Characterization of Ethylene in EP and in iPP/EP Systems by Deconvolution of IR Spectra

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ABSTRACT: The purpose of this study is to propose a correlation between IR spectra and molecular structure of ethylene-propylene (EP) copolymers possibly blended with isotactic polypropylene (iPP). The method is based on the deconvolution of the spectrum in the CH_2-rocking range, i.e., $800-680$ cm^{-1}, where the bands of interest overlap. The six bands present in this region were signal averaged in position and width. The spectra were then deconvoluted (curve fitted) assuming a Lorentzian shape for the bands. The band at 1167 cm^{-1} (with a shoulder at 1156 cm^{-1}) corresponding to a CH_3 vibration is considered as an internal standard. The method was checked by varying some fitting parameters. In order to realize some quantitative measurements, calibration curves were established with some EP samples, characterized by ^{13}C NMR, which were used as standards. The amounts of total $-(CH_2-CH_2)-$ units (ethylene units), isolated ethylene and structural defaults in PP were determined for different iPP/EP blends. Ethylene crystallinity has also been determined. A good correlation was evidenced between infrared and ^{13}C NMR measurements. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 75: 96–106, 2000

Key words: EP; iPP/EP; PE; IR; deconvolution; crystallinity

INTRODUCTION

The enhancement of isotactic polypropylene (iPP) impact properties by introduction of a finely dispersed rubbery phase (EP) is a well-known process that is widely commercialized. The preparation of such blends (iPP/EP) directly in the polymerization reactors by means of a two-stage process with Ziegler-Natta catalysts gives rise to products that exhibit a particularly good compromise between stiffness and impact resistance at low temperature. The mechanical properties of these products are strongly affected by the proportion, the molecular structure, and the morphology of the elastomeric component. As a consequence of the heterogeneity of active sites in Ziegler-Natta catalysts, the presence of crystalline polyethylenic subinclusions can be visualized in the elastomeric phase.[1,2]

These inclusions could stiffen the amorphous matrix and modify properties, such as surface hardness,[3] scratch resistance, tensile elongation,[4] and impact behavior[5] of compression-molded samples or stress whitening[6] behavior of injection molded products. It is quite obvious that a precise knowledge of the amount of such a type of crystallinity will be helpful in the context of structure-properties relationship studies.

A fair number of different methods using infrared spectroscopy purport to determine quantitatively the total ethylene content, the distribution of ethylene and propylene units along the chain,

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and the ethylene crystallinity.[7–10] One of these is based on a mathematical curve fitting (deconvolution) of the complex infrared absorption of the CH_2-rocking vibration (800–660 cm^{-1}).[9,11,12] The most important requirement of this method is that the number of bands must be known, before curve fitting is even contemplated.[13] A review by Tosi and Ciampelli[7] lists all bands so far utilized for analytical determinations on EP copolymers. In the region under study, four peaks are distinguished: a band at 722 cm^{-1} is usually assigned to long CH_2 sequences (in an amorphous state), whereas the bands at 720 and 729 cm^{-1} clearly result from ethylene crystallinity in the sample, i.e., orthorhombic phase.[8,9,12] The band near 735 cm^{-1} is due to the $(CH_2)_3$ sequence, characteristic of ethylene units isolated between two head-to-tail propylene units.

In order to apply a proper curve-fitting, enabling the resolution of individual absorption bands, it is also necessary to know the bands' profile. In a general view, collisions between molecules in liquids give rise to a Lorentzian shape infrared absorption band. However, besides instrumental band-widening effects, even molecular effects, such as rotational fine structure, hydrogen bonding, and the possible existence of multiple conformations, affect the shape of the absorption band, so that true Lorentzian shape is not always encountered.[14] In fact, most of the infrared bands can be described by the product or the sum of a Gaussian and a Lorentzian functions.[13,15–17] However, Van der Ven[9] has shown that a pure Lorentzian function described satisfactorily the CH_2 rocking vibration of an hydrogenated polyisoprene. Vandeginste and De Galan[13] also have shown that the ratio of the Lorentzian to the Gaussian contribution has only a minor influence. As a consequence, in their work, they use pure Lorentzian shapes.

To determine the composition of an EP or an iPP/EP system, a quantification of these polymers is required beyond their total ethylene content. Following Tosi and Ciampelli[7] and Van der Ven,[9] the determination of the total amount of copolymer phase, the content of random copolymer in this copolymer phase, and the ethylene crystallinity (720 and 729 cm^{-1} bands) can be determined. Unfortunately, they have never published any indication about the procedure to follow. But in a general view, an internal standard is necessary to avoid the thickness measurement. Bands arising from CH_3 units at 973, 1167, or 4391 cm^{-1} are currently used for this purpose.[18,19]

The aim of this paper is to propose a practical method for studying polymers such as EP and iPP/EP by the Fourier transform-infrared (FTIR) technique. After having briefly described the FTIR spectra of EP and iPP, the bases of the deconvolution are detailed. Furthermore, by comparison with ^{13}C nuclear magnetic resonance (NMR) results, some quantitative aspects are also presented about the total amount of ethylene units, isolated ethylene, and structural defaults in PP. An attempt is also made to determine the ethylene crystallinity.

