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Polymerization of 2-Allylnorbornane Using Ziegler−Natta Catalysts: Copolymerization with Ethylene[†]

S. Marathe, T. P. Mohandas, and S. Sivaram*

Division of Polymer Chemistry, National Chemical Laboratory, Pune 411008, India

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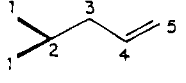
ABSTRACT: The copolymerization of ethylene with 2-allylnorbornane (2-ANB) was studied using Ziegler−Natta and homogeneous metallocene catalysts. The copolymers were characterized by IR, NMR, XRD, GPC, and thermal methods. It was found that the copolymers obtained using the $TiCl_4$/TIBAL catalyst were heterogeneous and blocky in nature while those obtained using Cp_2ZrCl_2/methylaluminoxane (MAO) were homogeneous and random in nature. A comparison between ethylene−2-ANB (norbornyl pendant) and ethylene−4-methyl-1-pentene (isopropyl pendant) copolymers led to the conclusion that both the isopropyl and norbornyl pendant give rise to a similar lowering in the values of ΔH_f and T_m.

Introduction

The copolymerization of ethylene with linear α-olefins to produce polyethylene with substituted alkyl side groups (linear low-density polyethylene) has gained considerable commercial importance in the last 15 years. Linear α-olefins such as 1-butene, 1-hexene, and 1-octene are the most widely studied in the literature, whereas, α-olefins containing cyclic and bicyclic groups have attracted less attention.

Recently, reports[1,2] have appeared on the copolymerization of ethylene with vinylcyclohexane. The interest in these copolymers arises because of the expectation that the bulky cyclohexyl substituent might lower the melting point and density of polyethylene more effectively than linear α-olefins at similar levels of incorporation. With this aim in mind, Mani and Burns[1] synthesized copolymers of ethylene and vinylcyclohexane using the soluble catalyst systems Cp_2ZrCl_2/MAO and Cp_2ZrMe_2/MAO. They found up to 1.7 mol % vinylcyclohexane could be incorporated into the polyethylene chains. The comonomer was found to be statistically distributed with the formation of short blocks at high comonomer concentrations. They found that the cyclohexyl branches affect the physical properties of the copolymer by decreasing the melting point and crystallinity of the polymer. At 1.7 mol % incorporation they obtained a copolymer with a T_m of 119 °C. Nekhaeva *et al.*[2] also obtained similar results using the Cp_2ZrCl_2/MAO catalyst. On going from 0 to 1 mol % vinylcyclohexane incorporation, they found the melting point decreased from 127 to 122 °C and density from 0.98 to 0.96 g/cm^3. They also noted that the addition of vinylcyclohexane led to centers of higher activity. A similar rate-enhancing effect of comonomer has been reported by many authors for both homogeneous and heterogeneous catalysts.[3−9]

An ethylene−α-olefin copolymer wherein the α-olefin is a bicyclic olefin such as 2-propenylbicyclo[2.2.1]heptane or 2-ANB has not been reported. We reasoned that the norbornyl pendant may cause some interesting perturbations in copolymer melting points and densities. It was also of interest to compare the properties of the ethylene−2-ANB copolymers with those of ethylene−4-methyl-1-pentene copolymers at similar mol % incorporation. This could elucidate the specific effect of the bicyclic pendant. 4-Methyl-1-pentene (**1**) was chosen because it is the acyclic analogue of 2-ANB (**2**).



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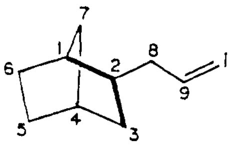

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Ethylene−4-methyl-1-pentene copolymers prepared with conventional Ziegler−Natta catalysts have been extensively studied.[10] Copolymers were synthesized using the homogeneous $V(acac)_3/(i\text{-}Bu)_2AlCl$ catalyst as well as the heterogeneous $TiCl_3$/DEAC catalyst. Copolymerization of ethylene and 4-methyl-1-pentene using supported catalysts was studied by Mulhaupt *et al.*[11] They found that using $MgCl_2$/2,6-di-*tert*-butyl-4-methylphenol/$TiCl_4$ (a highly isospecific catalyst) produced a copolymer with a low density (0.919 g/cm^3).

Since the mol % incorporation and changes in melting point/crystallinity are known to be dependent on the catalyst and conditions used, it was decided to synthesize ethylene−4-methyl-1-pentene copolymers in our laboratory under conditions identical to those used for the synthesis of ethylene−2-ANB copolymers.

It is well-known that the homogeneous metallocene catalysts result in copolymers which have a more random distribution of comonomers when compared to the heterogeneous Ziegler−Natta catalysts. Therefore, the present study was undertaken with heterogeneous and homogeneous catalysts.

Experimental Part

All manipulations were performed using standard inert atmosphere benchtop techniques.

1. Materials. *N*-Heptane (S.D. Chemicals, India) was washed with concentrated sulfuric acid and then neutralized with Na_2CO_3, washed with water, and dried over anhydrous $CaCl_2$. It was distilled over sodium−benzophenone prior to use. Toluene (S.D. Chemicals, India) was also distilled over sodium−benzophenone prior to use. Preparation and purification of 2-ANB has been described.[12] 4-Methyl-1-pentene (98% purity, density = 0.665 g/cm^3, Fluka, Switzerland) was distilled over triisobutylaluminum prior to use. Polymerization grade ethylene was obtained from Indian Petrochemical Corp. Ltd., Nagothane, India (O_2 < 3 ppm, H_2O < 4 ppm). Triisobutylaluminum (TIBAL), diethylaluminum chloride (DEAC), methylaluminoxane (MAO) (Me/Al = 1.54, 15 wt % Al solution in

