Physicochemical characterization of polypropylene films grafted by poly(acrylic acid): 2

Marie-Ange Romero and Alain Domard*
Laboratoire d'Etudes des Matériaux Plastiques et des Biomatériaux, URA CNRS No. 507, Université Claude Bernard Lyon 1, 43 Boulevard du 11 Novembre 1918, 69622 Villeurbanne Cédex, France
(Received 31 December 1993; revised 18 May 1994)

Various analyses were used to characterize polypropylene films grafted with poly(acrylic acid): infra-red spectroscopy (by means of transmission, total attenuated reflection and microscopic techniques), permeation and optical microscopy on coloured samples. We have compared the results obtained when the film to be modified was initially treated to eliminate incorporated additives with those obtained when the additives were not removed. In addition to the progressive propagation of the grafting previously evidenced, we have shown that the solubility parameter plays the major part in the transport of the monomer molecules from the surface to the bulk.

(Keywords: polypropylene; poly(acrylic acid); grafting)

INTRODUCTION

Polyolefin surfaces are well known to be chemically inert and hydrophobic. For some applications, they need to be more hydrophilic. Examples include required improvement to their printability, paintability or adhesion to substrates. For such purposes, radiochemical grafting is one of the methods often used. In the case of polypropylene (PP), several authors have expressed interest in the kinetics of radiochemical grafting of acrylic acid (AA) onto PP fibres[1–8]. Thus, the aim of this work is to try to characterize the mechanism of grafting as well as to identify the locus of the grafting of PP films by AA.

In the first part of this work[9], we demonstrated the coexistence of two types of copolymer. The first copolymer is very highly grafted, resulting in a chemical structure very close to poly(acrylic acid) (PAA), and is present at the film surface. The second is grafted to a lesser degree with a broad distribution of grafting ratios, corresponding probably to grafting in the bulk of the material. According to other authors, grafting seems to be a progressive phenomenon starting at the surface and leading to the bulk of the material. The propagation is easier when additives (mainly antioxidants), introduced into the polymer during its processing, are extracted before irradiation. At the same time, grafting at the surface is favoured compared to the case of the unextracted films.

In the second part of this work, results from other analyses are presented in order to confirm and specify the mechanism of the grafting propagation of AA onto PP films. We have also attempted to provide an understanding of the effect of the extraction of the antioxidants.

EXPERIMENTAL

Materials

The PP films used in this work contained approximately 1000 ppm of antioxidants. They were 50 μm thick, having been processed by extrusion and flow onto a cooled cylinder. They were approximately 50% crystalline and the crystalline phase was smectic. Acrylic acid was from Coatex and contained 200 ppm of stabilizer. All the other products were commercial samples of reagent grade. All the aqueous solutions were prepared using deionized water. Two kinds of films were used, those without any pretreatment and others after extraction of the additives.

Methods

Before treatment, the films were washed in methanol at ambient temperature for 40 min, rinsed in methanol and then dried under vacuum at ambient temperature. The extraction of the additives was carried out by placing the PP samples in glass tubes containing chloroform followed by rotating them in an oven thermostated at 30°C for 15 h. They were finally submitted to a subsequent washing with chloroform.

The effectiveness of the extraction of the additives was verified by chromatography of the extracts (after concentration). The chromatograms were compared to those obtained with solutions of commercial standards of the same chemical structure. Another verification was also made from the comparison of the i.r. spectrum of each additive to the spectrum of the solid mixture obtained after complete evaporation of the extracts.

The samples were irradiated by means of an electron-beam accelerator, the extracted films at 2 Mrad and the others at 2 and 4 Mrad; 2 and 4 Mrad correspond to optimal low- and high-irradiation conditions. They allow

* To whom correspondence should be addressed

0032-3861/94/24/5342–07

a minimal grafting for the former and a sufficient preservation of the physical properties of the films for the latter. Unfortunately, in the case of extracted films, irradiations over 2 Mrad led to an important loss of mechanical properties of the film. The films were then introduced into glass tubes containing aqueous solutions of acrylic acid (AA) of various concentrations. The tubes were allowed to rotate in an oven thermostated at 99°C for 2 h. In order to remove the residual monomer and extractable homopolymer[9], the grafted films (PPg) were washed thoroughly in running water. The free acidic form of the PPg films was then prepared by soaking the films in 1.25×10^{-2} M HCl followed by washing with deionized water. This treatment was performed to suppress any possible ionization that could have occurred during the various steps of preparation of the PPg films, in particular during the washing in tap water.