EXPERIMENTAL

Material

With the exception of samples EP15 to EP18 VISTALON EP504, 606, 719 and 805, respectively), which are commercial EPR supplied by EXXON, all the products used in this study were provided by SOLVAY. All of them are lab scale samples produced in a batch gas-phase process with steady-state (co)monomer feed ratio. All samples of iPP/EP have been produced similarly at SOLVAY by a two-stage polymerization.

The Tables 1(a) and 1(b) report the characteristics of all samples of EP and iPP/EP that are used in this paper. The compositions were determined by ^{13}C NMR in 1,2,4-trichlorobenzene solution according to Ray et al.[20] Fifty-megahertz ^{13}C NMR spectra were recorded at 130°C using a BRUKER AC200 NMR spectrometer under the following conditions: pulse angle: 60°, pulse delay: 10 s, acquisition time: 1.47 s, sweep width: 11,000 Hz. Deuterated *para*-dibromobenzene was used as an internal lock.

The polymer composition (ethylene content and triads distribution) is reported in Tables 1(a) and 1(b) using the following notations:

C_2X_3: mole fraction of ethylene present as single units between two propylene units

C_2X_5: mole fraction of ethylene present as double units between two propylene units

$C_2X_6^+$: mole fraction of ethylene present in sequences of three or more between two propylene units

C_2X_4: mole fraction of ethylene present as single units between two propylene units, one of them being inverted (i.e. other than head-to-tail)

Table Ia   Molecular Structure of EP Samples

Sample Ref.	Ethylene Content	C_2X_3	C_2X_2	C_2X_4	C_2X_5	C_2X_{6+}	$[\eta]$ (dL/g)	n^{2+}
EP1	7.0	4.8	0.0	0.0	1	2	—	3.9
EP2	10.5	5.5	0.0	0.0	2	3	—	3.9
EP3	13.2	6.2	0.0	0.0	3	4	—	4.1
EP4	29.0	10.0	0.0	0.0	6	13	—	4.6
EP5	32.2	10.0	0.0	0.0	8	14.2	0.554	4.9
EP6	47.6	9.8	0.0	0.0	6.2	31.6	0.670	6.0
EP7	19.8	6.8	0.2	0.3	3.2	9.3	0.468	4.8
EP8	24.1	7.2	0.2	0.4	3.7	12.6	0.401	5.2
EP9	28.5	7.1	0.2	0.0	4.6	16.6	0.524	5.7
EP10	33.9	7.0	0.2	0.2	4.1	22.4	0.434	6.2
EP11	42.4	6.4	0.1	0.3	4.7	30.9	0.472	7.5
EP12	48.4	6.5	0.1	0.3	5.3	36.2	0.662	8.1
EP13	56.0	5.0	—	—	5.0	46.0	—	10.0
EP14	70.0	2.0	—	—	3.0	64.8	0.534	11.5
EP15	58.9	5.7	1.4	1.6	6.9	42.9	0.209	(*)
EP16	53.3	6.7	1.8	1.9	8.3	34.6	0.270	(*)
EP17	77.4	2.1	0.4	1.1	2.0	71.7	0.158	(*)
EP18	77.0	1.8	0.4	1.0	3.2	70.6	0.208	(*)

(*), not determinable.

C_2X_2:   mole fraction of inverted propylene sequences (i.e. other than head-to-tail)

The EP samples (EP1–EP14) differ by their ethylene content.

The intrinsic viscosity of EP samples was determined at 140°C in tetraline, using a LAUDA Automatic Viscometer.

The mean length of sequences of at least two CH_2 groups, i.e., insertion of at least one ethylene

Table Ib   Molecular Structure of iPP/EP Blends

Sample Ref.	MFI (g/10 min)	$[\eta]_{EP}/[\eta]_{PP}$	% EP	Ethylene Content (%)		C_2X_3	C_2X_5	C_2X_{6+}	n^{2+}
				EP	PP/EP				
PP/EP1	4.0	2.20	25.0	55.0	13.8	1	0.5	12.3	11.2
PP/EP2	5.7	2.15	18.0	45.0	8.0	1	1	5.3	7.3
PP/EP3	6.2	2.19	19.0	45.0	8.7	1	1	6.7	7.6
PP/EP4	6.2	2.23	18.0	57.0	9.0	1	1	7.0	8.4
PP/EP5	5.9	1.12	14.0	50.0	7.0	1	1	5.6	7.1
PP/EP6	6.3	1.02	16.0	8.0	7.5	1	1	6.0	7.5
PP/EP7	5.9	1.40	12.4	58.0	7.2	1	1	6.2	8.9
PP/EP8	6.4	1.63	13.6	57.0	7.2	1	1	6.0	7.7
PP/EP9	5.7	1.21	14.9	57.0	8.4	1	1	6.3	8.5
PP/EP10	6.8	2.24	14.7	58.0	8.0	1	1	6.9	8.1
PP/EP11	12.0	2.75	16.6	56.0	7.5	1	1	6.6	8.2
PP/EP12	6.0	2.45	15.7	56.0	8.8	1	1	8.5	8.4
PP/EP13	4.7	0.97	13.9	56.0	7.7	1	1	5.6	8.3
PP/EP14	5.2	0.76	12.1	57.0	6.9	1	1	5.2	8.6
PP/EP15	2.7	1.21	30.5	62.0	18.9	1	2	14.5	10.0
PP/EP16	2.5	1.25	30.0	55.0	16.3	2	2	12.9	8.7
PP/EP17	2.6	1.24	28.7	44.5	12.9	2	2	10.3	7.0
PP/EP18	2.9	1.15	24.3	37.0	9.0	3	2	6.3	5.7
PP/EP19	3.0	1.84	26.2	38.0	9.7	3	2	7.0	5.7