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Table 1. Copolymerization of Ethylene with 2-ANB Using the $TiCl_4/(i\text{-}Bu)_3Al$ Catalyst System[a]

sample no.	2-ANB in feed: M	2-ANB in feed: mol %	yield (g)	activity [(kg/g of Ti)/h]	% conv	mol % 2-ANB in copolymer: IR	mol % 2-ANB in copolymer: NMR	$[\eta]$[b] (dL/g)	T_m (°C)	% cryst[c]
1			0.52	2.0	100			7.6	131.6	45
2	0.127	56.9	0.70	1.7	69	6	7	5.3	127.3	31
3	0.254	72.5	0.85	2.0	60	11	12	4.3	127.2	21
4	0.509	84.0	0.67	1.6	34	18	19	3.3	128.0	16
5	0.636	86.8	0.81	1.9	32	20		2.8	126.5	13
6	0.764	89.0	0.71	1.7	25	26		2.1	126.0	10

[a] Copolymerization conditions: temperature = 35 °C, pressure = 1 atm, solvent = heptane (25 mL), time = 10 min, [ethylene] = 0.096 M, [Ti] = 2×10^{-3} M, [Al] = 6×10^{-3} M. [b] In 1,2,4-trichlorobenzene at 135 °C. [c] % Crystallinity calculated from $\Delta H_{\text{fsample}}/\Delta H_{\text{fstd}} \times 100$.

toluene) all from Schering A.-G. (Germany), $TiCl_4$ (99%, Aldrich), $TiCl_3{\cdot}0.33AlCl_3$ (Toho Titanium Co.), and Cp_2ZrCl_2 (98%, Aldrich) were used as received.

2. Analytical Techniques. IR spectra were recorded on a Perkin-Elmer PC 16 FTIR on films (150–200 μm in thickness) compression molded on a Carver hydraulic press at 155 °C and 150 kg/cm² pressure. Copolymer ^{13}C NMR spectra were recorded using a 300 MHz Bruker MSL spectrometer at 120 °C on 10 wt % samples in 1,2,4-trichlorobenzene containing about 10% by volume of deuterated benzene for lock purposes. Spectra were recorded under quantitative conditions (pulse delay $>5T_1$). Thermogravimetric analysis was carried out using a Netzsch thermal analysis apparatus model STA 409. Differential scanning calorimetric analysis was done on a Perkin-Elmer DSC-7 with a heating and cooling rate of 10 °C/min. X-ray diffraction patterns were recorded on a Philips X-ray diffractometer. Gel permeation chromatograms of copolymer samples were run on a Water Associates model ALC GPC 150C at 135 °C using 1,2,4-trichlorobenzene as the mobile phase and μ-Styragel columns (10^5, 10^4, 10^3, and 500 Å) at a flow rate of 1 mL/min using an RI detector. A universal calibration was used. Intrinsic viscosity measurements were done using an Ubbelohde viscometer in 1,2,4-trichlorobenzene or decalin at 135 °C.

3. Copolymerization of Ethylene with 2-ANB Using $TiCl_4$/TIBAL. A 75 mL three-necked jacketed reactor connected to a 1 L gas buret was used for the copolymerizations. *n*-Heptane (25 mL) was syringed into the reactor and saturated with ethylene. Into this was syringed 0.86 g (6.6×10^{-3} mol) of 2-ANB followed by 0.6 mL of a 5 wt % TIBAL solution in heptane (1.5×10^{-4} mol). The copolymerization was initiated by the addition of 0.1 mL of a 10 wt % $TiCl_4$ solution in heptane (5.2×10^{-5} mol). Consumption of ethylene was noted at various intervals of time. The copolymerization was terminated after 10 min by pouring the contents of the reactor into acidified methanol. Yield of the copolymer = 0.86 g (60% conversion), $[\eta]$ = 4.3 dL/g (in 1,2,4-trichlorobenzene at 135 °C).

4. Copolymerization of Ethylene with 2-ANB Using Cp_2ZrCl_2/MAO. Toluene (25 mL) was syringed into the reactor and allowed to saturate with ethylene. Into this was syringed 0.86 g (6.6×10^{-3} mol) of 2-ANB followed by 0.82 mL (1.87×10^{-3} mol) of a 6.2 wt % Al solution of methylaluminoxane. The copolymerization was initiated by the addition of 0.4 mL of a Cp_2ZrCl_2 solution in toluene (1.25×10^{-6} mol). Consumption of ethylene was noted at various intervals of time. The copolymerization was terminated after 10 min by pouring the contents of the reactor into acidified methanol. Yield of copolymer = 0.81 g (57% conversion), $[\eta]$ = 0.32 dL/g (in 1,2,4-trichlorobenzene at 135 °C).

5. Copolymerization of Ethylene with 4-Methyl-1-pentene Using the $TiCl_4$/TIBAL Catalyst. *n*-Heptane (25 mL) was syringed into the reaction cell and allowed to saturate with ethylene. This was followed by addition of 0.5 mL of 4-methyl-1-pentene and 0.6 mL of 5 wt % TIBAL solution (1.51×10^{-4} mol), and copolymerization was begun by addition of 0.25 mL of 4 wt % $TiCl_4$ solution (5.27×10^{-5} mol). The copolymerization was terminated after 10 min by addition of acidified methanol. Yield = 0.54 g (66% conversion), $[\eta]$ = 4.8 dL/g (in decalin at 135 °C).

6. Copolymerization of Ethylene with 4-Methyl-1-pentene Using the Cp_2ZrCl_2/MAO Catalyst. Toluene (25 mL) was syringed into the reaction flask and allowed to saturate with ethylene. This was followed by addition of 0.4 mL of 4-methyl-1-pentene and 0.85 mL (1.87×10^{-3} mol) of methylaluminoxane solution in toluene. Copolymerization was initiated by addition of 0.75 mL (1.25×10^{-6} mol) of Cp_2ZrCl_2 solution in toluene. The copolymerization was terminated after 10 min by addition of acidified methanol. Yield = 0.54 g (77% conversion), $[\eta]$ = 2.7 dL/g (in decalin at 135 °C).

