

Study on a Novel N-Functionalized Multilithium Initiator and Its Application for Preparing Star-Shaped N-Functionalized Styrene-Butadiene Rubber

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ABSTRACT: A novel N-functionalized multilithium (N-M-Li) initiator was synthesized from divinylbenzene (DVB) and lithiohexamethyleneimine (LHMI), and its microstructure and molecular weight distribution were characterized by ¹H-NMR and GPC, respectively. Reaction kinetics of synthesis of N-M-Li was also studied and the apparent propagation rate constants of different monomers in this reaction were obtained. Star-shaped N-functionalized styrene-butadiene rubber (SBR) was prepared by anionic polymerization using N-M-Li as initiator, *N,N,N',N'*-tetramethylethylenediamine (TMEDA) as polar additive, and cyclohexane as solvent. The molecular weight distribution

of the target product was measured by GPC and the result showed that it contained a certain amount of star-shaped polymers. Three types of SBR were initiated by N-M-Li, LHMI, and *n*-BuLi, respectively, and then were contrasted in terms of the loss factor (tan δ) by DMA, which demonstrated that N-M-Li initiator could provide rubbers with improved hysteresis characteristics. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 820–824, 2008

Key words: anionic polymerization; initiators; functionalization of polymers; star polymers; high performance polymers

INTRODUCTION

It is desirable to produce tires with low hysteresis loss to decrease rolling resistance for economical consideration. A major source of hysteresis loss has been established to stem from the "free end" of the polymeric chain, which cannot effectively participate in the elastically recoverable process.^{1,2} Because star-shaped polymer has fewer free ends and therefore lower hysteresis loss than linear polymer,³ many researches have been developed for preparing star-shaped elastomers using multilithium initiators in anionic polymerization.^{4–7} Another practical method for reducing hysteresis loss is to introduce a cyclic amine group into the end of the polymeric chain by functionalized organolithium initiators.^{8–13} The functional groups have two effects: one is to anchor the free ends and the other is to improve the affinity of elastomer for compounding ingredients, both of which are conducive to reducing hysteresis loss.

In this study, we synthesized a novel N-functionalized multilithium (N-M-Li) initiator and used it for preparing the star-shaped N-functionalized SBR.

This type of SBR, which combines the advantages of both star-shaped polymer and functionalized polymer, exhibits commendable hysteresis characteristics, and thereby tires made from this SBR can be provided with reduced rolling resistance.

EXPERIMENTAL

Materials

Cyclohexane, butadiene (Bd), styrene (St), and *n*-butyllithium (*n*-BuLi) were obtained from Beijing Yanshan Petrochemical Corp., China. Isoprene (Ip) was obtained from Shanghai Jinshan Petrochemical Corp., China. Cyclohexane was dried by 5 Å molecular sieves for 2 weeks. The water content in cyclohexane was kept below 5 μg/g. The solvent was also purged with highly purified nitrogen for more than 15 min before use to keep oxygen content below 10 μg/g. St and Ip were treated with the similar method of cyclohexane. Bd was purified with a small amount of *n*-BuLi and then vaporized to keep water content below 10 μg/g. The concentration of *n*-BuLi was calibrated by the Gilman double titration method.

Divinylbenzene (DVB, Shanghai Chemical Reagent Factory, China) was dried by γ-Al₂O₃ for several weeks and then distilled over CaH₂ under vacuum.

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Hexamethyleneimine (HMI, Jiangsu Sheyang County Chemical Factory, China) was refluxed and then distilled over CaH_2 . Tetrahydrofuran (THF, Beijing Yili Fine Chemicals Co., China) was refluxed over CaH_2 and then diluted with cyclohexane. N,N,N',N' -tetramethylethylenediamine (TMEDA, Beijing Daxing Xingfu Fine Chemical Research Institute, China) was purified with the similar method of HMI and then dried by 5 Å molecular sieves for more than 2 weeks.

