

# Investigation of Grafted Impact-Resistant Polypropylene by Temperature Rising Elution Fractionation

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## SYNOPSIS

The goal of the present work is the examination of maleic anhydride (MAN) grafted impact-resistant polypropylene (I-PP), consisting of amorphous rubber and semicrystalline matrix. A special instrument to separate the rubber from the matrix is preparative temperature rising elution fractionation (TREF). Investigations of the isolated fractions permit conclusions on the course of the grafting reaction and side reactions during the modification. The present work has shown that the fractionation is just as possible in the modified products as in the raw material. It has also shown that a grafting reaction occurs mainly in the rubber phase of this two-phase polypropylene. During the grafting reaction, only small degrees of radical degradation of the homopolymeric polypropylene matrix could be detected. © 1997 John Wiley & Sons, Inc.

## INTRODUCTION

Modification of nonpolar polyolefines with maleic anhydride (MAN) is an important possibility to improve the adhesion properties of polyolefines.<sup>1–3</sup>

Simultaneously, with the production of impact-resistant, two-phase polypropylene, the concern was to graft such materials by extrusion. It is expected that the presence of a rubber phase ( $T_G \ll$  ambient temperature) in the semicrystalline matrix ( $T_G >$  ambient temperature) leads to a different grafting efficiency in these two phases. In the molten state, both phases remain immiscible. Consequently, it seems possible to modify the phases separately.

Successful characterization of the generated reaction products can be carried out only after complete separation of the rubber phase from matrix material. In the present work, the separation has been done by the temperature rising elution fractionation (TREF). This technique permits isolation of the components of the reaction products by separating the semicrystalline polymers ac-

ording to their crystallizabilities.<sup>4</sup> The graduation of solubility force results only from the extraction temperature. That means the separation is mainly determined by the chemical structure of the analyzed polymer (monomer sequence distribution in copolymers, branching degree in polyethylene, and tacticity in polypropylene).

Impact-resistant polypropylene (I-PP) can be made by blending rubbers in the polypropylene homopolymer<sup>5</sup> or directly during the synthesis in a two-reactor system. The material used for the present investigation is a reactor blend of ethylene-propylene rubber particles in a homopolymeric polypropylene matrix, generated in a polymerization process in the gas phase. It is a commercial product of BASF AG, Ludwigshafen.

The article describes the separation and following characterization of the isolated phases of grafted impact-resistant polypropylene. The results allow to describe the mechanism of the grafting reaction of MAN onto I-PP during melt modification.

## EXPERIMENTAL

### Materials

The I-PP was supplied by BASF AG, Ludwigshafen, and contained approximately 45 wt % dis-

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persely distributed ethylene-propylene rubber particles. The ethylene content of the commercial product was approximately 18 wt %; the melt flow index of the raw material was 4.2 g/10 min.

The I-PP was modified in a twin screw extruder (ZSK 30/Werner & Pfleiderer) at a temperature profile from 180 to 210°C by adding 0.1 wt % peroxide (di-*tert*-butyl-peroxide) and 2 wt % MAn. The titrated grafting degree was 0.93%. For comparison, a similar procedure was performed with only 0.1 wt % peroxide addition.

### Fractionation by TREF

The polymer was fractionated by preparative TREF. The polymer samples were dissolved in xylene at 125°C and introduced into the column of the apparatus, packed with an inert support (ballotini, diameter  $\sim 200 \mu\text{m}$ ). Subsequently, the column was closed and cooled to room temperature with a rate of 5°C per hour. The following fractionation was done with the same solvent by slow heating in incremental steps of temperature and removing the polymer phases at selected temperatures.

These fractions were precipitated with methanol, separated, and dried in vacuum at 60°C. The impact-resistant polypropylene was fractionated into three parts at the following temperatures: 60, 96, and 128°C.

### Characterization of the Separated Fractions

The MAn content of the isolated fractions was determined by titration with alcoholic KOH (0.05 *n*) to a thymol blue endpoint.<sup>6</sup>

Since PP undergoes chain scission during radical modification, the molecular weights of the fractions were checked by SEC using a Knauer high-temperature measurement equipment at 135°C. The eluent was 1,2,4-trichlorobenzene, stabilized with diphenylamine. The average molecular weight values were calculated by using polyethylene with known molecular weight distribution.