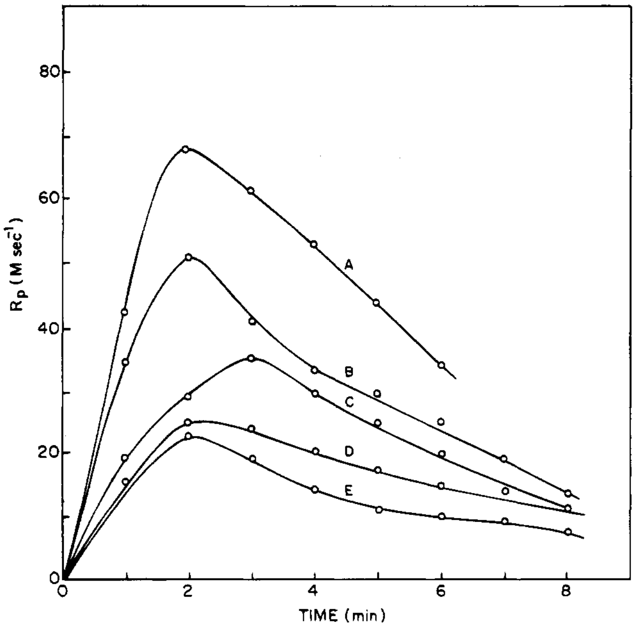

Figure 1. Plot of R_p vs time for ethylene 2-ANB copolymerization (catalyst: $TiCl_4$/TIBAL) at different 2-ANB feed concentrations: (A) 0.0 M, (B) 0.127 M, (C) 0.25 M, (D) 0.509 M, and (E) 0.76 M.

7. Quantitative Estimation of 2-ANB in the Copolymers. (a) ^{13}C NMR spectra of the copolymers recorded under quantitative conditions were used for estimating the mol % of 2-ANB in the copolymers. Though the spectrum is very crowded with a number of overlapping peaks, some characteristic signals such as endo and exo C_3, endo and exo C_4, and endo C_6 are easily distinguished and therefore can be used in quantitative estimation.

$$\text{mol \% of 2-ANB} = \frac{B}{1/2(A - 10B) + B} \times 100$$

where *A* is the sum of the integral over all C's and *B* is the integral of C_3(endo) + C_3(exo) or C_4(endo) + C_4(exo).

(b) An FTIR method for quantitative estimation of 2-ANB was also established. The absorption at 1308 cm^{-1} in the spectrum of poly(2-ANB) is characteristic of bridgehead −C−H bending.[13] The absorption at 720 cm^{-1} is characteristic of $(CH_2)_n$, i.e. long chain methylene sequences in the spectrum of polyethylene. Homopolymer mixtures of 0–80 mol % poly(2-ANB) and polyethylene were prepared by heating the appropriate amounts of homopolymers in xylene and coprecipitating in methanol. These were then dried and the IR spectra recorded. A straight line fit was obtained for a graph

Table 2. Copolymerization of Ethylene with 2-ANB Using the Cp_2ZrCl_2/MAO Catalyst System[a]

sample no.	2-ANB in feed M	2-ANB in feed mol %	yield (g)	activity [(kg/g of Zr)/h]	% conv	mol % 2-ANB in copoly IR	mol % 2-ANB in copoly NMR	$[\eta]^b$ (dL/g)	T_m (°C)		% cryst[c]
1			0.48	25.2	100			1.60	132.5		67.0
2	0.101	47.8	0.75	39.2	80	3		0.92	110	116	28.6
3	0.178	61.8	0.79	52.1	62	4	4	0.71	103	108.4	24.1
4	0.254	69.7	0.81	53.4	57	5		0.32	97.1	104.3	15.8
5	0.382	77.6	0.86	45.5	47	11		0.28	91.0	99.5	8.6
6	0.509	82.2	0.72	37.7	33	18	16	0.19	86.9	94.8	3.4

[a] Copolymerization conditions: temperature = 35 °C, pressure = 1 atm, solvent = toluene (25 mL), time = 8–10 min, [ethylene] = 0.11 M, [Zr] = 5×10^{-5} M, [Al] = 0.075 M. [b] In 1,2,4-trichlorobenzene at 135 °C. [c] % crystallinity calculated from $\Delta H_{f\text{sample}}/\Delta H_{f\text{std}} \times 100$.

of A_{1308}/A_{720} versus mol % 2-ANB in the mixture of copolymers. By the method of interpolation, the composition of copolymers was found by using the value of A_{1308}/A_{720}.

Results and Discussion

Kinetics of Copolymerization of Ethylene with 2-ANB Using $TiCl_4$/TIBAL and Cp_2ZrCl_2/MAO Catalyst Systems. Effect of Comonomer Concentration. Kinetic experiments were conducted using the $TiCl_4$/TIBAL catalyst system. The $TiCl_3 \cdot 0.33AlCl_3$ catalyst was not used because of its insolubility in *n*-heptane and difficulties encountered in transferring the slurry. Since the amount of catalyst required for the kinetic runs was small (less than 10 mg), it was found more convenient experimentally to use the $TiCl_4$/TIBAL catalyst system.

Copolymerizations of ethylene with 2-ANB were performed at 35 °C and atmospheric pressure. Table 1 shows the effect of comonomer concentration on copolymer properties using $TiCl_4$/TIBAl catalyst. It can be seen that conversion, R_p (Figure 1), and $[\eta]$ decrease with an increase in the comonomer feed. This could be attributed to the increased rate of chain transfer reactions in the presence of 2-ANB. An increase in 2-ANB incorporation leads to a decrease in the value of % crystallinity. However, the decrease in T_m is not significant.

Table 2 shows the effect of comonomer concentration on activity and copolymer properties using the Cp_2ZrCl_2/MAO catalyst. It is observed that the catalyst activity and R_p (Figure 2) of copolymerization initially increase and then decrease with a further increase in 2-ANB feed concentration. A similar rate-enhancing effect of comonomer has been found by several authors.[3-9] Copolymer intrinsic viscosities obtained with Cp_2ZrCl_2/MAO are lower than those obtained with the $TiCl_4$/TIBAL catalyst. The DSC scans of the copolymers show that both T_m (two close melting points are observed) and % crystallinity decrease with increasing 2-ANB incorporation.