into the PP chain, was measured using the parameter n^{2+} as defined by Randall[21]:

$$n^{2+} = \frac{I_{\alpha\beta} + 3I_{\beta\beta} + 2I_{\beta\gamma} + 5I_{\gamma\gamma} + 3I_{\gamma\delta+} + I_{\delta\delta+}}{0.5I_{\alpha\beta} + I_{\beta\beta} + 0.5I_{\beta\gamma} + I_{\gamma\gamma} + 0.5I_{\gamma\delta+}}$$

where I_{ii} refers to the signal intensities corresponding to the carbons at the positions from the next two CH-groups as defined by the greek indices.

iPP/EP tested (PP/EP1–PP/EP19) differ by the type of catalyst used (PP/EP1–6), the viscosity ratio ($[\eta]_{EP}/[\eta]_{iPP}$) (see later) between the two components (PP/EP7–14), the amount of ethylene in the EP rubber (PP/EP15–18) or both (PP/EP19). The EP content in iPP/EP samples, as determined by mass balance, and the MFI (in g/10 min at 230°C) are reported in Table 1b.

A viscosity ratio ($[\eta]_{X_s}/[\eta]_{X_i}$) can be derived from the intrinsic viscosities (measured in tetraline solution at 140°C) of the "xylene soluble" ($[\eta]_{X_s}$) and "xylene insoluble" ($[\eta]_{X_i}$) fractions of the polymer. The soluble fraction is obtained by recrystallization at room temperature after complete dissolution in xylene. The soluble and insoluble fractions are known to be representative of the amorphous (EP) and of the crystalline (PP) parts, respectively, of the whole polymer. In this paper $[\eta]_{X_s}/[\eta]_{X_i}$ measurements are reported as $[\eta]_{EP}/[\eta]_{iPP}$.

FTIR

The FTIR used in this work was a Perkin-Elmer 1760 X spectrometer. The resolution was 1 cm^{-1} and 10 scans were signal averaged. Films of polymers were molded on a press with heated platens. The polymer was introduced in a metallic mold between two aluminum foils. The sample was then pressed between two flat mold plates at 200°C during 30 s and a final pressure of 10 tons (30 s). The molten sample was rapidly quenched in water. Film thicknesses are around 100 μm to obtain a sufficient absorbance of the 680–800 cm^{-1} region.

Software

The deconvolution curves were obtained with the IGOR software provided by WaveMetrics. A program has been established to analyze IR spectra with Lorentzian band shapes. First, the number of Lorentzian must be fixed. Second, initial values of the position, half-width, and intensity of each
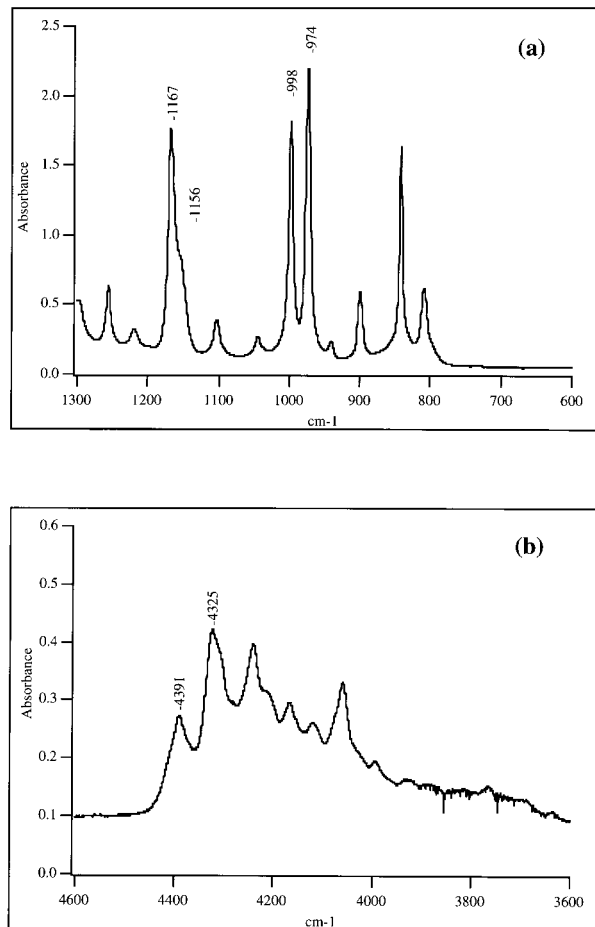

Figure 1 FTIR spectrum of a iPP sample in the range (a) 1600–600 cm^{-1} and (b) 4600–3600 cm^{-1}.

band have to be indicated. From this starting point, the program minimizes each value to obtain the minimal divergence between experimental spectrum and calculated curve. As written, this software performs the minimization until χ^2 reaches a value inferior to 10^{-3}.

