

Modification of Isotactic Polypropylene by a Cold Plasma or an Electron Beam and Grafting of the Acrylic Acid onto These Activated Polymers

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SYNOPSIS

Surface grafting of polymeric materials, such as films and fibers, may improve their reactive surface properties. Polypropylene active sites that should initiate a surface postgrafting can be formed by either nitrogen cold plasma or an electron-beam irradiation. The plasma-modified polymer surface is cross-linked and functionalized with primary amino groups and with oxidized groups, and it is almost not degraded. Electron-beam-modified polypropylene is also functionalized through an aging reaction, emphasized by a high radical concentration. In both cases, active surface films are susceptible to react with monomers in a postgrafting reaction. The grafting yield and rate of acrylic acid were shown to be dependent on the formed amino group concentration: The hydrophilic character of the modified polypropylene surface enhances the acrylic acid approach. The electron-beam treatment leads also to a reactive surface that can initiate a grafting reaction. But its yield and rate are dependent on the radical concentration: radicals formed during the irradiation. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Much recent research in the polymer field has been focused on blends of different polymers and has emphasized the need of compatibility in such systems to provide new materials. Modification or grafting of polymer films or fibers was proposed. However, most common polymers, such as polyolefins, are unreactive and the surface has to be modified to become reactive. Cold plasma treatment has been proposed,¹⁻³ but leads sometimes to a reactive and therefore unstable surface. Grafting a monomer onto this surface should prevent any aging process. This article describes a two-step surface modification of polypropylene: activation by a cold plasma or an electron beam, then grafting of acrylic acid onto these surfaces.

Polypropylene surface modification by a CO₂ or N₂ plasma^{1,4} is characterized by degradation, cross-

linking, functionalization, and activation. For a grafting reaction, activation of polypropylene with nitrogen plasma seems to be the most efficient treatment, as the modified surface presents efficient radicals for a grafting reaction through a radical mechanism and as nitrogen plasma treatment does not seriously degrade the polymer surface.

Electron beam and polymer interactions lead also to radical formation and could be helpful for a grafting reaction. Therefore, these two techniques that lead to two new materials will be compared in terms of degradation, cross-linking, functionalization, and activation for postgrafting applications. In this work, the reactivity of both materials was characterized by studying acrylic acid postgrafting.

EXPERIMENTAL

Apparatus

The plasma reactor (a 433 MHz microwave apparatus) (Fig. 1) and the polymer treatment have al-

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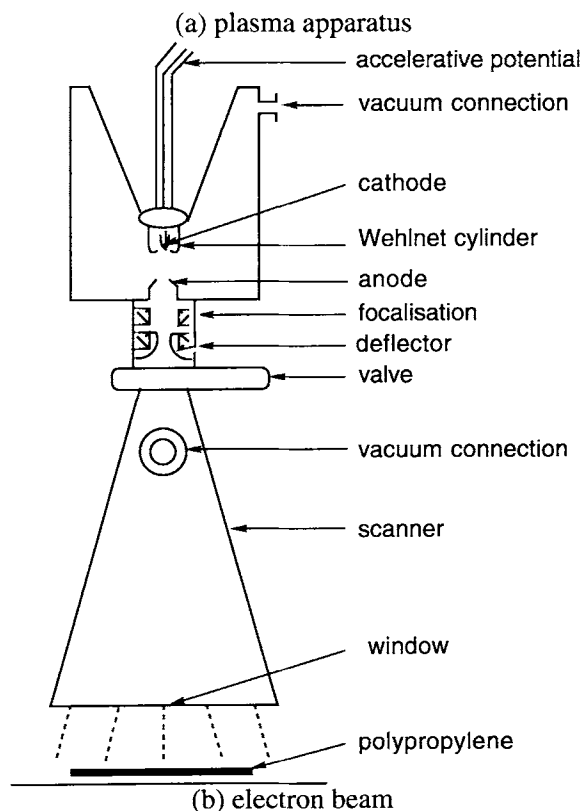
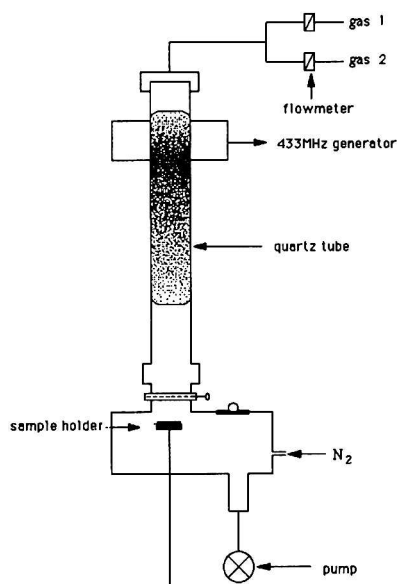


Figure 1 Plasma and Van de Graaff electron apparatus.

ready been described.⁴ The standard conditions were selected as follows:

- Incident power: $P_i = 60$ W.

- Reflected power: $P_r < 2 \cdot 10^{-2}$ W.
- Nitrogen flow: $Q = 20$ sccm; nitrogen purity: 99.985%.
- Distance between sample and surfatron: $d = 10$ cm.
- Duration: 3 min.
- Pressure during plasma: 0.3 mbar.
- System ultimate pressure: 10^{-5} mbar.

When a study was carried out with respect to one of these parameters, the other remained constant.

The electron beam in the Centre International d'Irradiation Electronique (Ecully, France) (Fig. 1) corresponds to a Van de Graaff accelerator with the following characteristics:

- Acceleration voltage: 200–350 keV.
- Electron current: 0–10 mA.
- Working width: 120 cm.
- Effective penetration depth: 15 mm.
- Passing through speed: 1–10 m/min.

Irradiation doses comprise between 5 and 200 kGy. Usually, doses higher than 20 kGy are not recommended but are used for the analysis of electron-beam modification of the polypropylene material.

Material

The polypropylene (PP, \overline{M}_n 50,000, $\overline{DP}_n = 1200$, $T_m = 160^\circ\text{C}$, crystallinity yield 62% [through ATD analysis] or 52% [through X diffraction]) supplied by ITF Lyon was synthesized by Ziegler-Natta catalysis in the heterogeneous phase. The PP is a film of 100 ± 10 μm thickness without additives. Each sample has a 15 cm^2 area and was washed with pure acetone before treatment.

Surface Analyzes

FTIR spectroscopy was run on Perkin-Elmer Model 1750 with a microcomputer Model 7700. Spectra are recorded with a specular cell with an IR beam incidence angle of 70° and resolution of 2 cm^{-1} and 100 scans were run. SEM pictures (magnification $\times 500$) were made on a Hitachi Model S 2300 in the Laboratoire de Physique des Matériaux (URA 807), Université du Maine, Le Mans, France.

Static secondary ions mass spectroscopy (SIMS, 4 keV xenon ions for primary beam, take-off angle 75° , total ion dose 10^{13} ions/ cm^2) was run on a Riber Q 156 (Unité de Physique et de Physicochimie des Matériaux, Université de Louvain-La-Neuve, Bel-

gium). Treated samples stored under reduced nitrogen pressure were analyzed 4 or 5 days after treatment.

XPS was performed on a Leybold LHS 12 in the Laboratoire de Physique des Couches Minces, Université de Nantes, France. The X-ray used corresponds to $MgK\alpha$ (1.2536 KeV) with a 90° electron take-off angle. A C—CH₂ reference at 284.6 eV was chosen. Samples stored under reduced nitrogen pressure were analyzed the day after treatment.

