

Poly(1-octene) Synthesis Using High Performance Supported Titanium Catalysts

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ABSTRACT: Poly(1-octene) was synthesized by polymerization of 1-octene using high performance MgCl_2 -supported TiCl_4 in combination with triethyl aluminum (TEAL) as cocatalyst in *n*-hexane for 2 h. Two catalysts, C_1 (diester catalyst) having di-isobutyl phthalate as internal donor and C_2 (monoester catalyst) having ethyl benzoate as internal donor were utilized for the atmospheric polymerizations to evaluate the influence of structurally different internal donors on the productivity, rate of polymerization and molecular weight profiles. The kinetic profile assessed in terms of variation of reaction parameters like temperature, cocatalyst to catalyst molar ratio and monomer concentra-

tion was found to be dependent on them. From these kinetic analyses, optimize conditions for polymerizations of 1-octene using diester as well as monoester catalyst were elucidated. The difference in the performance of diester and monoester catalyst system can be explained in terms of stability of active titanium species and chain transfer process. NMR spectroscopy of synthesized poly(1-octene) indicate predominantly isotactic nature. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 229–236, 2010

Key words: Ziegler-Natta polymerization; 1-octene; polymerization rate; isotacticity

INTRODUCTION

Poly(1-octene) based polymeric materials have wide range applications from usage in lubricating oil composition,^{1–5} adhesive,^{6–9} foams,¹⁰ valve seal¹¹ to being applied as one of the components of cosmetically suitable carrier in antiperspirants and deodorants.¹²

Multi sites Ziegler-Natta catalyst systems provide the opportunity for developing high yield process in addition to tailoring the critical characteristics of polymer such as stereoregularity and molecular weight characteristics. Polymerization of α -olefins using heterogeneous Ziegler-Natta catalysts is well known state of the art.^{13–18} The role of donors has been explored extensively for controlling the kinetic profile of lower α -olefins polymerization and polymer characteristics.^{19–24} Scientists worldwide have been working on understanding the mechanism of polymerization for effective utilization of the catalyst for the polymer production. But the main focus in this area remains on lower α -olefins that is propylene and ethylene. As for higher α -olefins like 1-octene, their copolymers with ethylene and propyl-

ene are well known for their wider applications at commercial level. However, limited studies are reported for the homopolymerization of higher olefins using the heterogeneous Ziegler-Natta catalyst systems.^{25,26}

Our interest in polyolefins synthesis using high performance catalytic systems led us to study the relationship of catalyst system, polymerization performance and product characteristics for higher poly(α -olefins). This article reports the results on polymerization of 1-octene using MgCl_2 supported TiCl_4 catalysts which are well established for propylene polymerizations. Our approach was to understand the influence of usage of two structurally different internal donors on moderating the activity of heterogeneous Ziegler-Natta catalysts for polymerization of 1-octene. The influences of the cocatalyst to catalyst molar ratio, reaction temperature, and monomer concentration were understood to have the optimized set of conditions for polymerization for two different catalyst systems.

EXPERIMENTAL

Materials

1-Octene (98%, Aldrich) was used as received. *n*-Decane (95%, Labort) and *n*-hexane (99%, Labort) were dried under nitrogen over molecular sieves. Triethylaluminum (TEAL, Witco) solution was used

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as 10% (v/v) in *n*-decane. Two MgCl₂-supported titanium catalysts, C₁ (Ti = 3.0 wt %; di-isobutyl phthalate (DIBP) = 12 wt %) and C₂ (Ti = 2.5 wt %; ethyl benzoate (EB) = 15 wt %) were used as 3 wt % catalysts slurry in *n*-decane.^{27,28}

Polymerization

All work relating to handling of air- and moisture-sensitive compounds were carried out in nitrogen atmosphere by using standard Schlenk techniques. A 1-L double-jacketed glass reactor equipped with a mechanical stirrer having glass stirrer with PTFE blade was used to polymerize 1-octene. The polymerization assembly was kept under nitrogen. Calculated amount of *n*-hexane, TEAL (cocatalyst) and 1-octene were added to the reactor. After the addition of catalyst, same amount of catalyst was taken in a volumetric flask for titanium estimation to calculate the amount of catalyst used for each polymerization. The reaction temperature was then set to the required degree. The polymerization was done for 2 h, after which the reaction was terminated by addition of methanol containing 5 wt % HCl. The polymer was dried under vacuum at 60°C until constant weight. The polymerizations are done in duplicates, and the data reported are the averaged one.

