^{13}C-{^1H} n.m.r. determination of the microstructure of poly(butene-I)

M. Mauzac
CDF Chimie, Centre de Recherches Nord, Département Polyoléfines, BP No 1, 62670 Mazingarbe, France
and J. P. Vairon and P. Sigwalt
Laboratoire de Chimie Macromoléculaire associé au CNRS, Université Pierre et Marie Curie, 4, Place Jussieu, 75230 Paris Cedex 05, France

INTRODUCTION

Industrially available poly(butene-1), obtained through Ziegler–Natta catalysis, is a highly isotactic material, with generally a very low soluble content (extraction by refluxing with Et_2O or CH_2Cl_2) assumed to be essentially composed of the amorphous part and of the low molecular weight stereoregular chains of the polymer. Thus an evaluation of the average tacticity of this soluble fraction might lead to the overall isotactic content of the crude polymer, and the ^{13}C n.m.r. technique appears to be the most reliable for this purpose. First published ^{13}C n.m.r. spectra of poly(butene-1)[1,2] concerned samples with very high isotactic content and no stereoregularity effect could be revealed on these spectra.

We intend to report here on the tacticity of the soluble fraction of poly(butene-1) as observed by ^{13}C n.m.r. and on the determination of the overall isotactic content of crude polymers.

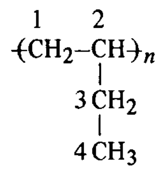
EXPERIMENTAL

Isotactic poly(butene-1) samples (CDF Chimie) with different soluble contents (1 to 25%, extracted by refluxing with CH_2Cl_2) were chosen for this study. The 25,15 MHz ^{13}C–{^1H} spectra of crude polymer, highly isotactic insoluble fraction and atactic soluble fraction were recorded on a JEOL PFT-100 spectrometer. *FID* were stored in 8K computer locations using a spectral window of 1 kHz, a pulse width corresponding to a ~90° flip and a pulse interval of 4.1 sec. Observations were performed at 100°C on 10% (w/v) solutions in 1,2,4-trichlorobenzene/benzene-d_6 mixtures (3:1 v/v) with TMS as internal standard. Overlapping peaks of the spectra were hand resolved and tacticity determination was performed from area measurements.

Polybutadiene RB 820, from JSR., with 92% 1,2 content* was hydrogenated in toluene solution at 80°C and under 100 bars hydrogen pressure using divided nickel as catalyst (promotors: $(acac)_2Ni$, $AlEt_3$). Hydrogenation yield was about 95% as determined by i.r. and ^1H n.m.r.

RESULTS

In *Figure 1* we compare the proton decoupled ^{13}C spectra of an isotactic industrial poly(butene-1) and its atactic extracted fraction. Chemical shifts and assignments of the different carbons (partial decoupling technique) agrees with previously reported data[1,2]. It appears here that the chain methylene carbon (1) is almost unsensitive to tacticity whereas the other carbons (2) (3) and (4) are differently sensitive to the expected triad effect, the largest effect being observed on side methylene carbon.



$$\overset{1}{\leftarrow CH_2}-\overset{2}{\underset{\substack{| \\ 3\,CH_2 \\ | \\ 4\,CH_3}}{CH}}\rightarrow_n$$

The single peak observed for chain CH (2) in the highly isotactic fraction splits into two peaks in the atactic sample. Assignment of the lowest field resonance to the isotactic triad is unequivocal as the chemical shift of this peak is exactly the same in the two spectra. The high field largest peak may be assigned to overlapping (*h* + *s*) triads resonances. This allows the determination of isotactic triad content in the extrac-

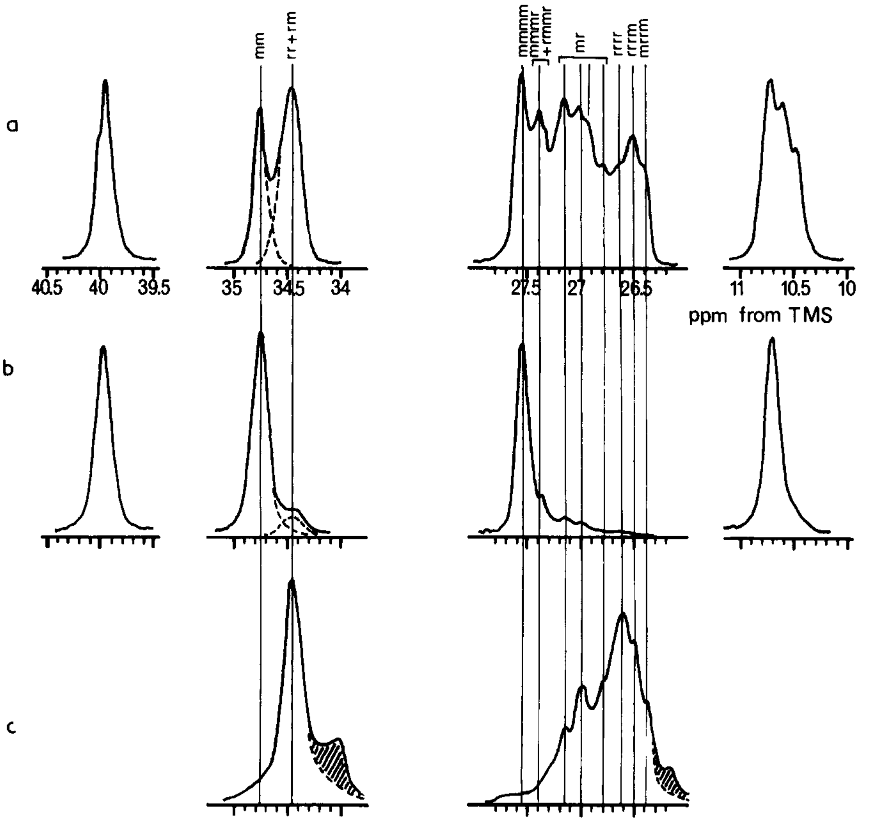


Figure 1 25.15 MHz ^{13}C n.m.r. spectra of crude poly(butene-1) (b) and of its atactic soluble fraction (a). Comparison with resonance patterns of stereosensitive carbons of a hydrogenated syndiotactic 1,2 polybutadiene (c). Peaks corresponding to ch–CH_2, ch–CH, s–CH_2, and s–CH_3 in order of increasing field. (Streaked peaks in spectrum (c) correspond to structural defects due to vicinity of hydrogenated 1–4 units. See refs 4 and 5)

