NMR Characterization of Ethylene/Propylene Copolymers and Propylene Impact Copolymers from $MgCl_2/TiCl_4/ID+AlR_3/ED$ Catalytic Systems

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Summary: The aim of this work was to study the comonomer distribution and the chemical composition distribution generated by different Ziegler-Natta (ZN) systems (different internal donors, ID, dicyclopentadienyl-dimethoxy silane, D donor, as the external donor) and to define the potentialities of different IDs to produce improved heterophasic copolymers (HECO). A methodology to quantify the amount of ethylene-propylene copolymer (EP) portion in ZN-HECO and ethylene content of the EP portion by ^{13}C-NMR was established. By using this method, it was possible to analyze the composition of ZN-HECO obtaining results comparable to those obtained with a more complex fractionation technique.

Keywords: Fractionation; Heterophasic Copolymers; NMR; polyolefin; Ziegler Natta catalysts

Introduction

Propylene heterophasic copolymers (HE-CO) are advanced polyolefin products composed by at least two different phases: a crystalline matrix (either isotactic polypropylene or a random propylene copolymer) and a rubber-like phase composed of an ethylene copolymer. A balanced combination of these phases in terms of both relative amount (the "Split") and comonomer content (copolymer(s) composition) generates products with an interesting balance of properties, unattainable for pure homo and co-polymers; for example, good impact resistance at low temperature (below 0 °C).[1]

HECOs are obtained in either fully gas-phase polymerization processes or in mixed processes composed of a liquid monomer polymerization step (for the crystalline phase), followed by one or more gas-phase reactor(s) for the copolymer synthesis.[2,3]

The best catalyst systems used for the preparation of HECOs are the classic heterogeneous $MgCl_2/TiCl_4/ID + AlEt_3/ED$ based systems (ID = internal donor, ED = external donor), taking advantage of the controllable porosity of these systems, which enable higher levels of rubber to be incorporated in the copolymer phase.[4]

The more diffused industrial catalytic systems are based on DIBP (di-isobutyl-phthalate) as the ID and are used in combination with a dialkyl dimethoxy silane as ED. More recent ID systems, even if less widely employed, are 1,3-diethers and succinate esters, also used in the presence of silanes as ED.[4,5]

The HECOs prepared using catalytic systems, which differ depending on the type of ID, could have a different balance of properties, even when they have the same "split" (relative amount of crystalline matrix and EP copolymer) and copolymer composition. For this reason, it is important to correlate the physical properties of the HECO with the type of catalyst employed and, hence, to develop methods able to describe the fine structure of these complex polymeric systems as the relative amount of

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crystalline and amorphous components, their composition and, more challenging, the intra and inter-molecular comonomer distribution of the rubber phase.[6]

The aim of this work is to contribute to the study of the influences of the catalytic system on the final properties of HECO impact copolymers: for this purpose three different $MgCl_2/TiCl_4/ID$ (ID = DIBP, 1,3-diether, succinate) catalytic systems were tested in combination with dicyclopentyl-dimethoxy-silane as external donor.

The first step was to prepare ethylene/propylene (EP) copolymers in slurry (70 °C, propane and hexane as diluents) targeting ethylene = 50%wt and IV = 2 dL/g. These copolymers were fractionated using different solvents[7] and the fractions characterized via ^{13}C NMR for comonomer content and distribution.

In the second step, the same catalytic systems were tested to produce HECOs in a sequential polymerization (in liquid propylene and ethylene/propylene in gas phase) step to reach 30%wt of EP rubber split, with a copolymer composition of about 50%wt of ethylene. The HECO samples were fractionated and characterized following the same approach applied to the pure copolymers.

This first part of the work represents a more classical approach to the analysis of EP copolymers via fractionation and analysis of the fractions with ^{13}C NMR analysis.[8,9] This well established method is very useful as several information on copolymer amount, composition and compositional heterogeneity are obtained but a lot of work and long analysis time are required. In the second part, a novel ^{13}C NMR approach was developed to evaluate the split and EP copolymer composition of HECOs directly from a single spectrum of the raw polymer without any fractionation. With this approach the information on copolymer heterogeneity are not achievable, but the analysis time is quite short.

