Metallocene catalysts - applications in the manufacture of polyethylenes and high-impact polypropylenes in gas-phase polymerization processes

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SUMMARY: The advent of single-site type metallocene catalysts has had a revolutionary impact on the manufacture of polyolefins[1)]. The impact is broad and includes polymer properties (rheological, mechanical) and productivity of polyolefin manufacturing processes. Constrained geometry catalysts with open and accessible active sites give random copolymerization of α-olefins and macromonomers giving narrow chemical composition and molecular weight distributions and long chain branching. Super condensation mode of heat removal is enhanced with metallocene catalysts. The use of metallocene catalysts and active site poisons can improve impact polypropylene properties (bulk density, powder flowability and impact strength). These topics will be discussed in some detail.

Introduction

Polyolefins are commercially produced using free-radical initiators, Phillips chromium oxide type catalysts, Ziegler-Naffa catalysts and more recently, metallocene catalysts[2)]. Industrial processes that use Ziegler-Natta catalysts are the most important ones because of the very broad range of applications of their products. Ziegler-Natta catalysts have evolved considerably since their discovery by K. Ziegler and G. Natta in the early fifties. These catalysts have been used in homogeneous, heterogeneous and colloidal forms to synthesize various types of homo and copolymers. In its broadest definition, Ziegler-Natta catalysts are composed of a transition metal salt of metals from groups IV to VIII (known as the catalyst) and a metal alkyl of a base metal from groups I to III (known as cocatalyst or activator). For industrial use, most Ziegler-Natta catalysts are based on titanium salts and aluminum alkyls. Many industrial processes using a variety of reactor types using Ziegler-Natta and Phillips

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chromium oxide catalysts are in use today for the production of polyolefins. Gas-phase processes appear to have greatest potential for growth because of the combination of excellent economic factors plus being environmentally friendly and therefore gas-phase processes will be considered exclusively in this manuscript.

Gas - phase polymerization of ethylene and propylene

Before the discovery of Ziegler-Natta catalysts, polyethylenes were produced commercially only with free-radical initiators at high polymerization temperatures and pressures. Polymer chains obtained with free-radical processes contain both short and long chain branches. The short branches which are formed by backbiting are 2 to 5 carbon atoms long while the long chain branches which are formed by chain transfer to polymer have a distribution of chain lengths which is comparable to the distribution of chain lengths for the main chains. From a rheological or polymer melt processing point of view, side chains with chain lengths smaller than the critical chain length for entanglement should not affect rheological responses [(zero shear viscosity, shear thinning (I_{10}/I_2), melt fracture, die swell and melt tension, for example)]. The critical molecular weight for chain entanglement in polyethylene melts is about 4000 (chain length of about 290 carbon atoms). Long chain branches are known to increase zero shear viscosity, increase shear thinning, delay melt fracture, increase die swell and increase melt tension. Free-radical polyethylenes have broad molecular weight distributions (M_w/M_n ~5) and very high levels of long chain branching LCB) (λ_n ~ 5 to 50 LCB per 10 000 C-atoms, or B_n ~ 1 to 20 LCB per polymer molecule). HP-LDPE (free-radical polyethylenes) are used predominantly for making films because of its limp feel, clarity and toughness. The high levels of long chain branching give excellent processability and high melt tension suitable for the manufacture of thin films.

The most important innovations introduced in the manufacture of polyolefins with ZieglerNatta catalysts are the synthesis of linear high density polyethylene (HDPE) with low levels of α-olefins comonomers and the copolymerization of ethylene with moderate levels of α-olefins to produce linear low density polyethylene (LLDPE) and the production of highly isotactic and syndiotactic polypropylene.

HDPE has few or no short chain branches and no long chain branches and polydispersities which can vary in the range, M_w/M_n ~3.5 to 9. These high polydispersities can give adequate levels of shear thinning (I_{10}/I_2 ~8). HDPE is used in structural applications because of its greater rigidity as compared to HP-LDPE and LLDPE. Copolymerization of ethylene with α--olefins disrupts the order of the linear polyethylene chain by introducing comonomer units that contain short chain branches. As a consequence, the density, crystallinity and rigidity of the polymer are reduced. By varying the amount and type of α-olefin, the catalyst type and the polymerization conditions, one can produce several grades of copolymers to meet specific market demands. LLDPE shares the market with HP-LDPE made by free-radical processes.

