

PREPARATION AND CHARACTERIZATION OF *cis*-1,4-POLYBUTADIENE CONTAINING A FRACTION OF *trans*-1,4-POLYBUTADIENE*

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ABSTRACT

Polymerization of butadiene catalysed first with $V(acac)_3-Al(i-Bu)_2Cl$, then with $Co(acac)_3-H_2O-Al(i-Bu)_2Cl$ has been studied. The polymer obtained was identified to be a new variety of *cis*-1,4-polybutadiene which contained a fraction of *trans*-1,4-polybutadiene chemically bonded to the *cis*-1,4-polybutadiene chains. Its molecular weight and *trans*-1,4 content can be regulated by varying the catalyst composition and concentration as well as other polymerization conditions. The *trans*-1,4 fraction, although it presents only in 9–16%, forms a crystalline phase in the matrix at room temperature and facilitates the crystallization of the polymer.

INTRODUCTION

Interest in preparing multiphase polymers, because of their special features not appearing in homogeneous polymers of similar compositions, has been stimulated since the sixties. For instance, in the synthetic rubber field, two new varieties of *cis*-polybutadiene, TAC^[1] and VCR^[2], have been produced in commercial scale. TAC was said to contain 9% *trans*-1,4-polybutadiene and VCR, 10% syndiotactic 1,2-polybutadiene. Both showed better physico-mechanical properties than conventional *cis*-polybutadiene.

Our interest is to explore the possibility of synthesizing a multiphase polybutadiene which has a *trans*-1,4-polybutadiene segment chemically bonded to a *cis*-1,4-polybutadiene chain and to study some of its properties in relation to its *trans*-1,4 content.

EXPERIMENTAL

Reagents

Butadiene was of solution polymerization grade. Toluene was of analytical grade, refluxed over $LiAlH_4$ and redistilled before use. $V(acac)_3$, $Co(acac)_3$ and $Al(i-Bu)_2Cl$ were prepared according to literature^[3, 4, 5]. $V(acac)_3$ was diluted to concentration of 1×10^{-4} mol/ml and $Co(acac)_3$ to 2.4×10^{-5} mol/ml with toluene respectively. The measured chlorine content and aluminium content of $Al(i-Bu)_2Cl$ were 5.22 g·atom/ml and 4.93 g·atom/ml respectively. H_2O -saturated toluene was kept at 38°C (abbr. Tol_w) and its H_2O .

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content was 3.95×10^{-5} mol/ml.

Polymerization

All glass apparatus used in polymerization were thoroughly dried and purged with nitrogen thrice before use. Polymerization was carried out at 40°C in glass ampoules having a volume of ca. 100 ml each, in which were added by syringes of different sizes 10 ml toluene solution of $V(acac)_3$ and $Al(i-Bu)_2Cl$ and 90 ml of toluene solution of butadiene. The concentration of butadiene in the mixture was 10 g/100 ml solution. After polymerization for one hour a required amount of Tol_w and toluene solution of $Co(acac)_3$ were added through the rubber stopper. The polymerization was continued for another three hours and then terminated with alcohol containing 2% antioxidant 2246. The product was washed with the same solvent and dried under vacuum below 40°C.

Characterization

Intrinsic viscosity was determined at 30°C using an Ubbelohde viscometer with toluene as solvent. Average molecular weight was calculated according to the following equation:

$$[\eta]_{tol}^{30^\circ C} = 3.06 \times 10^{-4} M^{0.725}$$

Microstructure was determined with Perkin-Elmer 599B infrared spectrometer. The contents of *cis*-1,4, *trans*-1,4 and 1,2 configuration were calculated according the following equations:

$$\begin{aligned} \text{Cis-1,4} & \quad (\%) = D_{738} / (D_{738} + 0.1464 D_{967} + 0.1883 D_{911}) \\ \text{Trans-1,4} & \quad (\%) = D_{967} / (D_{967} + 6.830 D_{738} + 1.285 D_{911}) \\ 1,2 & \quad (\%) = D_{911} / (D_{911} + 5.316 D_{738} + 0.7782 D_{967}) \end{aligned}$$

Solubility behavior was measured both in toluene at -20°C and in $CS_2-CH_3COC_3H_7$. The procedure for measuring solubility behavior in toluene was as follows: Several grams of dried polymer was weighed and dissolved in 250 ml of toluene in an Erlenmeyer flask at 50°C. The solution thus prepared was cooled to -20°C and centrifuged if precipitate appeared. The precipitate was redissolved in 100 ml toluene at 50°C, reprecipitated at -20°C and washed with small amount of toluene twice. The filtrates were combined and treated with alcohol containing antioxidant 2246 (2%) to precipitate the soluble portion. Both the soluble portion and insoluble portion were dried under vacuum below 40°C and their corresponding microstructures were determined.