All the results, whether they were obtained before or after grafting, are always averaged from several samplings corresponding to given conditions; thus, the errors due to the reproducibility of grafting as well as of sampling cannot exceed 15%.

Analyses

I.r. spectrophotometry. I.r. spectrophotometric analysis was performed using a Perkin–Elmer 1760-X *FT*i.r. spectrophotometer in three modes: transmission, attenuated total reflection (a.t.r.) and transmission coupled with a microscope for analysis of microtomic cuts. A resolution of 4 cm^{-1} was consistently used. Ten scans were realized per sample for the first two methods and 100 scans for the third.

For i.r. characterization of the grafting, the apparent grafting ratio (G) was considered to be the ratio of the absorbances at 1710 and 973 cm^{-1}: $A(1710\,cm^{-1})/A(973\,cm^{-1})$. These bands are characteristic of the C=O bond[10] of the carboxylic acid and of the CH_3 bonds respectively. The G values measured by transmission and a.t.r. were indexed as G_T and G_{ATR} respectively.

For a.t.r. analysis, a KRS-5 crystal was used. The incident beam was perpendicular to the bevelled surface, the angle of which was 45°. The sample was placed on only one side of the crystal and each face of the sample was submitted to analysis.

For i.r. microspectrophotometry, microtomic cuts 20 μm thick were performed perpendicular to the film surface on heavily ($G_T \geqslant 3$) and slightly ($G_T = 0.9$) grafted samples. The various cuts corresponding to each film were then placed flat on a KBr disc, covered by a second KBr disc and finally pressed at a pressure of 12 bar. The width of the sheared edge of the PPg film was different from that of the cut: 55 and 80 μm and 20 μm respectively. This difference allowed us to target the region we wanted to analyse, i.e. the film sheared edge. Before i.r. analysis, the sample was observed with the microscope. For analysis, a region was chosen that included a straight part of the PPg cut, which had to be as long as possible. The use of the window allowed us to analyse the cut along its width. The length and width of the window were 300 and 30 μm respectively. We first registered the background spectrum and then moved the sample in order to place the cut region of interest in the window centre.

Optical microscopy of coloured PPg samples. The PPg samples were immersed in an aqueous solution of methylene blue at 0.5 g dm^{-3} containing acetic acid at 0.5 g dm^{-3} and stirred for 30 min at ambient temperature. The samples were rapidly rinsed first with methanol and then with deionized water and finally dried at ambient temperature.

Microtomic cuts 10 μm thick of the coloured films were performed perpendicular to their surface. Each cut was then placed flat on a glass slide on which a drop of glue had been previously deposited, then covered by a second slide. The sheared edge of the coloured sample was then observed with an optical microscope using $\times 250$ magnification. A green filter was introduced in order to provide an image that could be photographed.

Thermogravimetric analysis. A DuPont thermal analyser was used for the thermogravimetric analysis (t.g.a.). Approximately 16 mg of product was placed in an aluminium pan and heated to 400°C with a 10°C min^{-1} temperature ramp under a continuous flow of helium.

Differential scanning calorimetry. A Perkin–Elmer DSC-4 analyser was used for the calorimetric analysis. Approximately 8 mg of product was placed in a pierced and clamped aluminium pan. An empty pan was used as a reference. They were then heated to 200°C with a 10°C min^{-1} temperature ramp under a continuous flow of nitrogen. All experiments were performed on triplicate sampling.

Permeation measurements. The permeation measurements were performed under two kinds of atmosphere: water vapour and nitrogen. The permeation cell was made up of two compartments (upstream = 1 and downstream = 2), which were separated by the polymeric membrane with an area of 3 cm^2. The cell was thermostated in a chamber heated at 23°C. A preliminary high-vacuum desorption was realized in order to ensure that the static vacuum pressure changes in the downstream compartment would be much smaller than pressure changes due to permeation: indeed, the static vacuum needs to be lower than 10^{-4} Torr min^{-1}. A pressure was then introduced in the upstream part: 17.9 Torr in the case of water vapour and 2280 Torr (3 bar) in the case of N_2. The pressure variation in the downstream volume V_2 (95 cm^3 in the case of water vapour and 144.4 cm^3 in the case of N_2) was measured by a Datametrics pressure sensor. By plotting the measured pressure P_2 *versus* t, the slope of the steady-state line enabled the calculation of the permeability coefficient (Pe)[11]. Pe is usually deduced from the ratio:

$$Pe = \frac{Je}{P_2 - P_1}$$

where J is the stationary flux, e is the thickness of the sample, and P_2 and P_1 are the pressures on both sides of the sample. The Barrer is a unit system that is defined by 1 Barrer = 10^{-10} cm^2 $cmHg^{-1}$ s^{-1}.

RESULTS AND DISCUSSION

Localization of the grafting

I.r. analysis of the films by the modes of transmission and a.t.r. allows us to study whether the apparent grafting

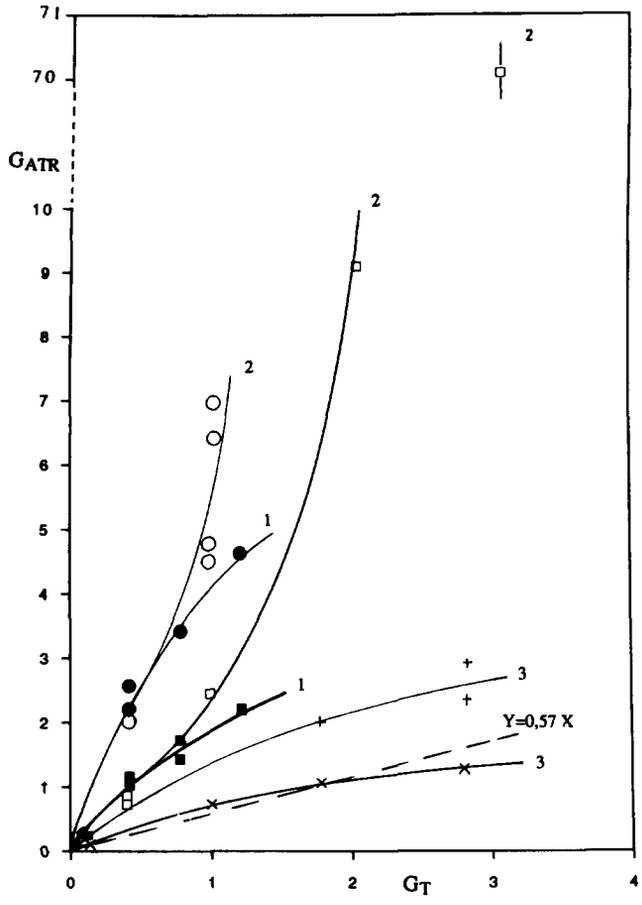

Figure 1 I.r. spectrometry analysis on various PPg films. Correspondence between the apparent grafting ratio measured by transmission (X) and by attenuated total reflection (Y) on each face: films irradiated at 2 Mrad (1) and 4 Mrad (2) without extraction of the antioxidants; films irradiated at 2 Mrad with a prior extraction of the antioxidants (3). Face A (■, □, +) and face B (●, ○, ×)

occurs at the surface or in the bulk of the material. Nevertheless, as detailed in part 1 of this series of papers[9], care must be taken when comparing the results obtained by these two techniques. Indeed, the penetration depth of the i.r. beam in the sample varies with the reciprocal of the wavelength. Thus, in the case of a homogeneously grafted PPg film, the relation between G_T and G_{ATR} becomes:

$$G_T = \frac{975}{1710} G_{ATR}$$

In part 1 of this series of papers[9], the relation between G_{ATR} and G_T for various PPg films has been studied using two samples of the same film placed on both sides of an a.t.r. crystal. We showed the coexistence of PP and PAA chains in the surface layer of the films and the enrichment of surface grafting of the films containing additives.

