

Propylene Polymerization Using Supported Ziegler–Natta Catalyst Systems with Mixed Donors

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ABSTRACT: Magnesium dichloride supported titanium catalyst incorporated with varying concentration of ethylbenzoate and diisobutyl phthalate together as internal donor are synthesized. The synthesized catalysts are characterized and compared with respect to composition, phase characteristics, crystallite size, and particle morphology. Performance of catalysts containing mixed donors is compared with the conventional single donor-based catalysts. The polymerization studies of the catalysts for propylene polymerization show dependence of polymerization

kinetics on relative concentration of diisobutyl phthalate and ethylbenzoate. Molecular weight characteristics of polypropylene obtained from these catalysts are studied and correlated with the nature and concentration of donors present in the catalyst. Morphology replication from catalyst precursor to polymer is observed irrespective of the nature of donor being incorporated in the synthesized catalyst. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 896–901, 2012

Key words: catalyst; mixed donors; poly(propylene)

INTRODUCTION

Polypropylene (PP) is among the fastest growing thermoplastics due to continued enhancement and tailoring of product characteristics in addition to improvements in production technology.^{1–4} One of the major factors for the growth is innovation in the high performance supported titanium catalyst leading to high catalyst productivity and tailored product characteristics.^{5–7} Initial generations of ZN catalysts were characterized by low activity and low stereoregularity. Introduction of MgCl₂ as support significantly improved the activity, but high stereoregularity could only come after introduction of organic electron donating component in the inorganic matrix.⁸ Today much of the catalyst development efforts are focused around modification of internal donor in solid catalyst composition. Successful commercial classes of catalyst systems are based on monoester, diester, diether type of internal donors.⁹ Studies on other types on internal donors such as triethers,¹⁰ ethyl propionate,¹¹ and mixed donors^{12,13} are also reported. Donors have a profound impact on polymerization kinetics and product properties for example ethyl benzoate (monoester)-based catalyst systems provide decay type of kinetics^{14,15} and

broad molecular weight distribution of the product where as diisobutyl phthalate (diester)-based catalysts show steady-state polymerization kinetics and produce polymer with narrower molecular weight distribution.^{16–18}

Current interest in tailoring molecular weight distribution characteristics of PP for high speed film¹⁹ making lines coupled with our studies on high performance supported titanium catalyst system prompted us to modify molecular weight distribution characteristics of PP through appropriate combination of different internal donors during catalyst synthesis. Ethyl benzoate and diisobutyl phthalate belong to two different classes of donors, i.e., monoester and diester, respectively. Both monoester and diester type of donors are used in supported Ziegler–Natta catalyst system for commercial scale usage. Monoester- and diester-based catalyst systems show significant differences in terms of catalyst activity, polymerization kinetics, and polymer characteristics. In this article, the authors have reported results on the development of catalyst system incorporated with both ethylbenzoate and diisobutyl phthalate donors together and influence of mixed donor on performance and product characteristics for propylene polymerization. Novelty of the work lies in affirming compatibility of two different classes of internal donors when incorporated together in a supported Ziegler–Natta catalyst system. Catalyst morphology is an important catalyst characteristic, which defines its operability, control over fines generation, rubber distribution in copolymer,

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and resin flow properties. In this study, the authors have also studied morphology replication from support to polymer to understand impact of internal donors on the shape replication characteristic.

EXPERIMENTAL

Materials

Titanium tetrachloride (Merck-Schuchardt, Germany) and triethyl aluminum (Crompton, Germany) were used as received. AR grade chlorobenzene, *n*-decane, hexane (Labort, India), diisobutyl phthalate (DIBP), ethyl benzoate (EB), benzoyl chloride (BzCl), phthaloyl chloride (PhCl), para ethoxy ethyl benzoate (PEEB), cyclohexylmethyl dimethoxy silane (C-Donor; Aldrich Chem., USA), and mineral oil (Witco, Germany) were used after treating with activated molecular sieves. Commercially available ultra pure propylene, nitrogen, magnesium ethoxide, and hydrogen were used as received. All the experimental manipulations were carried out under a high purity nitrogen atmosphere. Standard nitrogen atmos-bags and schlenk techniques were used for handling all the chemicals.

