

Comparative Studies on Ethylene/Propylene/Diene Terpolymerization

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ABSTRACT

A number of ethylene/propylene/diene elastomers (known as EPDM) were prepared in the presence of homogeneous $\text{VOCl}_3\text{-Al}_2\text{Et}_3\text{Cl}_3$ and indenyl, $\text{rac-EtInd}_2\text{ZrCl}_2$ -methylaluminoxane catalyst systems to compare their activity towards EPDM terpolymerization and their effects on the molecular weight distribution and the microstructure of the final products. 5-Ethyliden-2-norbornene (known as EBN) was used as the termonomer. Terpolymers prepared with the vanadium-based catalyst were of the higher molecular weight and more random in structure than those obtained with the zirconium catalyst. The latter catalyst system produced comparatively narrower molecular weight distribution. The loss in catalyst activity in presence of the non-conjugated diene was much higher than the anticipated amounts from kinetic parameters.

Key Words:

EPDM terpolymer; microstructure;
 $\text{VOCl}_3\text{-Al}_2\text{Et}_3\text{Cl}_3$; indenyl;
 $\text{rac-EtInd}_2\text{ZrCl}_2$ -methylaluminoxane;
molecular weight distribution.

INTRODUCTION

The terpolymers of ethylene with α -olefins and non-conjugated dienes are important commercial products and among them, there is an expanding demand for EPDM elastomers [1,2]. Uniform ethylene/propylene copolymers and the corresponding terpoly-

mers are commercially manufactured with homogeneous vanadium-based catalysts. The vanadium catalysts, however, require halogen containing activators and high catalyst residue must be removed from the final products due to its toxicity [3-5].

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The new zirconium/methylaluminoxane (known as MAO) catalysts have recently opened a fundamentally better synthetic approach to EPDM production [6-8]. They exhibit very high activity for random terpolymerization of ethylene with propylene and an unconjugated diene called termonomer. These catalysts systems differ from classical Ziegler-Natta catalysts at least in two important respects. First, only one type of active metal centre is generated and second, the ligand environment can be modified so that to rely stereochemical information to the active sites [9-10].

This article is a primary report on catalytic activity of a conventional Ziegler-Natta and a zirconium-based catalyst system and also the molecular weight of EPDM terpolymers synthesized in their presence.

EXPERIMENTAL

Chemicals

n-Heptane (from Fluka) used as polymerization solvent, was distilled twice over CaH_2 and Al_2O_3 and was finally dried by passing through a column containing a mixture of 4A and 13X molecular sieves. The catalysts VOCl_3 (from Aldrich), indenyl, $\text{rac-Et(Ind)}_2\text{ZrCl}_2$ (from Aldrich), sesquiethyl aluminium chloride (from ICI,plc) and methyl aluminoxane (from Witco) were used after dilution in toluene in a dry box under high purity grade argon atmosphere. Ethylene (from Air Products Ltd.) with 99.82% purity and propylene (from British Oxygen Company) with 99.50% purity were further purified by passing them through separate columns containing 4A and 13X molecular sieves. EBN (from Dutch State Mines) was received in a stabilized form and was claimed to be a mixture of nearly equimolar endo and exo forms. Before use, it was distilled over calcium hydride at reduced pressure.

Apparatus and Polymerization Technique

A 250 cm^3 capacity jacketed glass-reactor fitted with an efficient water-cooled condenser was used to conduct the polymerization in n-heptane. The reactor was of the open-ended flange top type to facilitate the addition of catalyst, cocatalyst and pure solvent or solution of the third monomer through individual inlets. In this flow method, ethylene and propylene monomers were supplied to the reactor semi-continuously via two

restricting valves and a 3-way tap. In the reactor, part of each monomer was polymerized and the rest was discharged and measured by a wet flowmeter. The product mixture was discharged after a certain time interval. More details of the polymerization system has been introduced in an earlier paper [11].

