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Polymer 46 (2005) 3782–3788

polymer

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Ultra high *cis* polybutadiene by monomeric neodymium catalyst and its tensile and dynamic properties

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Received 26 December 2004; received in revised form 4 March 2005; accepted 9 March 2005
Available online 7 April 2005

Abstract

The monomeric Nd-catalyst composed of Nd(neodecanoate)$_3$·(neodecanoic acid)(**NdV4**)/AlEt$_2$Cl/Al(*i*Bu)$_3$ showed a high activity (2.0×10^6 g/Nd mol h), and the monomeric active-center was proposed through density functional calculations (B3LYP/CEP-31G). The microstructure of polybutadiene was controlled by chain–transfer with **NdV4**, catalyst composition and phosphine compounds. As with increase in Nd concentration, increase in branchness and decrease in cold-flow were observed. A series of phosphine compounds was employed to control the microstructure of polybutadiene, and ultra high *cis* polybutadiene with over 99% *cis* content was obtained in the presence of tri-*p*-fluorophenyl phosphine.

The vulcanized properties of different microstructured polybutadienes were measured. Linear polymer, **Nd-BR1**, showed excellent tensile and dynamic properties such as low heat build-up and high abrasion resistance. However, poor processibility in view of high compound viscosity and hardness was obtained. **Nd-BR2**, designed to compromise both processibility and physical properties, exhibited improved processibility in terms of low compound viscosity with good tensile and dynamic properties.

Keywords: Neodymium; Polybutadiene; Vulcanized property

1. Introduction

Significant progress of lanthanide catalyst has been made in various homo- and co-polymerization from ethylene, butadiene, styrene to methyl methacrylate [1]. As for 1,3-butadiene polymerization, neodymium-based catalyst has also drawn particular interest since it gives a higher *cis* microstructure than any other catalysts such as Li-, Na-, Ti-, Co- and Ni-catalysts do, and exhibits pseudo-living character which is a very rare case in Ziegler–Natta catalyst reactions [2,3]. Nd-polybutadiene also shows high abrasion resistance, low heat build-up, and high resilience, which are very demanded properties for tire, golf-ball as well as high impact polystyrene (HIPS) applications [4]. Nd-polybutadiene, however, has cold-flow due to its linear structure, which causes continued deformation or movement under stress of a load, and thus cold-flow is a significant problem in the industry.

As for ultra high *cis* polybutadiene, many kinds of binary and ternary lanthanide-based catalysts have been developed including Nd(neodecanoate)$_3$/AlR$_2$Cl/AlR$_3$ (R = alkyl), which has been of particular interest in the rubber industry and intensively studied due to its higher solubility and better reactivity [3]. However, the neodymium compound Nd(neodecanoate)$_3$ (**NdV3**), exists as a mixture of hydrated oligomeric or polymeric forms, and its catalytic activity is needed to be further improved. Recently, we have developed a novel neodymium carboxylate, Nd(neodecanoate)$_3$·(neodecanoic acid)(**NdV4**), possessing a monomeric structure, and employed it for the preparation of ultra high *cis* polybutadiene [5]. Here, we report the physical and spectroscopic properties of the monomeric neodymium catalyst, controlling of the structure of ultra high *cis* polybutadiene with **NdV4**, a plausible monomeric active-site and vulcanized properties of branched and linear polybutadiene possessing ultra high *cis* structure.

2. Experimental

2.1. Materials

Diphenyl(2-methoxyphenyl)phosphine, tri(4-chlorophenyl)-

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0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.03.040

phosphine, tris-*o*-toylphosphine, tris(2,4,6-trimethylphenyl)phosphine, tris(4-fluorophenyl)phosphine, $Al(iBu)_3$, $Al(iBu)_2H$, $AlEt_2Cl$, and $AlEt_3$ were purchased from Aldrich. Cyclohexane and 1,3-butadiene were obtained from the Yeosu Plant of Korea Kumho Petrochemical Co., Ltd (KKPC). KBR-01 (**Ni-BR**) is a product of KKPC, and **Nd-BR1** and **Nd-BR2** are products of the rubber pilot plant.

