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CHARACTERIZATION OF POLYPROPYLENE BY PYROLYSIS
GAS CHROMATOGRAPHY

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SUMMARY

A new method for the determination of polypropylene tacticity has been developed. The ratio established for the C₄ hydrocarbon content in the pyrolyzate permits the identification of the individual types of polypropylene, and the quantitative determination of the isotactic polypropylene content.

INTRODUCTION

Great potentiality is offered by pyrolysis gas chromatography for the quantitative determination of the microstructure of polymers. Our previous investigations on polyethylene have shown, that the microstructural differences can be determined with high precision when the requirements on reproducibility are met¹. The published papers concerning the investigation of polypropylene by pyrolysis gas chromatography generally describe the identification of polypropylene specimens and the study of the degradation mechanism²⁻¹⁰.

There has been some attempt to determine the stereoregularity of polypropylene by pyrolysis gas chromatography^{20,23} but no results of this technique when applied as an analytical method for the identification and quantitative determination of polypropylene stereoregularity are given. The present work describes a simple pyrolysis gas chromatography method for the determination of polypropylene tacticity.

EXPERIMENTAL

The pyrolysis was carried out in a furnace type pyrolyzer²¹ within the temperature range of 300–500°. A short precut column was used to prevent the entry of the heavier fragments of pyrolyzate into the chromatographic column¹. The analyses of the light hydrocarbons were performed on a Perkin-Elmer Model 800 gas chromatograph under the following conditions:

Column: 2 m length, 6 mm O.D.; 5 % Carbowax 20 M on alumina 30–60 mesh pretreated with 50 % NaOH in methanol.

Carrier gas: He, 60 ml/min, 2.8 atm.

Sample weight: 0.5–1 mg.

Temperature program: 25–200° (2 min 25°, 2 min 50°), programming rate 5°/min.

The samples of polypropylene investigated were as follows:

Isotactic polypropylene: the insoluble part of a commercial type polypropylene (Moplen, Montecatini) which was dissolved in *n*-heptane.

Atactic polypropylene: the soluble part of the polymer when dissolved in propane.

Syndiotactic polypropylene SMC-77 with a syndiotacticity index of 1.8.

Blends of atactic and isotactic polypropylene prepared from solutions of atactic and isotactic polymers in xylene.

Polypropylene samples of the following different compositions:

No.	Atactic polymer (%)	Stereoblocs (%)
134	0.31	4.2
348	0.36	7.1
350	0.73	8.8

which were prepared in the Research Institute for Macromolecular Chemistry, Brno.

RESULTS

A typical pyrogram obtained under the above stated conditions is shown in Fig. 1.