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* As determined by i.r.; Technical notice on JSR RB 820 Japan Synthetic Rubber Co. Ltd, No.1,1 chome, Kyobashi, Chuo-ku, Japan.

ted atactic polymer.

The side methyl carbon (4) is much less stereosensitive than carbons (2) and (3) and does not allow any tacticity evaluation. The broad pattern which is observed for side $\underline{C}H_2$ (3) resolves into three main peaks corresponding to the expected triads resonances. Each of these peaks exhibits a pentad effect. Assignment of each main peak to separated iso-, hetero- and syndiotactic triads in order of increasing field might be doubtful as the nearest pentad resonances may overlap or mix. Such an assignment is nevertheless supported by the observed agreement between isotactic content determinations through the chain $\underline{C}H$ (2) and then through the side $\underline{C}H_2$ (3) patterns, on all the soluble extracts we examined. Typical results are given in *Table 1*.

Table 1 Comparison of tacticity determinations on chain methine and side methylene patterns

	Chain $\underline{C}H$ (2)*		Side $\underline{C}H_2$ (3)†		
Soluble extract of sample	*i*	*h* + *s*	*i*	*h*	*s*
I	0.27	0.73	0.29	0.35	0.36
II	0.37	0.63	0.35	0.34	0.31
III	0.51	0.49	0.48	0.25	0.27
Hydrogenated 1,2-Polybutadiene	Unmeasurable		0.06	0.34	0.60

* Accuracy: ±0.02;
† Accuracy: ±0.03

Table 2 Examples of microstructure determination on crude poly(butene-1) samples with various soluble contents (extraction by CH_2Cl_2)

Crude sample	Insoluble content (%)	Isotactic fraction of soluble extract (a)	Estimated* isotactic fraction of insoluble polymer (b)	Isotactic fraction of crude sample computed from (a), (b) values and soluble content	Isotactic fraction of crude sample (direct measurement)
IV	73.5	0.31 ± 0.02	0.86 ± 0.03	0.71 ± 0.03	0.70 ± 0.03
V	86.0	0.33 ± 0.02	0.86 ± 0.03	0.79 ± 0.03	0.81 ± 0.03
VI	91.8	0.39 ± 0.02	0.88 ± 0.03	0.84 ± 0.03	0.83 ± 0.03
VII	97.0	0.36 ± 0.02	0.96 ± 0.03	0.94 ± 0.03	0.92 ± 0.03

^{13}C n.m.r. analysis was performed on chain-$\underline{C}H$ pattern.
* Estimated from expanded spectra of the corresponding polymers.

A better confirmation is given by analysis of a model of syndiotactic poly(butene-1) obtained through catalytic hydrogenation of a syndiotactic 1,2-polybutadiene. ^{13}C n.m.r. tacticity determinations on this polybutadiene were performed on the vinyl ($=\underline{C}H_2$) carbon as reported in the literature[4–6]. Results ($i = 0.06$, $h = 0.31$, $s = 0.63$; accuracy, ±0.03) are in good agreement with values found for the corresponding hydrogenated polymer (*Table 1*).

A tentative assignment of side $\underline{C}H_2$ (3) resonance pentads of atactic polybutene, qualitatively obtained by comparison of spectra of isotactic, predominantly syndiotactic and atactic samples is given in *Figure 1*. Syndiotactic (*rrrr, mrrr, mrrm*) and isotactic *mmmm* pentads may be reasonably assigned, whereas isotactic *mmmm* and *rmmr* resonances are not resolved. The distribution of heterotactic pentads remains undetermined.

CONCLUSIONS

It appears from the above results that microstructure determination may be performed using the ^{13}C n.m.r. resonance patterns of the chain methine and side methylene carbons of atactic soluble fraction of industrial poly(butene-1). When the isotactic content of the crude polymer is equal or lower than 0.9, a direct determination of isotacticity is allowed by resolution of the peaks (or shoulder) on the chain $-\underline{C}H$ pattern. For the highest values, this leads only to a rough estimation. The average isotactic content of the crude polymer might be theoretically determined from that of the soluble extract, if the insoluble fraction could be considered as fully isotactic. It appears, in fact, that the heterotactic and syndiotactic residues of the insoluble fraction cannot be neglected (*Table 2*) and isotactic content of the crude sample may be reached by correcting the value accurately found for the soluble extract with that estimated from the expanded spectrum of the insoluble fraction. Results in *Table 2* show that isotactic contents measured using this method agree with directly determined values.

Thus, it may be concluded that, within the classical *NOE* and T_1 restrictions on quantitative comparison of peak areas, the pulsed ^{13}C n.m.r. is a reliable method for determining the absolute tacticity of poly(butene-1). We recently observed that *NOE* was close to its maximum value for all carbons of monomer unit and we are presently investigating the influence of tacticity on the T_1 of stereosensitive carbons[3].

ACKNOWLEDGEMENT

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