2.2. Preparation of $Nd(neodecanoate)_3\cdot(neodecanoic\ acid)$ (*NdV4*).

NdV4 was prepared in a ligand-exchange method with neodymium acetate and neodecanoic acid according to the literatures [5].

2.3. 1,3-Butadiene polymerization

Cyclohexane (450 g), 1,3-butadiene (90 g), **NdV4** (1.0% cyclohexane), diethyl aluminum chloride (1.0 M *n*-heptane), diisobutyl aluminum hydride (1.0 M *n*-heptane) and triisobutyl aluminum (1.0 M *n*-heptane) were added to a 1-l pressure glass reactor under a nitrogen atmosphere, and reacted at 60 °C for 2 h. The resulting polybutadiene was terminated by methanol.

2.4. Characterization

The microstructure of polybutadiene was measured in CS_2 solution by infra-red spectroscopy (Bio-Rad, FTS 60-A) according to the literature [6]. Gel permeation chromatography data were obtained using a Visotec system (TDA 300) employing connected TOSOH columns (G6000HHR, G5000HHR, G4000HHR, G3000HHR) with a refractive index detector. Tetrahydrofuran was used as solvent at the flow rate of 1.0 ml/min.

2.5. Cold flow and solution viscosity

Cold flow was measured through an orifice of 1/4 in in an oven at the temperature of 50 °C, and the flow rate was obtained by extruded amount of rubber. Polymer solution (5.3%) was prepared in toluene, and measured at 25 °C with a Ubbelohde viscometer.

2.6. Compound property

Mooney viscosities of raw polymers and their compounds were measured at 100 °C with a Mooney MV 2000 of Alpha Technologies. Physical properties of the compounds were measured with a universal testing machine (Instron 6021). Abrasion was measured according to ASTM with a Pico abrasion tester of BF Goodrich for 80 cycles.

2.7. Calculations

All calculations were performed with the density functional calculations using the Gaussian98 package with the CEP-31G basis set to obtain the structures and electronic properties of the monomeric neodymium active-site [7]. For graphical representation, the Cerius^2 software was utilized.

3. Results and discussion

3.1. $Nd(neodecanoate)_3\cdot(neodecanoic\ acid)$ (*NdV4*)

NdV4, monomeric Nd-compound used for 1,3-butadiene polymerization, is liquid at room temperature and highly soluble in cyclohexane, while the polymeric neodymium neodecanoate (**NdV3**) is solid. The absorption of **NdV4** is sharp and line-shape like that of a typical neodymium compound in Fig. 1. Sharp absorption peaks of **NdV4** at 527, 584, 741 and 801 nm, f–f electronic transitions of neodymium by spin-orbit coupling between $4f^n$ configurations, were observed at the same positions as that of **NdV3**. It is notable that the hypersensitive transition at 584 nm, attributed to $^4I_{9/2}\rightarrow{}^4G_{5/2}+{}^2G_{7/2}$, is particularly sensitive to changes in the coordination sphere [8]. The peak of **NdV4** at 584 nm is narrowed, which results from higher structural symmetry than that of **NdV3**. Contained impurities in **NdV3** show strong absorption in the region of below 325 nm. The concentration of neodymium in **NdV4** solution was determined with UV–visible spectroscopy at the peak position of 584 nm ($\varepsilon=11.1$ in cyclohexane).