RESULTS AND DISCUSSION

FTIR Results

Before studying blends of EP and iPP, FTIR spectra of these two compounds were recorded (Figs. 1 and 2). In the case of iPP (Fig. 1), usual infrared bands due to the isotactic phase are found.[18,22] The most meaningful are pointed out at 4391, 1167 (with a shoulder at 1156 cm^{-1}), 998, and 974 cm^{-1}. For the EP sample (Fig. 2), some bands previously observed in the iPP spectrum are
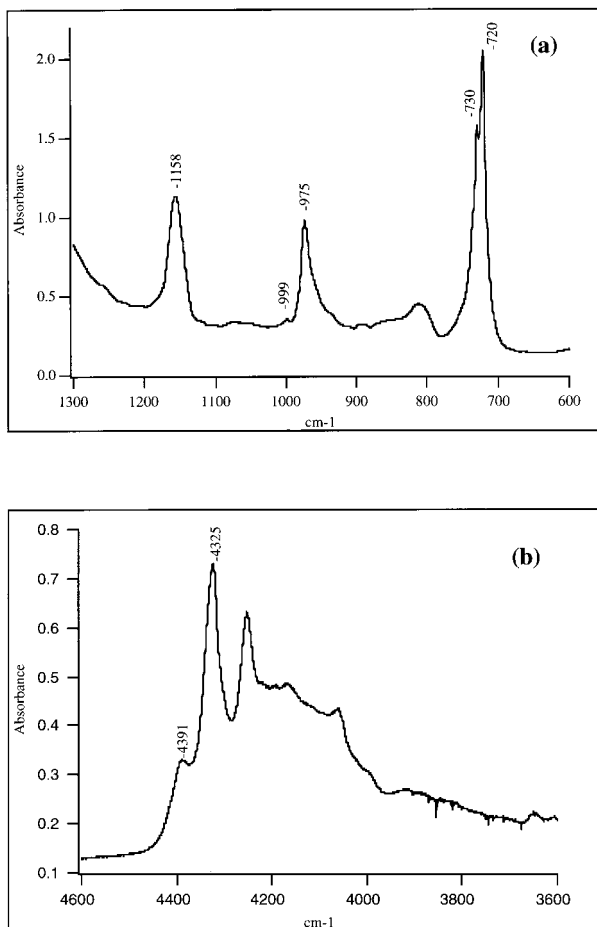
Figure 2 FTIR spectrum of an EP sample (EP6) in the range (a) 1600–600 cm^{-1} and (b) 4600–3600 cm^{-1}.

ethylene sequences. When the number of ethylene groups is low, and for the amorphous polyethylene sequences, only one band appears at 722 cm^{-1}. In the case of a single ethylene group between two propylene groups (i.e., —(CH$_2$)$_3$—), the band is pointed out at 735 cm^{-1}.[12] Bands arising from polypropylene are also detected. The 752 cm^{-1} band is assigned to the presence of two methylene groups (i.e., —(CH$_2$)$_2$—) between tertiary carbon atoms. This is characteristic of head-to-head inversions of propylene units.[23] A last band can be noticed at 770 cm^{-1}, which is the position of band assigned to pendant ethyl groups.[24,25] In an attempt to overcome the difficulties arising from the strong overlap of the bands of interest for elucidation of the constitution of ethylene-propylene copolymers, possibly with or without iPP, a computer curve-fitting (deconvolution) technique has been used.

Bases of the Deconvolution

Following the literature,[17] deconvolution can be made on the basis of a Lorentzian shape. Before beginning the deconvolution, this shape has been verified by considering the isolated band at 899 cm^{-1} in the iPP spectrum. A pure Lorentzian shape appears to describe properly this band. As a consequence, this shape has been applied to deconvolute the range of interest.

Van der Ven[9] has taken a baseline between 800 and 660 cm^{-1}. Because no peaks are present beyond 680 cm^{-1}, the range of interest has been reduced to 800–680 cm^{-1} to decrease fitting errors. This baseline corresponds to a straight line that is always close to horizontal. Further, no interference fringes came from the sample.

The procedure followed to determine the half width of bands is now described. First of all, the values corresponding to the 752 and 770 cm^{-1}

present but some new bands near 710–750 cm^{-1} are superimposed. From previous studies,[7,9] we are able to determine the number of bands in this region and their assignments as shown in Table 2. Bands at 720 and 730 cm^{-1} are representative of the ethylene crystallinity and correspond to long

Table II   Bands Assignments in the Range 800–680 cm^{-1}

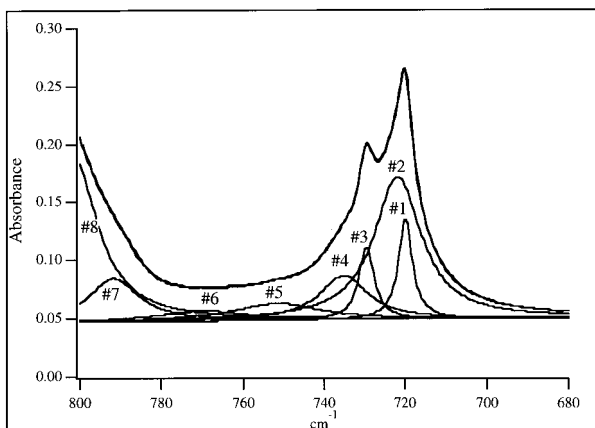| Lorentzian No.	Position (cm^{-1})	Half Bandwidth (cm^{-1})	Assignment
1	720	4.1	Ethylene crystalline units
2	722	14.1	Ethylene amorphous units
3	730	4.5	Ethylene crystalline units
4	735	14.3	Isolated ethylene
5	752	25.9	PP structural defaults
6	770	27.3	Pendant ethyl branched
7	± 790	—	PP contribution
8	± 800	—	PP contribution

