Polymer Journal, Vol. 5, No. 3, pp 231—242 (1973)

Equibinary (*cis*-1,4—1,2)Polybutadiene

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(Received December 25, 1972)

ABSTRACT: The equibinary (*cis*-1,4—1,2)polybutadiene was prepared using a catalyst of molybdenum compound—aluminum compound. The preparative conditions for this polybutadiene were studied. The catalyst of $R'_3Al/MoCl_3(OR)_2$ with molar ratio of less than 4 gave the 1,2-polybutadiene, whereas a molar ratio of more than 6 yielded the equibinary (*cis*-1,4—1,2)polybutadiene. Two kinds of catalytic species were formed by changing the Al/Mo molar ratio. The catalysts $MoCl_5$ and $MoO_2(AA)_2$ were also investigated. An experiment with a ternary catalyst of $MoO_2(AA)_2$—Et_3Al—Et_2AlCl suggests that the amount of Et and Cl is an influential factor in the catalyst for the preparation of equibinary (*cis*-1,4—1,2)polybutadiene. Various kinds of halogen compounds such as CBr_4, *t*-BuCl, and I_2 can be used as the halogen component. There was no temperature dependence for the microstructure of the polybutadiene.

The ^{13}C-NMR analysis of the polymer showed that the sequence distribution of the dyad was nearly random and far from an alternating one. The sequence distribution suggests that the polymerization proceeded *via* random polymerization of the *cis*-1,4- and 1,2-coordinated monomer or the head-to-head or the tail-to-tail polymerization of the monomer pair of the *cis*-1,4- and 1,2-coordinated on the catalyst.

KEY WORDS Equibinary Polybutadiene / (*cis*-1,4—1,2)Polybutadiene / Molybdenum Compound / Organoaluminum Compound / ^{13}C-NMR / Dyad Distribution / Random Distribution / Microstructure / Polymerization Mechanism /

In the polymerization of conjugated diolefins, the polymers having a 1 : 1 composition with respect to the unit of geometrical isomer, *i.e.*, *cis*-1,4—3,4-polyisoprene,[1] 1,2—3,4-polyisoprene,[1] and *cis*-1,4—*trans*-1,4-polybutadiene,[2] were named by Dawans, *et al.*, as equibinary polydienes. An alternating coordination mechanism was proposed[1,3,4] for their formation. The catalysts employed were CoX_2-Grignard reagent-alcohol and nickel complexes. On the other hand, the authors discovered independently[5] the formation of the equibinary (*cis*-1,4—1,2)polybutadiene using the $Co(AA)_3$—Et_3Al—H_2O catalyst system and proposed a random propagation mechanism, on the basis of the determination of the sequence distribution by gas-chromatographic analysis of the ozonolysis product of the polymers.[6] Takeuchi, *et al.*,[7] also reported the preparation of equibinary (*cis*-1,4—1,2)polybutadiene by the R_3Al—H_2O—CH_3SSCH_3—$CoBr_2(Ph_3P_2)$ catalyst.

The present paper deals with the preparation of the equibinary (*cis*-1,4—1,2)polybutadiene with a new catalyst system of molybdenum compound—organoaluminum compound and the determination of the sequence distribution of the polymers by means of ^{13}C-NMR analysis.

EXPERIMENTAL

Materials

Butadiene (Japan Synthetic Rubber Co.) was purified by being passed successively through columns packed with potassium hydroxide, activated alumina, and Molecular Sieves 3A, followed by standing for a night at −78°C in order to eliminate moisture in the monomer.

Commercial trichloromolybdenum dialkoxide

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($MoCl_3(OR)_2$), molybdenum pentachloride ($MoCl_5$) (Mitsuwa Chemical Reagents Co.), molybdenyl (VI) acetylacetonate ($MoO_2(AA)_2$) (Dotite), trimethylaluminum (Me_3Al), triethylaluminum (Et_3Al), tri-*n*-propylaluminum (*n*-Pr_3Al), tri-*n*-butylaluminum (*n*-Bu_3Al), tri-isobutylaluminum (iso-Bu_3Al), diethylaluminum ethoxide (Et_2AlOEt), diethylaluminum chloride (Et_2AlCl), and ethylaluminum sesquichloride ($Et_{1.5}AlCl_{1.5}$) (Texas Alkyls Inc.) were used without further purification. Ethylaluminum dichloride ($EtAlCl_2$) (Texas Alkyls Inc.) was purified by vacuum distillation.

Solvents (Guaranteed grade) were dried over Molecular Sieves 4A and bubbled with oxygen-free dry nitrogen.

Polymerization

The polymerization was performed under oxygen-free dry nitrogen atmosphere. At −78°C molybdenum compounds, solvent, organoaluminum compounds, and butadiene were placed successively in a 100-m*l* ampule. The ampule was sealed and subjected to polymerization. After polymerization reaction the reaction mixture was poured into methanol. Crude polymers often contained gels or solvent insoluble materials which were removed by extraction with isopropyl ether.

Properties of the Polymer

The microstructure of the soluble polymer in isopropyl ether was determined by infrared spectrophotometry according to the method of Morero, *et al.*[8] Intrinsic viscosity was measured in a toluene solution at 30±0.05°C with an Ubbelohde-type viscometer. ^{13}C-NMR spectrum of the polymer was measured by a pulsed Fourier transform NMR method with a JEOL-PS-100 NMR equipped with PFT-100-FT attachment and EC-6 computer[10] at a polymer concentration of *ca.* 30% (w/v) in deuterochloroform at *ca.* 30°C. Molecular weight distribution of the polymer was measured by gel permeation chromatography by the use of tetrahydrofuran as a solvent.

