cis—Vinyl-1 : 1 Polymer of Butadiene

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ABSTRACT: With the catalyst system, Co(acac)$_3$—AlEt$_3$—H$_2$O, cis-1,4—1,2-equimolar binary polybutadiene was obtained. The gas-chromatographic analysis of the ozonolysis product of the polymers showed that the sequence distribution was of the random but not alternating type. The preference of microstructure in polymerization is discussed briefly under the consideration of monomer coordination on the catalyst complex and the stability of the growing chain-end.

KEY WORDS   Equimolar Binary Polybutadiene/cis—Vinyl-polybuta-
diene / Cobalt Trisacetylacetonate / Triethylaluminum / Ozonolysis /
Dyad Distribution / Random Distribution / Rate / Mechanism /
Microstructure /

In the polymerization of diolefin, the polymer of a 1 : 1 composition of the geometrical isomer unit, i.e, cis-1,4—3,4-polyisoprene,[1] 1,2—3,4-polyisoprene,[1] and cis-1,4—trans-1,4-polybutadiene,[2] was reported by Dawans, et al. They called it equibinary polymer and they proposed an alternating coordination mechanism[1,3] for its formation. The catalysts employed were CoX$_2$—Grignard reagent—alcohol and nickel complexes, respectively. Takeuchi, et al.,[4] also reported the preparation of cis-1,4—1,2-equibinary polybutadiene with AlR$_3$—H$_2$O—CH$_3$SSCH$_3$—CoBr$_2$-(Ph$_3$P)$_2$ catalyst. On the other hand, the authors found independently[5] the formation of cis-1,4—1,2-equibinary polybutadiene by use of the Co-(acac)$_3$—AlEt$_3$—H$_2$O catalyst system, but the mechanism remained obscure.

This report is a detailed study of the equibinary polymer with the determination of sequence distribution.

EXPERIMENTAL

Commercial cobalt trisacetylacetonate (Co-(acac)$_3$) (Tokyo Kasei Chemicals Co.) and triethyl-

aluminum (AlEt$_3$) (Texas Alkyl Co.) were used without further purification. Butadiene (Japan Synthetic Rubber Co.) was purified by being passed successively through columns packed with KOH, activated alumina and Molecular Sieves 3A, followed by being trapped for a night at −78°C to exclude moisture in the monomer. Toluene was washed and distilled by conventional methods and stored over sodium wire.

Co(acac)$_3$, toluene, and AlEt$_3$ were placed in a 100 ml beverage bottle, and then aged for fifteen minutes at room temperature. After cooling to −78°C, a catalytic amount of water was added by use of a microsyringe under agitation by a high-rotation magnetic stirrer. Mixing was continued for forty minutes while the temperature was raised up to room temperature. After the bottle was cooled again to −78°C, butadiene monomer was added and it was sealed with a crown-cap and subjected to polymerization. The above procedures were carried out under nitrogen atmosphere. The microstructure of polybutadiene was evaluated by IR according to the method of Morero. Reduced viscosity was measured in toluene solution at 30±0.05°C with an Ostwald-type viscometer.

For the investigation of sequence distribution of polybutadiene microstructure, quantitative ozonolysis of the polymers followed by

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gas-chromatographic analysis of the ozonolysis products was carried out according to the modified Beroza—Bierl method.[6] The amount of 1,4—1,4-unit dyad was estimated by the amount of succinic dialdehyde, i.e.,