Catalyst preparation

Cat-A and Cat-E were prepared as reported earlier.^{20,21} Cat-B, Cat-C, and Cat-D with mixed internal donor were prepared by heating mixture of $\text{Mg}(\text{OC}_2\text{H}_5)_2$ and TiCl_4 ($\text{Mg}/\text{Ti} = 0.085$) in presence of equal volume of chlorobenzene at 120°C in a three-necked jacketed glass reactor. DIBP as internal donor was also added. The mole ratios of DIBP/ $\text{Mg}(\text{OC}_2\text{H}_5)_2$ was varied in every catalyst synthesis experiment to get varying degree of donor incorporation. The mole ratio of DIBP/ $\text{Mg}(\text{OC}_2\text{H}_5)_2$ in Cat-B, Cat-C, and Cat-D were kept as 0.28, 0.32, and 0.36, respectively. After 45 min of stirring, the reaction mixture by a mechanical agitator, the solids were allowed to settle, and the liquid was siphoned-off. The solid was again treated with TiCl_4 /chlorobenzene (1:1 v/v) and BzCl at 120°C for 45 min. The mole ratios of BzCl to $\text{Mg}(\text{OC}_2\text{H}_5)_2$ for Cat-B, Cat-C, and Cat-D were kept as 0.60, 0.40, and 0.20, respectively. The solid product was subsequently separated by settling followed by decantation of supernatant liquid and washed four times with 100 ml *n*-hexane. After washing catalyst was dried under nitrogen stream and stored as slurry in dried mineral oil. In Cat-E, the mole ratio of DIBP/ $\text{Mg}(\text{OC}_2\text{H}_5)_2$ was kept 0.40 and phthaloyl chloride was added in place of benzoyl chloride having mole ratio of PhCl to $\text{Mg}(\text{OC}_2\text{H}_5)_2$ as 0.1. In Cat-A, similar procedure was used only reaction temperature was 100°C in place of 120°C, EB was used in place of DIBP with mole ratio of 0.40 for EB/ $\text{Mg}(\text{OC}_2\text{H}_5)_2$ and 0.1 for BzCl to $\text{Mg}(\text{OC}_2\text{H}_5)_2$.

Polymerization

In 6.5 L stainless steel autoclave equipped with a stirrer, 2000 mL anhydrous hexane was added under nitrogen atmosphere followed by triethyl aluminum, external donor, and catalyst [$\text{Al}/\text{Ti} = 250$ and Al/D (C-Donor) = 30]. Calculated volume of hydrogen gas was introduced as chain terminating agent. Propylene pressure and reaction temperature were raised to the specified polymerization parameters. During polymerization, the total pressure was kept constant at 5.0 ± 0.1 bar at 70°C. On completion of reaction, the polymer product was separated and dried.

Characterization of catalysts

Magnesium and chlorine contents were determined by titration.²² For determination of titanium content in the catalyst, the catalyst was dissolved in an acidic media afterward all of the titanium contained in the catalysts was converted into Ti^{4+} by addition of H_2O_2 . UV-Vis spectra of the resultant solution of peroxotitanium complexes were recorded on a Perkin-Elmer UV Lambda-35 spectrophotometer. Intensity of the peak at 417 nm ($\epsilon = 782.7 \text{ L}^{-1} \text{ mol}^{-1} \text{ cm}^{-1}$) was used to quantify the titanium content. Solid samples were hydrolyzed in acidic solution for quantitative estimation of DIBP, EB, and ethoxy content as ethanol by gas chromatographic analysis.^{21,23,24} The morphology was examined by FEI Inspect scanning electron microscope before the measurements, the sample was fixed on the carbon tape under nitrogen atmosphere and quickly loaded in the chamber. The voltage and working distance were varied during the measurements and the images were recorded. The particle size and the distribution were determined by Cilas 1180 particle size analyzer using mineral oil as dispersing media for solid particles and applying laser diffraction technique. BET surface area of solid catalysts was measured on Carlo-Erba Sorptomatic 1900 model surface area analyzer.