Finally, data obtained from the different approaches were compared.

Experimental Part

The ZN solid catalyst precursors were obtained from the Ferrara industrial plant. Aluminium triethyl, dicyclopentyl dimethoxy silane (D donor), propylene, ethylene, propane and iso-hexane were obtained from the Ferrara industrial polymerization plants.

Slurry Copolymerization

About 10 mg of the solid catalyst precursor were reacted with 0.700 g of TEA and 70 mg of dicyclopentyl dimethoxy silane (Al/ED = 20 mol/mol) in about 10 mL of iso-hexane.

A 4.5 L stainless steel autoclave equipped with a magnetic stirrer was charged at room temperature with propane, of iso-hexane, propylene, ethylene and an amount of H_2 tuned according to catalyst hydrogen response (amounts are reported in Table 1). The autoclave was warmed up to 70 °C and the activated catalyst suspension was injected. The internal pressure was maintained constant by feeding a 55/45 ethylene/propylene mixture.

Table 1.
Ethylene/propylene copolymerization in slurry with different ZN catalysts.

Test	ID	Ethylene	H_2	Yield	IV	Ethylene	$r_1\ r_2$	time
		G	NL	kg_{pol}/g_{cat}	dl/g	%wt		min
1	DIBP	80	4.8	28.2	2.2	51.2	1.5	26
2	diether	70	3.0	15.4	1.8	48.9	1.9	20
3	succinate	75	3.2	19.5	2.3	49.6	1.8	27

Polymerization conditions: ED = Dicyclopentyl-dimethoxy silane (D donor), Al/ED = 20 mol/mol, TEA, 338 g propylene, 390 mL propane, 240 g iso-hexane, 70 °C, 25 min, autoclave 4.2 L, ethylene and propylene fed to keep constant the autoclave pressure.

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The polymerization was stopped after reaching 100 g of product (measured from the total amount of ethylene and propylene fed to keep the pressure constant) by venting off comonomers and solvents. About 2 L of cyclohexane was fed, the autoclave closed and warmed up to 100 °C to dissolve the polymer. The solution was discharged from the bottom of the autoclave to a separate vessel where the solvent was removed by feeding hot steam. The polymer was then recovered and dried at 80 °C under vacuum for 24 hours.

HECO Synthesis

About 6–8 mg of the solid catalyst precursor were reacted with 0.760 g of TEA and 76 mg of dicyclopentyl dimethoxy silane (Al/ED = 20 mol/mol) in about 10 mL of iso-hexane. The activated catalyst was transferred into a 4.5 L stainless steel autoclave at room temperature and, after closing the reactor, 1200 g of propylene and the desired amount of H_2 (tuned to reach MIL = 70 g/10, see Table 1) were added. The autoclave was warmed up to 75 °C in about 10 minutes and the polymerization was carried out at this temperature for 1 hour. At the end of this time the monomer was vented off and the temperature decreased, without control, to about 35–40 °C. After the complete venting of propylene, the procedure for the gas-phase reaction started: the autoclave was warmed to 80 °C, and, in the same time, the 30 g of ethylene and 40 g of propylene were fed to the autoclave. The conditions were chosen in order to reach at the same time the internal autoclave temperature of 80 °C and the total monomer feeding. This instant was set as the starting time of gas phase copolymerization that was conducted by feeding ethylene and propylene mixture in a 55/45 wt/wt ratio to keep the pressure constant and equal to 13 bar-g. The polymerization was stopped when at least 30%wt of split was reached. During the test, the split was calculated approximately from the amount of comonomers fed during the gas phase polymerization to keep constant the autoclave pressure and the activity of the catalyst in an independent liquid polymerization experiment.