Determination of Reactivity Ratios. Reactivity ratios were determined by terminating the copolymerization at less than 20% conversion (Table 3). In the case of copolymerization using the $TiCl_4$/TIBAL catalyst, analysis of data using the Fineman–Ross[14] method gave a value of $r_{\text{ethylene}} = 39.6$ and $r_{\text{2-ANB}} = 0.0706$ with $r_{\text{ethylene}}r_{\text{2-ANB}} = 2.8$, whereas the Kelen–Tudos[15] method gave $r_{\text{ethylene}} = 40$ and $r_{\text{2-ANB}} = 0.077$ with $r_{\text{ethylene}}r_{\text{2-ANB}} = 3.1$. An r_1r_2 value greater than 1 is indicative of block formation and is known to be more pronounced when the two comonomers have alkyl groups of different sizes, for example ethylene–4-methyl-1-pentene, propylene–styrene, propylene–4-methyl-1-pentene, and propylene–vinylcyclohexane. On the basis of this reasoning it is concluded that the ethylene–2-ANB copolymers also have a blocky microstructure.

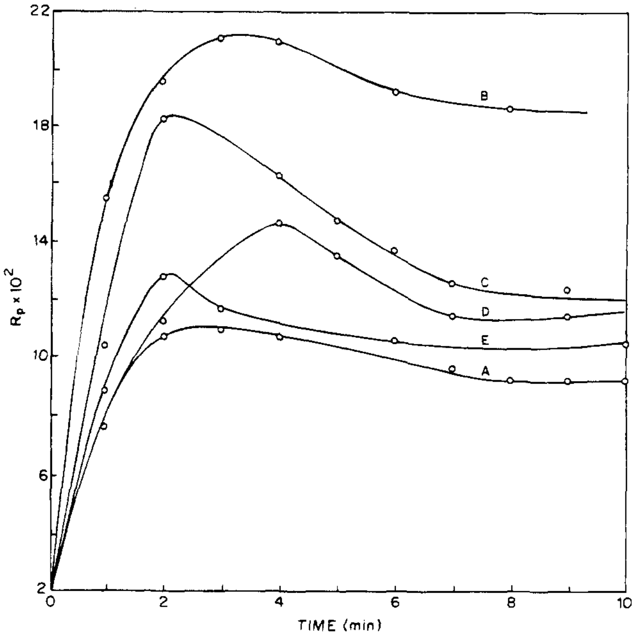

Figure 2. Plot of R_p vs time for ethylene 2-ANB copolymerization (catalyst: Cp_2ZrCl_2/MAO) at different 2-ANB feed concentrations: (A) 0.0 M, (B) 0.101 M, (C) 0.18 M, (D) 0.38 M, and (E) 0.509 M.

In the case of copolymerizations using the Cp_2ZrCl_2/MAO catalyst the treatment of data according to the Fineman–Ross method (Table 4) gave $r_{\text{ethylene}} = 43.7$ and $r_{\text{2-ANB}} = 0.038$ with $r_{\text{ethylene}}r_{\text{2-ANB}} = 1.62$. Treatment of data according to the method of Kelen and Tudos gave $r_{\text{ethylene}} = 42.6$ and $r_{\text{2-ANB}} = 0.027$ with $r_{\text{ethylene}}r_{\text{2-ANB}} = 1.15$. The value of r_1r_2 being close to 1.0 indicates that the copolymers formed are random in nature.

Kinetics of Copolymerization of Ethylene with 4-Methyl-1-pentene Using $TiCl_4$/TIBAL and Cp_2ZrCl_2/MAO Catalyst Systems. Copolymerization of ethylene with 4-methyl-1-pentene was carried out under conditions similar to those used for copolymerization of ethylene with 2-ANB. Addition of 4-methyl-1-pentene caused a decrease in copolymerization rate with the $TiCl_4$/TIBAL catalyst. Reactivity ratios were calculated to be $r_{\text{ethylene}} = 58.0$, $r_{\text{4MIP}} = 0.105$, $r_1r_2 = 6$ (Finemann–Ross); $r_{\text{ethylene}} = 53.4$, $r_{\text{4MIP}} = 0.073$, $r_1r_2 = 3.89$ (Kelen–Tudos) (reported $r_1r_2 = 4.8$ using the $TiCl_3 \cdot 0.33AlCl_3$ catalyst).[10] This suggests that the ethylene–4-methyl-1-pentene copolymers obtained using the $TiCl_4$ catalyst are also blocky in nature. The same conclusion is reached upon a close examination of the 730–720 cm^{-1} doublet region in the infrared spectrum. These results imply long crystalline methylene sequences, even at a 4-methyl-1-pentene concentration of 18 mol %.

The copolymers obtained with the Cp_2ZrCl_2/MAO catalyst, however, were again found to be random in nature. A rate-enhancing effect of 4-methyl-1-pentene

Table 3. Ethylene 2-ANB Copolymerization (at Low Conversion) Together with the Evaluation of Some Parameters (Catalyst: $TiCl_4(i\text{-}Bu)_3Al$)[a]

sr no.	conc of 2-ANB in heptane (M)	2-ANB in copolymer (mol %)[b]	$F_1 = (m_1/m_2)$	$f_1 = (M_1/M_2)$	10^2F^c	G^c	$F/(F+\alpha)^d$	$G/(F+\alpha)^d$
1	0.127	3.5	0.76	27.57	2.09	0.732	0.67	23.6
2	0.191	5.0	0.50	19.00	1.31	0.473	0.56	20.3
3	0.254	5.5	0.38	17.18	0.84	0.357	0.45	19.3
4	0.331	8.5	0.29	10.76	0.78	0.263	0.44	14.7
5	0.407	11.5	0.24	7.69	0.75	0.208	0.42	11.8
6	0.509	15.5	0.19	5.66	0.63	0.156	0.38	9.5
7	0.636	18.0	0.15	4.55	0.49	0.117	0.33	7.8

[a] Copolymerization conditions: temperature = 35 °C, pressure = 1 atom, solvent = heptane (25 mL), time = 2 min, [ethylene] = 0.096 M, [Ti] = 2×10^{-3} M, [Al] = 6×10^{-3} M. [b] Calculated from IR. [c] $F = F_1^2/f_1$, $G = [(f_1 - 1)/f_1]F_1$. Fineman–Ross equation: $G = -r_{\text{comonomer}} + r_{\text{ethylene}}F$. [d] Kelen–Tudos equation: $G/(F + \alpha) = (-r_{\text{comonomer}}/\alpha) + (r_{\text{ethylene}} + r_{\text{comonomer}}\alpha^{-1})(F/(F + \alpha))$, where $\alpha = (F_{\min}F_{\max})^{1/2}$.

