

Synthesis of Butyl Rubber in Hexane Using a Mixture of Et_2AlCl and EtAlCl_2 in the Initiating System

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ABSTRACT: A method was studied to obtain butyl rubber in hexane at -75 and -60°C using a mixture of a major amount of diethylaluminum chloride and a minor amount of ethylaluminum dichloride in the initiating system. The Jaacks method was used to determine the monomer reactivity ratio of isobutylene in copolymerization with isoprene in hexane at -75°C with the above initiating system; $r_{\text{IB}} = 1.54 \pm 0.06$. This value was different from a literature value $r_{\text{IB}} = 1.08$ when just EtAlCl_2 was used in hexane at -80°C . The mixture of both alkylaluminum chlorides in the initiating solution was subsequently directly activated with minute amounts of water or methylaluminoxane (MAO). The use of

the modified initiators resulted in higher molecular weights, higher degrees of conversion, and higher isoprene contents in the butyl rubber. At the same time, temperature control was good during polymerizations. With modified alkylaluminum halides, the monomer reactivity ratio of isobutylene in copolymerization with isoprene in hexane at -75°C was close to unity, similar to the reported case with just EtAlCl_2 . The system activated with MAO made it possible to synthesize butyl rubber in hexane at -60°C having main characteristics typical of commercial butyl rubber manufactured in methyl chloride at -95°C . © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 2360–2364, 2003

INTRODUCTION

Commercial butyl rubber, poly(methylpropene-co-2-methyl-1,3-butadiene), is a copolymer of isobutylene and a small amount of isoprene (<2.5 mol %). It provides excellent air retention, heat and steam resistance, ozone and weathering resistance, and outstanding dampening characteristics. It is used mainly in the automotive industry (inner tubes, curing bladders, body mounts), as well as for electrical insulation and roof sheeting.¹

Almost all world production of butyl rubber utilizes methyl chloride (MeCl) as a diluent and aluminum chloride as the cointiator. The growing health concerns² regarding MeCl stimulate the search for an alternative reaction medium in the process of manufacturing butyl rubber.

Presently, there is only one industrial process for butyl rubber without the use of methyl chloride. The solution process developed by Scherbakova et al.³ takes place in isopentane at -85 to -80°C . The initiating system is composed of ethylaluminum sesquichloride [$(\text{C}_2\text{H}_5)_2\text{AlCl} \cdot \text{Cl}_2\text{AlC}_2\text{H}_5$] with the addition of water or hydrogen sulfide.

Parker and Hanan⁴ described the synthesis of butyl rubber in hexane using a mixture of major amount of dialkylaluminum halide and minor amount of mono-

alkylaluminum dihalide. The patent claimed high molecular weights of the rubber obtained at a relatively high temperature (ca. -75°C) and a very good temperature control over polymerization reaction.

The goal of this study was to investigate the synthesis of butyl rubber in hexane using a mixture of Et_2AlCl and EtAlCl_2 , both in a nonactivated and the activated form.

EXPERIMENTAL

Reagents

Hexane (Aldrich, 99+%) used as a reaction medium was dried over Molecular Sieves 3A overnight, then distilled under nitrogen atmosphere using a Vigreux distilling column with an overhead Allihn condenser. The content of water in such distilled hexane was about 11 ppm, as determined by the Karl-Fischer method. The distilled hexane was kept in a tightly closed flask in a dry box.

Isobutylene (Matheson, 99.9%) was transferred as a vapor from a cylinder and condensed in the dry box.

Isoprene (Aldrich, 99%) was passed through an inhibitor remover disposable column (Aldrich, catalog no. 30,632-0).

Et_2AlCl and EtAlCl_2 were delivered from the manufacturer (Aldrich) as 1.0 molar solutions in hexanes.

Methylaluminoxane (Aldrich) was in the form of 10 wt % solution in toluene.

Copolymerizations

The typical composition of the monomer feed:

- 40.0 mL isobutylene at -75°C
- 8.0 mL hexane measured at room temperature
- 1.0 or 1.2 mL of isoprene measured at room temperature

The reactions were carried out in the MBRAUN glove box, in a 500-mL three-necked flask equipped with an overhead stirrer. The temperature changes during the reactions were followed by a thermocouple. The polymerizations were terminated by adding 5 mL of ethanol. The polymer solution was poured on an aluminum tare lined with Teflon, and the solvent and unreacted monomers were allowed to evaporate at room temperature. The obtained polymer was dried in a vacuum oven at about 70°C . Yields were determined gravimetrically.

