Novel Potassium-Based Catalyst Generated from Alkylmagnesium Compounds for the Preparation of Highly Crystalline *trans*-1,4-Polybutadiene

Dennis B. Patterson[†] and Adel F. Halasa[*]

Corporate Research Center, The Goodyear Tire & Rubber Company,
Akron, Ohio 44305-0001

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ABSTRACT: *trans*-1,4-Polybutadiene was prepared in quantitative yield using an alkylmagnesium/potassium *tert*-amyloxide catalyst in hydrocarbon solvent at 10 and 50 °C. The polymer was highly crystalline with two melting points at +70 and +150 °C. Several organomagnesiate complexes such as potassium alkylmagnesiate and sodium alkylmagnesiate were found to be active catalyst components for *trans*-1,4-polybutadiene when used in conjunction with potassium *tert*-amyloxide. It was concluded that the initiating species for the preparation of *trans*-1,4-polybutadiene is an alkylpotassium/potassium *tert*-amyloxide complex, whereas the propagating species is an allylpotassium complex.

Previously published reports discussed the modification of organosodium and potassium compounds with alkoxides of lithium in the polymerization of 1,3-butadiene. In these publications a detailed study was presented on the effects of several alkoxides of group I metals on the stabilization of the allylic anion.[1–4]

The purpose of this study was to examine the effect of alkoxides of group I on unsolvated dialkylmagnesium in the polymerization of 1,3-conjugated dienes, in hydrocarbon solvents.

Organomagnesium compounds have been reported by Tsuruta and co-workers[5,6] to initiate the polymerization of 1,3-butadiene in polar media, at low conversion. The resulting polybutadiene microstructure obtained by this system is high in 1,2 addition. Similarly, the same authors[7] have shown that organomagnesium compounds initiated the polymerization of styrene in the presence of *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) and 2-methoxyethanol. They have also reported that alkylmagnesium compounds do not polymerize 1,3-butadiene in hydrocarbon solvents. We have confirmed their finding.

Several publications[8,9b] discuss the polymerization of 1,3-butadiene with a combination of dialkylmagnesium and organolithium compounds. The "ate" complexes formed dissociate readily under polymerization conditions. However, it was not known whether the polymer obtained was initiated with RLi or R_2Mg even though it showed characteristics of polybutadiene made by organolithium compounds. The relationship between initiator levels and the molecular weight of the polymers made was not discussed.

Experimental Section

Butadiene/hexane premix was made by dissolving Bd in hexane and after drying (see Results and Discussion sections for details of premix purification) was 16 ± 2% butadiene by weight (by GLPC).

Potassium *tert*-amyloxide (*tert*-amylate, *tert*-pentoxide), KOAm, was obtained as a 18–20% solution in cyclohexane from the Callery Chemical Corp. Rectification was carried out by sealing several hundred milliliters of the solution in a 28-oz "pop" bottle with potassium metal and tumbling shielded for a few hours at 68–70 °C (mp of K metal = 63.7°). The potassium metal remained dispersed as a "sand" upon cooling and was left in the bottle. The solution was analyzed by diluting 15-fold in water and titrating with 0.1 N HCl to the phenolphthalein end point. (The treatment with potassium metal did not significantly change the titer.)

Dibutylmagnesium (with the butyl groups a mixture of *n*-butyl and *sec*-butyl), Bu_2Mg, was obtained as a 21.1% (1.11 M) solution in heptane and sodium trialkylmagnesiate, R_3MgNa, with the alkyl groups a mixture of butyl and 2-ethylhexyl, as a 0.47 M solution in methylcyclohexane/heptane from Lithco. Both solutions were used as received.

Potassium tributylmagnesiate was prepared freshly and used immediately from potassium metal and the Lithco dibutylmagnesium using a procedure adapted from ref 19a. An 8-oz septum-sealed (Viton A gasket) screw-cap bottle fitted with a metal safety shield and containing 100 mL of 1.11 M dibutylmagnesium in heptane and 4.5 g of potassium metal was tumbled in a rotary bath at 69 °C for 7 h. At room temperature the bottle contents was transferred under nitrogen atmosphere to a fritted filter using a double-tipped needle. Dry hexane was used to rinse all the solid onto the frit and to wash it. Two portions of dry benzene, 50 and 30 mL, respectively, were used to carry benzene-soluble material through the frit, yielding a benzene solution of the product. This solution was transferred to a septum-sealed "pop" bottle and stored at −10 °C for use directly in polymerizations.

TMEDA (*N,N,N′,N′*-tetramethylethylenediamine) was distilled from sodium metal and made up as a 1.0 M solution in dry hexane.

Polymerizations were carried out in oven-dried, nitrogen-flushed, septum-sealed, screw-cap bottles, 32-oz size (800-mL charged). Premix was charged through the cap first. Catalyst components were then injected through the cap at ambient temperature (see Tables I–V for details of catalyst components), the cap was quickly changed, and the bottle was transferred to a rotary bath and tumbled at the desired temperature.