The catalyst/cocatalyst components and the unconjugated diene were fed to the reactor as dilute solutions. Terpolymerization experiments were performed at 25 C for a mean residence time of 40 min with an ethylene/propylene gas mixture constituted of 0.3 bar of ethylene and completed to 1 bar with propylene, whereas, the initial diene concentration was varied from 1.5×10^{-2} to 2 M. High purity grade argon gas was further purified on molecular sieves and was used to provide a dry atmosphere in the reactor. The product of each polymerization run was immediately quenched by blowing off the monomers and adding CH_3OH . The obtained polymer was stirred in $\text{C}_2\text{H}_5\text{OH}/\text{HCl}$ in order to kill the catalyst residue, washed thoroughly with deionized water and dried overnight in vacuum oven at 65 C .

Characterization of Polymers

The MWD of the terpolymers were determined using gel-permeation chromatography (Waters Associates, model ALG- GPC- 150 C). The EPDM samples were dissolved in 1,2,4-trichlorobenzene (TCB) at 135 C. The instrument was equipped with five μ -styragel (500, 10^3 , 10^4 , 10^5 and 10^6 A pore size) columns in series. The flow rate of TBC was kept constant at 1.0 cm^3/min . The columns were calibrated universally with five broad-molecular weight distribution EPDM standards of propylene content ranging 15-50 mol%.

The composition of each terpolymer was determined by ^{13}C NMR on a Jeol FX-90Q spectrometer with hexamethyldisiloxane as internal standard. The solutions were made in *o*-dichlorobenzene-*d* to a maximum of 15 wt%. Elution column fractionation was applied with xylene as solvent and ethylene glycol monobutyl ether as non-solvent. 2,6 Di-tert-butyl-*p*-cresol (0.15 %) was used as antioxidant. The samples were dissolved completely in n-heptane and the solutions were mixed with 2500 g glass beads. n-Heptane was evaporated from the mixture with the aid of a hot-air-blower. The fractionation temperature was 120 C and was fixed over the melting area of the polyethylene

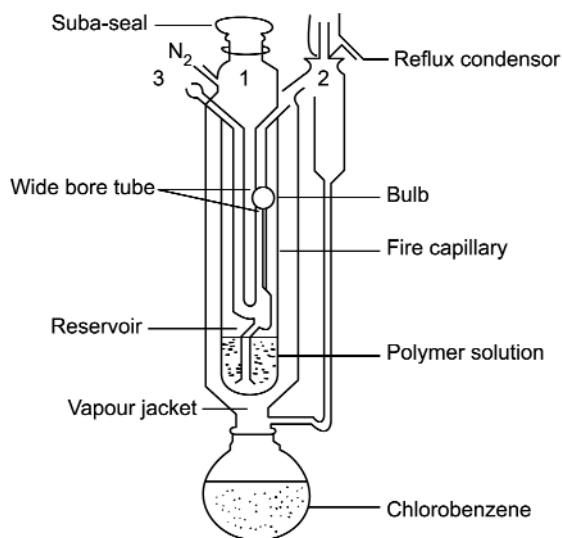


Figure 1. Ubbelohde suspended level viscometer.

blocks in the terpolymer samples.

The viscosity, $[\eta]$, of 0.1 g/dL polymer solution in decalin was determined with a jacketed Ubbelohde suspended level viscometer at 135 C by a one-point intrinsic viscosity method. Direct application of Mark-Houwink equation of the form $[\eta] = 3.8 \cdot 10^{-4} \bar{M}_v^{0.74}$ dL/g displayed the so-called viscosity average molecular weight, \bar{M}_v , as shown on Figure 1.

Differential scanning calorimetry (DSC) analyses of several selected terpolymers prepared with each catalyst system were measured using a Mettler thermal analyzer 3000 coupled to a DSC 20 at a heating rate of 10 C min⁻¹.

Rate and Yield Calculation

The volumetric flow rate of the monomers supplied to the reactor was controlled by means of a system of pressure gauges. The calibration of each monomer-orifice combination was carried out by measuring the volumetric flow rates. Monomer molar feed ration (C_3/C_2) of 70/30 was employed in this study. The total monomers volumetric flow rate was always checked at the start of any polymerization run. After purging the system with argon for about 20 min, n-heptane and the liquid diene were transferred from their reservoirs to the reactor by applying excess of argon gas pressure. Once the temperature of the circulating water around the reactor had reached the required polymerization temperature, a run started by switching the argon supply with the monomer gas mixture. After steady state

conditions in the reactor had been established, a 40 cm³ polymerization sample was collected into a 250 cm³ conical flask and it was quenched according to the procedure described earlier in experimental part.