Characterization of poly(1-octene)

Percentage polymer conversion was measured gravimetrically. Productivity for each polymerization was calculated as weight of polymer obtained per gram of catalysts. Rate of polymerization was calculated²⁵ using the equation

$$R_p = \frac{1000 \times w}{M \times t \times v}$$

where, R_p is the rate of polymerization; w is the weight of polymer obtained after the desired reaction time (g); M is the molecular weight of the monomer (g/mol); t is the reaction time (sec); v is the volume of reaction mixture (L; kept constant for all polymerization).

Molecular weight of the polymers was determined by Size Exclusion Chromatography with Polymer Laboratories PL-GPC220 High Temperature Chromatograph instrument (columns: 3×PLgel Mixed-B 10 μm) with two detectors (viscometer and refractometer) in 1, 2, 4 - trichlorobenzene at flow rate of 1 mL/min at 145°C. The system was calibrated with polystyrene standards using universal calibration. Titanium content in the catalyst was determined by dissolving the solid in an acidic media afterward; all of the titanium contained in the catalysts was con-

verted into Ti⁴⁺ by addition of H₂O₂. UV-Vis spectra of the resultant solution of peroxotitanium complexes were recorded on a Perkin-Elmer UV Lambda 12 spectrometer. The intensity of a peak at 417 nm ($\epsilon = 782.7 \text{ L}^{-1} \text{ mol}^{-1} \text{ cm}^{-1}$) was used to quantify the titanium content. All the NMR spectra were recorded on a Bruker Avance-400 spectrometer in CDCl₃ at frequencies of 400 and 100 MHz for ¹H and ¹³C, respectively, at 45°C. A delay time of 10 s was given for recording ¹H-NMR spectra, whereas for ¹³C{¹H}-NMR spectra, a 2 s delay time was given, and 5000 scans were accumulated. DEPT-90 and 135 spectra were recorded using standard pulse sequence with J modulation time of 3.7 ms ($J_{\text{CH}} = 135 \text{ Hz}$) with a delay time of 2 s.²⁹⁻³¹ The signal intensities of the spectral peak were measured from the integrated areas calculated with electronic integrator. NMR measurements were made on 10% (w/v) polymer solutions.

RESULTS AND DISCUSSION

Poly(1-octene) was synthesized by the polymerization of monomer using MgCl₂-supported TiCl₄ catalysts with different nature of incorporated internal donor (Table I). The solid catalysts comprise of the magnesium dichloride as support matrix with incorporated titanium (IV) chloride and internal donor. One catalyst consist of diester functionality as internal donor (C₁; diester DIBP), whereas the other catalyst was synthesized with monoester functionality (C₂; monoester – EB).

The effect of various reaction parameters like cocatalyst to catalyst (Al/Ti) molar ratio, monomer concentration, and temperature on the polymerization was studied to understand the catalysts behavior in absence of any external donor. A comparative study on the activity of two catalysts was also investigated in terms of productivity and rate of polymerization. The reaction time was kept fixed as 2 h for the polymerizations.

Effect of Al/Ti molar ratio on polymerization

Al/Ti mole ratio has an important function in heterogeneous Ziegler-Natta polymerization, as this is the crucial factor for the activation of catalysts. It is reported in the literature that triethylaluminum or TEAL activates the titanium species by shifting the alkyl group to Ti leading to the formation of active site for monomer addition. Furthermore, TEAL also reacts with impurities such as moisture to eliminate its poisoning effect on the catalyst performance.³²⁻³⁵ 1-Octene polymerizations were conducted for 2 h at 30°C at five different molar ratios of Al/Ti (50/1; 100/1; 250/1; 300/1; 400/1) with diester as well as monoester catalyst.

