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L. S. Bresler, E. N. Kropacheva, I. Ya. Poddubnyi, V. N. Sokolov

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Abstract

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On the Mechanism of Diene Polymerization under the Influence of Complex Catalysts Based on Cobalt Compounds

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To elucidate the mechanism of the propagation reaction in the polymerization of dienes under the influence of complex catalysts based on cobalt compounds, the method of deactivation of growing chains by an alcohol labeled either in the hydroxyl hydrogen or in the alkoxyl group has recently been used (^{1}-^{3}). This method, first applied by Feldman and Perry to study the mechanism of ethylene polymerization under the influence of the catalytic system AlR_3 + $TiCl_4$ (^{4}), is based on the fact that, during deactivation of the catalyst by an alcohol, the hydroxyl hydrogen interacts with the negatively polarized active end of the polymer chain, whereas the alkoxyl interacts with the positively polarized end.

The studies (^{1}-^{3}), however, led to contradictory results: according to Childers (^{1}), alkoxyl becomes attached to the polymer and the hydroxyl hydrogen does not; according to Cooper and co-workers (^{2}) and Natta and co-workers (^{3}), polybutadiene after deactivation contains only hydroxyl hydrogen. It therefore seemed important to determine the reason for the discrepancy that had arisen in the results, to define the limits of applicability of the Feldman–Perry method for studying the sign of the charge of the growing chain in ionic polymerization, and to establish the actual mechanism of the propagation reaction of the polymer chain in the presence of cobalt catalysts. For this purpose a series of catalytic systems was selected, including catalysts with a definitely known mechanism of action (an anionic-type catalyst, LiC_4H_9; cationic catalysts, $AlCl_2C_2H_5$ with the cocatalyst HCl; $TiCl_4$ with the cocatalysts HCl or H_2O), as well as complex coordination catalysts—TiJ_4 + $Al(iso\text{-}C_4H_9)_3$ and cobalt catalytic systems—cobalt naphthenate or an alcoholic complex of cobalt chloride in the presence of $AlCl(iso\text{-}C_4H_9)_2$.

Polymerization was carried out by the usual procedure. Butadiene and isoprene were used mainly as monomers, and benzene as the solvent. To terminate the polymerization, labeled ethanol was added to the reaction mixture in an amount of 10–20 moles per 1 mole of catalyst.

The commercial reagent $CH_3C^{14}H_2OH$, upon deactivation of a lithium-organic catalyst, caused radioactivity to appear in the polymer (1100 imp/min), which indicated the presence of carbonyl-containing impurities in the alcohol. Aldehydes were removed by boiling the alcohol with aluminum powder in an alkaline medium (⁵); the alcohol was freed from an ethyl acetate impurity by double isotopic dilution: nonradioactive ethyl acetate was added to the alcohol, then alkaline hydrolysis of the mixture and distillation of the purified alcohol were carried out. After this purification the amount of radioactive impurity was insignificant, and the radioactivity obtained upon deactivation of lithium-polyisoprene with purified $CH_3C^{14}H_2OH$ was subsequently taken by us as the background (40 imp/min for ethanol of activity 45 mCi/mole and 15 imp/min for a sample of activity 90 mCi/mole, Table 1).

$C_2H_5OH^3$ was prepared by exchange between tritium water and inactive ethyl alcohol. The alcohol obtained was absolutized by azeotropic distillation with benzene, followed by storage over amalgamated

Table 1

Radioactivity of the polymer upon deactivation of various catalysts

Catalyst	Cocatalyst	Monomer	Rel. (mol.) monomer/catalyst	Activity of alcohol, mCu/mol	Radioactivity of polymer, imp/min
$CH_3C^{14}H_2OH$	**$CH_3C^{14}H_2OH$**	**$CH_3C^{14}H_2OH$**	**$CH_3C^{14}H_2OH$**	**$CH_3C^{14}H_2OH$**	**$CH_3C^{14}H_2OH$**
LiC_4H_9	tetrahydrofuran	isoprene	100	45	40
LiC_4H_9	–	»	25	90	15
$AlCl_2C_2H_5$	HCl	»	330	45	90
$TiCl_4$	HCl	»	100	45	130
$TiCl_4$	H_2O	styrene	100	90	0
TiJ_4	Al(iso-$C_4H_9)_3$	butadiene	840	90	15
$CoCl_2 \cdot C_2H_5OH$	AlCl(iso-$C_4H_9)_2$	isoprene	200	45	350
$CoCl_2 \cdot C_2H_5OH$	AlCl(iso-$C_4H_9)_2$	butadiene	280	45	150
Co^{2+} naphthenate	AlCl(iso-$C_4H_9)_2$	»	600	90	330
Co^{2+} naphthenate	AlCl(iso-$C_4H_9)_2$	»	2500	90	55
$C_2H_5OH^3$	**$C_2H_5OH^3$**	**$C_2H_5OH^3$**	**$C_2H_5OH^3$**	**$C_2H_5OH^3$**	**$C_2H_5OH^3$**
LiC_4H_9	tetrahydrofuran	isoprene	100	45	150
LiC_4H_9	–	»	25	700	80000
$AlCl_2C_2H_5$	HCl	»	120	45	90
$TiCl_4$	HCl	»	100	45	250
$TiCl_4$	HCl	polyisoprene	50	45	250
$TiCl_4$	H_2O	styrene	100	700	65
TiJ_4	Al(iso-$C_4H_9)_3$	butadiene	840	700	30

