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Comparison of ethylene-propylene copolymers obtained with Ti, V and Zr catalyst systems

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Summary

Ethylene and propylene were copolymerized in n-heptane in the presence of high activity heterogeneous $MgCl_2/TiCl_4$ catalyst and homogeneous $VOCl_3$ and Cp_2ZrCl_2 catalysts to study the effect on the catalyst to the microstructure and molecular weight distribution of the copolymer. The copolymer obtained with the zirconium catalyst was much more random in structure than that obtained with the vanadium and titanium catalysts and the molecular weight distribution was very narrow. Ethylene and propylene were also copolymerized in liquid propylene with $MgCl_2/TiCl_4$ and $VOCl_3$ catalyst systems. These copolymers were column fractionated and the fractions were analysed by NMR spectroscopy and DSC. The fractions of the copolymer obtained with the titanium catalyst was found to have broader distribution in composition than the copolymer obtained with the vanadium catalyst. This probably explains the traces of crystallinity in the copolymer prepared with the titanium catalyst. However, no effect was seen on the glass transition temperature.

Introduction

It is well known from earlier studies that random or moderately altering copolymers of ethylene and propylene(1,2) or higher 1-alkenes(3) can be obtained with vanadium catalysts. Zirconium-based catalysts are another group of homogeneous catalysts(4-6) that produce a random distribution of monomers(7). The situation is quite different, however, for titanium-based heterogeneous catalysts. Apparently because they have multiple active species, blocks of ethylene and propylene are formed in the copolymer(8-12). Fractionation techniques are usually applied in studying the microstructure of olefin-based homo- and copolymers(13). Ethylene-propylene copolymers are usually studied with a solvent-nonsolvent system(14-16) and homopolymers or copolymers containing only small amounts of comonomer by temperature rising elution fractionation(17-19), direct extraction(20) or continuous polymer fractionation(21).

The purpose of the work described here was to compare the microstructure and molecular weight distributions of low- and moderate-molecular-weight ethylene-propylene copolymers obtained with titanium, vanadium and zirconium catalysts.

Experimental

Apparatus and method of copolymerizations: Copolymerizations in n-heptane were performed in a 0.5 dm^3 reactor 45 min at 40°C under a constant absolute pressure of 2 to 6 bars. A mixture of ethylene, propylene and, with the titanium and vanadium

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catalysts, also hydrogen, was bubbled through the reactor until equilibrium was reached. The hydrogen was added as chain transfer agent. After a five-minute preactivation, the mixture of catalyst and cocatalyst was added. Reactor temperature was controlled automatically with a thermostat connected to a Pt-100 resistance thermometer. Reactor pressure and the feeds of ethylene, propylene and hydrogen were controlled automatically with electronic pressure and mass flow controllers. Temperature was accurate to within ±0,05 °C and pressure to within ±0,03 bars. After polymerization the reactor was degassed, the reaction mixture was washed with dilute hydrochloric acid and water and the n-heptane was evaporated. The product was dried in a vacuum oven at 60°C overnight.

Copolymerizations in liquid propylene were performed in a 2 dm^3 reactor at 15°C, and under a constant ethylene partial pressure. Total pressure and the amount of hydrogen added were fixed so that the copolymers had the same ethylene contents and intrinsic viscosities. An appropriate amount of hydrogen was added, and immediately afterwards liquid propylene was added batchwise. The catalyst and cocatalyst mixture was then blown into the reactor with nitrogen and the ethylene feed was started semibatchwise. The pressure of the reactor was maintained constant with an electronic pressure controller and the temperature was controlled manually by circulating water-ethanol mixture in the jacket of the reactor. Accuracy of the pressure control was ±0.05 bar and the temperature ±0.3°C. Part of the copolymers were dissolved into n-heptane and washed with diluted hydrochloric acid and water, precipitated with acetone and milled to get the pure product for the characterization.

