Quantitative analysis of mixtures of ethylene- and propylene-based polymers by temperature-rising elution fractionation and ^{13}C nuclear magnetic resonance

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The fraction soluble in boiling heptane of a mixture of polypropylene, polyethylene and ethylene–propylene copolymer was characterized by ^{13}C nuclear magnetic resonance (n.m.r.) combined with temperature-rising elution fractionation. Two mathematical models were used to achieve quantitative analysis of the fractions from n.m.r. triad data. The result indicates that the ethylene–propylene copolymer made with an $MgCl_2/TiCl_4$-supported catalyst contains two or three major components and that the polypropylene exhibits high compositional heterogeneity. Simulation of the ^{13}C n.m.r. spectrum was successfully used to confirm the results.

(Keywords: ^{13}C nuclear magnetic resonance; polymer mixtures; polypropylene; polyethylene; ethylene–propylene copolymer; temperature-rising elution fractionation; mathematical modelling)

INTRODUCTION

Polymers produced by an $MgCl_2/TiCl_4$-supported catalyst are known to exhibit compositional heterogeneity. In an attempt to study such materials, the combination of ^{13}C n.m.r. and temperature-rising elution fractionation (t.r.e.f.) has been successfully applied to polypropylene[1–3], ethylene–propylene copolymer[3–5] and polyethylene[6–9], providing very detailed information about their microstructure. In that sense, Kakugo[2] showed that polypropylene produced by a heterogeneous catalyst contained two isotactic species arising from two isotactic sites. Kakugo and Cheng[4,5] found that ethylene–propylene copolymer produced by a δ-$TiCl_3$ catalyst could be readily described as a polymer blend of random copolymer components produced by three or four active catalytic sites.

As all those studies were performed on 'individual polymers' and considering the increasing development of industrial polymer mixtures such as high-impact modified polypropylene, we decided to evaluate the ability of ^{13}C n.m.r. combined with t.r.e.f. to characterize such materials.

EXPERIMENTAL

Polymeric material

The pilot product studies was made in the Groupement de Recherches de Lacq (GRL; Atochem Research Centre) with an $MgCl_2/TiCl_4$-supported catalyst. The material was produced in three steps, consisting of a propylene homopolymerization followed by on-line ethylene–propylene copolymerization and addition of linear polyethylene by extrusion. The final product will be designated as PP mixture.

Extraction and fractionation

Heptane extraction. A Kumagawa extractor was used to separate the boiling-heptane-soluble fraction (SH) of PP mixture from the boiling-heptane-insoluble fraction (IH). The SH fraction was found to represent 13% by weight of the PP mixture.

Temperature-rising elution fractionation. The PP mixture SH fraction was dissolved into 1 litre of boiling xylene. The solution was poured into a silica-filled column heated at 130°C. The column temperature was decreased from 130 to 10°C over 100 h. Then the column was washed with xylene at a flow rate of 1.2 litre h^{-1} while both solvent and column temperatures were increased. Fractions were collected according to the following:

F1: 3 h at 10°C + 1 h from 10 to 20°C
F2: 1 h from 20 to 28°C
F3: 1 h from 28 to 36°C
F4: 1 h from 36 to 44°C
F5: 1 h from 44 to 52°C
F6: 1 h from 52 to 60°C
F7: 1 h from 60 to 68°C
F8: 1 h from 68 to 76°C

