Copolymerization of ethylene and vinylcyclohexane using soluble Ziegler–Natta catalysts

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The copolymerization of ethylene and vinylcyclohexane has been investigated using soluble catalytic systems Cp_2ZrCl_2/MAO ($Cp = \eta^5$ cyclopentadienyl; MAO = methylaluminoxane) and Cp_2ZrMe_2/MAO at 70°C and room temperature. Under the reaction conditions employed, up to 1.7 mol% of vinylcyclohexane could be introduced into the polyethylene chains. The molecular structure and comonomer content of the copolymers were determined by ^{13}C nuclear magnetic resonance. The comonomer content of the polymers was found to increase with the comonomer concentration in the feed. The comonomer was found to be mainly statistically distributed. With samples containing higher comonomer content, however, the formation of a relatively very small amount of short blocks was noted. The average molecular weights of the copolymers were lower than those of pure polyethylene prepared under identical conditions. As expected, the vinylcyclohexane decreased the melting point and crystallinity of the polymers.

(Keywords: copolymerization; ethylene; Ziegler–Natta catalyst)

INTRODUCTION

The copolymerization of ethylene with linear α-olefins to produce polyethylene with substituted alkyl side groups at low pressures (linear low-density polyethylene) has gained considerable commercial importance in recent years[1]. Linear α-olefins such as 1-butene, 1-hexene and 1-octene are the most widely used comonomers, whereas the use of α-olefins containing alicyclic substituents like vinylcyclohexane as comonomer has not been reported in the literature to our knowledge. The reason may be due to the poor reactivity of conventional Ziegler–Natta catalysts towards such α-olefins complicated by unwanted side reactions[2]. Polyvinylcyclohexane is known to be a tough polymer with a melting point >300°C[3]. Hence the incorporation of vinylcyclohexane into the polyethylene backbone may bring about improvements in the mechanical toughness of the polymer. Also the bulky cyclohexyl substituent can be expected to lower the melting point and density of polyethylene more effectively than the linear α-olefins. Propylene has been copolymerized with vinylcyclohexane and very good improvements in properties such as lower brittleness temperature, greater heat resistance and better mechanical strength were observed[2,4].

Recently Kaminsky and Spiehl[5] have demonstrated the copolymerization of ethylene and cyclic olefins using highly active soluble zirconium catalysts. Appreciable amounts of the cyclic olefins could be incorporated without any ring-opening reactions. This paper deals with the copolymerization of ethylene and vinylcyclohexane taking advantage of the highly active soluble zirconium catalysts developed earlier by Kaminsky *et al.*[6].

EXPERIMENTAL

Cp_2ZrCl_2, trimethylaluminium, methyllithium and vinylcyclohexane were purchased from Aldrich Chemical Co. Toluene, which was used as the solvent for the polymerization reactions, was purified by refluxing over Na/benzophenone for 12 h followed by distillation. Cp_2ZrMe_2 was prepared according to procedures reported earlier[7]. Methylaluminoxane (MAO) was prepared by reacting trimethylaluminium with $Al_2(SO_4)_3 \cdot 16H_2O$ ($Al/H_2O = 1$) according to the procedure reported by Tsutsui and Kashiwa[8]. The supernatant liquid was separated by filtration under nitrogen atmosphere and stored as 1 M Al stock solution containing MAO and unreacted trimethylaluminium.

Polymerization procedure

The polymerization reactions were performed in a 500 ml glass reactor equipped with a magnetic stirrer. The dry glass reactor was baked in an oven at 150°C for 1 h and degassed with high-purity argon for 1 h. Toluene and vinylcyclohexane were placed in it and further degassed by bubbling with argon for 45 min. Methylaluminoxane stock solution was added through a syringe followed by the introduction of ethylene at atmospheric pressure. The contents were brought to the desired reaction temperature and the polymerization started by injecting the catalyst solution. The reaction was arrested by addition of a small amount of methanol.

