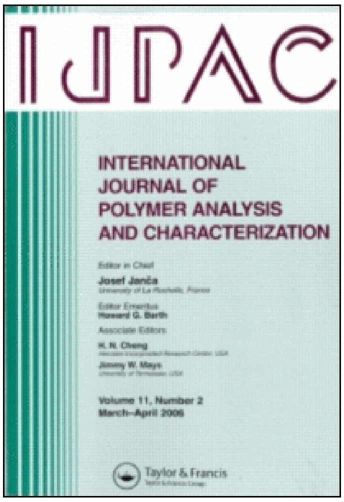

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Tacticity Distribution of Polypropene by Preparative and Analytical Temperature-Rising Elution Fractionation (TREF)

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(In final form 06 November 1996)

Several polypropene samples, synthesized with different catalytic systems based on $TiCl_4$ supported on activated $MgCl_2$ and different electron donors, were studied using both preparative and analytical temperature-rising elution fractionation (TREF). The experimental results show that each variation in the catalytic system is clearly reflected in the nature of the corresponding polymer, which can be distinguished by both preparative temperature rising elution fractionation and analytical temperature rising elution fractionation dissolution profiles.

Keywords: Polypropene, temperature rising elution fractionation (TREF), size exclusion chromatography

INTRODUCTION

It is known that heterogeneous Ziegler-Natta catalysts used in poly-α olefins production are characterized by the presence of a plurality of active species, each having its own kinetic constants and stereospecificity. In other words, each active site produces polymeric chains with different average molecular weight and stereoregularity and, consequently, polypropenes obtained by these catalysts show broad molecular weight and

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*Corresponding author.

tacticity distributions. Therefore, fractionation of these polyolefins is a necessary step to understand better both the mechanisms of the heterogeneous Ziegler-Natta polymerization and the property-structure relationships of the resulting polymers.

The molecular weight distribution of a polymer is generally studied by size exclusion chromatography (SEC), which separates polymer chains on the basis of their hydrodynamic volume in the solvent used.

To evaluate the stereoregularity of polypropene many studies have been performed using conventional fractionation techniques, such as successive solvent extraction with n-alkane solvents and temperature-rising elution fractionation (TREF) [1-8]. TREF, which has been reviewed by several authors [4,9-11], is a column fractionation technique especially suitable to the analysis of semi-crystalline polyolefins and separates the macromolecules according to their solubility differences. The ideal TREF fractionation is controlled only by polymer microstructure, for example, chemical composition distribution (copolymers) and type and distribution of defects (homopolymers), and it is free of cocrystallizzation effects, molecular weight influences, and peak broadening phenomena.

As far as regioregular homopolypropene is concerned, the solubility of polymer chains is influenced only by the concentration of sterical defects; thus, its tacticity distribution can be studied by TREF.

The objective of this work was to fully characterize several homopolypropenes obtained with different $MgCl_2$-supported catalysts and to set up a simple but effective method to evaluate the tacticity distribution of their most stereoregular components (isotactic fraction, insoluble in xylene at 25°C) on an analytical scale. The influence of electron donor addition on the polymer tacticity and the tacticity distribution was also studied.

EXPERIMENTAL

The properties of the studied samples are reported in Table I. Polymerizations were carried out in liquid propene at 70°C for 2 h. The catalyst system used consisted of $TiCl_4$ supported on activated $MgCl_2$ and, optionally, an internal electron donor. The cocatalyst was triethylaluminium plus, optionally, an external electron donor.

TABLE I Intrinsic viscosities (IV), xylene solubles at 25°C (X.S.), melting points (Mp), molecular weight parameters (M_i), and catalyst systems of polypropene homopolymers

Sample	*IV (dL/g)*	*X.S. (wt%)*	*Mp (°C)*	*M_w (g/mol)*	*M_w/M_n*	*Catalyst*	
						Internal Donor	*External Donor*
A	1.11	58.3	158.0	205000	11.4	no	no
B	1.45	3.2	164.0	280300	5.3	diether	no
C	1.84	2.7	164.0	332900	5.2	diether	silane
D	1.78	1.8	165.6	329500	4.6	diester	silane

POLYMER CHARACTERIZATION

An outline of the experimental procedure is shown in Figure 1.

Preparative TREF

The home built P-TREF apparatus used, is shown in Figure 2 and several experimental conditions are listed in Table II. About 1.5 g of sample were dissolved at 135°C in 250 mL of *o*-xylene, stabilized with 0.1 g/L of Irganox 1010. The solution was loaded into a column packed with glass beads and subsequently cooled down slowly in 20 h to 25°C.

The first fraction was obtained at room temperature eluting with *o*-xylene. The second fraction was collected after having raised the column temperature up to 95°C. The semicrystalline polymer component soluble between 25° and 95°C was collected as a single fraction ("stereoblock").

The successive fractions were eluted with *o*-xylene in which the temperature was raised linearly between 95° and 125°C. Each fraction was recovered in which 185 mL of solution was collected at 1°C temperature increments.

The polymer fractions were subsequently precipitated with acetone, recovered by filtration on a 0.5-μm PTFE filter, dried under vacuum at 70°C, and weighed. All the recoveries were above 97%. Selected fractions were characterized by viscometry, SEC, ^{13}C-NMR, and DSC.

Analytical TREF

The apparatus was assembled by connecting a gas chromatography (GC) oven to a Waters 150C ALC/GPC (Waters, Milford, Massachusetts, USA) without the SEC columns. The Waters apparatus was used for mobile phase

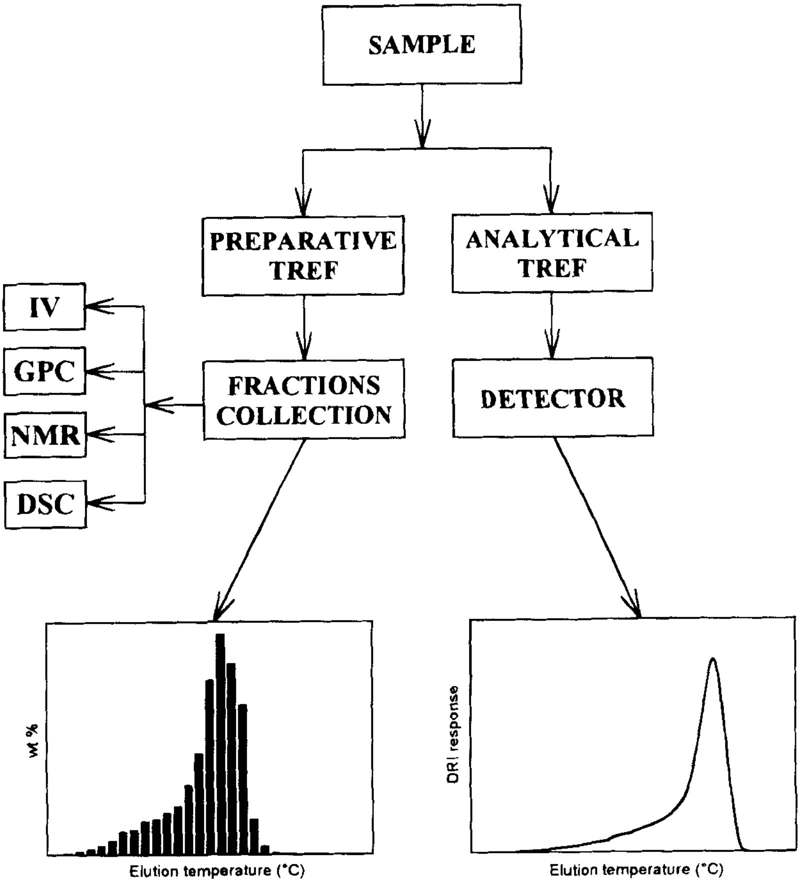

FIGURE 1 Schematic diagram of the experimental procedure.