Bottles were shortstopped with BHT 1% solution in 20% methanol in hexane. The contents of bottles having soluble PBd as the only product was decanted with hexane rinsing, allowed to dry down, and finally dried under aspirator vacuum at least overnight at 50–60 °C. Bottles containing both soluble PBd and precipitated *trans*-PBd resin were sometimes worked up in the same manner. Usually, however (see Tables I–V for details), the *trans*-PBd resin was strained off with Nylon mesh and washed at least twice with portions of fresh hexane by shaking thoroughly with the solvent. After each wash, the resin was again recovered with Nylon mesh and drained as thoroughly as possible by twisting the Nylon mesh tightly to wring out the resin. The hexane rinses and the original supernatant were combined, dried down, and vacuum dried as above. Finally, the resin was soaked in 1% w/v BHT in hexane, recovered and drained in the same manner as before (this hexane was discarded), and dried under aspirator

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[*] To whom all correspondence should be addressed.

[†] Present address: Revlon Science Institute, San Diego, CA 92121.

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Table I
Preliminary Butadiene Polymerizations with Bu_2Mg/KOAm Catalyst[a]

expt no.	Bu_2Mg, mmol/100 g of Bd	KOAm/Bu_2Mg, M	*trans*-PBd, %	soluble PBd, %	T_m,[b] °C	T_g,[c] °C
1	0.2	2.7	trace	50		−58
2	0.4	2.7	16	23	67, 152	
3	0.3	1.8	trace	89		
4	1.0	1.5	14	39	67, 151	
5	1.0	2.0	11	86		
6	1.0	1.6	14	69		
7	1.0	1.7	12	79		
8	1.0	1.8	12	78		
9	1.0	1.9	15	83		−54

[a] All experiments: Bu_2Mg was added first to the premix (15–19 wt % Bd in hexane and then KOAm used as received; polymerization time was 1 day or more at 10 °C. Latter KOAm was rectified by treatment with (liquid) potassium and stored over the metal "sand". [b] Resin fraction. [c] Soluble fraction.

Table II
Preliminary Butadiene Polymerizations with Bu_3MgK/KOAm Catalyst[a]

expt no.	Bu_3MgK, mmol/100 g of Bd	KOAm/Bu_3MgK, M	*trans*-PBd, %	soluble PBd, %	T_m,[b] °C	T_g,[c] °C
1	1.0	0.0	no polymn	no polymn		
2	1.0	0.5	17	68		−55
3	1.0	1.5	50	30	66, 151	−55
4	1.0	1.0	30	59		
5	1.0	2.0	33	51		
6	3.0	2.4	0	84		
7	4.0	2.4	0	86	66, 151	−55
8	2.0	2.0	6	82	66, 151	
9	1.2	1.8	47	25		−55
10	1.0	1.8	62	24	67, 152	
11	1.0	1.8	51	24		
12	1.0	1.8	32	39		−56
13	0.2	1.8	67	14		−56
14	0.2	2.3	48	52		

[a] All experiments: Catalyst components were added to the premix (15–19 wt % Bd in hexane); polymerization time was 1 day or more at 10 °C. Nos. 1–12: Bu_3MgK was added before KOAm; KOAm was added before Bu_3MgK. Nos. 13 and 14: premix was repassed (glass column); KOAm was treated with K metal per Table I. [b] Resin fraction. [c] Soluble fraction.

Table III
Principal Butadiene Polymerization Experiments[a] with Bu_3MgK/KOAm (1–14), R_3MgNa/KOAm (15–25), or Bu_2Mg/KOAm (26–28) Catalyst (10 °C in Hexane, 1 day or More)

expt no.	mmol of Mg/100 g of Bd	KOAm/Mg, M	*trans*-PBd, %	soluble PBd, %	T_m,[b] °C	T_g,[c] °C
1	0.2	2.3	86	<1	68, 155	
2	0.2	2.3	89	<1	67, 150	
3	0.2	2.3	65	<1	66, 149	
4	0.2	2.3	50	2		
5	0.2	2.3	84	1		
6	0.2	2.3	100	trace		
7	0.2	2.3	51	3	67, 149	
8	0.2	2.3	77	2		
9	0.2	2.3	92	1	67, 152	
10	0.3	1.5	68	4		
11	0.3	1.5	72	3	69, 150	
12	0.3	1.5	77	2		
13	0.3	1.5	90	2		
14	0.3	1.5	69	31		
15	0.3	2.4	84	16		
16	0.5	2.4	53	47	69, 150	60
17	0.15	3.0	88	12		54
18	0.15	3.0	83	17	68, 152	
19	0.25	3.0	70	27		
20	0.15	3.0	73	26	68, 152	
21[d]	0.15	10.0	69	2	76, 149	
22[d]	0.15	6.0	80	3	76, 151	
23[d]	0.15	10.0	42	6	68, 149	
24[d]	0.15	15.0	13	2	68, 149	
25[e]	0.15	12.0	11	1		
26	0.4	1.0	76	15		
27	0.4	1.0	84	6	67, 150	
28	0.4	1.0	80	2		

