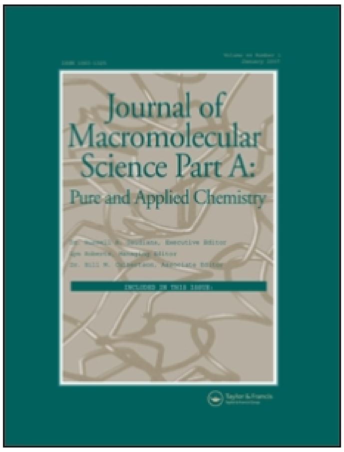

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SYNTHESIS OF HIGH - CIS - POLYBUTADIENE USING COBALT (II) -2-ETHYLHEXOATE MODIFIED TRIETHYLALUMINUM CATALYST

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ABSTRACT

Pretreatment of triethylaluminum with active chlorine bearing adjuvants led to the formation of an active cocatalyst for 1,3-butadiene polymerization to high - *cis* - polybutadiene using cobalt (II)-2-ethyl hexoate as catalyst. The features of the polymerization, namely, conversion, molecular weight and microstructure were found to depend on the Cl/Al ratio. Polymerization behaviour in both benezene and benzene-butene-1 mixture were similar and closely resembled that observed with the conventional cobalt (II)-2-ethylhexoate - diethylaluminum chloride catalyst system.

INTRODUCTION

High-*cis*-1,4-polybutadiene rubber is produced industrially using a Ziegler-Natta catalyst system comprising of diethylaluminum chloride (DEAC) and cobalt (II)-2-ethylhexoate in solution. Use of triethylaluminum with the cobalt catalyst system is reported to produce polybutadiene with high vinyl content. On the contrary nickel (II) napthenate, neodimium (II)-2-ethylhexoate[4] or lanthanum (II)-2-ethylhexoate[4] promote high-*cis*-1,4-polybutadiene formation in presence of trialkylaluminum cocatalyst. The inability of trialkylaluminum to promote polymerization

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of butadiene to high-cis-1,4-polybutadiene can be attributed to its high reducing power, causing over reduction of cobalt (II). A study was therefore undertaken to examine whether in presence of suitable adjuvants, the reducing power of trialkylaluminum could be moderated, so that high-cis-1,4-polybutadiene can be produced using cobalt (II)-2-ethylhexoate as catalyst. This paper reports the results of this study.

EXPERIMENTAL

Materials : Polymer grade 1,3-butadiene, butene-1 and cobalt-2-ethylhexoate were sampled from the operating high-cis-1,4-polybutadiene plant of Indian Petrochemicals Corporation Limited. Benzene was distilled over CaH_2, passed over molecular sieves 4 Å and stored over sodium wire. Diethylaluminum chloride and triethylaluminum (M/s. Ethyl Corporation) were sampled neat and used as 15% solution in benzene. All manipulations involving catalysts were performed in an inert atmosphere under a constant purge of high purity nitrogen.

Catalyst Preparation : (a) A known quantity of triethylaluminum in dichloromethane was taken in a 250 mL three neck flask. To this a known weight of t-BuCl in dichloromethane was added in instalments at 0°C over a period of 30 min. The bath temperature was slowly raised to 25°C. The reactants were further allowed to react under stirring for about 30-40 minutes. The product was recovered by evaporating the volatile reactants and solvent under a stream of dry nitrogen. The chlorine and aluminum content in the product were estimated volumetrically.

(b) A known quantity of anhydrous $AlCl_3$ was taken in a 250 mL flask containing benzene as solvent and kept in oil bath at 25°C. Based on anhydrous $AlCl_3$, a known quantity of TEAL in dry benzene was added in instalments and allowed to react for about 10-15 minutes under stirring. The reaction was further heated to 40°C for 20-25 minutes. The chlorine and aluminum content in the product were estimated volumetrically.

Polymerization : (a) In Benzene : 1:3 butadiene was bubbled through a trap containing 15% solution of diethylaluminum chloride/triethylaluminum in benzene and then into a flask containing dry benzene at ice-salt temperature. The concentration of dissolved butadiene 1:3 at room temperature was estimated bromometrically. The polymerization assembly consisted of a 250 mL round bottom flask fitted with a thermowell, rubber septum and a nitrogen outlet connected to a bubbler. Previously cleaned and oven dried glasswares were assembled inside inert atmosphere box and the flask was charged with the required amount of monomer solution and the synthesised catalyst. The polymerization was initiated at 25°C by addition of cobalt (II)-2-ethylhexoate. The reaction was terminated by addition of a small quantity of methanol containing 0.5% of ditertiary butyl p-cresol as an antioxidant.

(b) Benzene-Butene-1 : A jacketed 1 L laboratory glass reactor (Buchi SFS, Switzerland) provided with a variable speed magnetic agitator was used for these studies. The reactor was flushed thoroughly with N_2 at 90-95°C followed by repeated evacuation and filling with N_2. The reactor was cooled to -10°C. A measured amount of butene-1 and 1,3-butadiene was transfered to the reactor through a closed line by inverting the cylinder containing butene-1 and 1,3-butadiene. A mixture of benzene and modified co-catalyst was charged to reactor under N_2 pressure. The reactor temperature was brought to 7-8°C. Polymerization was initiated by adding a benzene solution of cobalt (II)-2-ethylhexoate through a syringe and increasing the reactor temperature rapidly to the desired level. The polymerization was terminated as described before.