Figure 3 Deconvolution of an iPP/EP sample (PP/EP2) in the range 800–680 cm^{-1}.

bands were determined using four samples including structural defaults (EP15–EP18) and pendant ethyl branches (EP15 and EP16). As a first step, allowing, for these five samples, all parameters to be freely calculated by the computer program, the values of half width were averaged, i.e., 25.9 cm^{-1} for the 752 cm^{-1} band and 27.3 cm^{-1} for the 770 cm^{-1} band.

In a second step, these four parameters were fixed for the determination of the other half widths. For six samples with well-defined crystalline bands (EP4, EP6, PP/EP1, PP/EP2, PP/EP3, and PP/EP5), the average value of the half widths are 4.1 cm^{-1} for the 720 cm^{-1} band and 4.5 cm^{-1} for the 730 cm^{-1} band.

Again these four parameters were fixed and the half width of 735 cm^{-1} band was determined at 14.3 cm^{-1} with six samples (EP1–EP6). For the last band at 722 cm^{-1}, all the samples were taken into account with all the previous parameters fixed. The half width at 722 cm^{-1} was finally

estimated to a value of 14.5 cm^{-1}. All these values are reported in Table 2 and agree with the results of Drushel et al.[26]

In order to complete the deconvolution, a contribution from iPP strong bands lying above 800 cm^{-1} has to be taken into account. The best results were obtained by defining two supplementary (fictious) Lorentzians. Their locations are marked at ca. 790 and 800 cm^{-1}. On the basis of this information, the deconvolution of the FTIR spectra of EP and iPP/EP systems with the IGOR soft was performed as shown in Figure 3.

Tests on the Robustness of the Method

Some fitting parameters were varied in order to test the robustness of the method used. For this purpose, two groups of experiments have been realized:

Group A: all parameters of bands at 720, 722, 730, and 735 cm^{-1} are fixed; the others were freely calculated by the computer program.

Group B: all parameters of bands at 752, 770, 790, and 800 cm^{-1} are fixed; the others were freely calculated by the computer program.

Results for group A with an EP copolymer (EP10) are given in Table 3. Large modifications are observed on the 752 and 770 cm^{-1} bands. If the Lorentzian #5 at 752 cm^{-1} is suppressed, it is immediately replaced by another one at the same location (e.g., the Lorentzian #7). This is a proof of the necessity of the band at 752 cm^{-1} to obtain a correct fitting and shows that structural PP defaults are undoubtedly present in some EP copolymers. With an iPP/EP sample (PP/EP3), both the Lorentzian #5 and #6 are needed. Then it is deduced that structural PP defaults are present in these systems and that some ethyl pendant groups could be present, although in a very small

Table III   Results Obtained on an EP Sample (EP10) in the Group A Experiments

Reference[a]	$S_{720+730}$	S_{722}	S_{735}	S_{752}	S_{770}
	0.185	0.78	0.32	0.2	0.1
A	0.183	0.77	0.30	0.3	0.06
B	0.182	0.77	0.29	—	0.06
C	0.182	0.76	0.29	—	—
D	0.184	0.75	0.29	—	—
E	0.185	0.78	0.32	0.2	0.1
F	0.184	0.76	0.29	—	—
G	0.183	0.79	0.32	0.2	—

^{a} A, all bands free; B, #6 fixed and #5 suppressed; C, #5 fixed and #6 suppressed; D, #5 suppressed; E, #5 and #6 fixed and #7 suppressed; F, #5 and #6 suppressed; G, #5 fixed, #6 and #7 suppressed.

Table IV   Influence of the IR Resolution on the Areas Measured After Deconvolution

Sample	Resolution (cm^{-1})	$S_{720+730}$	S_{735}	S_{722}	S_{752}	S_{770}	Σ $S(CH_2)$[a]
PP/EP1	1	0.130	0.03	0.20	0.03	0.01	0.39
	0.5	0.115	0.03	0.21	0.03	0.04	0.36
PP/EP5	1	0.062	0.03	0.11	0.01	0.01	0.21
	0.5	0.068	0.03	0.11	0.02	0.02	0.21
EP13	1	1.436	0.38	2.28	0.3	0.01	4.1
	0.5	1.604	0.35	2.35	0.3	0.04	4.3

[a] Σ $S(CH_2) = S_{720+730} + S_{722} + S_{735}$.

amount. They should come from the synthesis of these products. With group B, no significant effect either with EP nor with iPP/EP were observed.

Finally, we tested the influence of the IR resolution (Table 4). A group of experiments have been made at 0.5 cm^{-1} instead of 1 cm^{-1}. The total area of the ethylene units is unaffected. The only significant modification is observed on the 770 cm^{-1} band. The very low area under this band with a high value of half width represents a possible explanation. A slight modification in intensity implies a strong percentage deviation.