3.2. Polymerization

1,3-Butadiene polymerization was carried out at 60 °C for 2 h in the sequent addition of cyclohexane, butadiene, **NdV4**, $AlEt_2Cl$ as the halogen compound, and $Al(iBu)_3$ and $Al(iBu)_2H$ as alkylation compounds in a high-pressure reactor. The active neodymium-catalyst is formed in the in situ mixing of **NdV4**, alkyl aluminum halide and alkyl aluminum in the reactor. The concentration of neodymium,

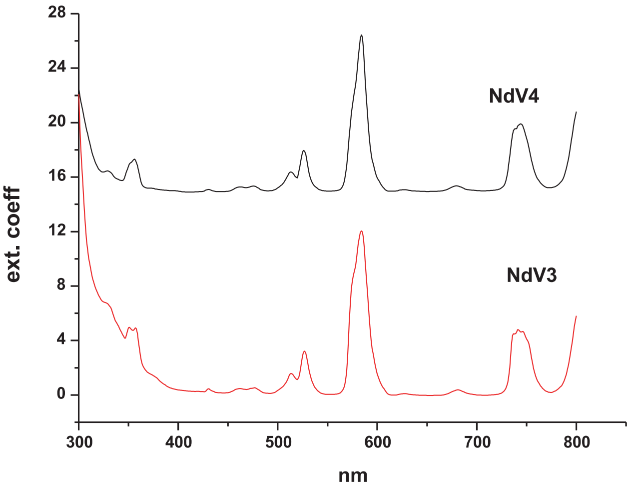

Fig. 1. UV–visible absorption spectra of **NdV3** and **NdV4**.

Table 1

1,3-Butadiene polymerization results by various Nd-catalyst concentration and the analysis of microstructure and cold-flow

Run	Cat. ratio[a]	Nd conc. ($\times 10^{-4}$ mol)	Conv.[b] (%)	*cis* (%)	ML ($_{1+4,\ 100\ °C}$)	*C*/*F*[c] (mg/min)	M_w	MWD
1	1/95/2/2.5	0.4	90	98.7	45.2	5.5	592000	2.55
2	1/30/13/2.5	0.6	91	98.5	44.0	3.6	571000	2.65
3	1/12/8/2.5	1.0	93	97.8	44.3	1.8	548000	2.88
4	1/12/10/2.5	1.1	97	97.5	47.6	1.9	595000	2.97
5	1/15/5/2.5	1.3	100	96.8	41.0	1.3	617000	3.32
6	1/95/2/2.5	0.4	55	94.5	65.6	2.1	956000	4.25

[a] Cat. ratio = Nd/TIBA/DIBAL/DIAE.

[b] 2-h.

[c] *C*/*F* = cold-flow.

the mol ratio of catalyst, and the polymerization results are summarized in Table 1. In the microstructure of polybutadiene, *cis* content is varied from ca. 97 to 98% by the concentration of **NdV4**. Mooney viscosity (MV) of 45, weight-average molecular weight (M_w) of ca. 500,000, and polydispersity (M_w/M_n) of 2.5–3.5 were controlled by the variation of catalyst composition.

In run 1, **NdV4** shows a high activity up to 2.0× 10^6 g/Nd mol h (first 1-h measurement), and produces polybutadiene with over 98% *cis* content and without gel. At a low concentration of neodymium, it proceeds propagation, 1,4-insertion of 1,3-butadiene as the main reaction, and thus produces a linear structure with a high cold-flow (5.5 mg/min). The high activity is attributed to the monomeric structure of neodymium catalyst resulting in every neodymium atom of **NdV4** readily working as an