The thermal behavior of the fractionated samples was determined on a Perkin-Elmer DSC 7 calorimeter. The samples were heated within a temperature range from -60 to 210°C with a heating rate of 10 K/min.

Fourier transform infrared (FTIR) spectroscopy was made on pressed films with a thickness of approximately 100  $\mu\text{m}$ . The films were pressed between aluminium sheets at 130°C. After storage of the pressed films in vacuum (120°C, 24 h), the

**Table I** Percentage of the Separated Fractions

Sample <sup>a</sup>	Amount of the Fractions (wt %)			Yield (%)
	60°C <sup>b</sup>	96°C	128°C	
A	36.5	7.9	55.6	100
P	34.8	7.6	57.6	100
G	25.8	4.4	51.8	82

<sup>a</sup> A, raw material; P, I-PP extruded with 0.1 wt % peroxide; G, I-PP grafted with 2 wt % MAn and 0.1 wt % peroxide.

<sup>b</sup> Temperatures are fractionation temperatures.

samples were scanned in an FTIR Perkin-Elmer 1700 in transmission mode. The amount of grafted anhydride was determined by the integral ratio of the carbonyl band at 1790  $\text{cm}^{-1}$  to the methyl band of polypropylene at 2722  $\text{cm}^{-1}$ . The size and shape of this band are not influenced by the modification reaction and can be used as an internal standard.

## RESULTS AND DISCUSSION

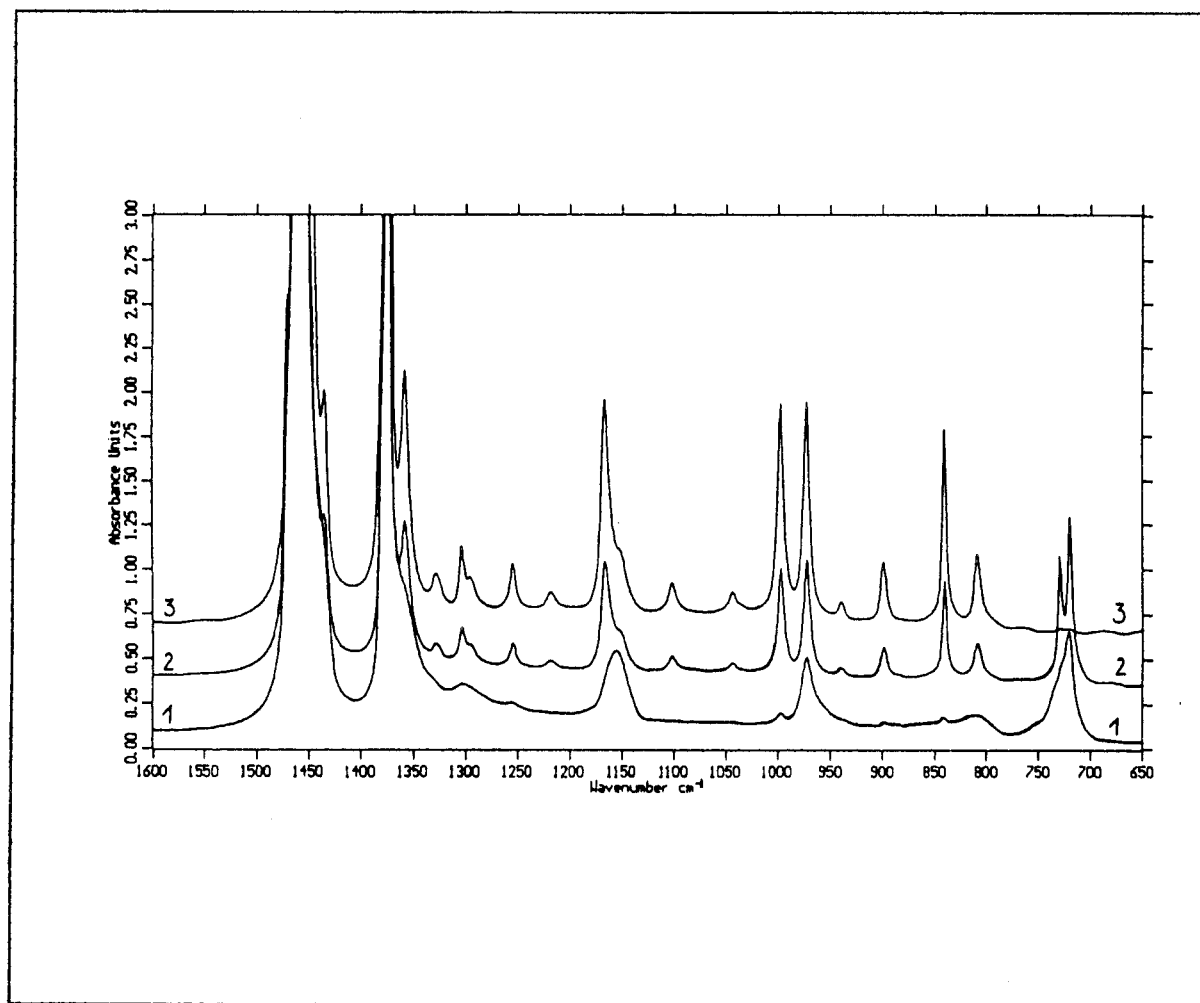
The primary object of the following study was to demonstrate the courses of both the grafting and degradation reactions in the two phases of I-PP.