RESULTS AND DISCUSSION

Catalysts

(*i*) *$MoCl_3(OR)_2$—R'_3Al Catalyst System.* When butadiene is polymerized by the $MoCl_3$(O*n*-Bu)$_2$—Et_3Al catalyst, equibinary (*cis*-1,4—1,2)polybutadiene is obtained depending on the polymerization condition, as shown in Table I. As the Al/Mo molar ratio is increased, the microstructure of the polymer changes from the 1,2-structure to the equibinary (*cis*-1,4—1,2)-structure. In all cases a small amount of *trans*-1,4-structure existed. Figure 1(a) illustrates the microstructure of the resulting polymer prepared at 0°C with various amounts of Et_3Al added to $MoCl_3$(O*n*-Bu)$_2$. Below the molar ratio of 6 the polymer is exclusively 1,2-polybutadiene and above this ratio it forms equibinary (*cis*-1,4—1,2)polybutadiene. Figure 1(b) shows the polymer yield as a function of $Et_3Al/MoCl_3$(O*n*-Bu)$_2$. There are two peaks, at molar ratios of 3 and 10. These results suggest that the active species for the equibinary polymer is not a mixture of that for 1,2-polymer and that for 1,4-polymer. Indeed, the polymer has a unimodal distribution

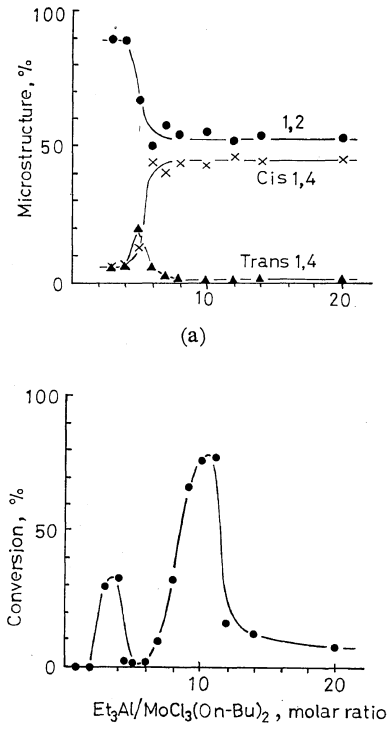


Figure 1. Effect of $Et_3Al/MoCl_3$(O*n*-Bu)$_2$ molar ratio on microstructure (a) and conversion (b) (from Table I): polymerization conditions, 0°C, 48 hr.

Table I. Polymerization by $MoCl_3(On\text{-}Bu)_2$—Et_3Al catalyst[a]

Polymn. temp. °C	Al/Mo,[b] molar ratio	Polymn. time, hr	Polymer conv, %	(iso-Pr)$_2$O-insoluble part,[c] %	Microstructure, %			
					cis	1,2	*trans*	[η]
−30	1	50	0					
−30	4	50	0					
−30	8	50	6.8	11.6	42.2	56.6	1.2	—
0	1	48	0					
0	2	48	0					
0	3	48	29.2	28.9	5.6	89.6	4.8	—
0	4	48	32.5	—	6.2	89.2	4.6	—
0	4.5	48	1.7	44.6	—	—	—	—
0	5	48	0.4	66.3	12.8	67.4	19.8	—
0	6	48	1.3	54.8	44.5	50.2	5.3	—
0	7	48	9.1	50.8	39.6	58.5	1.9	—
0	8	48	32.0	45.5	44.0	54.5	1.5	1.04
0	9	48	66.9	41.4	—	—	—	0.78
0	10	48	76.2	55.3	42.6	56.0	1.4	0.78
0	11	48	76.5	34.1	—	—	—	0.55
0	12	48	16.1	15.4	46.2	52.5	1.3	—
0	14	48	11.9	61.1	44.0	54.2	1.8	—
0	20	48	7.4	57.7	44.9	53.7	1.4	—
30	1	18	0					
30	2	18	60.2	0	8.4	85.3	6.3	—
30	3	18	100	0	8.0	85.9	6.1	—
30	4	18	14.6	—	4.1	88.4	7.5	—
30	4.5	18	13.1	18.6	—	—	—	—
30	5	18	2.6	43.3	8.2	79.1	12.7	—
30	6	18	5.5	49.8	40.3	56.6	3.1	—
30	7	18	3.9	52.9	39.0	57.2	3.8	—
30	8	18	41.7	23.6	43.3	54.8	1.9	0.85
30	9	18	52.5	39.5	—	—	—	0.80
30	10	18	52.6	59.9	42.9	55.9	1.2	0.71
30	11	18	30.3	44.5	—	—	—	—
30	14	18	12.4	43.1	44.9	52.9	2.2	—
30	20	18	10.8	41.7	44.6	53.5	1.9	—
60	5	7	6.7	48.6	8.5	73.1	18.4	—
60	6	7	3.3	41.4	33.3	50.5	16.2	—
60	7	7	6.6	43.4	32.1	55.2	12.7	—
60	8	7	19.8	56.3	42.5	55.1	2.4	—
60	10	7	21.3	48.1	41.5	56.4	2.1	—
60	20	7	2.1	73.1	45.3	50.6	4.1	0.70

[a] $MoCl_3(On\text{-}Bu)_2$, 0.2 mmol; butadiene, 64.7 mmol; toluene, 20 ml.
[b] $Et_3Al/MoCl_3(On\text{-}Bu)_2$.
[c] In total polymer.

curve for molecular weight, from the results of gel permeation chromatography as shown in Figure 2. Polymerizations at 30° and 60°C afforded results for the microstructure and the yields similar to those at 0°C.

