ELSEVIER

Polymer 43 (2002) 7111–7118

polymer

www.elsevier.com/locate/polymer

Synthesis of high vinyl elastomers via mixed organolithium and sodium alkoxide in the presence of polar modifier

A.F. Halasa*, W.L. Hsu

Chemical R&D, The Goodyear Tire & Rubber Co., 142 Goodyear Boulevard, Akron, OH 44305, USA

Received 16 November 2001; received in revised form 22 April 2002; accepted 21 May 2002

Abstract

The effect of incorporating a small amount of alkali metal alkoxides into a diene polymerization catalyzed by *n*-butyllithium in the presence of a polar modifier was investigated. It was found that the addition of sodium alkoxide significantly enhanced the polymerization rate of the monomers (1,3-butadiene, isoprene and styrene) and increased the vinyl content of the resulting polymers. It was also found that almost any sodium salt of an alcohol (cyclic or acyclic alcohols) or alkylphenol provided the similar 'synergistic' effects of improving polymerization rate and the vinyl content of polymer product. The rate enhancement was attributed to the super basicity from a superbase generated with sodium alkoxide and organolithium. Since other heavier alkali metal alkoxides, such as potassium or cesium alkoxide did not exhibit the similar synergistic effects, it suggested that only sodium is small enough to form a complex with lithium which can coordinate effectively with the polar modifier to yield high vinyl structures. The polymers prepared using the current catalyst system are branched which may have resulted from the backbone metallation by sodium metal or the superbase involved in the catalyst system. Since the current catalyst system is not monomer-specific, a variety of high vinyl elastomers containing diene(s) with or without vinyl aromatic monomers can be prepared at very fast rates. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Anionic polymerization; Sodium alkoxide; High vinyl elastomer

1. Introduction

The interest in anionic polymerization has grown tremendously in recent years because it can be employed to tailor-make polymers of controlled properties. Because of demands on tire skid resistance, elastomers with a high glass transition temperature (T_g) or high vinyl content are of particular interest to the tire industry due to their inherently better grip properties [1]. It is well known that polar modifiers, such as amines or ethers, are needed to increase the vinyl content of the diene polymers produced from anionic polymerization by organolithium [2]. However, it was found that most of these modifiers often failed to yield a high enough vinyl content at commercially feasible polymerization temperatures. Some of these modifiers even retarded the polymerization rates of monomers at higher modifier concentrations required to obtain higher vinyl contents [3,4]. It was our objective to explore means of making high T_g tire elastomers at fast rates. For commercial process, the catalysts should be stable and preferably soluble in aliphatic solvents. Although higher vinyl containing elastomers can be prepared with polar modifiers at lower polymerization temperatures, longer polymerization time and additional cooling requirements are needed. This is obviously not a viable means for use in commercial process. Heavier alkali metals, such as, Na, K, Rb and Cs are known to provide polydienes with much higher vinyl contents than Li [5]; however, the organoderivatives of these alkali metals were seldom employed towards diene polymerization [6]. This might be attributed to their very limited stability and solubility in most of organic solvents. The use of heavier alkali metal alkoxides to effect the reactivity of alkyllithium catalyzed polymerization has been known for more than 30 years [7]. The adducts (RM·LiOR′) of heavy metal oxides (R′OM; M = Na, K, Cs, Rb), and organolithium (RLi) are extremely strong bases (the so-called 'superbases'); they readily react with many organic compounds and thus represent useful tools in organic synthesis and in polymerization [8]. The superbase approach appears to be an excellent way to overcome the stability and solubility problems associated with the organo-compounds of heavier alkali metals (e.g. alkylsodium) since the more active alkylsodium is generated in situ and used immediately for

---

* Corresponding author. Tel.: +1-330-796-1253; fax: +1-330-796-7060.
E-mail address: adel.halasa@goodyear.com (A.F. Halasa).

PII: S0032-3861(02)00451-2

polymerizing diene monomers. Although the superbase concept was utilized in diene polymerization [7–12], the effect of polar modifiers in these polymerizations was seldom mentioned in the literature. The current paper will address this issue [13].