Catalyst	Cocatalyst	Monomer	Rel. (mol.) monomer/catalyst	Activity of alcohol, mCu/mol	Radioactivity of polymer, imp/min
$CoCl_2 \cdot C_2H_5OH$	$AlCl(iso\text{-}C_4H_9)_2$	»	280	45	0
$CoCl_2 \cdot C_2H_5OH$	$AlCl(iso\text{-}C_4H_9)_2$	»	250	700	0
Co^{2+} naphthenate	$AlCl(iso\text{-}C_4H_9)_2$	»	560	700	0
Co^{2+} naphthenate	$AlCl(iso\text{-}C_4H_9)_2$	»	2700	700	0
Co^{2+} naphthenate	$AlCl(iso\text{-}C_4H_9)_2$	»	2500	700*	45

* For decomposition a mixture of 80 wt.% alcohol and 20 wt.% water was used.

with aluminum shavings; it will be shown below that the use of ROH^3 containing water leads to incorrect information about the mechanism of polymerization, since the hydroxyl group of water containing tritium can add to the positively polarized end of the chain in the same way as an alkoxyl.

Two samples of $C_2H_5OH^3$ were used: with specific activities of 45 mCu/mol and 700 mCu/mol.

After decomposition of the catalyst with radioactive alcohol, the polymer was precipitated with inactive alcohol, washed, dissolved in benzene; the benzene solution was filtered through a paper filter to remove catalyst residues, and the polymer was reprecipitated twice more. It was established by a special experiment that the radioactivity of the polymer did not change further after twofold reprecipitation. Radiometric measurements were carried out in a polymer film with the aid of a gas-flow proportional counter using helium as the working gas and ethyl alcohol as the quenching additive. The electronic circuit of the apparatus, consisting of a non-overloading linear amplifier, discriminator, and scaling device with a PP-8 timer, had a dead time of about 3.5 μsec; the background during the measurements was 20–30 imp/min.

The results obtained by us are given in Table 1, from the data of which it follows that the polymer formed under the influence of an anionic catalyst is radioactive upon decomposition with $C_2H_5OH^3$, while its radioactivity upon deactivation with $CH_3C^{14}H_2OH$ is associated only with residues of carbonyl-containing impurities; however, polyisoprene obtained in the presence of typical cationic catalysts—Lewis acids—adds both tritium and the labeled alkoxyl. Along with this, polystyrene becomes radioactive only upon decomposition of the catalyst $TiCl_4$ by the alcohol $C_2H_5OH^3$, which is directly opposite to the result expected for a cationic process.

If, in anionic polymerization, the organometallic bonds of the active ends of "living" chains react with alcohol by only one pathway:

$$\sim CH_2Li + ROH \rightarrow \sim CH_3 + LiOR,$$

then the interaction of polymeric cations with an alkoxide can proceed in two ways:

$$\text{a)} \ \sim CH_2{-}C^+R_2 + R^{\otimes}O^- \rightarrow \sim CH_2{-}CR_2{-}OR^{\otimes}, \tag{1}$$

i.e., addition of the labeled alkoxide with formation of a labeled polymer, or

$$\text{b)} \ \sim CH_2{-}C^+R_2 + R^{\otimes}O^- \rightarrow ROH + \sim CH{=}CR_2, \tag{2}$$

i.e., abstraction by the alkoxide of a proton from the α-position with formation of an unlabeled polymer. Analogous reactions occur in the process of cationic polymerization between the growing cation and the counterion: reaction (2) is similar to transfer of a proton to the counterion with regeneration of the catalyst (a reaction inverse to initiation and thus reversible):

$$\sim CH_2{-}R_2C^+\,(TiCl_5)^- \rightleftarrows H^+\,(TiCl_5)^- + \sim CH{=}CR_2 \tag{3}$$

reaction (1) is analogous to addition of the counterion anion to the growing chain, associated with complete deactivation of the catalyst and the chain:

$$\sim CH_2{-}R_2C^+\,(TiCl_5)^- \rightarrow TiCl_4 \sim CH_2{-}R_2CCl. \tag{4}$$

Naturally, polymer formation is observed only when reaction (4) is considerably less probable than the propagation reaction, and thus, in cationic polymerization with formation of high-molecular products, reactions (1) and (4) are not the principal chain-termination reactions. This is consistent with only slight addition of $OR^{\otimes}$ to polyisoprene and the complete absence of $OR^{\otimes}$ in polystyrene (Table 1).