In Figure 3 it can be seen that the temperature has little effect on the microstructure of polymers produced between −30° and 60°C (at Al/Mo of 8). On the other hand, the authors reported[6] that the polymerization temperature in the $Co(AA)_3$—Et_3Al—H_2O catalyst system did not influence the constancy of 50-% *cis*-content,

Table II. Polymerization by $MoCl_3(OR)_2$—R'_3Al catalyst[a]

$MoCl_3(OR)_2$, mmol	R'_3Al, mmol	Al/Mo,[b] molar ratio	Polymer conv, %	(iso-Pr)$_2$O-insoluble part,[c] %	Microstructure, %		
					cis	1,2	*trans*
$MoCl_3(On\text{-}Bu)_2$—Me_3Al							
0.2	0.8	4	9.6	25.5	12.8	81.0	6.2
0.2	1.2	6	3.5	70.8	38.8	52.2	9.0
0.2	1.6	8	8.3	81.2	43.2	51.7	5.1
0.2	2.0	10	14.0	63.2	44.6	53.4	2.0
$MoCl_3(On\text{-}Bu)_2$—$n\text{-}Pr_3Al$							
0.2	0.4	2	83.1	0	7.9	83.4	8.7
0.2	0.8	4	5.4	36.8	7.8	77.7	14.5
0.2	1.2	6	2.6	22.2	37.0	52.7	10.3
0.2	1.6	8	15.1	52.8	45.7	50.4	3.9
0.2	2.0	10	4.0	50.0	55.3	41.0	3.7
0.2	4.0	20	15.7	96.4	56.2	39.1	4.7
$MoCl_3(On\text{-}Bu)_2$—$n\text{-}Bu_3Al$							
0.2	0.4	2	34.0	0	5.0	86.3	8.7
0.2	0.8	4	15.7	25.5	7.1	82.8	10.1
0.2	1.2	6	4.3	60.0	38.7	50.8	10.5
0.2	1.6	8	3.1	45.4	40.8	53.1	6.1
0.2	2.0	10	1.1	75.0	42.6	53.0	4.4
0.2	4.0	20	3.4	83.3	45.7	49.5	4.8
$MoCl_3(On\text{-}Bu)_2$—iso-Bu_3Al							
0.2	0.8	4	81.9	0	4.2	90.1	5.7
0.2	1.2	6	2.3	31.6	14.1	49.1	36.8
0.2	2.0	10	1.3	45.2	24.0	44.7	31.3
0.2	4.0	20	1.9	—		[e]	
$MoCl_3(OEt)_2$—iso-Bu_3Al							
0.2	0.8	4	71.9	0	9.7	84.0	6.3
0.2	1.2	6	1.5	17.6		[e]	
0.2	2.0	10	0.4	30.0		[e]	
$MoCl_3(OMe)_2$—Et_3Al							
0.2	0.8	4	100	0	8.3	85.7	6.0
0.2	1.2	6	17.9	13.7	7.6	85.6	6.8
0.2	1.6	8	6.9	36.5	13.6	79.9	6.5
0.2	2.0	10	50.4	46.5[d]	44.4	54.0	1.6
$MoCl_3(OEt)_2$—Et_3Al							
0.2	0.8	4	6.9	45.2	4.9	87.1	8.0
0.2	1.2	6	23.6	43.7	42.4	56.0	1.6
0.2	2.0	10	3.6	40.8	43.6	53.2	3.2

[a] Butadiene, 64.7 mmol; toluene, 20 m*l*; polymerization temp, 30°C; time, 22 hr.
[b] $R'_3Al/MoCl_3(OR)_2$.
[c] In total polymer.
[d] The sample was offered for ^{13}C-NMR measurement.
[e] Not characteristic.

but that above −15°C the *trans*-content increased at the expense of the 1,2-content. Considering the temperature effect, the regulation of the microstructure of the molybdenum catalyst system seems to be stronger than that of the cobalt catalyst system.

Table II summarizes the results of polymerization by the $MoCl_3(OR)_2$—R'_3Al system. Me, Et, and *n*-Bu radicals can be used as R and Me, Et, *n*-Pr, and *n*-Bu radicals can be used as R′

Table III. Effect of organometallic compounds[a]

Organometallic compound, mmol	Me/Mo,[b] molar ratio	Polymer conv, %	Microstructure, %		
			cis	1,2	*trans*
Et_2AlCl					
1.6	8	3.9		[c]	
2.0	10	1.2	43.0	24.0	33.0
4.0	20	0.7	51.6	36.0	12.4
$Et_{1.5}AlCl_{1.5}$					
1.6	8	24.9	37.0	13.1	49.9
2.0	10	30.3		[c]	
4.0	20	7.4	35.5	14.6	49.9
$EtAlCl_2$					
1.6	8	100	33.3	24.7	42.0
2.0	10	84.0	43.6	10.2	46.2
4.0	20	83.4	—	—	—
Et_2AlOEt					
0.4	2	0			
0.8	4	86.9	6.2	85.9	7.9
1.2	6	73.1	7.6	85.0	7.4
1.6	8	50.3	7.9	83.3	8.8
2.0	10	100	11.5	78.2	10.3
4.0	20	100	9.7	82.2	8.1
BuLi					
1.0	5	trace	—	—	—
2.0	10	trace	—	—	—
4.0	20	93.4	44.1	17.9	38.0
Et_2Zn					
1.0	5	0.6		[c]	
2.0	10	trace	—	—	—
4.0	20	trace	—	—	—

[a] $MoCl_3(On\text{-}Bu)_2$, 0.2 mmol; butadiene, 64.7 mmol; toluene, 20 m*l*; polymerization temp, 30°C; time, 30 hr (Et_nAlCl_{3-n}), 23 hr (the others).
[b] Organometallic compound/$MoCl_3(On\text{-}Bu)_2$.
[c] Not characteristic.

