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Diene Polymerizations with the Lanthanide Coordination Catalysts. I. Piperylene Polymerizations Effected by the Type of Lanthanide

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Abstract

The present paper concerns studies into piperylene polymerizations with the catalytic systems $LnHal_3 \cdot 3TBP-Al(i\text{-}C_4H_9)_3$ (Ln = Ce, Pr, Nd, Gd, Tb, Dy; Hal = Cl, Br, I; TBP = tributylphosphate) occurring in various solvents. The activity and stereospecificity of these catalysts have been found to depend on the composition of the initial lanthanide component $LnHal_3 \cdot 3TBP$ and mostly on the lanthanide itself. With other conditions being equal, the highest polymerization rates are provided by the Nd catalyst, and the Gd catalyst favours the formation of polypiperylene with the maximum content of *cis*-1,4-units. The data obtained have proved the dependence of anti–sin isomerization of π-allyl active centres on the types of the lanthanide, halogen, hydrocarbon solvent and diene monomer used.

Introduction

Recent research has resulted in further development of new types of Ziegler–Natta catalysts based on f-orbital elements such as lanthanides and actinides. With stereospecific diene polymerizations, some of the catalysts represent binary systems consisting of a combination of the $LnHal_3 \cdot nL$ lanthanide complex (L = electron-donor ligand) and trialkylaluminium.

Reference 1 (a review) and some subsequent papers published are a vivid demonstration that the potentials of these catalysts have been generally investigated with respect to the butadiene and isoprene *cis*-polymerizations. The data concerning piperylene (1,3-pentadiene) polymerizations appear very scanty. There exists some information that with chlorine-containing lanthanide catalysts the formation of isotactic polypiperylene takes place, that being preferably built of *cis*-1,4-units coupled head-to-tail [2–7], but other detailed information has not been found. The $LnCl_3 \cdot 3L-AlR_3$ catalysts used therein contain alcohols [3], tributylphosphates or sulphoxides [4] as electron-donor ligands.

The present paper reports some results on how the activity and stereospecificity of the considered catalysts is effected by their compositions in piperylene polymerizations.

Experimental

The starting piperylene consisted of a mixture of *cis*- and *trans*-isomers. The content of the proper monomer, *i.e.* *trans*-piperylene, was 60%. The *cis*-isomer does not polymerize with the lanthanide catalysts and represents an inert component, therefore the isomers were not separated. Piperylene was treated with maleic anhydride to remove catalyst-desactivating cyclopentadiene. Boiling in the presence of an NaOH–water–ethanol solution caused release of the monomer from carbonyl impurities. Piperylene and hydrocarbon solvents were distilled in the presence of triisobutylaluminium immediately before the polymerization started. Every procedure was carried out in an argon atmosphere. Catalysts such as $LnHal_3 \cdot 3TBP-Al(i\text{-}C_4H_9)_3$ (Al/Ln = 30; TBP = tributylphosphate) were used.

Complexes $LnHal_3 \cdot 3TBP$ were prepared according to the method published in ref. 8. Similarly [2], the contents of *cis*- and 1,4-units in the polymer were determined by IR and ^1H NMR spectroscopic methods, respectively. The difference in the content of 1,4- and *cis*-1,4-units corresponds to the *trans*-1,4-units.

Results and Discussion

The activity of the catalysts studied greatly varied from one to the other metal within the lanthanide series. Thus, polymerizations in toluene at 25 °C with the catalytic systems based on $LnCl_3 \cdot 3TBP$ resulted in a lowering of the polypiperylene yield in the order: Nd > Gd > Pr > Tb > Ce > Dy. Other lanthanides revealed much less activity than Dy. With polymerizations in n-heptane, the order is: Nd > Pr >

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Ce > Gd > Tb > Dy. With respect to the polymerization conditions, e.g. the solvent and temperature used, the activity series slightly changed with the following regularities retained. Maximum polymerization rates can be reached with Nd catalysts when other conditions are equal. The catalyst activity for the cerium subgroup increases from lanthanum to neodymium, while that for the yttrium subgroup shows an opposite trend and the Gd catalyst provides the highest activity. Samarium and europium fail to give a polymer due to the reduction of trivalent Sm and Eu to their divalent states with AlR_3. The catalysts based on erbium, and especially on the metals neighboring that, are really inactive. It is known that in the heavy lanthanides the f-orbitals are well shielded and thus their participation in chemical bond formation is strongly limited. The catalytic activity may be assumed to occur owing to participation of the f-orbitals in the formation of a coordination linkage between the lanthanide and diene. The piperylene polymerizations may be considered with respect to the recent conclusion [9] that the position of any lanthanide in the activity series is first of all determined by the dependence of the active centre reactivities (rate propagation constant k_p) on the lanthanide ordinal number.