transport through the A-TREF column and for the detection of the eluted sample. The insulated GC oven was modified and equipped with a six-port sampling valve, an A-TREF column, and a temperature programmer. The A-TREF stainless steel column (250 × 9.7 mm) was packed with solid-glass beads (40–80 μm). By means of the temperature programmer, an accurate control of the cooling and the heating steps was obtained. The eluted sample solution was directed, via a heated transfer line, to the differential refractive index detector of the Waters instrument. The block dia-

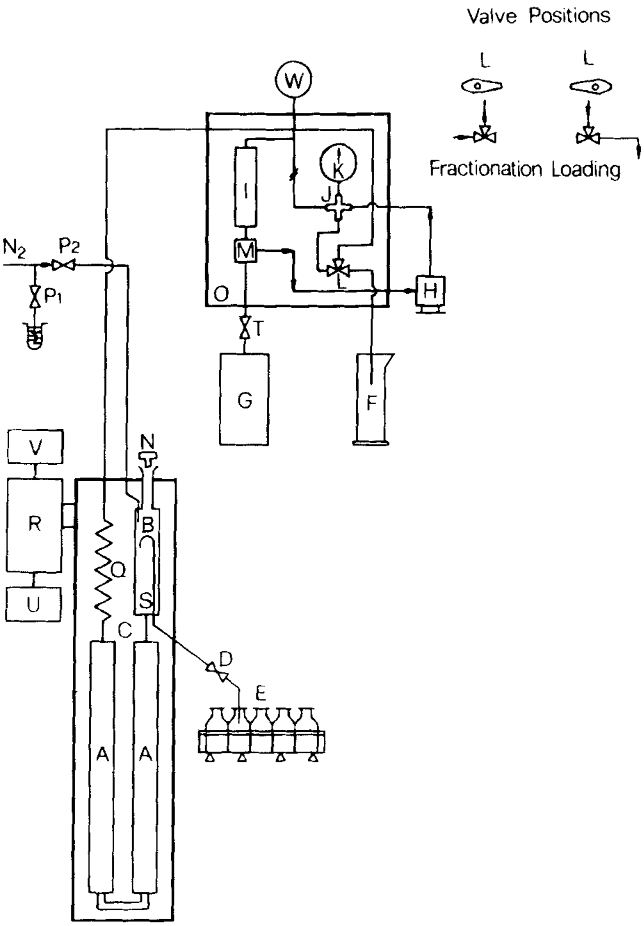

FIGURE 2 Scheme of the P-TREF apparatus: (A) column; (B) column vessel; (C) thermostated jacket; (D) siphon valve; (E) fraction collector; (F) graduated cylinder; (G) solvent reservoir; (H) pump; (I) safety valve; (J) four-way connector; (K) pressure gauge; (L) flow-reversal valve; (M) multiple-way connector; (N) vessel plug; (O) aluminium panel; (P) nitrogen valves; (Q) pre-heating; (R) thermostat; (S) siphon; (T) feeding valve; (U) temperature programmer; (V) recorder; (W) pressure switch.

gram of this A-TREF apparatus is shown in Figure 3 and several operating parameters are listed in Table II.

The polymer, 5 mg, was loaded as a 0.12% solution in *o*-dichlorobenzene (ODCB) into the A-TREF column. The cooling step was performed at

TABLE II Characteristic and operating conditions of the TREF methods.

Conditions	*A-TREF*	*P-TREF*
Column length (cm)	25	80×2
Internal column diameter (cm)	0.78	2.7
Support type	Glass beads	Glass beads
Support diameter (µm)	$36 \div 80$	≥1000
Support bulk volume (cm^3)	18.1	840
Solvent type	ODCB	*o*-xylene
Polymer (g)	0.005	1.5
Solution concentration (%)	0.12	0.75
Injected solution volume (mL)	4	200
Cooling rate (°C h^{-1})	6	6
Heating rate (°C h^{-1})	48/18	3
Solvent flow rate (mL min^{-1})	1.0	10
Overall eluate volume (mL)	110	4600
Elution time (min)	138/150	480

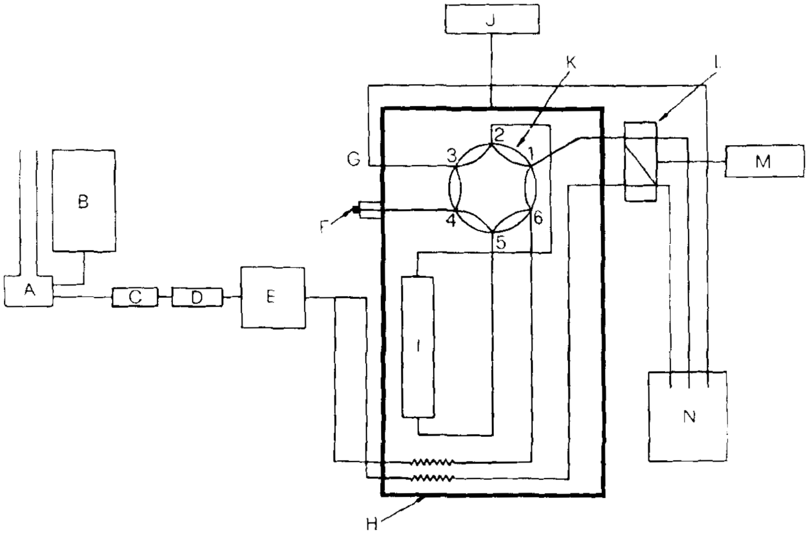

FIGURE 3 Scheme of the A-TREF apparatus: (A) solvent degasser; (B) solvent reservoir; (C) filter; (D) prepump; (E) pump; (F) sample inlet; (G) sample overflow; (H) insulated oven; (I) column; (J) temperature programmer; (K) sample loop; (L) differential refractometer; (M) personal computer; (N) waste.

6°C/h from 140° to 25°C and the subsequent elution step was carried out by pumping ODCB at a flow rate of 1.0 mL/min, and raising the temperature in two different ways: *i*, from 25° to 130°C at 0.8°C/min or *ii*, from 25° to 90°C quickly and from 90 to 130°C at 0.3°C/min. The eluted polymer was continuously monitored by the on-line differential refractive index detector connected to a data station. No further analyses of the fractions were carried out.

To evaluate the A-TREF results the detector signal was recorded as a function of elution time. The relationship between time and temperature allowed the conversion of any elution time in the corresponding temperature. Finally the area under the data curve was normalized to unity to allow comparison among the samples.