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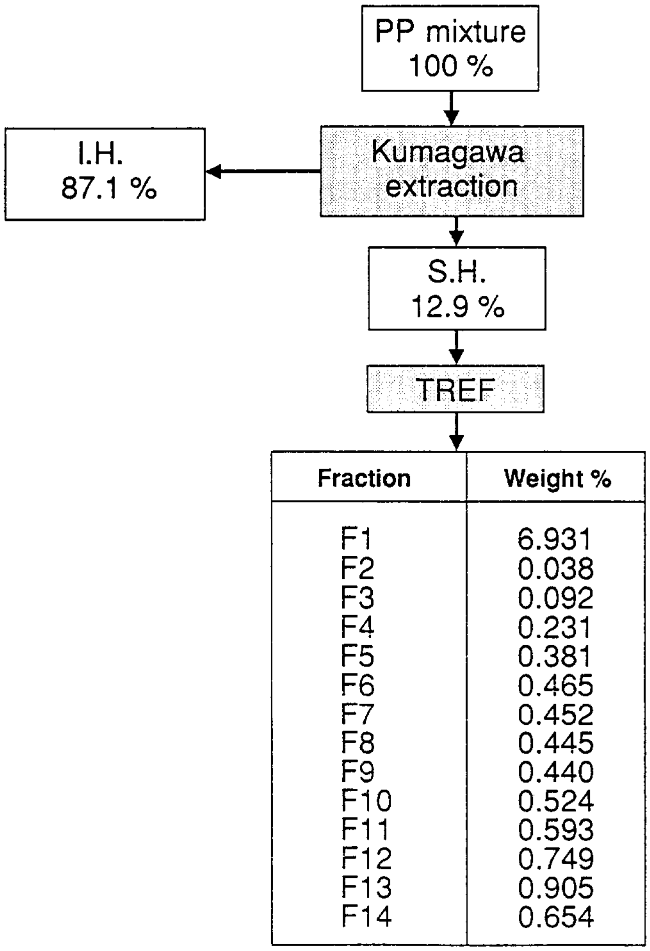
F9: 1 h from 76 to 84°C
F10: 1 h from 84 to 92°C
F11: 1 h from 92 to 100°C
F12: 1 h from 100 to 108°C
F13: 1 h from 108 to 116°C
F14: 1 h from 116 to 120°C

Figure 1 shows a summary of the extraction and fractionation of PP mixture with the weight percentage of each fraction.

Analytical methods

Size exclusion chromatography. Each fraction was analysed in the s.e.c. laboratory of the GRL using a Waters 150C equipped with a differential refractometer and a continuous viscosimeter. The separation was performed by two Touzart and Matignon columns (60 cm–mixed, and 30 cm–500 Å) with trichlorobenzene (TCB) as eluant at 145°C and a flow rate of 1 ml min^{-1}. The samples were prepared at 0.1% in TCB (w/w) and the injection volume was 0.2 ml.

Liquid-state ^{13}C nuclear magnetic resonance. Analyses were performed on a Bruker AC-250 equipped with an Aspect 3000 computer and operating at 62.89 MHz with quadratic detection. For each fraction, a 10% (w/w) solution was prepared in a mixture of hydrogenated and deuterated *o*-dichlorobenzene (*o*-DCB/*o*-DCB-d$_4$; 80/20, v/v); *o*-DCB-d$_4$ provided the signal for the ^{2}H n.m.r. internal lock. Composite pulse decoupling was used to remove ^{13}C–^{1}H couplings. The pulse angle was 90° with a 28 s delay to allow complete relaxation. Analyses of several polypropylenes showed that the nuclear Overhauser enhancement (NOE) was equivalent for the three carbons within 1% error. Free induction decays were recorded at 125°C and stored in 64K data points using a spectral width of 10 kHz (0.152 Hz/point digital resolution). Processing was preceded by 64K zero-filling and exponential weighting using a line-broadening factor of 0.5 Hz.