[a] KOAm (purified per Table I) was the first catalyst component except in nos. 25 and 26; all premixes were repassed through metal columns. [b] Resin fraction. [c] Soluble fraction. [d] About 45 min in 10 °C bath (no. 21, 90 min) and then overnight in a 50 °C bath. [e] Shortstopped at 45 min.

Table IV
Butadiene Polymerizations[a] with Bu_3MgK/KOAm (1–4) or R_3MgNa/KOAm (5–9) Catalysts Wholly or Partially at 50 °C

expt no.	mmol of Mg/100 g of Bd	KOAm/Mg, M	*trans*-PBd, %	soluble PBd, %	T_m,[b] °C	T_g,[c] °C
1[d]	0.20	2.3	15	6	62, 139	
2[d]	0.20	2.3	8	37	75, 134	
3[d]	0.20	2.3	~2[e]	~98[e]	73, 173	−71[f]
4[d]	0.20	2.3	~2[e]	~98[e]	73, 138	−71[f]
5[g]	0.10	(0.0)	0	16		−76[f]
6[h]	0.10	3.0	48	50	76, 149	−72
7[h]	0.10	6.0	80	3	76, 151	
8[h]	0.10	10.0	42	6	68, 149	
9[h]	0.10	15.0	13	2	68, 149	

[a] In hexane, 1 day or more; the premix and KOAm (first catalyst component) were of the purity per Table III. [b] Resin fraction. [c] Soluble fraction. [d] Placed in a 50 °C bath immediately after charging at room temperature. [e] Product is isolated as a resin/elastomer blend; composition was estimated from DSC data. [f] Microstructure as in Table VI; molecular weight as in Table VII. [g] 3.9 mole of KOAm added after 48 h at 50 °C; however, the aliquot at this point showed no polymerization after KOAm addition (24 h). [h] After 45 min in a 10 °C bath (no. 7, 90 min) and then overnight in a 50 °C bath.

vacuum at least overnight at ambient temperature.

Discussion

The interaction of organometallics of group I and groups II and IIB to form coordinated complexes is well documented in the literature.[10] These complexes are known as "ate" complexes and have fully been characterized, and their reactions have been extensively studied.[11] In the present studies we are dealing in the use of these "ate" complexes for polymerization of 1,3-butadiene to prepare highly crystalline *trans*-1,4-polyBd in hydrocarbon media.

Highly *trans*-1,4-polybutadiene is a resin rather than a rubber at room temperature by virtue of its high degree of crystallinity.[12]

trans-Polybutadiene is typically prepared by means of any of several transition metal[13] or rare-earth[14] coordination catalysts. However, preparation of *trans*-polybutadiene by an anionic route is attractive from the standpoints of (1) molecular weight control, including the preparation of material of higher molecular weight than that typically obtainable by means of coordination catalysts, and (2) the preparation of block, random, or graft copolymers containing *trans*-polybutadiene.

To these ends, an investigation of the preparation of *trans*-polybutadiene under anionic polymerization conditions was undertaken. This report deals with work based on organomagnesium compounds, in which the work of Halasa and Hall[15a] was used as a starting point. These workers reported in a 1980 U.S. Patent the preparation of *trans*-polybutadiene by means of an ostensibly anionic catalyst system, namely dialkylmagnesium compounds in tandem with potassium *tert*-amyloxide. A subsequent publication[16] will deal with work based on organolithium compounds, work which does much to elucidate matters

Table V
Butadiene Polymerization[a] with R_3Na/TMEDA or R_3MgNa/TMEDA/KOAm (except as Noted, 10 °C in Hexane, 1 day or More)

expt no.	mmol of Mg/100 g of Bd	KOAm/Mg, M	KOAm added at (h)	TMEDA[b]/Mg, M	*trans*-PBd, % (T_m, °C)	soluble PBd, % (T_g, °C)
1	0.15	0.0		1.0	0	100 (-21)
2	0.13	0.0		1.0	0	93 (-21)
3	0.15	0.0		4.0	0	98 (-25)
4[c]	0.10	0.0		1.0	0	94 (-36)
5	0.13	0.0		1.0	0	93 (-36)
6	0.10	3.9	init.	1.0	79 (69, 152)	1
7	0.15	3.0	init.	1.0	87 (69, 152)	13
8	0.15	3.0	init.	1.0	80	5
9	0.15	3.0	3.3	1.0	53 (68, 150)	47 (-23)
10[d]	0.15	3.0	7	1.0	46 (66, 151)	~52 (-20)
11[d]	0.15	3.0	7	1.0	50 (65, 151)	~49 (-21)
12	0.15	10.0	5.5	1.0	trace	63 (-25)
13	0.13	10.0	24	1.0	0	62
14	0.15	15.0	5.5	1.0	trace	65 (-24)
15	0.15	20.0	6	1.0	0	63
16	0.13	20.0	24	1.0	0	23
17	0.15	50.0	6	1.0	0	54

