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Ethylene and isoprene copolymerization by homogeneous metallocene catalysts

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Abstract – The metallocene compounds $Ph_2C(Flu,Cp)ZrCl_2$ (cat 1) and $Et(Flu)_2ZrCl_2$ (cat 2) activated with methylaluminoxane (MAO) were evaluated in ethylene and isoprene copolymerization. The comonomer concentration varied from 2.2 to 8.7 M and the polymerization temperature from 40 to 80 ºC. Ethylene concentration (0.135 M) was maintained constant in the reaction medium by adjusting the monomer pressure. The thermal properties and specific gravities of the synthesized materials were measured. Most of the copolymers obtained with catalyst 1 were amorphous, however those obtained with catalyst 2 at the same reaction conditions presented melting temperature lower than that of polyethylene. The properties of the synthesized copolymers were compared with those of polyethylene which was obtained at the same reaction conditions.

Metallocene systems have been studied in copolymerization of ethylene with comonomers such as alpha-olefins, cyclic or acyclic dienes [1-3]. Efforts have been developed in order to improve ethylene copolymer materials with significant incorporation of diene comonomers resulting in special mechanical and thermal properties [4-6]. Many authors [10-12] refer to copolymerization of ethylene with dienes but the reaction with isoprene is still not usually reported in the literature [13]. In the present work, we have studied the performance of the catalysts $Ph_2C(Flu,Cp)ZrCl_2$ and $Et(Flu)_2ZrCl_2$ in ethylene/isoprene copolymerization varying the comonomer content and polymerization temperature with the aim to observe the influence of these parameters on thermal properties and specific gravities of the synthesized materials.

The two homogeneous catalyst systems studied were very active for homo and copolymerization of ethylene and isoprene, although the complex 1 ($Ph_2C(Flu,Cp)ZrCl_2$/MAO) was more active than 2 ($Et(Flu)_2ZrCl_2$/MAO), at all temperatures employed.The melting temperatures of the copolymers obtained with catalyst 1 were lower than those with catalyst 2. Amorphous polymers were obtained with cat 1 at high concentrations of comonomer. It is possible that the catalyst 1 produced ethylene-isoprene copolymers containing higher amounts of comonomer in the polymer chain compared with the copolymer synthesized with catalyst 2. This effect can be justified by the bulkier bis-fluorenyl ligand of catalyst 2, which difficult the incorporation of the diene comonomer. Furthermore, it should be considered that the longer bridge in the structure of catalyst 2 results in a smaller angle of aperture which also influences the diene incorporation.

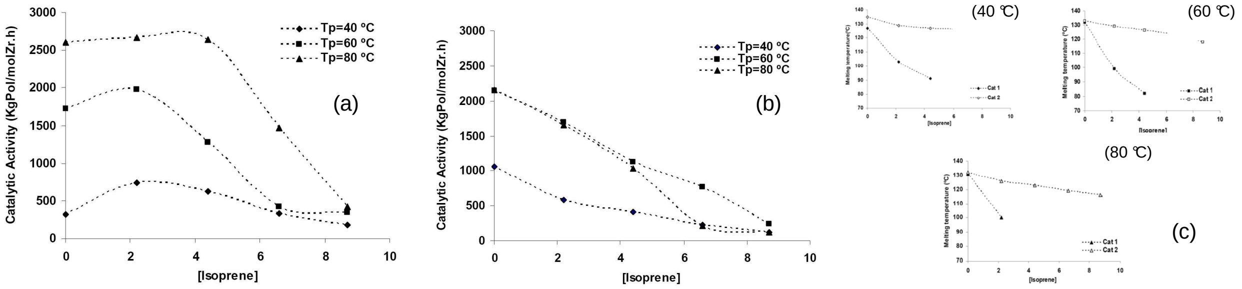

Figure 1: Catalytic activity and Melting temperature (c) *versus* molar concentration of isoprene in copolymerization with $Ph_2C(Flu,Cp)ZrCl_2$/MAO (a) and $Et(Flu)_2ZrCl_2$/MAO (b)

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