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Effect of reaction parameters on the solution polymerization of 1,3-butadiene using cobalt (II)-2-ethylhexoate-diethylaluminum chloride catalyst

V K Upadhyay & S Sivaram[a]
Research Centre, Indian Petrochemicals Corporation Ltd, P.O. Petrochemicals, Vadodara 391 346, India

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Polymerization of 1,3-butadiene to high-*cis*-1,4-polybutadiene initiated by cobalt (II)-2-ethylhexoate-diethylaluminum chloride was studied as a function of catalyst/cocatalyst concentration and reaction temperature in benzene-butene-1 mixed solvent system. Molecular weight was unaffected by cobalt (II) concentration. However, increasing concentration of organoaluminum as well as temperature depressed molecular weight. The *cis*-content was invariant with reaction conditons. A series of olefins and diolefins were examined for their relative efficacy as chain transfer agents. Allenic hydrocarbons were superior to olefins. Dicyclopentadiene showed desirable features of a good chain transfer agent.

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 diethylaluminum chloride[1]. In spite of the widespread use of this chemistry in industrial practice, little systematic information is available in the literature on the effect of various reaction parameters on the course of this polymerization[2]. We, therefore, undertook a detailed study of the effect of catalyst/cocatalyst concentration and reaction temperature on molecular weight, molecular weight distribution and microstructure of polybutadiene. We also examined the efficacy of various mono- and di-olefins as chain transfer agents in butadiene polymerization. All these studies were conducted in a mixed solvent system consisting of 70/30% wt/wt benzene-butene-1. Unlike laboratory studies, industrial polymerization of 1,3-butadiene is inveriably performed in mixed solvents[2,3]. This paper reports the results of this study.

Experimental Procedure

Materials—1,3-Butadiene (inhibitor free) was sampled from IPCL and stored in laboratory with 40 ppm *t*-butylcatechol. Butene-1 (Polyolefins India Ltd, >99% pure by GC) was used as received. Benzene dried over molecular sieves was stored over sodium wire in an atmosphere of nitrogen. Diethylaluminum 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 other chemicals used were reagent grade. All manipulations involving catalyst were performed in an inert atmosphere box purged continuously with high purity nitrogen.

Polymerization—The detailed procedure for polymerization of 1,3-butadiene in benzene-butene-1 mixture has been described[2]. Chain transfer agent (methylallene or C_4 raffinate) was charged as gas through injection port fitted with a rubber septum using a long stainless steel needle the tip of which was immersed in the liquid feed in the reactor at −5°C. The other side of the needle was connected to a cylinder containing the chain transfer agent through a gas flow meter. The order of addition was feed (butadiene + solvent), followed by chain transfer agent, diethylaluminum chloride and lastly cobalt-2-ethylhexoate. The chain terminator was added last when ethylene/propylene was used as chain transfer agents since they had to be charged under pressure. Ethylene or propylene was charged under pressure. Ethylene or propylene was charged through a calibrated bomb which was connected to the reactor using high pressure needle valves.

Polymer recovery and characterization—The polymer recovery procedure and characterization were as described before[2].

Results and Discussion

Effect of catalyst concentration—Cobalt (II)-2-ethylhexoate concentration was increased

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[a] Present address: Division of Polymer Chemistry, National Chemical Laboratory, Pune 411 008, India

from 0.026 mmole phgm to 0.090 mmole phgm at constant Al/Co ratio. Conversion showed a steady increase but molecular weight, its distribution and microstructure were invariant (Table 1). In the range of concentration studied cobalt (II) salt had no molecular weight depressing effect[4]. However, when the concentration of diethylaluminum chloride was increased at constant cobalt (II) concentration, conversion increased steadily, molecular weight decreased and the *cis* content was unaffected (Table 2). The ability of organoaluminum compounds to act as chain transfer agent in Ziegler-Natta polymerization is well documented in the literature[5].

Effect of temperature—The effect of polymerization temperature in the range 5-15°C was studied. The results are shown in Table 3. Whereas conversion increased and molecular weight decreased with temperature, the *cis* content was unaffected. At higher reaction temperatures, rate of chain transfer to both solvent and cocatalyst increases resulting in a decrease in molecular weight. However, temperature has little influence on the stability of the π-allyl cobalt complex which is responsible for the repetitive *cis* insertion of 1,3-butadiene.