The i.r. analysis of each side of the samples and the comparison with their G_T value (*Figure 1*) show other results. First, for all the PPg films, the surface grafting varies from one side to the other. This must be related to the difference of the surface tension (γ_s) of each face (3.2×10^{-2} and 3.5×10^{-2} mN m^{-1}) obtained using contact angle measurements. A peroxidation heterogeneity cannot explain such a result. Indeed, the films are thin enough to be fully traversed by the irradiation beam and to allow a homogeneous diffusion of O_2 through the whole thickness[12]. Moreover, the difference of γ_s is only 3×10^{-3} mN m^{-1} whereas the G_{ATR} value can double from one face to the other. The surface tension of each face does not therefore seem to be the main parameter. The results support the hypothesis that the surface morphology plays the most important role in relation to the difference of morphology between the two faces probably created during the film processing. The face that has been cooled the most rapidly would contain the most abundant amorphous phase and therefore the highest amount of antioxidants, all the additives being excluded from the crystalline regions[13]. Nevertheless, it is difficult to verify such a hypothesis as the film is not thick enough to allow the X-ray diffraction (x.r.d.) analysis of each face with the usual techniques. Moreover, in the case of antioxidants homogeneously distributed in the film, the amount of additives at the film surface is too small to be detected by electron spectroscopy for chemical analysis (e.s.c.a.).

Contrarily to the method we used in part 1 of this series[9], in this part, the a.t.r. analysis is performed by placing a PPg film on only one side of the crystal and by analysing each face of the former. The results obtained by this method show a much larger enrichment of surface grafting for the unextracted films, in particular, for those films irradiated at 4 Mrad. In the case of the extracted films, an acceleration of the surface grafting ratio could exist but should only appear for higher G_T values ($G_T \geqslant 3$).

Thus, the results obtained confirm those noted in our previous work[9]: in the case of the PP sample containing antioxidants, the chemical modification seems to predominate at the surface of the film, while, for extracted ones, the grafting seems to occur more homogeneously in the bulk.

A comparison of the results obtained by the two techniques, transmission and a.t.r. i.r. spectrometry, leads to very important conclusions. However, it allows neither the determination of the exact chemical nature of the surface layer (largely grafted PP or PAA homopolymer) nor that of the inner layers of the films. In order to answer these questions, we must study the PPg film sheared edge. For this purpose, microtomic cuts are performed perpendicular to the film surface and then analysed by i.r. microspectrometry. Cuts performed in previously coloured films are also observed with an optical microscope. For good interpretation of the results, film dimensions that could have changed during grafting must be controlled.

Table 1 Thickness (e) *versus* grafting ratio (G_T) of different PPg films

Unextracted films irradiated at 2 Mrad		Unextracted films irradiated at 4 Mrad		Extracted films irradiated at 2 Mrad	
G_T	e (μm)	G_T	e (μm)	G_T	e (μm)
0.1	48±1	0.1	50±2	0.1	53±2
0.4	49±1	0.1	50±1	1.0	50±1
0.9	52±1	0.3	51±2	2.1	52±1
1.4	55±1	1.0	53±1	3.5	55±1
		1.2	55±3		
		1.9	64±2		
		3.0	77±6		