[a] Premix and KOAm were of the purity per Table III. [b] TMEDA initially present. [c] Transferred to a 50 °C bath immediately after charging at room temperature. [d] Product was isolated as a resin/elastomer blend; composition was estimated from DSC data.

for the organomagnesium compounds.

Results

Organomagnesium/Potassium *tert*-Amyloxide Systems at 10 °C. Initially it was found here that *trans*-polybutadiene can indeed be generated by using the dibutylmagnesium/potassium *tert*-amyloxide catalyst system, in agreement with Halasa and Hall[15] (Table I). In these initial experiments, however, *trans*-polybutadiene proved to be the minor product of the polymerization if it was in fact generated at all. The principal and often sole product was a medium vinylpolybutadiene (soluble, of course, in the hexane polymerization medium, unlike *trans*-polybutadiene).

These experiments were carried out before it was realized how crucial system purity is to the partitioning of the product between *trans*-PBd resin and the hexane-soluble medium vinylpolybutadiene. Although the systems used in these experiments were generally adequate for lithium-catalyzed polymerizations, more stringent measures were required in order to obtain good yields of *trans*-polybutadiene with the present catalyst.

The first response, however, to the disappointing results of Table I was to give some consideration to the possible catalyst chemistry here. Perhaps the most straightforward possibility, and one which was cited by Halasa and Hall,[15] is coordination of alkoxide to magnesium to form "ate" complexes

$$R_2Mg + KOAm \rightarrow R_2AmOMgK \quad (1)$$

$$R_2AmOMgK + KOAm \rightarrow R_2(AmO)_2MgK_2 \quad (2)$$

Arguably, this could increase the ionic character of the magnesium–alkyl bonds sufficiently that initiation of anionic polymerization becomes possible. (Dialkylmagnesium compounds alone will not polymerize diene monomers,[9] a fact that facilitates their use in the purification of such monomers.) A further possibility, however, is disproportionation of an intermediate "ate" complex, for example

$$2R_2MgOAmK \rightarrow R_3MgK + RMg(OAm)_2K \quad (3)$$

to yield species differing in the degree of alkylation at magnesium. Analogous disproportionations can be brought about by suitable neutral ligands.[17]

Among the organomagnesium compounds generated here, as well as, perhaps, those generated by even further disproportionation, the active polymerization catalyst or catalysts could conceivably be found. Trialkylmagnesiate compounds (such as R_3MgK above) are reported to polymerize dienes and styrene[9,18] and seemed particularly promising candidates. Direct investigation of these species was thus undertaken.

Alkali-metal trialkylmagnesiates may be prepared from the dialkylmagnesium and excess alkali metal[19a,b]

$$3R_2Mg + 2M^0 \rightarrow 2R_3MgM + Mg^0 \quad (4)$$

which at least formally represents the sum of the formation of the alkali-metal alkyl from the alkyl of a less electropositive metal in the usual manner

$$R_2Mg + 2M^0 \rightarrow 2RM + Mg^0 \quad (5)$$

and subsequent complexation of the alkali-metal alkyl with dialkylmagnesium

$$R_2Mg + RM \rightarrow R_3MgM \quad (6)$$

In the present work, examples with M = sodium or potassium were examined. The initial experiments (Table II) were done with potassium tributylmagnesiate, Bu_3MgK, prepared from commercial dibutylmagnesium and potassium metal. Later a mixed trialkylsodium compound, R_3MgNa, was purchased from Lithco. (A U.S. patent[19c] claims that the use of alkyl halides with dialkylmagnesium and alkali metal

$$R_2Mg + RX + 2M^0 \rightarrow R_3MgM + MX \quad (7)$$

converts ALL the dialkylmagnesium to trialkylmagnesiate and obviates the formation of magnesium metal.)

Potassium tributylmagnesiate proved capable of generating *trans*-polybutadiene but, like dibutylmagnesium, required potassium *tert*-amyloxide as a cocatalyst. However, an immediate improvement in the yield of *trans*-polybutadiene was seen (Table II). The yields still were well short of quantitative, however, and medium vinylpolybutadiene was still the dominant product in most instances. More stringent purification procedures were instituted at this point. These consisted largely of (1) rectification of the commercial cyclohexane solution of potassium *tert*-amyloxide used by treatment with molten potassium metal and subsequent storage of the solution over the resulting potassium "sand", and (2) further drying of the hexane–Bd solution over baked silica gel, which had already been dried (typically triple passed). Such a solution was repassed, at first through laboratory glass columns; later a dual-metal column system packed with baked alumina and 3-Å molecular sieves was used.