2. Experimental

2.1. Materials

Isoprene was supplied by the Goodyear Tire and Rubber Co. and was freshly distilled and dried as described previously [3,4]. 1,3-Butadiene, received from the Goodyear Tire and Rubber Co., was premixed with hexanes and dried by passing through a column containing activated silica gel, alumina and molecular sieve 3 Å. Styrene, purchased from Aldrich, was premixed with hexanes and dried with a column containing activated alumina, molecular sieve and sodium hydroxide pellets. TMEDA (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine) purchased from Aldrich, was distilled from calcium hydride prior to use. Sodium *t*-amylate (NaOAm) and potassium *t*-amylate (KOAm) are in hexane solution and were purchased from Callery Chem. Co., Pittsburgh, PA. They were dried over sodium or potassium metals, respectively. Ethyl tetrahydrofurfuryl ether (ETE), provided by QO Chemicals, Memphis, TN was dried over 3 Å molecular sieve and calcium hydride. Cesium 2-ethylhexoxide (CsOR) in cyclohexane was purchased from Strem Chem. Inc., Newburyport, MA and used as received. *N*-butyllithium (*n*-BuLi), purchased from Chemetall Foote Co., was diluted with predried hexanes. The concentration of *n*-BuLi was determined by Gilman's double titration method [14].

2.2. Synthesis of sodium phenoxides and alkoxides

Sodium *p*-dodecylphenoxide (SDDP) and sodium *p*-nonylphenoxide (SNP) were prepared by refluxing *p*-dodecylphenol or *p*-nonylphenol with excess of NaOH in ethylbenzene until the calculated amount of byproduct water was collected from a Dean-Stark receiver. Sodium 2,4-dimethyl-3-pentoxide (SDMP) and 2-ethylhexoxide (SEH) were prepared by reacting 2,4-dimethyl-3-pentanol or 2-ethylhexanol with excess of sodium metal in ethylbenzene at the reflux temperature of ethylbenzene. Sodium mentholate (SMT) was prepared by reacting menthol with excess of sodium metal in *n*-heptane at the reflux temperature of *n*-heptane. The concentrations of these sodium salts hydrocarbon solutions were determined by titrating the hydrolyzed sodium salts with a standardized HCl solution.

2.3. Polymerization

All polymerizations were conducted in a 1 gallon stirred batch reactor at the desired temperature according to the procedures described previously [4,15]. Polymerization kinetics measurement (e.g. plots of monomer conversion vs. polymerization time) was obtained as described previously [15].

2.4. Characterization

The polymers were characterized by various analyses including T_g by DSC, molecular weight by GPC and microstructure by proton NMR. It is known that a small amount of cyclic vinyl structure is generated during the preparation of high vinyl polybutadiene [16]. The vinyl contents of polybutadienes reported in this paper represent the total amount of vinyl structures which contain 2–6% of cyclic vinyl structure.

3. Results and discussion

3.1. Isoprene polymerization

It was previously shown that TMEDA did significantly slow the polymerization rate of isoprene at high TMEDA concentrations required to obtain higher vinyl contents (Fig. 1) [4]. We have later discovered a more effective modifier, ethyl tetrahydrofurfuryl ether (ETE) for isoprene polymerization [3]. Based on kinetic studies, ETE was about four times faster than TMEDA for making polyisoprenes having similar microstructures. The rate difference was mainly attributed to the 'steric effect' [3]. The total vinyl structures of polyisoprenes prepared by either TMEDA or ETE were about 63% (3,4- +1,2-PI) which is the highest vinyl content for the polyisoprenes prepared by organolithium catalyst modified by polar modifiers at 65–70 °C. However, as shown in Fig. 2, by adding a small amount of NaOAm (0.5 molar ratio to *n*-BuLi) to the TMEDA modified system, isoprene polymerized much faster than in the ETE modified system. It took only 10 min to convert 90% isoprene to polyisoprene instead of 45 min for ETE and more than 4 h for TMEDA to reach the same monomer

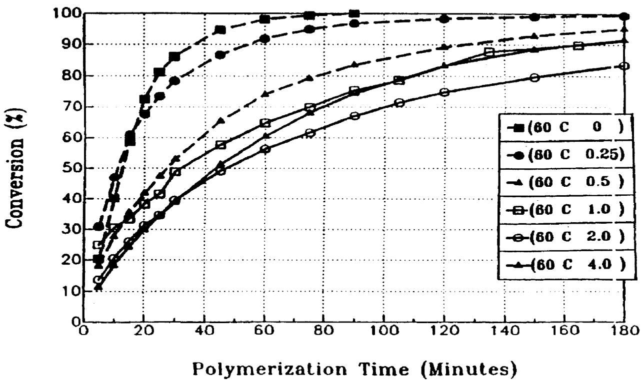

Fig. 1. Conversion data of TMEDA modified isoprene polymerization. Parameters are temperature and modifier ratio.

