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Kurzmitteilung

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by

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## *Cis*-1,4-Polybutadiene from Cobalt Catalysts. Some Remarks on the Termination of Growing Chains by C<sup>14</sup>- or Tritium-labelled Alcohols

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In a recent communication<sup>1)</sup> CHILDERS reported that the soluble cobalt catalysts used for the preparation of *cis*-1,4-polybutadiene are cationic, not anionic as previously believed<sup>2)</sup>. This conclusion was based on the fact that when in his experiments C<sup>14</sup>-methanol was used to terminate the growing polymer chains initiated by Al<sub>2</sub>Cl<sub>3</sub>(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>-cobalt octoate, C<sup>14</sup> was found in the polymer, while when hydroxyl tritiated butanol was used, inactive polymer was obtained.

More recently, COOPER, EAVES, and VAUGHAN<sup>3)</sup> reported the results of similar experiments on the Al(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Cl-cobalt naphthenate-water system. Contrary to CHILDERS, these authors did not find C<sup>14</sup> activity in the polymers, while tritium activity was present. They conclude that the polymerization is anionic, as we previously proposed<sup>2)</sup>, and that all the cobalt is active in the polymerization.

Since the appearance of CHILDERS' communication we too have performed some termination experiments on polymers initiated by the Al(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Cl-cobalt diacetylacetonate, (Co(acac)<sub>2</sub>), system. Our results differ from those of CHILDERS, in that they have provided no evidence against our hypothesis<sup>2)</sup> that a cobalt-carbon bond is involved in the chain growth. However, as they also differ in some respect from those of COOPER *et al.*, we wish to report them in this communication.

The polymerization experiments were performed in 100 ml. glass vessels under N<sub>2</sub> by the usual technique. Some runs were terminated by an-

Tab. 1. Radioactivity of polybutadienes formed by soluble cobalt catalysts and terminated by radioactive compounds<sup>a)</sup>

No.	Aluminum compound <sup>b)</sup> (moles · 10 <sup>3</sup> )	Co(acac) <sub>2</sub> (moles · 10 <sup>5</sup> )	Butadiene <sup>c)</sup> (g.)	Polymerization		Termination		Polymer				
				Temp. (°C.)	Time (min.)	Reagent	(ml.)	Activity (mC./mole)	Contact time (min.)	(g.)	% <i>cis</i> -1,4	Ac- tivity <sup>d)</sup> (mC./g.)
1	1.7	1.7	3.3	0	7	<sup>14</sup> C <sub>4</sub> H <sub>9</sub> OH	0.5	2.6	10	0.7	97.2	1.5 · 10 <sup>-7</sup>
2	2.1	2.1	6.0	0	6	<sup>14</sup> C <sub>4</sub> H <sub>9</sub> OH	0.5	2.6	30	0.3	97.5	2.7 · 10 <sup>-7</sup>
3	1.9	2.5	6.5	0	105	<sup>14</sup> C <sub>4</sub> H <sub>9</sub> OH	1.5	2.6	10	0.3	96.5	1.1 · 10 <sup>-7</sup>
4	6.3	6.3	3.5	-10	20	<sup>14</sup> CH <sub>3</sub> OH	1	17.8	5	0.9	97	2.0 · 10 <sup>-6</sup>
5	5.5	0.19	2.5	0	35	CH <sub>3</sub> OH <sup>e)</sup>	0.4	28	15	0.5	98.5	7.6 · 10 <sup>-6</sup>
6	5.5	0.19	2.5	0	35	CH <sub>3</sub> OH <sup>e)</sup> , then contaminated with CH <sub>3</sub> OH <sup>3</sup>	0.4	28	15	0.5	98.5	0.7 · 10 <sup>-6</sup>
7	2.1	2.1	2.7	0	5	CH <sub>3</sub> OH <sup>3</sup>	1.5	24	360	0.4	97.5	2.8 · 10 <sup>-5</sup>
8	6.3	6.3	3.6	-10	8	CH <sub>3</sub> OH <sup>3</sup>	1.5	39	10	0.6	96.5	7.1 · 10 <sup>-5</sup>
9	6.3	6.3	3.6	-10	8	CH <sub>3</sub> OH <sup>e)</sup> , then contaminated with CH <sub>3</sub> OH <sup>3</sup>	1.5	39	10	0.6	96.5	6.6 · 10 <sup>-5</sup>
10	2.1	2.1	3.2	-15	12	CH <sub>3</sub> COOH <sup>3</sup>	0.9	21	360	0.8	97	4.7 · 10 <sup>-5</sup>
11	2.1	2.1	3.2	-15	12	CH <sub>3</sub> OH <sup>e)</sup> , then contaminated with CH <sub>3</sub> COOH <sup>3</sup>	0.9	21	360	0.8	97	7.1 · 10 <sup>-6</sup>