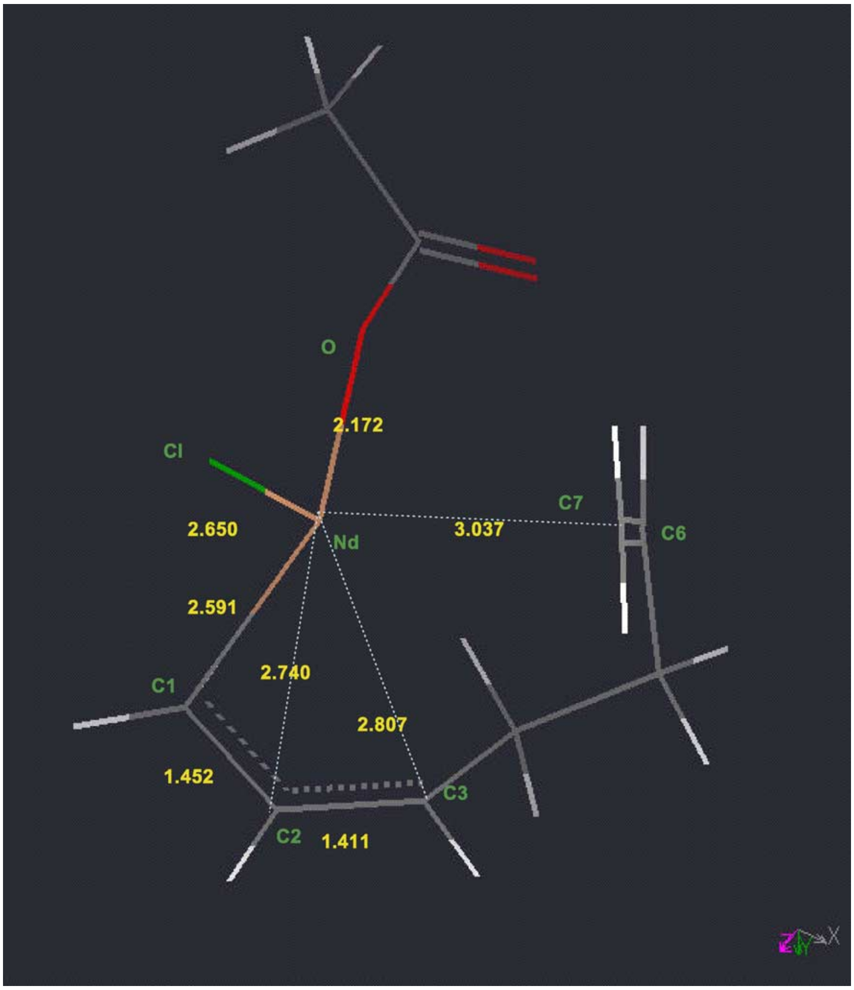

Fig. 2. Calculated a plausible active-center of the monomeric Nd-catalyst: The bond distances are Nd–C_1 2.59 Å, Nd–C_2 2.74 Å, Nd–C_3 2.81 Å, Nd-η^2-(C_6–C_7) 3.04 Å, Nd–Cl 2.65 Å, Nd–O_1 2.17 Å, C_1–C_2 1.45 Å, and C_2–C_3 1.41 Å, respectively.

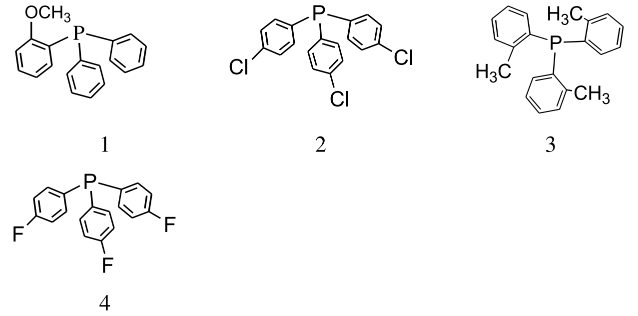

Fig. 3. Phosphine ligands, as electron donor, were used for stereoregularity.

active center, and thus yields a low value of polydispersity. Low activity of lanthanide catalysts mainly due to aggregation, a crucial disadvantage, was overcome by the monomeric structure [9]. However, cold-flow was too high to be used in practical. Cold-flow, solid-state deformation, can be described by reptation of a polymer chain within the mesh of constraints by the surrounding chains [10]. Thus, cold-flow of rubber depends strongly on its topological structure, primary related with and controlled by molecular-scale structure such as *cis* content, linearity and polydispersity. Degree of branch is represented by the ratio of solution viscosity (SV) over molecular weight or roughly by SV over MV. Catalyst composition of Ziegler–Natta is a prime factor to control polymer structure, because chain-transfer reaction is facilitated by increase in active species. In run 2, neodymium concentration was increased to lower cold-flow (3.6 mg/min). Simultaneously, decrease in Al(iBu)$_3$ and increase in Al(iBu)$_2$H were required to meet a suitable molecular weight and a Mooney viscosity (ML$_{1+4,\ 100\ ^\circ\mathrm{C}}$, 40). As the concentration of over 1.0×10^{-4} Nd mol was used in runs 3–4, a suitable cold-flow (ca. 1.8 mg/min) was obtained. These cold-flow results suggest that the chain-transfer to Nd is an important factor for controlling cold-flow and microstructure with broadening MWD and generating long chain branching.

