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Free radical grafting of maleic anhydride in vapour phase on polypropylene film[☆]

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Abstract

The formation of a graft polymer is observed when polypropylene as a film reacts with maleic anhydride in the vapour phase in the presence of peroxide. The activity of the employed peroxides decreases in the order: dicumylperoxide > bis(tert. butylperoxy-isopropyl)benzene > benzoylperoxide. The grafting reaction is not limited to the surface, but also takes place inside the film. Besides this reaction takes place on the film surface the formation of groups which give in ATR spectra a diffuse absorption band in the range between 1664 and 1500 cm^{-1}. The modified film is characterised by a wetting tension of 35 dynes/cm and exhibits the anhydride group characteristic properties. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Grafting; Polypropylene; Maleic anhydride

1. Introduction

The homogeneous grafting of maleic anhydride (MA) on atactic polypropylene dissolved in xylene was investigated by using benzoyl peroxide as the initiator [1]. Isotactic polypropylene as a powder was modified using high concentrations of initiator at temperatures lower than the melting temperature of the polymer [2]. Strongly oriented polypropylene fibers were modified with MA in the vapour phase [3]. The photografting reaction of polyethylene or polypropylene film with acrylic monomers [4] using UV radiation took place after deposition on the surfaces of controlled quantity of benzophenone as a sensitizer from an acetone solution. A mechanism of the grafting reaction of MA or related compounds on polyolefins or model substances [6] and some hypothesis on the grafted polymer structure were set forth in other articles [1,5]. Polypropylene grafted with MA may be used to prepare incompatible polymer alloys like polypropylene and polyamides [7] or as coupling agent to bond metallic surfaces or the glass fiber to the polypropylene matrix. An index of many applications is reported in the article of Rengarajan et al. [2].

Polypropylene is an ideal polymer for packaging film. It is resistant to moisture permeation but is not effective in inhibiting the passage of oxygen: This gas may adversely affect foods or others materials. Coating must be applied if oxygen barrier properties are required to protect the content. Obtaining adhesion of coating or inks or of other polar materials is of great importance for the development of new application of polypropylene film.

The aim of this article is to study the MA grafting reaction in the vapour phase onto a polypropylene film using low peroxide concentrations. Another objective of the article is the evaluation of the chemical reactivity of the modified film.

2. Experimental part

Isotactic polypropylene cast film: mean tickness, 60 μm; M_n 25 700 Da; M_w 2 31 000 Da from Moplefan.

The content of stabilizer may be evaluated in few ppm and is probably a residue of the processing antioxidant. In fact the IR spectra of the film as received and after extraction with ethyl ether (eight hours at boiling temperature) show negligible differences.

MA 99% from Fluka, dicumylperoxide (DICUP) 98% from Aldrich, and bis(tert. butylperoxyisopropyl)benzene (PEROXIMON) 98%, a mixture of *meta* and *para* isomers

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Table 1
Grafting reaction of MA on the polypropylene film in the presence of: DICUP, T°C 150, time 2 h, $[\mathrm{MA}]_{\mathrm{vap}}$ 7.2×10^{-3} mol/1; PEROXIMON, T°C 160, time 4 h, $[\mathrm{MA}]_{\mathrm{vap}}$. 9.4×10^{-3} mol/1

	DICUP				PEROXIMON		
Peroxide g/100 g PP	0.2	0.6	0.8	1	0.1	0.45	0.6
Grafted MA concentration (g/100 g)	0.18	0.42	0.5	0.8	0.27	0.62	[a]

[a] The film melts and decomposes.

from Ausimont, were used as received. Benzoylperoxide (Bz_2O_2) 98% was obtained by crystallization from a solution in chloroform of a commercial product containing 25% of water.

The surfaces of a weighted sample of the film (0.6 g on average) were treated with 0.46 g of 0.26% peroxide solution in toluene. This quantity was used when the weight of the added peroxide was 0.2% of the polymer. After evaporation of the solvent, the film covered with a layer of peroxide was placed in a pyrex glass reactor containing at the bottom 0.3 g of MA as a solid. A film sample was extracted with ethyl ether at reflux for two hours and the peroxide was determined iodometrically. The analysis result showed that the peroxide was about 98% of the calculated quantity.