Table 4. Ethylene 2-ANB Copolymerization (at Low Conversion) Together with the Evaluation of Some Parameters (Catalyst System: Cp_2ZrCl_2/MAO)[a]

sr no.	conc of 2-ANB in toluene (M)	2-ANB in copoly (mol %)[b]	$F_1 = (m_1/m_2)$	$f_1 = (M_1/M_2)$	10^2F^c	G^c	$F/(F+\alpha)^d$	$G/(F+\alpha)^d$
1	0.101	2.0	1.09	49.0	2.42	1.067	0.65	28.74
2	0.178	4.0	0.62	24.0	1.60	0.594	0.55	20.54
3	0.254	5.0	0.43	19.0	0.97	0.407	0.43	18.00
4	0.331	6.0	0.33	15.6	0.70	0.308	0.35	15.46
5	0.407	7.5	0.27	12.3	0.60	0.248	0.32	13.10
6	0.484	12	0.23	7.6	0.69	0.199	0.35	10.04

[a] Copolymerization conditions: temperature = 35 °C, pressure = 1 atm, solvent = toluene (25 mL), time = 1–2 min, [ethylene] = 0.11 M, [Zr] = 5×10^{-5} M, [Al] = 0.078 M. [b] Calculated from IR. [c] $F = F_1^2/f_1$, $G = [(f_1 - 1)/f_1]F_1$ Fineman–Ross equation: $G = -r_{\text{comonomer}} + r_{\text{ethylene}}F$. [d] Kelen–Tudos equation: $G/(F + \alpha) = (-r_{\text{comonomer}}/\alpha) + (r_{\text{ethylene}} + r_{\text{comonomer}}\alpha^{-1})(F/(F + \alpha))$, where $\alpha = (F_{\min}F_{\max})^{1/2}$.

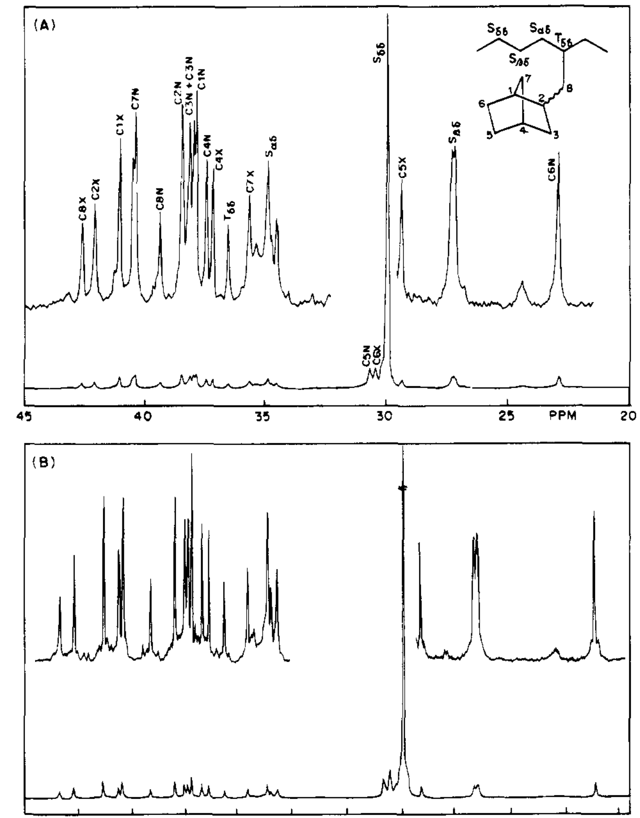

Figure 3. ^{13}C NMR spectrum of poly(ethylene-*co*-2-ANB): (A) catalyst, $TiCl_4/(i\text{-}Bu)_3Al$; (B) catalyst, Cp_2ZrCl_2/MAO.

on the copolymerizations was also observed. At a 4-methyl-1-pentene incorporation of 7.5 mol % the doublet at 730–720 cm^{-1} disappeared with only a broad peak centered at 725 cm^{-1} in the IR spectrum. The melting points of the copolymers also decreased with an increase in 4-methyl-1-pentene incorporation.

Comparison of the Structure of Ethylene–2-ANB Copolymers Obtained Using the $TiCl_4$/TIBAL and Cp_2ZrCl_2/MAO Catalyst Systems. The structures of the ethylene–2-ANB copolymers, obtained using the $TiCl_4$/TIBAL and Cp_2ZrCl_2/MAO catalysts were characterized by fractionation, infrared and nuclear magnetic resonance spectroscopy, differential scanning calorimetry, and gel permeation chromatography.

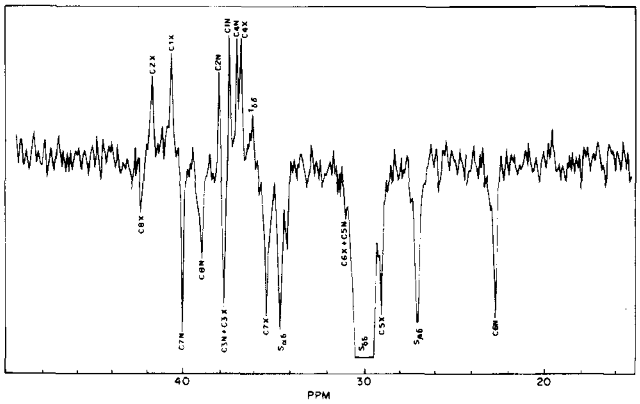

Figure 4. DEPT spectrum of poly(ethylene-*co*-2-ANB).