SEC Measurements

The experimental measurements of molecular weight parameters and molecular weight distribution (MWD) for all the samples were carried out at 135°C using a Waters 150C ALC/GPC (Waters, Milford, Massachusetts, USA). A set of three mixed gel columns GMHXL-HT (TosoHaas GmbH, Stuttgart, Germany) was used. The dimensions of each column were 300 × 7.8 mm and the estimated exclusion limit of the column packing for polystyrene standards was 4×10^8. The mobile phase used was vacuum distilled ODCB and the flow rate was kept at 1.0 mL/min. In each case, 300 μL of sample solution prepared with ODCB, at a concentration of 0.1 g/dL, were injected. To prevent degradation, 0.1 g/dL of BHT was added. The column set was calibrated using a broad molecular weight polypropene sample. Data acquisition and analysis were performed using a Maxima 820 software.

Viscometry

Viscosity measurements were made at 135°C using an Ubbelhode modified capillary viscometer and a Sematech Cinevisco system (39 Chemin du Terron, Nice, France) for the automatic recording of the flow time to the accuracy of 0.01 s. The solvent used was tetrahydronaphthalene with 0.1 g/L added Irganox 1010 as stabilizer. Elapsed time from preparation of the sample solution to final viscosity measurement was about 1 h. The silicon oil thermostatic bath was regulated to 0.1°C. The intrinsic viscosity values were estimated from single concentration viscosity measurements and the calculations were performed using the Huggins equation and taking into account the kinetic energy correction.

Xylene Soluble Content Determinations

The xylene soluble content determinations for all the samples were carried out by dissolving a weighed amount of each sample in o-xylene at 135°C. Solution concentrations were 1 g/dL and no antioxidant was added. After 1 h at 135°C the solution was cooled down under controlled conditions up to 25°C so that the sample insoluble fraction was precipitated. The precipitate and the solution then were separated by means of filtration on a paper filter. After carrying out the filtration, an aliquot of the solution was evaporated to dryness at 140°C, dried in an oven at 70°C under vacuum, and weighed.

Calorimetry

Thermograms were recorded at a heating rate of 20°C/min in order to measure melting point temperatures for the samples on a Perkin Elmer DSC-7 differential scanning calorimeter (Bodenseewerk Perkin Elmer & Co. GmbH, Ueberlingen, Germany). The instrument was calibrated by measurements of the melting points of indium and lead.

^{13}C NMR Measurements

^{13}C NMR spectra were recorded at 120°C on a Bruker AC 200 spectrometer (Bruker Franzen Analytik GmbH, Bremen, Germany) operating at 200 MHz with proton decoupling.

RESULTS AND DISCUSSION

In this report, the fractions are qualitatively defined by their solubility in *o*-xylene as follows:

i Atactic, the soluble at 25°C. The term "atactic" is not referred to its microstructure, but only to its property to be soluble even at room temperature. Actually it has been observed that this component does not often contain only atactic sequence configurations.

ii Stereoblock, the insoluble at 25°C, soluble at 95°C.
iii Isotactic, the insoluble at 95°C.

Figure 4 shows the weight percent of the so-called atactic, stereoblock and isotactic fractions in polypropene samples determined by P-TREF. The amounts of the less stereoregular fractions (atactic and stereoblock) decrease and, consequently, the most stereoregular fraction (isotactic) increases, going from sample A to D. In other words, sample D, which was polymerized with the catalyst containing both internal and external donors, shows the lowest content of atactic fraction and the highest content of isotactic fraction.

This result indicates that the samples, obtained with different catalytic systems, also have different tacticities. Even though these solubility differences can be taken as a qualitative indication of the degree of stereoregularity, detailed P-TREF dissolution profiles were obtained and compared for the isotactic fractions of the polymers (the "low-temperature" tail in the

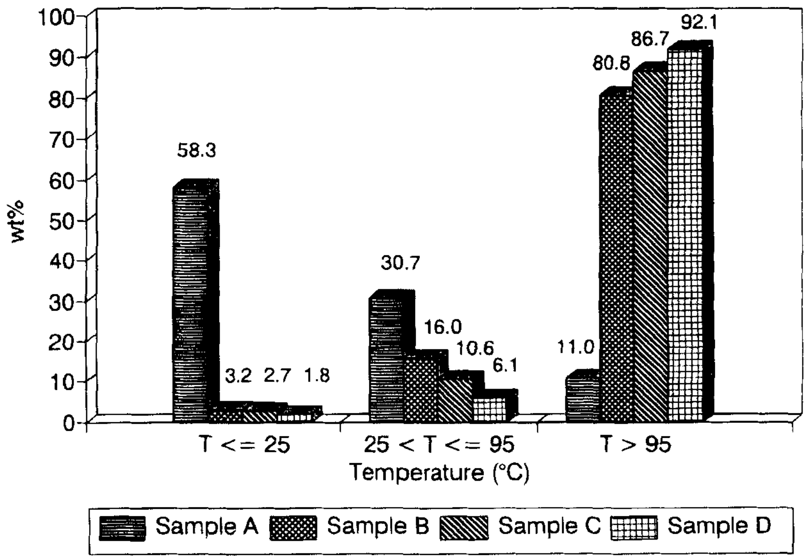

FIGURE 4 Atactic, stereoblock and isotactic fractions for all the samples obtained by P-TREF.

TREF distribution of the samples was not studied in detail as the samples obtained in the presence of donors contain only a small amount of the "atactic" plus "stereoblock" fractions). This allowed the study of the effects of the electron donor, which was added to the parent catalyst, on the stereoregularity of the isotactic polymer fraction.

The P-TREF results are listed in Tables III-VI. Figure 5 shows the distributions of the fractions as a function of the elution temperature (histograms) of all the samples. Figure 6 shows the differential distribution curves, which were derived from the cumulative distributions reported in Tables III-VI. For each sample, the area under the data curve was normalized to unity. In Figures 5 and 6, the less stereoregular fractions, eluted at a temperature lower than 95°C, were not drawn.

The TREF dissolution profiles reported in Figure 6 show the following features:

i Sample A, produced without electron donors, exhibits the broadest TREF distribution and the lowest "mean" elution temperature. This can be attributed to both the poor stereocontrol and the low stereospecificity of the catalyst without donors.

TABLE III Experimental results of the sample A and its fractions

N° [1]	*T* (°C)	*P%* [2] (*wt%*)	M_w (*g/mol*)	M_w/M_n	*IV* (*dL/g*)	*Mp* (°C)
1	25	58.30				
2	95	30.70	119500	3.5	1.03	155
3	96	0.10				
4	97	0.10				
5	98	0.10				
6	99	0.10				154
7	100	0.20	142500	2.5		154
8	101	0.40				
9	102	0.80			1.42	157
10	103	1.20	273600	2.5		
11	104	1.50				157
12	105	1.60			2.11	
13	106	1.70	475000	2.3		160
14	107	1.90			3.56	161
15	108	1.10	913000	3.0	3.90	
16	109	0.20				
17	110	0.00				
Whole Sample		100	205000	11.4	1.11	158.0

[1] Fraction number: 1 atactic, 2 stereoblock, 3-25 isotactic.

[2] Weight percent of eluted polymer.