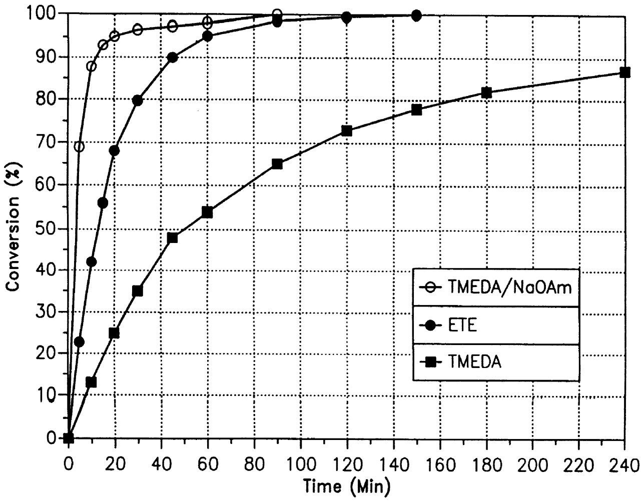

Fig. 2. Effect of NaOAm on isoprene polymerization at 70 °C; Modifier/*n*-BuLi = 3/1 (Modifier = TMEDA or ETE), NaOAm/*n*-BuLi = 0.5/1.

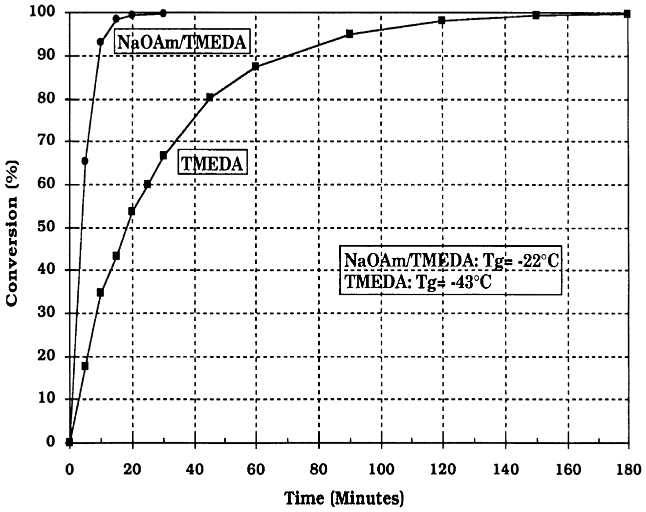

Fig. 3. Effect of NaOAm on 1,3-butadiene polymerization at 50 °C; TMEDA/*n*-BuLi = 3/1, NaOAm/*n*-BuLi = 0.5/1.

conversion. Furthermore, the glass transition temperature of the resulting polyisoprene increased from −15 °C (for either TMEDA or ETE modified systems) to 0 °C when sodium *t*-amylate was used in combination with TMEDA. As indicated in Table 1, the synergistic effects of increasing both rate and vinyl content by NaOAm was also seen in other chelating diamines, such as 2-(dimethylaminomethyl)-*N*-methylpiperdine (DMAMP) and Sparteine. Both the polymerization rate of isoprene and the T_g of the resulting polyisoprenes were greatly enhanced with the addition of NaOAm.

A +30 °C T_g polyisoprene containing virtually all vinyl structures (98% 3,4- + 1,2-PI) could also be prepared in less than 20 min at 50 °C using the combination of NaOAm and DPE (1,2-dipiperidinoethane) as the modifier.

3.2. 1,3-Butadiene polymerization

Similar to isoprene, the highest vinyl content for polybutadiene is around 65% with a modified organolithium catalyst at 65 °C ($T_g = -43$ °C). Again, NaOAm also exhibited synergistic effects on TMEDA modified 1,3-Bd polymerization. As indicated in Fig. 3, the time needed to reach 90% monomer conversion was reduced from 70 min to less than 10 min whereas, the T_g of the PBd was increased from −43 to −22 °C when a small amount of NaOAm was added. As with the PIs discussed earlier, a PBd with extremely high vinyl content (95%; $T_g = -6$ °C) could also be easily made at 50 °C in less than 20 min using a 0.5/3/1 NaOAm/DPE/*n*-BuLi catalyst system. Without the use of NaOAm, it took about 20 h at room temperature to prepare the similar high vinyl polybutadiene.