Fractionation of Copolymers

The following solvents and solvent mixtures were used: diethyl ether and acetone 90/10 wt/wt, diethyl ether, diethyl ether and *n*-hexane 90/10 wt/wt, *n*-heptane. Under nitrogen atmosphere, 6.0–6.5 g of copolymer and 600 mL of the first solvent mixture were transferred into a flask. The flask was warmed, under nitrogen, at the boiling temperature of the solvent mixture and then kept to solvent reflux for 6 hours. The flask was then cooled down to room temperature and kept at this temperature overnight. The solvent was then removed from the flask and the remaining polymer treated in the same way with the new solvent mixture. The solution was evaporated under vacuum and the residual polymer collected, weighted and analyzed for composition.

To remove the crystalline polymer, the HECO samples were fractionated with xylene: the polymer was dissolved at the reflux temperature of the solvent and the fraction soluble at room temperature was collected and fractionated following the method described above.

NMR Analysis of HECO and Copolymers

^{13}C-NMR spectra were acquired on a Bruker DPX-400 spectrometer operating at 100.61 MHz in the Fourier transform mode at 120 °C. The peak $S_{\delta\delta}$ carbon[10] was used as internal reference at 29.9 ppm. The samples were dissolved in 1,1,2,2-tetrachloroethane-d2 at 120 °C with a 8% wt/v concentration. Each spectrum was acquired with a 90° pulse, 15 seconds of delay between pulses and CPD (WALTZ 65_64pl) to remove ^{1}H-^{13}C coupling. About 1500 transients were stored in 32K data points using a spectral window of 6000 Hz. The assignments of the spectra of EP copolymers were made according to Kakugo[11] and Sacchi,[12] the evaluation of triad distribution and the composition was based on Kakugo.[11] The product of reactivity

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ratio r_1 r_2 was calculated according to Carman[10].

Intrinsic Viscosity (IV)

IV was determined in tetrahydronaphthalene at 135 °C.

Results and Discussion

The pure copolymers were prepared at 70 °C via EP copolymerization in propane/iso-hexane slurry. In order to maintain the copolymerization conditions constant as much as possible, a 50/50 wt/wt mixture of ethylene and propylene was fed during the test to keep the autoclave pressure constant. The results are reported in Table 1. A slightly low IV was obtained for the copolymer prepared with the diether based catalyst.

The copolymers were fractionated using a sequential non-exhaustive fractionation based on different solvents or solvent mixtures with increasing strength.[7] This approach enabled fractionation of the polymer mainly according to composition as shown by the spectra of the different fractions reported in Figure 1.

The solvents and the fractionation results are reported in Table 2. Some common features of the fractions of copolymers from different catalytic systems can be identified looking at the values of the product of reactivity ratios r_1r_2 calculated from NMR triad distribution. It is well known that r_1r_2 values indicate the type of comonomer distribution in ''single site'' copolymers (e.g. ''blocky'' copolymers for $r_1r_2 > 1$). On the other hand, it can be taken as an index of the heterogeneity of comonomer distribution in ZN, ''multi site'', copolymers (see values in Table 1) as pointed out by Cozewith[13] that showed that $r_1r_2 \approx 1$ is most probably due to either an almost pure copolymer or, in the worst case, to a mixture of copolymers with quite similar compositions, while $r_1r_2 \gg 1$ is a