The reaction was carried out in nitrogen atmosphere in an oven heated at the selected temperature. Solid MA quickly reaches equilibrium with its vapour phase, which is in contact with the polypropylene film. The film surface was about 90 cm^2 and the film was separated from the walls of the reactor in which some protrusions were obtained. After reaction the film was washed twice for two hours with ethyl ether or methanol in a rotovapor in order to eliminate the unreacted monomer and peroxide residues. Then the film was dried at 40°C under vacuum. The right extraction time was established in preliminary experiments with a film containing dissolved MA.

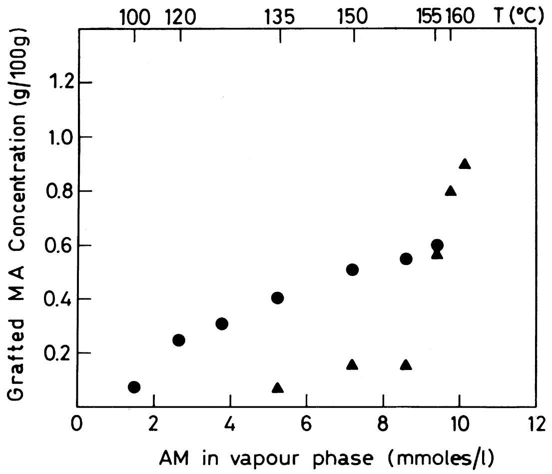


Fig. 1. Content of MA in the grafted copolymer vs. MA concentration in vapour phase. Reaction conditions: ● DICUP 0.881%, time: 2 h; ▲ PEROXIMON 0.513%, time: 4 h.

The grafted MA content was determined by using a solution in xylene of the film to which there was added a small quantity of water. In average was used a mixture of 70 ml of xylene and 25 ml of water. The titration of the acidity was made with a 0.01 N solution of KOH in isopropyl alcohol at 60°C using phenolphtalein as indicator. The contact between the two phases being obtained by magnetic stirring of the mixture.

The reactivity of the modified film was shown by reaction with selected reagents in the conditions indicated in the text. After treatment the film was washed and dried under vacuum for eight hours at 40°C.

The polymers MMD's were measured at 135°C by gel permeation chromatography (GPC Waters 150) using *o*-dichlorobenzene as solvent. Molecular weights were calculated with Benoit universal calibration.

IR transmission spectra of the film were recorded between 1530 and 1830 cm^{-1} using a FT-IR Nicolet 20SXB spectrometer. ATR measurements were taken on an accessory equipped with an internal reflection element KRS-5 with variable incident angle furnished by Harrich Co. In order to remove the volatiles from the surface, the film to be analysed was placed under high vacuum at room temperature for 72 h in the presence of silicagel.

The wetting tension was measured by ASTM D2578 procedure using liquids having a known value of surface tension. The wetting tension of the polypropylene film will be approximated by the mixture surface tension, which just wets the film surface for exactly two seconds.

The tensile properties were measured by ASTM D 638 procedure using an INSTRON 4302 dynamometer at the rate of 50 mm/min.

3. Results

The reaction was carried out with MA in the vapour phase. The concentration of the monomer is constant and determined by its vapour pressure at reaction temperature [8]. The reaction times were selected on the basis of the known values of half-life time and decomposition kinetic constants of the peroxides found in the literature [9,10].

Table 1 shows the percentage of monomer grafted with different concentrations of DICUP and 1-3 bis(*tert*-butylperoxyisopropyl) benzene after reaction times sufficient for a realistic total decomposition of the initiators. Experiments with 0.6% of Bz_2O_2 after a reaction time of one hour gave a product containing only 0.2% of grafted monomer. This result indicates that Bz_2O_2 is less active than other initiators in the grafting reaction.

The film modified using Bz_2O_2 shows values of tensile properties $\sigma_r = 36.3$ Mpa and $\epsilon_r = 606\%$ which are very close to the properties of the as-received film $\sigma_r = 45.4$ Mpa and $\epsilon_r = 606\%$.