Apparatus and method of fractionation: Elution column fractionation was applied with xylene as solvent and ethylene glycol monobutyl ether (butylcellosolve) as nonsolvent. 2,6-Di-tert-butyl-p-cresol (0,2%) was added as antioxidant. The sample was dissolved completely in n-heptane and the solution was mixed with 2500 g glass beads (Ø 0.4-0.5 mm). n-Heptane was gently evaporated from the mixture with the aid of a hot-air blower. After drying, the glass beads were introduced into a column (90 mm in diameter and 450 mm in height) equipped with a temperature probe and an oil jacket. The fractionation temperature was 120°C and was fixed over the melting area of the polyethylene block traces in the copolymer samples. The preheated solvent-nonsolvent mixture (total amount 700 ml) was led to the column. After 35 min the bottom valve was opened and first fraction was collected. The consecutive fractions were obtained in a similar manner by increasing the proportion of xylene in the mixture, the last fraction being eluted with pure xylene. The polymers were precipitated with acetone, filtered, and dried under vacuum at 60°C.

Chemicals: $MgCl_2/TiCl_4$ catalyst system was a typical supported Ziegler-Natta catalyst without internal or external donor. Cocatalyst was triethylaluminium (TEA) and the catalyst/ cocatalyst mole ratio was 100 (Ti). Titanium content of the catalyst was under 10 wt.-%. $VOCl_3$ catalyst was combined with diethylaluminium chloride (DEAC) with a catalyst/ cocatalyst mole ratio of 10 (V). Cp_2ZrCl_2 catalyst was combined with methylaluminoxane (MAO) and the catalyst/ cocatalyst mole ratio was 3000 (Zr). All ratios are typical values for these catalyst systems. The homogeneous catalysts were commercially available chemicals (from Aldrich Chemie). TEA and DEAC were 10 wt.-% solutions in n-heptane and MAO was 10 wt.-% in toluene (all from Schering AG). n-Heptane was grade GR (from J.T. Baker) and was further purified by conducting it through columns containing molecular sieves, CuO and Al_2O_3. Ethylene was grade 2.7 (from Aga), propylene 2.5 and hydrogen 5.0 (both from Messer Griesheim) and, just before being introduced to the reactor they were conducted through columns containing molecular sieves, CuO and Al_2O_3.

Polymer characterization : The ethylene contents and triad sequence distributions were determined with a Jeol GSX-400 nuclear magnetic spectrometer and calculated according to Cheng (22). A Waters GPC operating at 135°C and equipped with three Tosoh TSK-gel mixed bed columns was used to determine the molecular weight distributions. 1,2,4-Trichlorobenzene was used as solvent with flow rate of 1.0 ml/min. The columns were calibrated with linear low density polyethylenes with broad molecular weight distribution and monomer composition was taken into account according to the literature(23). The viscosity-average molecular weights were determined by intrinsic viscosity measurements at 135°C with decahydronaphthalene as solvent.

Results and discussion

The results from the copolymerizations in n-heptane and the fractionated copolymers are seen in Table 1. The characterization of the fractionated copolymers shows the properties to be about the same. The reproducibility of the fractionation method was checked with two parallel runs. Data from the test are collected in Figure 1 and confirm that the method is accurate.

Table 1. Results of polymerizations in n-heptane and the fractionated copolymers.

Catalyst system	Ethylene content in mole-%	Activity in kg/(g cat•h•bar)	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$
			g/mole		
(Ti)	42	0.83	19900	2700	7.4
(V)	37	0.02	6200	600	10.3
(Zr)	40	1.60	1300	500	2.6
(Ti)	51	1.30	23900	2700	8.9
(V)	53	0.05	6900	700	9.9
(Zr)	51	2.08	2900	700	4.1
(Ti)	67	1.13	34100	7700	4.4
(V)	69	0.10	18400	4500	4.1
(Zr)	68	2.68	5000	1400	3.6
(Ti)	70	2.06	211200	20600	10.3
(V)	67	0.17	959400	36100	26.6
(Zr) (-15°C)	76	0.27	227600	119300	1.9

Property	Ti	V
Ethylene content, mole-%	55	55
Intrinsic viscosity, dl/g	2.54	2.62
$\overline{M}_w$, kg/mol	260	300
$\overline{M}_n$, kg/mol	27	28
Polydispersity	9.6	10.7
Density, g/cm^3	0.859	0.857
Mooney viscosity, ML 1+4(100°C)	41	44
Hardness, Shore A	43	35
Polyethylene-based crystallinity	traces	none
Glass transition temperature, °C	-57	-58