TABLE IV Experimental results of the sample B and its fractions

N°[1]	*T* *(°C)*	*P%*[2] *(wt%)*	M_w *(g/mol)*	M_w/M_n	*IV* *(dL/g)*	*Mp* *(°C)*
1	25	3.19				
2	95	16.03	78400	3.4	0.56	159
3	96	0.01				
4	97	0.06				
5	98	0.17				149
6	99	0.32			0.61	
7	100	0.57	67000	1.8	1.14	163
8	101	0.94				
9	102	1.47				160
10	103	1.64			0.66	
11	104	2.22				160
12	105	2.33	116000	1.9	1.28	163
13	106	2.81				
14	107	3.23				
15	108	4.70	178000	2.0	1.80	164
16	109	6.91				
17	110	11.99	273000	1.9	1.90	164
18	111	15.13				
19	112	13.09	492000	2.2	2.28	167
20	113	10.27				
21	114	2.31	869000	2.1	3.39	167
22	115	0.55				
23	116	0.08				
24	117	0.00				
Whole Sample		100	280300	5.3	1.45	164.0

[1] Fraction number: 1 atactic, 2 stereoblock, 3–25 isotactic.

[2] Weight percent of eluted polymer.

ii For samples B, C and D, the TREF curves tend to shift to higher temperatures. This confirms that polymerization in the presence of electron donors leads to a significant increase in the stereoregularity of the isotactic fraction.

iii The differences in the elution temperatures among the samples reflect the relative effectiveness of the different donors used. Thus, each variation of the catalytic system which influences polymer stereoregularity, can be investigated by TREF dissolution profiles.

Several selected fractions, obtained by P-TREF, were extensively studied by viscometry and SEC with the aim to determine their MWDs. To evaluate the stereoregularity degree, ^{13}C NMR analyses were performed on the sample C fractions. In addition, since thermal properties of homopoly-

TABLE V Experimental results of the sample C and its fractions

N^{o1}	T °C	$P\%^2$ $(wt\%)$	M_w (g/mol)	M_w/M_n	IV (dL/g)	M_p (°C)
1	25	2.72				
2	95	10.65	87000	4.9		161
3	96	0.00				
4	97	0.06			0.75	
5	98	0.01				154
6	99	0.18			0.53	
7	100	0.38	68500	1.9		159
8	101	0.65			0.75	159
9	102	0.83			0.75	
10	103	1.14				160
11	104	1.48			0.78	
12	105	1.78	107900	2.2	0.71	162
13	106	2.06				161
14	107	2.44				
15	108	2.78			1.03	
16	109	3.24				
17	110	4.13	216500	2.5	1.58	164
18	111	6.83				
19	112	16.03				166
20	113	23.04			3.09	
21	114	14.94	800800	2.7	3.33	167
22	115	3.95	816000	2.7		168
23	116	0.56			2.86	
24	117	0.11				
25	118	0.00				
Whole sample		100	332900	5.2	1.84	164.0

[1] Fraction number: 1 atactic, 3 stereoblock, 3-25 isotactic.

[2] Weight percent of eluted polymer.

olefins are mainly dependent on isotacticity, several fractions of each sample were analyzed by DSC.

The parameters obtained by this characterization, reported in Table III-VI, showed the following features:

i The isotacticity-related parameters ([mmmm]-pentad content and melting point) of the fractions increase with elution temperature (Figs. 7 and 8), suggesting that the fractionation is mainly controlled by the crystallinity derived from the stereoregularity of the chains. Therefore, we can assume that TREF distributions can provide a qualitative description of tacticity distribution, which reflects the catalyst stereospecificity.

TABLE VI Experimental results of the sample D and its fractions

N°[1]	*T* (°C)	*P%*(2) (wt%)	M_w (g/mol)	M_w/M_n	*IV* (dL/g)	*Mp* (°C)
1	25	1.79				
2	95		62000	4.6		164
3	96	0.00				
4	97	0.01				
5	98	0.04				155
6	99	0.11			0.55	
7	100	0.20	48100	1.9		160
8	101	0.48			0.62	
9	102	0.80				161
10	103	1.16				
11	104	1.38				
12	105	1.30	86900	2.4		163
13	106	1.50				
14	107	1.86				163
15	108	2.42			1.17	
16	109	2.67				
17	110	4.08	136200	2.2	1.06	164
18	111	5.95				164
19	112	11.83			1.44	
20	113	28.56			1.94	
21	114	14.11				167
22	115	9.83	719700	2.6	3.01	168
23	116	3.40	962900	2.7	3.71	169
24	117	0.39				
25	118	0.00				
Whole Sample		100	329500	4.6	1.78	165.6

[1] Fraction number: 1 atactic, 2 stereoblock, 3-25 isotactic.

[2] Weight percent of eluted polymer.

ii The values of the molecular weight parameters (IV and M_i) also increase with elution temperature, which suggests that the most stereoregular chains also have the highest molecular weights (Figs. 9 and 10). Moreover, as can be seen from Figures 11-14, which show the SEC results, the individual fractions have narrower MWDs than the original samples (the values of M_w/M_n range from 1.8 to 2.7 for samples B, C and D).

All the A-TREF profiles are relative to the insoluble fraction in ODCB at 25°C of the sample. In fact the noncrystalline part of the polymers was eluted at room temperature before the heating program was initiated.

The analytical TREF profiles shown in Figures 15 and 16 reflect the

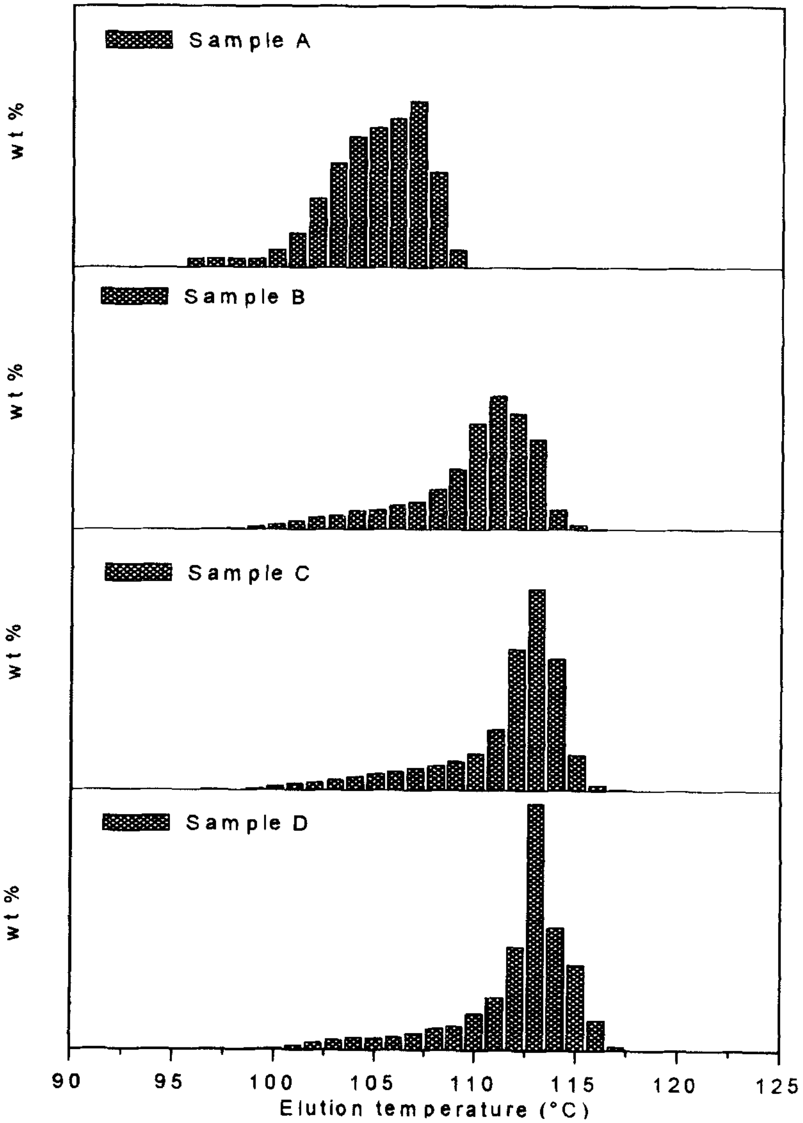

FIGURE 5 Distributions of P-TREF fractions as a function of elution temperature for all the samples. For Sample A the graph was magnified by 10.

