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Solvent Effects in the Polymerization of 1,3-Butadiene with Cobalt(II) 2-Ethylhexoate-Diethylaluminium Chloride Catalyst

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Polymerization of 1,3-butadiene to high-cis-1, 4-polybutadiene initiated by cobalt(II)2-ethyl hexoate-diethylaluminium chloride has been studied in benzene-butene-1, benzene-butane, benzene-hexene-1 and benzene-hexane solvent mixtures of different compositions. With olefinic cosolvents, conversions show pronounced maximum at a defined solvent composition. Molecular weights rapidly decrease with increasing proportion of olefinic cosolvents. Aliphatic solvents are relatively inefficient. The results are explained in terms of the relative π complex stabilities of the active Co (I) species in aromatic, diene and olefinic solvents.

1,3-Butadiene undergoes stereospecific polymerization to high molecular weight *cis*-1,4-polybutadiene (>97% *cis*-1,4 content) in presence of soluble catalysts comprising cobalt(II) salts and diethylaluminium chloride[1]. The nature of solvents employed in polymerization plays a definitive role in determining the polymerization rate, polymer molecular weight and its microstructure. The most commonly used solvents are benzene or toluene. However, the use of aliphatic solvents such as *n*-hexane, *n*-heptane or cyclohexane is also mentioned in the literature[2-4]. The *cis* content and molecular weight of polymers obtained with aliphatic solvents are lower than those obtained with benzene, although high conversions can be obtained. The rate of polymerization depends on the aromatic solvent used and decreases in the order: benzene >toluene >xylene >mesitylene[1]. Dielectric constant of the solvent has no effect on polymer *cis* content. However, conversion decreases with increasing solvent dielectric constant[4]. Chlorinated methanes or ethanes are reported to have an accelerating effect on polymerization[5]. The molecular weight of the polymers decreases with increasing chlorine content of the solvents. However, *cis* content is not affected. With cobalt (II) acetylacetonate-tri-*i*-butylaluminium catalyst system in toluene as the solvent, the monomer conversion shows a sharp increase when about 6% by volume of toluene is replaced by cyclohexane[6]. *Cis* content also shows an increase.

Unlike laboratory studies, industrial polymerization of 1,3-butadiene is invariably performed in mixed solvents[7,8]. Typically, a mixture of benzene and low boiling olefin is employed. Little is known in the published literature regarding the influence of such mixed solvents on the course of butadiene polymerization. Racanelli and Porri[9] studied the polymerization of 1,3-butadiene to high-*cis*-polybutadiene using cobalt(II) acetylacetonate and an organoaluminium catalyst containing Al-O-Al bonds in aromatic, aliphatic and olefinic solvents. Aliphatic solvents produced high-*cis*-polymers, but with molecular weights lower than that of the polymers obtained by the same system in benzene. *Cis*-butene-2 was found to be a particularly suitable solvent giving high *cis* content (at least 99%) and a very high molecular weight ($[\eta]>5$). Furthermore, polymerization rate was also much higher. Butene-1 and *trans*-butene-2 were less efficient. More recently, Horne[10] reported, butadiene polymerization in benzene, heptane, cyclohexane, 20% benzene-80% butane and 10% benzene-90% butene-1 with alkylaluminium compounds with different Cl/Al ratios. He showed that polymer molecular weight is solvent dependent.

The present study was undertaken with a view to delineating the role of olefinic solvents in butadiene polymerization using cobalt (II)-2-ethylhexoate-diethylaluminium chloride system. Effect of incremental substitution of benzene with butane or butene-1 and hexane or hexene-1 on polymer properties is reported.

Experimental Procedure

Materials — 1,3-Butadiene (IPCL) was sampled inhibitor free and stored in laboratory with 40 ppm-*t*-butylcatechol. Butene-1 (Polyolefins India Limited ,>99% pure by GC) and butane (Philips' Petroleum Company, 99 mol% minimum) were used as received.