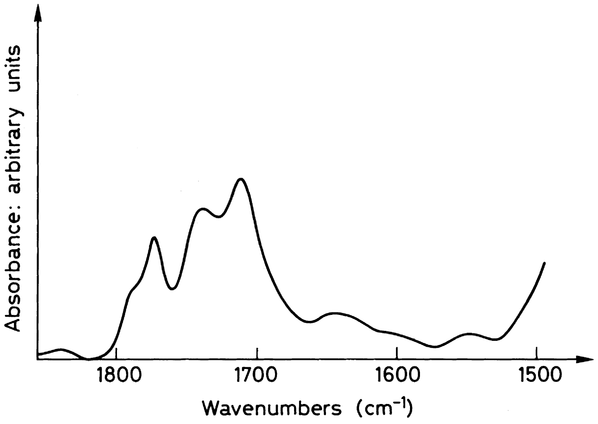


Fig. 2. IR transmission spectrum of polypropylene film grafted with MA and washed with methanol.

Grafting reaction does not take place in the absence of a peroxide. The IR spectrum of a film heated for 1 h at 120°C with only MA and washed by static contact with methanol at room temperature shows the bands characteristic of the monomer. These bands disappear after the film has been washed for 2 h at 40°C in rotavapor. This result indicates that the monomer has been dissolved in the polymer. The content of MA is 0.35 g/100 g polypropylene and this value may be assumed as the solubility of MA in the polymer at 120°C with a partial pressure of 8.106 KPa. Fig. 1 shows the variation of the grafted monomer content with the temperature and consequently with the monomer concentration in the vapour phase. Experiments lasted for 2 h using 0.85% of DICUP and for 4 h. using 0.5% of PEROXIMON. The weight of the added peroxides gives about the same concentration of radicals bearing in mind that the decomposition of a mole of PEROXIMON gives four radicals while two radicals come from the decomposition of a mole of DICUP. The results obtained indicate that the grafting efficiency of PEROXIMON is lower than that of DICUP at temperatures below 160°C. In average about 4% of MA in the vapour phase participates in the grafting reaction.

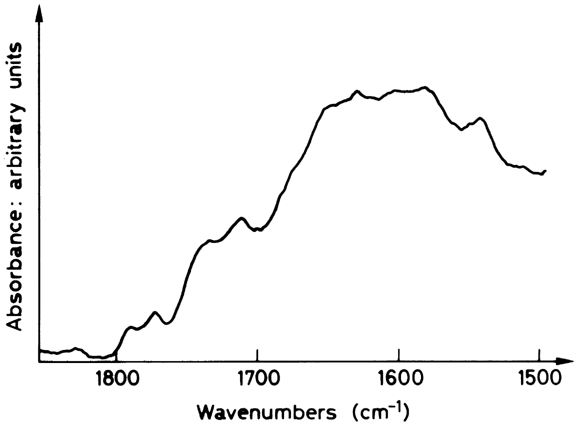


Fig. 3. IR–ATR spectrum of polypropylene film grafted with MA and washed with methanol; penetration depth: 2.3 μm; incidence angle 40.8°.

4. IR spectroscopy of grafted polymer

The monomer distribution in the film grafted and then washed with methanol was studied by ATR technique at incidence angles of 45 and 40.8° which allows one to ascertain the presence of grafted MA at the depth of 1.6 and 2.3 μm, respectively. Figs. 2 and 3 show transmission and ATR IR spectra in the interval 1800–1500 cm^{-1} normalised with reference to the band at 1165 cm^{-1} of isotactic polypropylene.

The ATR spectrum (Fig. 3) shows bands attributed to carbonyl functions between 1819 and 1664 cm^{-1} and a diffuse absorption between 1664 and 1500 cm^{-1}.

The groups which originated this absorption have not been identified.

The ratios of the integrated areas of these absorptions to the integrated area of the polypropylene band at 1165 cm^{-1} are collected in Table 2.

Results indicate that in the region 1819–1664 cm^{-1} the ratios calculated from the transmission and ATR spectra are practically equal and allow one to conclude that the grafting is equally distributed on the surface and in the bulk of the film. The ratio calculated from the transmission spectra of the treated film in the interval 1664–1530 cm^{-1} has the value of 0.34 equal to that of the non modified film. On the contrary the ratio obtained from ATR spectra has the value of 2.29 and 3 which indicates a modification limited to the depth analyzed which takes place at the same time of the grafting reaction. The main band in IR spectrum (Fig. 4 (d)) shows a principal peak at 1784 cm^{-1} and a shoulder at 1792 cm^{-1} which is due to the overlapping of two different bands. Roover et al. [13] after studying the infrared spectra of various polypropylene –g-MA suggested that single units grafts absorb at 1792 cm^{-1} whereas MA oligomers absorb at 1784 cm^{-1}. Applying these conclusions to the analysis of the spectrum shown in Fig. 4 (d) it results that MA was incorporated as a mixture of single units and oligomeric grafts (MA). Yoshi [11,12] carried out at 75.4°C the homopolimerization of MA in absence of solvent by using as initiator also large amounts, 5–10% of Bz_2O_2. The molecular weight of the oligomers obtained was comprised between 500 and 700 Da. These results may suggest that also in our conditions the value of the polymerization degree of grafted MA may be $n < 10$.