Several types of Ziegler-Natta catalysts are stereoscopic, i.e. the insertion of asymmetric monomers into the growing chain in a given orientation is favoured over all possible orientations. This characteristic of Ziegler-Natta catalysts permitted for the first time the production of highly isotactic and syndiotactic polypropylene. Isotactic polypropylene is used in several injection molding and extrusion processes due to its excellent rigidity, toughness and temperature resistance. To improve the impact strength at lower temperatures, impact polypropylene is produced in a 2-stage process. Isotactic polypropylene particles having a porosity of about 30 % are made in stage-1. These porous particles flow into stage-2 where the active sites in these particles experience an atmosphere of ethylene/propylene monomers and an ethylene/propylene rubber of about 50 mole % ethylene is synthesized. When the pores are filled with incompatible copolymer, a shell layer of rubber may form on the surface of the polymer particles. Smaller polymer particles tend to accumulate excessive levels of rubber and become sticky, causing wall fouling and particle agglomeration. The latter adversely affects bulk density and flowability of the powdered polymer product. Larger polymer particles lose more of their active sites in stage-1 due to thermal deactivation and hence accumulate inadequate levels of rubber in stage-2. This poor dispersion of rubber among polypropylene particles of different size may result in lower impact strength and loss in flexural modulus 2). The multi-site type titanium-based Ziegler-Natta catalysts used for the manufacture of impact polypropylene may given copolymer chains with sufficiently long sequences of either ethylene or propylene to obtain some crystallinity 3,4) which is undesirable for an impact modifier. Ideal copolymer chains should not crystallize and have as high a level of propylene as possible for reasons of compatibility when used as an impact modifier. A single site type metallocene catalyst system should permit the synthesis of a random copolymer of ethylene/propylene with a very narrow chemical composition distribution. It should also be possible to optimize the combination of low ethylene content with low crystallinity to maximize impact strength. Another important factor in maximizing impact strength is to make the distribution of ethylene/propylene rubber among the polypropylene particles more uniform in the powdered product, leaving stage-2(5). This can be done with the proper selection design of catalyst and reactor system in stages-1 and -2. Low catalyst active site thermal deactivation rates and narrow residence-time distributions in stages-1 and -2 are desirable. Poisons can be used in stage-2 to overcome design features which are less than optimal. It has been shown that the use of a poison in stage-2 can reduce reactor fouling and polymer particle agglomeration and improve powder bulk density and flowability as well as impact strength with minimal loss in flexural modulus(6).

Super condensation mode of heat removal in gas-phase polymerization processes is enhanced with the use of appropriate metallocene catalysts with an open metal centre which gives high incorporation rates of α-olefins. With classical Ziegler-Natta catalysts, high levels of α-olefin comonomers had to be used in the gas phase to achieve the desired level of α-olefin incorporation in the copolymer. This had an adverse effect on the dew point reducing the level of saturated hydrocarbon (such as a pentane) that could be used for direct contact heat removal via its evaporation. With the appropriate metallocene catalysts, the desired level of α-olefin in the copolymer can be achieved using appreciably lower α-olefin monomer levels in the gas phase permitting higher levels of saturated hydrocarbon to be employed. This could permit a doubling or more of the production rate.

We have already but briefly discussed the high levels of long chain branching and the beneficial effects on polymer melt processability which one finds for polyethylenes synthesized via free-radical mechanisms. Classical Ziegler-Natta and Phillips chromium oxide catalysts produce linear homo and copolymer chains. There is no evidence of any significant level of LCB. Metallocene catalysts of the constrained geometry type(7) have been shown to give polyethylenes with LCB less than about 1.0 per 10 000 as measured by C^{13}-

NMR on homopolyethylenes. These polymers were synthesized via continuous solution polymerization. These polyethylenes although having relatively narrow MWD's (M_w/M_n ~ 2) gave I_{10}/I_2 values as high as 11.5 [8)] Melt tension values [(MT (190 °C) (g)] of about 3.5 were much lower than those obtained with highly branched HP-LDPE of about 10.8. It is of interest to speculate about whether appreciable LCB might be obtained with a supported constrained geometry catalyst in a gas-phase polymerization. The important difference between gas-phase and solution polymerization processes is the concentration of polymer which is much greater in the polymer particles in a gas-phase process. Polymer chains are highly entangled and those with a higher molecular weight might be immobile (negligible self-diffusion of the centre of a mass of a highly entangled chain). When polymer chains grow on the active sites of a catalyst fragment, monomer(s) diffuse into the subparticle causing the subparticle to grow in volume. A dead polymer with terminal unsaturation caused by β-hydride elimination or chain transfer to monomer, or both, will be dragged away from expanding subparticle and as a consequence, the terminal carbon-carbon double bond may remain in the reaction volume for the active site for too short a time to add to the growing chain to form a trifunctional long chain branch. A shorter macromonomer chain may have too few entanglement points to render it immobile and it can add to the active centre to form an LCB. In other words, the incorporation of macromonomer and its rate may be chain length-dependent. The consequences of this are that most of the LCB will be shorter than the average chain length of macromonomer and that the branches may have a dendritic structure. It can also be shown that the frequency distributions of chain length for growing and dead polymer chains follow the Schultz-Flory most probable distribution when chain length dependence is ignored. However, recent information suggests that in the gas-phase process significant levels of long chain branching may be obtained with catalysts other than metallocenes even when incorporation of higher α-olefins is difficult. A possible explanation for this is that terminal carbon-carbon double bond on a recently formed macromonomer which is highly entangled cannot diffuse away from the reaction volume of the active centre making reincorporation in a newly growing chain quite likely. The steric barrier is thus of little consequence.

Conclusion

A number of examples of the use of metallocene catalysts for commercial manufacturing processes for polyolefins and the benefits derived therefrom have been illustrated.

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