Fractionation gives an idea of the heterogeneity of the copolymers. In the case of copolymer samples obtained using $TiCl_4$/TIBAL, catalyst sample nos. 2 and 5 (from Table 1) were subjected to a fractionation in a Soxhlet extraction unit using heptane for 12 h. It was found that the sample containing the higher amount of 2-ANB had a larger heptane soluble fraction. This could be because the 2-ANB disrupts the crystallinity of polyethylene, thus rendering it more soluble. Also, the comonomer addition depresses the molecular weight, increasing the solubility.

In the case of copolymer samples obtained using the Cp_2ZrCl_2/MAO catalyst, sample nos. 2 and 6 (Table 2) were fractionated. Both the copolymers were found to be completely soluble in heptane. Extraction using acetone or ether gave a negligible amount of soluble copolymer. These results are consistent with homogeneous copolymers possessing narrow molecular weight distribution and uniform compositional distributions.

Table 5. Chemical Shifts of the Comonomer (2-ANB) and Copolymer (E2−ANB)

sample		C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	$T_{\delta\delta}$	$S_{\alpha\delta}$	$S_{\beta\delta}$	$S_{\delta\delta}$
2-ANB	exo	40.6	41.6	37.7	36.6	28.8	30.0	35.1	41.0	137.9	114.7				
	endo	39.8	39.9	36.8	37.2	30.1	22.4	39.9	37.3	138.6	114.2				
E2−ANB	exo	41.05	42.11	38.05	37.1	29.3	30.6	35.6	42.6			36.4	35.34−34.84	27.12−27.22	29.91
	endo	37.78	38.4	37.89	37.3	30.6	22.9	40.4	39.3			36.4	35.34−34.84	27.12−27.22	29.91

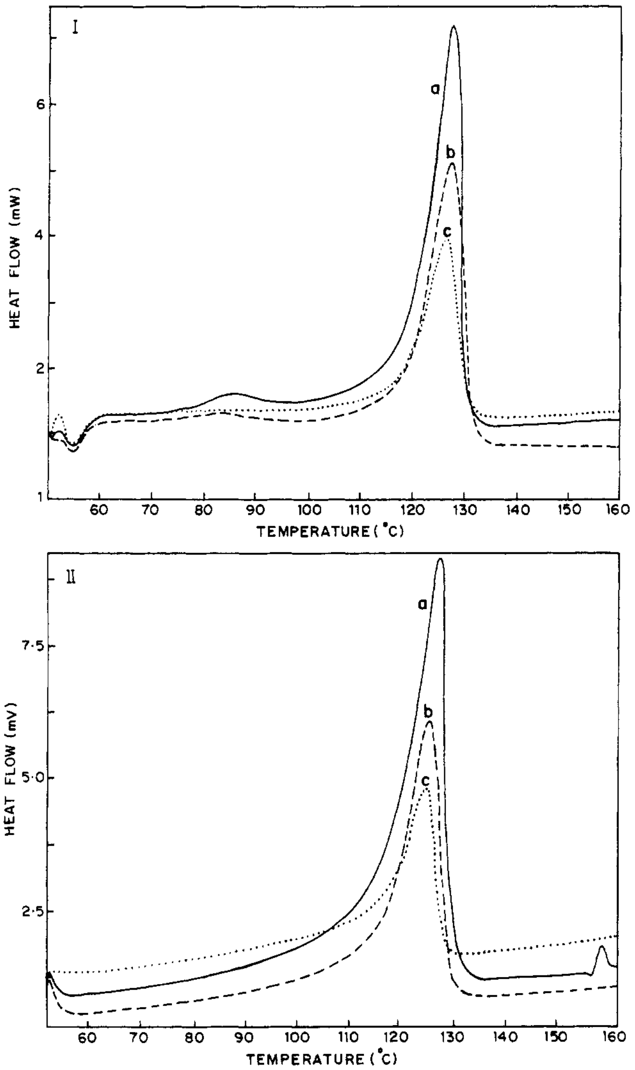

Figure 5. DSC scans of (I) ethylene−2-ANB copolymers (catalyst: $TiCl_4$/TIBAL) having (a) 7 mol %, (b) 11 mol %, and (c) 20 mol % of 2-ANB incorporation and (II) ethylene−4-methyl-1-pentene copolymers (catalyst: $TiCl_4$/(i-Bu)$_3$Al) having (a) 6 mol %, (b) 11 mol %, and (c) 19 mol % of 4M1P incorporation.

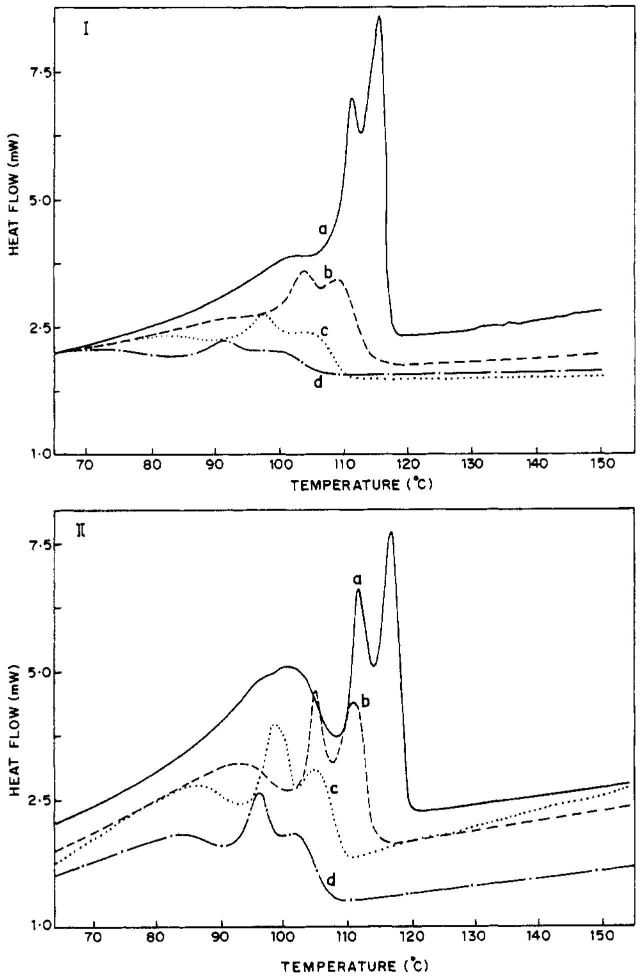

Figure 6. DSC scans of (I) ethylene−2-ANB copolymers (catalyst: Cp_2ZrCl_2/MAO) having (a) 3 mol %, (b) 4 mol %, (c) 5 mol %, and (d) 9.5 mol % of 2-ANB incorporation and (II) ethylene−4-methyl-1-pentene copolymers (catalyst: Cp_2ZrCl_2/MAO) having (a) 2.5 mol %, (b) 3.8 mol %, (c) 5.7 mol %, and (d) 7.5 mol % of 4M1P incorporation.