Procedure used in $CS_2-CH_3COC_3H_7$ was: Several grams of sample was weighed and dissolved in 200 ml CS_2 at 50°C and then another 50 ml methyl propyl ketone was added to precipitate the insoluble portion.

Degree of crystallinity was determined with a Rigaku X-ray diffractometer, CuK_α radiation with Ni filter, 35 KV, 15 mA; T_g and T_m with torsional pendulum apparatus and half crystallization time with a linear expansion apparatus.

RESULTS AND DISCUSSION

Polymerization of butadiene with dual catalyst systems

It is well known that in the polymerization of butadiene $V(acac)_3-Al(i-Bu)_2Cl$ catalyst

system favours the formation of high *trans*-1,4-polybutadiene^[6] which is a crystalline polymer having a melting point of 145°C and $\text{Co}(\text{acac})_3\text{-H}_2\text{O-Al}(\text{i-Bu})_2\text{Cl}$ system leads to *cis*-1,4-polybutadiene^[7], a commercial synthetic rubber with its melting point close to 0°C. When both of these catalysts are present, polymerization of butadiene may give a multiphase polybutadiene or only one species when the activity of one catalyst prevails over that of the other. In order to prepare a polymerization product having both *trans*-1,4 and *cis*-1,4-polybutadiene chains, the initiation method mentioned in the experimental part was adopted in the present work.

Effect of $\text{Co}(\text{acac})_3/\text{Bd}$ on yield and molecular weight

As found in preliminary experiments a polybutadiene containing 80–95% *cis*-1,4- and 20–5% *trans*-1,4-polybutadiene with good yield could be prepared with catalyst of the following composition range:

$$\text{V}(\text{acac})_3/\text{Bd} = 0.5\text{--}1.0 \times 10^{-4}; \quad \text{Co}(\text{acac})_3/\text{Bd} = 2\text{--}4 \times 10^{-5};$$

$$\text{Al}(\text{i-Bu})_2\text{Cl}/\text{Bd} = 6\text{--}10 \times 10^{-3}; \quad \text{and} \quad \text{H}_2\text{O}/\text{Al}(\text{i-Bu})_2\text{Cl} = 0\text{--}0.15$$

(all in mol/mol; Bd=butadiene)

The effect of $\text{Co}(\text{acac})_3/\text{Bd}$ ratio on the yield and intrinsic viscosity of the polymerization product is shown in Fig. 1.

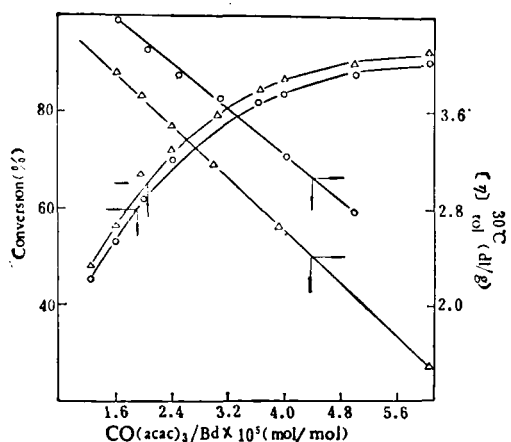


Fig. 1 Effect of $\text{Co}(\text{acac})_3/\text{Bd}$ ratio on the yield and intrinsic viscosity of the product

Catalyst composition: $\text{V}(\text{acac})_3/\text{Bd} = 8 \times 10^{-5}$; $\text{Al}(\text{i-Bu})_2\text{Cl}/\text{Bd} = 6 \times 10^{-3}$;
 $\text{H}_2\text{O}/\text{Al}(\text{i-Bu})_2\text{Cl}$, $\triangle = 0.10$, $\circ = 0.15$.