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The polymer was isolated by pouring the reaction mixture into excess methanol containing 10% HCl. The polymer was washed thoroughly with methanol and dried in a vacuum at 40°C for 24 h.

Differential scanning calorimetry (d.s.c.) analysis of the polymer samples was done on a Perkin–Elmer Model DSC-4 instrument with a Perkin–Elmer thermal analysis data station TADS-101. The samples, 4–5 mg in size, were heated at 20°C min^{-1} to 180°C, cooled to room temperature and heated again to 180°C at the same rate. The ^{13}C nuclear magnetic resonance (n.m.r.) analyses of the polymer samples were carried out on a Bruker AC-300 or a Bruker AM-250 instrument operating at 75.5 MHz or 62.9 MHz, respectively. The spectra of the polymers were recorded for 10–15% w/v solutions in trichlorobenzene at 125°C in 10 mm diameter sample tubes. The comonomer contents of the polymers were estimated from the peak areas in the ^{13}C n.m.r. spectra.

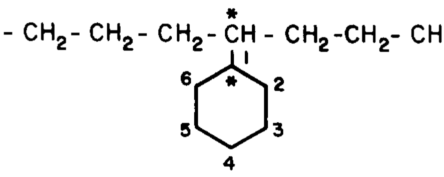
The molecular weight averages and the molecular weight distributions were determined by gel permeation chromatography (g.p.c.) using a Waters 150C instrument equipped with a Viscotek continuous viscometer and Chromatix KMX-6 LALLS and Waters RI detectors. A JORDI mixed bed column was used and the solvent 1,2,4-trichlorobenzene was stabilized with Irgonox 1010 (0.1%).

RESULTS AND DISCUSSION

The polymerization of ethylene and vinylcyclohexane using the catalytic systems Cp_2ZrCl_2/MAO and Cp_2ZrMe_2/MAO was studied at both 70°C and room temperature and the results are presented in *Table 1*. For comparison, the results of the homopolymerization of ethylene under identical conditions are also included in *Table 1*. It can be seen, with both catalytic systems and also at the two different temperatures, that the addition of vinylcyclohexane decreases the catalytic activity when compared with ethylene homopolymerization. Increasing the comonomer concentration in the feed clearly decreases the catalytic activity further but increases the comonomer content of the polymer. The above trend in reactivity has also been noted for copolymerization reactions of ethylene and linear α-olefins using Ziegler–Natta catalysts[9]. The room temperature study was carried out to discover whether lowering the reaction temperature would improve the comonomer incorporation as has been observed by Kaminsky and Spiehl[5] for copolymerization of ethylene and cyclic olefins. In the present study, however, the opposite trend is noted. Identical behaviour should not be expected, however, since vinylcyclohexane is an α-olefin and is structurally different from a cyclic olefin.

Structure identification by ^{13}C n.m.r.

The ^{13}C n.m.r. spectrum of the copolymer containing 1.7 mol% comonomer is shown in *Figure 1*. The nomenclature for assigning the peaks has been adopted from the literature as reported by Randall[10]. In most cases the assignments have been achieved by comparison of the experimental values with those of theoretical ones calculated by the method of Grant and Paul[11]. The J-modulated spin-echo spectrum (*Figure 2*) of the above mentioned sample indicates the presence of four methine carbons at 44.9, 43.8, 41.4 and 38.0 δ. The peaks at 43.8 and 41.4 δ have been assigned respectively to the cyclohexyl and branching methine carbons of structure **1** wherein the comonomer is statistically distributed along the polymer chain. The peaks at 33.7 (C_2, C_6), 26.7 (C_3, C_5) and 26.4 δ (C_4) of the pendent cyclohexyl group are in agreement with the literature report for n-butylcyclohexane[12]. The peaks at 38.0 and 37.7 δ have been assigned to the methine and methylene carbons of structure **2**. In order to explain



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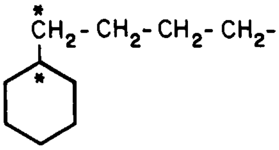