$$\sim\sim CH_2CH=CHCH_2-CH_2CH=CHCH_2\sim\sim$$
$$\longrightarrow OHCCH_2CH_2CHO$$
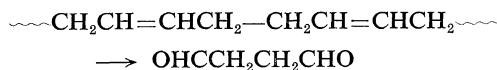
An example of the experimental procedure is as follows. Ozone prepared by Ozone Generator (Nippon Ozone K. K.) was introduced into 5 m*l* of dichloromethane solution containing 27 mg cis-1,4-polybutadiene (cis-1,4 content 98%) at -30——$50°C$ until the red colour of the indicator changed to blue. One drop of dichloromethane solution of Suden red was used as an indicator. The reduction of ozonides to aldehydes was carried out by the addition of triphenyl phosphine to the solution of ozonides followed by standing at room temperature for one night. Here, the amount of triphenyl phosphine was 1.5 times as much as the theoretical one based on the content of C=C unit in the original polymer. The amount of succinic dialdehyde produced was measured by 100-Mc NMR with use of toluene as an internal standard as well as by gas-chromatographic analysis. In the experiments with varied amounts of sample, the value in both analyses were identical. The yield of succinic dialdehyde based on the content of C=C unit in the original polymer was ca. 80%. Similar procedures were used for the analysis of samples 1 to 11. F_{AA} was calculated by the following equation with use of the gas-chromatographic peak area of succinic dialdehyde.

$$F_{AA}(\%)=\frac{\dfrac{\text{Peak area of a sample}}{\text{Amount of a sample}}}{\dfrac{\text{Peak area of }cis\text{-1,4-polybutadiene}}{\text{Amount of }cis\text{-1,4-polybutadine}}}\times 96$$

Details of the experimental procedures will be published elsewhere.

Catalyst

Among various kinds of catalysts investigated, a ternary system of $Co(acac)_3$—$AlEt_3$—H_2O was found to be one of the best for equibinary polybutadiene. The experimental data obtained under several conditions with catalysts having various compositions are summarized in Tables I and II. It was found that the addition of water is an essential factor for equibinary polymerization, since a simple mixture of $Co(acac)_3$ and a large amount of $AlEt_3$ in the absence of water affords a linear dimer of butadiene, i.e., 3-methylheptatriene-1,4,6.[7] The ternary catalyst yields almost an equimolar binary cis-1,4—1,2 polymer in a wide range of catalyst composition. Table I indicates that the activity runs parallel to the amount of $Co(acac)_3$ and is enhanced by the addition of a large amount of $AlEt_3$ (more than ten times as much as $Co(acac)_3$), while the microstructure is independent of the ratios of both catalyst components.

The amount of water added to $AlEt_3$ seems to be important, since the catalyst activity attains its maximum at about an equimolar water content, as shown in Figure 1.

The microstructure is slightly affected by added water, and an equimolar amount of water to $AlEt_3$ is favorable for the equibinary polymerization as illustrated in Figure 2. The polymer

Table I. Effect of $AlEt_3$ and $Co(acac)_3$[a]

Expt no.	$AlEt_3$, mmol	$Co(acac)_3$, mmol	Polymerization time, hr	Yield, %	Reduced viscosity, η_{sp}/c	Microstructure, %		
						trans	1,2	cis
K-289-1	13.3	0.33	2	14.3	18.3 (0.229)[b]	7	48	45
-2	13.3	0.66	2	50.0	64.9 (0.463)	4	41	55
-3	13.3	0.88	2	75.7	27.9 (0.384)	4	40	56
-4	6.7	1.33	18	15.7	3.8 (0.468)	3	45	52
-5	5.3	1.33	18	4.3	7.6 (0.421)	4	43	52

[a] $H_2O/AlEt_3$ molar ratio, 0.9; butadiene, 133 mmol; toluene, 25 m*l*; polymerization temp, $-15°C$.
[b] Polymer concentration, g/100 m*l*.