Table IV. Effect of solvents[a]

Solvent	Polymer conv, %	$(iso\text{-}Pr)_2O$ insoluble part,[b] %	Microstructure, %		
			cis	1,2	*trans*
Toluene	52.6	59.9	42.9	55.9	1.2
Hexane	4.3	36.4	42.3	53.3	4.4
Anisole	1.5	65.4	24.4	62.0	13.6
$ClCH_2CH_2Cl$	23.3	39.3	46.9	51.0	2.1
$Cl_2C{=}CHCl$	1.3	46.2	40.6	51.6	7.8
C_6H_5Cl	40.2	32.1	46.9	51.5	1.6
o-$Cl_2C_6H_4$	32.7	34.4	46.4	52.0	1.6

[a] $MoCl_3(On\text{-}Bu)_2$, 0.2 mmol; Et_3Al, 2.0 mmol; butadiene, 64.7 mmol; solvent, 20 m*l*; polymerization temp, 30°C; time, 18 hr.
[b] In total polymer.

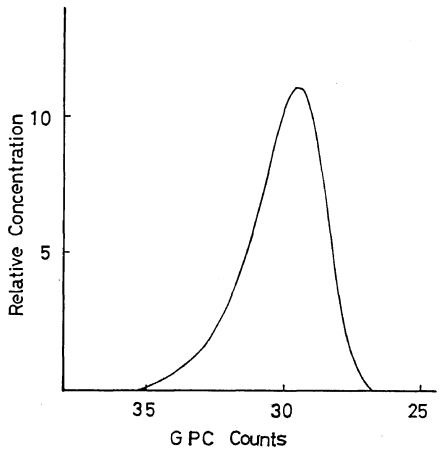


Figure 2. GPC curve of equibinary (*cis*-1,4—1,2) polybutadiene. Measured at 35°C in tetrahydrofuran solvent, preparation conditions of polymer: $MoCl_3(On\text{-}Bu)_2$, 0.5 mmol; Et_3Al, 4 mmol; butadiene, 64.7 mmol; toluene, 20 m*l*; polymerization temp and time, 30°C and 19 hr; polymer conv, 81%; *cis*- and 1,2-content, 44.7 and 54.1%.

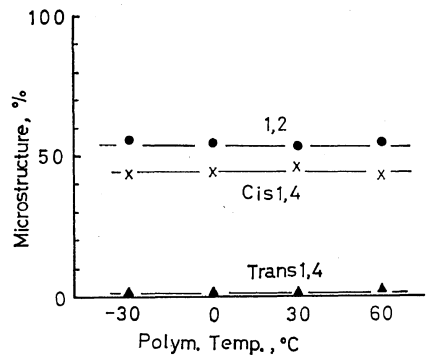


Figure 3. Effect of polymerization temperature on microstructure (from Table I): $Et_3Al/MoCl_3(On\text{-}Bu)_2=8$.

for the preparation of the equibinary polybutadiene. When R′ is a bulky group such as the iso-butyl radical, the 1,2-polybutadiene is obtained and the equibinary polybutadiene cannot be obtained. These facts suggest that the alkyl of the catalyst complex may play an important role in the selection of the monomer, perhaps due to selective coordination.

The organometallic compounds other than trialkylaluminum were also examined with $MoCl_3(On\text{-}Bu)_2$ Using Et_2AlCl, $Et_{1.5}AlCl_{1.5}$, $EtAlCl_2$, Et_2AlOEt, BuLi, and Et_2Zn, the equibinary polybutadiene is not obtained, as shown in Table III. In particular, Et_2AlOEt gives the 1,2-polybutadiene, but not the equibinary polybutadiene, irrespective of the Al/Mo molar ratio (Al/Mo=2—20), although it exhibits high polymerization activity.

Table IV shows the effect of polymerization solvents on the polymerization activity and on the polymer microstructure. Aromatic hydrocarbons or halogenated hydrocarbons yield a homogeneous polymerization system for the equibinary polybutadiene. Hexane decreases the polymerization activity, because its poor solvating power for the molybdenum compound, gives a heterogeneous dispersion. Anisole has a large effect on the microstructure of the resultant polymer, probably owing to its high coordination power to the catalyst. Trichloroethylene diminishes the polymerization activity very much.