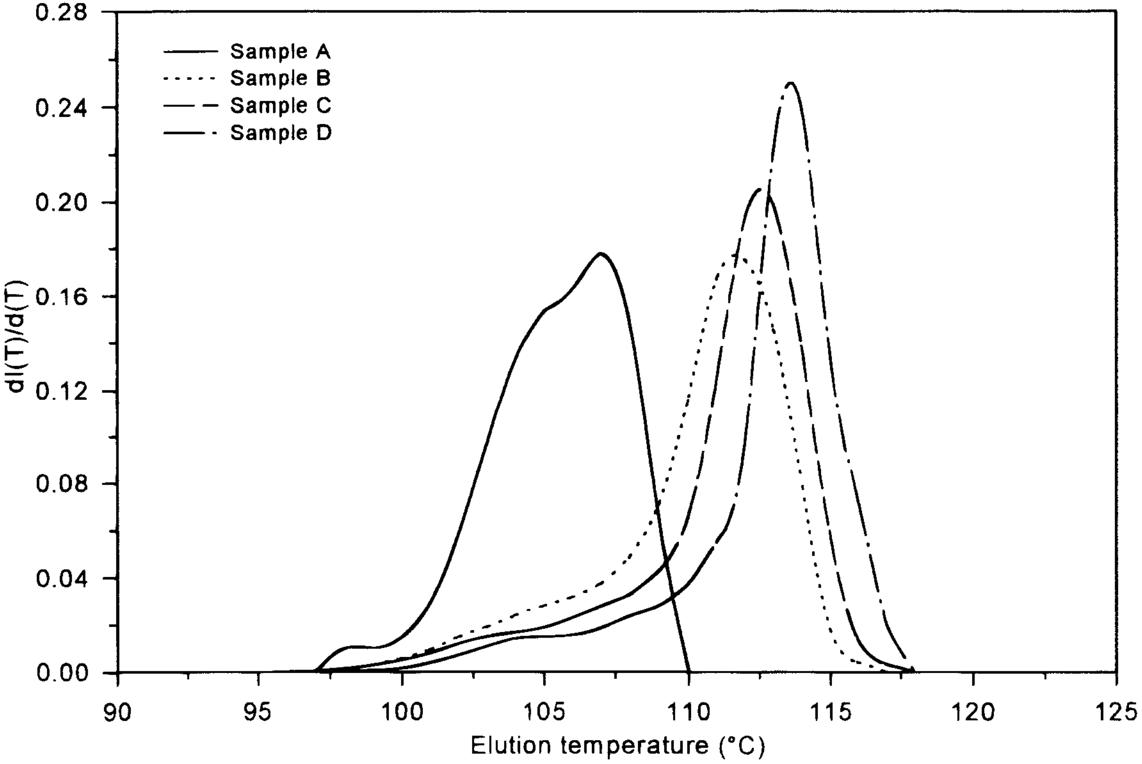

FIGURE 6 P-TREF profiles of all the samples (fractions insoluble at 95;°C).

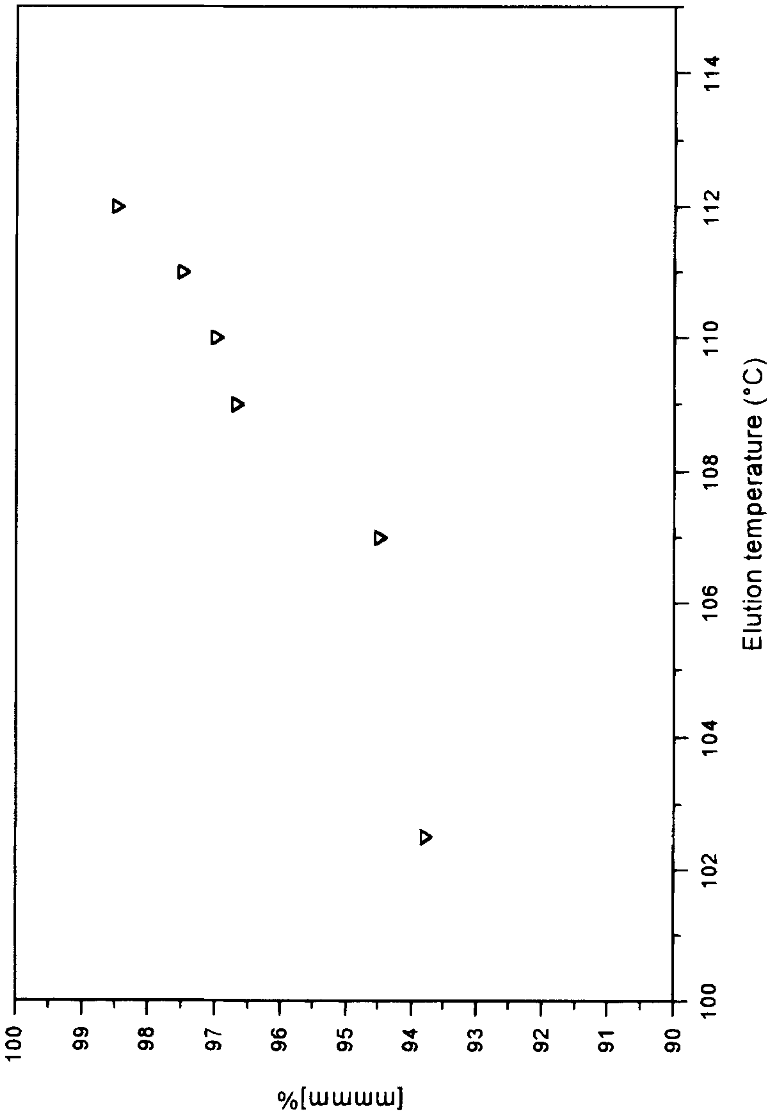

FIGURE 7 Isotactic [mmmm] pentad content of sample C.