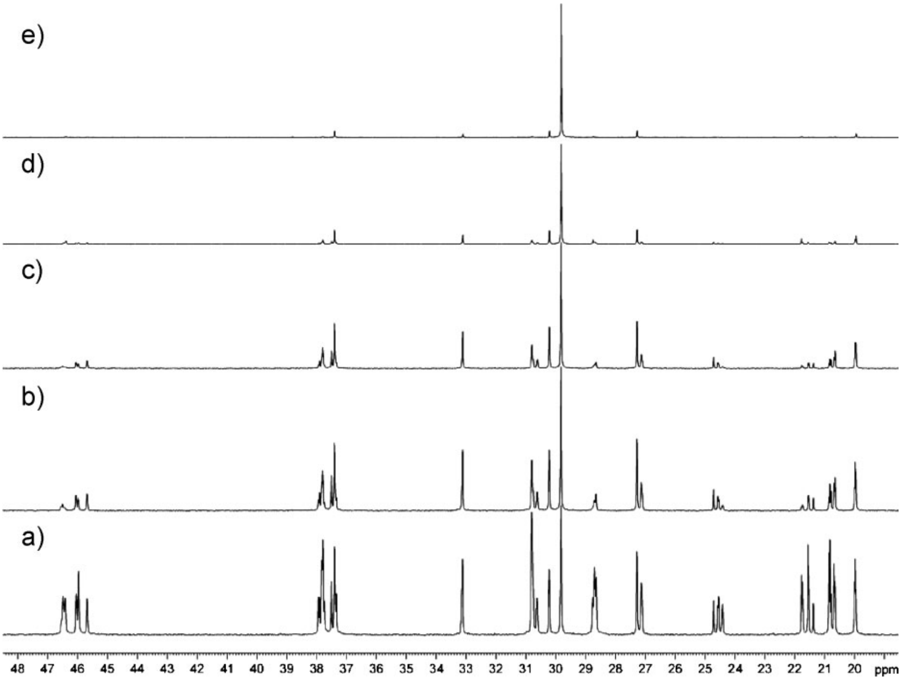

Figure 1.
^{13}C NMR spectra of soluble fractions of sample 1 diethyl ether/acetone (a), diethyl ether (b), diethyl ether/n-hexane (c), n-heptane (d) and of the insoluble fraction (e).

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Table 2.
Results of the fractionations of ethylene/propylene copolymers obtained with different ZN catalysts.

	Solvent	ID = DIBP			ID = diether			ID = succinate		
		Fraction	E	$r_1 r_2$	Fraction	E	r_1r_2	Fraction	E	r_1r_2
	type	%wt	%wt		%wt	%wt		%wt	%wt	
I	eth/ace[a]	17.5	35.6	1.3	33.9	34.7	1.4	30.3	32.3	1.0
II	ether	44.1	48.6	1.0	29.5	45.7	1.0	36.0	47.2	1.0
III	eth/hex[a]	12.3	55.6	1.0	8.0	58.7	1.3	6.8	58.3	1.1
IV	heptane	15.8	65.1	2.7	17.1	66.5	4.3	20.2	58.6	3.5
V	insoluble	10.4	88.8	4.7	11.5	86.4	7.3	6.7	86.4	7.5

[a] mixture 90/10 wt/wt of diethylether with either acetone (ace) or n-hexane (hex).

strong indication of a mixture of copolymers having very different compositions. In the following the r_1r_2 value is used with this meaning to classify the fractions according to their compositional homogeneity (or their dishomogeneity).

In the samples of this work it is easy to note that fractions I - III have $r_1r_2 < 2$ thus suggesting a quite homogeneous chemical composition. Fractions IV has a more ''blocky'' comonomer distribution ($r_1r_2 > 2$) indicating a broader distribution of intermolecular composition (it is a more heterogeneous copolymer fraction). Finally, the insoluble fraction V has the highest r_1r_2 values, symptomatic of the coexistence of both propylene and ethylene rich crystalline copolymers.

The results of the fractionation of copolymers from different IDs are compared in Figure 2, where the diameter of the circle is proportional to the amount (%wt) of each fraction and the composition (%wt of ethylene from ^{13}C NMR) is represented by the position with respect to the x-axis. The superposition of circles of different diameter indicates that different fractions having a different amount have an equal or similar composition (e.g. Fractions III and IV of succinate based copolymer).