Polymer recovery : The volatile solvents were allowed to evaporate and the preciptated rubbery polymer was sqeezed free of solvents and dried at 40°/10 nm Hg pressure for 8 h.

Polymer characterization : Intrinsic viscosity was determined in toluene at 30° using an Ubbelohde viscometer. The cis, trans and vinyl contents were determined on Beckman 4220 IR spectrometer using the frequencies at 740, 965 and 910-915 cm^{-1} respectively. Gel content in polymer was determined by dissolving 0.4 g of the rubber in 100 mL toluene and filtering, the solution through a clean stainless steel 180 mm sieve previously dried to a constant weight. The sieve was again dried at 120°C for 45 min. and weighed. The gel content was calculated from the difference in weight of the sieve.

RESULTS AND DISCUSSION

Organoaluminum compounds undergo facile redistribution reaction with active halogen compounds[5]. Increasing the halogen content in organoaluminum compounds is known to moderate its reducing power. We therefore pretreated triethylaluminum with anhydrous aluminum chloride and t-butyl chloride, thereby increasing the Cl/Al ratio in the range of 1.1 to 1.5 (eqn 1 and 2).

$$AlEt_3 + AlCl_3 \longrightarrow Al_{n+1}Et_3Cl_{3n} \quad \text{-------}(1)$$

$$AlEt_3 + \underline{t}BuCl \longrightarrow AlEt_{3-n}Cl + \quad t\text{-}Bu\text{-}Et \quad \text{------} \ (2)$$

The reaction according to equation (2) has been well documented in the literature[6].

Control experiments established that triethylaluminum alone did not initiate butadiene polymerization. However, when triethylaluminum was pretreated with varying quantities of t-BuCl, vigorous exothermic polymerization ensued (Table 1). Results show that

TABLE 1

Polymerization of 1,3-butadiene using cobalt-2-ethylhexoate/ triethylaluminum/t-butylchloride or anhyd. aluminum chloride in benzene[a]

Expt. No.	TEAL, mmoles	tBuCl or $AlCl_3$ phgm	Cl/Al	Time, min.	Conv.,	$[\eta]^b$ $dl\ g^{-1}$	% cis	% trans	% vinyl
1	25.1	27.7 (tBuCl)	1.1	6	31	0.4	89	2	9
2	25.4	33.0 (tBuCl)	1.3	6	30	4.0	98	1	1
3	25.4	37.8 (tBuCl)	1.5	6	22	3.1	97	2	1
4[b]	25.5	10 ($AlCl_3$)	1.1	10	21	2.1	97	1	2
5[c]	25.1	12.5 ($AlCl_3$)	1.3	10	13	4.0	97	2	1
6[c]	25.4	15.1 ($AlCl_3$)	1.5	10	10	3.9	97	2	1
7	25 (Diethylaluminum chloride)		1.33	10	20	4.0	97	2	1

[a] Feed : 10g 1,3-butadiene in 60 mL benzene; cobalt-2-ethylhexoate:0.17 mmoles phgm, reaction temperature : 28±2°C

[b] in toluene at 30°C

[c] cobalt-2-ethylhexoate : 0.04 mmole phgm.

TABLE 2

Polymerization of 1,3-butadiene using cobalt-2-ethylhexoate-triethylaluminum - anhyd.aluminum chloride in benzene[a]

Expt No.	Feed Composition 1,3-BD	B-1 mL	Benzene mL	Temp°C	Time, min.	Conv., %	$[\eta]^{b}$ dl g^{-1}	% cis	% trans	% vinyl
1	142	218	250	10	24	36	3.9	98.6	0.6	0.8
2	142	218	250	20	15	36	3.4	98.2	0.8	1.0
3	107	165	188	30	10	65	2.2	96.1	1.3	2.6
4	142	218	250	40	10	70	2.2	97	1.3	1.7

[a] Cobalt (II) -2-ethylhexoate, 0.04 mmoles phgm; cocatalyst : 15 mmoles phgm; Cl/Al=1.3

[b] in toluene at 30°C

increasing Cl/Al ratio has negligible effect on conversion. However, molecular weight initially increases with Cl/Al ratio and then levels off. Cis content is also generally invariant with Cl/Al ratio. It was found that when anhydrous aluminum chloride was used, a lower cobalt-2-ethylhexoate concentration was necessary to initiate polymerization.

Industrial polymerization of butadiene is generally carried out in mixed benzene-butene-1 solvent[7]. Therefore, polymerization was conducted under these conditions using anhydrous aluminum chloride modified triethylaluminum at 10, 20, 30 and 40°C at Cl/Al ratio of 1.31 (Table 2). The reaction exotherm was difficult to control above 25°C. The results are essentially similar to that observed in pure benzene. As expected, conversion increased and intrinsic viscosity decreased with increasing temperature. Cis - content was invariant with temperature and uniformly high.

Our observations indicate that it is possible to modify triethylaluminum by treating with suitable adjuvants containing reactive chlorine to an active cocatalyst for polymerization of 1,3-butadiene to high - cis - polybutadiene. As observed with diethylaluminum chloride, best results are obtained when Cl/Al ratio is about 1.3. These results also have a practical significance. With progressive shift in polyolefin processes towards high efficiency catalysts, use of diethylaluminum chloride as cocatalysts for polyolefins is fast diminishing. Cobalt based polybutadiene thus remains one of the last processes that will still need diethylaluminum chloride as cocatalyst. Our results establish the feasibility of using modified triethylaluminum in cobalt based polybutadiene process thereby also eliminating the dependence of this process on diethylaluminum chloride.

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