The surface energy was calculated from the Dupré equation. The surface energies of different liquids, nonsolvents of PP, and their dispersive (d) and polar (nd) components are as follows:

- Distilled H₂O: $\gamma = 72.8 \text{ mJ m}^{-2}$; $\gamma^d = 21.8 \text{ mJ m}^{-2}$; and $\gamma^{nd} = 51.0 \text{ mJ m}^{-2}$.
- Diiodomethane (Aldrich, spectrophotometer grade): $\gamma = 50.8 \text{ mJ m}^{-2}$; $\gamma^d = 49.5 \text{ mJ m}^{-2}$; $\gamma^{nd} = 1.3 \text{ mJ m}^{-2}$.

Amine or Radical Titration

Surface amines and radicals were titrated separately using Ponceau 2R acidified with 0.1N HCl solution (Fluka) and diphenylpicrylhydrazyl (DPPH, Aldrich, 99%), respectively.

Immediately after treatment and without contacting the air atmosphere, the PP sample was dipped into a 10 mL solution of reagent (DPPH concentration in benzene: $1.2 \times 10^{-4} \text{ mol L}^{-1}$; Ponceau 2R concentration in water: $2.0 \times 10^{-6} \text{ mol L}^{-1}$). After degassing, the solution was heated to 70°C for 12 h while stirring. Then, a back titration of the solution, giving a high sensitivity, was made on a UV spectrometer (Varian DMS 100). A temperature effect should be negligible because these titrations are run below the α phase transition of PP (80°C); treated surfaces were not altered by exposure to water and weak acidic solutions. A blank titration was run. The amino group concentration on the virgin PP was found to be negligible (practically zero), whereas the radicals concentration of treated samples was calculated from the difference between the experimental values for the treated sample and the virgin PP because virgin samples present radicals as many polymers. The purity, stability, and activity of each reagent solution were checked before titration.

Extraction of the Amorphous Phase

The amorphous phase was extracted in a Soxhlet with dichloromethane (500 mL) freshly distilled

during 44 h. The crystalline phase remained insoluble.

Grafting Reaction

After plasma activation, the samples were brought back to atmospheric pressure by nitrogen introduction. The sample was then dipped in an acrylic acid solution (15 wt % acrylic acid freshly distilled, 0.1% Mohr salt, an inhibitor of homopolymerization, 84.9% of 2-butanol or water). The electron-beam-irradiated PP samples were dipped in the solution in contact with an air atmosphere. Possible traces of homopolyacrylic acid were extracted with water using a Soxhlet extractor for 48 h. Mohr salt adduct should decrease the homopolyacrylic acid formation.

Radiocounting is carried out as follows: As silver ions can be complexed by carboxylic groups, a radiotitration of $^{110}\text{Ag}^+$ complexed onto the acrylic acid graft was performed in a scintillator solution (Instagel, Amersham Packard Instruments). Samples to be titrated were dipped for 5 min in a radioactive silver nitrate solution (1 m Ci of $^{110}\text{AgNO}_3$ dissolved in 100 cm³ of 0.1N AgNO_3 solution). Then, the $^{110}\text{Ag}^+$ excess was washed off twice with distilled water in an ultrasonic bath. After drying in air, the grafted PP samples were dipped in 10 cm³ of a scintillator solution and titrated with a radiocounting apparatus (Tri-Carb Model 1900 CA) for β -emission. The estimated error in the measurements is $\pm 2\%$.

For size exclusion chromatography (SEC), the grafted samples were prepared as follows: After plasma treatment, irradiated samples were brought back to atmospheric pressure by nitrogen or oxygen introduction. Samples were then dipped in acrylic acid solution (10% acrylic acid freshly distilled, 90% of water). The bath temperature was 90°C . No Mohr salt was added because of a possible disturbance of SEC analysis detection. SEC analysis of grafting solutions was run on two columns (HAB Waters UHG 250 and TSK PW 5000; dimension: 30 cm) in ammonium acetate (0.1M) and NaN_3 (100 mg/L) aqueous solution. Molecular weight was calculated from the equivalent molecular weight of polysaccharide (Pullulan) between 342 and 853,000.

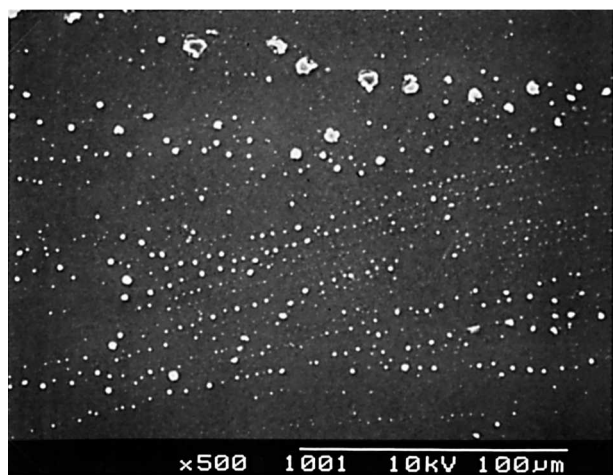
RESULTS AND DISCUSSION

Degradation and Cross-linking

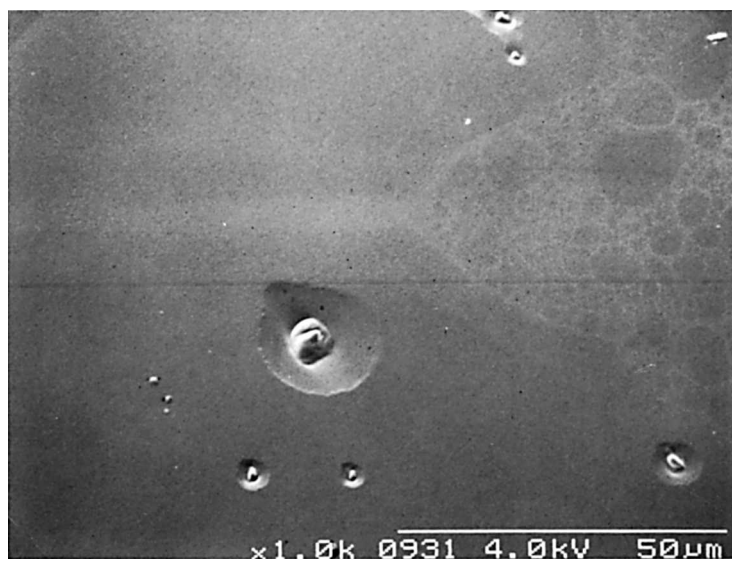
The first step of this study is a description of the treatment consequences on the PP surface with scanning electronic microscopy. The virgin film



(a) virgin PP



(b) plasma treated PP



(c) electron beam PP

Figure 2 SEM photographs: (a) virgin sample; (b) plasma-treated film; (c) electron-beam-treated film (20 kGy).

shows a smooth and homogeneous surface. But the effects of the two irradiations are different (Fig. 2). A relatively smooth surface is observed in the case of plasma treatment while craters and holes of 2 μm diameter appear even for weak electron-beam irradiation doses (less than 10 kGy). PP seems to be stable in a nitrogen plasma treatment as predicted by Yasuda et al. for semicrystalline polymers.⁵ However, some particles are observed when experimental conditions (time and power) are severe, as noticed before.^{5,6}

The amorphous phase, extracted in dichloromethane, is present in a lower proportion for the plasma-treated sample than for the virgin sample (4.9% instead of 6%), showing the presence of an insoluble tridimensional network and cross-linking reactions. Its chemical structure is practically equal to that of the virgin one. No oxidation is noticed by NMR or FTIR spectroscopies. The conclusions of SIMS analysis on this surface¹ were a decrease of methyl group concentration and branching reactions. A cross-linking reaction⁷ rather than an oxidation or a degradation occurs when PP film is treated in nitrogen plasma.

The extracted amorphous phase is in the same proportion in electron beam-treated or blank samples (6%); cross-linking seems to be weak. But oxidation is present, as evidence of carbonyl and hydroxyl groups is given by NMR and FTIR spectroscopies.

