

ABSTRACT

Four chromium-based oxo-trinuclear carboxylate complexes were prepared by reacting $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ with acetic acid and substituted carboxylic acids to produce $[\text{Cr}_3\text{O}(\text{CH}_3\text{COO})_6 \cdot 3\text{H}_2\text{O}]\text{NO}_3 \cdot 7\text{H}_2\text{O}$, $[\text{Cr}_3\text{O}(\text{ClCH}_2\text{COO})_6 \cdot 3\text{H}_2\text{O}]\text{NO}_3 \cdot 3\text{H}_2\text{O}$, $[\text{Cr}_3\text{O}(\text{Cl}_2\text{CHCOO})_6 \cdot 3\text{H}_2\text{O}]\text{NO}_3 \cdot \text{H}_2\text{O}$ and $[\text{Cr}_3\text{O}(\text{Cl}_3\text{CCOO})_6 \cdot 3\text{H}_2\text{O}]\text{NO}_3 \cdot 2\text{H}_2\text{O}$, which were characterized by infrared spectroscopy (FT-IR) and thermal analysis (TGA). Chromium content in each complex was determined by titrimetry method and the result was in good agreement with that from TGA. Chromium(III) monochloroacetate complex, $[\text{Cr}_3\text{O}(\text{ClCH}_2\text{COO})_6 \cdot 3\text{H}_2\text{O}]\text{NO}_3 \cdot 3\text{H}_2\text{O}$ in combination with diethylaluminium chloride formed heterogeneous catalyst system for ethylene polymerization and ethylene-propylene copolymerization. Both Al/Cr ratio and temperature influenced the catalytic activity. The maximum activity of ethylene polymerization was 1768 gPE/gCr/hr/atm, achieved by polymerizing ethylene at 29°C with Al/Cr ratio 30.8. Effect of chloro-substituent groups on carboxylic ligand was studied by using chromium(III) dichloroacetate, chromium(III) trichloroacetate and chromium(III) acetate as catalyst. Ethylene polymerization is first order with respect to ethylene during the initial stage. A decay-type of curve was observed when activity was plotted against reaction time. Incorporation of propylene into ethylene has yielded ethylene-propylene random copolymers with lower melting temperatures and lower degree of crystallinity than polyethylene homopolymer. Differential Scanning Calorimetry (DSC) thermograms showed that E-P samples in higher propylene content consists two or more melting peaks. Increasing mol% of propylene used would lead to a decrease in the catalytic activity and lower the product yield. Effect of catalyst aging time and Al/Cr molar ratio in ethylene-propylene copolymerization were studied. Composition of E-P copolymers

were determined by FT-IR and an almost linear relationship was obtained between the absorbance ratios (A_{720}/A_{1376} and A_{1376}/A_{1463}) and ethylene content.