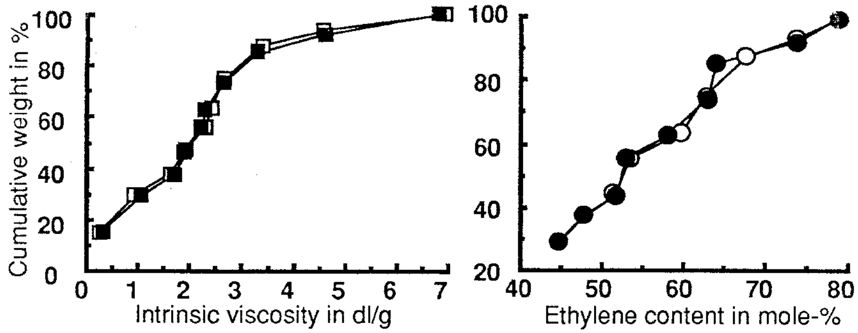

Fig. 1. Reproducibility of the fractionation method used; parallel fractionations.

The monomer distributions of the copolymers are displayed in Fig. 2. Figure 2 shows that the titanium catalyst gives copolymer with a very high proportion of polyethylene and polypropylene sequences compared with the homogeneous catalyst systems. Zirconium catalyst gives very low proportions of these homopolymer blocks and, at an ethylene content of 70 mole-%, there is no PPP at all. With the vanadium catalyst the proportions of these blocks lie between the two extremes. However, the PPE and PEE triads in all the copolymers, and the EPE triads in the copolymers obtained with the homogeneous catalysts, are present in about the same level. For the homogeneous catalysts, the main difference lies in the PEP triads; i.e., the proportion of PEP triads obtained with the zirconium catalyst is higher than the proportion obtained with the vanadium catalyst, which is about the same as for titanium. The triad distribution of the copolymers shows that highly random copolymer can be obtained with zirconium catalyst.

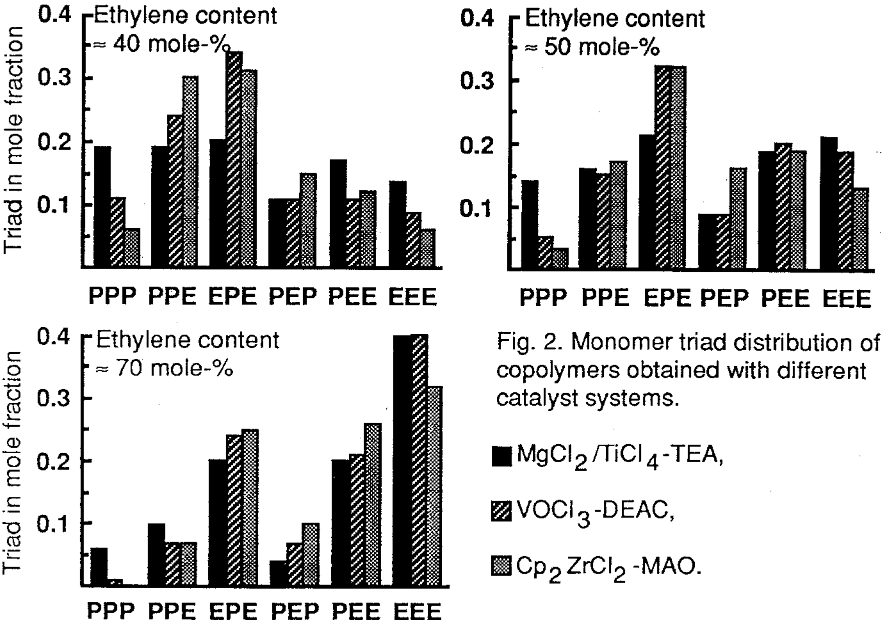

Fig. 2. Monomer triad distribution of copolymers obtained with different catalyst systems.

■ $MgCl_2/TiCl_4$-TEA,

▨ $VOCl_3$-DEAC,

▩ Cp_2ZrCl_2-MAO.

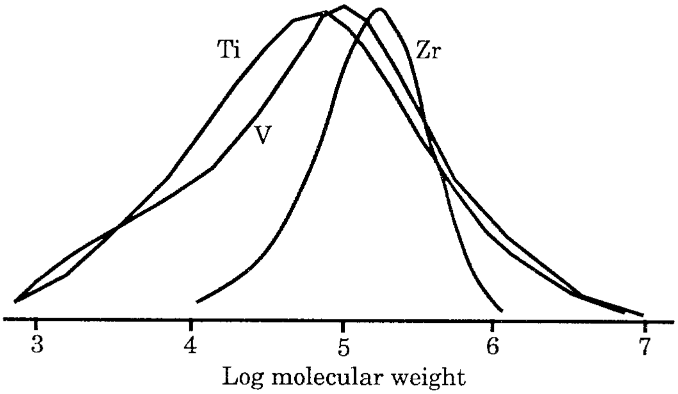

Fig. 3. GPC curves of the fractionated copolymers and the copolymer made at -15°C with zirconium catalyst.