Polymerization procedures

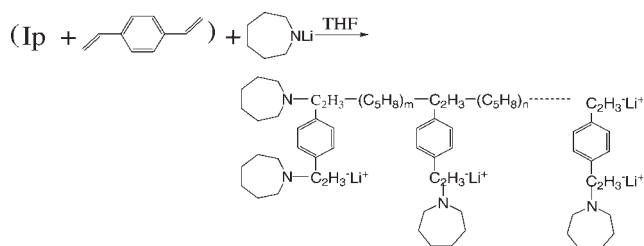
Synthesis of lithiohexamethyleneimine initiator (LHMI)

A stainless glass reactor that was dried and purged with purified nitrogen was charged with equal amount of *n*-BuLi (0.1 mol/L in cyclohexane) and HMI, and then was stirred for 10 min at room temperature to obtain LHMI initiator. The LHMI had the good solubility and stability in cyclohexane. The reaction was represented as follows:



Synthesis of N-M-Li initiator

The glass reactor was well-dried and carefully purged with purified nitrogen before use to ensure the reaction was performed without water and oxygen. The stoichiometric amount of cyclohexane, Ip, THF, DVB, and LHMI (molar ratio Ip/THF/DVB/LHMI = 15/0.5/0.8/1) were successively transferred into the reactor by syringes. A water bath with magnetic stirring apparatus was used to keep the reactor's temperature at about 30°C. After 1.5 h the N-M-Li initiator was obtained. The reaction was represented as follows:



Synthesis of star-shaped N-functionalized styrene-butadiene rubber (star N-SBR)

A 5L stainless steel reactor was washed by cyclohexane and purged by purified nitrogen before the reaction. A solution of 10 wt % styrene/butadiene (molar

TABLE I
SBR Vulcanizate Recipe Used in This Research

Content	Parts by weight
SBR	100
Zinc oxide	3
Stearic acid	1
Accelerator (<i>N</i> -cyclohexyl-2-benzothiazole sulfonamide)	1.2
Antioxidant (2,6-dibutyl-4-methylphenol)	1
Sulfur	1.75
N550 carbon black	50

ratio St/Bd = 25/75) in cyclohexane and polar additive TMEDA (molar ratio TMEDA/Li = 0.5/1) were sequentially charged into the reactor under the protection of nitrogen, and then preheated to the polymerization temperature (50°C). A stoichiometric amount of N-M-Li was added into the reactor to initiate the polymerization. After 4 h, when the polymerization was completed, a small amount of methanol was added to terminate the living polymers. The product was precipitated in ethanol with 1 wt % of antioxidant 264. After evaporating cyclohexane, the resulting copolymer was dried in a vacuum oven at 50°C to a constant weight.

Characterization

The molecular weight and its distribution were determined by gel permeation chromatography (GPC; Maxims 820, Waters) using three Waters μ -Styragel Columns at a nominal flow rate of 1 mL/min with a sample concentration of 0.1% in THF solvent. The GPC instrument was calibrated with monodisperse polystyrene standards. The microstructure of N-M-Li was analyzed by $^1\text{H-NMR}$ (AM-400, Bruker) spectroscopy at room temperature. The sample was dissolved in CDCl_3 to prepare a solution with a concentration of 150 mg/mL. The reaction kinetics of synthesis of N-M-Li was studied by gas chromatogram (GC; 6890N, Agilent). The entire vulcanizate recipe in this research is described in Table I. The vulcanization of SBR was performed at 145°C for 45 min. To determine the loss factor ($\tan \delta$) of SBR vulcanizates, dynamic mechanical analysis (DMA) was conducted with a viscoelastometer (TA2980, USA).