Hexane (S.D.Chemicals, >99% pure by GC) and hexene-1 (Gulf Chemical Company,>98.6% pure, 97% 1-olefin content) were distilled by refluxing over triethylaluminium and stored under nitrogen over activated molecular sieves (4Å). Benzene dried over molecular sieves was stored over sodium wire. Diethylaluminium chloride (Ethyl Corporation) was sampled neat and used as 15% solution in benzene. Cobalt(II)-2-ethylhexoate was used as 5% solution in benzene. All operations involving catalysts were performed in an inert atmosphere box purged continously with high purity nitrogen.

Polymerization

(a) *In benzene-hexene or hexene-1*—1:1-3 Butadiene was bubbled through a trap containing 15% solution of diethylaluminium chloride in benzene and then into a flask containing the requisite mixture of solvent. The concentration of dissolved butadiene 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 glassware were assembled inside an inert atmosphere box and was charged with the required amount of monomer solution and diethylaluminium chloride. The polymerization was initiated by addition of cobalt(II)-2-ethylhexoate. Conditions were so adjusted that the desired quantity of water, necessary to activate the catalyst was present in the system. Polymerization temperature was maintained at 25°C. The reaction was terminated by addition of a small quantity of methanol containing 5% di-*t*-butylcatechol as an antioxidant.

(b) *Benzene-butane or butene-1*—An all glass jacketed 2L laboratory reactor (from M/s Buchi SFS, Switzerland) provided with a variable speed magnetic agitator was used for these studies (Fig. 1). The reactor was flushed thoroughly with N_2 at 90-95°C followed by repeated evacuation and filling with N_2. A mixture of benzene-diethaluminium chloride was charged to the evacuated reactor under nitrogen. The reactor was cooled to below-5°C. Necessary quantities of butene-1 or butane and 1,3-butadiene were transferred to the reactor through a pump. The reactor was brought to 7-8°C. Polymerization was initiated by adding a benzene solution of cobalt(II)2-ethylhexoate through a syringe and bringing the reactor rapidly to the desired reaction temperature. The polymerization was terminated as described before.

Polymer recovery—The volatile solvents were allowed to evaporate and the precipitated rubbery polymer was squeezed free of solvents and dried at 40°C/10 mm Hg pressure for 8 hr.

Polymer characterization—Intrinsic viscosity was determined in benzene at 30°C using an Ubbelhode viscometer. The *cis*, *trans* and *vinyl* conten was determined using a Beckman 4220 IR spectrometer using the frequences at 735-740, 965 and 910-915 cm^{-1} respectively. A typical infrared spectrum is shown in Fig. 2 for a polymer having 96.3% *cis*, 2.4% *trans* and 1.3% *vinyl* content. (S.No. 2, Table 1). GPC measurements (polydispersity) were carried out on a Waters Associate ALC/GPC 244 at 25°C using toluene as a solvent. The rubber concentrations was

Table 1 — Polymerization of 1,3-Butadiene in Benzene-Butene-1 Solvent[a]

No.	Butene-1 in benzene, wt%	Conv. %	$[\eta]$[b] $dl.g^{-1}$	gel wt%	Microstructure %cis	%trans	%vinyl
1	90	21	1.0	0	-	-	-
2	65	47	1.9	0.2	96.3	2.4	1.3
3	50	39	1.9	0.1	95.5	0.7	3.8
4	40	24	2.9	n.d.	97.4	1.5	1.1
5	30	16	2.5	0.2	96.8	0.8	2.4
6	0	7	4.2	0.1	97.4	1.0	1.6

[a] Butadiene: 22% by wt of total feed; Co (II): 0.05 m moles per 100g of monomer; diethylaluminium chloride: 10.6 m moles per 100g of monomer: reaction time: 20 min, temp: 10°C