Effect of chain transfer agents—Chain transfer agents are employed in 1,3-butadiene polymerization to regulate polymer molecular weights[1]. A number of compounds, mostly organic, are reported to be useful for this purpose. They include water[6], hydrogen[7], ethylene[8], propylene[8],

Table 1—Effect of cobalt (II)-2-ethylhexoate concentration[a]

No.	DEAH phgm	Co(II) phgm	Time, min	Conv., %	$[\eta]^b$ dl g^{-1}	Microstructure			$\bar{M}_w$
						% *cis*	% *trans*	% vinyl	$\bar{M}_n$
1	5.45	0.026	15	0.3	—	—	—	—	—
2	8.18	0.039	15	4	3.5	98.2	0.8	1.0	—
3	10.90	0.052	15	21	3.3	97.9	0.8	1.3	2.7
4	13.62	0.065	12	23	3.2	98.4	0.5	1.1	2.3
5	16.35	0.078	12	34	2.4	97	1.0	2.0	2.2
6	19.07	0.090	10	28	3.2	97.5	0.8	1.7	2.9

[a] Butadiene: 22.3% wt in benzene-butene-1 (70/30 by % wt), temperature = 10°C.
[b] in toluene at 30°C

Table 2—Effect of diethylaluminum chloride concentration[a]

No.	DEAH mmole phg	Al/Co	Time, min	Conv. %	$[\eta]^b$ dl g^{-1}	Microstructure		
						% *cis*	% *trans*	% vinyl
1	10.9	210	25	23	4.1	98.0	0.5	1.5
2	21.8	420	20	29	3.5	97.8	0.7	1.5
3	32.7	629	15	40	1.9	96.1	0.9	3.0
4	43.6	838	15	41	2.2	97.4	0.7	1.8
5	54.5	1048	10	36	2.7	97.1	0.7	2.2

[a] Butadiene: 22.3% in benzene-butene-1 (70/30 % wt), temperature = 10°C.
[b] in toluene at 30°C.

Table 3—Effect of temperature[a]

No.	Temp., °C	Conv., %	$[\eta]^b$ dl g^{-1}	Microstructure			$\bar{M}_w$
				% *cis*	% *trans*	% vinyl	$\bar{M}_n$
1	5	3	3.4	98.3	0.5	1.2	2.3
2	10	20	3.2	98.4	0.9	0.7	2.4
3	15	23	2.9	98.5	0.9	0.6	2.4

[a] Butadiene: 22.3% wt in benzene-butene-1 (70/30 wt %), Cobalt (II)-2-ethylhexoate: 0.05 mmole phgm, DEAC: 10.9 mmole phgm, time = 20 min
[b] in toluene at 30°C

higher alpha olefins[8], allenes[8], cyclooctadiene[9], imides[10], ketones[11], alcohols[12], esters[13] and nitriles[13], thiophene[14], triethylamine[14] and anisole[14]. No information is available in the literature on the relative efficiencies of these diverse range of chain transfer agents. To generate this result, a series of olefinic and diolefinic organic compounds were examined for their relative chain transfer efficiency. Methylallene, C_4 raffinate from naphtha cracker containing 0.6% wt of methylallene, ethylene and propylene were studied at various concentrations. The results are shown in Tables 4-7. The results show that either neat methylallene (500 ppm) or methylallene (100-150 ppm) contained in 2-3 mole % C_4 raffinate is sufficient for the desired level of molecular weight reduction (from an intrinsic viscosity of 4 to 2.5 corresponding to a Mooney viscosity of 40-50) without affecting either the extent of conversion, microstructure or molecular weight distribution. Ethylene was effective at 1 mole %

Table 4—Effect of methylallene on polymerization of 1,3-butadiene[a]

No.	Methylallene ppm (based on monomer	Conv. %	$[\eta]^b$ dl g^{-1}	Microstructure			$\overline{M}_w/\overline{M}_n$
				% *cis*	% *trans*	% vinyl	
1	Nil	41	4.2	98.3	0.6	1.1	2.95
2	500	40	2.5	98.2	0.6	1.2	2.57
3	1000	44	2.0	98.3	0.6	1.1	2.43
4	1500	49	1.4	98.1	0.8	1.1	2.09
5	2000	49	1.3	97.1	1.0	1.9	1.94

[a]Butadiene: 22.8% wt in benzene-butene-1 (70/30 % wt), Co(II): 3.02 mg phgm, DEAC: 10.6 mmole phgm, temperature = 10°C, time = 10 min.