RESULTS AND DISCUSSION

Structure of N-M-Li initiator

The N-M-Li consists of prepolymer of Ip and DVB with different numbers of active anionic center,

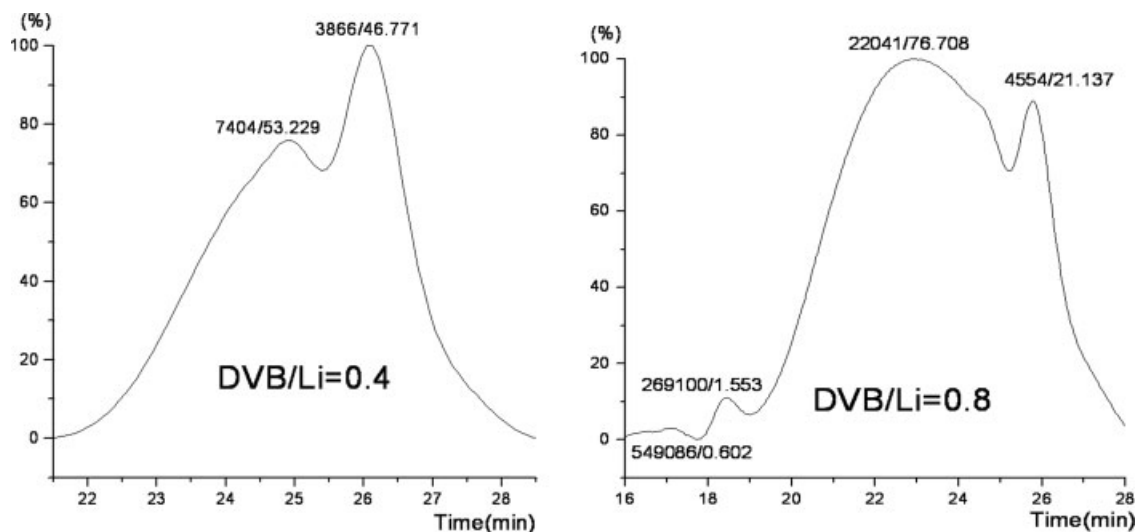


Figure 1 GPC spectra of terminated N-M-Li at different DVB dosage.

which can initiate further polymerization to prepare star-shaped polymers. The N-M-Li was terminated by methanol and the resulting polymer was characterized by GPC. The GPC spectra of terminated N-M-Li with different DVB dosage are shown in Figure 1. The high molecular weight proportion increases with the augment of ratio of DVB to LHMI (DVB/Li), which indicates that the average number of arms of the star-shaped initiator can be adjusted by the DVB dosage.

Butadiene was polymerized ($M_n = 4000$) using N-M-Li as initiator and the resulting polymer was analyzed by $^1\text{H-NMR}$. As shown in Figure 2, there are two small peaks at 2.6 and 3.1 ppm in the $^1\text{H-NMR}$ spectrum, which demonstrates that the cyclic amine group has been introduced into the polymer by N-M-Li.¹⁴

Reaction kinetics of synthesis of N-M-Li initiator

To acquire detailed information about the reaction of synthesis of N-M-Li, kinetic behavior of this copolymerization was studied by the method of gas chromatography. There are four kinds of monomers, *p*-DVB, *m*-DVB, *p*-ethylvinylbenzene (EVB), and *m*-EVB in the commercial DVB. As for this reaction, *p*-DVB and *m*-DVB are the effective components. The

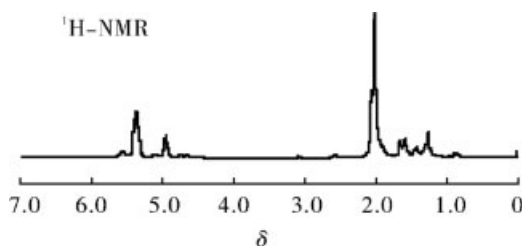


Figure 2 $^1\text{H-NMR}$ spectrum of polybutadiene initiated by N-M-Li.

relationship between time and conversion is shown in Figure 3. This study indicates that the N-M-Li can be effectively prepared at 100 min because at that time *p*-DVB and *m*-DVB have almost completely participated in the reaction.