To compare the results, three different samples were fractionated: the virgin material, the sample extruded with 0.1 wt % peroxide, and the one with 2 wt % MAn and 0.1 wt % peroxide. In the following, the investigated samples will be referred to by letters which designate the sample (A, raw material; P, with peroxide treated sample; and G, grafted sample) and by numbers which give the fractionation temperature. For instance, the sample "A-60" is the rubber fraction of the raw material fractionated at 60°C.

### Fractionation by TREF

The fractionation was carried out as described. The percentages of the separated fractions are listed in Table I.

Both the raw material and the material containing peroxide were completely extracted. The MAn modified sample was only partially removed from the fractionation column. The reason for this effect is the known good adhesion of the grafted anhydride groups onto the hydroxyl groups of the glassy support material of the column. Pyrolytic investigations of similarly treated ballotini-sup-



**Figure 1** FTIR spectra of the fractions of raw material: 1, A-60; 2, A-96; 3, A-128.

port showed the existence of MAN-*g*-PP after reiterated washing in hot xylene. This result indicates the partial coupling of grafted chains onto glass material of the column.

### Structural Investigations of the Fractionated Samples

FTIR analyses were performed for all fractions. The spectra of the fractions of raw material are given in Figure 1.

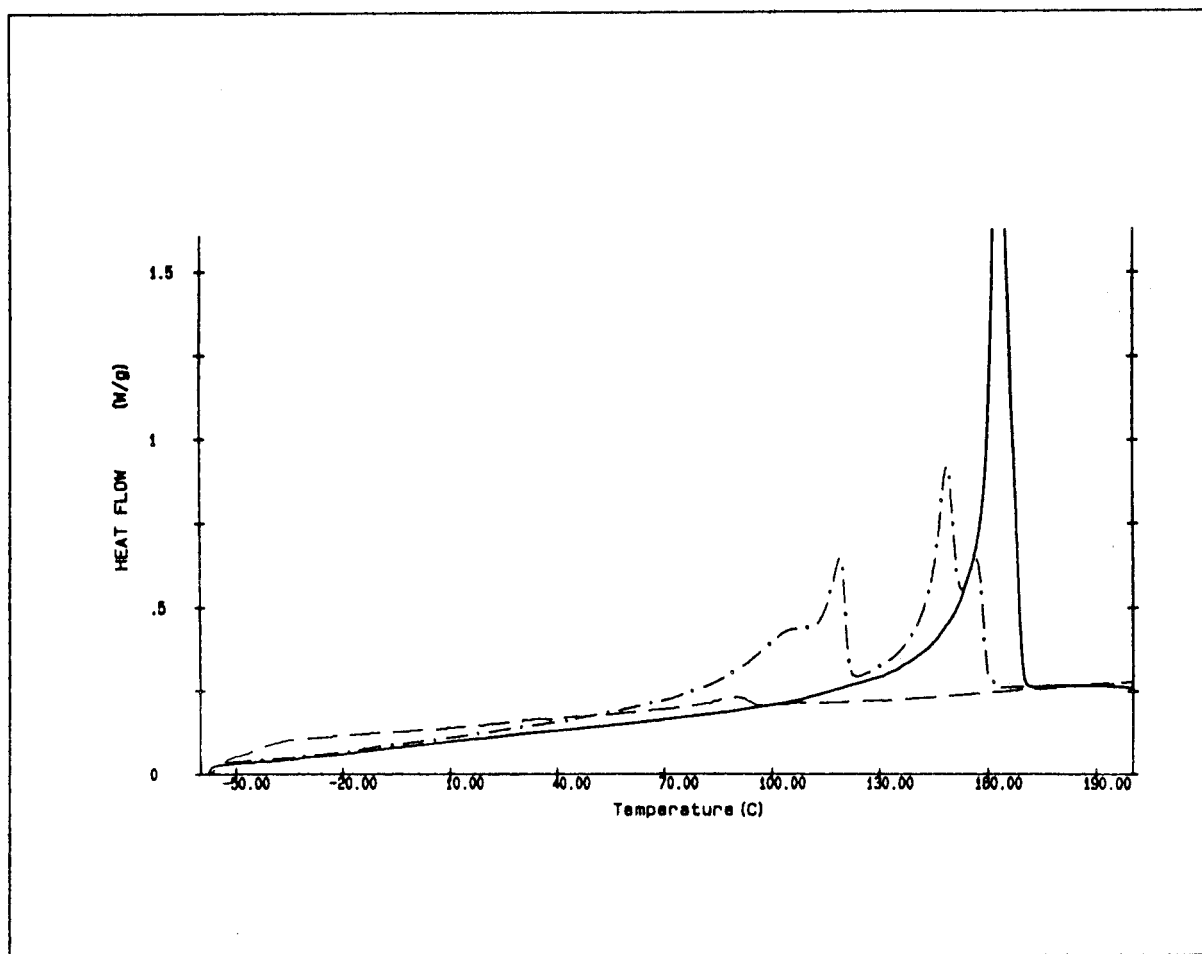