Fraction	Weight %
F1	6.931
F2	0.038
F3	0.092
F4	0.231
F5	0.381
F6	0.465
F7	0.452
F8	0.445
F9	0.440
F10	0.524
F11	0.593
F12	0.749
F13	0.905
F14	0.654

Figure 1 Extraction and fractionation of PP mixture (weight per cent yielded by PP mixture)

Data treatments. The compositions of the t.r.e.f. fractions were determined from n.m.r. triad data according to two models:

Model 1. The t.r.e.f. fraction consists of a mixture of polypropylene (hPP), polyethylene (hPE) and a Markovian ethylene–propylene copolymer (copo). The molar fraction of each component and the copolymer insertion probabilities were calculated from triad and diad data (detailed mathematics in Appendix):

$$\text{copo:}\quad X = \frac{\text{PE}^2(\text{EPE} + \text{PEP})}{4.\text{EPE}.\text{PEP}} \qquad P_{33} = \frac{\text{PPE}}{\text{PE}}$$

$$P_{22} = \frac{\text{PEE}}{\text{PE}}$$

$$\text{hPE}: Y = \text{EEE} - \frac{\text{PEE}^2}{4.\text{PEP}}$$

$$\text{hPP}: Z = \text{PPP} - \frac{\text{PPE}^2}{4.\text{EPE}}$$

Model 2: The t.r.e.f. fractions consist of mixtures of polypropylene (hPP), polyethylene (hPE) and up to three Bernoullian copolymers (copo1, copo2 and copo3). A simplex routine was written with Microsoft Quick Basic software on a Macintosh Classic computer to fit the unknown parameters to the triad data in a way similar to the one described by Cheng[5] (additional information available from the authors).

For each fraction, the polypropylene tacticity was determined from the CH$_3$ region of ^{13}C n.m.r. spectra. For that purpose, we measured the integrals H_1, H_2 and H_3 of the regions from 22 to 21.2 ppm, 21.2 to 20.5 ppm and 20.5 to 19 ppm respectively. In order to calculate the mm, mr and rr polypropylene triads, it is necessary to subtract the copolymer triad contributions to these three regions. This can be done if one of the two following statements could be assumed:

(i) The copolymers are nearly isotactic so that their PPP contributions in regions H_2 and H_3 can be neglected.

(ii) The molar fractions of the copolymers or their PPP triad values are low, so that the assumption that PPP contributes only in the first region leads to a negligible error.

In our case the first assumption was valid since the catalytic system was highly isotactic. Moreover, the second assumption was found to be valid also for most of the fractions.

Then, the polypropylene triads can be calculated for each fraction:

$$\text{mm} = (H_1 - \text{PPP})/Z$$

$$\text{mr} + \text{rm} = [H_2 - (\text{PPE} + \text{PPE})]/Z$$

$$\text{rr} = (H_3 - \text{EPE})/Z$$

where Z is the molar fraction of polypropylene.

^{13}C n.m.r. spectral simulation. For both models, the compositions are calculated from the n.m.r. triad data obtained by integration of eight regions of a spectrum as described by Randall[10]. These integrals provide us with a small amount of information compared to the relative intensities of all the signals of each region. Therefore, an obvious way to check the accuracy of the molar fractions and insertion probabilities would be to simulate a spectrum and compare it in every detail with an experimental one. The aim of such an approach being to recover the maximum amount of information using a few parameters obtained from a small piece of information, we called our program 'Maximum Information Recovery' (MIR).

The MIR program was written with Microsoft Quick Basic software on a Macintosh Classic computer. It simulates the spectrum of a multipolymeric component mixture given the molar fractions and insertion probabilities (except for linear polyethylene). Depending on its nature (polypropylene, polyethylene or ethylene–propylene copolymer), the program loads a reference file containing chemical shift and assignment information specific to each polymer (mmrm, EEEPE, ...). These assignments can go from triads to nonads depending on the spectral region and result from a review of assignments proposed by many authors over the past 20 years. Few adjustments were necessary to take into account differences in experimental conditions with those authors, and were confirmed by sample comparison. Then, for each chemical shift, the assignment name is translated by the program into a product of probabilties and multiplied by molar fraction to give peak area. When all the polymeric components have been treated, the chemical shifts are sorted and area of equal chemical shifts are cumulated. The spectrum or part of the spectrum is calculated by summing the Lorenztian curves corresponding to each chemical shift with the ability to use different linewidths for each spectral region. During this process, satellites due to ^{13}C–^{13}C couplings are added. The program has full viewing capabilities (scrolling, X and Y axis expansion and contraction, ...). The calculated and experimental spectra can be superposed as well as each peak of the polymeric components, which was found to be very useful for assignment adjustments.