It is interesting to note that other sodium alkoxides, such as sodium 2,4-dimethyl-3-pentoxide (SDMP), sodium 2-ethylhexoxide (SEH) and sodium mentholate (SMT) or alkylphenoxides, such as sodium *p*-nonylphenoxide (SNP) and sodium *p*-dodecylphenoxide (SDDP) behaved similarly to sodium *t*-amylate for enhancing both the polymerization rate and polymer vinyl content. As shown in Table 2, polybutadienes having vinyl contents of 82–83% can be easily prepared with the modifier system containing TMEDA and any sodium alkoxide (cyclic or acylic) or sodium alkylphenoxide.

It is also noteworthy that all these various sodium salts also worked similarly to NaOAm in the isoprene homopolymerization described above for making high T_g polyisoprenes at very fast rates.

The effect of varying the amounts of NaOAm and

Table 1
Effect of NaOAm on isoprene polymerization

Modifier system	T_g (°C)	Microstructure (%)			Time needed for 90 + % conversion (min)
		1,2-PI	1,4-PI	3,4-PI	
TMEDA	−15	4	39	57	240
NaOAm/TMEDA	0	14	10	76	10
DMAMP	−32	2	54	44	120
NaOAm/DMAMP	−2	9	24	67	30
Sparteine	−60	0	87	13	180
NaOAm/Sparteine	−12	5	36	59	45

Polymerization was done at 70 °C with 3/1 modifier/*n*-BuLi and 0.5/1 NaOAm/*n*-BuLi, $M_n = 300\,000$.

Table 2
Butadiene polymerization via varied sodium salts

Modifier system	Microstructure (%)		Time needed for 90 + % conversion (min)
	1,2-PBd	1,4-PBd	
NaOAm/TMEDA	83	17	15
SDMP/TMEDA	83	17	13
SEH/TMEDA	83	17	15
SMT/TMEDA	83	17	13
SNP/TMEDA	82	18	13
SDDP/TMEDA	82	18	13

Polymerization was done at 60 °C with 0.5/3/1 sodium salt/TMEDA/*n*-BuLi *n*-BuLi, $M_n = 250\,000$.

TMEDA was also studied in the polymerization of 1,3-butadiene at 75 °C. As expected, all polymerizations proceeded extremely fast. Complete monomer conversion (100%) for all runs was achieved in 10 min or less. However, as shown in Table 3, it was surprisingly found that the T_g (−27 to −28 °C) or the vinyl content (82–83%) of the resulting polybutadienes was not affected at the molar ratios of NaOAm to *n*-BuLi of 0.5:1 or higher and TMEDA to *n*-BuLi of 2:1 or higher. Our further studies indicated that polybutadienes with lower vinyl contents can be prepared using *n*-BuLi with sodium-*t*-amylate alone or a much lower amounts NaOAm and TMEDA as modifiers. The finding will be published later.

3.3. Co-polymerization of 1,3-butadiene with styrene

Although homo-polymerization rate of styrene is much higher than that of 1,3-butadiene, styrene polymerizes much slower than 1,3-butadiene in the co-polymerization of styrene and 1,3-butadiene [15]. As a result, a styrene–butadiene copolymer (SBR) with up to 70% blocky polystyrene at the end of polymer chains was formed. Polar modifiers, such as TMEDA, are needed to randomize styrene along the polymer chain to form random SBR. As shown in Fig. 4, by using a combination of NaOAm and TMEDA as the modifiers, a high T_g (−12 °C) 35/65 SBR was rapidly produced. It took about 10 min to reach 90% monomer conversion at 70 °C. The polymerization rates of 1,3-butadiene and styrene were nearly identical; a true random SBR can be expected with the current mixed catalyst system. Without the use of NaOAm, it would take about 1 h to make a lower T_g 35/65 SBR (−23 °C) under similar polymerization conditions.

The random styrene distribution in the polymer chains can also be seen from the plot of polymer composition versus total monomer conversion. As demonstrated in Fig. 5, a constant polymer composition of 35/65 styrene/1,3-butadiene was obtained at any given total conversion (or polymerization time). Thus, a totally random SBR was produced. It was found that random SBRs containing 5–50% styrene can be prepared using the current catalyst system.

Again, other sodium alkoxides and sodium alkylphenoxides described earlier also worked similarly to NaOAm in the styrene-1,3-butadiene co-polymerization.