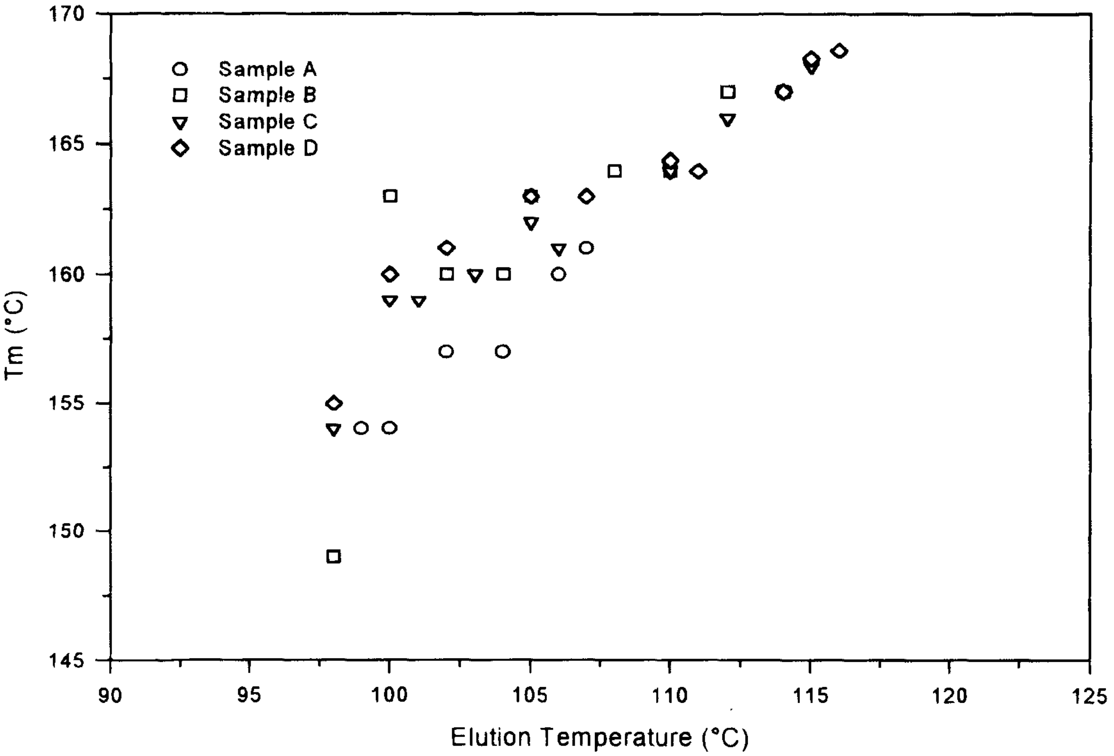

FIGURE 8 Relationship between melting temperature (T_m) and elution temperature of the fractions obtained by P-TREF.

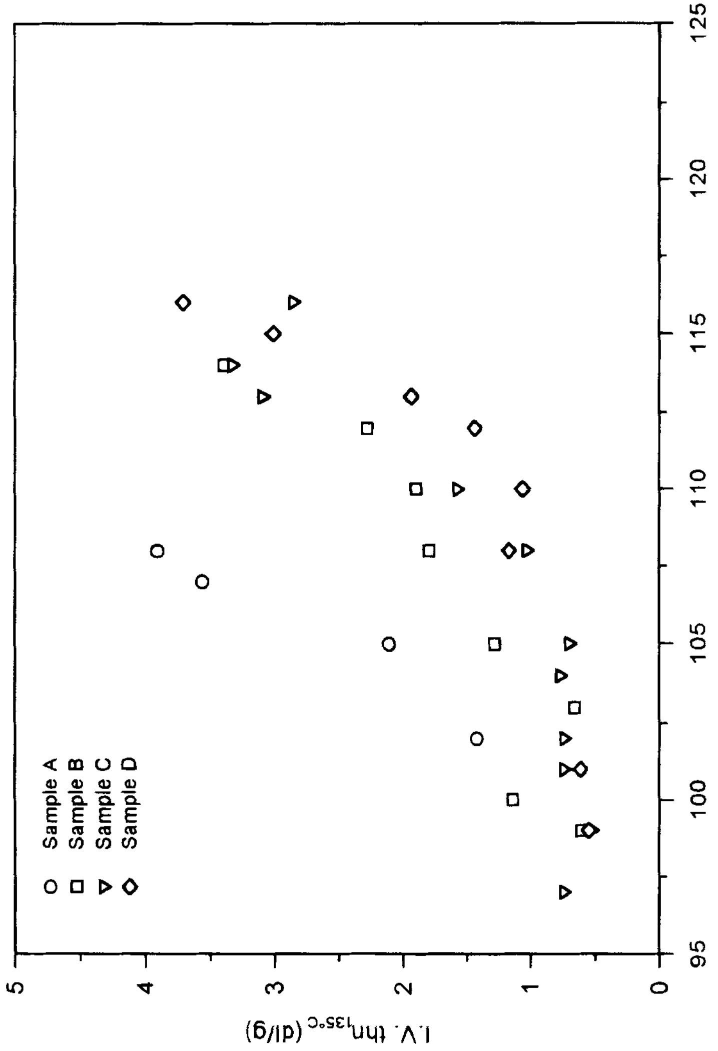

FIGURE 9 Intrinsic viscosities (IV) for the P-TREF fractions.

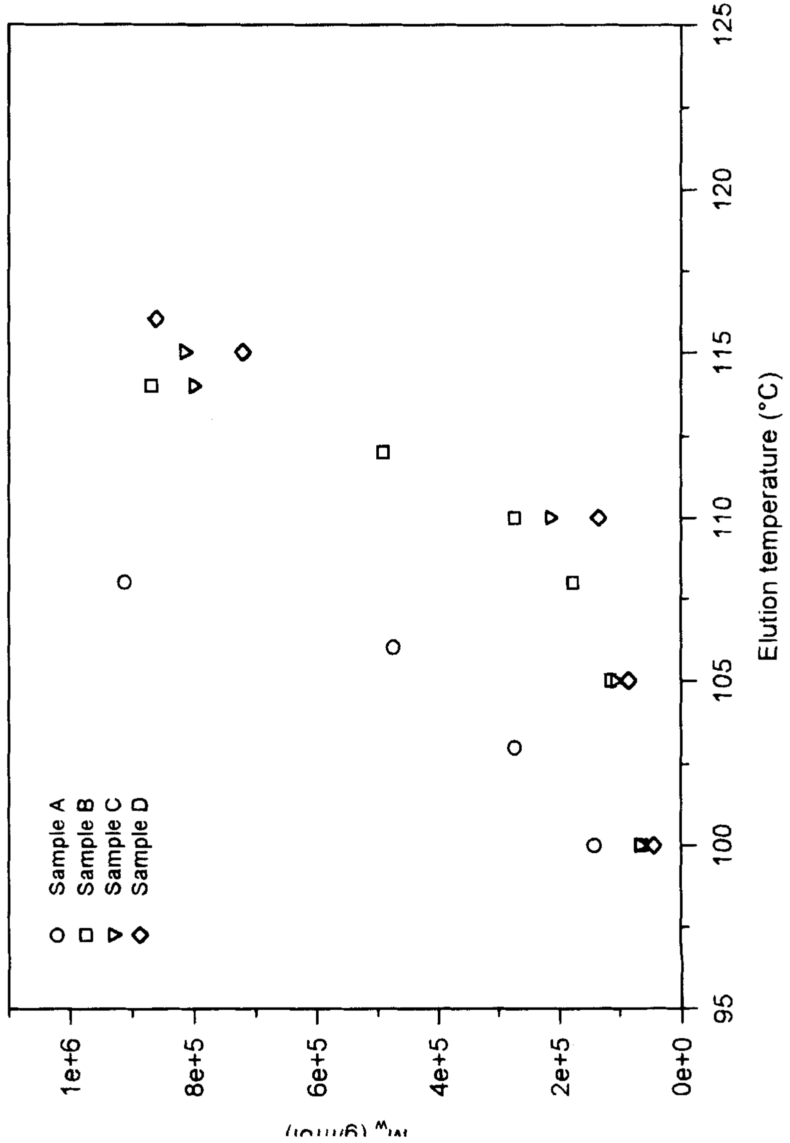

FIGURE 10 Weight-average molecular weight (M_w) for the P-TREF fractions.