(*ii*) *$MoCl_5$—Et_3Al Catalyst System.* $MoCl_5$ can be used as a molybdenum compound. As shown in Table V, butadiene polymerized to give the equibinary (*cis*-1,4—1,2)polymer by the $MoCl_5$—

Table V. Polymerization by $MoCl_5$—Et_3Al catalyst[a]

Et_3Al, mmol	Al/Mo,[b] molar ratio	Polymer conv, %	(iso-Pr)$_2$O-insoluble part,[c] %	Microstructure, %		
				cis	1,2	*trans*
0.4	2	8.7	44.2	41.5	54.3	4.2
0.8	4	7.2	53.7	42.9	54.0	3.1
1.2	6	3.6	66.6	45.5	49.8	4.7
2.0	10	4.3	94.0	47.8	47.3	4.9

[a] $MoCl_5$, 0.2 mmol; butadiene, 64.7 mmol; toluene, 20 m*l*; polymerization temp, 30°C; time, 21 hr.
[b] $Et_3Al/MoCl_5$.
[c] In total polymer.

Et_3Al catalyst system in the Al/Mo molar ratio of 2 to 10. The 1,2-polybutadiene was not produced at varied molar ratios. This catalyst system gave the equibinary polybutadiene at a lower Al/Mo molar ratio than that of the $MoCl_3(OR)_2$—R'_3Al catalyst system, as is mentioned

Table VI. Polymerization by $MoO_2(AA)_2$—Et_2AlCl catalyst[a]

Et_2AlCl, mmol	Al/Mo,[b] molar ratio	Polymer conv, %	(iso-Pr)$_2$O-insoluble part,[c] %	Microstructure %		
				cis	1,2	*trans*
0.4	2	100	0	2.5	92.4	5.1
0.8	4	100	0	6.9	88.0	5.1
1.2	6	8.7	29.6	7.5	86.1	6.4
1.6	8	4.1	27.3	30.3	63.9	5.8
2.0	10	5.3	42.1	41.8	55.0	3.2
2.4	12	4.7	19.3	45.9	50.0	4.1
2.8	14	5.5	22.7	45.4	50.5	4.1
3.2	16	5.4	24.8	46.2	50.0	3.8
4.0	20	5.3	33.6	43.3	53.6	3.1
6.0	30	3.9	34.9	44.5	51.4	4.1
8.0	40	2.1	38.4	47.4	48.8	3.8
10.0	50	1.4	32.0	48.2	48.0	3.8

[a] $MoO_2(AA)_2$, 0.2 mmol; butadiene, 64.7 mmol; toluene, 20 m*l*; polymerization temp, 30°C; time, 23 hr.
[b] $Et_2AlCl/MoO_2(AA)_2$.
[c] In total polymer.

Table VII. Effect of alkylaluminum compounds[a]

Et_nAlCl_{3-n}, mmol	Al/Mo,[b] molar ratio	Polymer conv, %	(iso-Pr)$_2$O-insoluble part,[c] %	Microstructure, %		
				cis	1,2	*trans*
Et_3Al						
0.4	2	0.8	70.5	14.5	48.4	37.1
0.8	4	4.4	83.1		[d]	
1.2	6	2.1	93.4		[d]	
1.6	8	2.2	90.8		[d]	
2.0	10	1.9	89.1	46.8	42.5	10.7
$Et_{1.5}AlCl_{1.5}$						
0.4	2	100	0	3.0	90.4	6.6
0.8	4	5.4	18.5	6.0	79.3	14.7
1.2	6	2.2	29.7	18.8	72.5	8.7
1.6	8	0.8	68.9	36.9	47.3	15.8
2.0	10	1.0	63.3	41.7	41.4	16.9
4.0	20	0.2	67.6	44.6	23.7	31.7
$EtAlCl_2$						
0.4	2	10.8	10.0	6.3	87.0	6.7
0.8	4	4.2	59.0	11.9	61.0	27.1
1.2	6	trace	—	33.6	21.6	44.8
1.6	8	trace	—	42.9	12.2	44.9
2.0	10	trace	—	54.1	9.3	36.6
4.0	20	trace	—	48.9	9.8	41.3

[a] $MoO_2(AA)_2$, 0.2 mmol; butadiene, 64.7 mmol; toluene, 20 m*l*; polymerization temp, 30°C; time, 23 hr.
[b] $Et_nAlCl_{3-n}/MoO_2(AA)_2$.
[c] In total polymer.
[d] Not characteristic.

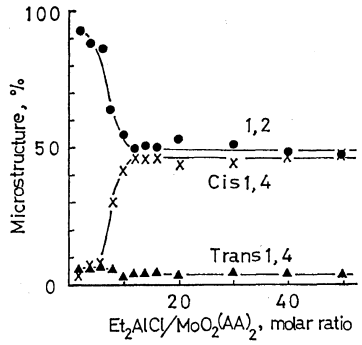


Figure 4. Effect of $Et_2AlCl/MoO_2(AA)_2$ molar ratio on microstructure at 30°C (from Table VI.)

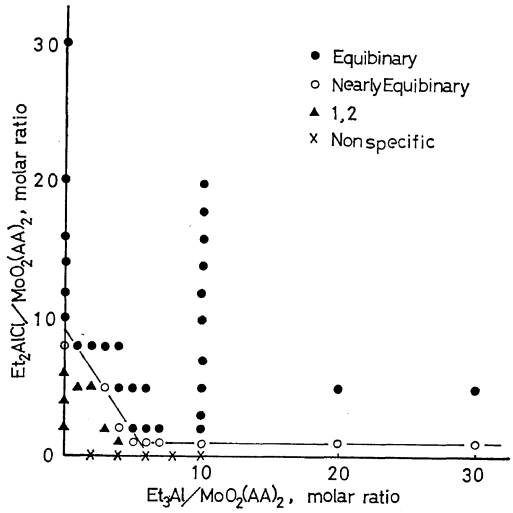


Figure 5. Effect of catalyst composition on polymer structure. Polymerization conditions: $MoO_2(AA)_2$, 0.2 mmol; butadiene, 64.7 mmol; toluene, 20 ml; polymerization temp, 30°C.

in the previous section. This might come from fact that $MoCl_5$ had such a poor solubility to the solvent, so that the effective Al/Mo molar ratio in the solution became considerably higher.