These different analyses lead to different conclusions in terms of degradation and cross-linking of PP modified by nitrogen plasma or electron beam irradiation:

Plasma: a weak degradation, a decrease of methyl group, and a surface cross-linking.

Electron beam: a weak degradation, an oxidation, and no cross-linking.

Functionalization

As we are looking for surface postgrafting of PP film, the chemical structure of the surface and sub-surface must be characterized for materials treated by nitrogen plasma or by an electron beam. Both surface and bulk analyses were used.

Plasma modification leads to surface functionalization depending on the chemical nature of the plasma gas. Amino groups, like primary amines, were noted as well as by ESCA or SIMS spectroscopies.¹ ESCA analysis (Table I) shows a nitrogen incorporation with a plateau around 18 atomic % but also an oxidation (11 atomic %). The nitrogen concentration is somewhat weak in comparison in regard to the literature on plasma modification.⁸⁻¹¹ But because ESCA analysis was not run *in situ*, an aging could be possible through hydrolysis of imine groups¹² or by an *in situ* oxidation described in Ref. 1. High resolution of the C_{1s} and O_{1s} peaks shows that amino groups are only in a reduced form, as primary amines and oxide groups are carbonyl (aldehyde, ketone) and C—O (alcohol and/or peroxide). A chemical titration of these amino groups¹ shows a dependence of amino group concentration on the plasma treatment parameters (time, power, etc.), and the milder the last one is, the higher the functionalization is.

Table I ESCA of Virgin, Plasma-treated and Electron-beam (10 kGy)-treated PP (Plasma: $P_i = 24$ W, $d = 5.5$ cm, $Q = 23$ sccm, $t = 60$ mn; Electron Beam: 10 kGy $\sigma =$ Full-Width at Half-Peak Maximum)

Peak	Sample	Position (eV)	σ (eV)	Assignment	Intensity (%)
C _{1s}	Virgin	284.6	1.35	C—C, C—CH	95
	Plasma-treated	284.6	1.80	C—C, C—CH	71
		286.9–287.9		C—O, C=O, C—N, C=N	
	Electron-beam-treated	284.6	2.00	C—C, C—CH	83
287.4–288.5			C=O, COOH		
O _{1s}	Virgin	531.9	2.55	C—O, C=O	5
	Plasma-treated	532.0	3.10	C—O, C=O	11
	Electron-beam-treated	531.6	2.90	C—O, C=O	11
N _{1s}	Virgin	—	—	C—O, C=O	0
	Plasma-treated	399.5	2.65	C—NH	18
	Electron-beam-treated	399.5	1.90	C—NH	6

FTIR-ATR spectroscopy leading to information on thickness does not reveal new band or peak vibrations corresponding to a functionalization. Whatever the penetration depth of the electron beam is, information given by ESCA spectroscopy on the chemical structure of the PP surface is useful, as the grafting of a monomer depends on the chemical structure of the modified PP surface at the beginning of the postreaction. As irradiation is performed in an air atmosphere, an oxidation is noted through the appearance of carbonyl and carboxyl groups. The oxygen concentration (11%) is similar to that observed in plasma modification. Nitrogen is also incorporated (6%) as primary amines. FTIR analysis on transmission or reflection modes shows the appearance of hydroperoxide groups (3350 cm^{-1}), carbonyl (1740 cm^{-1}), and double bonds (1630 cm^{-1}). The oxidation takes place also in the bulk of PP film, and insaturation and hydroperoxide groups are detected and could influence aging (Fig. 3). Later than 18 months after the irradiation, double-bond concentration nearly reaches zero and, on the contrary, concentrations of carbonyl and peroxide groups are strongly increased. In a manner opposite to that of the plasma-modified samples, the aging of the electron-beam-irradiated sample is slow, and after 1 week, the peroxidation of formed radicals is not complete. This evolution is followed by a degradation of the material, which becomes crumbly, phenomena emphasized with a high dose of irradiation and similar to that observed with γ irradiation.¹³⁻¹⁵

The most important conclusion of functionalization under plasma or an electron beam that can be drawn is that oxidation and nitrogen incorporation takes place in both systems, but, with the electron-beam irradiation, the bulk is affected and the aging mechanism cannot be neglected.

Activation

Dependence of radical concentration on different treatment parameters (duration, power, flow, and distance) was studied.¹ An example is given in Figure 4. For plasma treatment, the effect of discharge power leads to an exponential increase of radical concentration. The dependence of radical concentration on the other experimental conditions is fully described in Ref. 1 and can be summarized as follows: The more drastic are the treatment conditions, the higher is the radical concentration, but these conditions lead also to competitive reactions such as degradation or cross-linking.

For electron-beam doses lower than 80 kGy, sur-

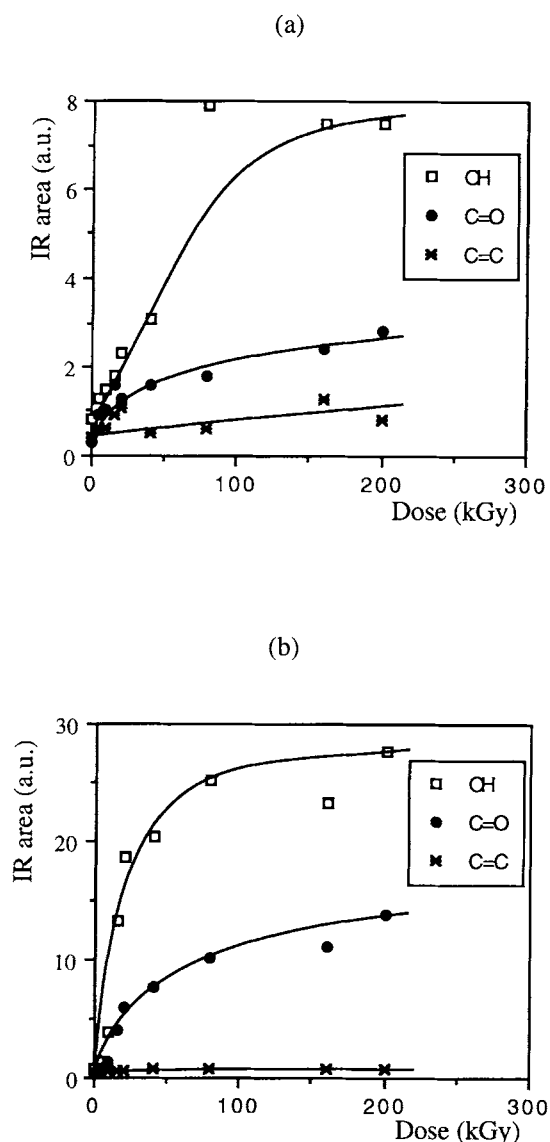


Figure 3 Aging phenomenon of electron-beam-irradiated PP, followed by FTIR absorption of hydroperoxides, carbonyls, and double bonds: (a) after 1 week; (b) after 18 months.

face radical concentration increases with the dose. Then, a plateau ($23 \cdot 10^{-8}$ mol equiv/cm²) is reached as degradation consumes radicals leading to an equilibrium state (Fig. 4). This concentration is nearly 10 times higher than for a PP surface treated in a nitrogen cold plasma, but degradation appears when PP is irradiated at 80 kGy or higher doses.