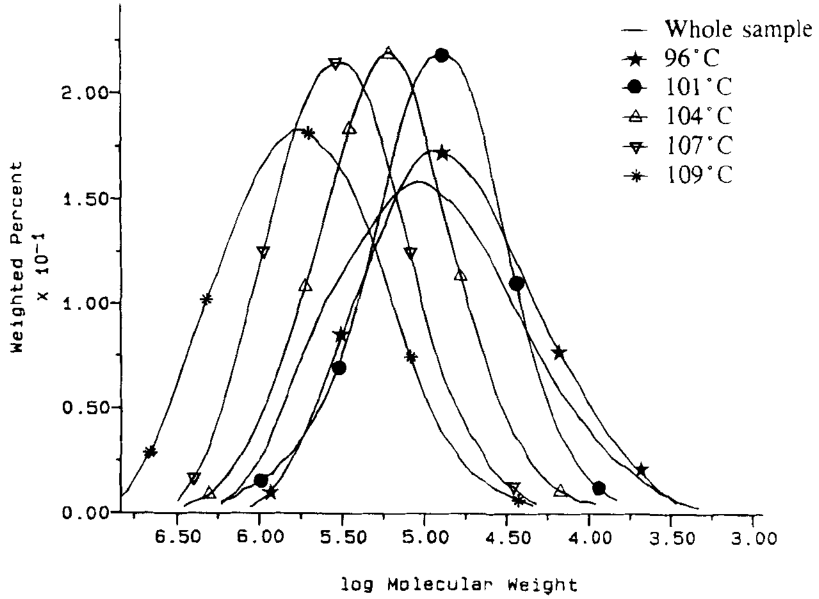

FIGURE 11 Molecular weight distributions for sample A and its selected fractions obtained by P-TREF.

shape of dissolution curves generated by preparative TREF analysis (Figs. 5 and 6). These figures clearly show that samples B, C and D are eluted at higher and narrower temperature ranges than sample A. Therefore, the relative degree of stereoregularity decreases in the order: D > C > B > A. This order reflects the catalyst stereospecificity.

CONCLUSIONS

The effect of the internal and external electron donors on the stereoregularity of the most isotactic fraction of polypropenes obtained with different $MgCl_2$-based catalysts, was studied by both P-TREF and A-TREF. Experimental results show that both the developed methods can be used to evaluate the tacticity distribution of polymer and, therefore, each variation in the catalytic system can be distinguished by the polymer dissolution TREF profiles, which clearly reflect the nature of the parent catalyst system.

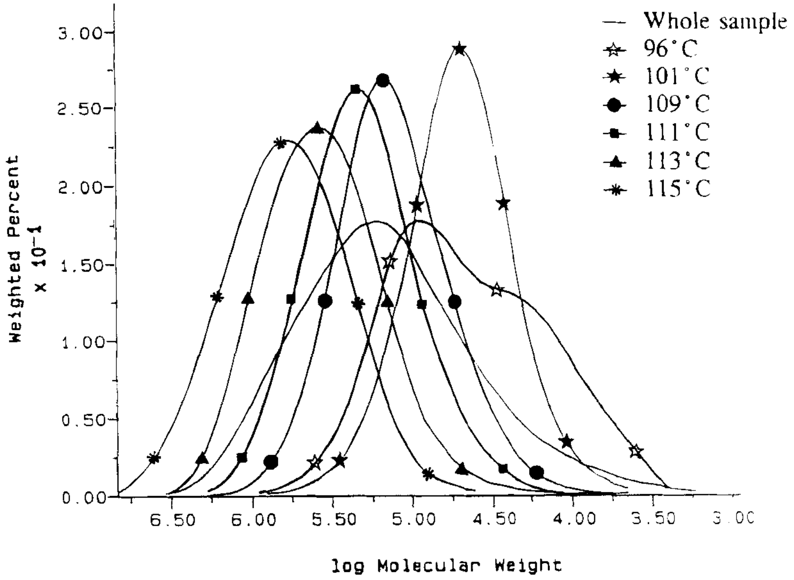

FIGURE 12 Molecular weight distributions for sample B and its selected fractions obtained by P-TREF.

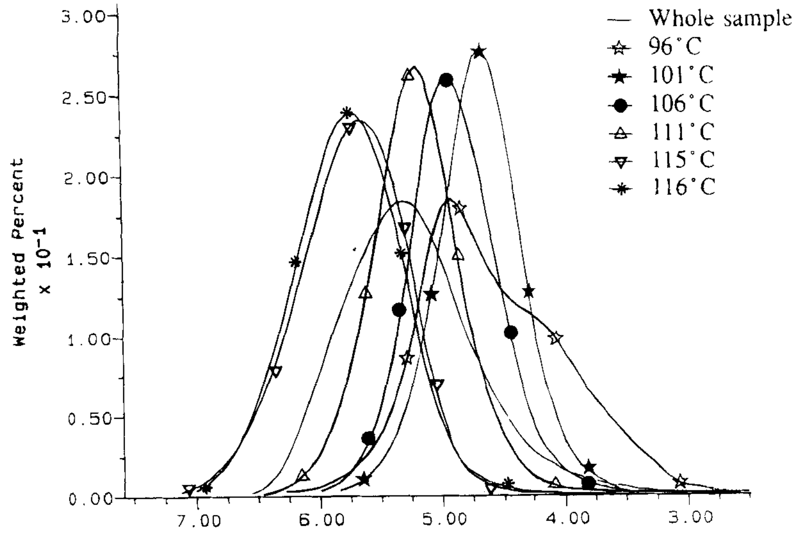

FIGURE 13 Molecular weight distributions for sample C and its selected fractions obtained by P-TREF.

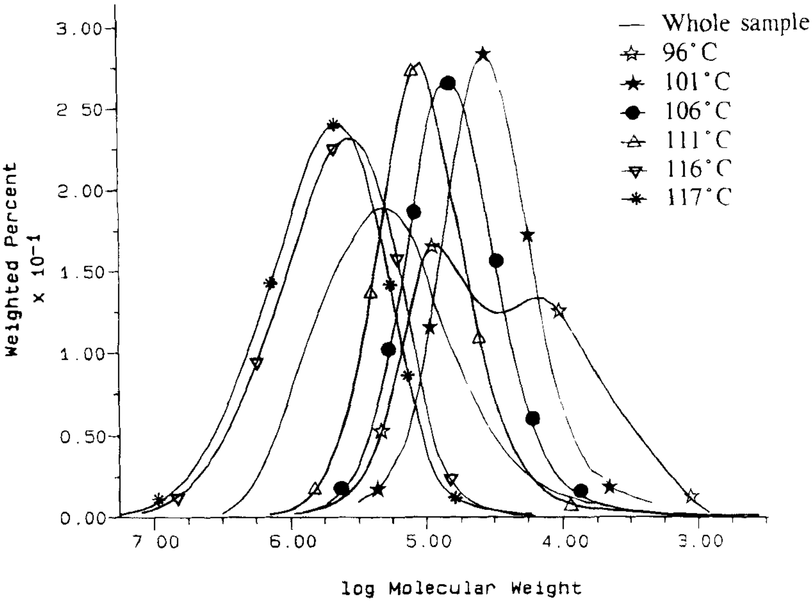

FIGURE 14 Molecular weight distributions for sample D and its selected fractions obtained by P-TREF.