Generally 3-5 samples were collected for a specific set of polymerization conditions which normally showed almost identical yields (within - 2%). The mean polymer yield was calculated as follows:

$$\text{Yield/g(mmol cat.)}^{-1} = \frac{\text{Mean polymer yield (g dm}^{-3}\text{)}}{[\text{cat.}] \text{ in total liquid stream (mmol dm}^{-3}\text{)}}$$

Values of the polymerization rate, R_p , under steady state conditions were calculated using the following expression:

$$R_p = \frac{\text{Mean polymer yield (g dm}^{-3}\text{)}}{\text{Mean time (s)} \times [\text{cat.}] \text{ in total liquid stream (mol dm}^{-3}\text{)}}$$

The R_p has then units of g mol⁻¹ s⁻¹.

The reproducibility of the method established for determination of yield, viscosity and monomer content of terpolymers was checked via conducting two parallel polymerization runs for each set of reaction conditions. The data obtained from the test methods are collected in Table 1 and this confirms that the method is accurate and valid.

Table 1. Reproducibility of the data obtained from identical parallel runs.

Catalyst ratio	Cumulative (weight %)	$[\eta]$ in g/dL	Ethylene content in mole (%)
[Al]/[V]=10	20	0.250	40
	20	0.250	38
[Al]/[V]=15	39	1.02	46
	39	1.04	46
[MAO] / [Zr] = 1 × 10 ³	80	2.50	53
	80	2.52	53
[MAO] / [Zr] = 3 × 10 ³	86	4.33	68
	86	4.33	65

Polymerization conditions: $C_3/C_2 = 70/30$; temp = 25 C.

Polymerization time = 40 min; [catalyst] = 5 × 10⁻⁴ mol/dm³.

RESULTS AND DISCUSSION

The ability of EBN termonomer for polymerization with ethylene and propylene in the presence of the two catalyst systems under study was investigated. The results are shown graphically in Figures 2-6.

Soluble vanadium catalyst system ($\text{VOCl}_3\text{-Al}_2\text{Et}_3\text{Cl}_3$ $\text{Al}/\text{V}=10$) was selected for comparison with indenyl, $\text{rac-EtInd}_2\text{ZrCl}_2$ ($\text{ind} = \text{C}_6\text{H}_7$) in the presence of MAO, since the former catalyst with the mentioned Al/V ratio is the most commonly used catalyst in EPDM production due to its ability to yield a more homogeneous comonomer unit distribution along the polymer chain [12].

The losses of catalyst activity and productivity in the presence of the non-conjugated diene are too drastic to result solely from kinetic parameters associated to the incorporation of the diene into the polymer chain [13].

Figure 2 shows that the Zr-catalyst gives terpolymers with slightly higher catalytic activity and higher ethylene content than the V-based catalyst system, whilst the situation is reversed for propylene content (Figures 2 and 3).

As Figure 4 shows, a notable difference between the two catalyst systems under study is the amount of diene incorporation into the terpolymers produced by them.

The diene content of terpolymers increases with catalytic activity in the case of the zirconium-based catalyst, but remains almost constant with the other catalyst under almost identical conditions of polymerization. This view of the zirconium catalyst is an important finding and must be taken into account since the diene content of industrial EPDM terpolymers is one of the determining parameters of their usefulness. How-

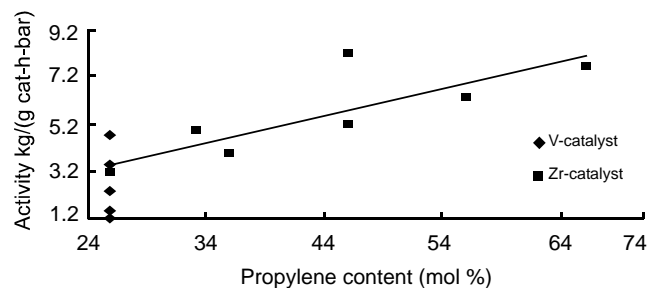


Figure 3. Variation of propylene content of terpolymers with catalyst activity.

ever, Figure 5 shows that the molecular weights of the terpolymers are very low even though no hydrogen was used as chain shortener. Under the same polymerization conditions, the molecular weight of the final polymers produced with the vanadium-based catalyst is about twice that obtained with the zirconium catalyst. This phenomenon is thought to be due to the chain transfer processes to propylene monomer which takes place frequently in the presence of metallocene catalysts [7,8,10]. This conclusion may be confirmed by the narrower molecular weight distribution of terpolymers obtained with the said catalyst system (Figure 6).