[b]in toluene at 30°C.

Table 5—Effect of C_4 raffinate on polymerization of 1,3-butadiene[a]

No.	C_4 raffinate mole % based on monomer	Conv. %	$[\eta]^b$ dl g^{-1}	Microstructure			$\overline{M}_w/\overline{M}_n$
				% *cis*	% *trans*	% vinyl	
1	Nil	32	4.1	98.4	0.5	1.1	3.56
2	1	38	3.6	97.9	0.9	1.2	2.89
3	2	30	3.0	98.2	0.7	1.1	3.14
4	3	33	2.6	98.6	0.5	0.9	2.97
5	4	26	2.4	98.3	0.7	1.0	2.62
6	5	30	2.2	98.3	0.7	1.0	3.17

[a]Butadiene: 21.3% wt in benzene-butene-1 (70/30 % wt), Co(II): 3.1 mg phgm, DEAC: 10.9 mmole phgm, temperature = 10°C, time = 30.60 min.

[b]in toluene at 30°C.

Table 6—Effect of ethylene on polymerization of 1,3-butadiene[a]

No.	Ethylene, mole % based on monomer	Conv., %	$[\eta]^b$ dl g^{-1}	Microstructure		
				% *cis*	% *trans*	% vinyl
1	—	23	4.0	98.2	0.7	1.1
2	1.0	29	2.8	97.8	0.9	1.3
3	2.0	29	2.6	98.1	0.6	1.3
4	3.0	35	2.45	98.1	0.7	1.2
5	4.1	40	2.2	97.5	0.9	1.6
6	5.2	27	2.1	98.1	0.8	1.1

[a]Butadiene: 22.5% wt in benzene-butene-1 (70/30 wt %), Co(II): 3.1 mg phgm, DEAC: 10.9 mmole phgm, temperature = 10°C, time = 30.60 mm.

[b]in toluene at 30°C.

concentration. Propylene showed no molecular weight depression even up to 7 mole % concentration. A series of liquid olefins and dienes, namely, styrene, divinylbenzene, dicyclopentadiene, and norbornadiene, were examined as chain transfer agents at 1 mole % concentration in benzene (Table 8). Clearly, styrene, divinylbenzene and norbornadiene were ineffective as they caused significant lowering of conversion. However, dicyclopentadiene at 0.25 mole % concentration reduced the molecular weight to the desired level without any adverse effect on either conversion or microstructure (Table 9).

These results clearly establish the superiority of allenic hydrocarbons as efficient chain transfer agents in butadiene polymerization. Ethylene is effective at higher concentrations. Higher alpha olefins and aromatic olefins are ineffective. Among the liquid dienes, dicyclopentadiene show good promise as a potentially useful chain fransfer agent.

The mechanism of chain transfer in 1,3-butadiene polymerization is best understood in terms of a stable propagating π-allylic cobalt complex which is intercepted by insertion of an olefin to form a less stable σ-complex[2]. The latter spontaneously undergoes β-hydrogen scission to form a terminal unsaturation in the polymer and an active Co^{I}-H species capable of initiating fresh polymerization. The higher chain transfer efficiency of allenes or ethylene could be due to the ease of insertion of these less olefins into the active centre compared to α-substituted olefins such as propylene or styrene or

Table 7—Effect of propylene on polymerization of 1,3-butadiene[a]

No.	Propylene mole % based on monomer	Conv., %	$[\eta]^b$ dl g^{-1}	Microstructure		
				% *cis*	% *trans*	% vinyl
1	—	23.0	4.0	98.2	0.7	1.1
2	3.0	33	3.7	98.0	0.6	1.4
3	4.4	26	3.7	97.8	0.9	1.3
4	6.0	26	3.7	98.6	0.5	0.9
5	7.3	55	3.5	98.6	0.9	1.5