Definition of the Postgrafting Conditions

Two corresponding solvents were tested: 2-butanol and distilled water. Since PP swells in 2-butanol,

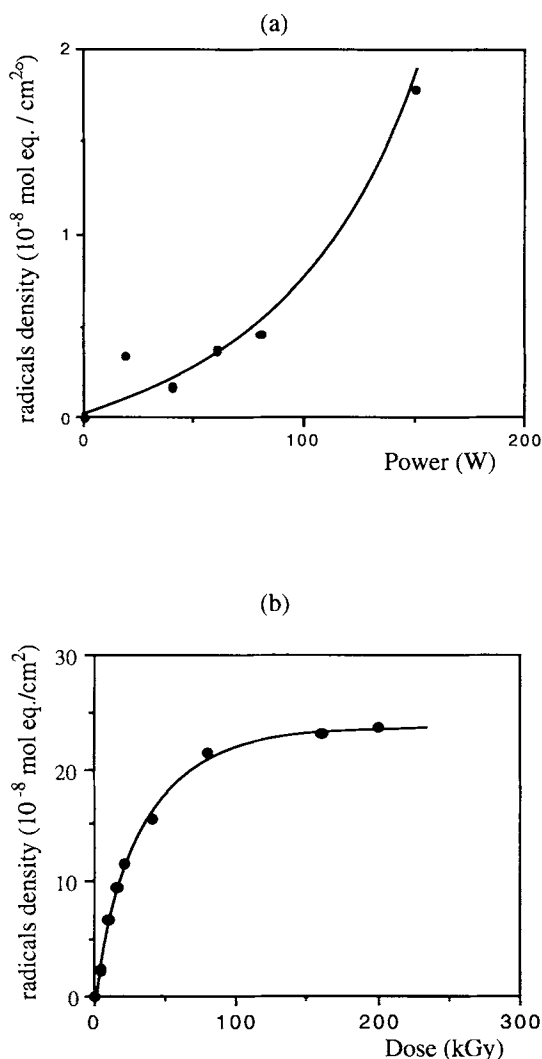


Figure 4 Dependence of radical concentration on treatment: (a) nitrogen plasma; (b) electron-beam irradiation.

diffusion of the monomer toward reactive sites is emphasized, whereas the growth of grafted chains soluble in water could be larger.

As the α transition of PP is around 80°C , two grafting temperatures (70 and 90°C) were tested. A reflection FTIR study of the absorption between 1808 and 1592 cm^{-1} , characteristic of the acrylic acid vibration, was performed (Table II). The weak absorption around 1640 cm^{-1} observed on blank PP, as noted in Refs. 4 and 16, is not really explained. A more important absorption is obtained when the postgrafting is carried out at 90°C , due to the monomer diffusion to initiator sites increasing when the temperature is higher than the α transition temperature. A temperature of 90°C was finally chosen.

Characterization of the Grafted Layer

The plasma-irradiated samples grafted in 2-butanol showed some ungrafted areas [Fig. 5(a)]. In contrast, when samples were grafted in water [Fig. 5(b)], the surface is rough, but completely grafted. In the case of electron-beam preactivation [Fig. 5(c) and (d)], identical conclusions can be drawn but the grafting occurs also in the bulk, since electron-beam irradiation affects the thickness of the PP sample. Homopoly(acrylic acid) seems to be still present on the surface whatever the extraction conditions.

ESCA analysis (Table III) of plasma-irradiated PP grafted in 2-butanol shows a new peak (288.7 eV) corresponding to a COOH function of the grafted layer. The grafted layer is thinner than the analyzed one, as the nitrogen peak is always observed and as the carbon and oxygen relative intensities are close to those of a blank sample. A fraction of the amino groups was still present after the post-grafting reaction or during extraction. Since the diffusion should be negligible, the presence of the N_{1s} peak means that the thickness of the poly(acrylic acid) layer is lower than the analyzed one. However, when water is used as the grafting solvent, the ESCA nitrogen peak (Table III) is negligible and the ratio of COOH (288.6 eV) to C—C (284.6 eV) bond intensities (0.37) corresponds exactly to the COOH/C—C ratio of poly(acrylic acid).¹⁷ In such conditions, the grafted PP surface has a chemical structure close to that of poly(acrylic acid).

With electron-beam activation, grafting rates seem to be slower than with plasma initiation. The nitrogen peak is still present but at low intensity (Table III).

Study of the Grafting Kinetics of Electron-beam-irradiated Polypropylene

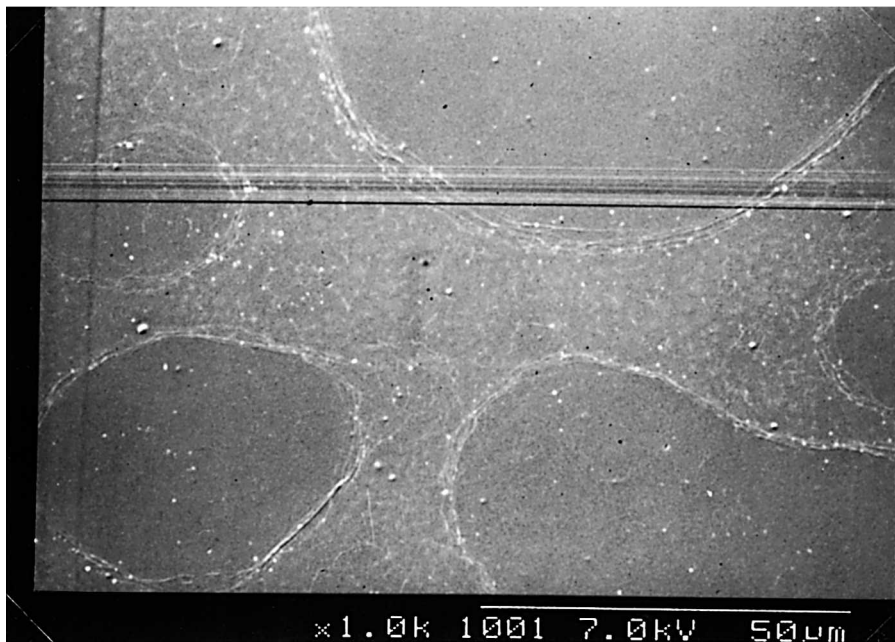
The dependence of the postgrafting yield on parameters like the monomer concentration (Fig. 6), the

Table II Dependence of the Acrylic Acid IR Absorption on the Grafting Temperature

Grafting Temperature ($^\circ\text{C}$)	IR Area (au)	
	Blank ^a	Treated
70	5.7	7.3–6.9
90	7.3	13–11.5

^a The blank sample was also dipped into the grafting solution.

(a)



(b)