Differential scanning calorimetry data of typical terpolymers with almost the same ethylene, propylene and EBN unit contents, prepared with the two catalyst systems are presented graphically in Figure 7a,b. As it can be observed, the product of indenyl, $\text{rac-EtInd}_2\text{ZrCl}_2/\text{MAO}$ is completely amorphous and does not exhibit any crystallization domain, as it is the case for products of the $\text{VOCl}_3\text{-Al}_2\text{Et}_3\text{Cl}_3$. This feature in turn indicates that in addition to other advantages, the metallocene catalyst also enables the polymer chemist

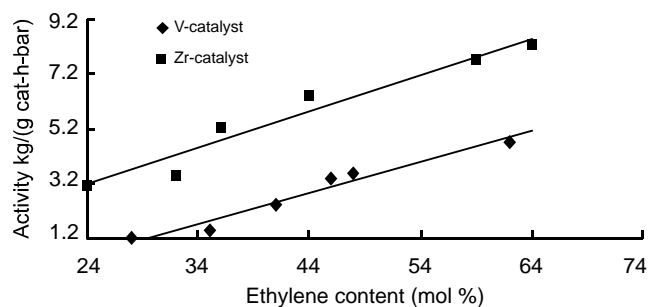


Figure 2. Variation of ethylene content of terpolymers with catalyst activity.

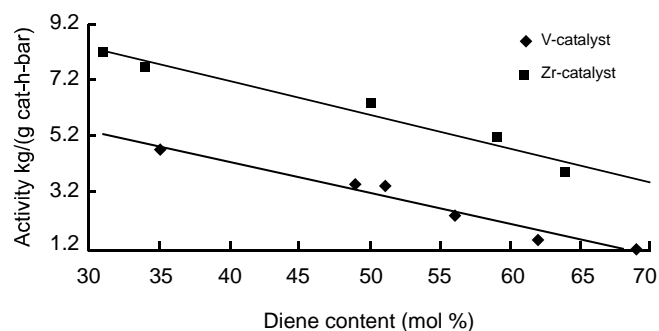


Figure 4. Variation of diene content of terpolymers with catalyst activity.

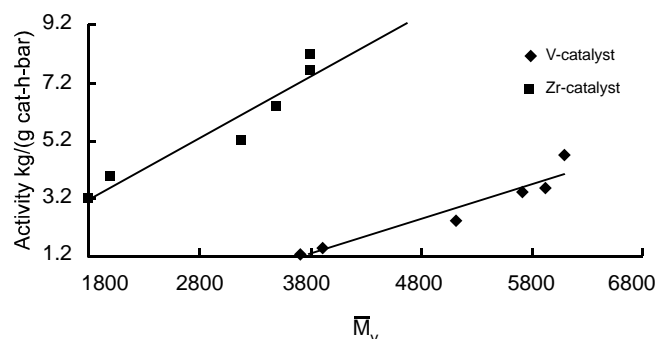


Figure 5. Variation of number average molecular weight of terpolymers with catalyst activity.

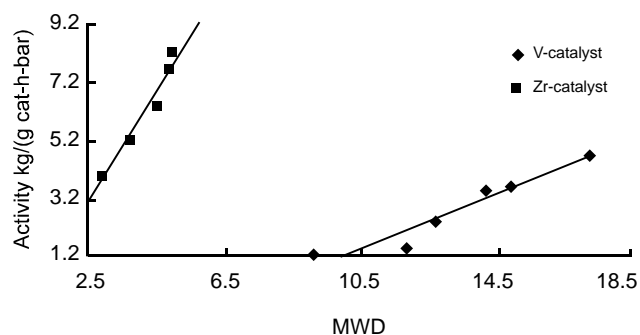


Figure 6. Variation of molecular weight distribution with catalyst activity.