Wide angle X-Ray diffraction measurements were carried on Bruker AXS, D8 Advance X-ray diffractometer. To perform analysis in nitrogen atmosphere, the catalyst samples were placed on the zero background, X-ray transparent airtight sample holder in the glove box in nitrogen environment.² The step size in WAXD measurements was 0.02° and the time per step of 12s. Component analysis was performed using TOPAS v3.0 software by Bruker AXS.

Polypropylene characterization

PP samples were dissolved in boiling xylene and then cooled down for precipitating the insoluble

TABLE I
Characteristics of Synthesized Supported Titanium Catalysts

Characteristics	Cat-A	Cat-B	Cat-C	Cat-D	Cat-E
Mg (wt %)	18.1	18.1	17.8	17.9	18.8
Cl (wt %)	62.0	61.0	61.0	60.0	62.0
Ti (wt %)	2.8	3.2	3.1	2.6	2.5
Ethoxy (wt %)	0.5	0.4	0.5	0.7	0.6
DIBP (wt %)	–	8.2	9.8	13.6	14.6
DIBP mol fraction (w.r.t. total internal donor)	0	0.4	0.5	0.8	1.0
EB (wt %)	15.5	6.9	5.0	2.0	–
EB mol fraction (w.r.t. total internal donor)	1.0	0.6	0.5	0.2	0
Particle size ^a	26	28	25	30	26
Polymerization activity ^b (kg PP/g catalyst)	5.2	7.5	7.8	8.5	10.0
Isotactic index (%) ^c	96.5	97	98	97	98.6

^a Particle size in μm .

^b Polymerization conditions – pressure = $5.0 \pm 0.1 \text{ kg/cm}^2$, $\text{H}_2 = 210 \pm 10 \text{ mL}$, $\text{Et}_3\text{Al} = 12 \text{ mmol}$, cyclohexyl(methyl)dimethoxy silane (for Cat-B to E) = 0.6 mmol , para ethoxy ethyl benzoate (for Cat-A) = 1.8 mmol , time = 120 min , catalyst = $70 \pm 5 \text{ mg}$, temperature = 70°C .

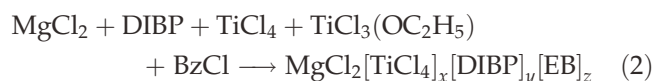
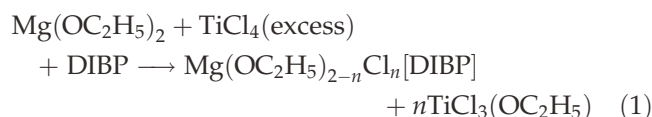
^c Xylene-insoluble content of the polymer.

fraction, the weight percentage of precipitated fraction was reported as xylene insoluble (%XI). Molecular weight distributions were determined using Polymer Laboratories PL-GPC220 High Temperature Chromatograph instrument (columns: $3 \times \text{Plgel Mixed-B } 10 \mu\text{m}$) and using 1,2,4-trichlorobenzene as solvent at a flow rate of 1 mL/min at 145°C . The system was calibrated with polystyrene standards using universal calibration. The polymer morphology was examined with FEI Inspect scanning electron microscope.

RESULTS AND DISCUSSION

Solid catalyst compositions containing varied amount of EB and DIBP were synthesized using different reactant ratios. A sequence of reactions eqs. (1) and (2) can occur simultaneously in the reaction mixture to yield a solid catalyst.^{21,23–25} EB is generated *in-situ* through reaction of added BzCl with

partial chlorinated magnesium ethoxide and/or titanium chloroethoxide species in the reaction mixture.²⁴



Two solid catalysts with only EB in one and DIBP in other were also prepared for comparison.