IR spectra of the polypiperylene samples obtained show no bands at 910 cm^{-1}, thus giving evidence of the absence of 3,4-units in the polymer. Its macrochains contain 1,4- and 1,2-units; 1,4-units can possess *cis*- and *trans*-geometry, while 1,2-units represent *trans*-geometry only, as reported in ref. 2. Although polypiperylenes contain preferably *cis*-1,4-units (Fig. 1), this property, as well as the content of the total 1,4-units (Fig. 2), is inferior to polybutadiene and polyisoprene produced under similar conditions [1]. Therefore, lanthanide catalysts lose their high stereospecific properties in piperylene polymerizations and the regular chain structure is broken, generally due to the appearance of 1,2-units (*ca.* 20%).

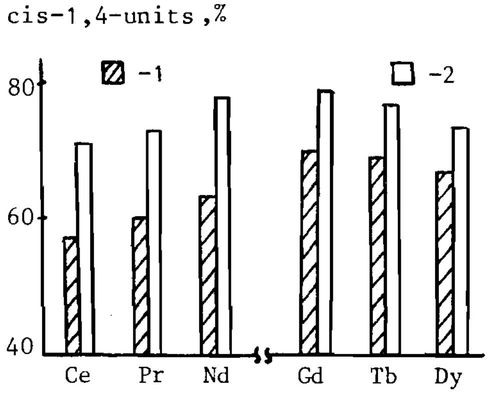

Fig. 1. The dependence of the *cis*-1,4-unit content in polypiperylene (15–20% yield) on the lanthanide used for polymerizations in toluene (1) and n-heptane (2) with the $LnCl_3 \cdot 3TBP–Al(i\text{-}C_4H_9)_3$ catalytic system at 25 °C.

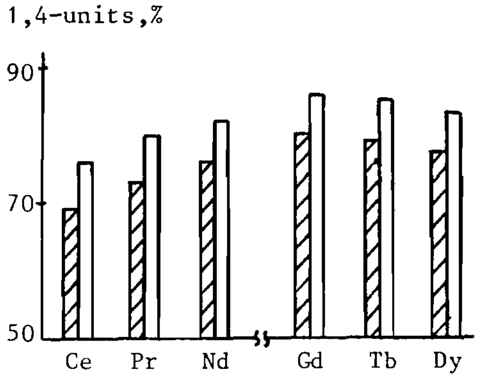

Fig. 2. The dependence of the 1,4-unit content in polypiperylene on the lanthanide used (under conditions analogous to those of Fig. 1).

In contrast to butadiene and isoprene [1], piperylene polymerization reveals the pronounced dependence of catalyst stereospecific properties on the lanthanide involved (Figs. 1, 2). These dependences correspond to the ones drawn with studies of the effect of the lanthanide type on catalyst activity; *i.e.* the content of *cis*-1,4-units increases and decreases in polypiperylene with increasing lanthanide number in cerium and yttrium subgroups, respectively. Similarly, the content of 1,4-units varies as well. In general, the investigated catalysts with lanthanides of the yttrium subgroup give polypiperylenes with a higher content of *cis*-1,4-units (Fig. 1). The most stereoregular polypiperylene is formed with a Gd catalyst. Thus, the highest activity and the highest stereospecificity are not inherent to the same lanthanide in piperylene polymerization. This is probably conditioned by the dependence of anti–sin isomerizations of active centres on the lanthanide type.