The absorbances at 1720 and 1640 cm^{-1} (Fig. 5) are, respectively, attributed to the carboxyl groups formed by the reaction of the anhydro groups with moisture and to the unsaturated groups formed by the scission of the chain as shown at the point (c) of the scheme of reaction.

5. Chemical reactivity of the grafted film

The modified film is characterised by a 35 dynes/cm wetting tension. This value is very close to that of 30 dynes/cm of untreated polymer, and may be due to the

Table 2
Distribution of the chemical modifications of the film as measured by IR–ATR spectroscopy

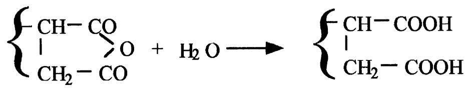
Sample	Depth analyzed μm	Ratio of the integrated areas in the indicated intervals to the integrated area of the polypropylene band at 1165 cm^{-1}	
		1819–1664 cm^{-1}	1664–1530 cm^{-1}
PP untreated	Transmission spectrum	0.20	0.33
PP untreated	ATR spectrum 2.3 μm	0.27	0.58
PP grafted[a]	Transmission spectrum	1.27	0.34
PP grafted[a]	ATR spectrum 1.6 μm	1.17	2.29
PP grafted[a]	ATR spectrum 2.3 μm	1.27	3.00

[a] Reaction conditions: 2 h at 150°C—%DICUP = 0.8 washed for 2 h with methanol in rotovapor at 40°C—MA grafted 0.5%.

low concentration on the surface of MA grafted polypropylene. However grafted polypropylene works rather well as a functionalized substrate as shown by the following results.

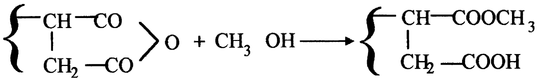
Fig. 4 (e) shows a part of the IR spectrum of a modified film in which the bands at 1792 and 1865 cm^{-1} are attributed to the succinic anhydride.

Fig. 4 (a) and (b) was obtained from the modified film with MA then treated for 3 h at 90°C with 0.5 N hydrochloric acid and water. The absorption bands at 1720 cm^{-1} are attributed to carboxyl groups formed as follows:



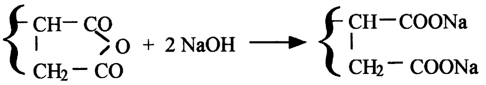
$$\left\{\begin{array}{l}\mathrm{CH-CO}\\ |\qquad\quad >\mathrm{O}\\ \mathrm{CH_2-CO}\end{array}\right. + \mathrm{H_2O} \longrightarrow \left\{\begin{array}{l}\mathrm{CH-COOH}\\ |\\ \mathrm{CH_2-COOH}\end{array}\right.$$

Fig. 4 (c) was obtained from the modified film then treated for 3 h with methanol. The bands at 1720 and 1735 cm^{-1} are attributed to the carboxyl and ester groups formed by the reaction of anhydrosuccinic groups.



$$\left\{\begin{array}{l}\mathrm{CH-CO}\\ |\qquad\quad >\mathrm{O}\\ \mathrm{CH_2-CO}\end{array}\right. + \mathrm{CH_3\ OH} \longrightarrow \left\{\begin{array}{l}\mathrm{CH-COOCH_3}\\ |\\ \mathrm{CH_2-COOH}\end{array}\right.$$

Fig. 4 (d) shows the spectrum of the modified film after reaction for for 3 h at 90°C with a 10% aqueous solution of NaOH. The two bands at 1630 cm^{-1} and at 1720 cm^{-1} are attributed to the carboxylate ions and carboxylic acids formed by reactions of the anhydrogroup with sodium hydroxide and water.



$$\left\{\begin{array}{l}\mathrm{CH-CO}\\ |\qquad\quad >\mathrm{O}\\ \mathrm{CH_2-CO}\end{array}\right. + \mathrm{2\,NaOH} \longrightarrow \left\{\begin{array}{l}\mathrm{CH-COONa}\\ |\\ \mathrm{CH_2-COONa}\end{array}\right.$$

All the spectra show the absorption bands at 1784 and 1792 cm^{-1} characteristic of the succinoanhydro group. This result indicates that in the mild experimental conditions used only the MA present on surface is active.