3.4. Co-polymerization of 1,3-butadiene with isoprene

Similar to styrene, isoprene polymerizes faster than 1,3-butadiene in homo-polymerization but much slower than 1,3-butadiene in the co-polymerization of isoprene and 1,3-butadiene [17]. Thus, isoprene–butadiene copolymers (IBR) with random monomer sequence distribution along the polymer chains were seldom achieved via an organolithium catalyst, either with or without polar modifier. The IBR polymer thus produced normally contained a tapered polyisoprene segment at the end of polymer chains. However, as demonstrated in Fig. 6, an IBR with less

Table 3
Butadiene polymerization via varied modifier ratio

NaOAm/TMEDA/*n*-BuLi ratio	T_g (°C)	Microstructure (%)		ML_{1+4} at 100 °C
		1,2-PBd	1,4-PBd	
0.5/3/1	−28	82	18	49
1/3/1	−28	82	18	54
2/3/1	−27	83	17	65
3/3/1	−27	82	18	68
1/2/1	−27	82	18	49
1/3/1	−28	82	18	54
1/5/1	−27	83	17	57

Polymerization was done at 75 °C with target M_n of 200 000.

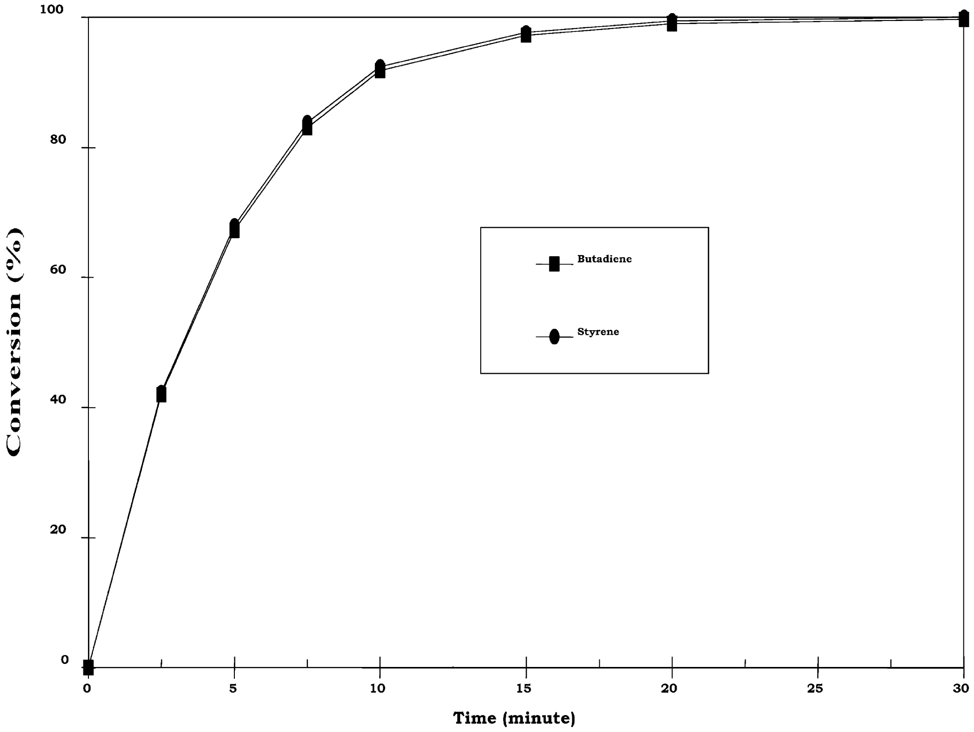

Fig. 4. 35/65 SBR via 0.5/1/1NaOAm/TMEDA/*n*-BuLi at 70 °C.

blocky polyisoprene segment can be formed with the NaOAm/TMEDA/*n*-BuLi catalyst system. In addition, a significant reduction in polymerization time along with enhancement in polymer T_g (e.g. from −25 to −16 °C for a 50/50 IBR) resulted from the use of NaOAm.

3.5. Effect of NaOR on ether modified polymerization

The effect of NaOAm on polymerizations using chelating oxygenated modifiers, such as ETE was also investigated. Although the synergistic effects were also found in the ETE/*n*-BuLi system (Table 4), the effects were not as pronounced as those found in the diamine modified systems. In addition, an incomplete polymerization of isoprene was observed when NaOAm was used in conjunction with Diglyme (2-methoxyethyl ether) as modifiers. As shown in Fig. 7, at 70 °C and 0.5/3/1 NaOAm/Digyme/*n*-BuLi catalyst ratios, the isoprene conversion reached around 70% in less than 5 min but polymerization died off afterward. The premature termination of polymerization may be due to chain transfer reaction as a result of Diglyme metallation by sodium metal (see discussion below). This is evidenced by an extremely low molecular weight polyisoprene produced under these polymerization conditions.