The results show that all of the catalytic systems behave in a fairly similar way, as the composition and the 'structure' or, better, the homogeneity from r_1r_2 of the fractions are very similar among the three copolymers. In Figure 2 it appears that the phthalate based system has a slightly narrower distribution of the fractions; in particular, a lower amount of the ethylene-poor fraction is present and most of the copolymer has a composition close to the average. It is interesting to note that all of

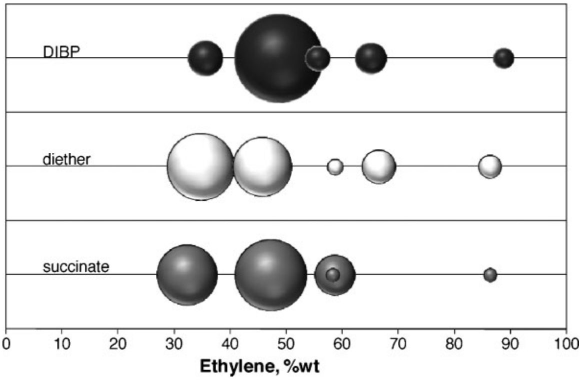

Figure 2.
Comparison of the results of fractionations of pure EP copolymers obtained in slurry from catalysts with different ID: the diameter of the sphere is proportional to the amount of the fraction; the position on the x axis is the fraction composition. The graph is based on the values reported in Table 2.

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these observations are in agreement with the lowest r_1r_2 value on the starting copolymer sample ($r_1 r_2 = 1.5$), also indicating the narrower intermolecular distribution of composition.

In the second part of the work the copolymer structure in HECO samples obtained from the same catalysts were investigated. The synthesis was made in autoclave using two sequential polymerization steps. The bulk homopolymerization of propylene was carried out at 75 °C and hydrogen was dosed in order to obtain an *i*-PP matrix with MIL = 75 g/10 min. After the monomer was vented, in the second step a gas-phase copolymerization was carried out at 80 °C and 13 bar-g of pressure. Hydrogen was fed to achieve a copolymer IV = 3–4 dL/g. The gas phase polymerization was carried out for the time needed to reach about 30%wt of rubber in the final HECO. The values of split and copolymer composition were obtained from ^{13}C NMR spectrum of the unfractionated samples according to Method B described in the following. The results are collected in Table 3.

The amorphous rubber of the HECO was then extracted with xylene: the sample was dissolved at 130 °C in xylene and then the crystalline fraction was separated with a slow cooling to room temperature and filtered. The soluble polymer was recovered by treating the solution with excess acetone. The amorphous polymer was then fractionated using the same approach applied for the pure copolymers.

In order to have a more complete description of the copolymer structure, the composition and amount of EP copolymer insoluble in xylene was estimated from the ^{13}C NMR spectra of the HECO Xylene Insoluble fractions, where the signals of both the *i*-PP matrix and the insoluble portion of the EP copolymer are present. Due to the high ethylene content expected for an insoluble EP copolymer ($E > 75\%$wt), it can be assumed that there was no contribution from the PPP triad, so the PPP triad is totally attributed to the *i*-PP matrix, while all the other triads were due to the copolymer. After having transformed the "molar fraction" triad distribution to "weight fraction" triad distribution:

$$i\text{-PP matrix } (\%\text{wt}) = \text{PPP} \tag{1}$$

$$\text{EP copolymers } (\%\text{wt}) = \text{PPE} + \text{EPE} + \text{PEP} + \text{PEE} + \text{EEE} \tag{2}$$

The weight composition of the EP insoluble fraction is then obtained from equation 2 after re-scaling the triad distribution to 100.

The complete fractionation results are reported in Table 4 and compared in Figure 3.

As in the case of pure copolymers, the donor systems behave in a comparable way as the compositions and the 'structure' of the fractions are very similar. Also in this case the DIBP based system shows slightly narrower distribution of the fractions due to the lower amount of the ethylene-poor, propylene-rich fraction and with a predominant contribution of fraction 2.

