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INTEGRATED ANALYTICAL SCHEME FOR THE DEVELOPMENT OF AN ATACTIC POLYPROPYLENE-BASED OLEFIN-POLYMER PRODUCING TECHNOLOGY

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SUMMARY

An integrated analytical scheme has been elaborated to facilitate the development of a polypropylene waste-based medium-molecular-weight olefin-polymer producing technology. The scheme integrates classical petrochemical test methods (ASTM distillation, fluorescent indicator analysis, iodometric titration), gel and capillary gas chromatography, and both infrared and mass spectroscopic methods, into a comprehensive system which allows both the sufficiently detailed characterization of the product and the optimization of the various stages of the production process. The applicability of the system is demonstrated by the test results of a characteristic production batch.

INTRODUCTION

Some 4-10% (w/w) atactic polypropylene (APP) is formed during polypropylene production. Since the mechanical characteristics and thermal stability of APP are poor, it cannot be used for the same purposes as tactic polypropylene. The volume of the Hungarian polypropylene production is significant, and so is that of APP which, so far, has been considered as a hard-to-dispose-of waste. With the present, ever-increasing emphasis on non-waste or low-waste technologies, the possibilities of utilization of APP have gained in importance.

APP is utilized as a solid fuel, an additive in bitumens, oils or plastics, a component of adhesives, plasticizers and paints, and, after thermal decomposition, as a petrochemical raw material or liquid fuel. Since properly controlled pyrolysis seems to yield products which are both cost-effective and have a good market, experiments were carried out to modify existing Hungarian pyrolysis equipment and make use of the free capacity. This project required a powerful analytical scheme which, on the

one hand characterized the products in sufficient detail, and on the other, could be used to optimize the key steps of the entire production process. This scheme is described here.

EXPERIMENTAL

Raw materials

Atactic polypropylene with a viscosity-averaged molecular weight (MW, \bar{M}_v) of 26,000 was obtained from TVK (Tiszaszederkeny, Hungary). The major steps of the technology developed here are shown in Fig. 1. Details of this process will be described elsewhere¹. Only the liquid fraction obtained in the second separator is dealt with here.

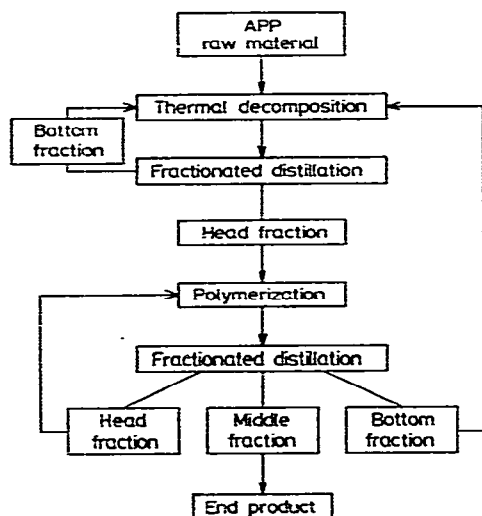


Fig. 1. Scheme of the technological process.

Individual analytical methods

- (1) ASTM distillation².
- (2) Iodometric titration³.
- (3) Fluorescent indicator analysis (FIA)⁴.
- (4) Infrared (IR) spectroscopy. A Specord IR-75 recording IR spectrophotometer (Carl Zeiss, G.D.R.) equipped with sodium bromide cells (pathlength 0.1 mm) was used. The $3200\text{--}2700\text{ cm}^{-1}$ and $1400\text{--}400\text{ cm}^{-1}$ spectral regions were recorded and evaluated as described^{5,6}.
- (5) Gel chromatography. A custom-made gel chromatograph⁷ was used. The column train consisted of two 500-\AA and two 10^4-\AA nominal pore size μ Styragel columns (Waters Assoc., Milford, MA, U.S.A.) connected in series. The eluent was tetrahydrofuran, at a flow-rate of 2.0 ml/min. The calibration curve of the column system was determined with $C_{10}\text{--}C_{24}$ α -olefin standards (Polyscience, Evanston, IL, U.S.A.), polyethylene glycol (molecular weight per angstrom chain length, $Q = 23$)

standards nominal MW = 600–6000) (Serva, Buchs, Switzerland) and polystyrene ($Q = 41$) standards (nominal MW = 4000–17,500) (Waters Assoc.). It can be expressed by the equation where

$$\log M = 10.7078 - 0.2465 V + 1.0084 \cdot 10^{-3} V^2$$

where V is the elution volume in cm^3 and $30 \leq V \leq 44 \text{ cm}^3$.