The rectified *tert*-amyloxide was used along with premix repassed through glass columns for experiments 9–14 in Table II. This resulted, on the average, in further shifts in the yield in favor of *trans*-PBd. However, use of premix repassed through the dual-metal columns (and rectified *tert*-amyloxide), as was done for all the examples in Table III, resulted in dramatically increased yields of *trans*-PBd (essentially quantitative in at least one case, no. 6, and near 90% in several others).

Moreover, these results were obtained in the presence of potassium *tert*-amyloxide with either the potassium or the sodium trialkylmagnesiate or with dibutylmagnesium (experiments 26–28, Table III, contrast sharply with the results in Table I). These results raised the possibility that the alkylmagnesium compound, of whatever type, serves merely to alkylate the alkali-metal cation (the lower case mg denotes a generalized single bond to magnesium)

$$R_2Mg + 2MOAm \rightarrow 2RM + Mg(OAm)_2 \qquad (8)$$

followed by the initiation of polymerization by the RM species.

Alkoxide–alkyl exchanges of the type depicted in eq 8 are well-known for organolithium compounds[20–22]

$$RLi + MOR' \rightarrow RM + LiOR' \qquad (9)$$

and for M = Na or K are in fact synthetically significant. Upon examination of catalysts based on various butyllithiums and potassium *tert*-amyloxide, it was quickly found that entry into what is for all practical purposes the same catalyst system as obtained with the organomagnesiums and potassium *tert*-amyloxide could be gained.[16] Since the butyllithium undoubtedly undergoes exchange with the alkoxide, the organomagnesium compounds likely do so as well to generate alkylpotassium species, which are the true initiators of the polymerization in all cases. As a final piece of evidence, it proved possible to generate *trans*-polybutadiene from a purely potassium catalyst derived from potassium metal and potassium *tert*-amyloxide. The process giving rise to *trans*-polybutadiene is thus a potassium-based anionic polymerization. The catalyst that gives rise to the medium vinylpolybutadiene is also a potassium species, based on the fact that the catalyst derived from potassium metal also yields medium-vinyl PBd and the results of the work with lithium compounds.[1–4]

Thus this work provides a successful anionic route to *trans*-polybutadiene. Either trialkylmagnesiates or dialkylmagnesiums may serve as the catalyst precursor. Dialkylmagnesiums are the more economical and accessible although the trialkylmagnesiates appear to be somewhat more tolerant of impurities. System purity, while always critical in anionic polymerization, is particularly so here. Typically the penalties for inadequate purity are incomplete conversion and a missed molecular weight target. Here the penalties include as well the (perhaps exclusive) production of byproduct polybutadiene of undesired microstructure.

Finally, the fact that these magnesium compounds readily generate organometallic compounds of higher alkali metals via alkyl (likely also aryl) alkoxide exchange suggests that the domination of this route to such compounds by exchanges involving organolithium compounds may not be fully warranted. Beyond the simplest alkyl groups, organomagnesium compounds are in general more readily obtained than are the corresponding lithium compounds.

Nevertheless, with respect to anionic polymerization, interest shifted at this juncture from these organomagnesium-based catalysts to the more convenient and more versatile organolithium-based catalysts. Detailed presentation of the results for the lithium-based catalysts is deferred to future publication.[16] The balance of this publication deals with some additional aspects of butadiene polymerization with catalysts derived from the trialkylmagnesiate compounds.

Trialkylmagnesiate/Potassium *tert*-Amyloxide Catalysts at 50 °C. It was hoped that increasing the polymerization temperature would change the microstructure from *trans*-polybutadiene to some mixed form. If so, changing the temperature sufficiently during the course of the polymerization could conceivably produce a diblock copolymer having both crystalline and rubbery blocks. Polymerization with $Bu_3MgK/KOAm$ at 50 °C did show a tendency toward the production of hexane-soluble elastomer, experiments 1–4 in Table IV. However, the diverse results for these four ostensibly replicated experiments show a pronounced inverse correlation between the yield of *trans*-PBd resin and both conversion to hexane-soluble polymer and total conversion. This is consistent with an original partitioning of the catalyst between that yielding hexane-soluble PBd and that yielding *trans*-PBd resin followed by inactivation of the latter upon heating to 50 °C). It is unclear whether inactivation at 50 °C of the catalyst producing *trans*-PBd reflects thermal instability or simply stems from the catalyst being effectively trapped in its own product, which coalesces somewhat in the polymerization medium at 50 °C.