It is seen from Fig. 1 that the conversion of monomer increases steeply with increase of $\text{Co}(\text{acac})_3/\text{Bd}$ ratio up to 3.0×10^{-5} and then moderately with further increase in the ratio. As to the effect on intrinsic viscosity, a linear relationship is observed.

*Effect of $\text{V}(\text{acac})_3/\text{Bd}$ on *trans*-1,4 content, yield and intrinsic viscosity of the polymerization product*

The effect of $\text{V}(\text{acac})_3/\text{Bd}$ on *trans*-1,4 content, yield and intrinsic viscosity is shown in Table 1. It is seen that with increase in $\text{V}(\text{acac})_3/\text{Bd}$ ratio, both the yield and intrinsic

viscosity are somewhat decreased, while the *trans*-1,4 content is increased.

Table 1 Effect of $V(acac)_3/Bd$ on conversion, intrinsic viscosity and *trans*-1,4 content on the product

$V(acac)_3/Bd$ (mol/mol) $\times 10^{+5}$	Conversion (%)	$[\eta]_{tol}^{30^\circ C}$ (dl/g)	Microstructure (%)		
			<i>cis</i> -1,4	1,2	<i>trans</i> -1,4
1	87.0	2.3	91.9	2.1	6.0
3	84.3	2.5	89.8	3.5	6.7
5	78.7	2.2	87.8	4.1	8.1
7	76.7	2.2	85.1	4.9	10.0
9	71.3	1.4	80.1	6.2	13.7
10	73.0	1.6	78.4	6.6	15.0

Catalyst composition: $Co(acac)_3/Bd = 3 \times 10^{-5}$; $Al(i-Bu)_2Cl/Bd = 6 \times 10^{-3}$; $H_2O/Al(i-Bu)_2Cl = 0.05$.

Increase in *trans*-1,4 content with increase in $V(acac)_3/Bd$ seems reasonable because active centers leading to *trans*-1,4 configuration in the first stage of polymerization are increased with the increase in $V(acac)_3/Bd$ ratio. Decrease in conversion with increase in this ratio may be explained by the fact that the more the active centers formed vanadium compound, the higher the consumption of the co-catalyst $Al(i-Bu)_2Cl$, thus leaving less co-catalyst to activate the $Co(acac)_3$ in the second stage of the polymerization.

Data shown above indicate that a polybutadiene having suitable intrinsic viscosity and *trans*-1,4 content can be prepared in good yield using present dual catalyst system and polymerization procedure. It is interesting to investigate whether this product is a blend of homopolymers or they are chemically bonded. According to traditional view, a polymer chain propagates through the insertion of monomer into the metal-carbon bond of a Ziegler-Natta catalyst. Thus each catalyst species will propagate independently and the product we prepared is seemingly to be a mixture of polybutadienes. However, it is also known that the inner double bond of polydienes could be attacked by Ziegler-Natta catalyst^[8], and the formation of branched polybutadiene cobalt catalyst, i.e., grafting of active polymer chains to the existing polybutadiene, is not impossible. The following experiments were carried out to characterize our product.

Identification of the polymerization product

Solubility behavior: The difference in solubility behavior between the present product and a blend of *trans*-1,4- and *cis*-1,4-polybutadienes in toluene at $-20^\circ C$ is listed in Table 2.

The difference in solubility behavior between the present polymer and the blend is obvious on comparison. For the blend, the *trans*-1,4- and *cis*-1,4-polybutadiene are separated completely into respective insoluble and soluble portions having *trans*-1,4 and *cis*-1,4 contents corresponding to their original compounds respectively. Whereas for the present polymer there is less *trans*-1,4 content in the insoluble portion and less *cis*-1,4 content

Table 2 Solubility behavior of polymer prepared and a blend of *trans*-1,4- and *cis*-1,4-polybutadienes in toluene at -20°C

Sample	Original				Insol. portion				Sol. portion			
	wt (g)	<i>cis</i> -1,4 (%)	1,2 (%)	<i>trans</i> -1,4 (%)	wt (g)	<i>cis</i> -1,4 (%)	1,2 (%)	<i>trans</i> -1,4 (%)	wt (g)	<i>cis</i> -1,4 (%)	1,2 (%)	<i>trans</i> -1,4 (%)
1)	5.04	—	—	—	0.49	5.3	2.2	92.4	4.42	94.9	2.0	3.1
2)	4.03	79.6	4.6	15.6	0.57	44.5	3.2	52.3	3.32	84.6	6.2	9.2
3)	3.96	84.4	3.9	11.7	0.38	48.3	1.3	50.4	3.41	86.9	4.6	8.5