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Table 1 Results of polymerization reactions using toluene as the solvent

Catalyst Zr ($\mathrm{mol\,l^{-1}}$) × 10^5	 Al[a] ($\mathrm{mol\,l^{-1}}$) × 10^2	VC[b] ($\mathrm{mol\,l^{-1}}$)	Reaction temperature (°C)	Reaction time (min)	Yield (g)	Comonomer content (mol%)
Cp_2ZrCl_2						
1.5	2.5	0	70	30	6.0	–
1.5	2.5	0.73	70	30	3.5	1.1
1.5	2.5	1.83	70	30	2.9	1.7
3.0	5.0	0	25	45	3.6	–
3.0	5.0	1.83	25	45	0.95	0.6
Cp_2ZrMe_2						
0.2	5.0	0	70	60	0.8	–
0.2	5.0	1.83	70	120	0.65	1.4

[a] Methylaluminoxane/Me_3Al
[b] Vinylcyclohexane

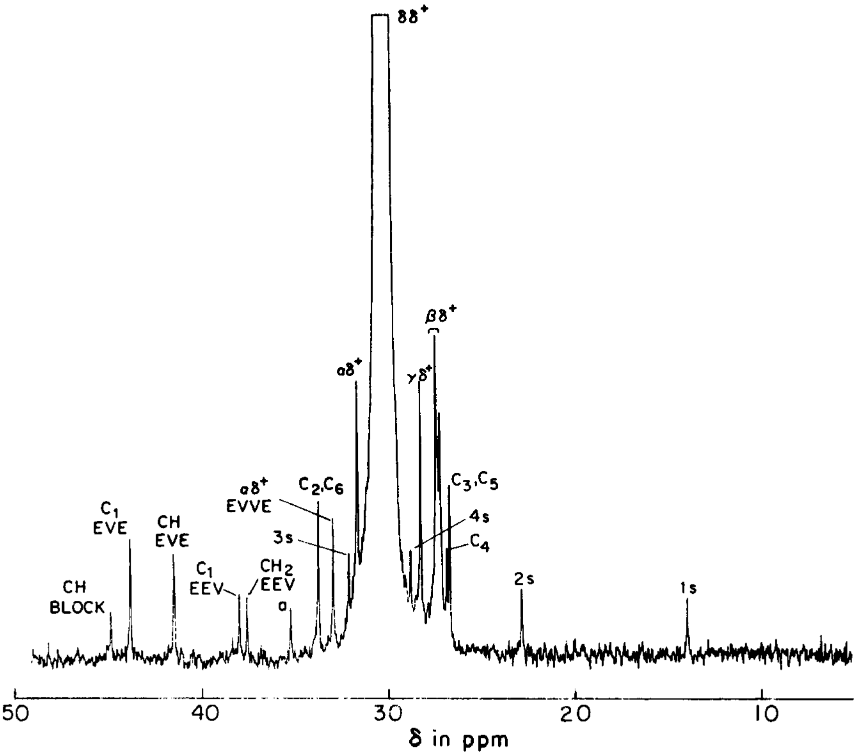


Figure 1 ^{13}C n.m.r. spectrum of ethylene/vinylcyclohexane copolymer. s, a, E and V represent saturated, allylic, ethylene and vinylcyclohexane, respectively. C_1–C_6 represent the cyclohexyl carbons