Compositional characteristics of prepared solid catalysts are shown in the Table I. Ti (wt %) for all the catalysts varies in optimum range of 2.8–3.2, EB amount in the catalyst varies from 2.0 to 6.9 (wt %), while DIBP found to vary from 13.6 to 8.2 (wt %). This resulted in the synthesis of solid catalysts with DIBP mol fraction of 0, 0.38, 0.51, 0.78, and 1.00 for

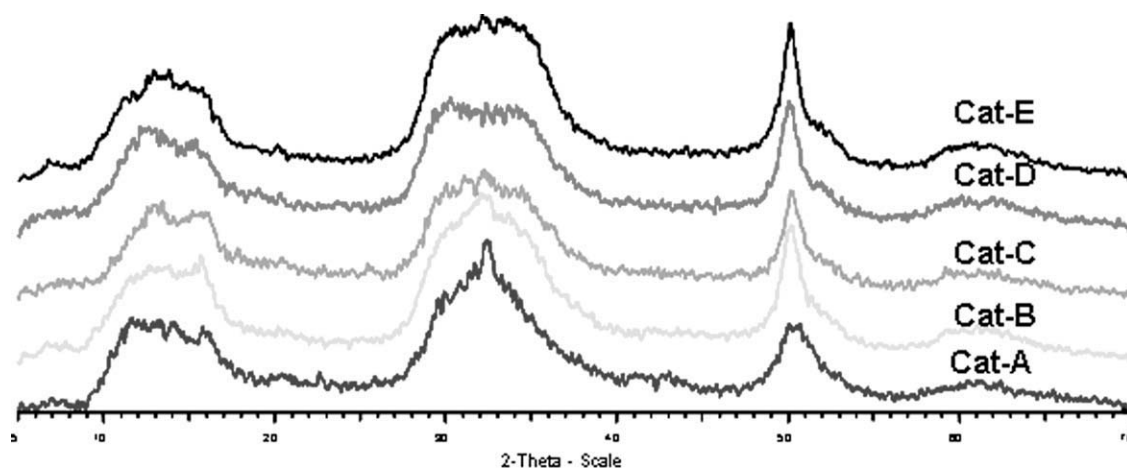


Figure 1 XRD patterns of Cat-A, Cat-B, Cat-C, Cat-D, and Cat-E.

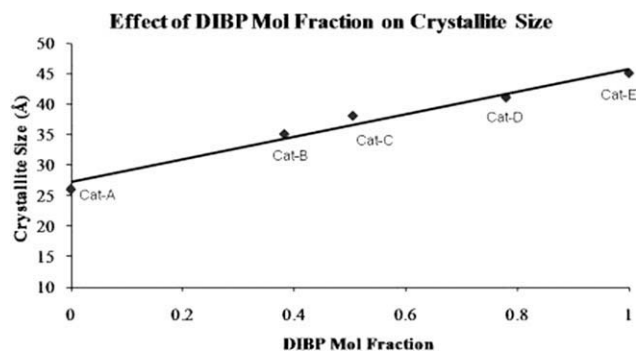


Figure 2 Effect of DIBP mol fraction on crystallite size.

Cat-A to Cat-E, respectively. The slight reduction in Ti from Cat-B to Cat-E can be a result of increase in DIBP content. As DIBP increases, it occupies more coordination sites on which otherwise Ti could have co-ordinated.²¹ Mg (wt %) remains in the range of 17.9–18.8 indicating comparable yield for all the catalysts system. Impurities in the form of ethoxy remains below 1.0 (wt %).^{21,24} Surface area was also measured through nitrogen sorption for Cat-A and Cat-E. The surface area of Cat-A remains in the range of 220–250 m² g⁻¹, whereas, it remains in the range of 270–300 m² g⁻¹ for Cat-E. The hysteresis shape of nitrogen adsorption desorption isotherm for these catalysts was correlated with pore structure. The hysteresis shape is of type H3²⁶ for both the catalyst, which characterizes solids consisting of aggregates or agglomerates of particles forming slit-shaped pores (plates or edged particles like cubes), with nonuniform size and shape.²⁶

From Table I, the particle size (by laser light scattering) remains almost constant from the support to each catalyst, which shows that there is no significant difference at different donor concentrations and it remains constant during the catalyst synthesis. The mean particle size of catalyst was found to be in the range of 25–30 μm.