- 1) Contains 90% Ni-BR (*cis*-1,4, 96%; *trans*-1,4, 2.8%; 1,2, 1.2%) and 10% high *trans*-1,4-polybutadiene (*trans*-1,4, 95.5%; 1,2, 4.5%) (t-PB).
 2) Prepared with catalyst composition: $\text{V}(\text{acac})_3/\text{Bd} = 8 \times 10^{-3}$; $\text{Co}(\text{acac})_3/\text{Bd} = 2 \times 10^{-3}$; $\text{Al}(i\text{-Bu})_2\text{Cl}/\text{Bd} = 6 \times 10^{-3}$; $\text{H}_2\text{O}/\text{Al}(i\text{-Bu})_2\text{Cl} = 0.05$.
 3) Similar to sample 2 except $\text{H}_2\text{O}/\text{Al}(i\text{-Bu})_2\text{Cl} = 0.10$.

in soluble portion then the respective homopolymers. These results lead to assume that the insoluble portion of the present polymer is the *trans*-1,4-polybutadiene containing *cis*-1,4-polybutadiene sequence, and the soluble portion *cis*-1,4-polybutadiene containing *trans*-1,4-polybutadiene sequence.

The solubility behavior of the present and that of the blend in $\text{CS}_2\text{-CH}_3\text{COC}_3\text{H}_7$ also differ markedly as shown in Table 3. It is seen from the table that Ni-BR and *trans*-1,4-polybutadiene of the blend are quantitatively separated in the $\text{CS}_2\text{-CH}_3\text{COC}_3\text{H}_7$ of the proportion of 200:50, while the present polymer remains soluble even in a $\text{CS}_2\text{-CH}_3\text{COC}_3\text{H}_7$ of a proportion of 200:200.

Table 3 Solubility behavior of the present polymer and a blend in $\text{CS}_2\text{-CH}_3\text{COC}_3\text{H}_7$ at room temperature

Sample	Original				$\text{CS}_2\text{:CH}_3\text{COC}_3\text{H}_7$ (v/v)	Insol. portion		Sol. portion	
	wt (g)	<i>cis</i> -1,4 (%)	1,2 (%)	<i>trans</i> -1,4 (%)		wt (g)	<i>trans</i> -1,4 (%)	wt (g)	<i>cis</i> -1,4 (%)
1	4.00	—	—	—	200:50	0.39	97.5	3.50	94.5
2	4.00	86.6	2.1	11.3	200:50	0	—	—	—
					200:200	0	—	—	—

Thus, it leads us to believe that *trans*-1,4 units are chemically bonded to *cis*-1,4-polybutadiene.

Degree of crystallization

Based on the catalyst system used, the polymerization procedure adopted and the solubility behavior mentioned above, it is reasonable to believe that the chemically bonded *trans*-1,4 units are linked in sequences. A comparison of wide angle X-ray diffraction spectra of *trans*-1,4-polybutadiene, a blend and the present polymer confirmed this view (see Fig. 2). Besides the amorphous band of *cis*-1,4-polybutadiene the present polymer shows also

a characteristic peak of crystalline *trans*-1,4-polybutadiene at $2\theta = 22^\circ 36'$, though weaker than that of the blend of similar *trans*-1,4 content.

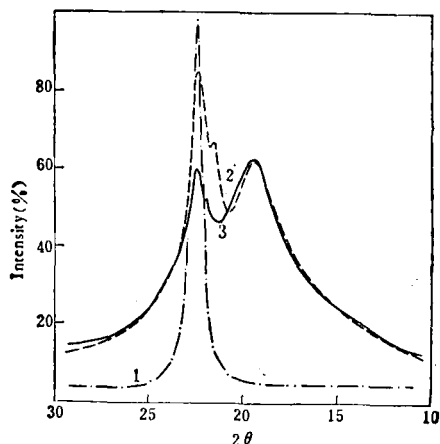


Fig. 2 X-ray diffraction spectra of *trans*-1,4-polybutadiene (curve 1), a blend (curve 2) and the present polymer (curve 3) having 15% *trans*-1,4 content

Table 4 lists the data concerning the degree of crystallization with respect to *trans*-1,4 content of the present polymer having close molecular weight. The fact that the degree of crystallization is increased with increase of *trans*-1,4 content supports the above conclusion.