TABLE I
Experimental Conditions for Ziegler-Natta Polymerization of 1-Octene Using Diester and Monoester Catalyst^a

Entry no.	Monomer (mol L ⁻¹)	C ₁ ^b (×10 ⁻³ g)	C ₂ ^c (×10 ⁻³ g)	TEAl ^d (mL)	Al/Ti molar ratio	Temp (°C)
1	1.4	69.4	68.2	15.5	250	30
2	1.4	71.0	70.5	15.5	250	40
3	1.4	70.6	71.3	15.5	250	50
4	1.4	70.3	72.1	15.5	250	60
5	1.4	70.4	70.4	15.5	250	70
4	1.4	70.8	69.9	3.0	50	30
5	1.4	71.6	70.6	6.0	100	30
6	1.4	70.3	71.7	18.1	300	30
7	1.4	70.6	70.6	24.1	400	30
8	0.7	68.4	69.5	15.5	250	30
9	1.0	70.2	70.3	15.5	250	30
10	1.7	69.9	70.7	15.5	250	30
11	2.1	69.1	70.0	15.5	250	30

^a Polymerization time: 2 h; Total volume = 300 mL.

^b C₁: Diester catalyst (Ti = 3.0 wt %; di-isobutyl phthalate (DIBP) = 12 wt %).

^c C₂: Monoester catalyst (Ti = 2.5 wt %; di-isobutyl phthalate (DIBP) = 15 wt %).

^d 10% v/v in *n*-decane.

Boldface show change in reaction parameters.

Figure 1(a) shows the effect of variation of Al/Ti ratio with productivity while the outcome of varying Al/Ti on the rate of polymerization for both diester as well as monoester system is depicted in Figure 1(b). In case of diester catalyst (C₁), increase in productivity is observed as Al/Ti ratio changes from 50 to 250. When the ratio is increased to 400, marginal increase is observed in polymerization rate as well as productivity. For monoester catalyst system (C₂), increase in productivity is being observed when Al/Ti molar ratio changes from 50 to 250. Fur-

ther increase of Al/Ti molar ratio does not affect productivity of the system.

The results indicate that the increase in the mole ratio of Al/Ti up to 250 results in the formation of AlEt₂Cl along with the active species Ti³⁺ (formed by reduction of Ti⁴⁺) which leads to increase in productivity and rate in both the catalyst systems till optimum ratio is achieved.^{36–39}

The molecular weight profile of the polymers [Fig. 1(c)] obtained by varying Al/Ti ratio also exhibits the similar trend as observed above. As the ratio

