OLIGOMERIZATION OF BUTADIENE IN THE PRESENCE OF METAL COMPOUNDS IMMOBILIZED ON POLYMERIC CARRIERS. COMMUNICATION 1. IRON COMPLEXES IMMOBILIZED IN THE BULK OF A POLYMER GEL IN THE REACTION OF LINEAR DIMERIZATION OF BUTADIENE

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The oligomerization of conjugated dienes in the presence of Ziegler-Natta catalytic systems in a homogeneous reaction medium is a well-studied process. A significant disadvantage of homogeneous catalytic systems is their insufficient stability in the catalytic process and the technological difficulties involved in separating the components of the catalytic system from the products of the reaction. The major possibility of creating and using microheterogeneous catalytic systems for the hydrogenation and oligomerization of some  $\alpha$ -olefins was demonstrated in [1, 2].

Such catalytic systems, prepared from cross-linked synthetic rubber with grafted units of a polymeric ligand, can swell in the reaction medium and form sufficiently strong metal complex compounds. The conditions for maximum utilization of the catalytic sites in the entire volume of the polymer gel are created in the swollen state [2]. The gel-immobilized catalytic systems (GCS) associate the best properties of the usual homogeneous and heterogeneous metal-complex catalysts.

GCS which we synthesized were studied in the oligomerization of 1,3-butadiene, and the effect of the structure of the polymeric ligand of the catalyst on the activity of the GCS and the selectivity of the process were determined.

Catalytic systems containing iron complexes and phosphonites chemically grafted to the polymer were studied. The structure of the phosphorus-containing ligands of the GCS is shown in Table 1. The data in Table 1 indicate that GCS containing complex-bound Fe(acac)<sub>3</sub> exhibited different activity and selectivity in the oligomerization of 1,3-butadiene (BD). For all of the GCS, the predominant product of oligomerization was 3-methyl-1,4,6-heptatriene (I). When the contact time of the BD with the GCS was increased, other oligomers were also formed in the reaction medium: 4-vinyl-1-cyclohexene (II), 1,3,7-octatriene (III), 1,5cyclooctadiene (IV), 1,5,9-cyclododecatriene (V), and linear trimers (VI). The highest rate of oligomerization of BD was attained when a GCS containing dibutylphosphonite ligands was used.

The organophosphorus ligands can be placed in the following order with respect to their effect on the value of the catalytic activity:

 $PC-P(OBu-n)_2 > PC-P(OC_8H_{17})_2 > PC-P(OC_3H_5Cl_2)_2 > PC-P(OBu-t)_2,$ 

where PC is the polymeric carrier.

This effect of the ligand environment of the catalytic site on the activity and selectivity is due to a change in the electron-acceptor or steric properties of the substituents on the phosphorus atom, as found previously in the study of hydrogenation of alkylbenzene in the presence of GCS containing phosphonite complexes of iron of similar structures [1].

For comparing the catalytic activity, oligomerization of BD in the presence of the Fe(acac)<sub>3</sub>-P(OBu-n)<sub>3</sub>-TEA (triethylaluminum) homogeneous system was carried out in the same conditions. It was found that oligomerization of BD stopped relatively rapidly due to the formation of significant amounts of polybutadiene.

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Fig. 1. Dependence of the rate of oligomerization of butadiene on the time on the GCS: EPTSR-P( $OC_3H_5Cl_2$ )<sub>2</sub>-Fe(acac)<sub>3</sub>-Et<sub>3</sub>Al. Solvent: benzene, 50°C, Fe:Al = 1:4 (molar); Pbutadiene = 7.3°10<sup>2</sup> GPa. Point \* with the arrow corresponds to the time of periodic activation of the GCS.

Fig. 2. Dependence of the rate of oligomerization of butadiene on the time on GCS No. 1:  $EPTSR-P(OBu-n)_2-Fe(acac)_3-Et_3A1$  and GCS No. 2:  $EPTSR-P(OC_8H_{17})_2-Fe(acac)_3-Et_3A1$ . Solvent: benzene, 50°C, Fe:A1 = 1:4 (molar);  $p_{butadiene} = 7.3 \cdot 10^2$  GPa. Point \*: cf. Fig. 1.

The fact that linear oligomerization takes place in the presence of GCS with a significant rate and selectivity confirms the efficiency of organophosphorus macroligands in stabilization of the Fe ion in lower degrees of oxidation. The metal-complex structure of the synthesized gel-immobilized catalytic systems was confirmed by the possibility of their repeated reactivation on addition of TEA.

The dependence of the rate of oligomerization of BD on the time in conducting three successive experiments and removing the products of oligomerization formed is shown in Figs. 1 and 2. These data indicate that partial restoration of the catalytic activity occurred after each addition of TEA. The slight decrease in the catalytic activity in time is probably due to the partial migration of the Fe chelate compound into the solution due to formation of a complex with TEA and accumulation of an insignificant amount of polybutadiene, which blocks some of the active sites. In our opinion, the second cause has the greatest effect on the deactivation of the catalytic sites.