The results obtained upon heating ongoing resin-producing polymerizations at 10–50 °C are consistent with this picture of inactivation of the catalyst that yields *trans*-PBd but not with that which produces soluble PBd. Such heating of a polymerization catalyzed by R_3MgNa/OAm at an OAm/Mg ratio of 3 M resulted in a mixture of *trans*-PBd and hexane-soluble PBd of essentially the same T_g as that obtained in the experiments with $Bu_3MgK/KOAm$ (Table IV, no. 6). The use of R_3MgNa alone at 50 °C led solely to soluble polymer, again of essentially the same T_g (and microstructure) in low conversion (Table IV, no. 5). Using higher OAm/Mg ratios in temperature jump polymerizations (nos. 7–9) resulted in steadily decreasing yields of resin accompanied by only small amounts of hexane-soluble polymer.

Thus, if the OAm/Mg ratio is low enough, active catalyst that yields hexane-soluble polymer at 50 °C remains. Essentially the same microstructure is obtained whether one has excess catalyst precursor or simply starts with R_3MgNa alone. At higher OAm/Mg ratios, however, virtually all of the catalyst is of the type producing *trans*-PBd resin, and thus the system becomes essentially completely deactivated upon heating to 50 °C.

Thus, heating the system from 10 to 50 °C does not bring about a simple, substantial shift in microstructure for the catalyst producing *trans*-PBd resin. Instead, this catalyst becomes deactivated with at most a slight shift in the microstructure of the resin produced (Table IV). Any soluble PBd is apparently produced, as is the case at 10 °C, by an alternative catalyst. Thermal jumping is

Table VI

Microstructures[a,b] of Soluble Polybutadienes Generated via Catalysts Derived from Organomagnesiums

expt no.	catalyst, polymn temp	polybutadiene microstructure, % vinyl	trans	cis	T_g, °C
1	Bu_3MgK, 1.8 mol of KOAm, 10 °C	54	33	13	-55
2	Bu_3MgK, 2.3 mol of KOAm, 10 °C	53	34	13	-56
3	same, 50 °C	39	41	20	-71
4	as preceding	38	41	21	-72
5	R_3MgNa, 1.0 mol of TMEDA, 10 °C	85	7	8	-21
6	as preceding	89	6	5	-21
7	R_3MgNa, 4.0 mol of TMEDA, 10 °C	70	16	23	-25
8	R_3MgNa, 50 °C	36	39	25	-76
9	R_3MgNa, 1.0 mol of TMEDA, 50 °C	76	15	9	-36
10	as preceding	79	16	13	-36
11	Bu_2Mg, 2.7 mol of KOAm, 10 °C	52	33	15	-58
12[c]	Bu_3MgK, 3.0 mol of KOAm, 10 °C	<2	>96	<2	68, 152[d]

[a] Infrared analyses. [b] Molecular weight data in Table VII (for nos. 1–10). [c] *trans*-PBd resin; analysis by NMR. [d] T_m values.

Table VII

Molecular Weight Data[a] for Soluble Polybutadienes Generated via Catalysts Derived from Trialkylmagnesiates

expt no.	catalyst, polymn temp	product, %	$M_n \times 10^{-3}$	H_i	KM_n[b] $\times 10^{-3}$	chains[c]/Mg atom	chains[d]/R group
1	Bu_3MgK, 1.8 mol of KOAm, 10 °C	100	106	1.57[e]	156	1.44	0.48
2	Bu_3MgK, 2.3 mol of KOAm, 10 °C	52	267	2.06[e]	536	3.21	1.07
3	same, 50 °C	~98	167	2.79	536	3.21	1.23
4	as preceding	~98	131	3.26	487	2.18	0.73
5	R_3MgNa, 1.0 mol of TMEDA, 10 °C	100	230	1.40	661	2.87	0.96
6	as preceding	100	263	1.29	784	2.98	0.99
7	R_3MgNa, 4.0 mol of TMEDA, 10 °C	100	209	1.35	687	3.29	1.10
8	R_3MgNa, 50 °C	100	62	1.48	154	2.48	0.83
9	R_3MgNa, 1.0 mol of TMEDA, 50 °C	100	295	1.42	934	3.17	1.06
10	as preceding	100	236	1.24	785	3.32	1.11

[a] GPC (no. corresponds to those in Table VI). [b] Kinetic M_n; calculated from grams of soluble PBd per moles of Mg charged. [c] Ratio of KM_n to M_n. [d] Ratio of KM_n to M_n divided by 3. [e] Bimodal peak: high molecular weight shoulder.

therefore wholly useless for the preparation of diblock copolymers.