The peak broadening correction function, H , was determined^{8,9} as:

$$H = 9.5692 - 0.4067 V + 0.0063 V^2$$

The response coefficient of the Fresnel-type differential refractometer was considered constant over the entire polyolefin molecular weight range tested. The molecular weight distribution (MWD) function and the average MWs were calculated as described¹⁰ by an EMG 666 desk top calculator (EMG, Budapest, Hungary).

(6) *Capillary gas chromatography (GC)*. A custom-made¹¹ Pyrex capillary (15 m \times 0.27 mm I.D., 0.9 mm O.D.) (Sovirel, France) was persilylated^{12,13} with hexamethylene disilazane and statically coated with a 0.2- μm thick layer of OV-1 as stationary phase (Applied Science Labs., State College, PA, U.S.A.). Separations were carried out on a custom-modified GCHF-18.3 gas chromatograph (Chomatron, Berlin, G.D.R.) using a splitting ratio of 1:50, initial and final temperatures of 80°C and 320°C and a programme rate of 6°C/min. The carrier gas was hydrogen with a linear gas velocity of *ca.* 50 cm/sec.

(7) *Mass spectrometry*. A MAT 111 gas chromatographic-mass spectrometric (GC-MS) system (Varian MAT, Bremen, G.D.R.) equipped with a 45-m glass capillary column (OV-1, film thickness 1 μm)⁶ was used.

RESULTS AND DISCUSSION

The integrated analytical system developed here is shown in Fig. 2. At first the propylene oligomer mixture (POM) obtained during the thermal decomposition of APP is characterized by relevant analytical methods. ASTM-distillation indicates the distillation limits for the next technological step, fractional distillation. The MWD curve, number and weight-averaged molecular weights, \bar{M}_n and \bar{M}_w , as well as the polydispersity factor, $\alpha = \bar{M}_w/\bar{M}_n$, characterize the product formed. There is a fairly close correlation between the ASTM-distillation limits and the MWD, so in the second stage, during the optimization of the pyrolysis conditions, only the MWD is determined for each sample. Once the final pyrolysis conditions are established, another ASTM-distillation is carried out.

FIA and iodometric titration yield the class composition of the sample and the total of amount unsaturation. Using this value, the average molecular weight and the absorbance values at 967 and 890 cm^{-1} taken from the IR spectra, the distribution of unsaturation by bond-type (% w/w *trans*-olefin and vinylidene) can be determined⁶. The average number of methyl and methylene groups in an average molecule can also be determined according to Bélafiné-Réthy⁵ from the absorbances at 2958 and 2927 cm^{-1} , and the average molecular weight.

The next step is the determination of the oligomer-distribution of the POM. It is known¹⁴⁻¹⁶ that, depending on the pyrolysis conditions, polypropylene decomposes in a characteristic fashion. Since the technological aim is the production of as much of a selected oligomer as possible, the oligomer distribution (fingerprint chro-

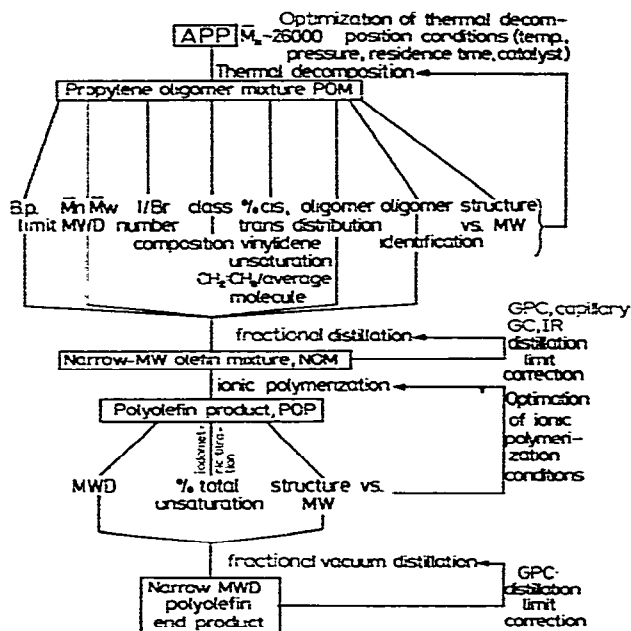


Fig. 2. Scheme of the integrated analytical method.

matogram) as determined by capillary GC is very informative. Combined GC-MS was used to establish the chemical identity (carbon number) of the major peaks in the capillary chromatogram of the POM. Thus, in further tests capillary GC alone, based on the elution temperatures, proved sufficient for the characterization of the oligomer distribution of the sample.