RESULTS AND DISCUSSION

In this paper, we only discuss the study concerning the SH fraction of PP mixture, since it is the one that exhibits the higher compositional heterogeneity and since our purpose is to evaluate the ability of ^{13}C n.m.r. combined with t.r.e.f. to analyse such complex mixtures.

Size exclusion chromatography

We have shown in *Figures 2* to *4* chromatograms of the t.r.e.f. fractions. Fractions F1 and F3 (fraction F2 could not be analysed because of lack of product) are characterized by a peak of high molecular weight and large polydispersity, with a rather important quantity of low-molecular-weight product (*Figure 2*). Fractions F4 to F11 are characterized by a double distribution, for which intensities vary with elution temperature (*Figure 3*); and fractions F12 to F14 by a monodistribution, with an increase of the mean molecular weight with elution temperature (*Figure 4*).

Obviously, these results confirm the compositional heterogeneity of the t.r.e.f. fractions. It is important to note that, if we sum up the chromatograms of the fractions (obtained by t.r.e.f. or Kumagawa extraction), taking into account their weight percentages, we

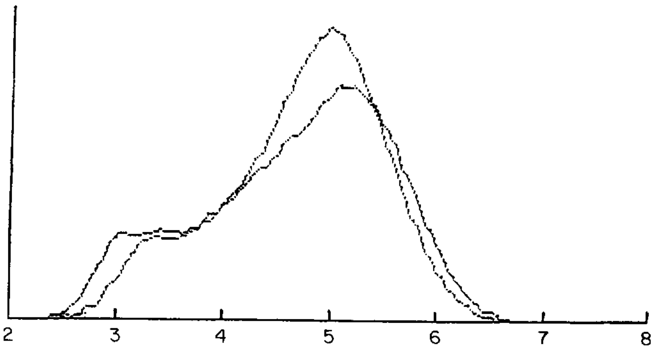


Figure 2 S.e.c. chromatograms of fractions F1 and F3

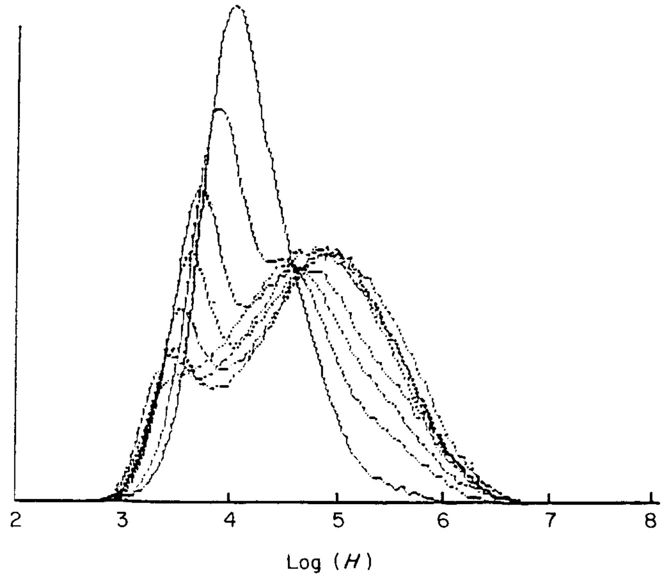


Figure 3 S.e.c. chromatograms of fractions F4 to F11

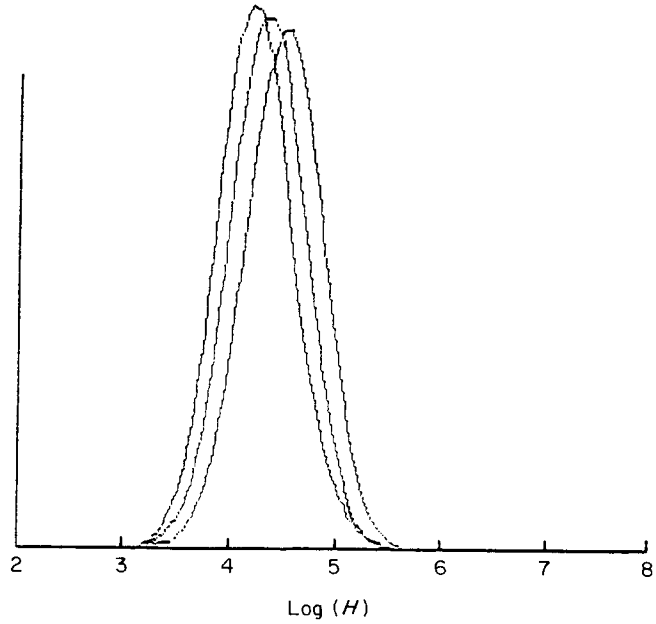


Figure 4 S.e.c. chromatograms of fractions F12 to F14

get a chromatogram similar to the one of the unfractionated product. This means that both t.r.e.f. and Kumagawa extraction do not modify the molecular-weight distribution of the product.

Liquid-state ^{13}C n.m.r.

Tables 1 and *2* give for each fraction the results obtained by models 1 and 2 (fractions F2 and F3 could not be analysed because of lack of product). *Figures 5a* and *5b* show the weight distribution of each component obtained from models 1 and 2, respectively. In order to ease the interpretation of *Figures 5a* and *5b*, fraction F1 was omitted and copolymers with very low propylene content in model 1 were plotted as polyethylene. It is clear from these figures that both models give similar results.