The robustness of the method described above was also tested by scanning 10 samples of a same iPP/EP blend (PP/EP4). Each sample was molded independently with a thickness in the range 56–135 μm. Table 5 reports the values for all bands. The reproducibility is very high, particularly on narrow bands like the crystalline ones (720 and 730 cm^{-1}). With the increasing of the band half-width, the error on the peak areas becomes more important.

From the above results, the deconvolution process seems correct. Some quantitative measurements can now be performed.

Quantitative Measurements

Normalization

As the IR absorption bands are dependent on the sample thickness, a preliminary normalization is necessary. Bands due to the CH$_3$ group can be used as references. In general, bands at 4391, 1167, and 973 cm^{-1} are often used as internal standards. These three possibilities were thus examined. Figure 4 outlines that the area of the 973 cm^{-1} band is not always measurable (depending on the sample) and then cannot be taken as a good reference. In the case of the 4391 cm^{-1} band, the strong overlap of this band with the others located at lower frequency induces a large error in the estimation of the intensity, and then this 4391 cm^{-1} peak can not be kept as a standard (Fig. 5). On the contrary, with the 1167 cm^{-1} band linked to the isotactic helix of the polypropylene, no experimental problem has been encountered with different samples (Fig. 4). The shoulder at 1156 cm^{-1} (amorphous phase of polypropylene) is associated to a complex band with C—CH$_3$ stretching and CH$_3$ twisting.[7] To take into account all the propylene units, the sum of the areas of 1167

Table V   Reproducibility of Measurements Realised on the PP/EP4 Sample

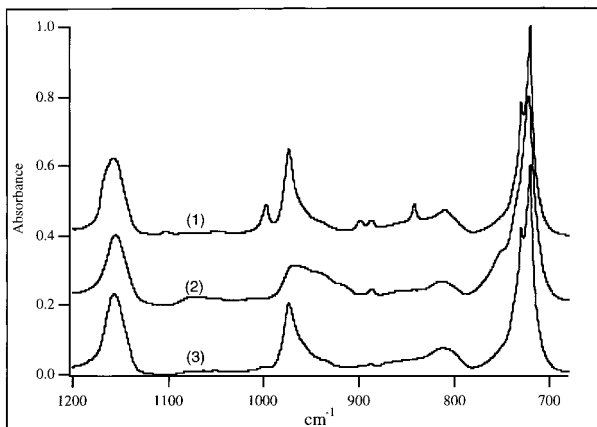| Sample	$S_{720+730}/S_{1167}$	S_{735}/S_{1167}	S_{722}/S_{1167}	Σ $S(CH_2)/S_{1167}$	S_{752}/S_{1167}	S_{769}/S_{1167}
1	0.056	0.03	0.15	0.24	2×10^{-2}	3×10^{-2}
2	0.056	0.04	0.15	0.25	3×10^{-2}	5×10^{-2}
3	0.056	0.04	0.15	0.24	2×10^{-2}	4×10^{-2}
4	0.060	0.04	0.14	0.24	3×10^{-2}	4×10^{-2}
5	0.059	0.04	0.15	0.24	2×10^{-2}	5×10^{-2}
6	0.055	0.04	0.15	0.24	2×10^{-2}	4×10^{-2}
7	0.057	0.03	0.14	0.23	1×10^{-2}	3×10^{-2}
8	0.056	0.03	0.14	0.23	2×10^{-2}	3×10^{-2}
9	0.056	0.04	0.14	0.24	2×10^{-2}	4×10^{-2}
10	0.055	0.03	0.15	0.24	3×10^{-2}	4×10^{-2}

Figure 4 FTIR spectra of EP samples with similar ethylene content: (1) EP12: 48.4% C_2; (2) EP16: 53.3% C_2; and (3) EP6: 47.6% C_2 in the range $1200–600$ cm^{-1}.

and 1156 cm^{-1} bands was measured, as Skaare et al.[25] have already proposed. In this case, it is assumed that molar extinction coefficients of these bands are identical or at least of comparable values. By convenience, the sum of the areas of 1167 and 1156 cm^{-1} bands was named S_{1167}. In order to assess the use of this last band area, the thickness of 10 samples of a same blend (PP/EP4) has been measured by a mechanical technique. Figure 6 outlines the good correlation between S_{1167} and the measured thickness. To check the thickness, the film was embedded in an epoxy resin matrix. A cut of the sample was carried out by microtome and then observed by optical microscopy (Leitz Orthoplan Pol). Values obtained by mechanical measurements (micrometer) are
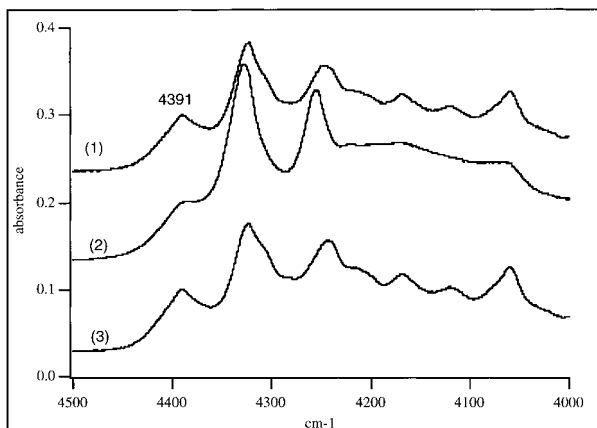