As a final step in the characterization of the sample, narrow molecular weight fractions were obtained by semi-preparative gel chromatography (using the same column train, but increased sample loadings and combining the fractions taken from 50 successive separations of the same sample). Only IR spectra and capillary gas chromatograms were taken for these fractions. It could be concluded that the general structure (regarding the olefinic bond) of the pyrolysis product (POM) was approximately identical over the entire molecular weight range of the sample.

Once the main characteristics of the POM became known the pyrolysis conditions were modified so as to maximize the amount of the target oligomer (C_9 and C_{15} , respectively). Therefore, the reaction temperature, average residence time, reactor pressure, feed rate and separator temperatures were varied, and the MWDs and the capillary chromatograms of the products were determined. These two plots proved sufficiently informative, fast and simple to allow for a fairly detailed technological optimization.

Once the pyrolysis conditions yielding the POM are optimized, this fraction is subjected to fractionated distillation. ASTM-distillation, MWD and oligomer distribution by capillary GC were used to determine the optimum distillation parameters. The narrow MW olefin mixture (NOM) was then again analysed by IR, but later on, during production, only the MWD and oligomer distribution by capillary GC were taken.

In the next stage the NOM is subjected to batchwise ionic polymerization and a polyolefin with $\bar{M}_w \approx 500$ is produced. Since the volatility of this product is low only gel permeation chromatography (GPC), iodometric titration and combined semi-preparative GPC-IR spectroscopic examinations were carried out. The latter showed that the average structure of the polyolefin molecule (regarding the olefinic bond) is approximately constant over the entire MW range of the sample. Therefore, GPC alone proved sufficient for the optimization of the polymerization conditions.

Once the polymerization conditions were optimized the polyolefin product (POP) was subjected to vacuum distillation. The distillation fractions were once again analysed by GPC and the distillation conditions were optimized. Eventually, the end product was characterized by its MWD, \bar{M}_n , \bar{M}_w and iodine/bromine number.

In order to demonstrate the use of the system a few analytical results for a typical sample are shown here (Figs. 3-10, Table I).

The 859-kg/m³ APP ($\bar{M}_z \approx 26,000$) was pyrolyzed yielding the POM. Its ASTM-distillation curve is shown in Fig. 3, the MWD in Fig. 4, IR spectra in Fig. 5 and capillary gas chromatogram (oligomer distribution) in Fig. 6. The MWD of the NOM sample after fractionated distillation is shown in Fig. 7, its capillary gas chromatogram in Fig. 8 and the mass spectrum of the main chromatographic peak in Fig. 9. The NOM

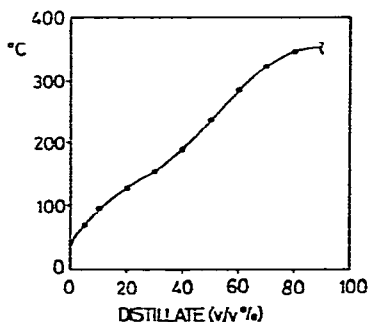


Fig. 3. The ASTM-distillation curve of the POM².

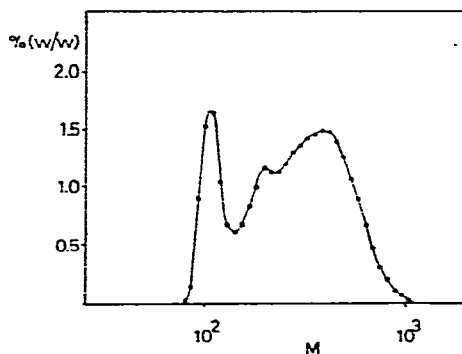


Fig. 4. The molecular weight distribution of the POM.

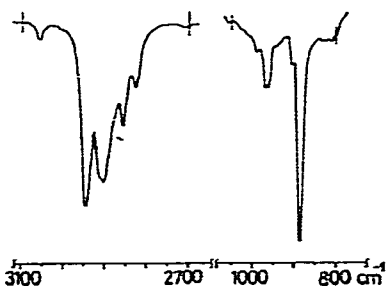


Fig. 5. Parts of the IR spectrum of the POM.