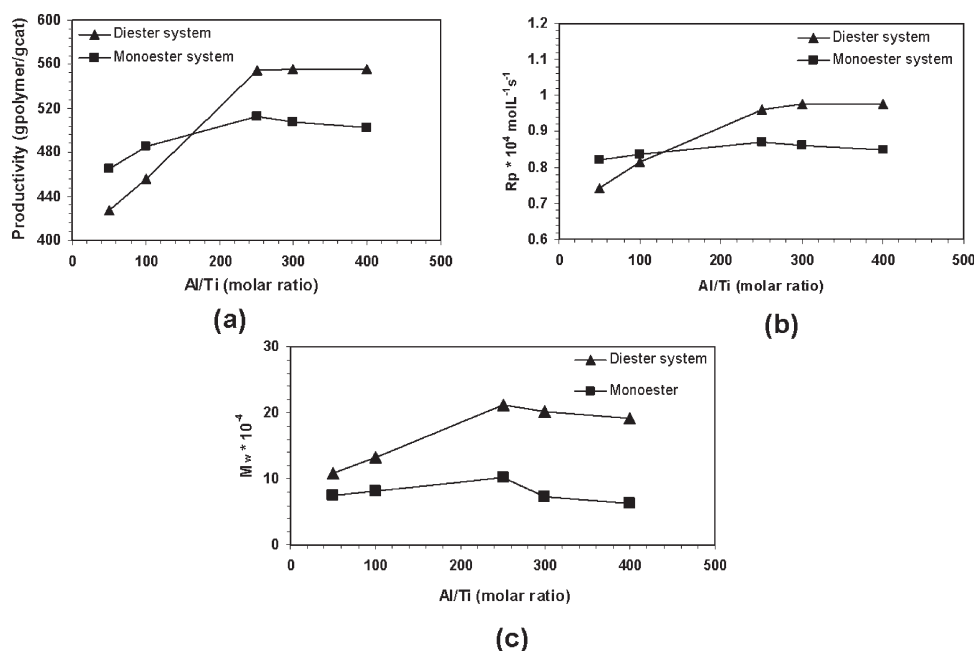


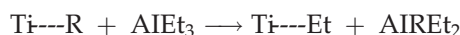
Figure 1 Plot of variation of Al/Ti molar ratio with (a) productivity, (b) polymerization rate, and (c) molecular weights in polymerization of 1-octene with diester and monoester catalysts.

TABLE II
Trend of Productivity with Varying Monomer Concentration for Ziegler-Natta Polymerization of 1-octene

Catalyst ^a	Monomer (mol L ⁻¹)	Productivity (g polymer/g cat)
C ₁	0.7	301
C ₁	1.0	467
C ₁	1.4	559
C ₁	1.7	796
C ₁	2.1	984
C ₂	0.7	274
C ₂	1.0	410
C ₂	1.4	526
C ₂	1.7	625
C ₂	2.1	717

^a C₁: Diester catalyst; C₂: Monoester catalyst.

changes from 100/1 to 250/1, the molecular weights increases supporting the assumption that active Ti³⁺ species is being formed leading to increase in rate of polymerization. Further as the ratio is increased, molecular weights decreased probably because of increased rate of termination reaction to TEAL.



where R is polymer chain.

The productivity, polymerization rate, and molecular weights of diester catalyst system are found to be higher as compared with monoester catalyst. This can be ascribed to higher stability of active sites in diester system due to lesser leaching out of DIBP as compared with EB during addition of cocatalyst which leads to deactivation of active sites in monoester case resulting in lowering of polymerization performance.

Effect of monomer concentration on polymerization

Ziegler-Natta catalysts have been widely explored for polymerization of lower α -olefins especially pro-

pylene. The aim of above pursuit was to explore how the polymerization rate and molecular weights behaved with varying monomer concentration for 1-octene polymerization using two different catalyst systems. For this study, the polymerizations were carried out at five different concentrations of 1-octene at polymerization temperature as 30°C, Al/Ti molar ratio as 250/1 and for 2 h. The productivity data with monomer concentration is summarized in Table II. With increase in monomer concentration, the productivity increased for both diester as well as monoester catalyst system. Diester catalyst showed higher activity compared with monoester catalyst which can be explained in terms of better stability of C₁ due to bidentate nature of internal donor as compared with monodentate internal donor of C₂.⁴⁰

For both the catalysts systems, the plot of rate of polymerization with respect to monomer concentration, [Fig. 2(a)] is a straight line passing from the origin indicating that the order of the reaction with respect to monomer concentration is one.

The molecular weight of the polymers increased with increasing monomer concentration [Fig. 1(b)], indicating that chain transfer to 1-octene is insignificant.

Effect of temperature on polymerization

Polymerization temperature plays a very crucial role as it directly affects the kinetics. Many reactions like chain transfer, propagation rate, etc., behave differently with change of temperature of the system. The effect of temperature on productivity and rate of polymerization of 1-octene was studied in the temperature range of 30–70°C. The variation of the above parameters with temperature change is shown in Figure 3.