Both the process rate (Fig. 3) and the microstructure of polypiperylene (Figs. 1, 2) are effected by the type of solvent in which polymerization occurs. The solvents may be divided into two groups. With the first group, including aliphatic hydrocarbons and chlorobenzene, higher polymerization rates and the formation of a polymer with a higher content of *cis*-1,4- and 1,4-units become achievable. This group provides really equal rates and the formation of polymers of similar microstructure. In aromatic hydrocarbons, polymerization proceeds more slowly and the resulting polymers possess lower stereoregularities. The difference in microstructures of polypiperylenes obtained in toluene and n-heptane increases with the increase in polymerization temperature (Fig. 4). With a Gd catalyst (in contrast to that of Nd), the polymers obtained in toluene and

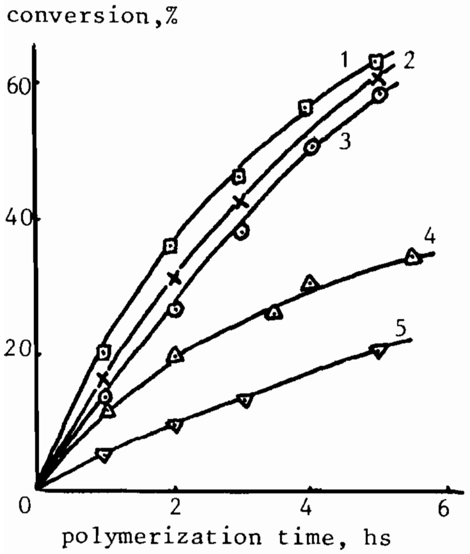

Fig. 3. The kinetics of piperylene polymerizations with the $NdCl_3 \cdot 3TBP-Al(i\text{-}C_4H_9)_3$ catalytic system in isopentane (1), n-heptane (2), chlorobenzene (3), benzene (4) and toluene (5) at 25 °C.

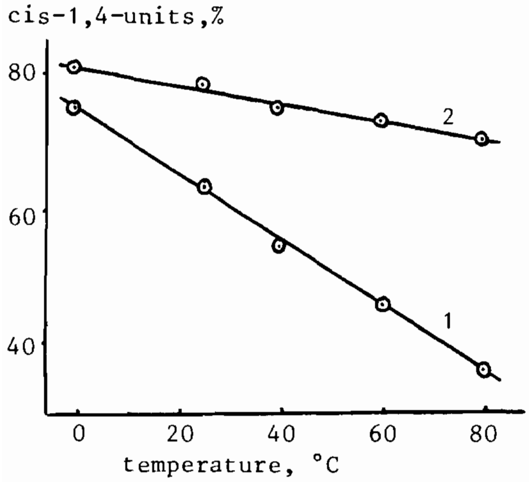

Fig. 4. The dependence of the *cis*-1,4-unit content in polypiperylene (15–20% yield) on the polymerization temperature in toluene (1) and n-heptane (2) with the $NdCl_3 \cdot 3TBP-Al(i\text{-}C_4H_9)_3$ catalytic system.

n-heptane at 0 °C are of similar microstructures. The dependence of active centre functions on the lanthanide used is thus observable in the above aspect as well.

The total sum of the data obtained gives evidence of the formation of non-identical active centres with polymerizations in aliphatic and aromatic hydrocarbons. That non-identity results probably from the changing of the lanthanide ligand environment in the active centre due to the arene-type complexes formed. According to the idea of the π-allyl structure of lanthanide active centres [10], the dependence of activity and stereospecific properties of the catalysts studied on the hydrocarbon solvent type is evidently caused by the higher rate of anti–sin isomerization of active centres with arene ligands.

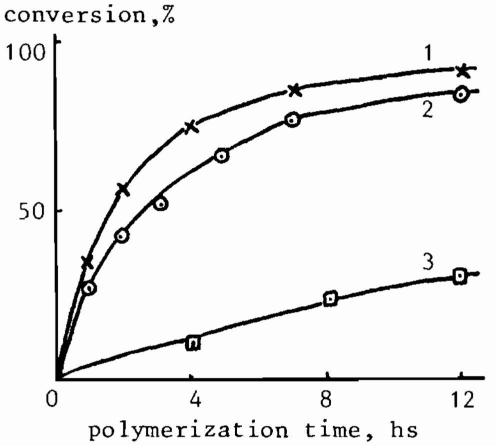

Fig. 5. The kinetics of piperylene polymerizations in n-heptane with the $PrHal_3 \cdot 3TBP-Al(i\text{-}C_4H_9)_3$ catalytic systems: Hal = Br (1), Cl (2) and I (3) at 25 °C.