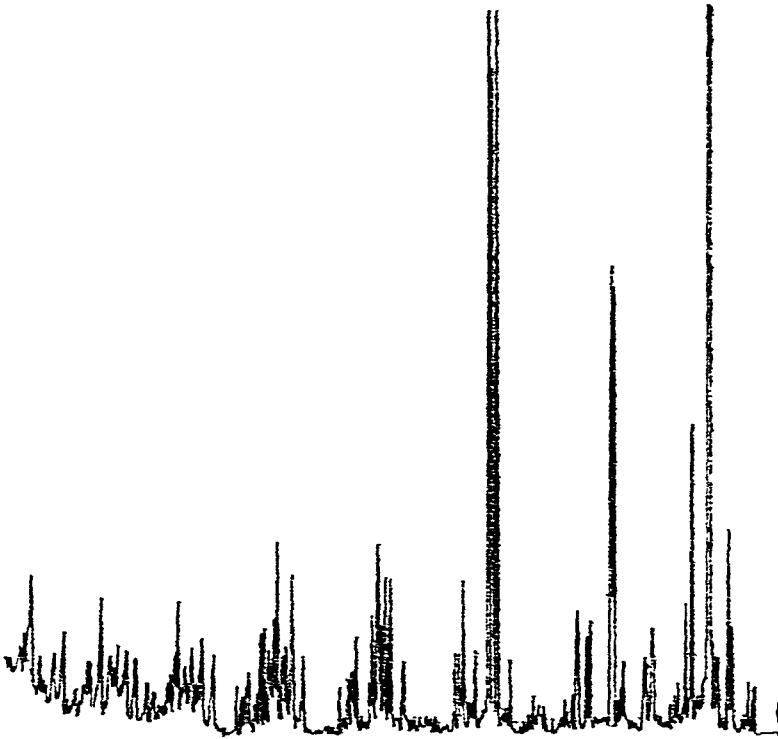


Fig. 6. Capillary gas chromatogram of the POM.

was subjected to ionic polymerization with AlCl_3 yielding the polyolefin mixture, whose MWD is shown in Fig. 10. The MWDs of the head, middle and bottom fractions of this POP are also shown in Fig. 10. It can be seen that the production goal set at the beginning, *i.e.*, the production of an olefin polymer with a fairly narrow MWD and predetermined average MW, could be achieved.

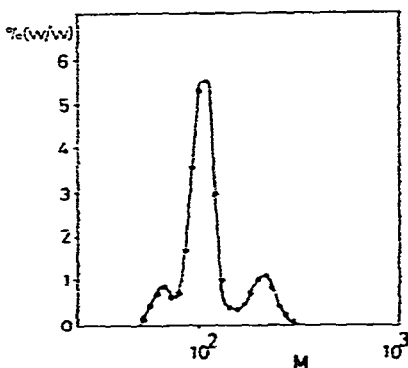


Fig. 7. The molecular weight distribution of the POM after fractionated distillation.

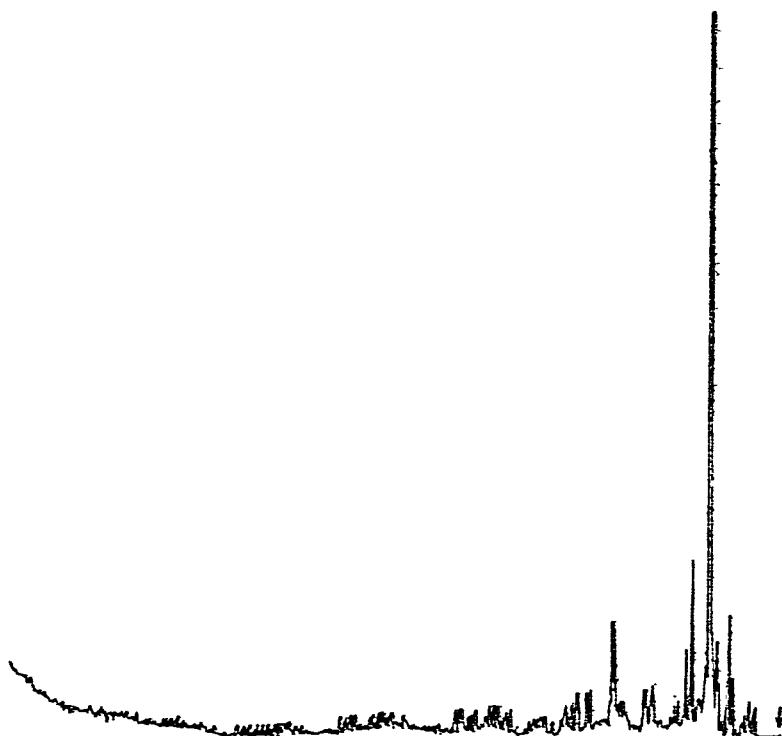


Fig. 8. The capillary gas chromatogram of the POM after fractionated distillation.