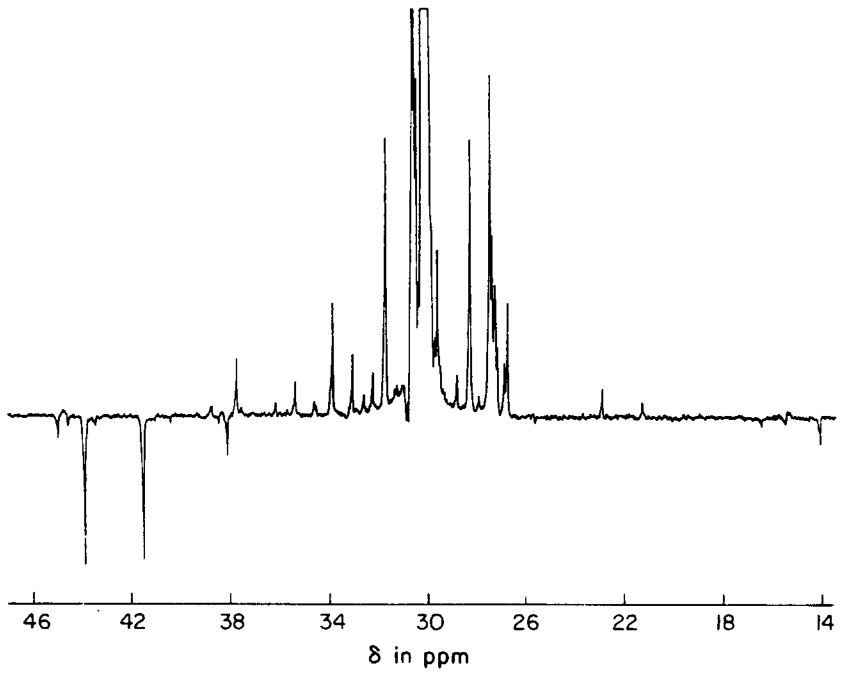
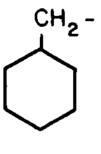


Figure 2 ^{13}C n.m.r. J-modulated spin-echo spectrum of ethylene/vinylcyclohexane copolymer

this structure one must consider the possible occurrence of chain transfer reactions with the comonomer as outlined by Böhm[13]. The observed values coincide well with those reported for the corresponding carbons of n-butylcyclohexane 3 which can best be considered as a model compound for structure 2. It should be noted here, however, that the observed chain transfer to the comonomer is not an exclusive mode of termination of the polymer chains in the present study. This is supported by the fact that the decrease in the mean molecular weight of the polymers was not proportional to the comonomer content. The relatively weak peak at 44.9 δ observed only in samples containing higher comonomer content (1.7 and 1.4 mol%) indicates presumably the formation of a very small amount of blocks of two comonomeric units (structure 4). The appearance of an additional peak at



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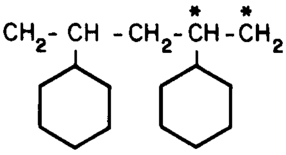

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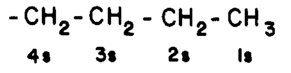
32.9 δ for these samples which can plausibly be assigned to the $S_{\alpha\delta}+$ of the blocks confirms their formation. The formation of blocks of vinylcyclohexyl units at such low levels of comonomer content is known in the literature with propylene[2] and thus is not without precedent. The peaks at 14.1, 22.9, 32.2 and 28.8 δ have been assigned to 1s, 2s, 3s and 4s carbons of the terminal polyethylene chains (structure 5)[14]. The foregoing n.m.r. results confirm


$$\underset{4s}{-CH_2}-\underset{3s}{CH_2}-\underset{2s}{CH_2}-\underset{1s}{CH_3}$$

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the structure to be the copolymer of ethylene and vinylcyclohexane without any noticeable ring-opening reactions of the cyclohexyl group.

The basic physical properties of the polymers synthesized are presented in *Table 2*. The melting point and heat of fusion (ΔH_f) of the copolymers decrease with increasing comonomer content as can be expected of the bulky pendent cyclohexyl groups. The number-average molecular weights of the copolymers are lower than those of the corresponding polyethylene samples although no direct relationship could be detected between the decrease in mean molecular weight and comonomer content. As is well known with linear α-olefins, vinylcyclohexane must be acting as a chain transfer agent for some of the growing polymer chains, thereby regulating the molecular weight. This conclusion is consistent with the n.m.r. studies already mentioned.