Figure 5 FTIR spectra of EP samples normalized on the 4391 cm^{-1} band: (1) PP/EP15, (2) EP15, and (3) PP/EP2.
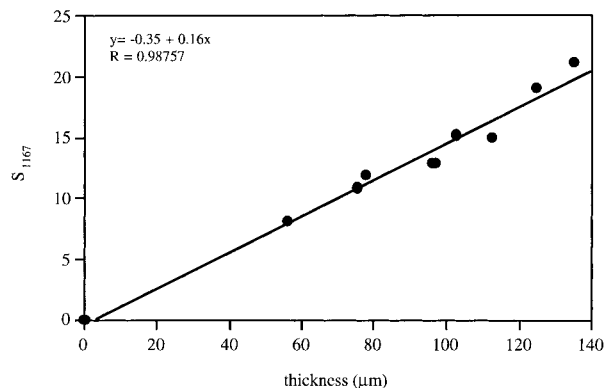

Figure 6 Relation between the sum of the area of the 1167 and 1156 cm^{-1} bands (S_{1167}) and the sample thickness measured by a mechanical technique.

very close to the one obtained by microscopy. This validates the protocol used in this work.

Calibration Curves

In order to establish calibration curves, the amounts of ethylene and propylene units have to be measured by another technique. The most powerful technique seems to be ^{13}C NMR,[27] which makes it possible to detect and quantify long-range chemical-shift effects on carbon atoms in different constitutional situations. Results are reported in Table 1a.

By FTIR, the total ethylene concentration is obtained by summation of the deconvoluted areas below the four Lorentzians corresponding to ethylene units (Lorentzians #1–4). The value has been divided by S_{1167} to avoid the influence of the sample thickness (normalization). A calibration curve (Fig. 7) has been established with six EP
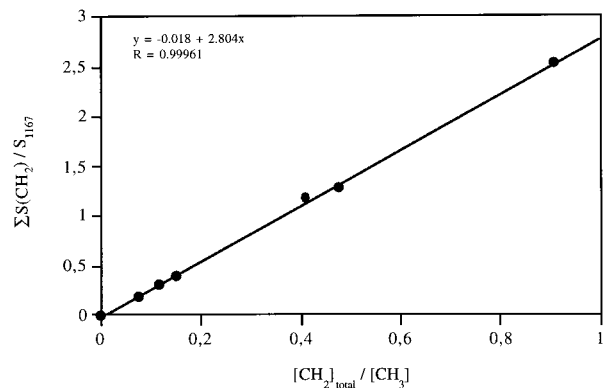

Figure 7 Calibration curve for the total ethylene content: FTIR data versus ^{13}C NMR data.
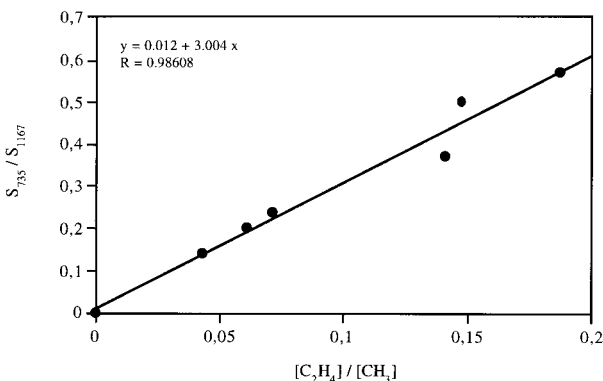
Figure 8 Calibration curve for the amount of isolated ethylene units: FTIR data versus ^{13}C NMR data.

samples (EP1–EP6). The straight line is described by the following relationship:

$$\frac{\sum S(CH_2)}{S_{1167}} = 2.80 \frac{[CH_2]_t}{[CH_3]} - 1.8 \times 10^{-2}$$

The amount of isolated ethylene units is provided by the ratio S_{735}/S_{1167}, calculated for the same six samples as above. A plot of this ratio as a function of ^{13}C NMR results is given in Figure 8. The result is

$$\frac{S_{735}}{S_{1167}} = 3.00 \frac{[C_2H_4]}{[CH_3]} + 1.12 \times 10^{-2}$$

The concentration in structural PP defaults has also been determined by the ratio S_{752}/S_{1167} on two specific samples with a relatively high concentration in PP defaults (EP15 and EP16). The results are also reported in Table 6. The lack of samples with different percentages in PP defaults did not allow the establishment of a true calibration curve.

The ethylene crystallinity was then directly determined from areas of the crystalline bands at 720 and 730 cm^{-1} and reported to the total ethylene content, given by $S_{720+730+735+752}$. As anticipated,[28] the crystalline bands (720 and 730 cm^{-1}) appear markedly narrower than the amorphous ones.

Validation of the FTIR Method

From the calibration curves, a simple FTIR spectrum is able to provide the percentage of ethylene units, isolated ethylene, the amount of PP structural defaults and the ethylene crystallinity. This method has been validated for a number of iPP/EP samples. Table 7 summarizes the results. In Figure 9, some of these measurements have been superimposed on the calibration curve of the total ethylene content (established in Fig. 7). Owing to the different distribution of ethylene units giving satisfactory fitting with the calibration line, it is clear that the molar extinction coefficients of ethylene units are close to each other whatever their position.

