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STEREOSPECIFIC POLYMERIZATION OF BUTADIENE IN THE PRESENCE OF CATALYTIC SYSTEMS BASED ON π-CYCLOPENTADIENYL COMPLEXES OF NICKEL

It was shown by us earlier that certain π-complexes of metals of variable valence, either by themselves or in combination with metal halides, are effective catalysts for the stereospecific polymerization of butadiene ([1], [2]). Depending on the nature of the metal bound in the π-complex, cis-1,4- or 1,2-polybutadienes were obtained.

Continuing the study of the catalytic activity of π-complexes of transition metals in processes of stereospecific polymerization of dienes, we found a new type of catalysts based on π-cyclopentadienyl complexes of nickel in combination with Lewis acids.

Table 1

Polymerization of butadiene by catalytic systems based on bis-π-cyclopentadienylnickel

MeX	Ni/Me (mol.)	Solvent	Polymer yield, %	1,2	trans-1,4	cis-1,4	Unsaturation, %
$TiCl_4$	4	Benzene	10	not determined	not determined	not determined	–
$TiCl_4$	2	»	32	3	8	89	–
$TiCl_4$	1	»	76*	3	4	93	96.5
$TiCl_4$	0.5	»	20	3	4	93	–
VCl_4	5	»	10	2	6	92	–
VCl_4	2	»	80	1	2	97	–
VCl_4	1	»	60	1.5	2	96.5	–
VCl_4	1	Heptane	32	2	4	94	–
$VOCl_3$	2	Benzene	37	not determined	not determined	not determined	–
$VOCl_3$	1	»	37	2	5	93	–
$SnCl_4$	2	»	48*	2	50	48	–

MeX	Ni/Me (mol.)	Solvent	Polymer yield, %	1,2	trans-1,4	cis-1,4	Unsaturation, %
$MoCl_5$	2	»	60	not determined	not determined	not determined	–
$MoCl_5$	1	»	96	6	42	52	–
WCl_6	4	»	43	not determined	not determined	not determined	–
WCl_6	2	»	57	3	22	75	–
WCl_6	1	»	60	2	20	78	–
$AlCl_3$	2	»	31*	2	5	93	–
$AlCl_3$	1	»	31*	2	5	93	–
$AlBr_3$	2	»	59	1	39	60	96.0
$AlBr_3$	1	»	94	1	30	69	97.0

* The interaction of the components was carried out at a temperature of 50° for 6–12 hours.

Bis-π-cyclopentadienylnickel was synthesized by the method of Górdes ([3]) from sodium cyclopentadienide and nickel hexammine chloride. For the preparation of the catalysts, a product twice sublimed in vacuum (2–3 mm Hg) was used.

π-Cyclopentadienyl-π-cyclopentenylnickel was obtained by the method of Fischer ([4]) from nickel carbonyl and cyclopentadiene.

By themselves, π-cyclopentadienyl derivatives of nickel do not initiate the polymerization of dienes. However, the products of interaction of nickel complexes with various metal halides are active catalysts for the polymerization of butadiene.

The catalysts were prepared in an argon atmosphere by mixing freshly prepared hydrocarbon solutions of the components. In all cases the interaction began at room temperature and was accompanied by the precipitation of abundant loose precipitates. In individual experiments the catalysts were kept at a temperature of 50° for 6–12 h. The color of the precipitates depended on the nature of the Lewis acid used. The solutions above the precipitates, depending on the amounts of nickel compounds used, were either colorless or colored in the color of the corresponding nickel complex.

Table 2

Polymerization of butadiene by catalytic systems based on π-cyclopentadienyl-π-cyclopentenylnickel (solvent—benzene)

MeX_n	Ni/Me (mol.)	Polymer yield, %	1,2	trans-1,4	cis-1,4	MeX_n	Ni/Me (mol.)	Polymer yield, %	1,2	trans-1,4	cis-1,4
$TiCl_4$	1	56	not determined	not determined	not determined	VCl_4	1	11	2	2	96
$TiCl_4$	2	57	3	7	90	VCl_4	2	10	3	5	92
$VOCl_3$	1	28	2	4	94	$MoCl_5$	1	50	3	5	92
$VOCl_3$	2	41	2	3	95	$MoCl_5$	2	18	not determined	not determined	not determined

The results of experiments on the polymerization of butadiene by catalytic systems based on π-cyclopentadienyl nickel complexes are given in Tables 1 and 2.

Polymerization was carried out at a temperature of 50° for 17 h. The concentration of butadiene in the solution was 2.5 mol/l; the concentration of metal halides was $5 \cdot 10^{-3}$ mol/l. After completion of the polymerization, the polymers were isolated from the solution by precipitation with ethyl alcohol acidified with hydrochloric acid.

The yields of the polymers and their molecular weight depend substantially on the nature of the Lewis acid used and on the molar ratio of the catalyst components.

For the catalytic system $(\pi\text{-}C_2H_5)_2Ni—TiCl_4$, the formation of polymers containing about 90% cis-1,4 units, 5–10% trans-1,4 units, and practically no pendant vinyl groups is characteristic.

The polymers have a comparatively low molecular weight (up to 100,000). The maximum yield of polymers was observed at the molar ratio $Ni : Ti = 1$.

The catalytic system $(\pi\text{-}C_5H_5)_2Ni—VCl_4$ affords polybutadienes with a content of cis-1,4 units up to 96%. The range of molar ratios $Ni : V$ at which maximum activity was achieved lies in this case between 1 and 2. The molecular weights of the polymers decrease with increasing $Ni : V$ ratio. Polymers with molecular weights of 400–500 thousand can be obtained at the ratio $Ni : V = 1$.

In contrast to catalysts prepared from titanium and vanadium compounds, catalytic systems based on halides of tin, molybdenum, and tungsten lead to the formation of polymers with a noticeable content of trans-1,4 units (20–50%), although the content of 1,2 units does not exceed 5%. In some cases the polymers obtained using molybdenum pentachloride and tungsten hexachloride at ratios $Ni : Me > 1$ had limited solubility.

In polymerization in the presence of the catalysts $(\pi\text{-}C_5H_5)_2Ni{-}AlX_3$ (where $X = Cl$ or Br), polymers with molecular weights of 20–50 thousand (depending on the reaction conditions) are formed.

Catalysts based on π-cyclopentadienyl-π-cyclopentenylnickel are analogous in their action to bis-π-cyclopentadienyl catalytic systems and lead to the formation of polymers containing 92–95% cis-1,4 units.

The results obtained in the present work on the polymerization of butadiene in the presence of catalytic systems based on π-cyclopentadienyl nickel complexes testify to the broad possibilities opening up for researchers in creating stereospecific polymerization catalysts that do not contain organometallic compounds with a metal–carbon σ bond.

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