The apparent propagation rate constants of *p*-DVB, *m*-DVB, *Ip*, *m*-EVB, *p*-EVB can be calculated from Figure 4 and the results are shown in Table II. The order of reaction velocity is *p*-DVB > *m*-DVB > *Ip* > *m*-EVB > *p*-EVB, which is in accordance with the similar reaction (identical monomers, polar additive, solvent, and temperature) initiated by *n*-BuLi.¹⁵

GPC analysis of star N-SBR

The star N-SBR was obtained by the use of N-M-Li as initiator in anionic polymerization. The molecular weight distribution of the star N-SBR was analyzed by GPC, as shown in Figure 5. The GPC spectrum indicates that there exists about 30% star-shaped polymers

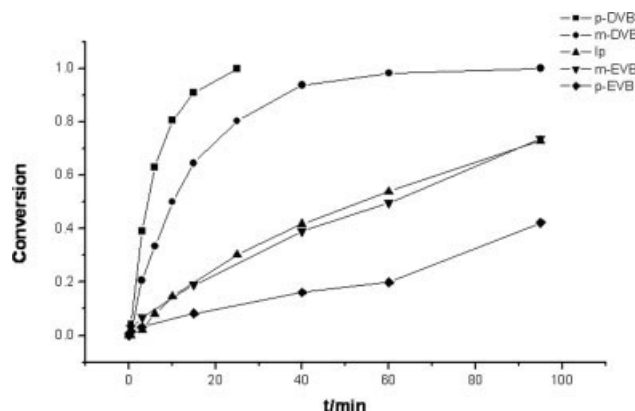


Figure 3 Relationship between time and conversion of different monomers.

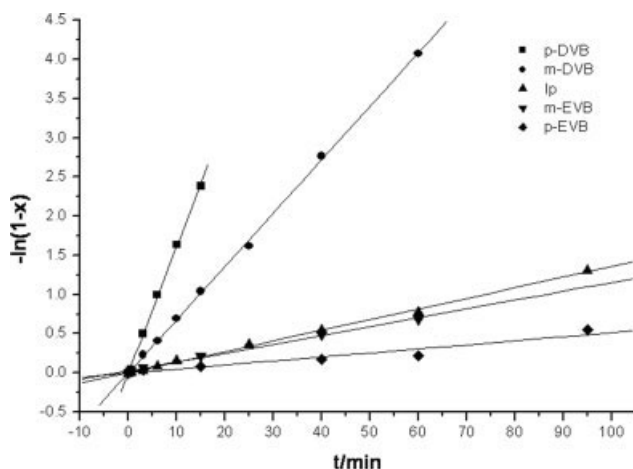


Figure 4 Curves of time versus $-\ln(1-x)$ of different monomers.

in the target product. In fact, the star N-SBR includes both star-shaped polymers and linear polymers.

DMA analysis of the vulcanized SBR initiated by different initiators

Three types of SBR were obtained by using N-M-Li, LHMI, and *n*-BuLi, respectively, as initiator, and then were vulcanized according to the recipe in Table I. The rolling resistance and wet skid resistance of the vulcanized SBR rubbers were estimated by DMA. Usually $\tan \delta$ at 60°C is a parameter for rolling resistance and $\tan \delta$ at 0°C is a parameter for wet skid resistance.¹⁶ The original DMA spectra are illustrated in Figure 6 and the corresponding data are shown in Table III.

The SBR-1 shows obviously reduced $\tan \delta$ at 60°C and slightly increased $\tan \delta$ at 0°C compared with the SBR-3, which indicates that the former has lower rolling resistance and higher wet skid resistance than the latter. The $\tan \delta$ at 60°C of the SBR-2 is lower than that of the SBR-3 but higher than that of the SBR-1. These data can be explained by the microstructures of these rubbers. The SBR-2 is initiated by LHMI and then has a cyclic amine group in the initial end of the polymeric chain. Such functional group can anchor the "free end" and improve the affinity of elastomer for compounding ingredients, and thereby reduce hysteresis loss. Thus, the rolling

TABLE II
The Apparent Propagation Rate k_p'' of Different Monomers

Monomer	k_p''/min^{-1}
p-DVB	0.161
m-DVB	0.068
p-EVB	0.00516
m-EVB	0.0113
Ip	0.0136