The WAXD patterns of catalysts shown in Figure 1 have following features: (1) 9–18 2θ: broad peak, (2) 27–38 2θ: broad peak, (3) 48–54 2θ: broad peak, and (4) 57–67 2θ: broad peak indicative of presence

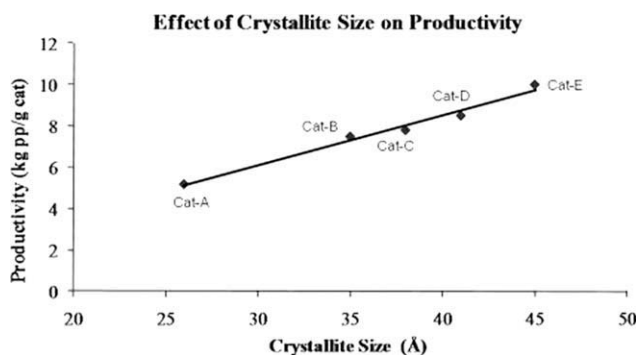


Figure 3 Effect of crystallite size on productivity.

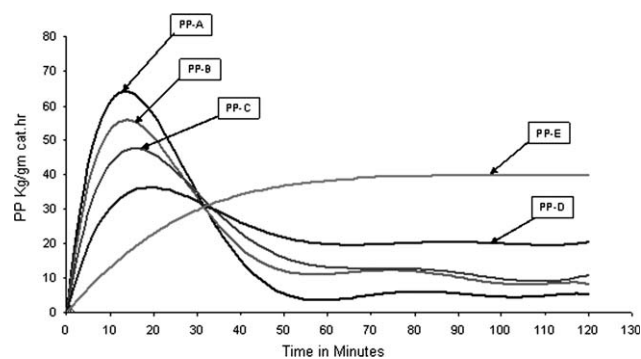


Figure 4 Polymerization kinetic for synthesized catalysts – PP-A, PP-B, PP-C, PP-D, and PP-E rate of polymerization curves for Cat-A, Cat-B, Cat-C, Cat-D, and Cat-E, respectively.

of MgCl₂ crystallites. Crystallite size has been calculated from the broad peak at 50.2 2θ [attributed to (110) planes of α-MgCl₂ and β-MgCl₂ and (018) plane of α-MgCl₂ phase].² Crystallite size (Å) of Cat-A, Cat-B, Cat-C, Cat-D, and Cat-E is 26, 35, 38, 41, and 45, respectively. Gradual increase in crystallite size is observed with increasing DIBP content (Fig. 2). Increase in crystallite size indicates toward higher structural stability in the catalyst having higher DIBP content.

The productivity of the prepared catalysts (Cat-B, Cat-C, Cat-D, and Cat-E) was examined for the homo polymerization of propylene using triethylaluminum as cocatalyst and C-donor as external donor. As shown in Table I, the productivity of catalysts (Cat-B to Cat-E) varies from 7.5 to 10.0 kg PP/g catalyst [at isotactic index as xylene insoluble (%XI) of polymer from 97.0 ± 1.0] with varying DIBP mol fraction. The productivity of catalyst containing only monoester (Cat-A) was also examined for the homo polymerization of propylene using triethylaluminum as cocatalyst and PEEB as external donor for the comparison, activity was found to be 5.2 kg PP/g cat.

The changes in productivity with varying donor(s) composition and content can be explained based on the fact that increased DIBP content stabilizes the matrix as indicated by increase in crystallite size. This enhanced stability can also help in improving the activity (Fig. 3). Thus, there is found to be a correlation between activity and crystallite size (Fig. 3) indicating higher activity with increasing crystallite size. The diester-catalyst systems follow a steady-state kinetic regime during polymerization, whereas monoester catalyst systems follow decay type kinetic curve. The difference in reaction kinetics⁸ is also one of the reasons for the higher activity of diester-catalyst systems.