The succinate based system is very similar to DIBP with most of the sample equally distributed between fractions 2 and

Table 3.
Sequential bulk propylene polymerization and gas phase ethylene/propylene copolymerization with different ZN catalysts.

Test	ID	H_2 bulk	H_2 GP	t GP	yield	MIL	XI	IV(XS)	E	E(bipo)	Split
		NL	NmL	min	kg_{pol}/g_{cat}	g/10'	%	dL/g	%wt	%wt	%wt
4	DIBP	20	240	55	84	13	75.5	3.6	15.5	52.5	29.5
5	diether	9	100	68	60	19	74.6	3.5	16.9	54.3	31.1
6	succinate	13	195	109	59	9	71.5	3.5	18.3	54.1	33.8

Polymerization conditions: ED = Dicyclopentyl-dimethoxy silane (D donor), Al/ED = 20 mol/mol, TEA, autoclave 4.2 L, Bulk polymerization, 1200 g propylene, 75 °C, 1 h, Gas phase polymerization: 30 g ethylene, 40 g propylene, 80 °C, ethylene and propylene fed to keep constant the autoclave pressure.

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Table 4.
Results of the fractionations of HECO samples obtained with different ZN catalysts

	Solvent	ID = DIBP			ID = diether			ID = succinate		
		Fraction	E	r_1 r_2	Fraction	E	r_1 r_2	Fraction	E	r_1 r_2
	type	%wt	%wt		%wt	%wt		%wt	%wt	
I	eth/ace[a]	7.4	33.1	1.5	15.6	23.5	3.6	12.5	35.2	2.0
II	ether	40.8	43.5	1.0	35.7	44.0	1.1	27.4	44.6	1.0
III	eth/hex[a]	21.5	50.1	1.1	15.9	50.8	1.1	27.8	50.4	1.0
IV	heptane	11.8	67.5	1.3	12.6	67.0	1.4	13.3	66.4	1.2
V	Insoluble[b]	18.5	80.0	nd	20.2	84.8	nd	19.0	81.0	nd

[a] mixture 90/10 wt/wt of diethylether (eth) with either acetone (ace) or n-hexane (hex).
[b] calculated from ^{13}C NMR spectrum of XI fraction, see text. b. Fraction Insoluble

3; the diether based system has a broader comonomer distribution and a higher amount of ''crystalline'' ethylene.

From the comparison of the fractionation of pure samples and HECO copolymers, it appears that the copolymers from slurry are more homogeneous than copolymers from gas phase process. In fact, a lower amount of the crystalline ethylene rich fraction is found in pure copolymers. This could be ascribed either to the different polymerization process or to a different distribution of active sites in the ''fresh'' catalyst (slurry process) with respect to the ''aged'' one (gas phase polymerization after a propylene homopolymerization step).

Finally, the similarity of the inter- and intra-molecular comonomer distribution observed for the three different catalytic systems seems to indicate that the internal donor has little effect on these properties.''

Determination of Split (F_c) and EP copolymer composition (E_c)

Xylene Fractionation (Method A)

The xylene fractionation technique combined with ^{13}C NMR on the fractions is a simple and widely used approach, even if quite time consuming, for estimating E_c and F_c of HECO.

This approach is based on the possibility of separating in the spectrum of each fraction, and therefore in the relative triad distribution, the contribution of the *i*-PP matrix from the contribution of the EP copolymer.

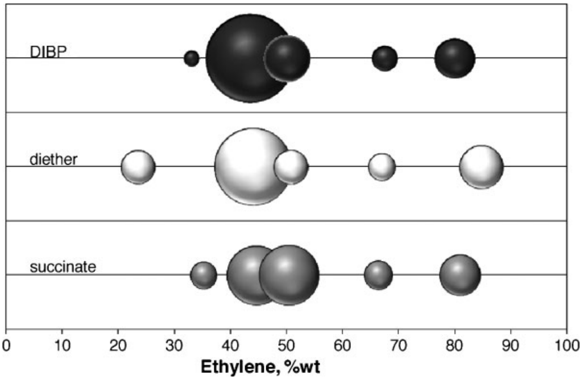


Figure 3.
Comparison of fractionation of EP copolymer of HECO obtained in a sequential copolymerization from catalysts with different ID: the diameter of the sphere is proportional to the amount of the fraction, the position on the x axis is the fraction composition.