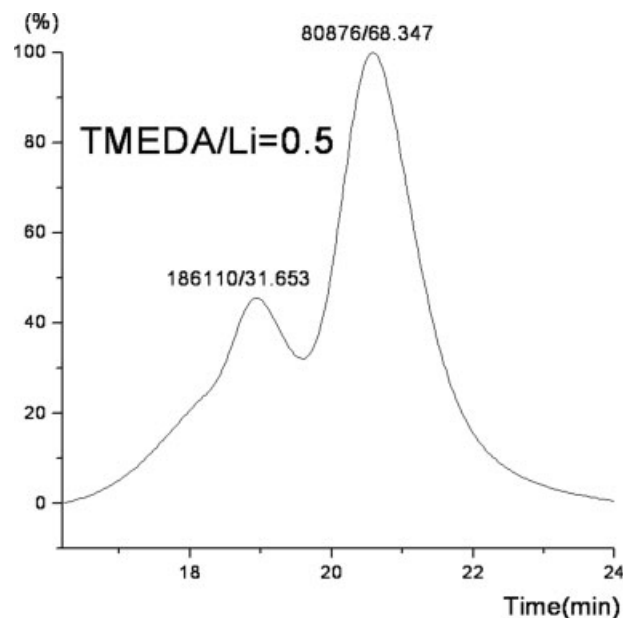


Figure 5 GPC spectrum of star N-SBR.

resistance of the SBR-2 is lower than that of the SBR-3. The SBR-1, which is initiated by N-M-Li, not only is introduced with functional groups but also involves a certain amount of star-shaped polymers. The star-shaped polymeric chains are also conducive to reducing hysteresis loss since they have fewer "free ends" than linear polymeric chains. Thus, under the dual effects, the SBR-1 exhibits the lowest hysteresis loss among the three types of SBR.

CONCLUSIONS

The novel N-M-Li initiator for anionic polymerization was prepared from DVB, Ip, and LHMI. The GPC spectra of the terminated N-M-Li implied that

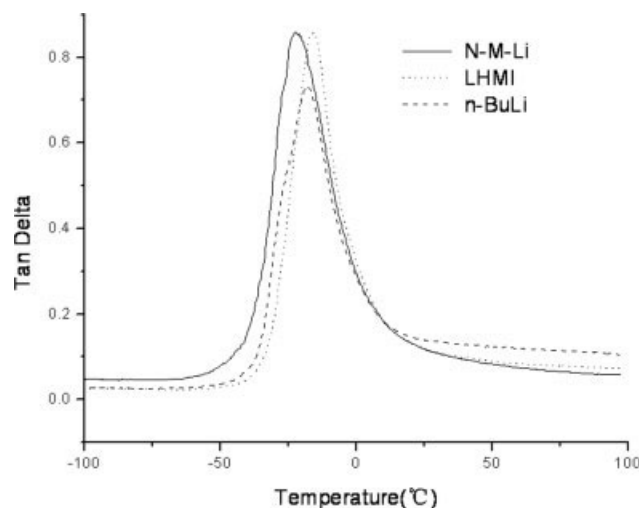


Figure 6 DMA spectra of vulcanized SBR initiated by different initiators.

TABLE III
DMA Analysis of Vulcanized SBR Initiated by Different Initiators

Sample	SBR-1	SBR-2	SBR-3
Initiator	N-M-Li	LHMI	<i>n</i> -BuLi
T_g (°C)	-22.25	-15.42	-17.63
Tan δ (0°C)	0.2952	0.3239	0.2881
Tan δ (60°C)	0.07426	0.08384	0.1194

this initiator contained prepolymers with different numbers of active anionic centers. The $^1\text{H-NMR}$ spectrum of polybutadiene initiated by N-M-Li demonstrated that the cyclic amine group had been introduced into the polymer. Kinetic study of the reaction of synthesis of N-M-Li determined the apparent propagation rate constants of different monomers in this reaction. Star N-SBR was obtained by N-M-Li as initiator and the GPC spectrum indicated that the target product was actually a mixture of linear polymers and star-shaped polymers. Three types of SBR initiated by different initiator were contrasted, the SBR initiated by N-M-Li exhibited better hysteresis loss characteristics than those initiated by LHMI or *n*-BuLi.

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