[b] in toluene at 30°C

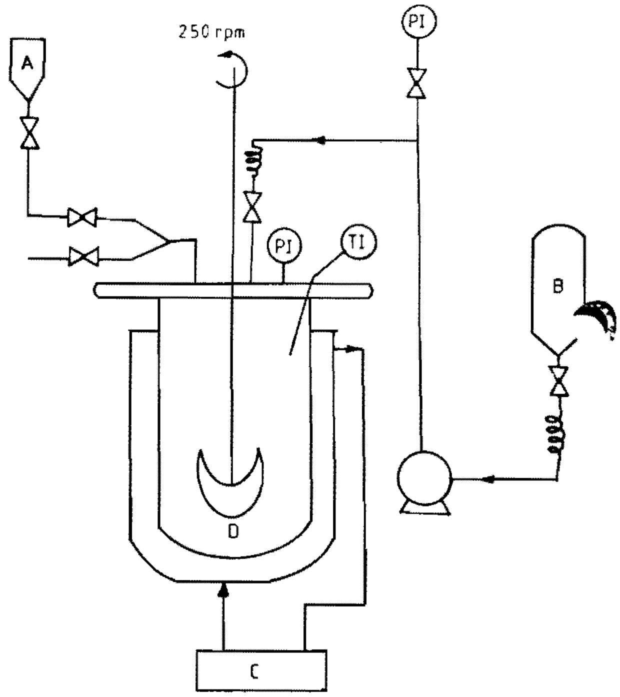


Fig. 1—Schematics of reactor system [A—Benzene and catalyst dosing tank; B—Butadiene and butene-1/*n*-butane dosing tank; C—Low temperature circulating bath; and D—Calibrated glass reactor]

0.4% and flow rate 2 mL/min. Five styrogel columns of pore size 10^5 (5), 10^4 (2), 10^3 (1) and 500° A were used and a universal calibration using standard polystyrene was employed. Gel content in polymer was determined as per ISI method DOC PCDG 14(387), April 1980. The procedure is as follows: 100 mL of toluene was taken in a clean and dry glass beaker. 0.4g of the rubber sample containing an antioxidant was cut into small pieces and added to the solvent without mechanical stirring. The solution was then filtered through a clean stainless steel 180 mm sieve, previously dried to a constant weight. The sieve was then dried at 120° C for 45 min and weighed. The gel content was calculated from the difference in weight of the sieve.

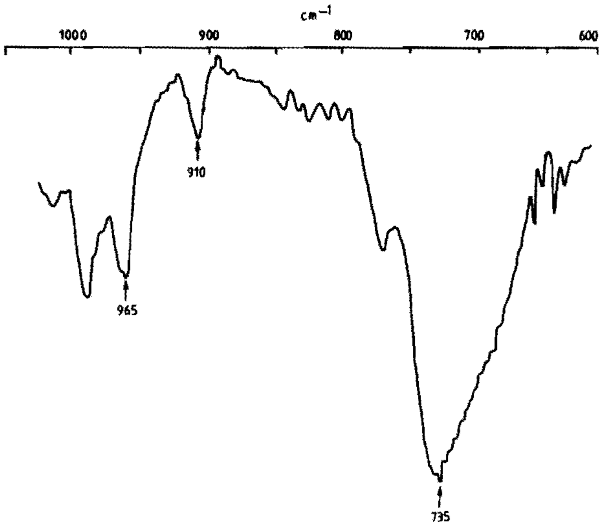


Fig. 2—Typical IR spectrum of high-*cis*-1,4-polybutadiene

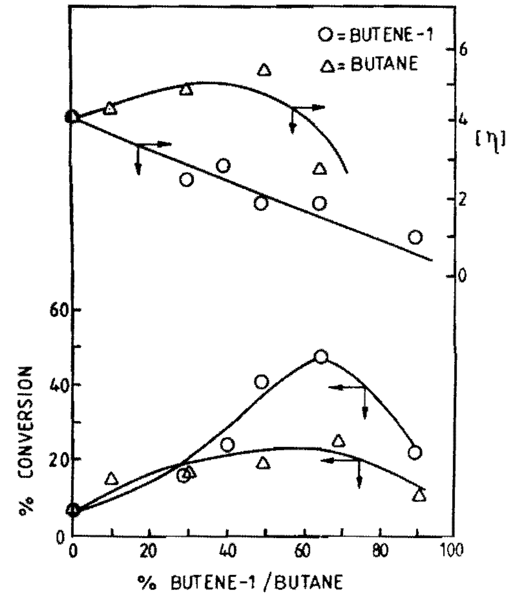


Fig. 3—Effect of butene-1/butane in benzene on conversion and intrinsic viscosity