In run 5, a high concentration of neodymium (1.3×10^{-4} Nd mol) produces a low cold-flow (1.3 mg/min) of polybutadiene. The low cold-flow results from a broad MWD (3.3) and a branched structure (96.8% *cis*, 1.3% vinyl contents), which increase entanglement of polymer chains. In run 6, structure of alkyl aluminum affects the activity of polymerization and the microstructure of polybutadiene. AlEt$_3$ showed a low activity (7.7×10^5 g/Nd mol h), and generated a high molecular weight, a high value of MV and a low *cis* content (94.5%). Triethylaluminum, dimeric in solution, would form aggregated catalytic species and promote chain-transfer in the aggregates, while the steric hindrance of Al(iBu)$_3$ plays an important role in forming the monomeric character of the neodymium active-site and in enhancing the catalytic activity with high *cis* content [11].

3.3. Active center

The monomeric active center composed of **NdV4** and Al(iBu)$_3$ is proposed on the basis of polymerization results, spectroscopic studies and through density functional calculations (B3LYP/CEP-31G) in Fig. 2 [12]. The optimized structure shows that the η^3-allyl ligand of the chain end, chloride, the penultimate double bond are coordinated to Nd(III), and Nd, O$_1$, Cl, and C$_4$ atoms are on the same plane. The bond distances are Nd–C$_1$ 2.59 Å, Nd–C$_2$ 2.74 Å, Nd–C$_3$ 2.81 Å, Nd-η^2-(C$_6$–C$_7$) 3.04 Å, Nd–Cl 2.65 Å, Nd–O$_1$ 2.17 Å, C$_1$–C$_2$ 1.45 Å, and C$_2$–C$_3$ 1.41 Å, respectively. Chlorine would induce 4f-orbitals of neodymium so as to enhance the *cissoid* coordination of monomer, and to facilitate the back-biting coordination that blocks *anti–syn* isomerization. In the η^3-allylic end, the bond length of Nd–C$_1$ is shorter than that of Nd–C$_3$, which implies 1,4-addition of 1,3-butadiene is favored over 1,2-addition. The significance of the penultimate double bond is well shown here, which stabilizes neodymium active-site and prevents *anti*/*syn* rotation for high *cis* stereoregularity [13].

3.4. Additive effects

It is well investigated that phosphine plays an important role in controlling the microstructure of polybutadiene using Co- and Nd-based Ziegler–Natta catalysts [14]. In the monomeric catalyst system, the effects of phosphine ligands on the active-site of neodymium are studied on the basis of stereoregularity, catalytic activity, and the molecular weight analysis of polybutadiene in Fig. 3 and Table 2. Phosphine compounds were mixed with tetrahydrofuran,

Table 2
Microstructure control of polybutadiene with phosphine compounds

Run[a]	Phosphine comp.	Conc. of phosphine comp. (mmol)	Conv.[b] (%)	M_w	MWD	*cis* (%)	*trans* (%)	Vinyl (%)
1	–	–	100	654000	3.42	97.1	2.3	0.6
2	1	5.1	85	1176000	3.13	99.4	0.2	0.4
3	2	6.0	83	816000	2.54	98.9	0.7	0.4
4	3	4.2	83	1330000	2.38	99.3	0.3	0.4
5	4	8.7	77	1417000	2.43	99.7	0.1	0.2

[a] Cat. ratio = Nd/TIBA/DIBAL/DIAE(1/33/7/2), Nd conc. = 1.5×10^{-4} mol.
[b] 2-h.