Trialkylmagnesiate/TMEDA Catalysts. Upon activation with *N,N,N′,N′*-tetramethylethylenediamine (TMEDA), the sodium trialkylmagnesiate compound, R_3MgNa, proved capable of initiating butadiene polymerization (Table V, nos. 1–5). No *trans*-polybutadiene was produced. Instead, the product consisted entirely of soluble, fairly high vinylpolybutadiene. The microstructure was only slightly dependent on the TMEDA/Mg ratio in the range of 1.0–4.0 M and, at a given temperature, similar to that obtained[23] at limiting TMEDA/Li ratios in lithium-catalyzed polymerizations. However, a quite different microstructure was obtained for R_3MgNa alone (slow polymerization at 50 °C; Table IV, no. 5).

Like the polymerizations involving KOAm cocatalysts, such TMEDA or thermally activated polymerizations appear to be essentially alkali-metal-catalyzed polymerizations rather than any sort of magnesium-based polymerization. It is unclear whether the liberation of sodium alkyl from R_3MgNa by TMEDA proceeds according to

$$R_3MgNa + TMEDA \rightarrow R_2Mg(TMEDA) + RNa \quad (10)$$

or

$$R_3MgNa + TMEDA \rightarrow R_2Mg + RNa(TMEDA) \quad (11)$$

with, in any case, subsequent sodium-catalyzed polymerization (it has been reported that TMEDA does not induce dibutylmagnesium to polymerize styrene).[5]

$$\text{RNa or RNa(TMEDA)} \xrightarrow{\text{Bd}} \text{PBdNa or PBdNa(TMEDA)} \quad (12)$$

The strong dependence of polymer microstructure on the presence or absence of TMEDA suggests complexation with sodium.

Molecular Weight Data for Soluble Polybutadienes. The high crystallinity and resulting insolubility of the *trans*-PBd resins prepared here precluded obtaining direct molecular weight data. Molecular weight data for soluble derivatized *trans*-PBd will be discussed in a future publication.[16] Molecular weight data (GPC) were obtained for some of the hexane-soluble polybutadienes (Table VII) and are discussed here.

The hexane-soluble medium vinylpolybutadiene polymers are generally of substantial molecular weight with M_n values on the order of 100 000–250 000. The molecular weight distributions are not monodisperse, although those from polymerizations with R_3MgNa/TMEDA catalyst do have HI values of 1.5 or lower. Those from Bu_3MgK/KOAm catalyst polymerizations are substantially broader with HI values in the 1.6–3.3 range. Of particular interest are the average number of polymer chains per catalyst moiety values, calculated from the measured M_n values and the weight of polymer per moles of catalyst ratios. In most cases, a value near one polymer chain per alkyl group on magnesium was obtained. The data for the Bu_3MgK/KOAm catalyst show more scatter in this respect than do those for the R_3MgNa/TMEDA catalyst. For no. 1 in Table VII, at a OAm/Mg ratio of 1.8 M, about one polymer chain is formed for every two R groups charged. However, the fact that only soluble polymer was formed here suggests that scavenging of the catalyst by impurities may have been particularly extensive. For no. 2, at a OAm/Mg ratio of 2.3 M, about one polymer chain per R group charged is found. Here the product composition was bout 50/50 resin/soluble PBd. If a substantial amount of the catalyst had been diverted to production of resin, a correspondingly larger number of polymer chains per R group for the catalyst actually involved in the production of soluble PBd would be required to accommodate the observed M_n. It is tempting to speculate that the resin here was produced by only a small fraction of the total catalyst charged; i.e., this is substantially the more active catalyst.

The foregoing assumes that chain transfer is unimportant in these polymerizations at 10 °C. The M_n values for two replicated experiments with the $Bu_3MgK/KOAm$ catalyst at 50 °C (nos. 3 and 4, same OAm/Mg as no. 2) yield comparable deviations (about 25%; positive in one case and negative in the other) from one polymer chain per catalyst alkyl group. Chain transfer thus appears to be unimportant even at 50 °C. There is some indication of chain transfer with organolithium/KOAm catalysts,[16] but substantially higher OAm (catalyst alkyl group) ratios were used there. (The question of activation of all the catalyst alkyl groups here despite a formal stoichiometric deficiency of KOAm is discussed below.)

The M_n values obtained from polymerizations with the $R_3MgNa/TMEDA$ catalysts at either 10 °C (nos. 5–7) or 50 °C (nos. 9 and 10) correspond within 10% to the formation of one polymer chain per alkyl group. The deviation for R_3MgNa alone (50 °C, no. 8) is somewhat larger but still less than 20% (negative).