Results and Discussion

Polymerization of 1,3-butadiene was studied with varying weight ratios of benzene-butene-1 and benzene-butane at 10° C. The results are shown in Tables 1-3 and Figs. 3-6. In both cases, conversions to polymer increased with increasing butene-1 or butane reaching a maximum around 60-70% beyond which conversion decreased (Fig. 2). However, absolute conversions were higher with benzene-butene-1. Butene-1 showed a pronounced molecular weight depressing effect indicating its involvement in chain transfer process (Fig. 3). On the contrary, with butane, molecular weight was practically invariant up to 50% by wt of butane in benzene. Whereas the tendency of the rubber to precipitate out of solution was more pronounced at 90% by wt butene-1 in benzene, such precipitation occurred even at 70% by wt butane in benzene. This was accompanied by progressive gelation of polymer with as much 80% by wt of polymer present as gel in

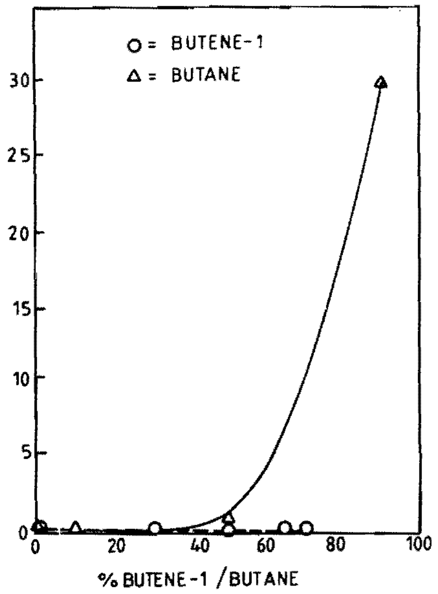


Fig. 4—Effect of butene-1/butane in benzene on gel content

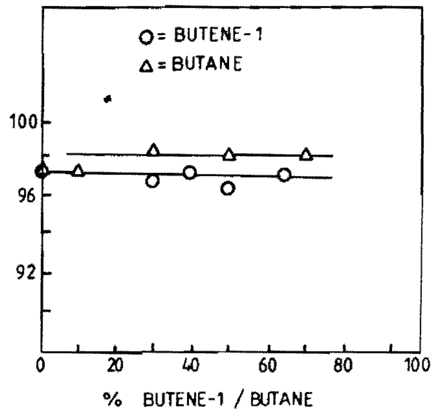


Fig. 5—Effect of butene-1/butene in benzene on *cis* content

Table 2 — Polymerization of 1,3-Butadiene in Benzene-Butane Solvent[a]

No.	Wt% butane-1 in benzene,	Conv., %	$[\eta]^b$ dl.g^{-1}	gel wt%	Microstructure %*cis*	%*trans*	%*vinyl*
1	90[c]	10	–	30	–	–	–
2	70	25	2.85	n.d.	98.0	0.8	1.2
3	50	19	5.5	1.0	98.3	0.9	0.8
4	30	17	4.8	n.d.	98.6	0.6	0.8
5	10	15	4.4	0.1	97.8	1.0	1.2
6	0	7	4.2	0.1	97.4	1.0	1.6

[a] Butadiene: 22% by wt of total feed; Co (II): 0.05 m moles per 100g of monomer; diethylaluminium chloride: 10.6 m moles per 100g of monomer; reaction time : 20 min; temp. 10°C