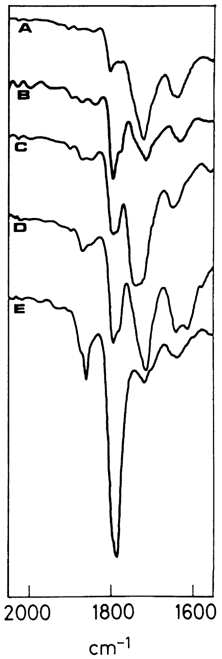


Fig. 4. Infrared spectra of grafted polypropylene in the carbonyl region after various treatments (see text).

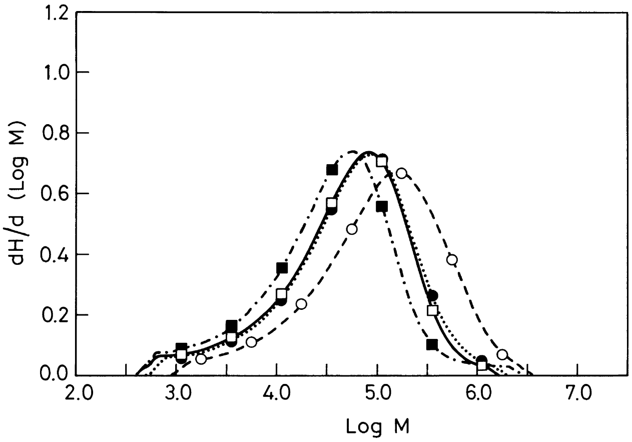


Fig. 5. GPC curves of untreated and modified polypropylene: ○ PP unmodified; ● PP grafted—reaction time 30 min, T 120°C, Bz_2O_2 0.62%; ☐ PP grafted—reaction time 60 min, T 120°C, Bz_2O_2 0.62%; ■ PP modified in the absence of MA—reaction time 60 min T 120°C, Bz_2O_2 0.62%.

Table 3
Molecular weight of treated and untreated polypropylene obtained by gel permeation chromatography

Sample	M_n	M_w	M_w/M_n
PP untreated	25 700	2 31 000	9
PP grafted 30′ 120°C, $\%Bz_2O_2 = 0{,}62$, %MA-grafted = 0.2	13 800	1 14 000	8.3
PP grafted 60′ 120°C, $\%Bz_2O_2 = 0{,}62$, %MA-grafted = 0.2	11 000	97 000	8.7
PP 60′ 120°C, $\%Bz_2O_2 =$ 0.62, absence of MA	9100	87 000	9.6

6. Grafting reaction mechanism

Fig. 5 shows the molecular weight distribution curves obtained by gel permeation chromatography of four polypropylene samples untreated or modified as described in Table 3. The curves show that in comparison with the unmodified polymer the molecular weight distribution and the maxima of the modified materials are shifted to lower values.

Table 3 collects the average molecular weight obtained from the GPC curves.

The M_n value of the polypropylene treated only with 0.62% of Bz_2O_2 in the absence of AM is very close to that estimated taking in to account only the beta scission reaction.

As a matter of fact with reference to a mixture containing 0.62% Bz_2O_2 one mole of the polymer having M_n = 25 700 Da is mixed with 0.637 mol of Bz_2O_2 which by heating gives 1.27 mol of benzoyloxy radicals.

The reaction of benzoyloxy radicals with a macromolecule of the polymer gives 2.27 macromolecular fragments having a calculated M_n 11 321 which is very close to the experimental result. The simple reaction leading to the macroradical scission gives two fragments, which may react with MA to give a modified polypropylene. The grafting reactions indicated G1, G2, G3 in the reaction scheme are possible. However in the presence of initiator the reaction G3 occurs at low extent [1] and is mainly influenced by temperature.