The polymerization reaction with different catalyst prepared was monitored as a function of time to get insight into rate of polymerization (Fig. 4). Polymerization is carried out in slurry phase. Initially solvent

TABLE II
Characteristics of Catalyst and Molecular Weight Characteristics of Corresponding Polypropylene

Catalyst	Polymerization batch	Activity (kg PP/g catalyst)	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	PDI
Cat-A	PP-A	5.2	366	53	6.9
Cat-B	PP-B	7.5	319	55	5.8
Cat-C	PP-C	7.8	307	58	5.3
Cat-D	PP-D	8.5	302	63	4.8
Cat-E	PP-E	10.0	203	68	3.5

(hexane) is saturated with propylene at 1.0–2.0 kg cm⁻² pressure. Catalyst is added and propylene is continuously fed in the reactor to maintain constant pressure of 5 kg cm⁻² at polymerization temperature of 70°C. Propylene feed rate is recorded with respect to time under studied conditions. The rate of polymerization is directly proportional to monomer feed rate per unit time [eq. (3)].

$$\begin{aligned} \text{Rate of polymerization (kg pp g}^{-1}\text{cat h}^{-1}) \\ = \text{propylene flow (kg h}^{-1}\text{)}/\text{catalyst added (g)} \quad (3) \end{aligned}$$

The catalyst with only DIBP show steady kinetics, i.e., slow initial increase in rate of polymerization reaching to optimum and then maintaining steady rate of polymerization. As the amount of EB in the catalyst is increased, the kinetic profile changes from

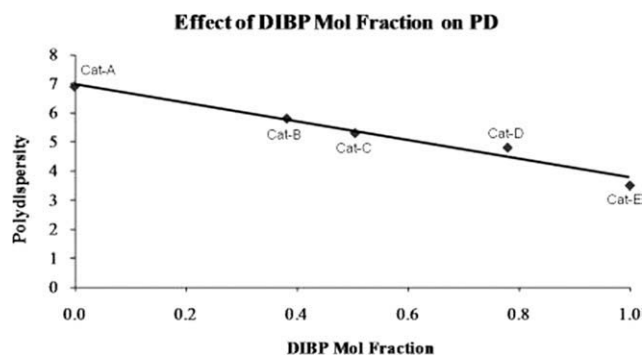


Figure 5 Effect of DIBP mol fraction on polydispersity.

steady to decay type. This indicated that presence of EB in the diester-catalyst system modifies the kinetic profile toward decay type and quantum of change in the kinetics depends upon the ratio of diester/monoester.

The polymer obtained as PP-A, PP-B, PP-C, PP-D, and PP-E by the respective catalyst was studied for their molecular weight characteristics by GPC as shown in Table II.

As given in Table II, as the amount of diester increases in the catalyst, the corresponding polymer has higher M_n values indicating a shift in molecular weight toward higher region with reduced number of chains and increased homogeneity in chain length distribution. In this study, it is also seen that as