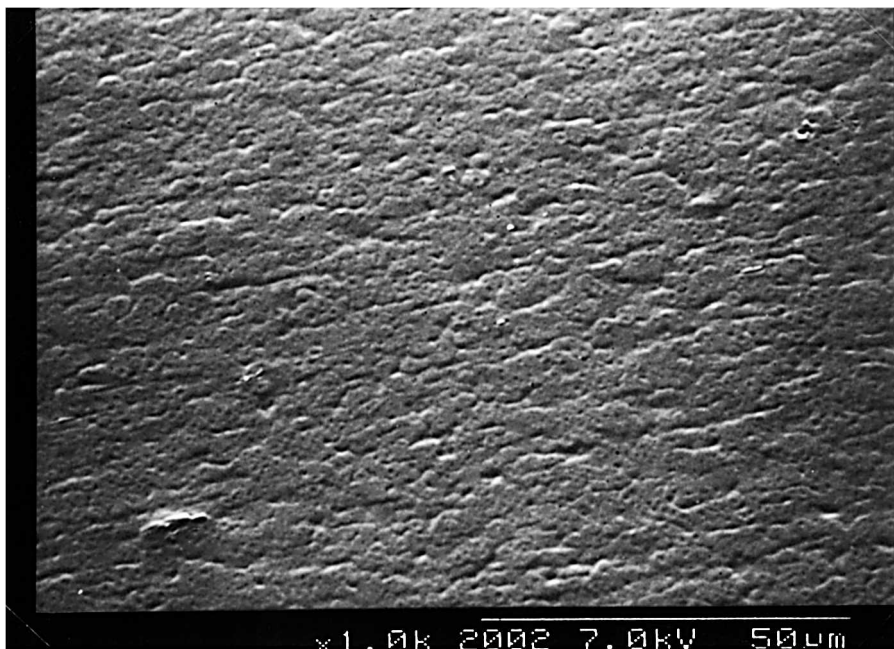
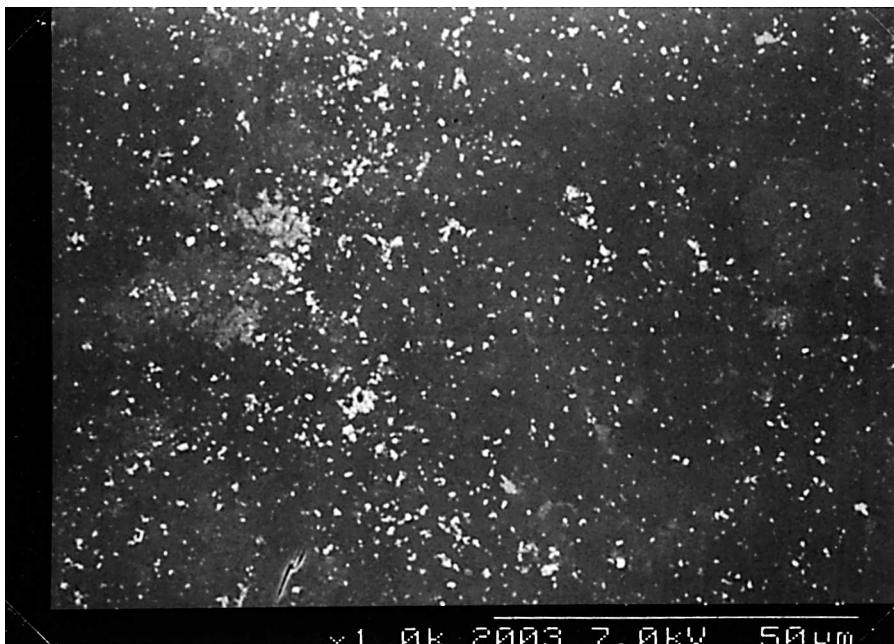


Figure 5 SEM pictures of (a) plasma-irradiated PP grafted in 2-butanol; (b) plasma-irradiated PP grafted in water; (c) electron-beam-irradiated PP grafted in 2-butanol; (d) electron-beam-irradiated PP grafted in water.

duration (Fig. 7), and the irradiation dose, i.e., radical concentration (Fig. 8), is marked. A 15% monomer concentration seems to be a good com-

promise between the grafting yield and the homopolymer concentration. A plateau is reached after 10 h of postgrafting. The grafting yield is maximum

(c)



(d)

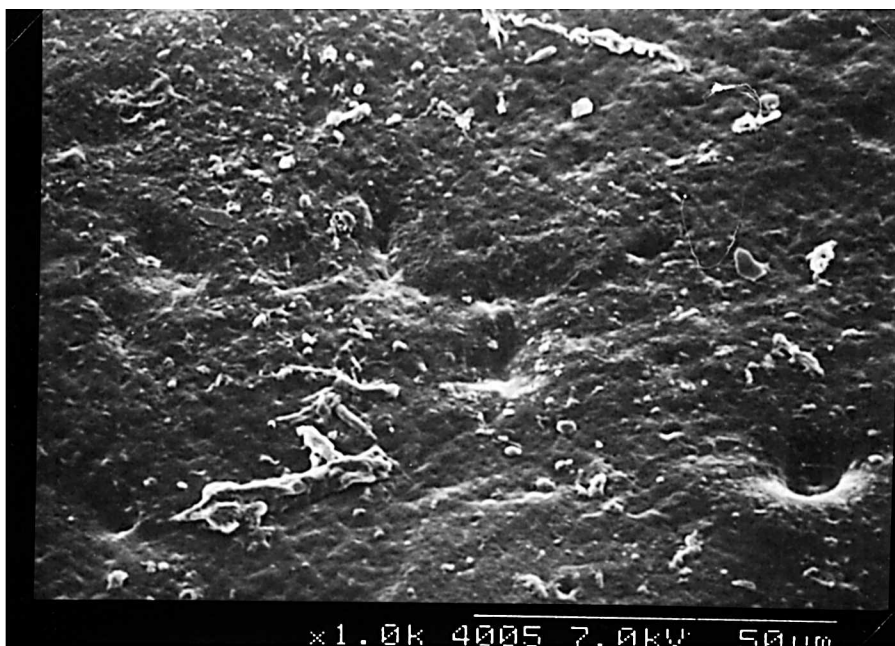


Figure 5 (Continued)

for irradiation doses between 15 and 40 kGy. With higher dose, the degradation decreases the grafting yield. Radiotitration confirms these results, and the

presence of a plateau rather than a maximum could be explained by the limitation of silver ion diffusion in the bulk.

Table III ESCA Data of Different Grafted or Ungrafted PPs

Sample	Peak	Position (eV)	σ^a (eV)	Assignment	Relative Intensity (%)
Poly(acrylic acid) ^b	C _{1s}	284.6	—	C—C, C—CH	60
		288.7	—	C—O	
	O _{1s}	532.2	—	COOH	40
	N _{1s}	—	—	—	0
Plasma-irradiated PP	C _{1s}	284.6	3.20	C—C, C—CH	63
		286.9		C—O	
		287.9		C=O	
	O _{1s}	532.9	3.20	C=O, C—O	18
	N _{1s}	399.4	3.35	C—NH	19
Plasma-irradiated PP grafted in 2-butanol	C _{1s}	284.6	2.05	C—C, C—H	84
		286.8		C—O	
		288.7		COOH	
	O _{1s}	531.9	3.15	COOH	12
	N _{1s}	399.6	2.90	C—NH	4
Plasma-irradiated PP grafted in water	C _{1s}	284.6	1.70	C—C, C—CH	69
		288.6		COOH	
	O _{1s}	532.1	3.00	COOH	31
	N _{1s}	—	—	—	0
Electron-beam-irradiated PP	C _{1s}	284.6	2.00	C—C, C—CH	83
		287.4		C=O	
		288.5		COOH	
	O _{1s}	531.6	2.9	C—O, C=O	11
	N _{1s}	399.1	1.90	C—NH	6
Electron-beam-irradiated PP grafted in 2-butanol	C _{1s}	284.6	1.80	C—C, C—CH	80
		288.7		COOH	
	O _{1s}	532.1	2.70	COOH	19
	N _{1s}	399.8	—	NH	1

^a σ : full-width at half-maximum.

^b Theoretical values.^{3,4}

In conclusion, the whole of the PP sample irradiated with an electron beam is grafted and uniform. Very high grafting yields (500% of initial PP weight

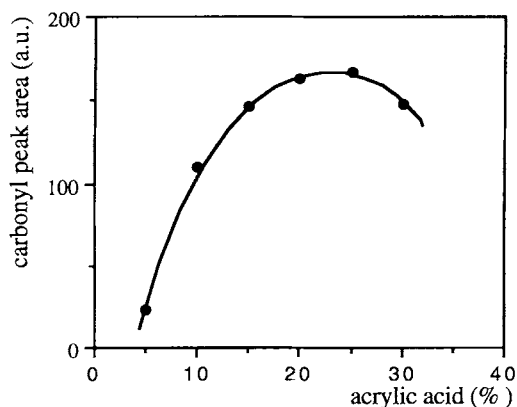


Figure 6 Dependence of the grafting yield on the monomer concentration (PP irradiated with electron beam; grafting solvent: H₂O).

after 72 h) can be obtained, but this material has physical properties close to the poly(acrylic acid) rather than to PP as has been noted previously.¹⁸⁻²⁰ For short grafting durations, water is advised as the solvent, and for longer grafting durations, 2-butanol leads to a more uniform surface but preserves the initial physical properties of PP.