Table II. Effect of polymerization temperature and $H_2O/AlEt_3$ molar ratio on microstructure[a]

Expt no.	Polymerization temp, °C	$H_2O/AlEt$, molar ratio	Polymerization time, hr	Polymer yield, %	Microstructure, %		
					trans	1, 2	*cis*
K-292-1	30	0	16	0.7	11	59	30
2	30	0.2	16	4.3	43	34	23
3	30	0.4	16	37.1	15	47	38
4	30	0.6	1.5	70.0	9	43	48
5	30	0.8	1.0	87.1	12	39	49
6	30	1.0	1.0	72.9	11	39	50
7	30	1.2	14	52.9	20	36	44
8	30	1·4	14	24.3	30	30	40
K-284-1[b]	0	0	42	2.9	3	49	48
2	0	0.2	42	9.9	6	49	45
3	0	0.4	42	21.4	8	47	45
4	0	0.6	42	30.0	5	35	60
5	0	0.8	18	35.7	5	52	43
6	0	1.0.	2	48.6	6	40	54
7	0	1.2	2	55.7	4	30	66
8	0	1.4	2	68.6	7	32	61
K-288-1[b]	−15	0	20.5	1.4	2	60	38
2	−15	0.2	20.5	15.7	4	47	49
3	−15	0.4	20.5	8.6	3	53	44
4	−15	0.6	20.5	26.7	3	50	47
5	−15	0.8	17	32.9	3	53	44
6	−15	1.0	3.25	37.1	2	48	49
7	−15	1.2	3.25	51.4	4	42	54
8	−15	1.4	17	40.0	3	44	53
K-302-1	−30	0	5	Trace	5	56	39
2	−30	0.2	5	Trace	—	—	—
3	−30	0.4	5	5.7	3	52	45
4	−30	0.6	1.5	35.7	3	50	47
5	−30	0.8	1	40.0	5	43	52
6	−30	1.0	1	75.7	4	41	55
7	−30	1.2	1.5	34.3	6	40	54
8	−30	1.4	2	15.7	5	38	57
K-318-1	−43	0	Several days	Trace	—	—	—
2	−43	0.2	18.5	3.0	1	68	31
3	−43	0.4	2	8.7	1	54	45
4	−43	0.6	1.25	22.8	1	53	46
5	−43	0.8	1	54.8	1	54	49
6	−43	1.0	17	21.4	4	48	48
7	−43	1.2	17	3.0	3	46	51

[a] $Co(acac)_3$, 1.33 mmol; $AlEt_3$, 13.3 mmol; toluene, 25 m*l*; butadiene, 133 mmol.

[b] In the K-284 and K-288 experimental series, polymer yields are lower than that of other series. This might be caused by the fact that mixing for catalyst preparation was not carried out with a magnetic stirrer but by hand-shaking. Effect of mixing for catalyst preparation on the microstructure of polymer obtained seems slight considering the linearities of the figures which show variations of microstructure.
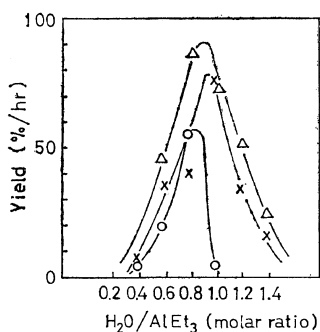
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Figure 1. Effect of water added to the activity. Polymerization temp: ◯, −43°C; ×, −30°C; △, 30°C.
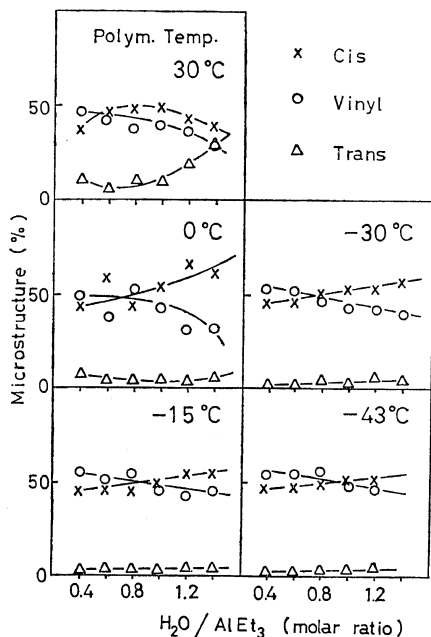
Figure 2. Effect of water added to the catalyst preference of microstructure.