Fractions F4 to F8 contain a copolymer with a medium propylene content (20 to 30%) and either a copolymer with low propylene content (copo3 in model 2) or a polyethylene (model 1). In fact there is no way to choose between these two possibilities since the contributions of copo3 to triads other than EEE are less than 0.004 and thus insignificant. Results for fractions F9 to F11 are more contradictory, but model 2 provides results more consistent with the compositions of the other fractions. Thus, fractions F4 to F11 appear to contain a regularly distributed copolymer with a medium content of propylene and polyethylene, the irregular distribution of which suggests the existence of a copolymer with a low propylene content (especially in fractions F9 to F11).

Fractions F12 to F14 can only be interpreted as mixtures of polypropylene and polyethylene since triads other than EEE and PPP are non-existent.

The compositions obtained by the two models for fraction F1 are somewhat different. In that case, we would prefer those of model 1 for three reasons. First, the calculated triad data obtained using model 2 do not perfectly fit the experimental ones. Moreover, the presence of a copolymer with a medium content of propylene in fraction F1 is not consistent with the regular distribution of the same copolymer among fractions F4 to F11. In addition, we fed the results of model 1 into the MIR program and obtained a spectrum that fits almost perfectly the experimental one (*Figures 6a* and *6b*).

Table 1 Model 1: composition of t.r.e.f. fractions

Fraction	Copolymer (mol%)	P_{33}	P_{22}	Polypropylene (mol%)	Polyethylene (mol%)
F1	60.0	0.50	0.45	35.5	4.5
F4	51.0	0.33	0.63	31.5	17.5
F5	51.5	0.27	0.72	33.5	15.0
F6	46.0	0.25	0.74	35.0	19.0
F7	34.5	0.19	0.71	42.0	23.5
F8	30.5	0.27	0.82	50.5	19.0
F9	39.5	0.06	0.94	60.5	–
F10	39.7	0.03	0.97	60.3	–
F11	42.3	0.02	0.98	57.7	–
F12	–	–	–	62.9	37.1
F13	–	–	–	91.1	8.9
F14	–	–	–	99.3	0.7