A possible explanation for the utilization of additional and even all the catalyst alkyl groups is provided by the mechanism put forth by Hsieh for lithium polymerizations carried out in the presence of a dialkylzinc compound.[24] Dialylzincs, like dialkylmagnesium, are not themselves initiators of diene polymerization. However, alkyl exchange between dialkylzincs and the polymeric lithium species occurs

$$PnLi + R_2Zn \rightarrow PnZn'R + RLi \qquad (13)$$

followed by initiation of a new polymer chain by RLi. Thus all the alkyl groups potentially may be brought into play. An analogous process may be occurring between the polymeric sodium species and the dialkylmagnesium in the present work, i.e.

$$PBdNa(TMEDA) + R_2Mg \rightarrow PBdMgR + RNa(TMEDA) \qquad (14)$$

followed by initiation per eq 12. In the case of the $Bu_3MgK/KOAm$ catalyst, analogous exchanges between polymeric potassium species and magnesium-bound butyl groups may be written.

In summary, molecular weight data for the hexane-soluble polybutadienes produced with either $Bu_3MgK/KOAm$ (presumably also $R_3MgNa/KOAm$) or $R_3MgNa/TMEDA$ catalysts indicate that each catalyst alkyl group is typically involved in the initiation of a polymer chain. Chain transfer appears to be insignificant.

These results are essentially bracketed by those of Liu, Kamienski, Morton, and Fetters, who report[9a] that, in the polymerization of styrene with Bu_3MgNa, only one polymer chain per magnesium is formed, whereas in the corresponding polymerization of isoprene typically more than one polymer chain per Bu group is formed. For isoprene they invoke alkyl group exchange with subsequent initiation as described above and chain transfer as well. No ligand such as TMEDA was used in their work. However, Hsieh reported[24] a ligand, THF, to be essential to alkyl group exchange in the dialkylzinc/lithium case. The results of Liu et al. plus one experiment here (Table VII, no. 8) suggest that a ligand is not essential in the magnesium/sodium system with diene monomers, although it certainly facilitates polymerization, at least in the R_3MgNa/butadiene case.

Trialkylmagnesiate/TMEDA–Potassium *tert*-Amyloxide Catalysts. The addition of 1 mol of TMEDA to an ongoing *trans*-PBd producing polymerization catalyzed by $R_3MgNa/KOAm$ had little effect on the outcome; a high yield of *trans*-PBd was nonetheless obtained, and only a trace of soluble PBd was produced (Table V, no. 7). Having the TMEDA present at the beginning of such polymerizations also had little effect (nos. 8 and 9). Clearly the effect of KOAm overwhelms that of TMEDA, at least at the molar ratios used here.

It was therefore hoped that this would hold true in the reverse situation and that a polymerization catalyzed by $R_3MgNa/TMEDA$, and thus producing a soluble polybutadiene, could be converted to the production of *trans*-PBd by the addition of KOAm. Ideally such a conversion would result in a diblock copolymer. However, as nos. 10–12 in Table V show, if such a conversion is effected (by the use of intermediate OAm/Mg ratios), one does not obtain a diblock copolymer but rather a blend of *trans*-PBd and the soluble PBd corresponding to catalysis by $R_3MgNa/TMEDA$.

It can be argued that such behavior has the same root cause as the thermal jump experiments discussed above, in which resin/elastomer blends were produced. That is, only a portion of the capacity of the trialkylmagnesiate is involved in the primary catalyst activation while the remainder becomes involved in the activation of a secondary catalyst, which produces PBd of a different microstructure. In the case of such a thermal jump experiment, the primary activation is by KOAm to produce *trans*-PBd resin while the secondary, thermal, activation produces a soluble PBd. In the present experiments, the primary activation is by TMEDA, to produce a soluble PBd, and the secondary activation is by KOAm, as usual to produce *trans*-PBd.

However, if all the alkyl groups in the $R_3MgNa/TMEDA$ catalyst eventually participate in initiation as discussed in the preceding section, the question arises as to the precursor(s) to the KOAm-generated *trans*-PBd-producing catalyst. It might have been thought that polymeric groups bound to sodium or magnesium (cf. eqs 12 and 14) would serve as precursors to diblock copolymers containing blocks of *trans*-PBNa rather than to discrete *trans*-PBd. Suffice to say at this point that studies with organolithium precursors indicate that polymeric organometals may apparently serve as precursors to *trans*-PBd[16] and its formation is thus not necessarily an argument against their being the sole type of organometallic group present.

In any case, the addition of KOAm at partial monomer conversion to butadiene polymerizations catalyzed by $R_3MgNa/TMEDA$ constitutes a route to in situ resin/elastomer blends prepared from a single monomer. Although the actual experiment of using a temperature other than 10 °C for the $R_3MgNa/TMEDA$-catalyzed portion of the polymerization was not done, it should be possible to vary the microstructure of the elastomer by the temperature used in the first stage of the polymerization.

The use of higher OAm/Mg ratios, as in nos. 12–17, Table V, results in a virtual quenching (as indicated by the moderate conversions) of the polymerization so that essentially only the hexane-soluble PBd corresponding to TMEDA mediation is obtained. Data in the absence of TMEDA (Table III) indicate that excessively high OAm/Mg ratio is deleterious to the polymerization.

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