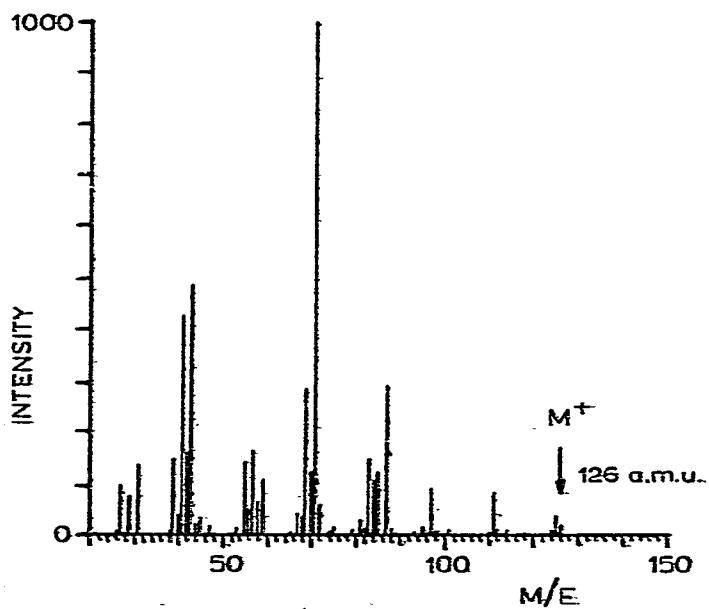


Fig. 9. Mass spectrum of the major chromatographic peak in Fig. 8.

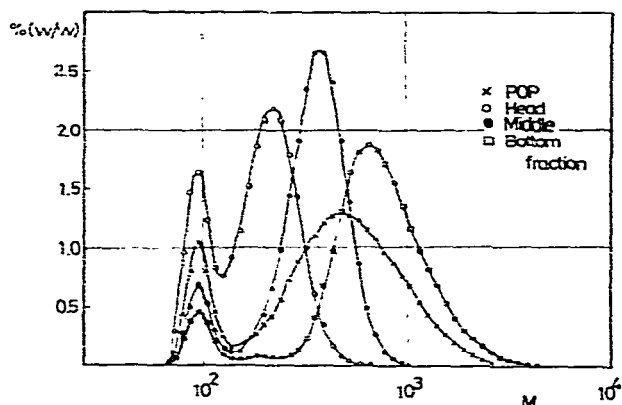


Fig. 10. The molecular weight distributions of the polymerization mixture, and of the vacuum distilled fractions.

TABLE I

SELECTED CHARACTERISTICS OF THE BATCHES SHOWN IN THE FIGURES

Atactic polypropylene

Density 859 kg.m³
 $\bar{M}_z \approx 26.0\%$

Propylene oligomer mixture (POM)

Density 768 kg.m³
 % distillation temp. 238°C
 $\bar{M}_n = 224$
 $\bar{M}_w = 305$
 $\alpha = 1.36$

FIA saturated 21% (w/w)
 unsaturated 79% (w/w)

Olefin distribution by IR

vinylidene (at 890 cm⁻¹) 69% (w/w)
 trans-vinylene (at 927 cm⁻¹) 8% (w/w)

Number of CH₃ groups in average molecule 3.6
 Number of CH₂ groups in average molecule 5.8

Narrow molecular weight oligomer mixture (NOM)

Density 760 kg.m³
 $\bar{M}_n = 120$
 $\bar{M}_w = 132$
 $\alpha = 1.10$

FIA saturated 18% (w/w)
 unsaturated 82% (w/w)

Olefin distribution by IR

vinylidene (at 890 cm⁻¹) 77% (w/w)
 trans-vinylene (at 927 cm⁻¹) 4% (w/w)

I:Br number 156

Polyolefin product (POP)

$\bar{M}_n = 278$
 $\bar{M}_w = 534$
 $\alpha = 1.92$

I:Br number 112

Middle fraction of POP

$\bar{M}_n = 267$
 $\bar{M}_w = 346$
 $\alpha = 1.29$

I:Br number 108

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