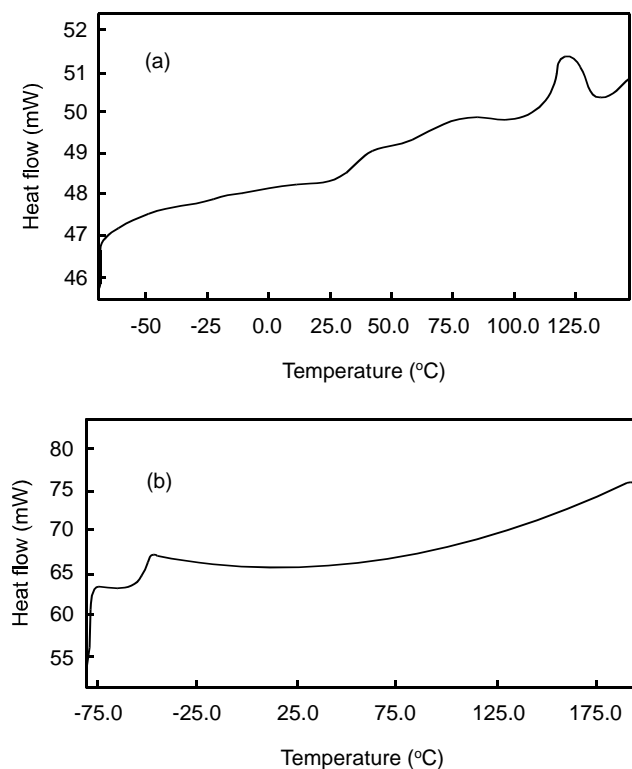


Figure 7. DSC Thermograms of EPDM terpolymer obtained with $\text{VOCl}_3\text{-Al}_2\text{Et}_3\text{Cl}_3$: (a) metallocene, and (b) catalysts.

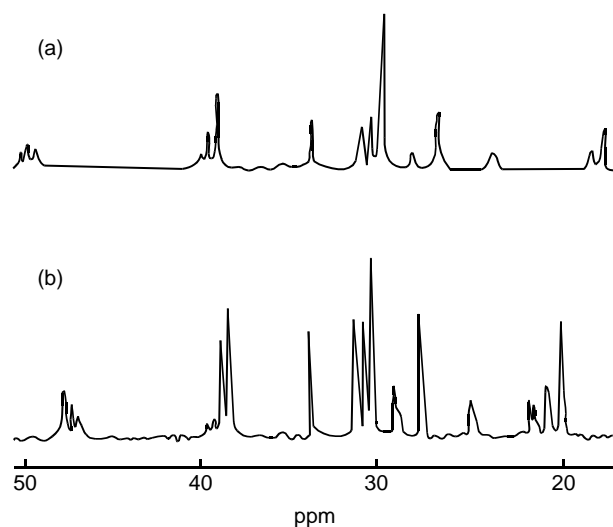


Figure 8. ^{13}C NMR Spectra of EPDM with 48 mol% of propylene: (a) produced with $\text{VOCl}_3\text{-Al}_2\text{Et}_3\text{Cl}_3$; and (b) produced with $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ catalyst system.

to obtain more random terpolymers with highly homogeneous composition which are true amorphous materials, the ^{13}C NMR spectra of two selected samples, each of which obtained with one of the two catalyst systems, are compared in Figure 8a,b. The analysis and assignment of peaks were carried out according to Cheng [14].

CONCLUSION

In conclusion, with indenyl, $\text{rac-EtInd}_2\text{ZrCl}_2/\text{MAO}$ catalyst system, very low molecular weight EPDM terpolymers are obtained while the $\text{VOCl}_3\text{-Al}_2\text{Et}_3\text{Cl}_3$ which is presently used in manufacture of this elastomer gives higher molecular weight products. Instead, the former catalyst produces more random terpolymers which may be more compatible with natural rubber for making rubber blends of industrial importance. Of course additional work should be carried out in this area for further conclusions. The molecular weight distribution of the terpolymers are also narrower in this case.

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