Since the two procedures gave similar TREF curves, the less cumbersome A-TREF can be used for a qualitative investigation of the polypropene microstructure. The time-consuming P-TREF, and the subsequent characterization of the individual fractions, should be performed only when more detailed information about polymer microstructure is required.

Fractionation results clearly indicate that the polymers obtained with different electron donors also contain different amounts of the various stereoregular fractions. In particular, the occurrence or not of some highly insoluble components is strongly affected by the presence and type of electron donor. This confirms that donors are actively involved in the generation of the isospecific sites and that their role is not limited to block or deactivate the aspecific sites of the catalyst.

The molecular weight–elution temperature relationship would also indicate that the most isospecific centers are also characterized by the highest propagation rate to transfer rate ratio. In addition, SEC results clearly show

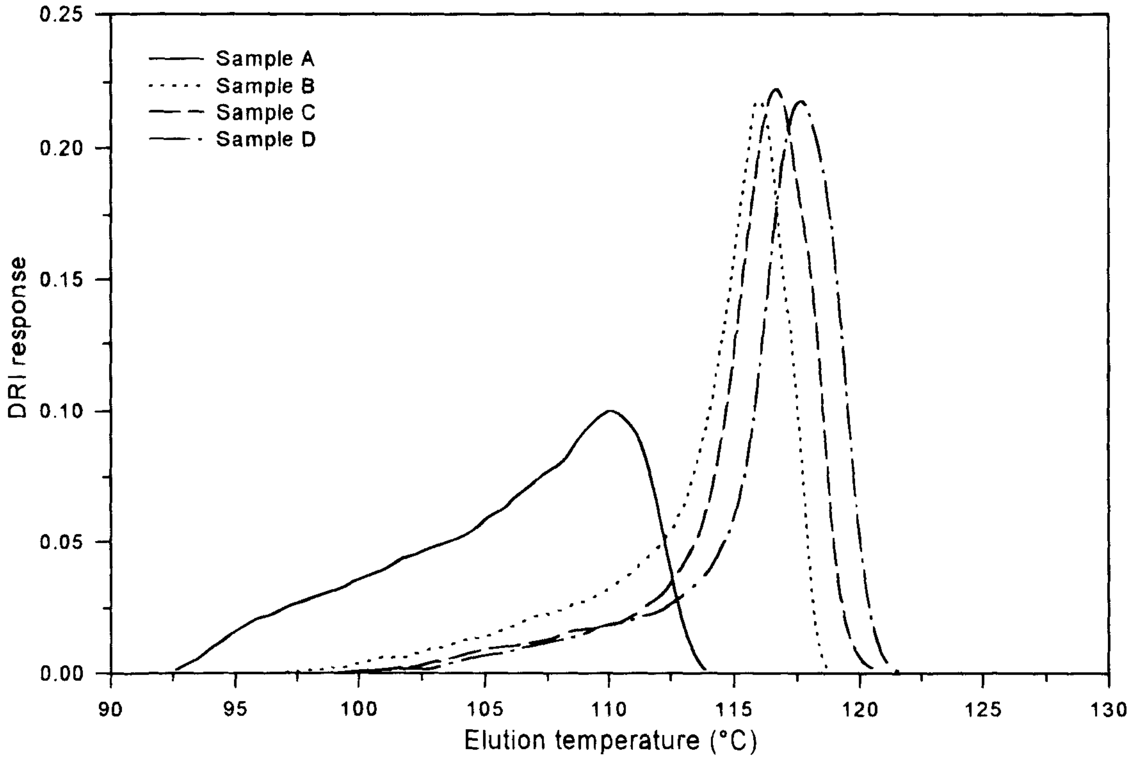

FIGURE 15 A-TREF profiles for the ODCB insoluble fractions at 90°C of all the samples.

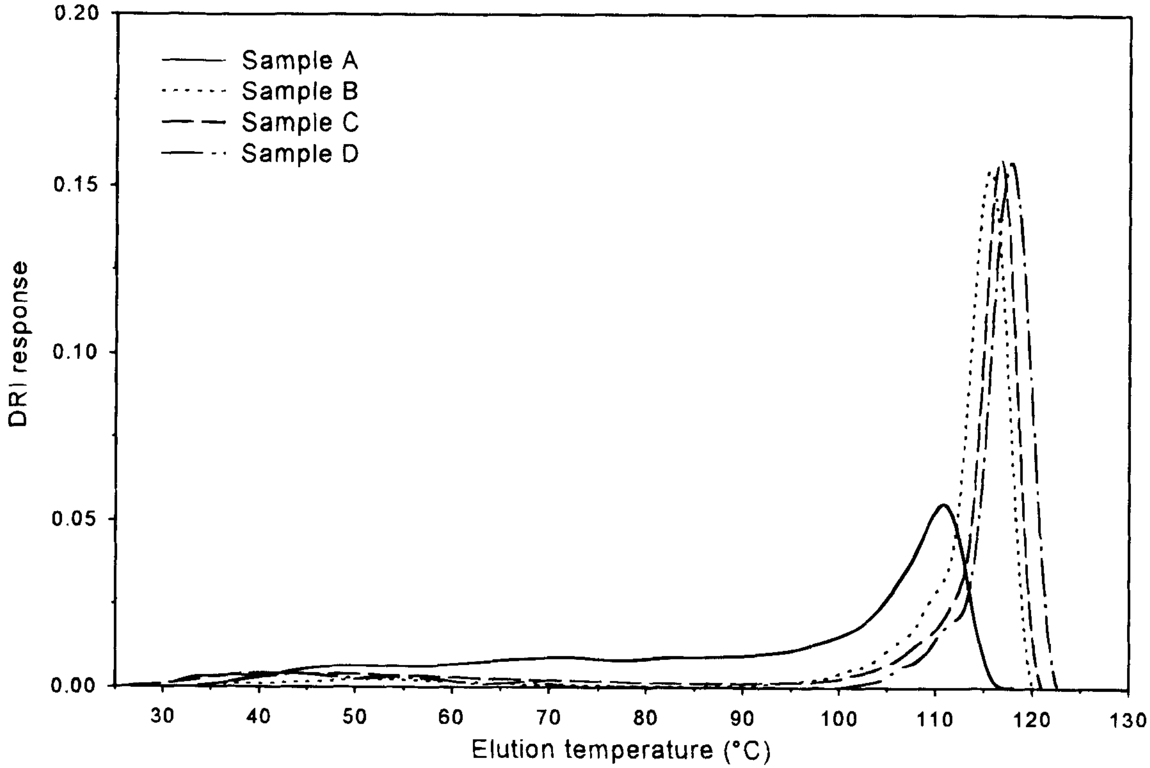

FIGURE 16 A-TREF profiles for the ODCB insoluble fractions at 25°C of all the samples.

that the individual polymerization centers tend to generate polymer fractions characterized by quite narrow MWDs.

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