<sup>a)</sup> Solvent 50 ml.; runs 1,2,7 benzene; runs 3-6, 8-11 toluene. In runs 1 and 2 the catalyst was aged for 20 min. before introduction of monomer; in run 3 the catalyst was aged for 24 hrs.; in runs 4-11 the catalyst was prepared introducing Co(acac)<sub>2</sub> in the solution containing the monomer and the aluminum compound.

<sup>b)</sup> Run 2 Al<sub>2</sub>(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>Cl<sub>3</sub>; all the other runs Al(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Cl.

<sup>c)</sup> Runs 2,7,10,11: butadiene from decomposition of the cyclic sulphone, chromatographically pure. Runs 1,3-6,8,9: PHILIPS "pure grade" butadiene, 99% pure.

<sup>d)</sup> Measurements were performed in toluene solutions containing PPO (2,5 diphenyloxazole) and POPOP (2,2 p-phenylenebis(5-phenyloxazole)) using a liquid scintillation counter "Tricarb". The reported data are the difference between the measured and the background activity. In some runs the gas counting method of BEVINGTON and EAVES<sup>8)</sup> was also employed.

<sup>e)</sup> The polymerizations were stopped with methanol, then the polymer was coagulated, purified and dissolved in 50 ml. of toluene. Al(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Cl (5.5 · 10<sup>-3</sup> moles in run 6, 6.3 · 10<sup>-3</sup> in run 9, 2.1 · 10<sup>-3</sup> in run 11) was added to this polymer solution which was then treated with CH<sub>3</sub>OH<sup>3</sup> in runs 6 and 9 (0.4 and 1.5 ml. respectively) and with CH<sub>3</sub>COOH<sup>3</sup> in run 11 (0.9 ml.). After the time indicated the polymer was coagulated, purified, and the radioactivity content measured.

hydrous C<sup>14</sup>-butanol or methanol, others by oxygen tritiated methanol (in one run CH<sub>3</sub>COOH<sup>3</sup> was used). The polymers, after coagulation by an excess of CH<sub>3</sub>OH, were purified by three times dissolving in benzene and reprecipitating with CH<sub>3</sub>OH. The experimental data concerning some typical runs are summarized in Table 1. The results show that the C<sup>14</sup> activity was of the same order as the background, while tritium activity was always above this level. These results are reverse to that of CHILDERS', and are in qualitative agreement with those of COOPER *et al.*

Control runs, however, have shown that in the reaction between the growing chains and CH<sub>3</sub>OH<sup>3</sup> in the presence of Al(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Cl contamination of the polymers occurs. These control runs were performed as follows: Al(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Cl was added to a benzene solution of non-radioactive *cis*-1,4-polybutadiene (the ratio polymer/solvent/Al(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Cl being the same as that used in the polymerization runs). Then CH<sub>3</sub>OH<sup>3</sup> was added, again in the amount usually used in the polymerization runs. After some minutes of contact the whole mixture was coagulated by excess of CH<sub>3</sub>OH. The polymer was found to be radioactive, the activity remaining constant even after a thorough purification.

