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1,3-Butadiene polymerization by Ziegler-Natta catalyst containing fluorine atoms as halogenating agent

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Abstract – In this work a Ziegler-Natta catalytic system constituted of neodymium versatate (NdV), diisobutylaluminium hydride (DIBAH) and an halogenation agent, has been studied with respect to the influence of halogen source and halogen:Nd molar ratio on the catalyst activity, polymerization constant rate, polymerization conversion, molecular weight characteristics and microstructure of polybutadiene. Using either pre-formed or *in situ* catalysts, it was compared the Fluor-containing catalysts systems with the Cloro-containing catalysts systems.

Among the isomeric forms obtained from butadiene polymerization, the polybutadiene with high content of *cis*-1,4 units has attracted attention due to its excellent physical properties, such as abrasion resistance and low heat build-up. These characteristics make this elastomer one of the most used in pneumatic industry [1].

The literature [2] shows that a neodymium-based catalyst system having tert-butyl chloride as halogenating agent produces polybutadiene with *cis*-1,4 units content higher than 95% depending on the catalyst system, catalyst's synthesis conditions, polymerization's conditions and on the molar ratio between the catalyst components. On the other hand, $BF_3.OEt_2$ based catalyst presents some advantages. The polybutadiene molecular weight and molecular weight distribution (MWD) can be controlled by simple variation of $BF_3.OEt_2$ concentration without accentuated effect on the activity and *cis*-1,4 units content [3].

In this work it was studied two catalysts systems containing $BF_3.OEt_2$ (one of them was activated *in situ* at F:Nd molar ratio=3:1 (A) and another one was pre-formed and aged for 5 days at F:Nd molar ratio=1:1 (B)) and two catalysts systems consisting of $THF.BF_3$ as halogenating agent (one of them was activated *in situ* at F:Nd molar ratio=3:1 (C) and another one pre-formed and aged for 24 hours at F:Nd molar ratio=3:1 (D)). All catalyst systems were compared with the catalyst consisting of t-BuCl at a Cl:Nd molar ratio=3:1 (E).This last one provided the highest conversion, and both BF3-based catalyst showed similar conversion values (Figure 1).

According to the literature [4] the F-based catalyst produces polybutadiene when the F:Nd molar ratio is higher than 10, and when the F:Nd molar ratio is 40 the highest catalyst activity is attained.That behavior was attributed to the fact that dialkylaluminium fluorides are associated as tetramers, because of that is necessary to use an excessive proportion of this component. The halogenating agent $THF.BF_3$ produces similar catalyst activity and stereoregularity as that produced by $BF_3.OEt_2$ [3].

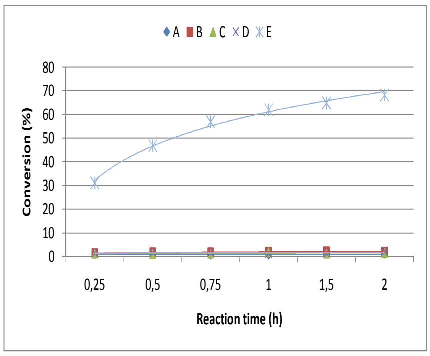

Figure 1: The influence of the catalyst system on the conversion

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