Catalyst solution

The composition of the catalyst solution:

- 3.75 mL hexane
- 4.62 mL Et_2AlCl (1.0M solution in hexanes)
- 0.38 mL EtAlCl_2 (1.0M solution in hexanes)

Usually, 1.8–2.2 mL of this solution was used to initiate the reaction.

Water or MAO was added directly to the initiating solution using a microsyringe. The solution was stirred and immediately used to start the copolymerization.

Determination of isoprene content

The isoprene content was determined using $^1\text{H-NMR}$ (Bruker AVANCE 500 MHz).

About 0.1 g of a polymer was dissolved in 3 mL of CDCl_3 . One hundred scans were accumulated with a relaxation delay of 8 s. The area for isoprene unsaturation was integrated at 5 ppm and compared to the aliphatic methyl region at 1.17–0.5 ppm. The relative ratio of the isoprene area to the isobutylene methyl area in a given polymer was calculated and expressed in mol % using a software program.

Determination of molecular weights

Molecular weights were measured by a Waters gel permeation chromatography (GPC) (size exclusion chromatography: SEC) instrument equipped with six Ultrastyrigel columns (100, 500, 10^3 , 10^4 , 10^5 , and 10^6 Å pore size) thermostated at 40°C and a DRI 410 detector. The mobile phase was tetrahydrofuran

TABLE I
Synthesis of Butyl Rubber in Hexane at -75°C Using Various Amounts of Isoprene in the Monomer Feed

Isoprene in the feed (mL)	Yield (wt %)	\bar{M}_n	\bar{M}_w	\bar{M}_w/\bar{M}_n	Isoprene in the rubber (mol %)
1.0	36.3	131,800	347,200	2.6	1.4
1.1	40.6	152,300	380,000	2.5	1.5
1.2	47.3	145,200	397,200	2.7	1.9
1.3	40.3	154,400	370,500	2.4	1.9
1.4	38.1	92,300	227,900	2.5	1.9

Reaction time = 40 min; 2.2 mL of the solution containing a mixture of Et_2AlCl and EtAlCl_2 used to start the reaction.

(THF) with 1 mL/min flow rate. The instrument was calibrated with narrow molecular weight distribution (MWD) polystyrene standards and sulfur was used as an internal reference. Molecular weights were calculated using Water's Maxima 820/GPC software and the universal calibration principle. The following values of K and α were used⁵:

$$\begin{aligned} \text{polystyrene: } K &= 1.12 \times 10^{-4} \text{ gL/g; } \alpha = 0.725 \\ \text{butyl rubber: } K &= 2.0 \times 10^{-4} \text{ dL/g; } \alpha = 0.67 \end{aligned}$$

RESULTS AND DISCUSSION

Copolymerization of isobutylene and isoprene in hexane at -75°C initiated using a mixture of Et_2AlCl and EtAlCl_2 by itself

Table I contains the results of copolymerizations leading to butyl rubber when the ratio of both components in the initiating solution is 92.5 mol % Et_2AlCl to 7.5 mol % EtAlCl_2 . This ratio was found to be advantageous from some preliminary experiments, and was also reported in the original patent by Parker and Hanan.⁴

The amount of isoprene in the monomer feed varied from 1.0 to 1.4 mL.

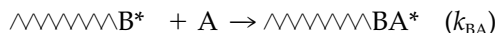
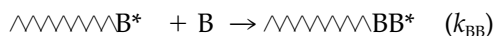
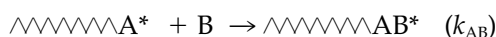
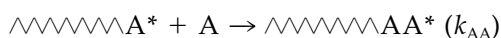
When the amount of isoprene added to the feed was 1.2 mL, the M_w , the yield, and the isoprene content in the rubber were the highest. Further increases of isoprene content in the monomer mixture (Table I) resulted in lower degrees of conversion and lower molecular weights. It has been demonstrated by other authors^{6–8} that isoprene acted both as a poison and a chain transfer agent in cationic copolymerizations with isobutylene.