A particular attention has been paid to PP/EP15 to PP/EP19 samples, which differ mainly by the amount of ethylene in the EP rubber (see Table 1b) and by the viscosity ratio of the last sample (PP/EP19), which is higher than for PP/EP18 sample.

As expected, there is an increase of crystalline PE with the amount of ethylene in the EP rubber. No difference is observable between the two samples with the same ethylene content but with different viscosity ratios.

A comparison was performed between the PE crystallinity measured by infrared—this method appeared as the most convenient using the experimental results of this study—and the n^{2+} parameter calculated from liquid phase NMR experiments and defined as the number-average sequence length for methylene sequences ($n^{2+} \geq 2$) (Fig. 10). It confirms the good correlation between PE crystallinity and ethylene content. Once again, there is no difference between PP/EP18 and PP/EP19 samples.

CONCLUSION

A method of deconvolute an FTIR spectrum was developed to study EP and iPP/EP systems. A number of points are well established, such as the method and the good correlation between FTIR and ^{13}C-NMR results for the total ethylene content. Moreover, structural defaults were evidenced by FTIR both in EP and iPP/EP. A crystallinity level can also be deduced from the ratio S

Table VI   Values of the PP Default Determined by FTIR and ^{13}C-NMR

Sample	S_{752}/S_{1167}	[PP Default]/[CH$_3$]
EP15	1	0.03
EP16	0.9	0.04

Table VII   Composition of EP and EP/iPP Samples After Deconvolution

Sample	Total Ethylene	Isolated Ethylene	PP Default	S (cryst)/S (total ethylene)	% Cryst
EP7	19	6.9	0.3	0.070	1.3
EP8	22	7.0	0.4	0.086	1.9
EP9	26	7.0	0.4	0.11	2.8
EP10	31	6.9	0.4	0.14	4.5
EP11	43	6.5	0.5	0.20	8.7
EP12	47	6.0	0.5	0.24	11
EP13	57	4.5	0.5	0.29	16
EP14	61	2.5	0.4	0.46	28
PP/EP1	12	0.50	0.1	0.25	3.0
PP/EP2	8.0	1.0	0.1	0.21	1.7
PP/EP3	8.3	1.1	0.1	0.16	1.4
PP/EP4	8.7	0.85	< 0.1	0.23	2.0
PP/EP5	7.2	0.62	< 0.1	0.23	1.7
PP/EP6	7.7	0.74	< 0.1	0.22	1.7
PP/EP7	6.6	0.37	< 0.1	0.27	1.8
PP/EP8	7.0	0.59	< 0.1	0.20	1.4
PP/EP9	7.8	0.61	< 0.1	0.22	1.8
PP/EP10	7.5	0.65	< 0.1	0.20	1.5
PP/EP11	7.4	0.65	< 0.1	0.20	1.5
PP/EP12	8.6	0.85	< 0.1	0.20	1.7
PP/EP13	6.9	0.43	< 0.1	0.24	1.6
PP/EP14	6.5	0.41	< 0.1	0.25	1.6
PP/EP15	16	0.84	0.1	0.29	4.6
PP/EP16	15	1.2	0.1	0.23	3.4
PP/EP17	13	1.8	0.1	0.17	2.3
PP/EP18	11	2.3	0.1	0.12	1.3
PP/EP19	12	2.7	0.1	0.12	1.4

(crystalline)/S (total ethylene). To progress in this field, it must be of interest, for example, to determine the molar extinction coefficients of the deconvoluted bands. A subsequent paper will be devoted to NMR, DSC, and FTIR char-

acterization of the crystalline degree and crystal dimensions of ethylene runs in iPP/EP samples.
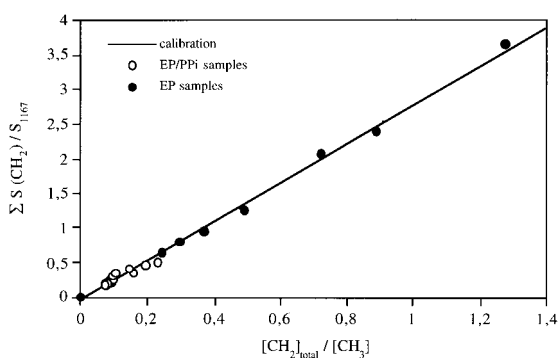

Figure 9   Comparison between calibration curve (established in Fig. 7) and FTIR and ^{13}C NMR results (validation).
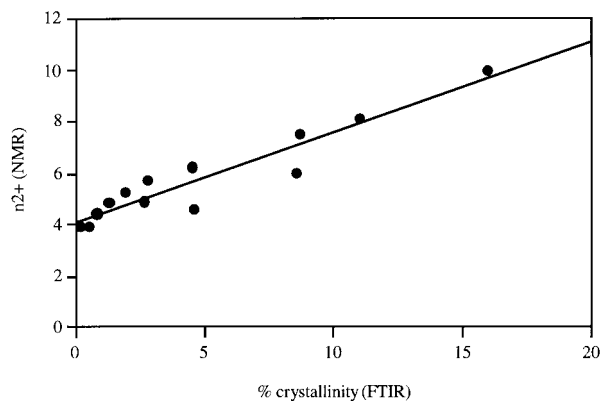

Figure 10   Correlation between the n^{2+} parameter calculated from liquid phase NMR and PE crystallinity measured by IR spectroscopy for all EP samples used in this work.

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