The molecular weight distributions of the polymer samples at two different temperatures are illustrated in *Figures 3* and *4*. The distributions are broader for the samples prepared at room temperature (*Figure 4*) than for those prepared at 70°C. The polyethylene samples prepared at 70°C showed bimodal distributions irrespective of the catalyst system. The molecular weight distributions for the homopolymer and copolymer samples prepared at this temperature, however, were quite narrow and nearly identical. This observation suggests that the nature of the active species may be the same for the homopolymerization and the copolymerization reactions.

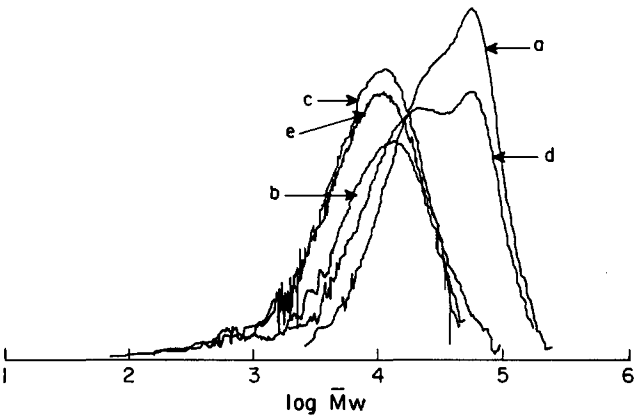

Figure 3 Molecular mass distribution of the polymers at 70°C. (a) Polyethylene (PE) ($T_m = 132.6$°C); (b) copolymer (1.1 mol% vinylcyclohexane (VC)); (c) copolymer (1.7 mol% VC); (d) PE ($T_m = 132.1$°C); (e) copolymer (1.4 mol% VC)

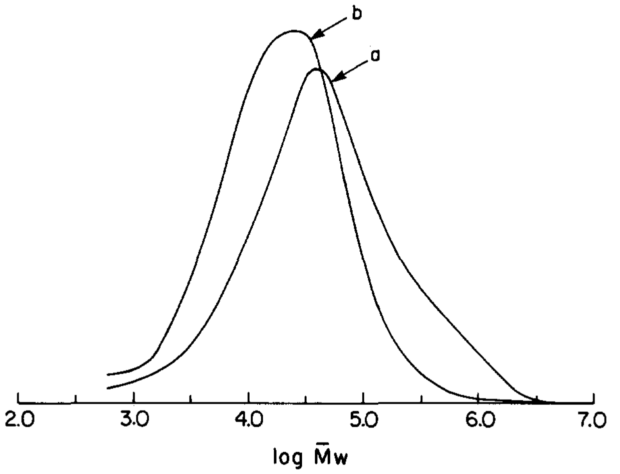

Figure 4 Molecular mass distribution of the polymers at room temperature using Cp_2ZrCl_2/MAO (*Table 1*). (a) Polyethylene; (b) copolymer

Table 2 Some basic physical properties of the polymers[a]

Comonomer content (mol%)	Melting point (T_m) (°C)	ΔH_f ($J g^{-1}$)	$M_n \times 10^{-3}$ ($g mol^{-1}$)	M_w/M_n
0	132.6	165.8	16.6	2.27
1.1	125.5	151.1	6.1	2.25
1.7	119.1	120.1	5.3	1.96
0	133.1	164.9	16.6	8.57
0.6	126.2	121.4	10.4	4.65
0	132.1	194.2	10.7	2.77
1.4	121.5	131.9	5.0	1.91

[a] Preparation conditions are given in *Table 1*, in which the polymers are reported in the same order

CONCLUSIONS

The copolymerization of ethylene and vinylcyclohexane has been achieved using soluble catalytic systems. The structure of the copolymer and the comonomer content were determined by a ^{13}C n.m.r. study. The cyclohexyl branches affect the physical properties by decreasing the melting point and crystallinity of polyethylene as expected.

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