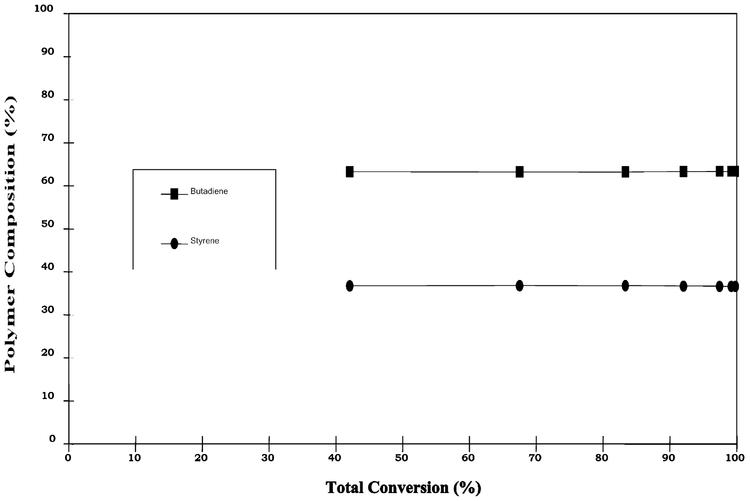

Fig. 5. 35/65 SBR via 0.5/1/1NaOAm/TMEDA/*n*-BuLi at 70 °C.

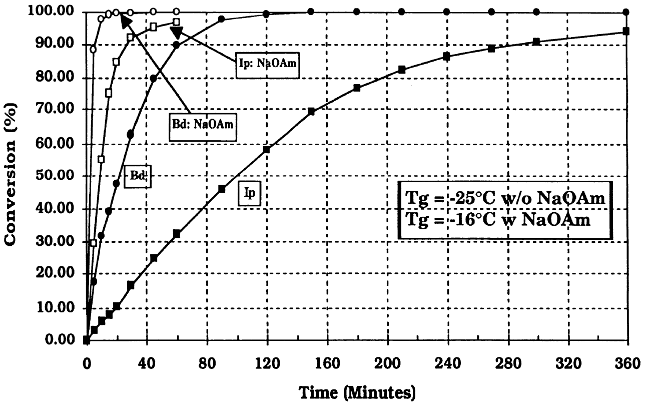

Fig. 6. Effect of NaOAm on 50/50 IBR via 3/1TMEDA/*n*-BuLi at 65 °C, NaOAm/*n*-BuLi = 0.5/1, M_n = 275 000.

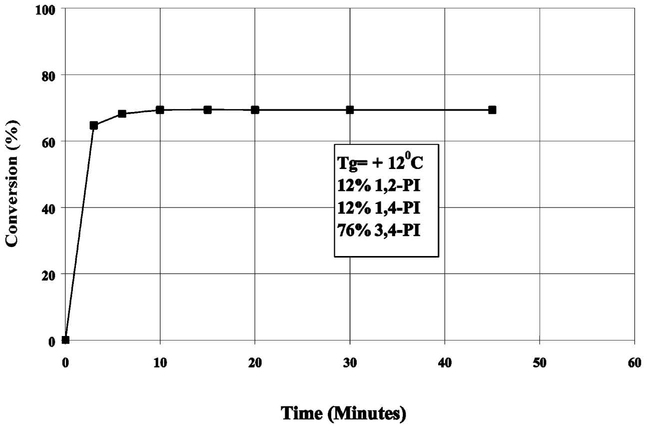

Fig. 7. Polyisoprene via 0.5/1/1NaOAm/Diglyme/*n*-BuLi at 70 °C, Target M_n = 300 000.

