-

lithium is dissolved in THF), then the first required loading of butadiene is $c_N \times V_{\text{THF}}$. Thus the mass concentration of butadiene cyclohexane solution (ρ) should be:

$$\rho = c_N \times V_{\text{THF}} \times 54 / V_{\text{cyclohexane}}$$

$$\rho \geq c_N \times V_{\text{THF}} \times 54 / 1.33 V_{\text{THF}} = 40.6 c_N \quad (9)$$

Preparation of Low Molecular Weight Polybutadiene Dilithium

The polybutadiene dilithium with an average polymerization degree of 8 was prepared using butadiene cyclohexane solution in two steps. Comparing to the one-time feeding method, the differences observed during the experiment are listed in Table 1.

Table 1. Comparison of the results for dilithium preparation *via* different feeding method

Method of feeding		$V_{\text{cyclohexane}}$ (mL)	React time (h)	Results
One-time feeding		20.0	1.0	Large amount of black precipitation, difficult to stir
Feeding in	First feed	6.0	0.5	Solution in brownish black, no precipitation
two batches	Second feed	14.0	0.5	Solution in dark brown, clear

Note: $c_N = 1.83 \text{ mol/L}$, $V_{\text{THF}} = 5.0 \text{ mL}$, $\rho = 100.0 \text{ g/L}$, $T = 30^\circ\text{C}$

The feeding method in two batches has significant advantages comparing with one-time feeding when the butadiene cyclohexane solutions were added, as shown in Table 1. In the experiment the concentration of naphthalene-lithium was 1.83 mol/L, totally 5.0 mL was added, thus the loading was 9.15 mmol. From Eqs. (8) and (9) the maximum allowable cyclohexane loading for the first batch should be $5 \times 1.33 = 6.7 \text{ mL}$, and the minimum dissolved butadiene should be $40.6 \times 1.83 = 74.3 \text{ g/L}$. In fact, the mass concentration of butadiene in the experiment was 100.0 g/L ($> 74.3 \text{ g/L}$), the total cyclohexane was 6.0 mL ($< 6.7 \text{ mL}$), the loading of butadiene was 11.11 mmol ($> 9.15 \text{ mmol}$). The reactions (4) and (5) were conducted in homogeneous phase and naphthalene-lithium was completely converted into polybutadiene dilithium. The system was in brownish black solution without precipitation. After 0.5 h, the rest of the butadiene was added in the second batch. As the increasing of the butadiene cyclohexane loading, the polymerization degree of butadiene continued to increase (Eq. 6), and the solubility of dilithium in cyclohexane gradually improved. As a result, the system became more and more clear. However, in case all of the 20 mL butadiene cyclohexane was added into naphthalene-lithium solution in one time, with a volume ratio of 20:5 for cyclohexane to THF, the solubility parameter of the solvent mixture was $17.5 (\text{J}/\text{cm}^3)^{0.5}$, which was lower than the minimum $18.3 (\text{J}/\text{cm}^3)^{0.5}$ required. Therefore naphthalene-lithium could not be well dissolved in the solution, resulting in large amount of black precipitation at the bottom of the reactor, and making it difficult to agitate. As a result, most of the naphthalene-lithium could not effectively initiate butadiene.

The above results demonstrated that adding the butadiene cyclohexane solution in batches according to the Eqs. (8) and (9) can resolve the solubility problem for naphthalene-lithium during preparation of polybutadiene dilithium, thus it is feasible to use cyclohexane instead of benzene for the preparation of low molecular weight polybutadiene dilithium.

Effect of Polymerization Degree of Butadiene

According to reaction kinetics, the reaction for polybutadiene dilithium and SnCl_4 to form multifunctional organolithium initiator and LiCl (Eq. 7) is easy to take place. However, the steric hindered effect plays an important role in this reaction, especially in the later periods. The length of dilithium molecule chain is controlled by the polymerization degree of polybutadiene in dilithium. The longer the dilithium molecule chain, the larger the steric hindrance in the coupling reaction. Thus the functionality of the multifunctional organolithium initiator is affected. The relationship between the polymerization degree of butadiene and the functionality of multilithium initiator is presented in Table 2.