The copolymers were characterized by infrared spectroscopy. Peaks attributed to $-CH_2-CH_2-$ and 2-ANB repeat units were easily identified. To determine the composition of the copolymers, the absorbances of peaks at 720 and 1308 cm^{-1} were used. The spectrum of polyethylene has very few characteristic infrared absorption peaks. The absorption peaks for poly(2-ANB), also a saturated hydrocarbon, occur mostly in the same regions. As the choice of peaks is limited, the peaks at 720 cm^{-1} (no absorption of poly(2-ANB) in this region) and 1308 cm^{-1} (marginal absorption by polyethylene in this region) were chosen. Wei and Gossl have also used the absorption at 720 cm^{-1} to determine the ethylene content in ethylene propylene copolymers.[16]

In the case of the copolymers derived from the $TiCl_4$/(i-Bu)$_3$Al catalyst, the 722 cm^{-1} polymethylene chain vibration band splits into a doublet at 730 and 720 cm^{-1} corresponding to the rocking models of the two chains in the crystal cell[23] even at high 2-ANB incorporation. But, in the case of the copolymers obtained using Cp_2ZrCl_2/MAO, at high 2-ANB incorporation only a broad peak centered at 725 cm^{-1} is obtained. The absence of a doublet indicates disruption of the polyethylene crystallinity. This indicates that the copolymers obtained with the Cp_2ZrCl_2/MAO catalyst are more random in nature.

The two copolymers were characterized by nuclear magnetic resonance spectroscopy. The ^{13}C NMR spectrum of an ethylene-2-ANB copolymer is shown in Figure 3. The assignments of the peaks in ethylene−2-ANB copolymers were done similar to those of ethylene−4-methyl-1-pentene copolymers.[17] The nomenclature for assigning peaks has been adopted from the literature.[18] A good agreement of the assigned experimental values with those calculated using Grant and Paul rules[19] is observed. Assignments for the norbornyl pendant were done in accordance with the chemical shifts of model compounds and monomer. A DEPT

Table 6. Comparison of the Thermal Properties of Ethylene–2-ANB Copolymers with Those of Ethylene–4-Methyl-1-pentene Copolymers

ethylene–2-ANB copolymers				ethylene–4-methyl-1-pentene copolymers			
mol % comonomer	T_m (°C)	ΔH_f (J/g)	% cryst	mol % comonomer	T_m (°C)	ΔH_f (J/g)	% cryst
			$TiCl_4(i\text{-}Bu)_3Al$ Catalyst System				
	131.6	128.6	45		131.6	128.5	45
6	127.3	86.2	30	6	126.6	89.4	31
11	126.7	61.0	21	11	125.2	60.0	21
20	126.0	37.6	13	19	124.0	38.4	13
			Cp_2ZrCl_2/MAO Catalyst System				
	132.5	194.7	67		132.5	194.7	67
3	110, 115	83	28	2.5	112, 117	96	33
5.7	97, 104	52	18	5.0	98, 104	51	17.5
9.5	91, 99.9	26	9	7.5	96, 101	41	14

(distortionless enhancement by polarization transfer) spectrum of the copolymer (Figure 4) was also obtained to distinguish between the methine and methylene signals. The assignments of the peak positions are shown in Table 5. The shifts of the main chain carbon atoms do not appear to be sensitive to the endo/exo isomerism in the pendant moiety. Here endo C_1 and C_2 are assigned values different from those of the homopolymer on the basis of the DEPT spectrum.

^{13}C NMR spectra were also used to determine the copolymer composition, as described in the Experimental Part. Further, based on integration of endo and exo C_3 or C_4, an endo:exo ratio of 55:45 for 2-ANB is obtained. This implies the absence of selectivity toward insertion of either the endo or exo isomer during copolymerization.

The X-ray diffraction patterns of the ethylene–2-ANB copolymers using the $TiCl_4$/TIBAL catalyst show the presence of two crystalline peaks (110 at $2\theta = 21.4°$ and 200 at $2\theta = 23.8°$) along with an amorphous halo in samples having low levels of comonomer. As the comonomer concentration increases, the peak positions of the 200 and 110 reflections shift to lower values, indicating an increase in the dimensions of the unit cell which could be a consequence of the reduced crystallite dimensions which decrease as branching increases.[20] At even higher 2-ANB concentrations a new reflection at $2\theta = 18.5°$ appears, and the intenisty of this peak increases as comonomer content increases. Clas *et al.*[20] have observed a similar peak at 19.4° in ethylene–1-octadecene samples of high comonomer content. This has been attributed to a triclinic form that competes in stability with orthorhombic polyethylene. At 26 mol % 2-ANB incorporation, a substantial loss in crystallinity is observed. On the other hand, the X-ray diffraction patterns of the copolymers obtained using the Cp_2ZrCl_2/MAO catalyst show almost total loss of crystallinity at 9.5 mol % incorporation of 2-ANB. A loss of crystallinity at a lower value of comonomer content could be attributed to a random incorporation of comonomer units when the Cp_2ZrCl_2/MAO catalyst is used.

Thermogravimetric analysis under a nitrogen atmosphere shows that the initial decomposition temperature of all copolymers is above 380 °C with a marginal decrease in the value of initial decomposition temperature with increasing comonomer concentration.