The XS fraction contains only the contribution of the EP component in addition to a negligible amount of the XS portion of the *i*-PP matrix that can be easily quantified from the peaks of the $T_{\beta\beta}$ (mr + rr) carbons of non isotactic PPP sequences at 28.59–28.35 ppm. The XI fraction contains the contribution of the *i*-PP matrix and of the insoluble portion of the EP copolymer. Assuming that no PPP triads are present in the insoluble portion of the EP copolymer due to the high ethylene content ($E > 75\%$wt), we can attribute the PPP triad entirely to the *i*-PP matrix and all of the other triads to the EP copolymer.

Therefore, triad distribution for the EP copolymer is obtained according the following equations, where the triad distributions are expressed as ''weight fraction'' instead of the more usual ''molar fraction'' and XS and XI are the relative amount of polymer respectively soluble and insoluble in xylene:

$$\mathrm{PPP_{EP} = PPP_{xs} \cdot XS(wt\%)}$$

$$\mathrm{PPE_{EP} = PPE_{xs} \cdot XS(wt\%) + PPE_{xi} \cdot XI(wt\%)}$$

$$\mathrm{EPE_{EP} = EPE_{xs} \cdot XS(wt\%) + EPE_{xi} \cdot XI(wt\%)}$$

$$\mathrm{PEP_{EP} = PEP_{xs} \cdot XS(wt\%) + PEP_{xi} \cdot XI(wt\%)}$$

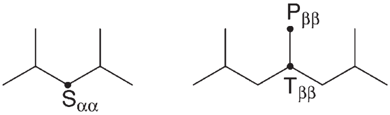
$$\mathrm{PEE_{EP} = PEE_{xs} \cdot XS(wt\%) + PEE_{xi} \cdot XI(wt\%)}$$

$$\mathrm{EEE_{EP} = EEE_{xs} \cdot XS(wt\%) + EEE_{xi} \cdot XI(wt\%)}$$

From these triads the copolymer composition E_c (%wt of ethylene) is directly obtained as $E_c = \mathrm{PEP_{EP} + PEE_{EP} + EEE_{EP}}$, while F_c is calculated as $F_c = 100 \times E(\mathrm{wt\%})_{\mathrm{HECO}}/E_c(\mathrm{wt\%})$.

Direct Determination from ^{13}C NMR of HECO (Method B)

A typical ^{13}C-NMR spectrum of a HECO sample appears as a superposition of the spectrum of an *i*-PP and the spectrum of an EP copolymer. In particular, the peaks due to $S_{\alpha\alpha}$, $T_{\beta\beta}$ and $P_{\beta\beta}$ carbons (associated with PP and PPP sequences, Scheme 1) are present in both spectra.



Scheme 1.

Therefore, if the HECO is described in terms of triad distribution, the contribution of *i*-PP and EP components to the PPP sequence (evaluated from the $T_{\beta\beta}$ area according to Kakugo's equations) has to be separated. The heterogeneous nature of EP copolymers from classical ZN systems prevents the use of simple statistical methods to model the triad distribution, but it is clear that, in a copolymer, triads and triad ratios are a function of the composition of the copolymer itself.