Figure 3. Effect of temperature on the catalyst preference of microstructure. $H_2O/AlEt_3$ (molar ratio): ◯, 0.8; ●, 1.0.
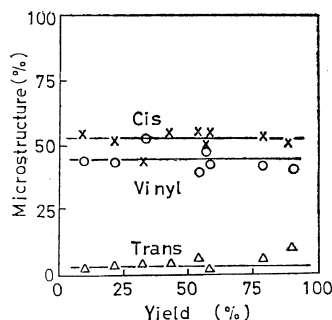
Figure 4. Microstructure independence of the extent of polymerization: $H_2O/AlEt_3$ (molar ratio), 0.8; polymerization temp, −15°C.

is composed of about 50% *cis*-1,4 and 50% 1,2 together with a small amount of *trans* unit.

The polymerization temperature does not influence the constancy of 50% *cis*-content, while above −15°C the *trans* structure increases at the expense of the 1,2-structure, as shown in Figure 3.

Polymer Homogeneity

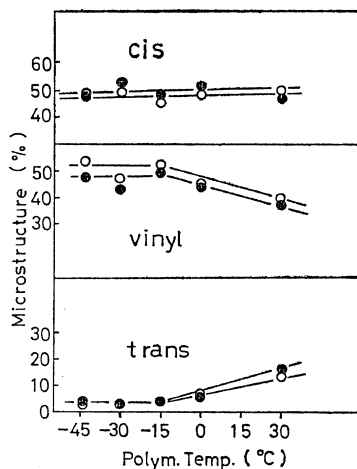It was found that the polymer is of homogeneous composition but not a mixture of the *cis*-, *trans*-, and 1,2-units. Figure 4 indicates that the microstructure is constant irrespective of the extent of polymerization or the polymer yield. The infrared spectrum of the polymer did not show the absorption due to syndiotactic 1,2-polybutadiene.[8]

The fractionation of the polymer by extraction with isopentane at room temperature keeps

Table III. Extraction with isopentane

Polymer, %	Original, 100	Extracted	
		Soluble, 70	Residue, 30
Microstructure	*cis* 48%	*cis* 41%	*cis* 64%
	1,2 49%	1,2 57%	1,2 32%

Table IV. Microstructure and succinic dialdehyde

Sample no.	Source	Microstructure, %		Succinic dialdehyde produced (%) based on *cis*-1,4-polybutadiene
		cis + *trans*	1,2	
		F_A	F_B	F_{AA}
1	BR 01	98.0	2.0	96.0
2	Diene NF-35	88.0	12.0	84.0
3	Emulsion polybutadiene	82.2	17.8	68.5
4[a]	BuLi—orthoacid ester catalyzed polybutadiene	63.5	36.5	45.8
5[a]	BuLi—orthoacid ester catalyzed polybutadiene	39.0	61.0	18.0
6[a]	BuLi—orthoacid ester catalyzed polybutadiene	20.0	80.0	6.0
7	Equibinary polybutadiene	47.1	52.9	22.4
8	Equibinary polybutadiene	52.9	47.1	26.2
9	Equibinary polybutadiene	52.1	47.9	23.9
10	Equibinary polybutadiene	53.7	46.3	25.1
11	Equibinary polybutadiene	51.3	48.7	28.8

[a] Polymers were prepared according to the method in ref 11.

the composition of the polymer almost constant, as shown in Table III. On the other hand, isopentane is known[4] to dissolve amorphous 1,2-polybutadiene but not syndiotactic 1,2- or *cis*-1,4-polybutadiene. In other words, the polymer is not a blend but a real "copolymer" of *cis*-1,4- and 1,2-units.