Determination of a monomer reactivity ratio for isobutylene in its copolymerization with isoprene in hexane at -75°C

In binary copolymerization there are four possible propagation reactions, with associated rate constants:

TABLE II
Cationic Copolymerization of Isoprene (IP) with an Excess of Isobutylene (IB) at -75°C in Hexane Initiated Using a Nonactivated Mixture of Et_2AlCl and EtAlCl_2

Unreacted IB (%)	Unreacted IP (%)	$-\log ([\text{IB}]_t/[\text{IB}]_0)$	$-\log ([\text{IP}]_t/[\text{IP}]_0)$	r_{IB}
100	100	0	0	
61.0	73.4	0.2147	0.1343	1.60
63.4	74.1	0.1979	0.1302	1.52
72.0	79.3	0.1427	0.1007	1.42
85.1	90.1	0.07007	0.04528	1.55
91.5	94.2	0.03858	0.02595	1.49



The reactivity ratio for monomer A (r_{A}) is defined as $k_{\text{AA}}/k_{\text{AB}}$ and the reactivity ratio for monomer B (r_{B}) is $k_{\text{BB}}/k_{\text{BA}}$. The value of r gives a measure of the preference for an active center to add on a monomer of its own type rather than to add on a monomer of the opposite type.

Jaacks developed a method to determine monomer reactivity ratios (r_1, r_2) in binary and ternary copolymerizations.⁹ It is applicable when there is a large excess of one monomer (M_1) in the feed so that the copolymer formed will have a very small content of the other monomer (M_2). The copolymer equation to determine the monomer reactivity ratio in such a case⁹ is

$$\log([M_1]_t/[M_1]_0) = r_1 \log([M_2]_t/[M_2]_0)$$

where $[M_1]_0$ and $[M_2]_0$ are the initial concentrations of monomers and $[M_1]_t$ and $[M_2]_t$ the concentrations of unreacted monomers after the polymerization. This integrated equation has unlimited validity up to high

conversions provided that the excess of M_1 over M_2 remains large enough throughout the reaction.

The above method was used to determine a monomer reactivity ratio for isobutylene (r_{IB}) in its copolymerization with isoprene in hexane, initiated by a nonactivated mixture of Et_2AlCl and EtAlCl_2 . Table II gives the data required to determine r_{IB} .

The concentration of unreacted monomers was plotted in a logarithmic scale and from the slope of the straight line ($R^2 = 0.9945$) the monomer reactivity ratio for isobutylene was determined as $r_{\text{IB}} = 1.54 \pm 0.06$. This is different from a literature value¹⁰ $r_{\text{IB}} = 1.08$ when just EtAlCl_2 was used in hexane at -80°C . Apparently, Et_2AlCl does not behave as an inert component in a mixture with EtAlCl_2 , even though the diethylaluminum chloride cannot initiate the reactions by itself.

Copolymerization of isobutylene and isoprene in hexane at -75°C initiated using a mixture of Et_2AlCl and EtAlCl_2 activated with water

The maximum value for M_w for butyl rubber synthesized under the conditions given in Table I was about 400,000. Typical commercial butyl rubber manufactured in methyl chloride has a M_w close to 600,000. It was of interest to see if the initiating system under study could be improved.

Several experiments were carried out when the mixture of Et_2AlCl and EtAlCl_2 was modified by a direct addition of minute amounts of water. The resulting solution containing suspended white particles was stirred and immediately used to initiate the copolymerization. This was different from the earlier mentioned industrial solution method³ where only clear supernatant solution was used for the initiation.

Table III contains the results of copolymerization experiments with various amounts of water added to the initiating solution, 1.8 mL of which was used to start the reaction. The monomer reactivity ratio for isobutylene was calculated from the Jaacks equation individually for each case.