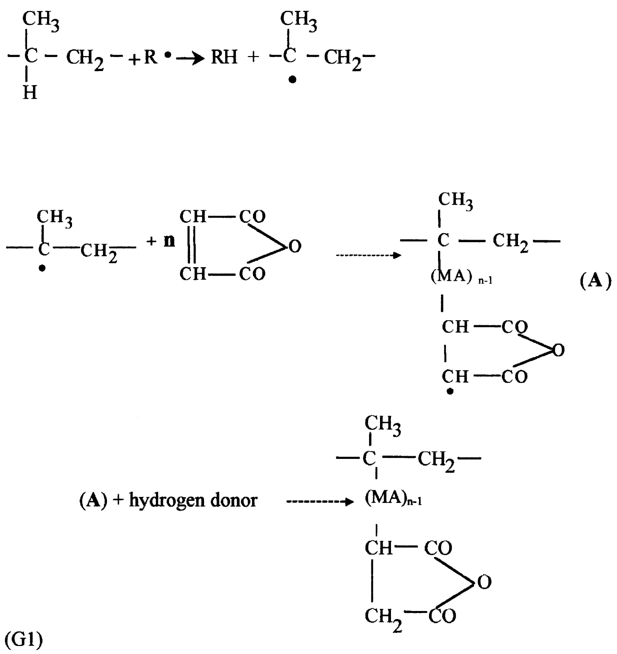
Whereas, grafting MA units without decrease in molecular weight G1 seems to remain negligible. Grafting anhydride units on the radical ended polypropylene chain (G2) may be considered very important in originating MA modified polypropylene.

The content of MA in the grafted polypropylene as determined by titration is 0.2%. The low percentage of the monomer grafted may be related to very poor tendency to MA homopolymerization and at its high chain transfer reactivity [11,12].

The results obtained suggest that the following reaction scheme may be considered as well.

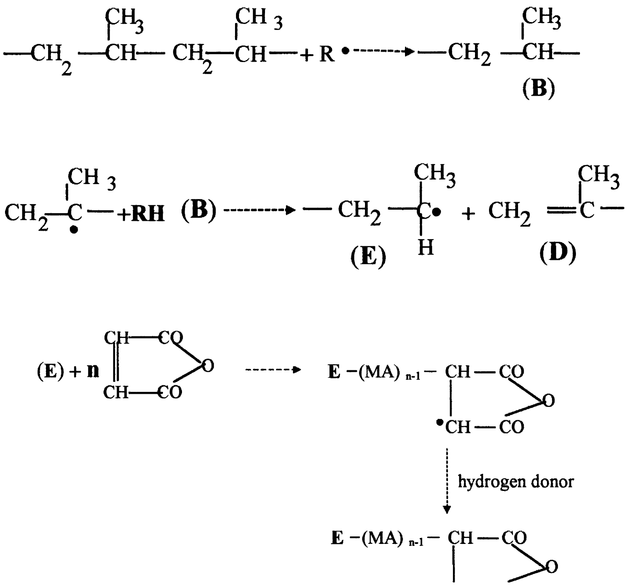
6.1. Graft copolymer formation:

1. Peroxides decomposition.
   1. $I \rightarrow 2R^{\cdot}$ (Bz_2O_2–DICUP);
   2. $I \rightarrow 4R^{\cdot}$ (PEROXIMON).
2. Transfer and grafting reactions.

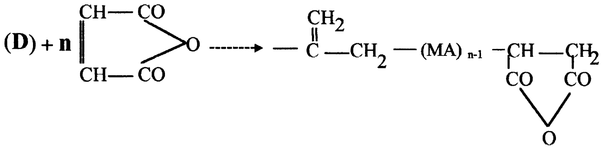


(G1)

3. Chain scission and formation of MA terminated polypropylene.



(G2)



(G3)

7. Conclusions

Film of polypropylene modified with MA may be prepared by the reaction of the polymer with the monomer vapour in the presence of a peroxide. The temperature of the reaction determines both the concentration of the monomer and of the radicals formed by the peroxide decomposition.

The grafting reaction takes place homogeneously with an accompanied degradation of polypropylene.

The ATR spectra show a diffuse absorption between 1664 and 1530 cm^{-1} due to a modification limited to the film surface. The chemical groups, which originated this absorption have not been identified.

The grafted film is reactive and exhibits the properties characteristic of the anhydro groups and a wetting tension of 35 dynes/cm.

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