Sequence Distribution

The polymer was a *cis*-1,4—1,2-equibinary polymer but the question, whether it is alternating or random cannot be answered until an analysis of the dyad or the higher sequence distribution is obtained. Up to the present, NMR analysis has not been sensitive to problems of this kind. The method of quantitative ozonolysis was found to be an effective tool for solving the problem. The amount of succinic dialdehyde obtained from the prepared polymers and commercially available polybutadienes is listed in Table IV. Since the yield in succinic dialdehyde does not exceed 80% of the theoretical values for 98% *cis*-1,4-polybutadiene as shown in the experimental section, the accuracy of the analytical results listed in Table IV is not sufficient to discuss the degree of randomnesss. However, it can be said at least that *cis*-1,4—1,2-equibinary polybutadiene contains a large amount of the 1,4—1,4 unit.
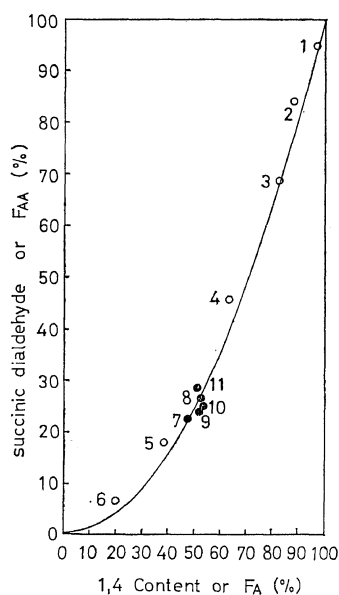

Figure 5. Bovey's relation between F_A and F_{AA}. Numbers in the figure are the same as that in Table IV.

Figure 5 demonstrates the correlation between 1,4—1,4- dyad (F_{AA}) and 1,4-fraction (F_A) and shows that the former is equal to the square of the latter. This means that the presence of 1,4-unit of the equibinary polybutadiene is

considerably random according to Bernoullian statistics.[9]

Polar Additives, Solvents, and Active Hydrogen Compounds

The effect of active hydrogen compounds, polar additives and solvents was investigated.

Active hydrogen compounds like halogeno-acetic acid, -phenol, -alcohol can be used in

Table V. Effect of active hydrogen compounds on microstructure[a]

Expt no.	Reactant	Time, hr	Yield, %	Microstructure, %		
				trans	1,2	cis
K-329-1	CF₃COOH	48	4.2	3	37	60
2	CCl₃COOH	48	21.1	5	40	55
3	CCl₂HCOOH	48	25.3	15	49	36
4	2,4,6-Trichlorophenol	24	11.3	3	60	37
5	2,2,2-Trichloroethanol	48	11.0	10	49	41
6	1,4-Butanediol	48	5.6	4	63	33
K-316-5	H₂O	1	69.4	3	49	48

[a] Co(acac)₃, 0.5 mmol; AlEt₃, 5 mmol; active hydrogen compound, 4.5 mmol; butadiene, 7.2 g; polymerization temp, −15°C.

Table VI. Effect of polar additives on microstructure[a]

Additive	Additive / Co(acac)₃, molar ratio	Time, hr	Yield, g	Microstructure, %		
				trans	1,2	cis
PPh₃	1.0	36	0.2	6	48	46
PiBu₃	1.0	36	0.1	19	37	44
Ph₂PCH₂CH₂PPh₂	1.0	48	0.2	11	45	44
NEt₃	2.0	2.5	1.3	3	49	48
C₅H₅N	1.0	—	nil	—	—	—
PhNMe₂	2.0	0.5	2.1	2	52	46
Me₂NCH₂CH₂NMe₂	0.5	48	0.6	15	43	42
PhOMe	2.0	0.5	1.5	2	51	47
PhCOOEt	2.0	0.5	2.3	3	49	48
PhSMe	2.0	19	1.3	3	52	45

[a] The order of addition is as follows: Co(acac)₃, 0.5 mmol; additive, AlEt₃, 5 mmol; H₂O, 4 mmol; butadiene, 7.2 g; toluene, 15 ml; polymerization temp, −15°C.