The origin of this contamination, which varies, depending mostly on the amount of Al(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Cl, but also on the polymer concentration and its molecular weight, was not investigated. Our data indicate that the tritium activity found in the contaminated polymers is generally lower than the activity found in closely parallel runs for CH<sub>3</sub>OH<sup>3</sup>-terminated polymers. This fact seems to indicate that the total observed activity arises in part from the chain termination, and hence that the polymerization is anionic\*). We do not think, however, that the termination by tritiated alcohols may be used for a quantitative measurement of the active centers. First of all, calculations of tritium activity arising from chain termination are extremely uncertain, due to the presence of the contamination. Furthermore, it does not seem that the reaction between the tritiated alcohol and the growing chains, at least for the conditions under which we operated, is quantitative, as the order of magnitude of the tritium activity attributable to termination is rather low.

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\*) Other facts lead to the same conclusion, *e.g.*, the effect of olefins on the termination of the chains<sup>4</sup>), the effect of some LEWIS bases on the catalytic activity<sup>5</sup>), the analogy with other polymerizations which are definitely anionic. All these facts will be examined in detail in future papers.

Even taking into consideration a kinetic isotopic factor<sup>\*)</sup> (which has not been determined for this reaction), the calculated ratio of active centers to total cobalt present would still be rather low.

On the other hand, our kinetic studies have shown that all or at least a large part of the cobalt is active in the polymerization. This difference seems to indicate that in the reaction between the tritiated alcohol and the active metal-carbon bond the tritium does not remain quantitatively bonded to the polymer chain.

We wish to point out here that although the termination by tritium-labelled alcohols has been widely used to determine the active centers in anionic polymerizations<sup>6a, b)</sup>, its use in the field of diolefin polymerization by catalysts based on metals of the 8<sup>th</sup> group requires some caution. In the case of diolefins, the bond between the metal and the monomeric unit is of the allylic type and it is known that such bonds are sometimes rather stable. For instance, when the metal is Rh, Pd, or Ir, the bonds of the allylic type are relatively stable even in the presence of water or alcohols, at room temperature. If, in a polymerization of a diene, a bond between one of these metals and the monomeric unit is involved, the reaction at room temperature with an oxygen-tritiated alcohol would be of no value in determining the number of active centers and even the nature of the polymerization. In other cases, the bond between the metal and the monomeric unit may not be so stable, but even then the reaction with alcohols may not be quantitative.

For example, it is known that the active catalyst is a complex between Al and Co<sup>2, 7)</sup>. A cobalt-monomeric unit bond, of the allylic type, is most probably present in the catalytic complex during the polymerization. The reaction with a tritiated alcohol destroys the complex, and hence stops the polymerization, but it has not been shown that the destruction of the cobalt-carbon bonds gives quantitative bonding of tritium to the polymer chain. This bond could break homolytically, at least in part, as a consequence of the destruction of the complex.

In conclusion: a) C<sup>14</sup> was not found in the polymers obtained by termination by C<sup>14</sup>-labelled alcohols. b) Tritium was present when the termination was effected by oxygen-tritiated alcohols. However, a tritium contamination was also detected, which invalidates the exact calculation

\*) COOPER *et al.*<sup>3)</sup> use 3.7 as isotopic factor in the calculation of the active centers. This figure was experimentally determined by FELDMAN and PERRY<sup>6a)</sup> for the case of ethylene polymerization by aluminum-alkyl-titanium tetrachloride catalysts. We do not know whether this figure may also be used in the case of butadiene polymerization by cobalt catalysts, but in any case the isotopic factor for this last reaction should not be much different from that used by COOPER *et al.*

of the number of active centers. Furthermore, it does not seem that the reaction between the alcohols and the active metal-carbon bond is quantitative in the case examined here.

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