For the diester catalyst system, as the temperature is increased, both the productivity as well as rate of polymerization increases. This trend is very different for what one observes in monoester catalyst system where both the productivity as well as rate of

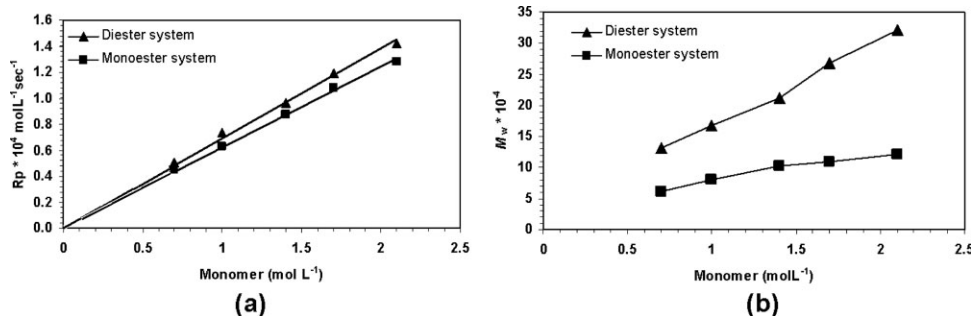


Figure 2 Plot of variation of monomer concentration with (a) rate of polymerization and (b) molecular weights in polymerization of 1-octene with diester and monoester catalysts.

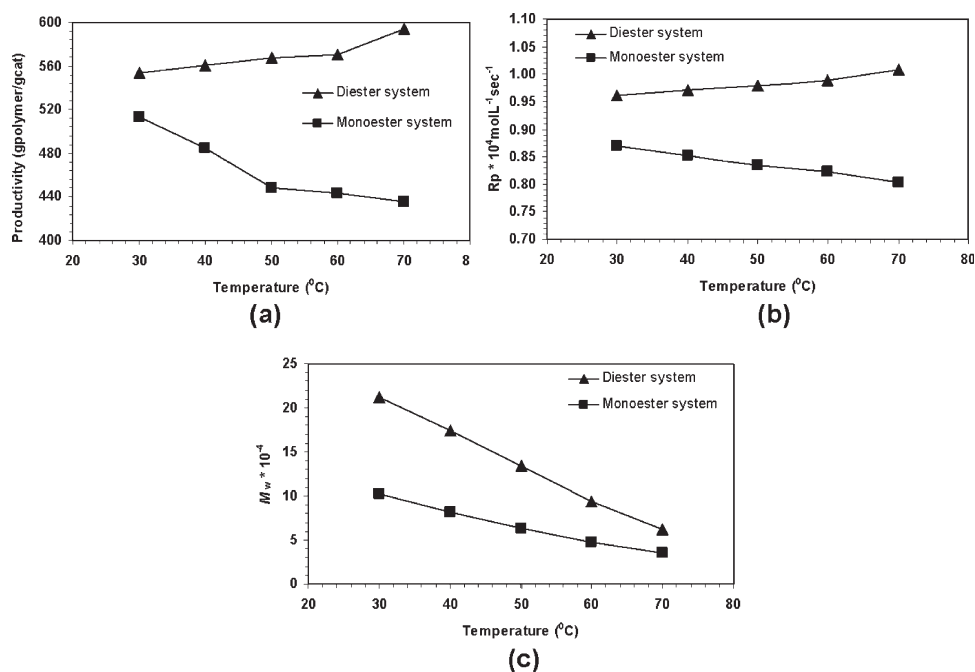


Figure 3 Plot of variation of (a) productivity, (b) polymerization rate, and (c) molecular weights with temperature in polymerization of 1-octene with diester and monoester catalysts.

polymerization decreases with increasing temperature.⁴¹ This indicates that the in situ generated active species in diester catalyst system is more stable at higher temperatures. This behavior reveals the binding feature of DIBP as bidentate chelate which provides more stability to the catalyst as compared with monodentate ethyl benzoate.