Table VII. Effect of solvents, on microstructure[a]

Solvent	Time, hr	Yield, %	Microstructure, %		
			trans	1,2	cis
Hexane	2.5	13.9	1	37	62
Benzene	0.5	36.1	3	48	49
Toluene	3.25	37.1	2	48	49
Cyclohexane	2	15.3	5	48	47
Anisole	0.5	36.1	3	42	55
Monochlorobenzene	14	13.9	6	33	61
1,1,2,2-Tetrachloroethane	2	25.0	1	2	97
Trichloroethylene	2	91.7	3	6	91
trans-Dichloroethylene	14	80.5	2	5	93

[a] Co(acac)₃, 0.5 mmol; AlEt₃, 5 mmol; H₂O, 5 mmol; butadiene, 133 mmol; solvent, 15 ml; polymerization temp, −15°C.

place of water as shown in Table V. Polar additives like alkyl or aryl phosphine, amine, sulfide, and ether were found to decrease the activity of the catalyst, but to have little effect on the microstructure of the resulting polymer, as shown in Table VI.

The polar solvents do not play an influential role except for the halogenated hydrocarbon solvents which modify the catalyst favorable to *cis*-1,4-polymerization, as shown in Table VII.

DISCUSSION

Experimental results show that the ternary system of $Co(acac)_3$—$AlEt_3$—H_2O, having a composition of about 0.3—2 : 10 : 10 in molar ratio, yields an equibinary polybutadiene of *cis*-1,4 and 1,2. The formation of *cis*-1,4 units seems to be controlled by the addition of water to the catalyst. The polar additives and active hydrogen compounds do not seem to be influential, but a large amount of chlorinated hydrocarbon used as solvent alters the catalyst so that it favors *cis*-1,4-polymerization, although detailed studies on the solvent effect are necessary to confirm this phenomena. Ozonolysis analysis shows the equibinary polymer to be not alternating but random.

The above facts suggest that unit preference is governed by a simple factor and not a cooperative one and, accordingly, alternating coordination seems in conceivable in this case. As controlling factors, the coordination of the catalyst to the monomer and that to the polymer end are important, and the effect of the catalyst may be concerned with either factor. The *cis* polymerization is interpreted by the concept involving *cis* coordination of butadiene monomer.[1] Accordingly, the equimolar preference of the *cis* unit is likely to arise from the equimolar coordination of the *cis* and vinyl units, as illustrated by (A) and (B) in Figure 6, respectively. The addition of water or active hydrogen compounds may adjust the acidity of the catalyst to equimolar coordination. The existence of the small temperature-coefficient of *cis*-1,4-preference suggests that the equimolar coordination is quite a strong one.

On the other hand, vinyl-preference concurs with *trans*-preference and much depends on the
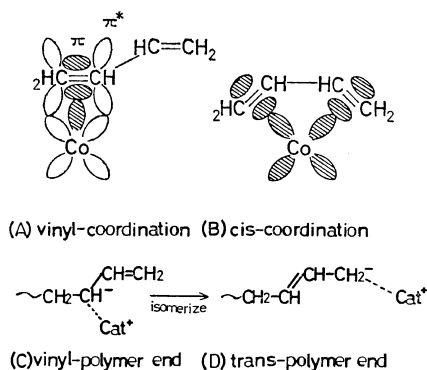

(A) vinyl-coordination (B) cis-coordination

(C)vinyl-polymer end (D) trans-polymer end

Figure 6. Schematic diagram of monomer coordination and polymer end.

temperature, high temperature favoring *trans*-preference. This phenomenon suggests that vinyl-*trans*-preference arises from factors other than coordination; for example, the growing chain end may exist favorably in 1,2-form (C), but is isomerized to *trans* form (D) at elevated temperature due to less steric hindrance in the *trans* form.

Marechal, *et al.*,[10] concluded from X-ray analysis that the equibinary polymer of *cis*-1,4- and *trans*-1,4-polybutadiene is an alternating copolymer. If so, there may be several cases for 1 : 1 equibinary polymers according to the preparation. In order to reach any conclusion on the structure of 1 : 1 copolymer, analysis is necessary for each copolymer and any further speculation should be based on the case in point.

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