The method presented is based on this observation and it starts from the evaluation of triad distribution of a set of reference pure copolymer samples produced in slurry polymerization conditions with a DIBP/D based catalytic system in a broad compositional range (26 wt% < ethylene < 68 wt%). In Figure 4, the ratios of selected experimental triads (EPE/PEP and PPP/PPE respectively) are shown as a function of copolymer composition. The relation in Figure 4a (EPE/PEP vs. E) contains only triads due to the copolymer counterpart and, therefore it can be used to obtain the copolymer composition from the experimental EPE and PEP values of the HECO. Using the obtained value of copolymer composition in the relation of Figure 4b, it is possible to estimate the PPP/PPE ratio of the copolymer. As the PPE triad in HECO is known, the PPP triad of the copolymer ($\mathrm{PPP_{EP}}$) can be easily calculated and used to evaluate the amount of *i*-PP matrix:

$$\mathrm{PPP}_{i\text{-PP}} = \mathrm{PPP_{HECO} - PPP_{EP}}$$

The new triad distribution for the EP copolymer is obtained rescaling to 100

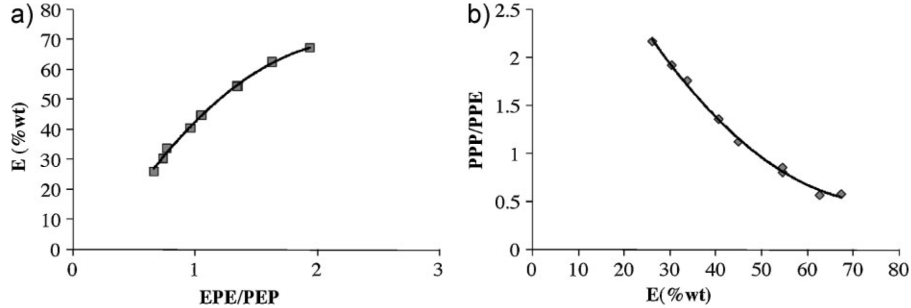


Figure 4.

Experimental relations between triad ratios and copolymer compositions used in the determination of split and copolymer composition from ^{13}C NMR spectra of HECO: **a** Ethylene (%wt) vs. EPE/PEP (mol/mol), **b** PPP/PPE (mol/mol) vs. Ethylene (%wt).

Table 5.

Comparison of the E_c and F_c obtained from Methods A and B.

ID	Whole Sample	Method A		Method B	
	E	E_c	F_c	E_c	F_c
	% wt	% wt	% wt	% wt	% wt
DIBP	15.5	53.8	28.8	52.5	29.5
diether	16.9	53.0	31.9	54.3	31.1
succinate	18.3	54.8	33.4	54.1	33.8

the triad distribution: PPP_{EP} PPE_{HECO} EPE_{HECO} PEP_{HECO} PEE_{HECO} EEE_{HECO} (the subscript HECO indicates the triad evaluated from the whole polymer).

The copolymer composition is then obtained from the rescaled triad distribution from the relation $E_c = EEE + PEE + PEP$ and the split F_c is calculated as $F_c = 100 \times E(wt\%)_{HECO}/E_c(wt\%)$.

Comparison of the Results

The values of E_c and F_c obtained with the two different methods for the three HECO samples obtained from different ID based catalytic systems are compared in Table 5.

A good agreement between the values obtained using the two different approaches is evident. This indicates that the proposed method for the evaluation of split and copolymer composition from a single ^{13}C NMR spectrum can successfully be used as an alternative to more time-consuming approaches. It is worth noting that Method B is based on the ‘‘calibration curves’’ obtained for DIBP/D catalytic system: the possibility to apply these relations to catalysts based on other IDs derives from similar comonomer distributions as evidenced by the fractionation results.

Conclusion

NMR combined with fractionation techniques, is a valuable approach to study comonomer distribution of copolymers. The fractionation method can provide a separation of an EP copolymer in fractions with different composition and allows comparing comonomer distributions generated by different catalyst systems.

DIBP based catalyst is able to produce copolymers either in slurry or in gas phase polymerizations with the narrower comonomer distribution.

The differences between different samples are due mainly to polymerization conditions, as the copolymers from slurry copolymerization seem to have a narrower comonomer distribution than those obtained in gas-phase. The influence of internal

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donor type is not evident and the ED (D donor) seems to play the main role in imparting the catalyst performance.

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