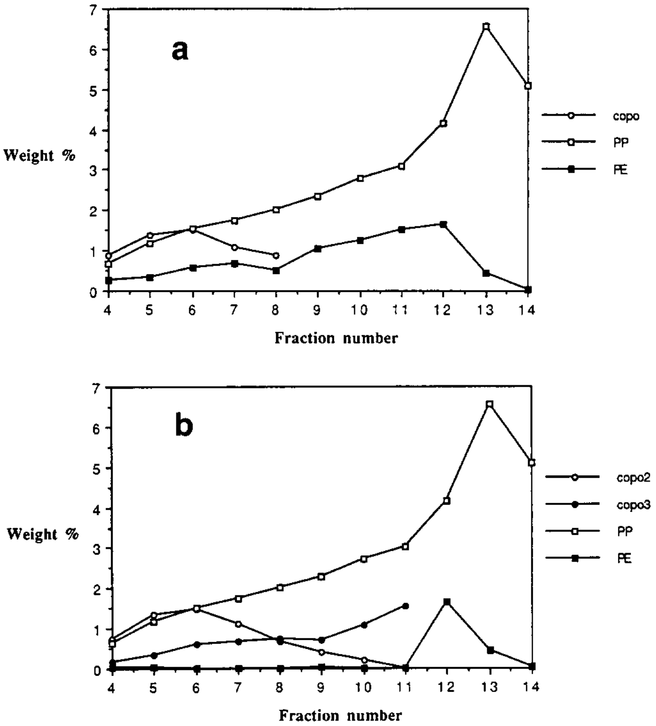


Figure 5 Weight distributions of polymeric components according to (a) model 1 and (b) model 2

Table 2 Model 2: composition of t.r.e.f. fractions

Fraction	Copo1, $P_3 = 0.604$ (mol%)	Copo2, $P_3 = 0.260$ (mol%)	Copo3, $P_3 = 0.014$ (mol%)	Polypropylene (mol%)	Polyethylene (mol%)
F1	47.2	20.9	–	31.9	–
F4	13.0	45.4	10.4	30.0	1.2
F5	1.7	50.6	14.0	32.9	0.8
F6	0.1	45.1	20.0	34.7	0.1
F7	–	34.8	23.4	41.7	0.1
F8	0.2	21.9	27.1	50.4	0.4
F9	–	13.3	26.8	58.5	1.4
F10	–	5.4	35.0	59.3	0.3
F11	0.1	0.4	42.9	56.4	0.2
F12	–	–	–	62.9	37.1
F13	–	–	–	91.1	8.9
F14	–	–	–	99.3	0.7