[a]Butadiene: 22.5% wt in benzene-butene-1 (70/30 wt %), Co(II): 3.1 mg phgm, DEAC: 10.9 mmole phgm, temperature = 10°C, time = 30.60 min.
[b]in toluene at 30°C

Table 8—Effect of other chain transfer agents on polymerization of 1,3-butadiene[a]

	Divinylbenzene 1 mole %	Styrene 1 mole %	Norbornadiene 1 mole %	No. Chain transfer agent
$[\eta]^b$, dl g^{-1}	3.9	2.99	—	4.2-4.5
Conv., %	10	3	3	25
cis, %	96	97	93	97

[a]Butadiene: 10 g in 65 mL benzene, Co(II): 0.04 mmole phgm, DEAC 12.5 mmoles phgm, temperature = 25°C, time = 20 min.
[b]in toluene at 30°C.

Table 9—Effect of dicyclopentadiene on polymerization of 1,3-butadiene[a]

	Mole % based on monomer	Conv. %	$[\eta]^b$ dl g^{-1}	Microstructure		
				% *cis*	% *trans*	% vinyl
a3	2	—	—	—	—	—
	1.0	4	2.5	—	—	—
	0.5	6	1.9	98.0	0.9	1.1
	0.25	23	2.2	97.6	1.0	1.4
	0.125	27	3.3	98.0	0.9	1.1
	Nil	25	4.2-4.5	97.4	1.0	1.6

[a]Butadiene: 10g in 65 mL benzene, Co(II): 0.04 mmoles phgm, DEAC: 12.5 mmoles phgm, temperature = 25°C, time = 30 min.
[b]in toluene at 30°C.

norbornadiene. Aromatic/bicyclic olefins also cause catalyst deactivation. The improved chain transfer efficiency of dicyclopentadiene is somewhat surprising. The fact that one of the double bonds, though disubstituted, is far removed from the C-7 carbon could be responsible for this observation.

References

1 Natta G & Porri L, *Polymer chemistry of synthetic elastomers*, edited by J P Kennedy and E Tornqvist (John Wiley and Sons, Inc. New York) 1969, Part 2, 597.

2 Upadhyay V K & Sivaram S, *Indian J Technol*, 25 (1987) 669.

3 *Belg Pat*, 876, 015 (1979) to Polysar; *Chem Abstr*, 92 (1979) 60147n; and *Ital Pat*, 594, 618 (1959) to Montecatini; *Chem Abstr*, 55 (1959) 12936i.

4 Hunig J A J, Burford R P & Chaplin J, *J Polym Sci Polym Chem Ed*, 21 (1983) 2559.

5 Boor J, *Ziegler-Natta catalysis and polymerizations* (Academic Press, New York) 1979.

6 Gippin M, *Ind Eng Chem Prod Res Dev*, 4 (1965) 160.

7 Natta G & Porri L, *Polymer chemistry of synthetic elastomers*, edited by J P Kennedy and E Tornqvist (John Wiley and Sons, Inc, New York) 1969, Part 2, 621.

8 Longiave C, Castelli R & Ferraris M, *Chim Ind (Milan)*, 44 (1962) 725.

9 *Ger Pat*, 1, 959, 932 (1970) to Japanese Geon Co; *Chem Abstr*, 73 (1970) 46414y.

10 *Jap Pat*, 6, 910, 277 (1969) to Mitsui Toatsu Chem Ind Ltd; *Chem Abstr*, 71 (1969) 82393h.

11 *Jap Pat*, 6, 910, 276 (1969) to Mitsui Toatsu Chem Ind Ltd; *Chem Abstr*, 71 (1969) 82392g.

12 *Jap Pat*, 13072 (1965) to Bridgestone Tire Co Ltd; *Chem Abstr*, 65 (1965) 12389c.

13 *Nath Pat*, 6 505, 496 (1965) to Chemische Werke Huls A-Z; *Chem Abstr*, 64 (1966) 14394e.

14 *E Ger Pat*, 99807 (1973); *Chem Abstr*, 81 (1974) 50295t.