Peculiarities of the composition heterogeneity of ethylene/1-hexene copolymers produced over supported catalysts of different composition.

Mikhail A. Matsko[1], Inna K Shundrina[2], Marina I Nikolaev[1], Ludmila G. Echevskaya[1], Kseniya I. Baskakova[3], Vladimir A. Zakharov[1]

[1]Boreskov Institute of *Catalysis SB RAS (Russia)*
[2]Vorozhtsov Instit. of Organic Chemistry, Russian Academy of Science (Russia)
[3]Novosibirsk State University (Russia)

The separation into narrow MWD fractions (liquid-liquid fractionation) and into fractions with different level of short chain branching (preparative TREF fractionation) with subsequent analysis of fractions by GPC, FTIR and ^{13}C NMR spectroscopy were used to study the comonomer distribution of ethylene/1-hexene copolymers produced over highly active supported titanium -magnesium catalyst $TiCl_4/MgCl_2$ (TMC), vanadium-magnesium catalyst $VCl_4/MgCl_2$ (VMC) and a supported zirconocene catalyst $Me_2Si(Ind)_2ZrCl_2/SiO_2$(MAO). These catalysts produce copolymers with different MWD: Mw/Mn values vary from 2.4-2.9 for zirconocene catalyst, 4.0-4.7 for TMC, and 22-25 for VMC. Hexene -1 increases Mw/Mn from 15 up to 25 for copolymer produced over VMC and hardly affects MWD of copolymer produced over TMC and zirconocene catalysts.

The most broad short chain branching distribution (SCBD) was found for ethylene/1-hexene copolymers synthesized over TMC. VMC and supported zirconocene catalyst produce copolymers with a uniform profile of SCB content vs. molecular weight in spite of great differences in Mw/Mn values (22 and 2.4, respectively). At the same time TREF data indicate a more homogeneous SCBD in copolymer produced over supported zirconocene catalyst in comparison with VMC.

Dynamic mechanical analysis (DMA) data confirm some peculiarities of ethylene/1-hexene copolymers produced over supported VMC in comparison with TMC. It was shown that the occurring relaxations correlate to the crystallinity, lamella thickness, and SCBD. It was demonstrated that the type of catalyst has a great influence on the α- and β-transitions in corresponding copolymers.

This work was supported by the Ministry of education and science of Russia, project 14.607.21.0046.