3.6. Mechanistic considerations

It is well known that the adducts (RM·LiOR′) of heavy metal oxides (R′OM; M = Na, K, Cs, Rb), and organolithium (RLi) are extremely strong bases. It was found that these so-called 'superbases' increase the reactivity of organolithium compounds to a great extent, by a factor of more than 10^6 [8]. As a result, the polymerization rate enhancement observed in our catalyst system might be attributed to the super basicity of the superbase generated from sodium alkoxide and *n*-butyllithium. To elucidate the mechanism of the current system, the effect of other alkali metal alkoxides (i.e. KOR, CsOR) on TMEDA modified systems towards diene polymerization at 70 °C was also studied. As shown in Table 5, although the polymerization time was reduced by about 50% with the addition of these heavier alkali metal alkoxides, the vinyl content of the resulting polymers were adversely affected. In fact, the glass transition temperatures of the resulting polymers were even lower than those of TMEDA alone modified polymers. It should be noted that although Hsieh [7] pointed out that, among the mixed alkali metal alkoxide/butyllithium system, sodium alkoxide provides PBd with the highest vinyl structure, the substantially lower T_gs for the KOR and CsOR systems with TMEDA (as shown in Table 5) was not expected. It was generally believed that a cyclic bimetallic intermediate was formed (i.e. Lochmann's base) as depicted in Fig. 8 [8], although a lithium 'ate' complex [18] as shown in Fig. 9 is also possible. But, in either case, the data illustrated in Table 5 have led us to speculate that only sodium is small enough to form a complex with Li which can then coordinate effectively with TMEDA ([RNa·R′OLi]·TMEDA) to yield high vinyl structures.

3.7. Polymer structures

Although the molecular weight distributions (MWD) were low (1.05–1.13) for PBds and SBRs using the current

Table 4
Comparison of conventional and mixed modifiers

Polymer type	Modifier system	PZN temperature (°C)	T_g (°C)	Time needed for 90% conversion (min)	
				1,3-Bd	Isoprene
PI	TMEDA	70	−15		270
	ETE	70	−15		40
	NaOAm/TMEDA	70	0		15
	NaOAm/ETE	70	−3		20
	NaOAm/DPE	50	+30		20
PBd	TMEDA	60	−43	70	
	ETE	60	−36	60	
	NaOAm/TMEDA	60	−22	15	
	NaOAm/ETE	60	−34	20	
	NaOAm/DPE	50	−6	15	
50/50 IBR	TMEDA	65	−25	210	300
	ETE	65	−26	60	90
	NaOAm/TMEDA	65	−16	20	30
	NaOAm/ETE	65	−25	20	30

Table 5
Effect of alkali metal on mixed modifier

Polymer	Modifier system	Time needed for 90% conversion (min)	T_g (°C)
PI	TMEDA	270	−15
	TMEDA/NaOAm	15	0
	TMEDA/CsOR	150	−36
50/50 IBR	TMEDA	210	−25
	TMEDA/NaOAm	20	−16
	TMEDA/KOAm	120	−46

Table 6
GPC data of polymers prepared in the batch reactor

Polymer[a]	M_n	M_w	M_w/M_n	T_g (°C)	ML-4[b]
PBd	189 000	202 000	1.06	−24	53
10/90 SBR	310 000	350 000	1.13	−20	88
10/90 SIR	156 000	328 000	2.10	+3	49
PI	163 000	382 000	2.34	0	62
50/50 IBR	181 000	342 000	1.90	−16	82

catalyst system in a batch reactor, the MWD was much higher (1.9–2.34) for isoprene containing polymers, such as PI, IBR and SIR (Table 6). MWD was also higher for all polymers prepared via continuous polymerization.[1] This clearly indicated that polymers made with the current catalyst systems are branched. The branching structures may have resulted from polymer backbone metallation by sodium metal or the superbase involved in the catalyst system, as the superbases are known to be good metallating agents [8,19–21], especially in the presence of TMEDA [8]. A possible scheme of polymer backbone metallation at the acidic hydrogen sites with a super base R^-M^+ is shown in Fig. 10.

With the continuous monomer addition employed in continuous reactors, long chain branching is also likely to take place. A recent rheological study of styrene–butadiene copolymers prepared using similar mixed catalysts has confirmed the branching nature of these polymers [22].

4. Conclusions

The combination of a polar modifier with the superbase generated from sodium alkoxide and organolithium has proven to be a synergistic catalyst for making high vinyl elastomers at very fast rates. Since it is also not monomer-specific, a variety of high T_g polymers including homopolymers (PBd, PI), co-polymers (IBR, SBR, SIR) and terpolymer (SIBR) can be prepared using the catalyst systems described in this paper.

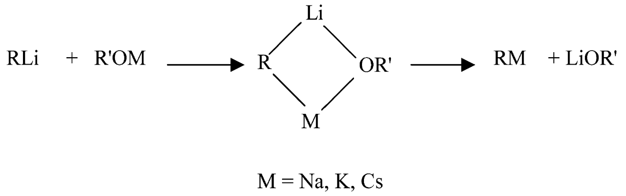

Fig. 8. Proposed structure of Lochmann's base (Superbase).