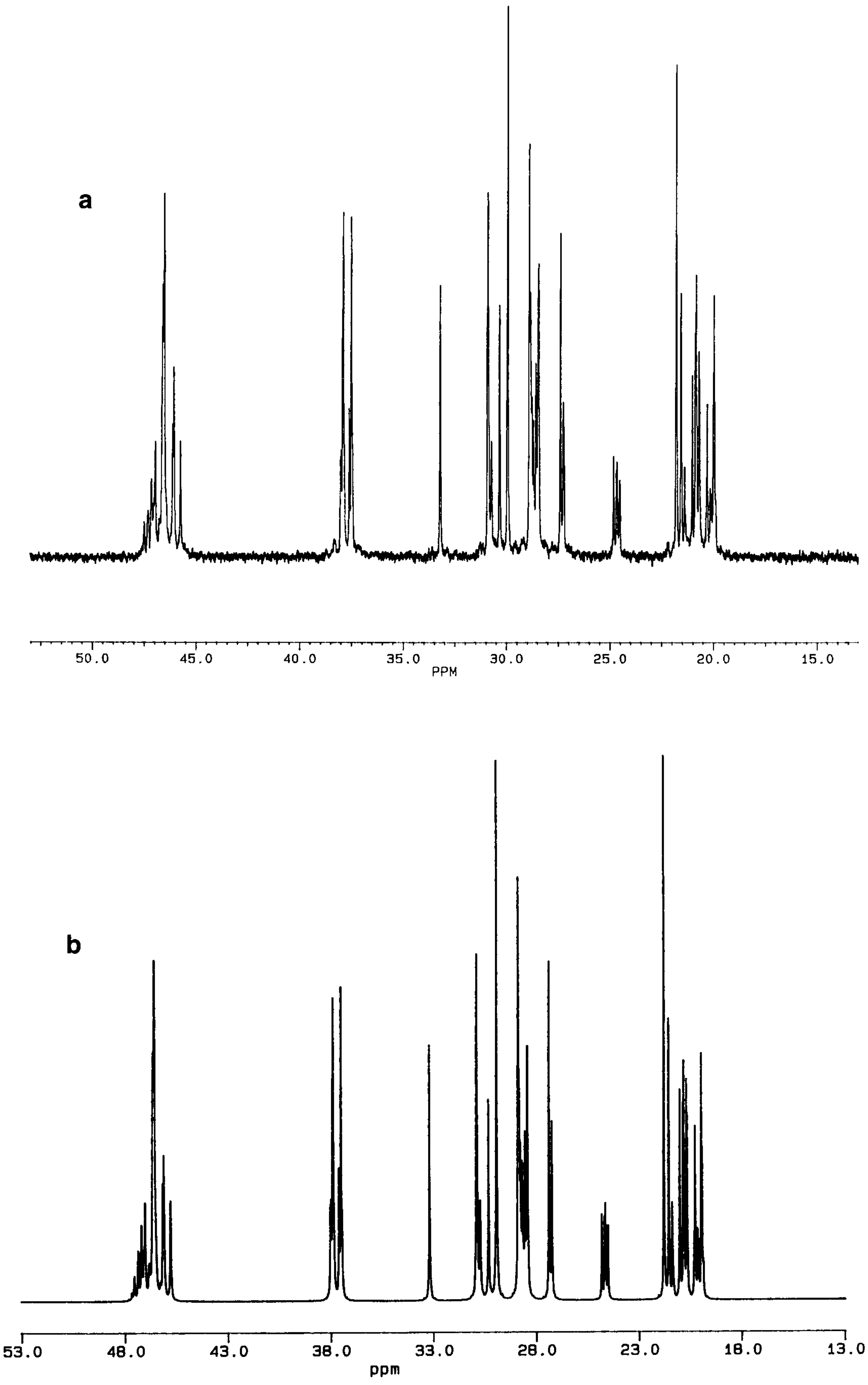


Figure 6 (a) Experimental spectrum of fraction F1. (b) Simulated spectrum of fraction F1 (molar percentages and probabilities are given in *Table 1*)

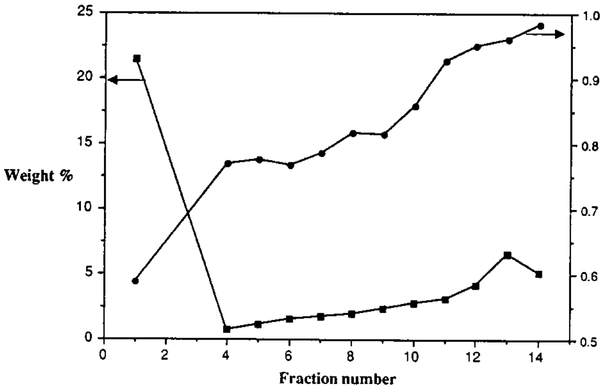


Figure 7 Polypropylene weight distribution and *meso* fraction *versus* fraction number

The polypropylene weight distribution and tacticity evolution are shown in *Figure 7*. The main component is a nearly atactic polypropylene (fraction F1). In fractions F4 to F10, there is a regular increase of low isotactic polypropylene, and a highly isotactic polypropylene appears from fraction F11. This confirms the highly heterogeneous composition of polypropylene obtained by an $MgCl_2/TiCl_4$-supported catalyst.