TABLE III
Synthesis of Butyl Rubber in Hexane at -75°C Initiated Using a Mixture of Et_2AlCl and EtAlCl_2 Activated with Water

H_2O added to initiating solution (μL)	Yield (wt %)	\bar{M}_n	\bar{M}_w	\bar{M}_w/\bar{M}_n	Isoprene in the copolymer (mol %)	r_{IB}
0 (control)	8.4	170,100	394,300	2.3	1.6	1.49
2	24.0	191,000	490,400	2.6	1.9	1.27
5	30.7	200,300	549,600	2.7	1.9	1.24
10	38.2	185,000	585,700	3.2	1.9	1.29
15	53.4	121,000	514,100	4.2	2.1	1.17
25	46.3	110,900	496,000	4.5	2.0	1.27
30	70.0	109,500	481,500	4.4	2.1	1.16
35	7.9	67,400	254,600	3.8	2.1	1.15
50	5.7	98,800	331,600	3.4	2.1	1.10

Reaction time = 20 min; 1.2 mL of isoprene in the feed; 1.8 mL of the initiating solution used to start the reaction

TABLE IV
Synthesis of Butyl Rubber in Hexane at -75°C Initiated Using a Mixture of Et_2AlCl and EtAlCl_2 Activated with Methylaluminumoxane (MAO).

MAO added to initiating solution (μL)	Yield (wt %)	\bar{M}_n	\bar{M}_w	\bar{M}_w/\bar{M}_n	Isoprene in the copolymer (mol %)	r_{IB}
0 (Control)	14.8	46,200	126,500	2.7	1.3	1.55
25	33.8	139,400	506,100	3.6	1.6	1.28
75	55.3	117,200	514,300	4.4	1.8	1.12
100	54.5	83,800	523,900	6.3	1.9	1.03
175	57.1	67,900	517,500	7.6	1.9	1.05
400	4.0	227,000	839,500	3.7	2.1	0.93

Reaction time = 20 min; 1.0 mL of isoprene in the feed; 1.8 mL of the initiating solution used to start the reaction

The initiating system containing proper amounts of water enabled us to achieve higher molecular weights and higher yields compared to the control reaction when no water was added.

Weight average molecular weights exceeding 500,000 could be obtained with the isoprene content in the rubber 2.1 mol %. Amounts of introduced water higher than about 30 μL in the initiating solution had a detrimental effect on M_w and the yield.

The data in the last column indicate that when increasing amounts of water were present in the initiating solution, the monomer reactivity ratio for isobutylene was decreasing from about 1.5 to 1.1. The last value of r_{IB} is almost identical with the literature value¹⁰ $r_{\text{IB}} = 1.08$ when EtAlCl_2 by itself was used in hexane at -80°C .

Copolymerization of isobutylene and isoprene in hexane at -75°C initiated using a mixture of Et_2AlCl and EtAlCl_2 activated with methylaluminumoxane

Aluminumoxanes are mixtures of components having Al-O-Al linkages. Their structure has not yet been fully understood. They consist of mixtures of linear, cyclic, and crosslinked species being in equilibrium with

each other. In the proposed structures, oxygen is often tricoordinated and aluminum tetracoordinated.¹¹ Even if aluminumoxanes could be isolated and studied in isolation, this provides little insight into the bonding and complex equilibria of alkylaluminumoxanes in solution.

Aluminumoxanes have been found to be excellent cocatalysts for the transition metal catalyzed polymerization of alkenes.¹¹ One of the patents of Langstein et al.¹² also teaches the beneficial use of methylaluminumoxane (MAO) to produce polyisolefins—in particular, polyisobutylene.

We used MAO as an activator for our initiating system composed of a mixture of Et_2AlCl and EtAlCl_2 . The addition of MAO had a pronounced effect on the process and rubber characteristics (Table IV).

Increasing amounts of MAO added to the initiating solution (up to about 175 μL) resulted in both higher polymer yields and molecular weights compared to the case when no methylaluminumoxane was added. Also, the isoprene content in the rubber was higher. This set of advantages obtained simultaneously, combined with a good temperature control during reactions, was rather surprising but it represents a very useful scenario from an industrial viewpoint.