The molecular weight of the polymers also decreases as temperature is raised from 30 to 70°C as in Figure 3(c). The lowering of molecular weights with increasing temperature could be due to an

increasing rate of chain transfer at higher temperatures. This behavior is observed in both diester as well as monoester catalysts system.⁴²

Stereoregularity of poly(1-octene)

The compositional and stereoregularity of obtained polymers were studied by NMR Spectroscopy. Figure 4 shows the $^{13}\text{C}\{^1\text{H}\}$ -NMR of the poly(1-octene) obtained using diester catalyst at 30°C having Al/Ti of 250 having weight average molecular weight

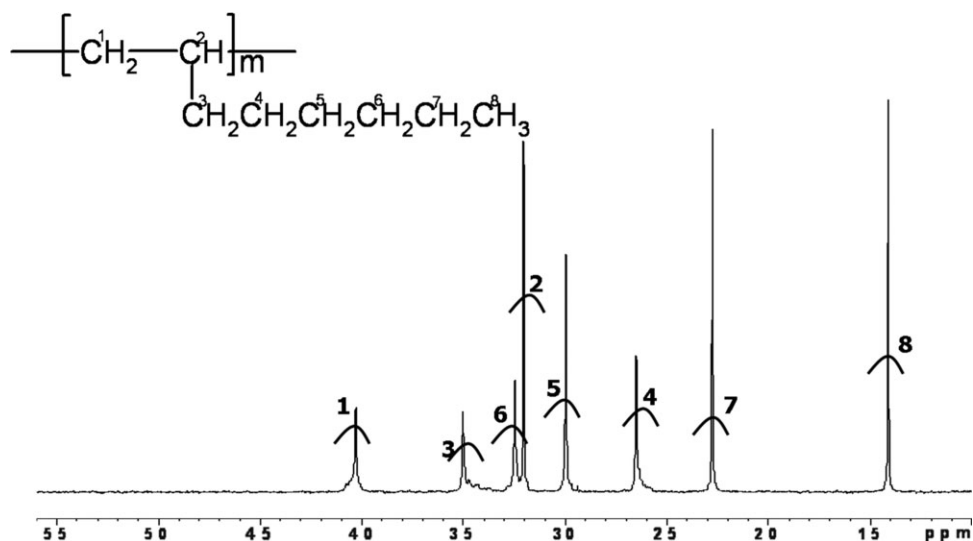


Figure 4 $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of poly(1-octene) polymerized using diester catalyst in CDCl_3 at 45°C.