Table 1 shows that the molecular weights of the copolymers are very low with the zirconium catalyst, even though no hydrogen was used, and the products were obtained as viscous liquids. To obtain a polymer with moderate average molecular weight copolymerization with the zirconium catalyst was done at -15°C. The molecular weight distribution of the low-molecular-weight copolymers obtained with titanium and vanadium catalyst was very broad, but with zirconium catalyst narrow. The broad molecular weight distribution was propably due to the high hydrogen partial pressure applied to obtain low molecular weights, this appears to cause tails in the molecular weight distributions.

The results from the fractionations of the copolymers obtained with vanadium and titanium catalysts are collected in Table 2. The differences between the ethylene contents of the two fractionated copolymers are seen in Figure 4. Figure 4a shows that both copolymers have broad distribution in composition of the fractions, with the distribution measured for the titanium copolymer being slightly broader. Whereas the curve for the copolymer obtained with titanium is nearly linear, however, that for the copolymer obtained with the vanadium catalyst is S-shape, with the inflection point near the average ethylene content of the copolymer. Most of the chains in the copolymer obtained with vanadium thus have the same ethylene content as the copolymer as a whole. To better visualize the differences in the polymers, third degree equations were fitted to the points and then differentiated. The shapes of the curves after the differentiation are seen in Figure 4b. The figure clearly shows that most of the copolymer obtained with the vanadium catalyst is concentrated at either sides of the average ethylene content of the copolymer, unlike the copolymer obtained with the titanium catalyst, which is evenly spread about the average content.

Table 3. Results from the fractionations of the copolymers obtained with vanadium and titanium catalysts.

Fract. no.	Xylene:butyl-cellosolve in ml	Fraction yield in mg Ti:V	Cumulative weight in %	Ethylene content in mole-%	$\overline{M}_w$ in 10^3 g/mol	$\overline{M}_w/\overline{M}_n$
1	75:625	375:281	9:8	43:42	22: 17	2.1:2.0
2	115:585	413:274	20:16	45:45	64: 43	2.8:2.1
3	140:560	341:197	28:21	45:47	170:105	4.2:2.8
4	160:540	305:181	36:26	49:51	217:247	4.1:4.0
5	185:515	415:231	46:33	53:54	245:264	3.6:3.5
6	210:490	364:422	55:44	56:57	267:282	3.4:3.1
7	230:470	405:424	65:56	59:58	282:311	3.0:2.8
8	245:455	278:354	72:66	62:59	317:360	2.9:2.5
9	270:430	363:510	81:80	67:62	377:480	2.6:2.5
10	290:410	297:335	89:90	70:67	456:559	2.4:2.3
11	310:390	319:366	96:100	76:71	682:907	2.4:2.3
12	700:0	141:-	100:-	79:-	1118:-	2.5: -

Figure 5 shows the DSC runs of the final fractions from the copolymer obtained with the titanium catalyst . The melting of polyethylene crystallites is clearly evident in the fractions containing over 75 mole-% ethylene. Fractions containing over 75 mole-% ethylene were not obtained from the copolymer made with vanadium catalyst and no crystallinity was observed. The fractions exhibiting crystallinity represent only 11 weight-% of the whole copolymer, however, and thus only traces of crystallinity are seen in the DSC run of the whole copolymer.

