Polymerization of 1, 3-Butadiene by Biscyclopentadienylnickel Compounds

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(Received September 17, 1966)

The polymerization of 1, 3-butadiene by a binary catalyst system of a biscyclopentadienylnickel compound and an organoaluminum compound has been studied. The nickel π-complexes used in the experiments were biscyclopentadienylnickel bromide (Cp_2NiBr_3), biscyclopentadienylnickel diammonotetrathiocyanochromate ($Cp_2Ni(NH_3)_2Cr(NCS)_4$), and biscyclopentadienylnickel tetraphenylborate (Cp_2NiBPh_4).

In an autoclave (100 m*l* volume), 50 m*l* of toluene as a solvent, 30 m*l* of liquid butadiene, 0.1 g of a nickel π-complex, and 1 m*l* of an organoaluminum compound ($AlEt_3$, $AlEt_2Cl$, or $AlEtCl_2$) were taken into an inert atmosphere. The reaction was then carried out at 110°C for 2 hr. After the termination of the reaction (by the addition of 10 m*l* of acetone), the products were analyzed. The results are shown in Table 1 and Table 2.

When the Cp_2NiX-$AlEt_3$ catalyst system was used, cyclooligomerization predominantly occurred, and cyclodimers (vinylcyclohexene and cyclooctadiene) and a cyclotrimer (cyclododecatriene) were produced. In the case of $AlEt_2Cl$ or $AlEtCl_2$, polymerization occurred, but the catalytic activity of Cp_2NiX-$AlEtCl_2$ systems was much inferior to that of Cp_2NiX-$AlEt_2Cl$ systems. The

TABLE I. Cp_2NiX-$AlEt_3$ CATALYSTS SYSTEM

Catalyst component	Conversion %	Content (%) of products			
		V·H	COD	CDT	Redidue
Cp_2NiBr_3-$AlEt_3$	89.0	14.5	24.2	47.3	14.0
$Cp_2Ni(NH_3)_2Cr(NCS)_4$-$AlEt_3$	75.6	13.9	26.5	12.0	12.0
CP_2NiBPh_4-$AlEt_3$	78.6	12.6	24.8	48.5	13.6

V·H: Vinylcyclohexene COD: Cyclooctadiene CDT: Cyclododecatriene

TABLE 2. Cp_2NiX-$AlEt_2Cl$ (OR $AlEtCl_2$) CATALYSTS SYSTEM

Catalyst component	Yield (%) of polymer formed	Microstructure (%) of polymer formed			[η]
		1.4 cis	1.2 cis	1.4 trans	
Cp_2NiBr_3-$AlEt_2Cl$	80.1	75.1	2.2	22.8	0.34
Cp_2NiBr_3-$AlEtCl_2$	15.1	74.8	4.5	20.7	0.16
$Cp_2Ni(NH_3)_2Cr(NCS)_4$-$AlEt_2Cl$	70.5	76.5	6.2	17.3	0.13
$Cp_2Ni(NH_3)_2Cr(NCS)_4$-$AlEtCl_2$	11.7	75.2	7.8	17.0	0.11
Cp_2NiBPh_4-$AlEt_2Cl$	63.2	75.2	4.5	20.3	0.28
Cp_2NiBPh_4-$AlEtCl_2$	9.8	78.9	7.5	13.6	0.20

[η]: Determined at 30°C in toluene solution. [η]: Intrinsic viscosity

microstructure of the polymer formed was determined by a study of its IR spectra. In each case of polymerization, 1.4 cis addition occurred mainly.

Biscyclopentadienylnickel bromide was prepared1) by oxidizing nickelocene in petroleum ether with Br_2. Biscyclopentadienylnickel tetraphenylborate or biscyclopentadienylnickel diammonotetrathiocyano chromate was prepared1) by reacting $(C_5H_5)_2NiBr_3$ with $NaBPh_4$ or $NH_4Cr(NCS)_4(NH_3)_2$.

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1) E. O. Fischer and W. Hafner, *Z. Naturforsch.*, 217 (1953); G. L. Hobbs, Brit. Pat. 733129 (1955).