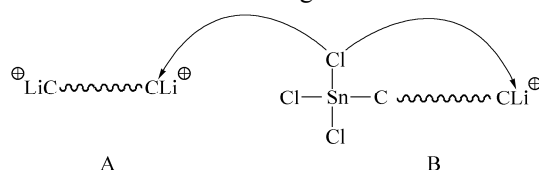
It can be seen from Table 2 that the functionality of the multifunctional organolithium initiator decreased with the increasing of polymerization degree of butadiene. Gel appeared when the polymerization degree was 15.

Table 2. Relationship between the polymerization degree of butadiene and the functionality of multilithium initiator

$\bar{X}_n$	Functionality	$\bar{X}_n$	Functionality
4	3.84	10	3.69
7	3.79	15	gel

Note: $n_{\text{Li}^+}/n_{\text{Cl}^-} = 2$

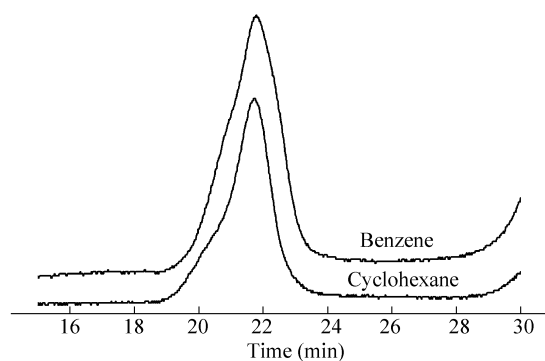
If $n_{\text{Li}^+}/n_{\text{Cl}^-} = 2$, ideally the functionality of the multifunctional organolithium initiator should be 4, but the actual measured value was 3.84. This is because the reaction (6) was completed in steps. The SnCl_4 molecule consists of four $\text{Sn}-\text{Cl}$ covalent bonds which form a tetrahedron structure. In the first step, a Cl^- ion in the SnCl_4 reacted with a Li^+ ion in dilithium to form the following substance B:



In the second step, the potential for the other Cl^- in the SnCl_4 to react with Li^+ in A is greater than that in B. However as the reaction continued, more dilithium molecule chains were connected together by Sn atom, and the steric hindrance increased consistently, making it more difficult for Cl^- to react with the Li^+ in A. Therefore for the polymerization degree of 4, 7, 10 for butadiene, the functionality of multifunctional organolithium initiator were 3.84, 3.79, and 3.69 respectively, which were all less than the theoretical value of 4. The dilithium used in this experiment was a butadiene oligomer, for which the flexibility increased with the length of molecule chain, and the molecule chain gradually curled to form random coil. Consequently, the potential for the rest Cl^- in SnCl_4 to react with the residue dilithium molecule decreased gradually, while the probability for it to react with the Li^+ in the dilithium molecule chain which had bonding linkage with Sn atom increased, and the inner ring structure in the multifunctional organolithium molecule was formed. As a result, the functionality of multifunctional organolithium initiator decreased consistently. In case the polymerization degree of the butadiene was greater than 15, a few of the Cl^- ions in SnCl_4 reacted with the Li^+ ion at the other end of the dilithium molecule chain. Then several of Sn atoms were connected by the polybutadiene molecule chain, and an inner ring structure with multiple layers was formed, leading to the formation of gels. As such, the optimum polymerization degree of butadiene should be in the ranged of 4 to 8.

Comparison in Benzene and in Cyclohexane

Two multifunctional organolithium initiators were prepared from the cyclohexane solution using the above-mentioned process and from the benzene solution^[8]. They were then used to produce star S-SBR ($w_{\text{St}} = 25\%$, $m_{\text{BV}}/m_{\text{BD}} = 0.45$) respectively by random copolymerization of butadiene and styrene under the same condition in

**Fig. 1** GPC traces of star S-SBR prepared with initiators from the different solvents

the experiments. The polymerization degree of the butadiene was 8, $n_{\text{Li}^+}/n_{\text{Cl}^-} = 2$. The molecular weight and molecular weight distribution of the two star S-SBR were analyzed by GPC, and the results are shown in Fig. 1.

It can be seen from Fig. 1 that the molecular weight and molecular weight distribution of the two star S-SBR are similar, which means that the multifunctional organolithium initiator prepared from cyclohexane using batch feeding method has the same functionality and activity as that prepared from benzene solution.

Properties of S-SBR

One of the important applications for the S-SBR is to produce high performance tire tread with low rolling resistance and high wet-skid resistance. Star S-SBR is a promising rubber that can improve both rolling resistance and wet skid resistance.