[b] in toluene at 30°C

[c] in 100% butane 80% by weight of polymer formed was in the form of gel

Table 3 — Effect of Solvent Composition on Polymer Polydispersity

Solvent composition	Q
Butene-1 in benzene, wt%	
100	3.6
65	2.8
30	3.7
0	3.3
Butane in benzene, wt%	
70	2.2
30	4.5
0	3,3

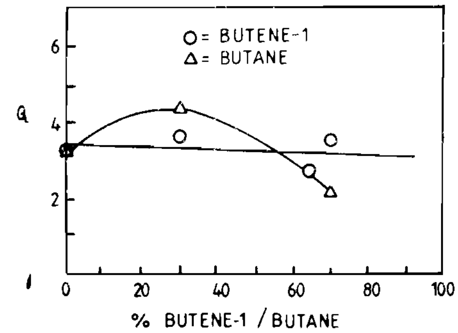


Fig. 6—Effect of butene-1/butane in benzene on polydispersity

Table 4 — Polymerization of 1,3-Butadiene in Benzene-Hexane-1 Solvent[a]

No.	Hexene–1 in benzene, wt%	Conv. %	$[\eta]^b$ dl g^{-1}	Microstructure %*cis*	%*trans*	%*vinyl*
1	100	12	0.5	93.7	2.1	4.2
2	70	30	0.6	94.0	3.5	2.5
3	50	53	1.5	94.0	1.6	4.4
4	30	59	1.4	95.5	1.5	3.0
5	0	26	3.5	97.4	1.0	1.6

[a] Butadiene : 22% by wt of total feed; Co(II) : 0.04 m moles per 100 g of monomer; diethylaluminium chloride:12.5 m moles per 100 g of monomer; reaction time:30 min, temp. : 25°C

[b] in toluene at 30°C

Table 5 — Polymerization of 1,3-Butadiene in Benzene-Hexane Solvent[a]

No.	Hexene benzene, wt%	Conv. %	$[\eta]^b$ dl.g^{-1}	Microstructure %*cis*	%*trans*	%*vinyl*
1	100	-	–	–	–	–
2	50	7	0.5	94.0.	2.4	3.6
3	30	27	3.2	96.0	1.5	2.5
4	0	26	3.5	97.4.	1.0	1.6

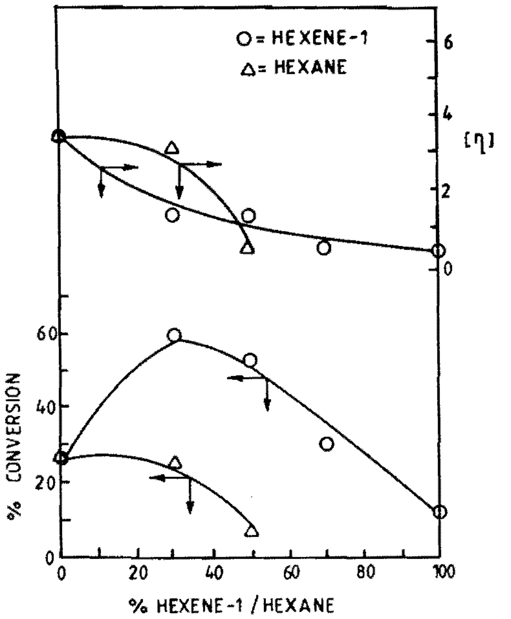
[a] Butadiene : 22% by wt of total feed; Co(II) : 0.04 m moles per 100g of monomer; diethylaluminium chloride; 12.5 m moles per 100 g of monomer; reaction time: 30 min, temp.:25°C

[b] in toluene at 30°C

100% butane (Fig.4). *Cis* content was generally high and invariant either with the nature or composition of solvent (Fig. 5). Polydispersity was practically invariant over the various composition ranges in case of butene-1; however, with butane, a slight broadening of distribution was observed at about 30% by wt butane in benzene (Fig. 6).