TABLE I. Microstructure of Polypiperylene Synthesized with $LnHal_3 \cdot 3TBP-Al(i\text{-}C_4H_9)_3$ Catalysts at 25 °C (60–70% conversion)

Solvent	Ln	Halogen	Unit content (%)		
			1,4-	*cis*-1,4-	*trans*-1,4-
Toluene	Pr	Cl	73	52	21
		Br	72	47	25
		I	64	27	37
n-Heptane	Pr	Cl	80	71	9
		Br	82	73	9
		I	69	35	34
	Gd	Cl	82	79	3
		Br	85	83	2
		I	80	69	11

The known peculiar feature of the catalysts based on f-element halogenides is revealed by the independence of their stereospecificities on the halogen type in butadiene polymerizations; the content of *cis*-1,4-units in polyisoprene increases slightly in the series of iodine-, bromine- and chlorine-containing catalysts [1]. It was found that there exists an intricate dependence of the lanthanide catalyst activity (Fig. 5) and polypiperylene microstructure on the halogen type. Chlorine- and bromine-containing catalysts favour similar polymerization rates and scarcely differ in their stereospecific properties when other conditions are equal. Polypiperylene produced with iodine-containing catalysts shows more *trans*-1,4-units especially with praseodymium (Table I). Thus, there arises evidence of a strongly pronounced anti–sin isomerization of active centres, which is in addition proved by the low polymerization rates. With iodine catalysts, the dependence of polypiperylene microstructure on the lanthanide also occurs to the highest degree.

Conclusions

Our studies of piperylene polymerizations have proved the lanthanide and halogen type as well as the hydrocarbon solvent influence the activity and, above all, the stereospecific properties of the lanthanide catalysts. According to information available, that influence on the stereospecific properties of such catalysts was either unobserved or extremely poor with butadiene and isoprene polymerizations. The difference in polymerizations of conjugated dienes is evidently explained by the higher anti–sin isomerization of active centres in the pentadienyl structure and by its dependence on the chemical individuality of the lanthanide.

References

1 N. G. Marina, Yu. B. Monakov, S. R. Rafikov and Kh. K. Gadeleva, *Vysokomol. Soedin., Ser. A, 26,* 1123 (1984).

2 A. A. Panasenko, V. N. Odinokov, Yu. B. Monakov, L. M. Khalilov, A. S. Bezgina, V. K. Ignatyuk and S. R. Rafikov, *Vysokomol. Soedin., Ser. B, 19,* 656 (1977).

3 D. Xie, C. Zhong, N. Yuan, Y. Sun, S. Xiao and J. Ouyang, *Kao Ken Tsu Tung Hsun, 4,* 233 (1979); *Chem. Abstr., 92,* 77008r (1980).

4 *U.S.S.R. Pat. 726110 (Cl.C08F 137/04)* to Yu. B. Monakov, S. R. Rafikov, A. S. Bezgina, G. A. Tolstikov, *et al.*; *Chem. Abstr., 93,* 72926z (1980).

5 A. Bolognesi, S. Destri, L. Porri and F. Wang, *Makromol. Chem., Rapid Commun., 3,* 187 (1982).

6 D. Xie and C. Zhong, *Gaofenzi Tongxun, 3,* 220 (1983); *Chem. Abstr., 99,* 159096b (1983).

7 H. C. Yeh and H. L. Hsieh, *Am. Chem. Soc. Polymer Prepr., 25,* 52 (1984).

8 Yu. I. Murinov, Yu. B. Monakov, Z. G. Shamaeva, N. G. Marina, V. S. Kolosnitsyn, Yu. E. Nikitin and S. R. Rafikov, *Izv. Akad. Nauk SSSR, Ser. Chim., 12,* 2790 (1977).

9 Yu. B. Monakov, N. G. Marina, I. G. Savel'eva, L. E. Zhiber, V. G. Kozlov and S. R. Rafikov, *Dokl. Akad. Nauk SSSR, 265,* 1431 (1982).

10 Yu. B. Monakov, N. G. Marina, I. G. Savel'eva, L. E. Zhiber, N. V. Duvakina and S. R. Rafikov, *Dokl. Akad. Nauk SSSR, 278,* 1182 (1984).