(iii) $MoO_2(AA)_2$—Et_2AlCl Catalyst System. $MoO_2(AA)_2$—Et_2AlCl catalyst system also afforded the equibinary (*cis*-1,4—1,2) polybutadiene, as shown in Table VI. In this case, there also exist two catalyst regions depending on the Al/Mo molar ratios: one for the 1,2-polybutadiene and another for the equibinary polybutadiene. Figure 4 shows the relation between the catalyst composition and the microstructure of the resultant polybutadienes. The Al/Mo molar ratio for the 1,2-polybutadiene is below 6 and that for the equibinary polybutadiene is above 9.

As a cocatalyst for $MoO_2(AA)_2$ catalyst, Et_3Al, $Et_{1.5}AlCl_{1.5}$ and $EtAlCl_2$ were examined, but they did not give the equibinary polybutadiene, as shown in Table VII. At low Al/Mo molar

Table VIII. Polymerization by $MoO_2(AA)_2$—Et_3Al—$EtAlCl_2$ catalyst[a]

Et_3Al, mmol	Al_1/Mo,[b] molar ratio	$EtAlCl_2$, mmol	Al_2/Mo,[c] molar ratio	Polymer conv, %	(iso-Pr)$_2$O-insoluble part,[d] %	Microstructure, %		
						cis	1,2	*trans*
2.0	10	0.1	0.5	2.0	50.5	47.5	48.7	3.8
2.0	10	0.2	1	7.3	65.6	48.4	49.4	2.2
2.0	10	0.3	1.5	10.0	65.0	47.3	50.5	2.2
2.0	10	0.5	2.5	16.9	69.7	47.6	50.0	2.4
2.0	10	1.0	5	21.2	50.6	44.5	53.8	1.7
2.0	10	2.0	10	10.1	40.9	43.9	54.4	1.7
0.2	1	1.0	5	0.9	66.7	35.9	43.1	21.0
0.4	2	1.0	5	1.4	80.0	29.5	62.2	8.3
0.6	3	1.0	5	2.7	30.0	42.1	52.7	5.2
0.8	4	1.0	5	7.1	24.0	48.8	47.6	3.6
1.0	5	1.0	5	10.0	10.0	48.9	47.7	3.4
1.2	6	1.0	5	15.4	27.8	48.7	48.2	3.1

[a] $MoO_2(AA)_2$, 0.2 mmol; butadiene, 64.7 mmol; toluene, 20 ml; polymerization temp, 30°C; time, 23 hr; condition of catalyst preparation, Mo—TL—$EtAlCl_2$—Et_3Al—BD.

[b] $Et_3Al/MoO_2(AA)_2$.

[c] $EtAlCl_2/MoO_2(AA)_2$.

[d] In total polymer.

Table IX. Effect of halogen compounds[a]

Halogen compound, mmol	X/Mo,[b] molar ratio	Polymer conv, %	(iso-Pr)$_2$O-insoluble part,[c] %	Microstructure, %		
				cis	1,2	*trans*
CBr_4						
0.2	1	2.3	50.0	52.8	42.7	4.5
0.6	3	2.6	88.9	51.4	38.7	9.9
1.0	5	trace	—	—	—	—
I_2						
0.2	1	2.9	90.0	49.1	47.6	3.3
0.6	3	3.4	66.7	56.2	40.7	3.1
1.0	5	2.9	90.0	57.7	38.2	4.1
t-C_4H_9Cl						
0.2	1	2.9	80.0	53.5	40.2	6.3
0.6	3	8.6	43.3	53.0	45.4	1.6
1.0	5	10.9	31.6	54.7	43.8	1.5
CCl_4						
0.2	1	5.7	45.0	52.6	36.2	11.2
0.6	3	1.7	90.0	36.2	39.6	24.2
1.0	5	3.1	54.5	36.7	27.4	35.9
CCl_3COOH						
0.2	1	trace	—	—	—	—
0.6	3	7.1	84.0	45.7	37.0	17.3
1.0	5	9.4	93.9	16.8	51.0	32.2
CCl_3CHO						
0.2	1	3.1	72.7	53.0	36.5	10.5
0.6	3	1.1	90.0	38.0	44.8	17.2
1.0	5	4.9	29.4	5.1	86.3	8.6
CCl_3CH_2OH						
0.2	1	2.9	80.0	47.7	43.5	8.8
0.6	3	8.6	43.3	35.5	52.6	11.9
1.0	5	10.9	31.6	48.3	42.4	9.3

[a] $MoO_2(AA)_2$, 0.2 mmol; Et_3Al, 2.0 mmol; butadiene, 64.7 mmol; toluene, 20 m*l*; polymerization temp, 30°C; time, 23 hr; condition of catalyst preparation, Mo—X—TL—(−78°C)—Al—BD.

[b] Halogen compound/$MoO_2(AA)_2$.

[c] In total polymer.

ratio, $Et_{1.5}AlCl_{1.5}$ and $EtAlCl_2$, together with $MoO_2(AA)_2$, gave the 1,2-polybutadiene, but Et_3Al provided neither the equibinary nor the specific polymer.