The multifunctional organolithium initiator prepared in this study was used to initiate butadiene and styrene to form star S-SBR. The synthesized star S-SBR was compared with commercial S-SBR SL552 and 2305 produced by coupling method. The structure parameters of S-SBR are listed in Table 3. The GPC curves of S-SBR and the properties of vulcanizates are shown in Fig. 2 and Table 4^[18].

Sample	w_{St} (%)	$m_{\text{BV}}/m_{\text{BD}}$
Star S-SBR	29.5	0.39
SL552	24.0	0.39
2305	25.0	0.34

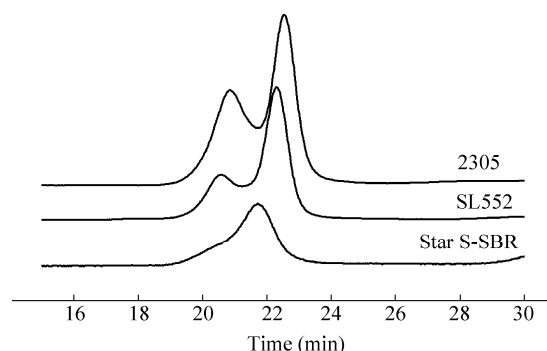


Fig. 2 GPC curves of S-SBR

It can be seen from Fig. 2 that the GPC curve for star S-SBR has a single peak, meaning that the structure is completely star shape. While the GPC curves for SL552 and 2305 both have two peaks. This is because they were prepared by arm-first method, and were consisting of both linear molecules and star-shape molecules.

The mechanical properties of vulcanizates in Table 4 show that comparing to SL552 and 2305, the compress permanent deformation and temperature rise at dynamic compression of star S-SBR were the lowest (1.2% and 13.1°C), lower than those of SL552 (2.1% and 15.6°C) and 2305 (2.7% and 15.8°C). This is because first, the weak Sn—C bond in star S-SBR molecule increased the amount of bonds between rubber and carbon black. Secondly, the higher coupling degree resulted in less deformation under certain stress; in addition, the molecule had less twist, and was easy to be loosed. Thus the friction between molecule chains was reduced, and less heat was generated in star S-SBR. Table 4 also shows that $\tan\delta$ at 60°C for star S-SBR was 0.08, lower than that of the other two rubbers. While at 0°C, $\tan\delta$ for star S-SBR was close to that of SL552 and 2305. According to the equivalent theory for time and temperature, at certain frequency, increasing the $\tan\delta$ value at 0°C can improve the wet resistance, while reducing the $\tan\delta$ value at 60°C can reduce the rolling resistance. Therefore as a tire tread, star S-SBR has better overall performance than commercial products, and is promising to be a better raw rubber for green and energy-saving tire tread.

Table 4. Mechanical properties and dynamic mechanical properties of S-SBR vulcanizate

Properties	Star S-SBR	SL552	2305
Hardness, Shore A	73	73	73
300% modulus (MPa)	16.4	16.8	15.4
Tensile strength (MPa)	23.9	23.2	23.2
Elongation at break (%)	482	428	496
Tear strength (kNm ⁻¹)	41.3	46.2	43.4
Permanent set (%)	12	12	12
Compress permanent set (%)	1.2	2.1	2.7
Temperature rise at dynamic compression (°C)	13.1	15.6	15.8
tan δ 0°C	0.26	0.26	0.25
tan δ 60°C	0.08	0.11	0.09

Formulation of S-SBR vulcanizate (phr): S-SBR 100, carbon black (N234) 50, ZnO 4, stearic acid 1, antioxidant 4010NA 1, accelerator DM/D 1.2/0.6, Paraffin wax 5, sulfur 1.8;

All were cured at 150°C for 8.0 min.

CONCLUSIONS

A new preparing method was developed to synthesize multifunctional organolithium initiator from naphthalene-lithium in this study. The synthesis process of the multifunctional organolithium initiator must satisfy the following conditions. The butadiene cyclohexane solution was fed in batches. In the first feeding, the maximum loading of cyclohexane and the least concentration of butadiene cyclohexane must be controlled under $V_{\text{cyclohexane}} \leq 1.33V_{\text{THF}}$ and $\rho \geq 40.6c_{\text{N}}$. Average polymerization degree for butadiene was 4–8, and $n_{\text{Li}^+}/n_{\text{Cl}^-} = 2$. Using this multifunctional organolithium initiator, star S-SBR is achieved with no linear-molecules and could be used for the high overall performance tire tread.

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