Study of the Grafting of the Plasma-irradiated Polypropylene

The grafting yield and its dependence on different plasma-treatment parameters (duration, discharge power, etc.) was determined by different methods:

- Measurement of the carboxyl group absorption in the reflectance FTIR mode (between 1808 and 1592 cm⁻¹).
- Global surface energy measurement.

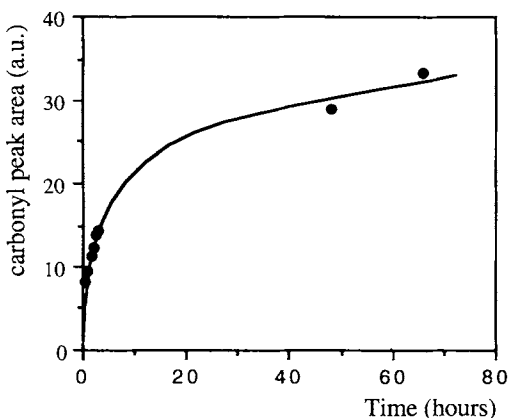


Figure 7 Dependence of the grafting yield on duration (PP irradiated with electron beam; grafting solvent: H₂O).

- Radiotitration with ¹¹⁰Ag⁺ ions chelated on carboxyl functions.

Higher grafting yields of acrylic acid on modified PP, calculated from IR absorption bands of carboxylic groups, were obtained for the following plasma treatment conditions (Fig. 9):

- Duration of plasma treatment: 8 min.
- Discharge power: 60 W.
- Sample at the edge of plasma.

No significant dependence on nitrogen flow was found.

Excessively long treatment and high discharge power do not enhance the grafting as they mostly produce surface cross-linking.^{1,21} The sample must

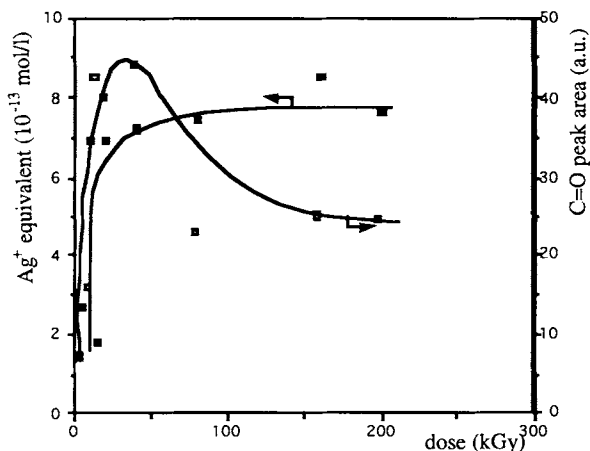


Figure 8 Dependence of the grafting yield on irradiation dose (PP irradiated with electron beam; grafting solvent: H₂O).

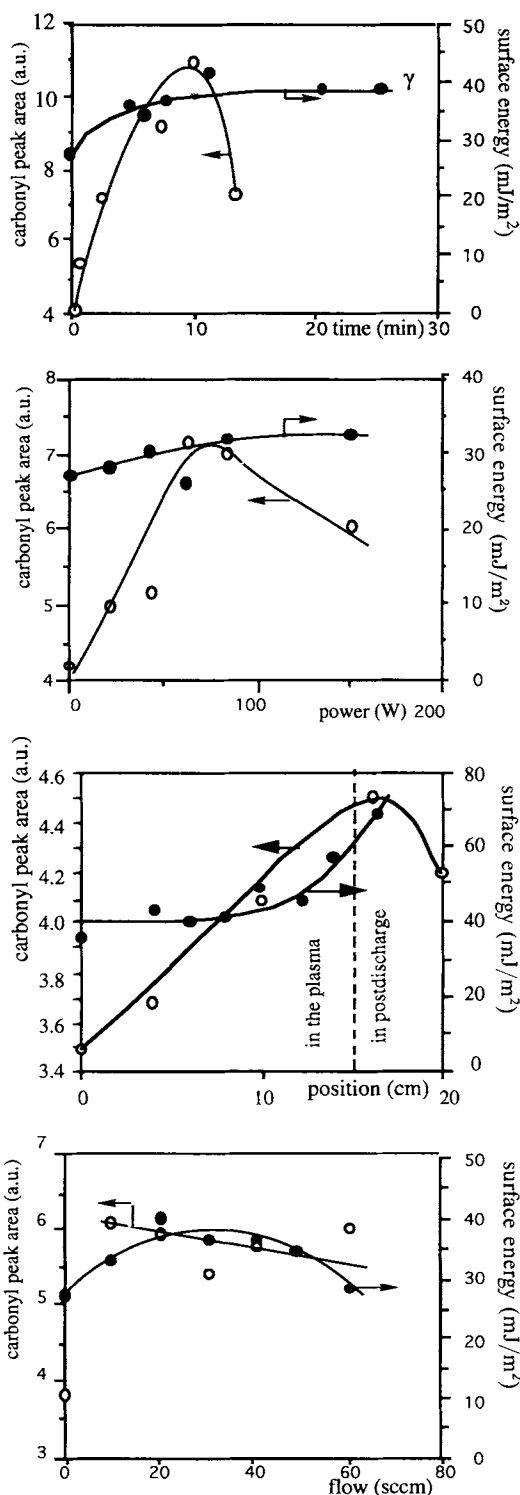


Figure 9 Dependence of the grafting yield on plasma parameters: FTIR and surface energy (grafting solvent: 2-butanol).

be at the edge of the plasma. The interpretation of the dependence of the grafting yield determined by surface energy variations is practically the same as

described above: initial increase followed by a plateau with power or duration. No maximum is observed since the surface is completely covered by poly(acrylic acid) and the surface energy remains constant at the value for poly(acrylic acid). Higher surface energy is obtained when working in the plasma and a decrease is noticed with the nitrogen flow.

Radiotitration of the grafted PP is not easy to set up as it is necessary to perform a blank titration. The chosen blank sample is PP modified in the same nitrogen plasma as used for the postgrafting reaction. Comparison of results from blank, activated, and grafted samples leads to different conclusions:¹

- Without plasma treatment, the sample does not chelate silver ions (radiocompter: 45 cps/s).
- Nitrogen plasma treatment leads to a silver complexation (radiocounter: 577 counts/s).
- After the grafting reaction, the complexation rate decreases (three times lower, radiocounter: 199 counts/s).

The first point to note is that radiotitration gives evidence of the functionalization of the cold plasma-modified PP and confirms the other analyses. The second point is the difference between the radiative emission yield of the grafted and the treated surfaces. The emission yield of the grafted surface is lower than for the treated surface, although the concentration of functional groups able to chelate silver ions is greater on the grafted layer than on the activated surface. This paradox can only be explained by a difference between the two surface densities that control the silver ion diffusion. The grafted layer must have a higher density, and as the radiotitration is controlled by the diffusion rate of silver ions, the measured concentration is lower than that of the treated surface.

It has also been noted that the extraction has an effect on the radiotitration. Extracted samples have a lower emission yield than that of the nonextracted ones, explained by the homopoly(acrylic acid) disappearance.

Remarks following this titration of samples treated in different plasma treatment conditions (Fig. 10) are similar to those obtained from other titrations. Optimum treatment conditions for the grafting are the following:

- Duration: 2 min.
- Discharge power: 60 W.
- Sample at the edge of plasma.
- Nitrogen flow has little influence.