However, the $MoO_2(AA)_2$—Et_3Al system in combination with a halogen compound such as $EtAlCl_2$, CBr_4, *t*-C_4H_9Cl, or I_2 gave the equibinary polybutadiene, as shown in Tables VIII and IX.

Moreover, the molar ratio of alkyl radical and molybdenum seemed to be an important factor in both the catalyst systems of $MoCl_3(OR)_2$—R'_3Al and of $MoO_2(AA)_2$—Et_2AlCl. The effect of the Et/Mo and Cl/Mo molar ratios in the $MoO_2(AA)_2$—Et_3Al—Et_2AlCl catalyst system on the characteristics of the resultant polymers is shown in Figure 5. Here, x and y indicate the $Et_3Al/MoO_2(AA)_2$ and $Et_2AlCl/MoO_2(AA_2)$ molar ratios respectively. The oblique line on the graph expresses $3x+2y=18$; in other words, one of preparative conditions for the equibinary polybutadiene is that $3x+2y>18$. This means the total number of ethyl radicals added to the molybdenum atom should be more than 18. In the case of the $MoCl_3(On\text{-}Bu)_2$—Et_3Al catalyst system, the preparative condition for the equibinary polybutadiene is that Al/Mo is more than 6, or Et/Mo>18 (see Figure 1). The horizontal

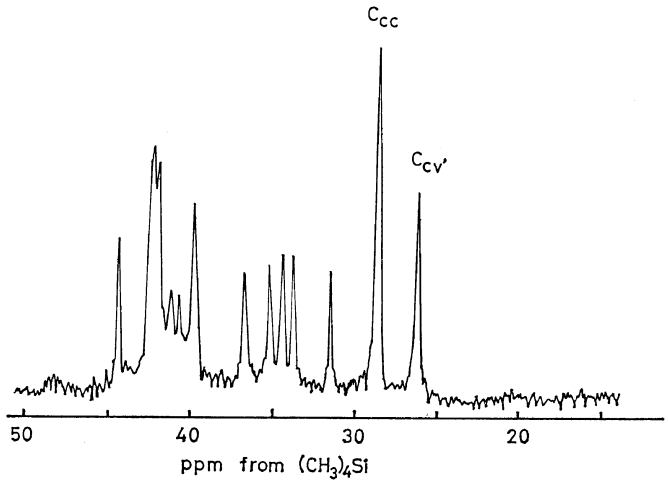


Figure 6. ^{13}C-NMR chart of equibinary (*cis*-1,4—1,2)polybutadiene (aliphatic part) (500 times accumulation): Preparative conditions of polymer; see Table II.

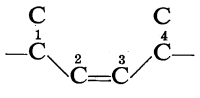
line in the graph expresses $y=1$, and indicates that the preparative condition for the equibinary polybutadiene is $y>1$. This means the chlorine atom per molybdenum atom ratio should be larger than 1. The chlorine atom would be related to bridge structures of active species.

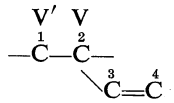
Characterization of Equibinary (cis-1,4—1,2) Polybutadiene

Intrinsic viscosities of the polymers were measured in toluene solution at 30°C and were found to be less than 1.1 d*l*/g. Total unsaturation determined by infrared spectrophotometry according to the method of Morero[8] is very close to the theoretical value of polybutadiene. This fact indicates that no cyclization is occuring in the polymers.

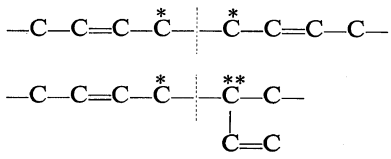
The equibinary polybutadiene is almost completely soluble in isopentane, unlike[9] *cis*-1,4-polybutadiene or syndiotactic 1,2-polybutadiene. Consequently, the equibinary polybutadiene is considered to be a 'copolymer' composed of equimolar amounts of *cis*-1,4-units and 1,2-units.

Figure 6 shows a ^{13}C-NMR chart of the aliphatic part measured with the equibinary polybutadiene. Assignment and analysis are based on the method of Araki, *et al.*[10] The *cis*-1,4-, *trans*-1,4-, and 1,2-content of the sample are 44.4, 1.6, and 54.0%, respectively, which were determined by the IR method. Here, C, V′ and V denote the aliphatic carbon (1,4-carbon) of *cis*-1,4-unit, the aliphatic head carbon (1-carbon) of 1,2-unit, and the aliphatic tail carbon (2-carbon) of 1,2-unit, respectively.



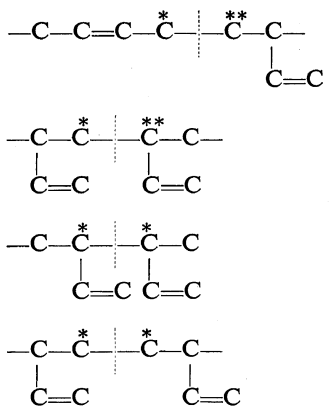


Then, each carbon of polybutadiene consisting of the *cis*-1,4- and 1,2-unit is discriminated among nine kinds of carbon, considering dyads of units, as follows: For instance, C· means 1 and/or 4 carbon of the *cis*-unit, and the suffix C—C means *cis*—*cis* dyad. According to this method, for example, C_{C-V} expresses the aliphatic carbon of the *cis*-unit bonded to the aliphatic tail carbon of the 1,2-unit and V_{C-V} is the aliphatic tail carbon of the 1,2-unit bonded to the *cis*-unit and so on.