The bands at 722 and 735  $\text{cm}^{-1}$  are characteristic of ethylenic structures with different lengths of the ethylenic sequences, and the bands in the range from 1350 to 1470  $\text{cm}^{-1}$  are characteristic of propylenic structures.

The ratio of the absorbances at 974 and 998  $\text{cm}^{-1}$  characterizes the crystalline form of polypropylene, and the ratio of the band at 1167  $\text{cm}^{-1}$  and

the shoulder at 1156  $\text{cm}^{-1}$  is influenced by the tacticity of the PP.<sup>7,8</sup>

The shape of spectrum 1 leads to the conclusion that the fraction A-60 can be characterized as an amorphous, atactic ethylene-propylene copolymer with ethylenic sequences of more than five units.

Spectrum 3 is a typical spectrum of an isotactic, partially crystalline homopolymeric PP. The shape of spectrum 2 shows that the fraction obtained at 96°C contains both ethylenic and propylenic structures with a high crystallinity (comparable with the homopolymeric PP). The final structure of the fraction collected at 96°C cannot be explained exhaustively by FTIR measurements alone. However, the investigation of the thermal behaviour of this fraction by DSC-measurements (Fig. 2; A-96) allows further conclusions on its probable composition.



**Figure 2** DSC thermograms of the fractions of raw material: - - -, A-60; - · -, A-96; —, A-128.

The thermogram of the sample A-96 shows two melting regions containing multiple melting peaks. This result indicates that the fraction collected at 96°C consists of at least two parts, probably some ethylene-propylene copolymers with different monomer distributions.

The other thermograms are the typical ones of amorphous rubber (Fig. 2; A-60) and crystalline polypropylene (Fig. 2; A-128), respectively.