TABLE V
Monomer Reactivity Ratios for Copolymerizations of Isobutylene with Isoprene

Reaction medium	Initiating system	Temperature ($^{\circ}\text{C}$)	r_{IB}	r_{IP}	Ref.
Methyl chloride	AlCl_3	-103	2.5 ± 0.5	0.4 ± 0.1	13
Methyl chloride (CH_3Cl): (hexane/heptane) (88 : 12)	EtAlCl_2	-100	2.17	0.5	14
(CH_3Cl): (hexane/heptane) (50 : 50)	EtAlCl_2	-80	2.15	1.03	10
CH_2Cl_2 : <i>n</i> -pentane (50 : 50)	EtAlCl_2	-80	1.75	1.02	10
(CH_3Cl): (hexane/heptane) (12 : 88)	EtAlCl_2	-70	1.56 ± 0.19	0.95 ± 0.17	15
Hexane	EtAlCl_2	-80	1.17	1.08	10
Hexane	EtAlCl_2	-80	1.08	1.28	10
Hexane	$\text{Et}_2\text{AlCl} + \text{EtAlCl}_2 + \text{H}_2\text{O}$	-75	$\rightarrow 1.10$		This work
Hexane	$\text{Et}_2\text{AlCl} + \text{EtAlCl}_2 + \text{MAO}$	-75	≈ 1.0		This work
Hexane	$\text{Et}_2\text{AlCl} + \text{EtAlCl}_2$	-75	1.54 ± 0.06		This work

TABLE VI
Synthesis of Butyl Rubber in Hexane at -60°C Initiated Using a Mixture of Et_2AlCl and EtAlCl_2 ,
With and Without H_2O or MAO

H_2O or MAO added to initiating solution (μL)	Yield (wt %)	\bar{M}_n	\bar{M}_w	\bar{M}_w/\bar{M}_n	Isoprene in the copolymer (mol %)	r_{IB}
0 (Control)	12.5	209,000	410,600	2.0	1.35	1.52
10 (H_2O)	39.5	169,100	504,600	3.0	1.65	1.30
150 (MAO)	36.3	230,300	620,200	2.7	2.1	0.94

Reaction time = 80 min; 1.0 mL of isoprene in the feed; 1.0 mL of the initiating solution used to start the reaction.

The addition of MAO to the solution also affected the \bar{M}_w/\bar{M}_n in the product. This is evident for the case with the polydispersity ratio equal to 4.4, 6.3, and 7.6 when the conversions are practically the same. Thus, methylaluminoxane can be used to broaden the molecular weight distribution of butyl rubber.

Similar to the case when water was added to the initiating solution, increasing amounts of MAO resulted in the decrease of the monomer reactivity ratio of isobutylene from a value of about 1.5 to a value close to unity.

A comparison of some published values of monomer reactivity ratios for copolymerization of isobutylene and isoprene with those obtained in this work is given in Table V.

The above results indicate that there is a significant influence of solvent polarity on reactivity ratios for isobutylene–isoprene copolymerizations.¹⁰

A mixture of a major amount of Et_2AlCl and a minor amount of EtAlCl_2 in the initiating solution has a different influence on the monomer reactivity ratio for isobutylene in its copolymerization with isoprene compared to the case when EtAlCl_2 is used by itself ($r_{\text{IB}} \approx 1.5$ vs $r_{\text{IB}} \approx 1.1$, respectively). However, when this mixture of ethylaluminum chlorides is modified by the addition of proper amounts of water or methylaluminoxane, the value of r_{IB} is close to unity. In such a case the rate constants of the growing polymer chain having an isobutylene-based active center with isobutylene monomer and that with isoprene monomer are almost equal. This resembles the situation when just EtAlCl_2 was present in the initiating solution and the reported¹⁰ value for r_{IB} was 1.08.

Copolymerization of isobutylene and isoprene in hexane at -60°C initiated using a mixture of Et_2AlCl and EtAlCl_2 by itself and with water or MAO

Finally, some copolymerizations of isobutylene and isoprene were carried out in hexane when the temperature was raised to -60°C (Table VI).

Again, the beneficial effect of the activation of the initiator on the degree of conversion, molecular weights, and the isoprene content in the rubber was evident. Using the MAO-activated catalyst system, it was possible to obtain butyl rubber in hexane at -60°C having $\bar{M}_w = 620,000$, polydispersity = 2.7, and isoprene content 2.1 mol %. This temperature is probably about 20°C higher than for the industrial solution process.³ The above rubber characteristics are comparable with those for commercial butyl rubber manufactured in methyl chloride at -95°C .

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