*→C_{C-C}

*→C_{C-V}, **→V_{C-V}



$*\rightarrow C_{C-V'}$, $**\rightarrow V'_{C-V'}$,

$*\rightarrow V'_{V-V'}$, $**\rightarrow V_{V-V'}$

$*\rightarrow V_{V-V}$

$*\rightarrow V'_{V'-V'}$

The NMR chart reveals the following facts. First, the peak assinged to $C_{C-V'}$ is observed at 26.2 ppm; this fact indicates the existence of the *cis*-1,4—1,2-dyad in the polymer. Second, the peak assigned to C_{C-C} is found at 28.6 ppm, illustrating the presence of the *cis*-1,4—*cis*-1,4-dyad in the polymer. Third, the peaks assigned to $V'_{V-V'}$ and $V_{V-V'}$ appear at 40.7—42.3 ppm and at 39.8 and 42.0—42.3 ppm, respectively, showing, that there is the 1,2—1,2-dyad in the polymer. However, the information contained in $V'_{V'-V'}$ and V_{V-V} has not yet been clarified. Consequently, the polymer is far from a block or an alternating polymer of the *cis*-1,4- and 1,2-unit. The assignments of other carbons than those mentioned above are now in progress,[12] but F_{CC}, F_{CV}, and F_{VV} can be calculated; These express the fractions of the *cis*-1,4—*cis*-1,4 dyad, the *cis*-1,4—1,2 dyad, and the 1,2—1,2 dyad, respectively. The fractions of the peak area of C_{C-C} and $C_{C-V'}$ are 0.16 and 0.09 respectively. From the relation $V'_{C-V'}=C_{C-V'}=0.09$, the following equations are derived.

$$\textit{cis}\text{-1,4-content } (0.45)=C_{C-C}+C_{C-V'}+C_{C-V}$$

And consequently,

$$C_{C-V}=0.45-C_{C-C}-C_{C-V'}=0.20$$

From the relations

$$V_{C-V}=C_{C-V}=0.20$$

and

$$\text{1,2-content } (0.55)=V_{V-V}+V_{V-V'}+V'_{V'-V'}+V'_{V-V'}+V_{C-V}+V'_{C-V'}$$

it follows that,

$$V_{V-V}+V_{V-V'}+V'_{V'-V'}+V'_{V-V'}=0.55-V_{C-V}-V'_{C-V'}=0.26$$

Then, the dyad fractions, (F_{CC}, F_{CV}, and F_{VV}) are given by the following equations:

$$F_{CC}=C_{C-C}=0.16$$

$$F_{CV}=C_{C-V}+C_{C-V'}+V_{C-V}+V'_{C-V'}=0.58$$

and

$$F_{VV}=V_{V-V}+V_{V-V'}+V'_{V'-V'}+V'_{V-V'}=0.26$$

On the other hand, if the sequence distribution of *cis*-1,4-unit and 1,2-unit of this polymer is random, each dyad fractions is calculated according to Bernoullian statistics.[11]

$$F_{CC}=0.45\times 0.45=0.20$$

$$F_{CV}=2\times 0.45\times 0.55=0.50$$

and

$$F_{VV}=0.55\times 0.55=0.30$$

The values of F_{CC}, F_{CV}, and F_{VV} estimated from ^{13}C-NMR are relatively close to those estimated by the random assumption. Therefore, the sequence distribution of the equibinary polybutadiene synthesized by the molybdenum catalyst system is thought to be mostly random.

Tentative Polymerization Mechanism

The equibinary (*cis*-1,4—1,2)polybutadiene synthesized by the molybdenum catalyst system is considered to be random with respect to the sequence distribution of *cis*-1,4- and 1,2-units. Consequently, the polymerization cannot be explained by an alternating coordination mechanism such as that proposed by Dawans, *et al.*[1,3,4]

There exist several possibilities for the pro-

duction of the equibinary (*cis*-1,4—1,2)polybutadiene through various structures of growing polymer terminals or various modes of monomer coordination. For example, when the polymer terminal forms a π-allyl complex in antiform, the *cis*-1,4- and 1,2-structures result from the attack of the 4-position and the 2-position of π-allyl, respectively, and the random equibinary polybutadiene may be formed if the reactivity of both positions is equal to each other. The mode of monomer coordination may also affect the structure of the polymer, depending on the 1,4- and 1,2-coordination on the catalyst; in this case the formation of the random equibinary polybutadiene requires equivalency in the coordination and the reactivity of coordinated monomers. The catalyst whose number of available sites for coordination is limited to three may be favorable for simultaneous coordination of 1,4- and 1,2-forms. In this case, the polymerization of the coordinated monomer pair may be favorable to form the equibinary polybutadiene having 50 mol% of the *cis*-1,4—1,2-dyads by its polymerization of the head-to-head or the tail-to-tail. However, such a mechanism as this should be considered with further NMR analysis in higher order, because the triad information, if available, might indicate the absence of C—C—C and V—V—V triads in this case. This is a subject for future study.[12]

Acknowledgement. We are grateful to Mr. M. Imanari (JEOL Co. Ltd., Tokyo) for his help in measuring the ^{13}C-NMR spectra. We also would like to express our appreciation to Messrs Y. Araki, K. Tanaka, and K. Yamamoto (Bridgestone Tire Co., Tokyo) for their helpful advice in analyzing the ^{13}C-NMR spectra.

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