### Investigation of the Grafting Reaction

The results obtained from titration of the grafted fractions are summarized in Table II. The values of grafting degree show that grafting of maleic anhydride takes place mainly in the rubber phase. Only a small part of MAn is grafted in the other phases. This is probably caused by different distributions of the monomer in the rubber and the

homopolymeric PP. The distribution of low molecular substances should be influenced by the different solubility of MAn in both phases (different solubility parameters of the polymers<sup>9</sup>), by the different molecular weights of rubber and homopolymeric polypropylene and the resulting different melt viscosities, and probably by various diffusion rates of the low molecular substances into the rubber or polypropylene. Summarizing, dur-

**Table II** Results of Titration of the Fractions of the Grafted Sample

Sample	Grafting Degree (wt %)
G-60	0.63
G-96	0.10
G-128	0.04

**Table III Molecular Weights of the Fractionated Samples**

Sample	$M_w \times 10^{-4}$ (g/mol)	$M_n \times 10^{-4}$ (g/mol)	$M_w/M_n$
A-60	17.15	3.01	5.7
A-96	28.2/11.1	—	—
A-128	17.6	4.27	4.1
P-60	3.76	1.17	3.2
P-96	20.9/1.0	—	—
P-128	14.0	3.67	3.8
G-60	2.8	1.06	2.6
G-96	1.48	0.69	2.1
G-128	9.40	2.87	3.3

ing extrusion, the monomer enriches in the rubber phase more than in the PP matrix.

Other indications for such a monomer distribution are the different grafting degrees of the phases containing ethylenic structures (G-60, G-96), which differ in their ethylenic contents (and also in the amounts of grafted MAn), and the very low grafting degree in the homopolymeric matrix (G-128).

Hence, a separate grafting reaction occurs only in the rubber phase of the two-phase material. Consequently, it is possible to carry out the separate grafting reaction in one processing step.

### Investigation of the Degradation Reaction

The mechanism of radically initiated degradation of polypropylene is well known in the literature.<sup>10</sup> On the other hand, polyethylenic macroradicals undergo chain branching reactions rather than scission of the polymeric backbone.<sup>11</sup> The reasons for the different radical reactions in these polymers are the different dissociation energies of the hydrogens on the secondary carbon of the polyethylenic and the tertiary carbon of the polypropylenic chain<sup>6</sup> and the differing stabilities of the generated macroradicals.<sup>12</sup>

The results in Table III show that addition of peroxide causes reduction of molecular weight in all fractions. However, in contrast to our expectations, this degradation is significantly higher in the rubber phase than in the other ones. The decrease of molecular weight is stronger than expected from the chemical structure of the rubber. Taking into account that chain degradation is more probable in PP sequences, a much stronger decrease in molecular weight should be expected