Results of the differential scanning calorimetric analysis of copolymers obtained using the $TiCl_4$/TIBAL catalyst are shown in Table 1 and Figure 5. It can be seen that the value of ΔH_f decreases with an increase in comonomer content. The percent crystallinity was estimated by assuming that $\Delta H_f = 290$ J/g for 100% crystalline polyethylene.[21] The calculated percentage of crystallinity from the ΔH_f values decreases with an increase in comonomer content. However, even in samples with a high comonomer content the depression in T_m is of the order of only 5.6 deg. From this observation it can be deduced that regardless of the composition of the copolymer, they appear to contain the same kind of larger crystallites. This can happen if the copolymers have a blocky microstructure. A similar observation has also been noted in the case of ethylene–hexene copolymers.[22] The decrease in the value of ΔH_f can then be explained by a dilution effect since at a high mol % incorporation of comonomer the mass fraction of ethylene-derived main chains is reduced.

The DSC of the fractions of samples 2 and 5 (Table 1) were also obtained. It was observed that the heptane soluble fraction did not show a noticeable T_m whereas the heptane insoluble fraction showed a slightly higher T_m than the unfractionated sample.

Results of the differential scanning calorimetric studies of copolymers obtained using the Cp_2ZrCl_2/MAO catalyst are shown in Table 2 and Figure 6. Upon comparison with the data in Table 1 and Figure 5 it is noted that at similar mol % incorporation of comonomer the copolymer obtained using the Cp_2ZrCl_2/MAO catalyst results in a larger decrease in the value of ΔH_f and percentage crystallinity than the copolymer obtained using $TiCl_4$/TIBAL. Further, the initial drop in crystallinity with mol % incorporation is very rapid in the copolymer obtained using the Cp_2ZrCl_2/MAO catalyst, whereas in the copolymer obtained using the $TiCl_4$/TIBAL catalyst the decrease is very gradual. This implies that the copolymers obtained using the Cp_2ZrCl_2/MAO catalyst are more random in nature, resulting in a large disruption of polyethylene crystallinity. This conclusion is also supported by the value of the product of the reactivity ratios. A prominent feature of all these copolymers is that the melting is observed as two endotherms separated by about 5 deg. The multiple melting endotherm did not disappear upon repeated cycles of heating and cooling. A similar observation was also made in the case of ethylene–4-methyl-1-pentene copolymers obtained with the Cp_2ZrCl_2/MAO catalyst (Figure 6). No prior literature report of such a behavior exists, though in some of the ethylene–hexadecene copolymers synthesized by Koivumaki and Seppala[24] a multiple melting endotherm can be seen. A multiple melting endotherm normally implies compositional heterogeneity, but fractionation results, reactivity ratios, and melting and ΔH_f values indicate that the copolymers are random and homogeneous in nature. The reason for this unusual observation is not apparent at present.

Gel permeation chromatography was used to determine the molecular weight distribution. Sample 2

(Table 1) was found to have a broad molecular weight distribution with $M_n = 48\,400$, $M_w = 322\,900$, and $M_w/M_n = 6.7$.

Sample 3 (Table 2) was analyzed by GPC. A narrow molecular weight distribution is obtained, as expected with homogeneous metallocene catalysts, with $M_n = 15\,500$, $M_w = 40\,200$, and $M_w/M_n = 2.6$.

Comparison of the Thermal and Crystalline Properties of Ethylene–2-ANB and Ethylene–4-Methyl-1-pentene Copolymers. A comparative evaluation of properties of ethylene–2-ANB and ethylene–4-methyl-1-pentene copolymers is shown in Table 6 and Figures 5 and 6. It can be seen that, contrary to expectation, at essentially similar mol % incorporations of comonomers, the depression in the value of T_m and ΔH_f (within the limits of experimental error) depends largely on the catalyst system used and not on the type of comonomer. A similar independence of crystallinity and ΔH_f of comonomer type was observed by Burfield[25] in his studies on a series of linear low-density polyethylenes containing propylene, 1-butene, or 4-methyl-1-pentene. He found that the disruption of polymer crystallinity is determined principally by the number and distribution of chain irregularities rather than branch length. He attributed this to the use of similar catalyst and reaction conditions, resulting in copolymers of similar molecular weights and molecular weight distributions.

On the other hand Clas *et al.*[26] observed that in a series of copolymers of ethylene and 1-alkene ranging from 1-butene to 1-octadecene prepared using the $VOCl_3/Et_3Al_2Cl_3$ catalyst, at low comonomer contents the melting points are independent of branch length but at higher comonomer contents the melting points decrease in the order 1-butene > 1-octene > 1-octadecene. For example, at 8 mol % comonomer the melting point of the ethylene–1-butene copolymer was 92 °C whereas for the ethylene–1-octadecene copolymer it was 65 °C. It can be concluded that the norbornyl ring acquires a compact structure, probably due to the bridging, and its influence on the folding of polyethylene chains is not very different from that of an isopropyl group.

Conclusions

The ethylene–2-ANB copolymers obtained using the $TiCl_4$/TIBAL catalyst and the Cp_2ZrCl_2/MAO catalyst were characterized by reactivity ratio analysis, fractionation, differential scanning calorimetry, gel permeation chromatography, and infrared and nuclear magnetic resonance spectroscopy. Interestingly, the ethylene–2-ANB copolymers obtained using Cp_2ZrCl_2/MAO showed a multiple melting endotherm which normally implies compositional heterogeneity, yet results from fractionation, reactivity ratios values, and melting and ΔH_f values indicate the copolymers are compositionally homogeneous in nature. The copolymers obtained using the $TiCl_4$/TIBAL catalyst were found to be heterogeneous and blocky in nature.

At the same mol % incorporation, the copolymers obtained using the Cp_2ZrCl_2/MAO catalyst have much lower values of crystallinity and T_m. The lower values of intrinsic viscosity would suggest a lower molecular weight.

Contrary to expectation, the bicyclo[2.2.1] pendant does not result in an additional lowering of crystallinity when compared to the isopropyl pendant. This conclusion is drawn on the basis of the comparison of the thermal properties of ethylene–2-ANB and ethylene–4-methyl-1-pentene copolymers at similar mol % incorporations.

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