## **EXPERIMENTAL**

Ethylene-propylene terpolymer synthetic rubber (EPTSR), purified by three reprecipitations from heptane solution, was used as the starting product for synthesis of the polymeric carrier.

Different phosphorus-containing ligands were attached to the purified and cross-linked EPTSR according to the method in [3]. The prepared polymeric carriers were treated in the swollen state with a solution of  $Fe(acac)_3$  in dehydrated toluene, the unattached  $Fe(acac)_3$  was then carefully washed off with toluene, and the product was vacuum dried. All operations related to the synthesis of the polymeric carriers and their complexing were conducted in an atmosphere of Ar. The physicochemical properties of the polymeric metal complexes are reported in Table 1.

The catalytic activity of the GCS was studied on a manometric installation with automatic stabilization of the pressure of the BD in the glass reactor. Before use, the moisture in the BD was again dried in columns containing silica gel and zeolites, and traces of  $O_2$  were removed on a special catalyst. Benzene was extracted with  $H_2SO_4$ , washed with water, passed through  $Al_2O_3$ , boiled over Na, and distilled in an Ar current in the presence of 0.5 g of triisobutylaluminum (TIBA) per liter. The solution of TEA in benzene was prepared immediately before use. For the tests, 0.5-1.0 g of swollen granules of the polymeric complex of Fe were used. The method of conducting the oligomerization of BD was similar to

TABLE ] [TEA cc	L. Physicochem catalyst, Fe:A	ical Proj 1 = 1:4	perties c (molar),	of GCS and TP 50°C, P <sub>buta</sub>	eir Catalyt: = 7.3	ic Activ •10 <sup>2</sup> GPa	rity in t 1]	he 01igom	erization	ı of Butad	iene	
Mainhor	Coordinate	Concent	ration, %	Swelling in				Compos	ition of ol	igomers		Total rate of
of GCS	group	đ	Fe	- benzene, ml/g	Reaction time. h	. (I)	(11)	(111)	(IV)	(11)	(X)	accumulation
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2	PC -P (OBu-t) 2	4	1,2	3,7	2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	22 22 22	11,3 1,3	111	0,4 4 0,4 7	7,3	1 8 1	47,6 24 6.6
c,	PC -P (0C <sub>8</sub> H <sub>1</sub> 7-n)	4	1,0	3,4	2.4	288	14 12,8 31	111	2,8 1 7,8 1 7	53.23	6,2 1 9,7 1 9,7	6,0 160 78,5
4	PC $-PC_{3}H_{5}Cl_{2})_{2}$	4	1,2	3,4	4 <del>-</del>	12 12 12 12 12 12 12 12 12 12 12 12 12 1	31 17	2,0	0,1	15 8,0	) [m]	30
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Physicochemical Properties of GCS and	atalyst, Fe:Al = 1:4 (molar), 50°C, p <sub>1</sub>
E 1. Physicochemical Properties of GCS and	cocatalyst, Fe:Al = 1:4 (molar), 50°C, P <sub>1</sub>

[4]. The GLC analysis of the products of oligomerization of BD was conducted on an LKhM-8MD chromatograph (column 2 m long, SE-30 stationary phase, programmed temperature of 8°C/min). The results of the experiments are reported in Table 1.

## CONCLUSIONS

1. Iron complexes immobilized in the bulk of a polymer gel and containing phosphonite groups are active catalysts of linear oligomerization of butadiene.

2. The nature of the coordinating group of the polymeric carrier has a significant effect on the rate and selectivity of the oligomerization of butadiene.

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## POLYHYDROXYNAPHTHOQUINONES - A NEW CLASS OF NATURAL

ANTIOXIDANTS

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Echinochrome (2,3,5,7,8-pentahydroxy-6-ethylnaphthalene-1,4-dione), a red pigment contained in the gonads, spines, and skeletons of various forms of sea urchins, has high antioxidant effectiveness that exceeds by several factors the effectiveness of the widely used synthetic inhibitor 2,6-di-tert-butyl-4-methylphenol (Ionol) in model reactions involving the autooxidation of mineral and plant oils and animal fats [1]. A number of other pigments, viz., spinochromes I-V (Table 1), which are also polyhydroxy derivatives of naphthoquinone, accompany echinochrome in sea urchins:



 $R^1$ ,  $R^4 = OH$ ,  $R^2$ ,  $R^3 = H$ , OH,  $C_2H_5$ ,  $COCH_3$ .

It seems of interest to verify whether spinochromes, like echinochrome, are antioxidants. The goal of our research was to study the characteristics of polyhydroxynaphthoquinones as antioxidants in the model reaction of oxidation of cumene.

The low-temperature initiated oxidation of alkylbenzenes is described by the following scheme, which has frequently been verified experimentally:

Initiator 
$$\rightarrow r^{*} \xrightarrow{RH} R^{*}$$
 (0)

$$R' + O_2 \rightarrow RO_2' \tag{1}$$

$$RO_2 + RH \rightarrow ROOH + R^{*}$$
 (2)

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1345