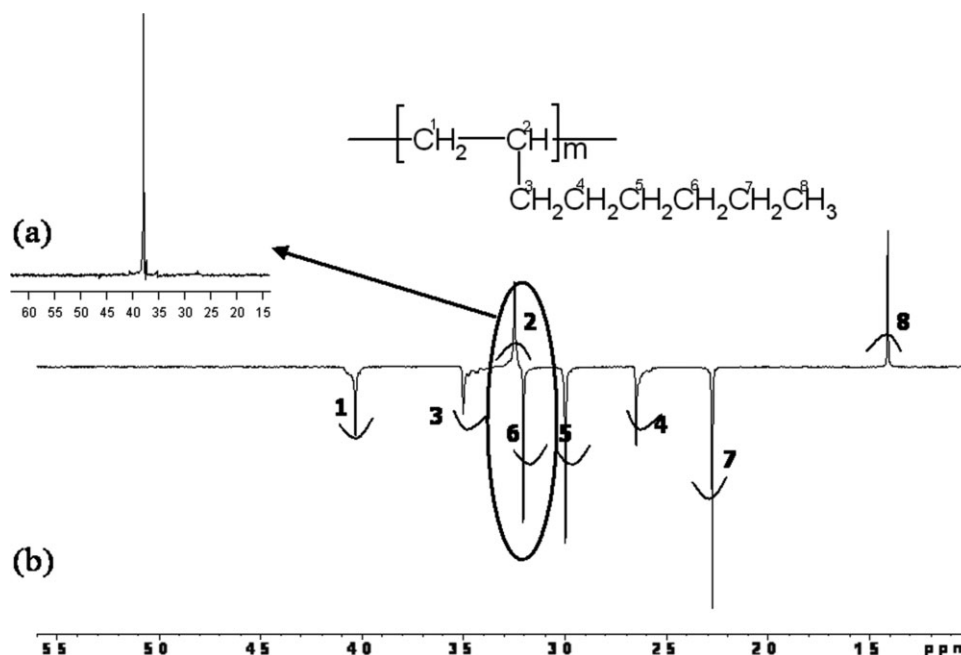


Figure 5 (a) DEPT-90 and (b) DEPT-135 spectrum of poly(1-octene) polymerized using diester catalyst in CDCl_3 at 45°C .

(M_w) of 2.1×10^5 and PDI = 9.8. The resonances obtained were assigned according to the literature.²⁵ To confirm the assignments given to various methyl, methylene, and methine groups, DEPT experiments were carried out. On comparing the $^{13}\text{C}\{^1\text{H}\}$ with DEPT-135 and DEPT-90, assignments were substantiated as shown in Figure 5.

For understanding of the configurational arrangement of 1-octene monomeric unit in the homopolymers obtained by using two different catalyst systems, the side chain methylene carbons that is C^3 and C^4 were analyzed as the carbon nuclei of pendant groups and α -carbon are observed to be highly sensitive to such type of stereoregularity. Figure 6

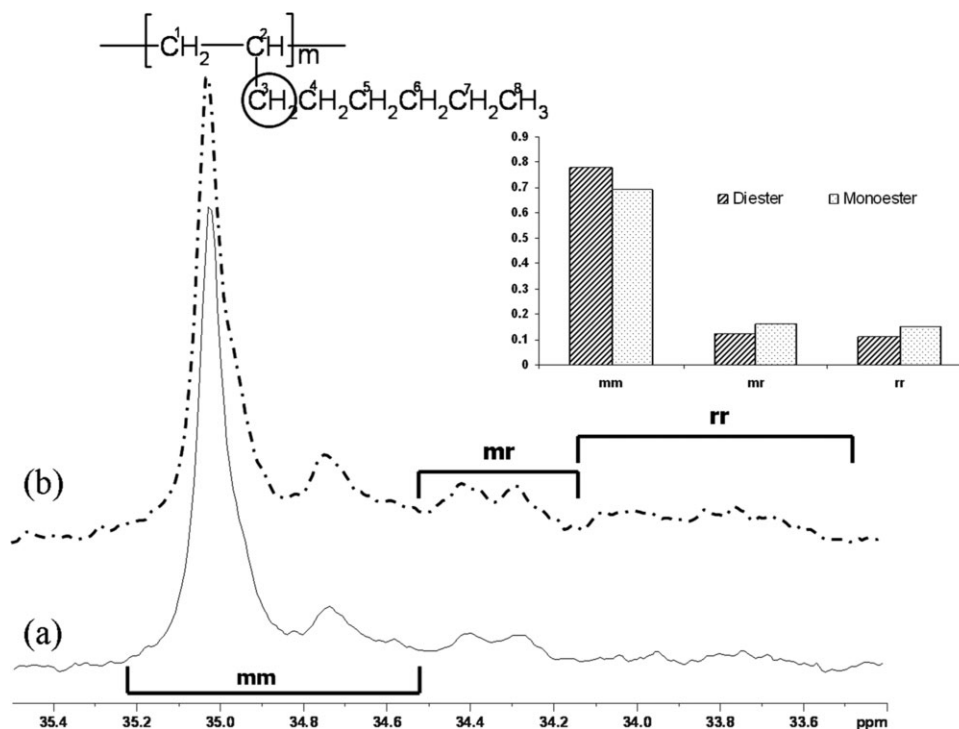


Figure 6 Expanded side chain methylene (C^3) resonance patterns of poly(1-octene) polymerized using (a) diester catalyst and (b) monoester catalyst showing sensitivity toward configuration.