On the other hand, as a consequence of reaction (3), in cationic polymerization the system always contains free catalyst bearing a proton, and dead chains with a double bond are capable of reacting with it. At the moment when labeled alcohol $C_2H_5OH^3$ is added to the reaction mixture, apparently the following reversible reactions take place:

$$C_2H_5OH^3 + H^+(TiCl_5)^- \rightleftarrows C_2H_5OH + H^{3+}[TiCl_5]^-,$$

$$H^{3+}(TiCl_5)^- + R_2C{=}CH \sim\rightleftarrows (TiCl_5)^- R_2C^+{-}CHH^3 \sim,$$

which leads to the introduction of tritium into the polymer chain. Such isotopic exchange with the polymer chain in cationic polymerization should be highly probable, since the reaction of addition of the catalyst to the terminal double bond corresponds to the initiation reaction. Isotopic exchange in the presence of Friedel-Crafts catalysts can also occur with the polymer. We observed this phenomenon when treating a solution of polyisoprene with $TiCl_4$ + HCl, and then $C_2H_5OH^3$ (Table 1); radioactive contamination discovered by Natta and co-workers ([3]) in the treatment of inactive polybutadiene first with $Al(C_2H_5)_2Cl$ and then with CH_3OH^3 probably arises in the same way.

Consideration of the results obtained on typical anionic and cationic catalysts makes it possible to systematize the information provided by the termination of ionic polymerization with labeled alcohols in the form of Table 2. From the data in this table it follows that the presence of a label in the polymer upon decomposition of the catalyst with ROH^3 and its absence upon treatment with alcohol labeled in the alkoxyl group cannot yet serve as proof of an anionic mechanism of chain growth.* However, in the case when the polymer adds

* See the data on styrene polymerization on $TiCl_4$, Tables 1 and 2. Thus, the proof of an anionic polymerization mechanism in the presence of the catalytic system TiJ_4 + Al(iso-$C_4H_9)_3$ should be considered not the fact of addition of tritium to the polymer and the absence of alkoxide in the polymer (Tables 1 and 2), but the carbonation of the organometallic active bonds upon treatment of the reaction mixture with $C^{14}O_2$ (specific activity of the $C^{14}O_2$ used: 4500 mCu/mol; radioactivity of the polymer: 7500 imp/min).

Table 2

Data on the polymerization mechanism obtained by deactivation of chains with labeled alcohol

Alcohol used for deactivation	Radioactivity of the polymer	Polymerization mechanism	Alcohol used for deactivation	Radioactivity of the polymer	Polymerization mechanism
$R^{\otimes}OH$	+	Cationic only	ROH^3	+	Anionic or cationic (owing to isotopic exchange)

Alcohol used for deactivation	Radioactivity of the polymer	Polymerization mechanism	Alcohol used for deactivation	Radioactivity of the polymer	Polymerization mechanism
$R^{\otimes}OH$	—	Anionic or cationic (if reaction (1) does not occur)	ROH^3	—	Nonionic

attaches the labeled alkoxide, the chain can carry only a positive charge; that is, the polymerization is cationic regardless of whether hydrogen from ROH^3 is added to the polymer. This is the case we observed in the polymerization of dienes in the presence of cobalt catalysts. Our results on the deactivation of cobalt catalysts agree with the data of Childers (^{1}) and differ from the results of Cooper (^{2}) and Natta (^{3}), who did not detect activity in the polymers when the catalyst was decomposed with $R^{\otimes}OH$ alcohol. However, when a more active alcohol was used (17.8 mCi/mole), Natta and co-workers obtained a polymer of appreciable activity. Only the use of low-activity $R^{\otimes}OH$ preparations (2.5 mCi/mole and 7 mCi/mole) did not allow Natta and Cooper to detect radioactivity in the polymers, since, according to our data, addition of alkoxide to the polymer chain during decomposition of the cobalt catalyst occurs in a non-quantitative manner.

When cobalt catalysts were deactivated with anhydrous $C_2H_5OH^3$, in contrast to Natta and Cooper, we did not detect radioactivity in the polymer, although we used a preparation of considerably higher radioactivity (700 mCi/mole instead of, respectively, 40 mCi/mole or 100 mCi/mole). Neither Cooper nor Natta, unlike Childers, mentions drying the ROH^3 they used. Apparently, the polymer radioactivity detected by them upon decomposition of the cobalt catalyst with this alcohol was caused by the presence of water in the latter. Indeed, when a catalyst based on cobalt naphthenate was deactivated with $C_2H_5OH^3$ alcohol containing water, we obtained radioactive polybutadiene (Table 1).

The results we obtained make it possible to conclude that the polymerization of dienes under the influence of cobalt catalytic systems proceeds by a cationic mechanism; in this case, initiation probably does not occur through addition of a free proton, since, when anhydrous ROH^3 is used, isotopic exchange of tritium with the polymer chain is not observed (as we found in the case of ordinary cationic polymerization).

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Note: Figure translations are in progress. See original paper for figures.