These observations were further confirmed by the study of butadiene polymerization with benzene-hexane and benzene-hexene-1 of varying compositions. The results are summarized in Tables 4-5 and grahically depicted in Figs 7-8. The conversion to polymer showed a maximum at around 30% hexene-1 in benzene. No such maximum was observed with hexane as cosolvent although conversion drastically dropped beyond 50% hexane-benzene (Fig. 7). In 100% hexane, polymerization could not be initiated. There was sharp decrease in polymer molecular weights with increasing weight proportion of hexene-1 in benzene. However, in case of hexane a dratic molecular weight reduction was observed only after hexane content has increased beyond 30% (Fig. 7). *Cis* content decreased with increasing hexane in benzene (Fig. 8). This is probably a consequence of the lower molecular weights of polybutadiene. It has been observed that in general when a *cis*-polybutadiene obtained by a catalyst has a lower molecular weight, it also has a lower *cis* content. Unlike with butene-1 or butane, polymers were completely soluble over the entire compositional range of benzene-hexene-1 and no tendency towards gelation was observed.

These results indicate that olefinic cosolvents in 1,3-butadiene polymerization increases conversions and decreases polymer molecular weights. The compositions at which conversion maxima are obtained de-



[illegible] 7—Effect of hexene-1/hexane in benzene on conversion and intrinsic viscosity

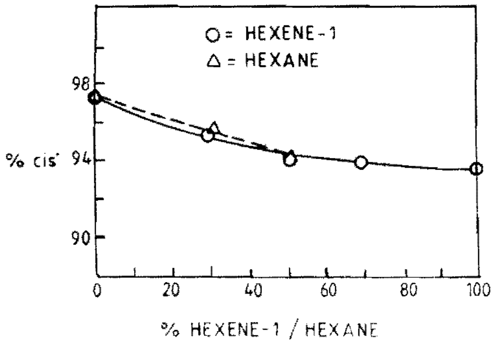


Fig. 8—Effect of hexene-1/hexane in benzene on *cis* content

pend on the nature of olefin cosolvents. The mechanism of butadiene polymerization to high *cis*-1,4 - p[illegible]utadiene by cobalt catalyst is best understood in terms of an active cobalt(I) species which is stabilized in solution as an aryl or alkenyl derivative by p→d bonding (π-bonding)[1]. Presence of an olefinic cosolvent is expected to confer lesser stability to the active species compared to a π-aryl (with benzene or π-alyl (with 1,3-butadiene) complex. The conversion maxima observed with olefinic cosolvents are indicative of a situation in which a subtle balancing of stability and lability of active species occurs at specific solvent compositions leading to rate enhancements. In aliphatic solvents, cobalt(I) is very unstable leading to precipitation of cobalt metal from solution. This

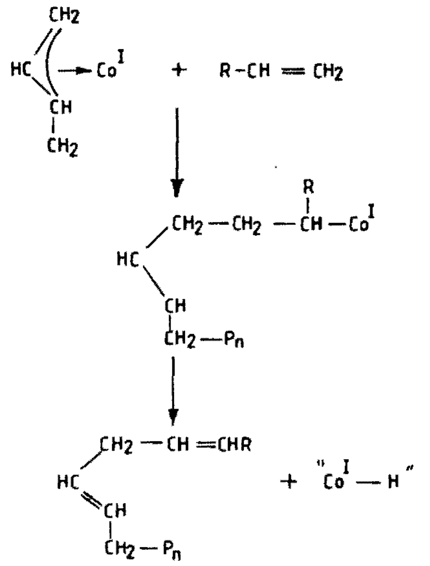


Fig. 9—Mechanism of chain transfer by olefins during butadiene polymerizations

renders these solvents unsuitable for butadiene polymerization. Lowering of molecular weights by olefinic solvents is related to its ability to act as chain transfer agents in butadiene polymerization[1-2]. Interception of a growing chain bearing a π-allylic cobalt complex with an olefin leads to an unstable complex. The latter spontaneously eliminates a Co^{I}-H species capable of initiating fresh polymerization (Fig. 9).

Acknowledgement

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