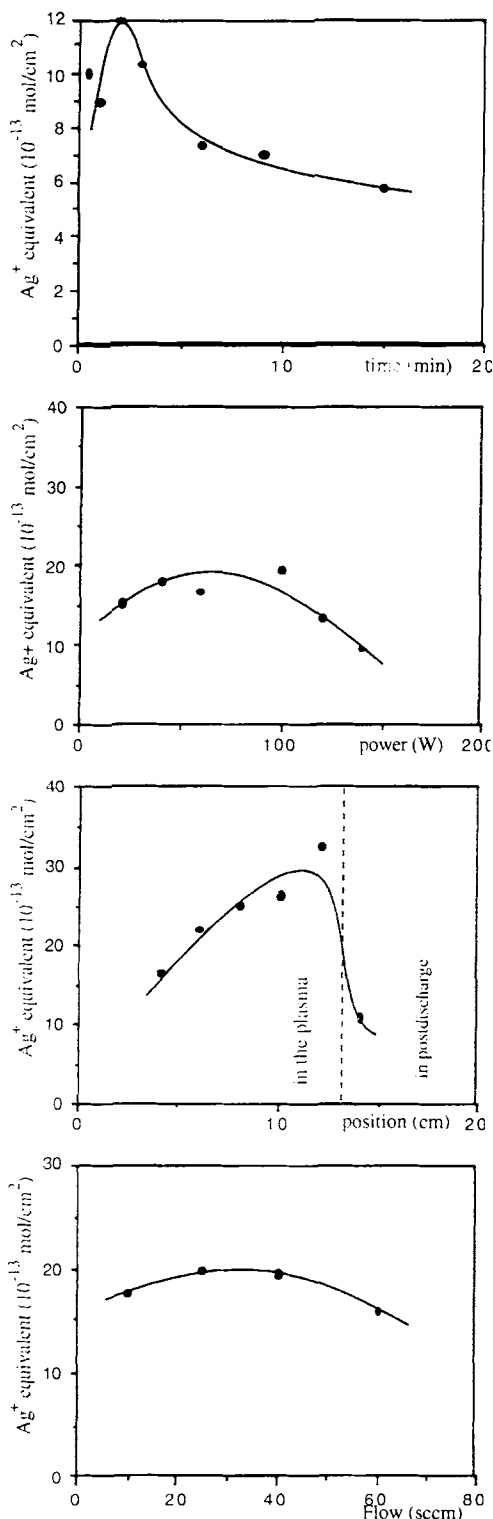


Figure 10 Dependence of the grafting yield on plasma parameters: radiotitration (grafting solvent: 2-butanol).

As for each plasma treatment condition, radical and amino groups formed on the PP surface are measured; the grafting yield variation can be also

described as a function of both the radical and amino group densities. The acrylic acid grafting should proceed via a radical mechanism. Therefore, the concentration of radicals created by the plasma interaction must control the grafting rate and, in particular, the initiation rate. If the grafting rate, determined by FTIR analysis or surface energy measurement or radiotitration, is plotted vs. the concentration of radicals created on the PP surface, calculated after a chemical titration,¹ no dependence is found. However, if the same grafting yield is plotted vs. the amino group concentration calculated by another chemical titration,¹ a linear dependence is found (Fig. 11) (an exception being the effect of the nitrogen flow, a parameter that leads mostly to degradation¹). An explanation based on the attraction of monomer carboxyl groups to the hydrophilic amino group on a hydrophobic PP surface can be given. The fixation of hydrophilic groups on hydrophobic surfaces should favor the hydrophilic monomer approach. In this way, the amino group concentration may affect grafting, and beyond a critical concentration, the radical concentration is not a predominant factor. The amines not only cause enhanced attraction due to the dipolar interaction but can also react with the acid by the Michael reaction. But since the grafted layer thickness seems to be 10–15 units (ESCA determination), the Michael reaction should be negligible.

Study of the Acrylic Acid Homopolymerization Kinetics

Even with a Mohr salt adduct, the homopolymerization of acrylic acid in the solution takes place together with grafting. Some authors²² described the methacrylic acid grafting on natural rubber under UV or γ irradiation. In such a system, the grafted chains have the same length as in the homopolymer obtained in solution. Therefore, the comprehension of the homopolymerization kinetics and mechanisms will be helpful in understanding the grafting and should allow us to find conditions where the homopolymerization will be negligible.

The grafting was performed without Mohr salt. Molecular weight is determined with SEC analysis (Table IV). Two kinds of initiating radicals on the PP surface were chosen: the peroxide and alkyl radicals. When PP is treated in nitrogen plasma, alkyl radicals are created. Then, before being dipped in the acrylic acid solution, the PP can be oxidized by an oxygen atmosphere, leading to peroxide radicals.

From SEC analysis, the homopolymer and monomer concentrations are determined as a func-

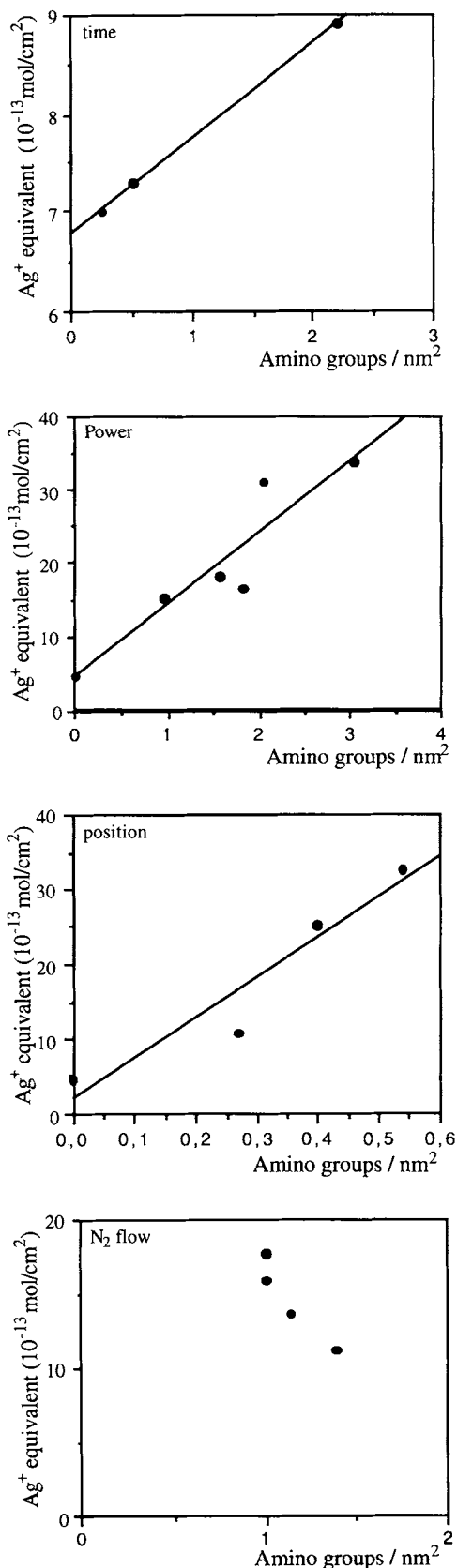


Figure 11 Dependence of the grafting yield on amino group concentration (grafting solvent: 2-butanol).

Table IV Molecular Weight of the Homopoly(acrylic acid) Formed During the Grafting

Time (h)	Homopolymer (%)	Monomer (%)	\overline{M}_n (10^6)	\overline{M}_p (10^6)
Initiation with peroxides				
0	0	100	—	—
2	6.9	93.1	0.988	1.323
4	8.8	91.2	1.275	1.509
12	9.6	90.4	1.217	1.603
20	12.6	87.4	1.182	1.670
30	14.3	85.7	1.164	1.482
44	26.4	73.6	1.225	1.516
70	65.2	34.8	0.892	1.209
Initiation with alkyl radicals				
0	0	100	—	—
2	9.3	90.7	0.849	1.208
4	37.4	62.6	0.123	0.853
15	65.3	34.7	0.043	0.723
20	78.5	21.5	0.029	0.525
30	86.1	13.9	0.046	0.694
43	87.4	12.6	0.042	0.733

tion of the postgrafting duration (Table IV). The equations of the polymerization mechanism are applied, and the propagation rate (V_p) is deduced from these equations:

$$V_p = -d[AA]/dt = k_p[P^*][AA]$$

$$\ln([AA]_0/[AA]) = k_p[P^*]t$$

with $[AA]$ the concentration of acrylic acid, $[AA]_0$ at $t = 0$ h; $[P^*]$ the growing sites concentration; and k_p the propagation constant.