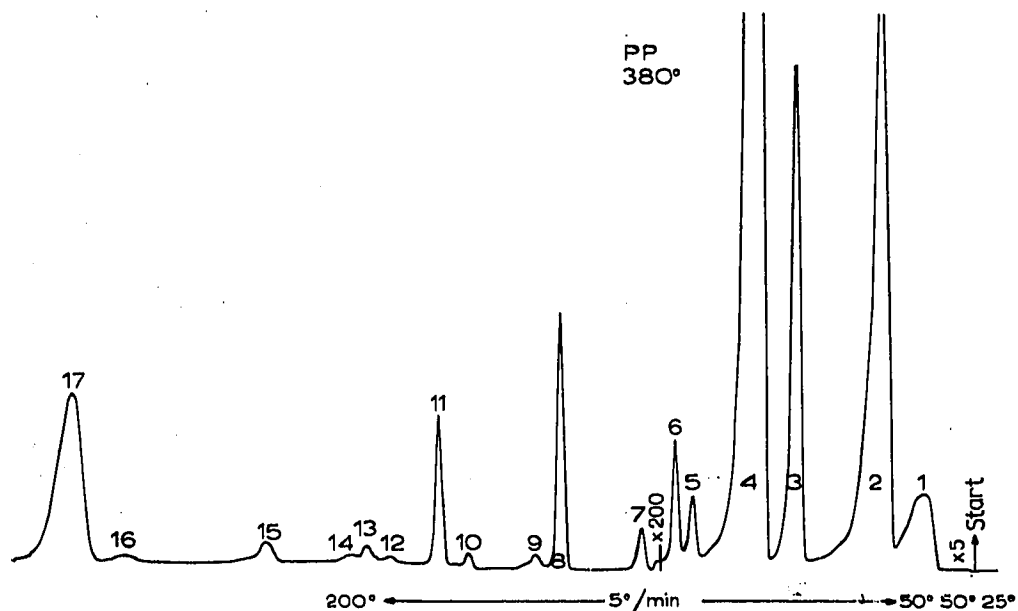


Fig. 1. Pyrogram of polypropylene. Peak No.: 1 = methane; 2 = ethane + ethylene; 3 = propane; 4 = propylene; 5 = isobutane; 6 = *n*-butane; 7 = butenes; 8 = *n*-pentane; 9 = pentenes; 10 = 3-methylpentane; 11 = hexenes; 12 = 2,4-dimethylpentane; 13 = 2-methylhexane; 14 = heptenes; 15 = 4-methylheptane; 16 = isononane; 17 = nonenes.

The lightest fraction of hydrocarbons originating from the pyrolysis of isotactic, atactic and syndiotactic polypropylene is shown in Fig. 2. The samples of isotactic polypropylene in relation to atactic and syndiotactic polypropylene showed a decidedly lower content of *n*-butane in the pyrolyzate. The characteristic relationships between isobutane and *n*-butane are evident for the individual polypropylene types. This relationship has been employed successfully for the identification of individual polypropylene types and for the determination of the isotactic polymer content in the polypropylene samples.

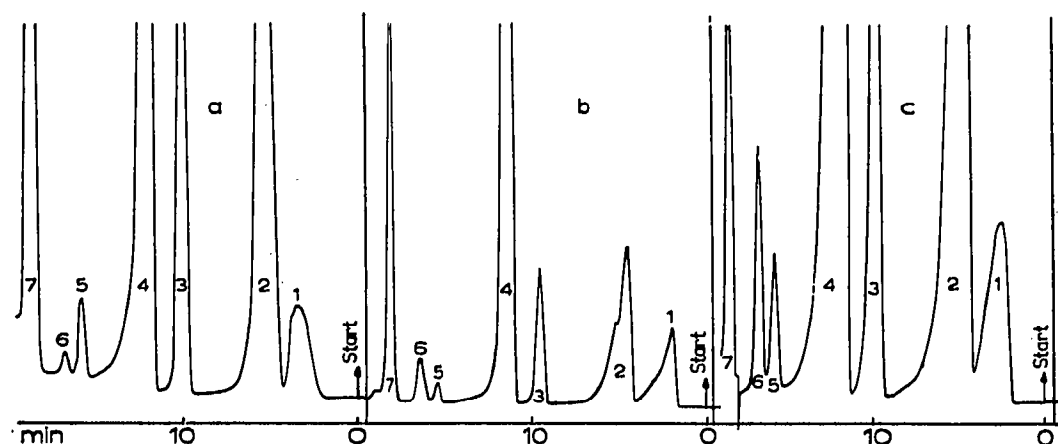


Fig. 2. Composition of the C_1 - C_4 hydrocarbon fraction in the pyrolyzate of (a) isotactic, (b) syndiotactic and (c) atactic polypropylene. Peak No. 1 = methane; 2 = ethane + ethylene; 3 = propane; 4 = propylene; 5 = isobutane; 6 = *n*-butane; 7 = butenes.

TABLE I

THE RELATIONSHIP OF THE CHARACTERISTIC PEAK RATIO $isoC_4/nC_4$ AND THE PYROLYSIS TEMPERATURE FOR ISOTACTIC, SYNDIOTACTIC AND ATACTIC POLYPROPYLENE

	300°	350°	420°	500°	550°
i-PP	4.10	3.10	2.30	1.80	1.68
s-PP	0.24	0.37	0.60	0.75	0.87
a-PP	0.25	0.39	0.66	0.90	0.93

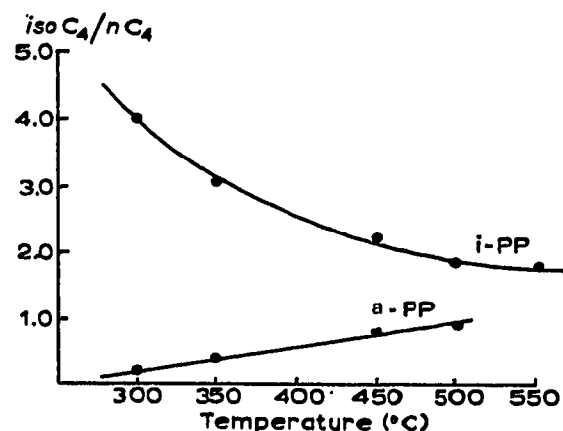


Fig. 3. Plot of $isoC_4/nC_4$ ratio versus temperature for isotactic and atactic polypropylene.