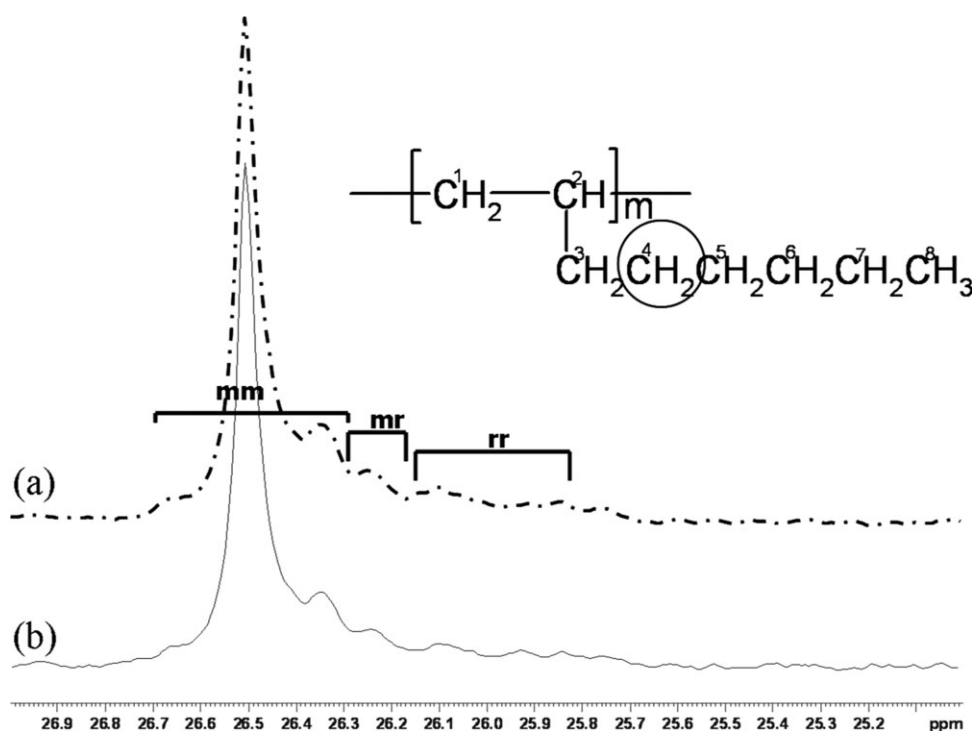


Figure 7 Expanded side chain methylene (C^4) resonance pattern of poly(1-octene) polymerized using (a) diester catalyst and (b) monoester catalysts systems showing sensitivity toward configuration.

shows the expanded region of side chain methylene carbon (C^3) of poly(1-octene) for both diester and monoester systems. The poly(1-octene) synthesized by monoester catalyst characterized for stereoregularity had average molecular weight (M_w) as 1.0×10^5 with PDI of 5.9. The resonance signals split into three peaks in the range of ~ 34.5 – 35.0 , 34.0 – 34.5 , and 33.4 – 34.0 ppm, which are assigned to isotactic (mm), heterotactic (mr) and syndiotactic (rr) triads, respectively.

Figure 7 shows configurational sensitivity of C^4 carbon which further substantiates the tacticity determination. The value of σ , defined by Bovey⁴³ and Coleman,⁴⁴ was found to be 0.78 for diester system and 0.69 for monoester system, which indicates that the polymer is largely isotactic in nature and isotactic content is on higher side for diester system as compared with monoester system.

CONCLUSIONS

Polymerization of 1-octene with heterogeneous Ziegler-Natta catalyst systems gave isotactic poly(1-octene) in hexane slurry process. The structural differences of the internal donors in the catalyst system are reflected in the performance of the studied systems. Diester catalyst showing better performance for polymerizing 1-octene as compared with monoester system. The kinetic understanding of the polymerization carried out in terms of temperature,

monomer concentration, and Al/Ti molar ratio variation resulted in setting optimize conditions for polymerizations using diester as well as monoester catalyst. The polymers obtained in both diester and monoester systems were predominately isotactic in nature as determined from the NMR spectral analysis.

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