CONCLUSIONS

The extraction and fractionation methods used were efficient in dividing a complex product into simpler and analysable fractions. Liquid-state ^{13}C n.m.r. combined with appropriate models enabled the identification and quantification of most of the components. We found as Cheng[5] that the copolymerization step led to the production of three or four nearly Bernoullian copolymers. However, some uncertainties remain since the precision of the n.m.r. triad data did not allow discrimination between polyethylene and ethylene–propylene copolymer with low propylene content. Therefore, a complete study of a polymer mixture by ^{13}C n.m.r. and t.r.e.f. can be difficult without prior knowledge of the compositional heterogeneity of the individual polymers or without complementary techniques like on-line s.e.c.-*F*Ti.r., which could provide such information.

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APPENDIX

Calculation of the molar fractions and insertion probabilities in model 1

If we call X, Y and Z the molar fractions of ethylene–propylene copolymer, polyethylene and polypropylene, respectively, and P_{ij} the insertion probability of monomer j after monomer i (with indices 2 and 3 standing respectively for ethylene and propylene), we can write the following expressions for the n.m.r. triad data:

$$2XP_{32}P_{23}P_{33}/(P_{23}+P_{32}) = \mathrm{EPP}+\mathrm{PPE} = a \quad \text{(A1)}$$

$$XP_{32}^2P_{23}/(P_{23}+P_{32}) = \mathrm{EPE} = b \quad \text{(A2)}$$

$$2XP_{32}P_{22}P_{23}/(P_{23}+P_{32}) = \mathrm{EEP}+\mathrm{PEE} = c \quad \text{(A3)}$$

$$XP_{23}^2P_{32}/(P_{23}+P_{32}) = \mathrm{PEP} = d \quad \text{(A4)}$$

$$XP_{32}P_{22}^2/(P_{23}+P_{32}) + Y = \mathrm{EEE} = e \quad \text{(A5)}$$

$$XP_{23}P_{33}^2/(P_{23}+P_{32}) + Z = \mathrm{PPP} = f \quad \text{(A6)}$$

Then:

$$(\mathrm{A2})/(\mathrm{A1}) \Rightarrow P_{32}/P_{33} = 2b/a$$

$$(\mathrm{A2})/(\mathrm{A3}) \Rightarrow P_{32}/P_{22} = 2b/c$$

$$(\mathrm{A2})/(\mathrm{A4}) \Rightarrow P_{32}/P_{23} = b/d$$

$$(\mathrm{A4})/(\mathrm{A1}) \Rightarrow P_{23}/P_{33} = 2d/a$$

$$(\mathrm{A4})/(\mathrm{A3}) \Rightarrow P_{23}/P_{22} = 2d/c$$

According to Markov statistics, $P_{32}+P_{33}=1$ and $P_{23}+P_{22}=1$, thus:

$$P_{33} = 1/(1+2b/a) = a/(a+2b)$$

$$P_{32} = 1-a/(a+2b) = 2b/(a+2b)$$

$$P_{22} = 1/(1+2d/c) = c/(c+2d)$$

$$P_{23} = 1-c/(c+2d) = 2d/(c+2d)$$

Replacing the probabilities by their expressions in one of equations (A1) to (A4), it can be established that:

$$X = (a+2b)^2(b+d)/(4bd) = (c+2d)^2(b+d)/(4bd) \quad \text{(A7)}$$

Replacing X by its expression in equations (A4) and (A5), one gets:

$$Y = e - c^2/(4d) \quad \text{(A8)}$$

$$Z = f - a^2/(4b) \quad \text{(A9)}$$