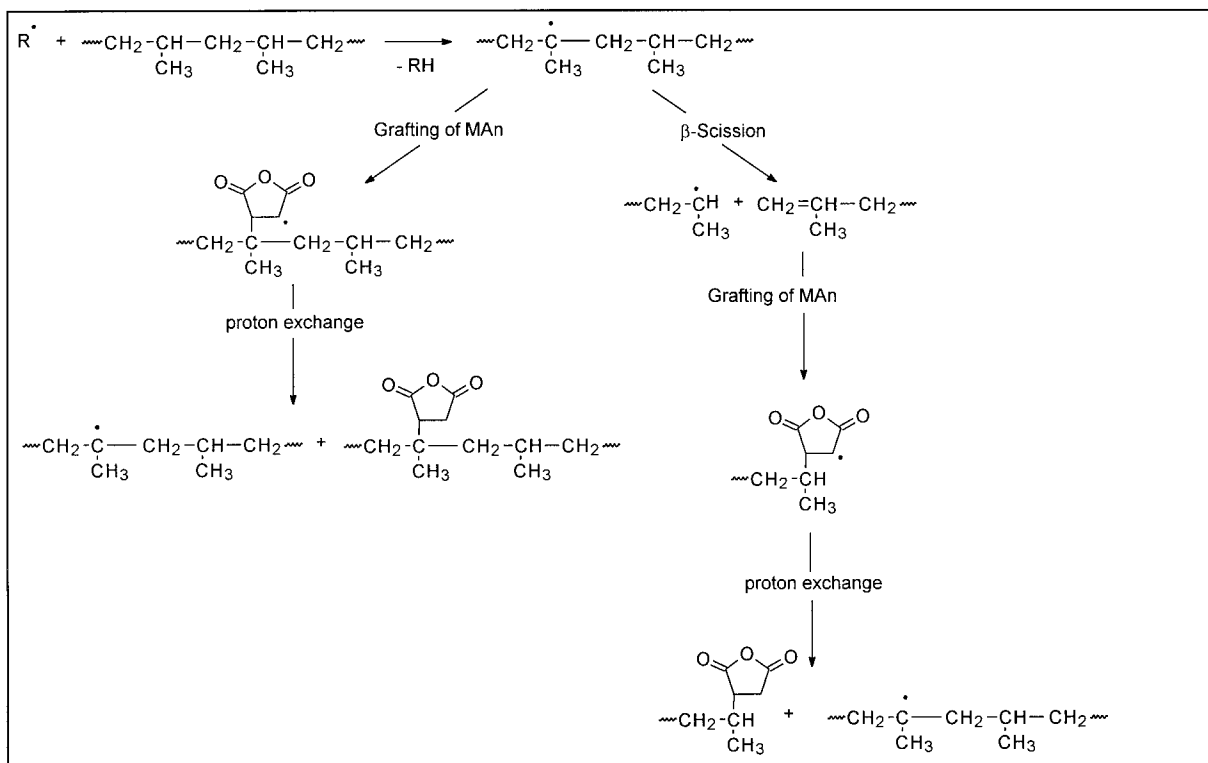
for the PP-matrix. However, just the opposite behaviour has been found. There are two possible explanations for this result. First, as mentioned above, the peroxide is distributed more in the rubber phase than in the PP matrix of the polymer blend. Second, the rate of degradation of the propylenic units in the rubber is higher than the chain branching rate of the ethylenic ones. The addition of MAn leads to a further decrease of the average molecular weight. The grafted succinic anhydride radical is known to withdraw intra- or intermolecularly a proton to generate a new radical center in the polymeric chain. When a molecule of MAn is not grafted onto this new radical, the chain can undergo  $\beta$ -scission at this radical centre (see also Fig. 3).

IR spectroscopy and differential scanning calorimetry (DSC) measurements have shown that the fraction collected at 96°C contains two phases with different chemical structures. This could also be confirmed by GPC. For both samples, A-96 and P-96, a bimolecular distribution in molecular weight has been found. After grafting reaction, the fraction G-96 shows only a monomolecular distribution and yields only one value of average molecular weight  $M_w$ . The reason for this change in molecular weight distribution is probably caused by interchain reactions between both phases. The bimolecular distribution confirms the existence of two different products in this fraction. The long-chain E/P copolymer with only few propylenic units ( $M_w = 28.2 \times 10^4$  g/mol) does not undergo a strong degradation as compared to the short-chain E/P copolymer with higher content of propylenic units ( $M_w = 11.1 \times 10^4$  g/mol). The strong decrease of average molecular weight in the short-chain copolymer (see Table III, A-96 to P-96) confirms the assumption that the scission of propylenic units takes place with higher rate than the chain branching of ethylenic macroradicals.

Radically initiated degradation in the homopolymeric PP phase is less significant as compared to the rubber phase (A-128/P-128 and A-60/P-60). The enrichment of peroxy radicals in rubber would lead to a lower level of free radicals in the surrounding matrix. Hence, the degradation reaction should be prevented in the homopolymeric phase.

### CONCLUSIONS

It has been shown that the distribution of low molecular substances in the polymer melt during



**Figure 3** Reaction scheme of grafting and degradation reaction.

extrusion has an important influence on the efficiency of the grafting reaction. The enrichment of monomer and peroxide in the amorphous rubber leads to a separate grafting reaction.

Consequently, the separate grafting of the disperse phase with maleic anhydride during one manufacturing step seems possible. The radically initiated degradation reaction of the surrounding matrix can be suppressed because the concentration of peroxide in the polymeric matrix is very low.

Thus, separate grafting of the rubber phase has been shown to be possible with a reduced tendency of radical degradation of the homopolymeric matrix.

The main mechanism of the grafting reaction seems to be a competition between grafting and degradation reaction.

In addition, TREF was an effective method to fractionate not only the virgin product, but also the modified one.

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