Table 4 Relationship between degree of crystallization and *trans*-1,4 content

Sample	$\overline{M}_n$ $\times 10^{-3}$	Microstructure (%)			Degree of crystallization (%)
		<i>cis</i> -1, 4	1,2	<i>trans</i> -1,4	
4	230	88.3	2.7	9.0	trace
5	202	85.4	4.5	10.1	0.8
6	241	81.4	5.1	13.5	1.5
7	270	77.8	4.7	17.5	2.5
8	180	74.2	5.0	20.8	4.7

The difference in "damping factor-temperature" curves of a blend and the present polymer determined with torsional pendulum apparatus (Fig. 3) gives another piece of evidence that the *trans*-1,4-polybutadiene block in the present polymer is chemically bonded and not in blend. The first transition of all the three samples lies at the same temperature, -96°C , which is usually considered to be the glass temperature of both *trans*-1,4- and *cis*-1,4-polybutadiene. The second transition of the present polymer occurred at -10°C , a temperature ten degrees lower than that of the blend, 0°C , which is known to be the melting point of normal high-*cis*-polybutadiene. The decrease in melting point in the present polymer shows that there is a change in regularity of *cis*-1,4-polybutadiene.

A comparison of half crystallization time among *cis*-1,4-polybutadiene (Ni-BR), blends

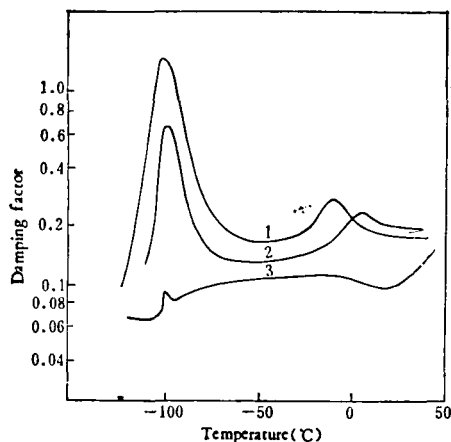


Fig. 3 Damping factor of polybutadiene as the function of the temperature
1. Present polymer (*trans*-1,4 content 15%); 2. Blend (85/15); 3. *Trans*-polybutadiene.

and present polymers reveals that the presence of *trans*-polybutadiene in the *cis*-polybutadiene either blended or chemically bonded, can shorten the half crystallization time (Table 5).

Morphology of the present polymer has also been studied [8]. The difference between the present copolymer and the blends of their corresponding homopolymers was also observed.

Table 5 Half crystallization time of polybutadiene at -26°C

Sample	Ni-BR/t-PBD* (wt/wt)	t-PBD Microstructure (%)			Half crystn. time (min)
		<i>cis</i> -1,4	1,2	<i>trans</i> -1,4	
Ni-BR	100/0	96.0	1.2	2.8	10.04
Blend	90/10	—	—	—	4.90
Blend	85/15	—	—	—	3.65
9	—	95.7	1.3	5.0	6.05
10**	—	83.5	1.4	15.1	5.27

* t-PBD *trans*-1,4-polybutadiene.

** Present polymers.

REFERENCES

- [1] 宇部兴产, 日本特许, 昭 46-42784, 43092; 昭 48-24831.
- [2] 化学工业(日本), 1979, 30 (9), 75.
- [3] Morgan, G. T. and Moss, H. W., *J. Chem. Soc.*, 1913, 10 (3), 78.
- [4] Sidgwick, N. V., "The Chemical Elements and Their Compounds", Vol. 2, 1406, 1952.
- [5] Bähr, G., Burba, P., Lehmkuhl, H. und Ziegler, K., in Müller, E., "Methoden der Organischen Verbindungen", Band 13/4, George Thieme Verlag, Stuttgart, 1970, 60.
- [6] Natta, G., Porri, L., Zanini, G. and Fiore, L., *Chim. et Ind.*, 1959, 41, 526.
- [7] Gippin, M., *Ind. Eng. Chem. Prod. Res. Develop.*, 1962, 1, 32.
- [8] 周恩乐, 金桂萍, 林云青, 李树汉, 胡振亚, 高分子通讯, 1983, (4), 281.