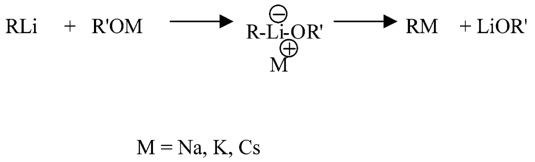

Fig. 9. Proposed structure of Lithium Ate complex.

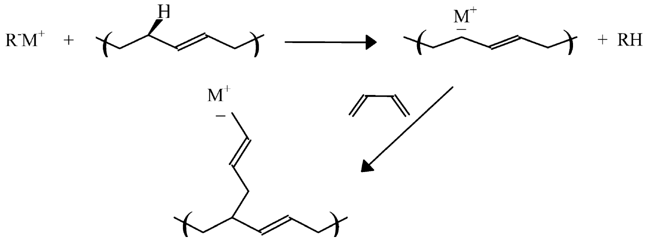

Fig. 10. Proposed metallation of the polymer backbone at the acidic hydrogen sites with a Superbase (R^-M^+).

Acknowledgments

The authors are grateful to The Goodyear Tire and Rubber Co. for granting permission to publish this work. The authors are indebted to their colleagues at The Goodyear Tire and Rubber Co. for their dedicated efforts to this work.

References

[1] Norsiek KH, Wolpers J. Proc Int Rubber Paris, France, June 1990;123.
[2] Halasa AF, Schulz DN, Tate DP, Mochel VD, Stone FGA, West R, editors. Adv Organomet Chem 1980;18:55–93.
[3] Hsu WL, Halasa AF, Wetli TT. Rubber Chem Technol 1977;71:62–9.
[4] Chang CC, Halasa AF, Miller JM. J Appl Polym Sci 1993;47:1589–99.
[5] Foster FC, Binder JL. Handing and uses of alkali metals. Advances in Chemistry, Series No. 19. Washington, DC: American Chemistry Society; 1957. p. 26.
[6] Arest-Yakubovich AA, Zoloareva IV, Pakuro NI, Nakhmanovic BI, Glukhovskoi VS. Chem Engng Sci 1996;51(11):2775–80.
[7] Hsieh HL, Wofford CF. J Polym Sci A-1 1969;7:449–60.
[8] Lochmann L. Eur J Inorg Chem 2000;1115–26. and references cited therein.
[9] Wofford CF. US Patent 3,295,768; 1963.
[10] Arest-Yakubovich AA, Zoloareva IV, Pakuro NI, Kristal'nyi EV, Nakhmanovich BI. Polym Sci A 1996;38(3):18.
[11] Pakuro NI, Zolotareva IV, Kitayner AG, Rogozhkina ED, Izyumnikov AL, Arest-Yakubovich AA. Macromol Chem Phys 1995;196:375.
[12] Nakhmanovich BI, Zolotareva IV, Arest-Yakubovich AA. Macromol Chem Phys 1999;200:2015 and the references cited therein.
[13] For related work, see Halasa AF, Hsu WL. Polym Mater: Sci Engng

---

[1] For detailed GPC data, see Ref. [22].

2001;84:839–40. US Patents issued to the Goodyear Tire and Rubber Co. 5 300 599, 1994; 5 534 592, 1996; 5 654 384, 1997; 5 906 956, 1999.

[14] Gilman H, Cartledge FK. J Organomet Chem 1964;2:447.

[15] Chang CC, Halasa AF, Miller JW, Hsu WL. Polym Int 1994;33:151–9.

[16] Oziomek J, Futamura S. Polym Prepr 1976;17:785.

[17] Hsieh HL, Quirk RP. Anionic polymerization. New York: Marcel Dekker; 1996. p. 442.

[18] Wilhelm D, Clark T, Schleyer PVR, Courtneidge JL, Davies AG. J Organomet Chem C1 1984;273 and references cited therein.

[19] Farral MJ, Frechet JM. J Organomet Chem 1976;41:3877.

[20] Schlosser M. Pure Appl Chem 1988;11:1627.

[21] Beinert GJ, Zilliox JG, Herz JE. Makromol Chem 1993;194:3184.

[22] Henning SK, Kerns ML. Presented at ACS Rubber Division Meeting, Providence, Rhode Island, Paper #52; April 2001.