Table 3
Vulcanized properties of linear and branched Nd-BR and Ni-BR

		Nd-BR1	**Nd-BR2**	**Ni-BR**
Raw Mooney viscosity	($ML_{1+4,\ 100\ °C}$)	45.2	44.3	46.5
cis(%)		98.7	97.8	95.5
M_w		592000	548000	567000
MWD		2.55	2.88	4.50
SV (SV/MV)		354 (7.81)	278 (6.28)	150 (3.22)
Cold-flow (mg/min)		5.5	1.8	0.1
Comp. Mooney viscosity	($ML_{1+4,\ 100\ °C}$)	97.7	92.6	82.5
Tensile property	Hardness (shore A)	63	63	60
	300%-modulus (kg_f/cm^2)	112	106.5	97.5
	Tensile strength (kg_f/cm^2)	158	140	127
	Elongation break (%)	386	365	365
Rebound	%	55.4	54.3	49.8
Heat build-up	(Δ °C)	27.0	27.7	34.0
Abrasion (PICO)	mg	11.3	13.0	17.0

and sequentially added after solvent, monomer and catalyst injections. In the absence of phosphine compound, 97.1% *cis* content was obtained with high conversion, in run 1. In runs 2–4, *cis* content was increased with a large decrease in *trans* and a slight decrease in vinyl, which suggests that phosphine promotes *anti*-conformation over *syn*. Regardless of phosphine structure, the similar high *cis* content was obtained, but conversion was decreased. It is a different result obtained by Quirk, in which tetrabutyl phosphine increases conversion by the formation of more soluble catalytic centers in the catalytic system composed of **NdV3** and alkyl aluminum [15]. In the monomeric neodymium catalytic system, the active species are highly soluble without phosphine compounds. Thus, it is understood that the bulky structure of phosphine ligand prevents coordination of 1,3-butadiene resulting in low reaction kinetics ($3.1–3.9\times10^5$ g/Nd mol h). In run 5, ultra high *cis* polybutadiene was prepared with a significant decrease in *trans* and vinyl contents, of which microstructure consisted of 99.7% *cis*, 0.2% *trans*, and 0.1% vinyl. This is one of highest *cis* contents ever reported. Tri-*p*-fluorophenyl phosphine would interact with neodymium active-site, and promote that 1,4-insertion step is predominantly faster than *anti–syn* rearrangement, chain transfer, or 1,2-insertion step [16].

3.5. Physical property

To understand the relationship between the structure and physical properties, the three different structural polymers of **Nd-BR1**, **Nd-BR2** and **Ni-BR** were studied. The catalyst and polymerization conditions for **Nd-BR1** (run 1) and **Nd-BR2** (run 3) are as described in Table 1. The catalyst for **Ni-BR** consists of Ni(naphthenate)$_2$/BF$_3$OEt$_2$/AlEt$_3$ (Ni conc. 0.6×10^{-4} mol, catalyst ratio 1/12/3). The microstructures, molecular weight analyses and the physical properties are compared in Table 3. **Nd-BR1**, **Nd-BR2** and **Ni-BR** are the same in Mooney viscosity and molecular weight. Significant differences are found in solution viscosity, molecular weight distribution (MWD) and microstructure. The order of high solution viscosity is **Nd-BR1** > **Nd-BR2** > **Ni-BR**, and the order of MWD is **Nd-BR1** < **Nd-BR2** < **Ni-BR**. The measurement of solution viscosity is directly related with hydrodynamic volume, sensitive to structural changes such as molecular weight and degree of branching. The *cis* contents of **Nd-BR1**, **Nd-BR2** and **Ni-BR** are 98.7, 97.8 and 95.5%, respectively. Both **Nd-BR1** and **Nd-BR2** has a higher *cis* content than **Ni-BR** does. **Nd-BR1** has a very linear structure (based on SV/MV and *cis* content) with a narrow MWD, while **Nd-BR2** is moderately linear with a broader MWD. **Ni-BR** has a relatively high degree of branching with a broad molecular weight distribution, and a low solution viscosity.