The established ratio of $isoC_4/nC_4$ was examined within the temperature range of 300–550° (see Table I).

It is of notable interest that not only do the differences between isotactic and both atactic and syndiotactic polypropylene become several times greater (Fig. 3) at lower temperatures, but that the existing differences in the $isoC_4/nC_4$ ratio between atactic and syndiotactic polypropylene become negligible (Table I). Likewise, no significant differences between stereoblocs and atactic polymer are noticeable.

From this it could easily be concluded that the quantitative determination of isotactic polypropylene in a mixture with atactic and syndiotactic would be much more convenient at lower pyrolysis temperatures.

However, some serious problems are encountered in performing the analysis at low temperatures. The slow degradation reactions result in broad overlapped peaks and prevent the precise measurement of the interesting peaks. Another problem is presented by the fact that in spite of the several times greater $isoC_4/nC_4$ ratio obtained with a low degradation temperature, the very small peaks obtained in the pyrograms, particularly in the case of isotactic polypropylene, strongly affect the precision and accuracy of results.

The difficulties in the chromatographic separation originating from slowly formed pyrolysis products can be avoided by a simple procedure: the inlet part of the chromatographic column is cooled in order to concentrate the pyrolysis products, and the dominant olefin components in the pyrolyzate are removed by a subtraction method²².

However, we could not make use of the great advantage of high difference in the $isoC_4/nC_4$ ratios for isotactic and atactic polypropylene at 300°, because of the very small amount of pyrolyzate formed. A higher pyrolysis temperature had to be used and therefore, the results presented were obtained with a pyrolysis temperature of 380°.

The investigation with blends of known structure was carried out to establish the relationship between the *iso*- and *n*-butane content, and the sample composition. The results obtained point to the existence of a linear relationship between the $(isoC_4 - nC_4)/isoC_4$ ratio and the amount of isotactic polypropylene in the sample (Fig. 4).

Owing to the linear relationship between $(isoC_4 - nC_4)/isoC_4$ ratio and the sample

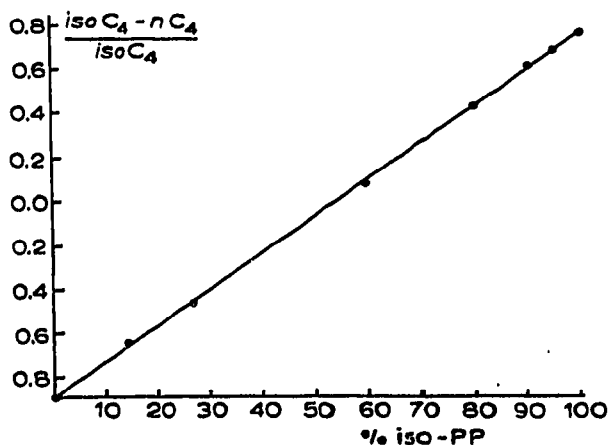


Fig. 4. Relationship between $(isoC_4 - nC_4)/isoC_4$ ratio and polypropylene blends composition.

composition, the procedure becomes very simple. In order to construct a calibration curve it is quite enough to determine the established ratio for pure isotactic and atactic polymer.

The agreement between the results obtained and the real blend composition is within $\pm 1.0\%$ of the isotactic polymer content. The maximum deviation in the results (Table II) does not exceed ± 0.020 , which corresponds to $\pm 1.0\%$ of the isotactic portion in sample. The validity of the results was confirmed with the samples of polypropylene of known composition (Table III). On the basis of the results obtained

TABLE II

REPEATABILITY OF THE INDEX $(isoC_4 - nC_4)/nC_4$

<i>Index value</i>	<i>Mean</i>	<i>Deviation</i>	<i>Standard deviation</i>
0.875		0.000	
0.887		+0.012	
	0.875		± 0.126
0.890		+0.015	
0.870		-0.005	
0.855		-0.020	

TABLE III

ANALYSIS OF POLYPROPYLENE SAMPLES OF KNOWN COMPOSITION

<i>Sample No.</i>	<i>% of isotactic polymer determined by</i>	
	<i>Extraction</i>	<i>PGC</i>
134	95.45	95.5
348	92.52	91.6
350	90.43	91.1

the pyrolysis gas chromatography procedure just described can be recommended as a new method for determination of the isotactic polypropylene content in polypropylene samples.

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