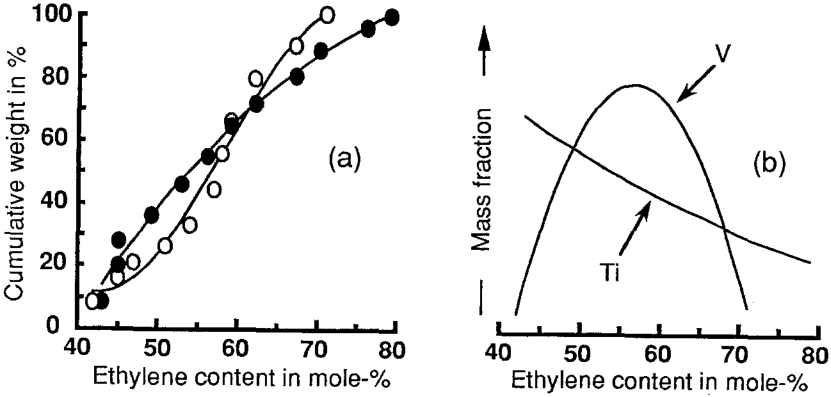

Fig 4. Fractionation of the copolymers: difference in ethylene contents (a) and the distribution in compositon (b). ● Ti, ○ V

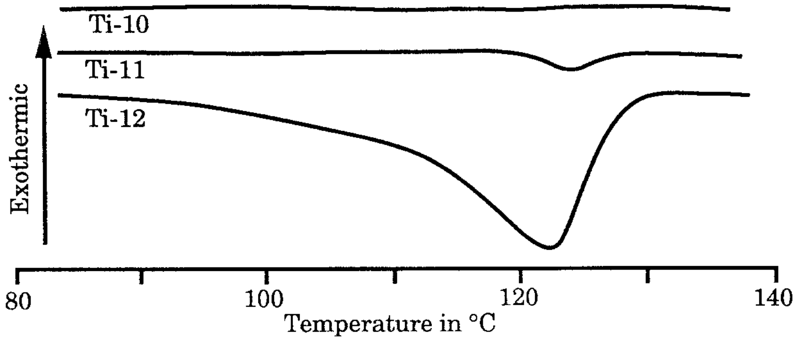

Fig. 5. The DSC runs of the last fractions (see Table 3). Heating rate 10°C/min.

Altogether, the results suggest that the different active species in the vanadium catalyst produce the same kind of copolymer chains, or else that the number of different active species is smaller in the vanadium than in the titanium catalyst and so that the copolymers differ distribution in composition of the fractions. The two copolymers particularly differ in the amount of EPE and homopolymer triads. The broader distribution in composition in the copolymer obtained with the titanium catalyst than in the copolymer obtained with the vanadium catalyst is the reason for the traces of crystallinity. However, the amount of these crystallites is not great enough to affect the glass transition temperature.

Table 3 shows the triad sequence distributions for the whole copolymer and the selected fractions. As stated earlier papers(6,7) and as seen in Table 3 more random distribution of the monomer units can be obtained with the vanadium catalyst than with the titanium. The main differences are in the PPP, EEE and EPE triads; the PPE, PEE and PEP triads are at the same level in the two copolymers. The same pattern of differences and similarities as in the whole copolymer is repeated in the triad distributions of the fractions.

Table 4. Sequence distribution of selected fractions.

Sample	E	PPP	PPE	EPE	PEP	PEE	EEE
V	0.55	0.03	0.14	0.31	0.12	0.22	0.18
Ti	0.55	0.08	0.12	0.24	0.10	0.22	0.24
V-1	0.42	0.10	0.22	0.32	0.12	0.14	0.10
Ti-1	0.43	0.16	0.17	0.26	0.12	0.16	0.13
V-2	0.45	0.08	0.19	0.33	0.10	0.18	0.12
Ti-2	0.45	0.14	0.16	0.27	0.08	0.19	0.16
V-11	0.71	0.00	0.06	0.24	0.08	0.27	0.35
Ti-11	0.76	0.00	0.04	0.20	0.06	0.26	0.44
Ti-12	0.79	0.00	0.04	0.18	0.02	0.17	0.59

Conclusions

The proportions of homopolyethylene and homopolypropylene triads are smaller and the proportion of the PEP triad is greater in the copolymer obtained with the zirconium catalyst than in that obtained with the titanium or vanadium catalysts. In other words, ethylene-propylene copolymer obtained with the zirconium catalyst system was more random than that obtained with conventional homogeneous vanadium catalyst.

With zirconium catalyst very low-molecular-weight copolymers are obtained even in the absence of hydrogen while vanadium catalyst gives very high-molecular-weight copolymers. The molecular weight distribution in the copolymers obtained with zirconium catalyst is extremely narrow. The wider use of these very homogeneous ethylene-propylene copolymers prepared with zirconium catalyst is limited, however, because of the low temperatures required for products with reasonable molecular weights.

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