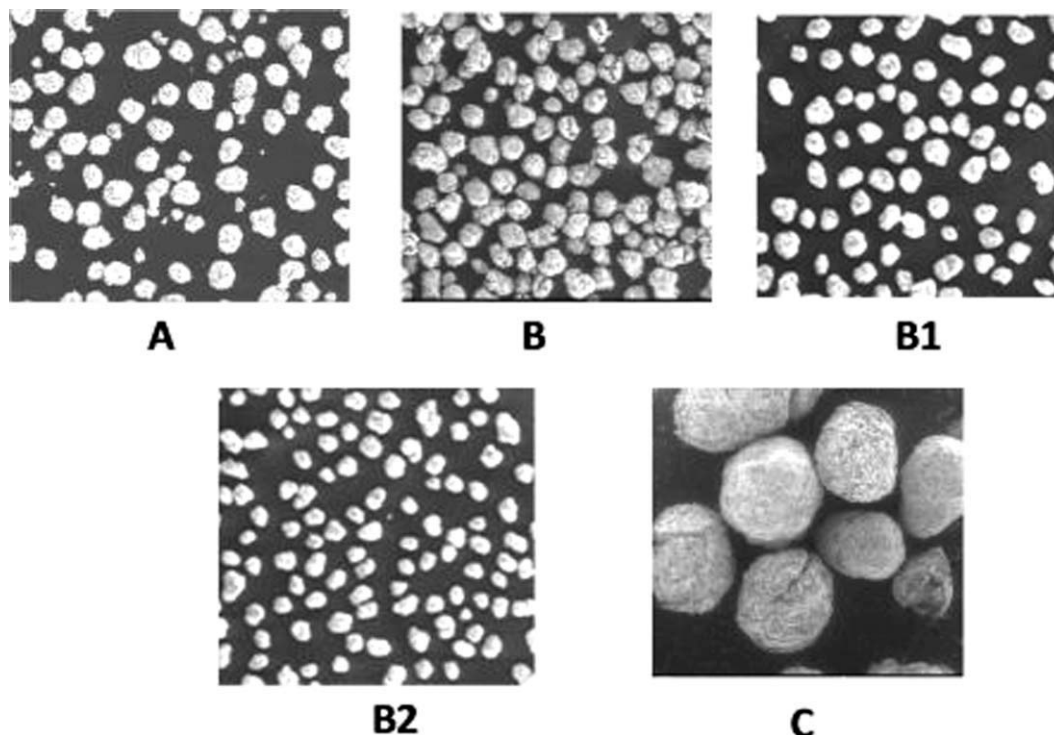


Figure 6 SEM images of (A) support at $\times 1000$ magnification, (B) catalyst with EB as internal donor at $\times 1000$ magnification, (B1) catalyst with mixed internal donor at $\times 1000$ magnification, (B2) catalyst with DIBP as internal donor at $\times 1000$ magnification, (C) polymer at $\times 100$ magnification.

monoester concentration increases, values of M_w increases that can be ascribed to a probability that the increased monoester concentration not only increases the chain length but also the number of chains. This phenomenon is caused by the heterogeneity of active titanium species distribution on the $MgCl_2$ matrix that leads the random chain propagation during the polymerization. Increase in DIBP content can also lead to more homogenous distribution of active sites thus giving polymer with narrow molecular weight distribution (Fig. 5). At the same time, activity increases with increased DIBP content, this fact can be contributed to structural stability of the catalyst and higher k_p , when DIBP is used as donor.⁸

From Figure 5, the polydispersity increases ($M_w/M_n = 4.8-5.8$) as the monoester amount increases in the catalyst having mixed donors, even though the xylene-insoluble content of the polymer remains almost constant (Table II). This indicates that the stereospecificity of the catalyst systems remains unaltered in spite of broadening molecular weight distribution. Thus, though the number of polymer chains is increasing, still the chains formed are primarily isotactic in nature.

The typical morphology of the catalyst system and its replication from support to polymer is studied using SEM. The morphology is studied for Cat-A, Cat-C, and Cat-E. The study (Fig. 6) shows that support has spherical shape and the catalysts from this support also have spherical-shaped particles. Similarly, the PP particles obtained from the other catalysts are also spherical in shape showing the replication of catalyst morphology in polymer. This replication in shape is found to happen irrespective of the donor being used. This validates that in slurry polymerization, the particle fragmentation and growth mechanism is similar for monoester as well as diester type of catalyst systems. The catalyst or polymer morphology does not depend upon the donor content of the catalyst.

CONCLUSIONS

Our studies demonstrate the high performance $MgCl_2$ supported titanium catalyst can be synthesized with two different generations of internal donors (EB and DIBP) incorporated together on the support matrix. Performance of catalyst containing mixed internal donor depends upon the amount of individual donors and their mole fractions. Catalyst active sites, polymerization kinetics, and polymer characteristics can be modified by changing ratio of the two donors incorporated in the catalyst matrix.

The polymerization kinetic study of these catalysts revealed that the nature of polymerization kinetic profile is more toward decay type as the concentration of EB increases in the catalyst. Similarly, catalyst having higher DIBP has kinetic profile closer to steady state. A catalyst having higher content of DIBP gives polymer with narrower molecular weight distribution. PP with tailored molecular weight and molecular weight distribution can be made by optimum combination of both the internal donors in the catalyst matrix. Replication of support morphology in the catalyst and polymer is observed, irrespective of type of internal donor used.

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