Taking the time derivation $[AA] = f(t)$ leads to the propagation rate. For postgrafting duration higher than 2 h, the monomer concentration dependence on time is described as

With peroxide initiation:

$$[AA] = -1.81 \cdot 10^{-4} t^2 + 13.8 \cdot 10^{-4} + 1.27$$

$$\Rightarrow V_p = -3.62 \cdot 10^{-4} t + 13.8 \cdot 10^{-4} \quad (\text{mol L}^{-1} \text{h}^{-1})$$

With alkyl radical initiation:

$$[AA] = -3.07 \cdot 10^{-5} t^3$$

$$+ 3.05 \cdot 10^{-3} t^2 - 0.102t + 1.37$$

$$\Rightarrow V_p = -9.21 \cdot 10^{-5} t^2$$

$$+ 6.10 \cdot 10^{-3} t - 0.102 \quad (\text{mol L}^{-1} \text{h}^{-1})$$

Therefore, the propagation rate increases linearly with the postgrafting time when the grafting is initiated with peroxide radicals. It results from an increase of the growing site concentration, which depends on the monomer diffusion rate and on the half-life of peroxide radicals. With alkyl radical initiation, the propagation rate decreases and reaches a plateau after 25 h and, in fact, depends directly on the monomer concentration decrease (Fig. 12).

Application of the radical polymerization mechanism can be only be developed for peroxide initiation, since with the alkyl radical initiation, the homopolymer yield is too great (this theory could only be applied in the case of a yield lower than 15%).

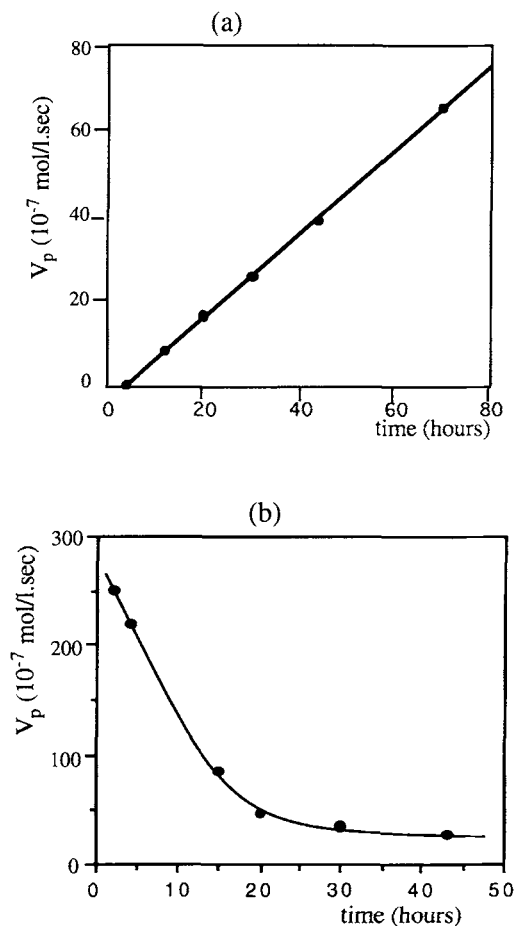


Figure 12 Dependence of the propagation rate on time: (a) peroxide initiation; solvent: H_2O ; (b) alkyl radical initiation; solvent: H_2O .

SEC analysis allows the study of transfer reactions, as described in the following equation:

$$1/\overline{DP}_n = V_p / (\sum \text{rates of any reaction leading to new chain})$$

$$1/\overline{DP}_n = 1/\overline{DP}_0 + C_{AA} + C_I[\text{O—O}]/[M] + \dots$$

$1/\overline{DP}_n$ variation vs. V_p (Fig. 13) does not pass through the origin and shows a transfer to the monomer. This curve is not linearly dependent on V_p , showing also the presence of other transfer reactions to the initiator or to the polymer.

The dependence of \overline{M}_n and \overline{M}_w on the postgrafting duration (Table IV) shows (with peroxide initiation) first an increase of molecular weight, then a decrease after 20 h. As the growing chain concentration is increased, most of these chains are short. The decrease of molecular weight with the alkyl radical initiation depends on the monomer concentration decrease and on the high homopolymer yield for a short postgrafting duration.

This kinetic study can be summarized as follows:

With peroxide initiation:

- The initiation rate depends mainly on monomer diffusion.
- The propagation rate increases linearly with time.
- The reaction of transfer to monomer is important, and other transfers to solvent or initiator are possible.
- For duration > 20 h, the concentration of growing sites increases and the molecular weight decreases.

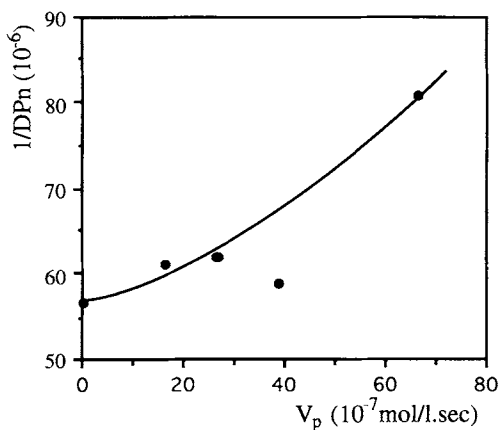


Figure 13 Dependence of $1/\overline{DP}_n$ on the propagation rate for AA postgrafting on PP; solvent: H_2O with peroxide initiation.

With alkyl radical initiation:

- Long chains are obtained for short duration.
- Monomer diffusion is not important.
- Transfer reactions are not negligible and do not allow an increase of molecular weight after 5 h of grafting.

If Cooper's hypothesis²² is true for such a system, these conclusions can be applied to the grafted chains.

CONCLUSION

Polypropylene modifications, either in a cold plasma or with an electron beam, are described as activation, degradation, functionalization, and cross-linking. This study shows that creation of initiators of grafting, radicals, can be obtained either with plasma treatment or with electron-beam irradiation, and the monomer accessibility was illustrated by the chemical titration of radical species initiating the grafting step. Sample oxidation after or during treatment was observed and leads, as the nitrogen incorporation does, to a higher surface energy of PP. During nitrogen plasma treatment, surface cross-linking was the prevalent reaction, through methyl group elimination or modification, which leads to different radical structures.¹ Electron-beam irradiation leads to chemical modifications of PP. Oxidation and nitrogen incorporation were observed. Aging is an important phenomenon leading to degradation, as radical concentration is high.

The grafting of acrylic acid onto different activated PP—modified by a cold plasma or irradiated with an electron beam—is possible either in 2-butanol or in water. The grafting yield is higher in the water solution.

For plasma-modified polymer, the kinetic study has shown that, above a critical concentration of initiator sites, grafting yield depends mostly on the concentration of polar groups fixed on the modified PP. Amino groups seem to induce a hydrophilic surface, which favor the acrylic acid approach, and, therefore, these surface groups control the grafting rate and yield. Further works are in progress to understand the mechanisms of these interactions. Grafting on the electron-beam PP sample depends on radical concentration and takes place at the PP surface but also in the bulk. The two preirradiation methods lead to two different grafted materials: One has a chemically modified surface and the other is completely affected.

A kinetics study of the homopolymerization of the grafted monomer shows that the molecular weight of the homopolymer in solution is high, and the homopolymer yield depends on time and corresponds to an increase in the number of chains rather than an increase in length. These results could be applied to the grafted chains. Homopolymerization depends on the nature of initiator sites on the surface: alkyl radicals or peroxides.

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Received September 13, 1993

Accepted March 1, 1994