Although **Nd-BR1** yielded a high compound viscosity, high tensile and dynamic properties such as high abrasion resistance and rebound were obtained. These excellent dynamic properties are attributed to ultra high *cis* and linear structure. Poor processibility can be expected by the high compound viscosity and hardness [17]. Abrasion resistance, one of the significant features of neodymium-polybutadiene, is used to predict the service life of rubber products such as tire tread, shoe soles, belts and hose [18]. Abrasion takes place on the surface of the test specimen, and can be described to friction coefficient and hardness: $A(\text{abrasion}) \sim \mu/H\sigma\varepsilon$ (H: hardness, μ: traction force, σ: tensile strength, ε: elongation) [19]. The high abrasion resistance of **Nd-BR1** is explained by high hardness, tensile strength, and elongation properties.

Nd-BR2 showed a moderate cold-flow, and better processibility with a suitable compound viscosity. These results imply that long branches are generated with increase in Nd concentration (see SV/MV). It was designed to improve processiblity for better mixing and milling with filler and other polymers. Processibility, primarily indicated with compound viscosity and hardness, depends on the structure of polybutadiene. Low *cis* content, high branch ratio, and high polydispersity decrease viscosity and hardness because of increased miscibility with carbon black. High elongation with high tensile properties suggests

			Physical Properties	Polymer Structure
Elasticity	Energy Stroage (Spring)		Tensile Modulus Rebound	Linear Cis Narrow MWD High M_w
Viscosity	Energy Relaxation (Dashpot)		Heat Build-up Abrasion	Branch Vinyl Broad MWD Low M_w

Fig. 4. A simple Maxwell model for explaining tensile and dynamic properties of vulcanized polybutadiene.

that cross-linking networking is made by the long chains of polybutadiene so as to maintain a high ultimate strength without break [20].

Ni-BR showed a very low cold-flow because of a broad MWD and high degree of branch structure increasing topological entanglement. Low compound viscosity and hardness indicate the advantage of nickel–polybutadiene, good processibility. However, low tensile and dynamic properties, especially high heat build-up (34.3 °C) and abrasion (17.0 mg), were obtained. Branching is known to suppress chain dimension as compared to the linear polymer of the same molecular weight, which would yield a low value of tensile strength [21]. High abrasion is mainly due to low hardness and tensile strength.

The tensile and dynamic properties of polybutadiene were well explained by a simple Maxwell model in Fig. 4. Elastic properties such as tensile, modulus, and rebound properties are compared to spring as energy storage, and heat build-up and abrasion to dashpot as energy dissipater. Neodymium-polybutadiene has ultra high *cis*, linear and narrow MWD, showing high elastic properties while nickel-polybutadiene with branched structure and a broad MWD shows relatively high viscositic properties.

4. Conclusions

The monomeric neodymium catalyst, **NdV4**, shows high activity in 1,3-butadiene polymerization, and overcomes one of disadvantages of lanthanide catalyst, which is primary related with catalyst aggregation. The monomeric active center is proposed that the η^3-allyl ligand of the chain end, chloride, penultimate double bond are coordinated to Nd(III). Chlorine would induce Nd orbitals so as to enhance the *cissoid* coordination of monomer, and facilitate the back-biting coordination that blocks *anti–syn* isomerization. The penultimate double-bond stabilizes the active site and prevents *anti–syn* rotation for high *cis* stereoregularity.

Cold-flow, a significant problem in the rubber industry, is greatly improved and the structure of polybutadiene is also controlled by increase in **NdV4** concentration, which facilitates chain-transfer and results in a broad MWD and branched structure. In the presence of tri-*p*-fluorophenyl phosphine, ultra high *cis* polybutadiene with 99.7% *cis* content is obtained. The physical and rheological properties are dictated by controlling the polymer structure. Highly linear neodymium-polybutadiene with a narrow MWD is desirable for high abrasion resistance, low heat build-up and high tensile properties. Although linear and ultra high *cis* polybutadiene possesses high compound viscosity, the disadvantage can be improved by introducing branch structure. **Nd-BR2** is an example to satisfy both good processibility and high physical properties.

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