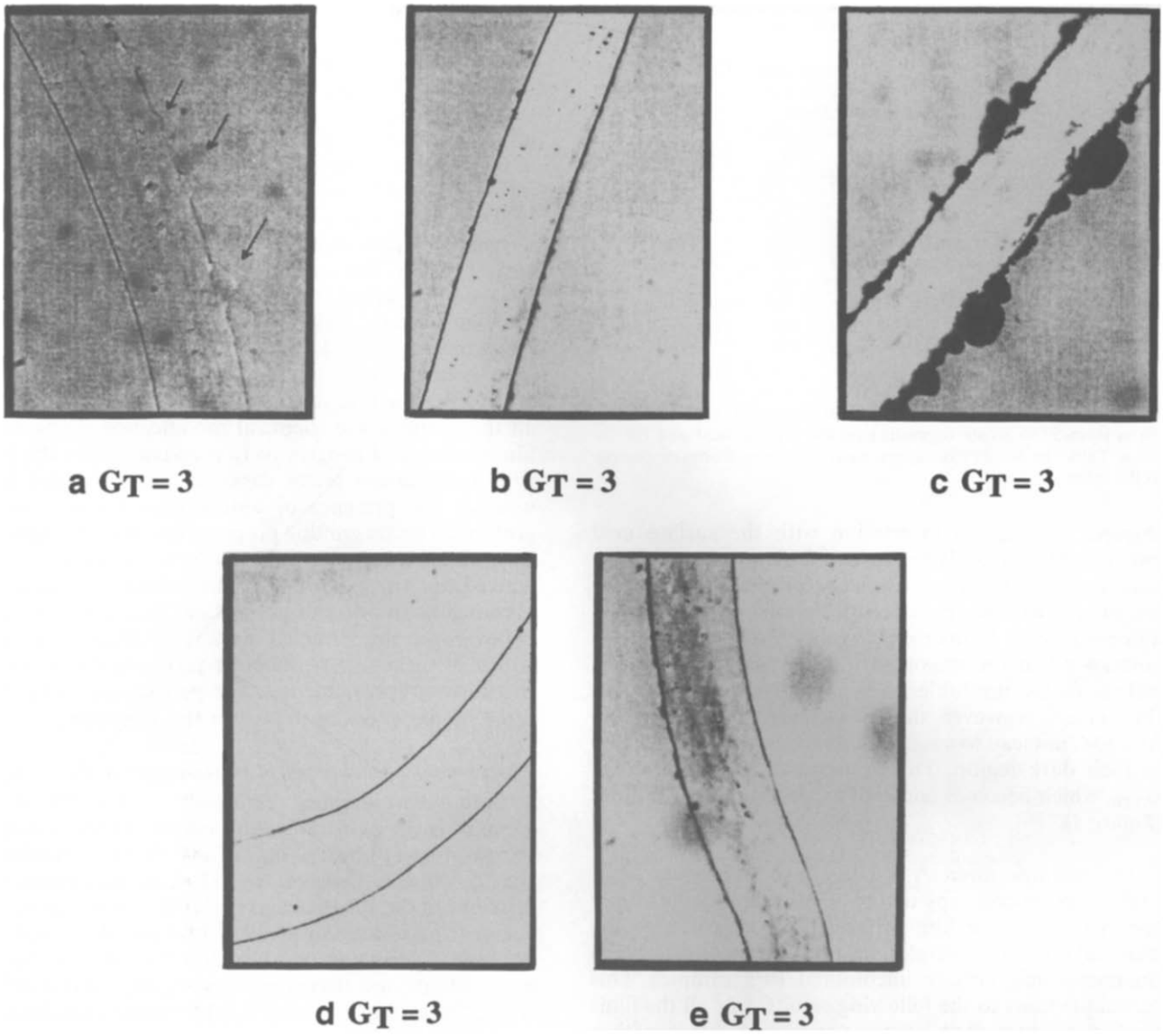

Figure 2 Optical microscopy analysis of microtomic cuts 10 μm thick performed in different PPg films (magnification $\times 250$): unextracted film irradiated at 4 Mrad and uncoloured (a); coloured and unextracted film irradiated at 4 Mrad (b, c); coloured and extracted film irradiated at 2 Mrad (d, e)

Control of the film dimensions. PAA is hygroscopic. Thus, during grafting, PP films swell in the reaction medium. Therefore, their dimensions must be controlled after being dried. We notice that only the film thickness increases with G_T (*Table 1*), their width and length being constant. As a consequence, this thickness increase does not correspond to swelling of the films, which should lead to a three-dimensional phenomenon. Moreover, we can observe that the thickness increase is much more important for the films charged with antioxidants than for the extracted ones. In the latter case, the increase is meaningful for the highest G_T values ($G_T \geqslant 3$). According to the results obtained by i.r. analysis, the extraction of the antioxidants seems to play an important role in the mechanism of grafting propagation.

Optical microscopy. Optical microscopy of microtomic cuts performed on the PPg coloured sample shows a dark region at the film surface (*Figure 2*). This colouring is characteristic of the presence of PAA grafts, but it is impossible to conclude whether the latter corresponds to the whole or only a part of the grafted region. We can compare two films with the same ratio of grafting ($G_T = 3$): one containing antioxidants and the second chemically modified after extraction of the additives. The thickness of the coloured region is higher on the former (*Figure 2c*) than on the latter film (*Figure 2e*) though their G_T values are similar. Thus, the colouring is limited to the uppermost layer of the PPg films, which, according to the i.r.-a.t.r. analysis, corresponds not only to the most grafted layer but also to the most hydrophilic layer. In fact, the inner chains of PP should not be hydrophilic enough to allow the diffusion of the dye molecules through the whole grafted region. This phenomenon is obvious in the extracted films but may also occur in the case of the unextracted ones. Thus, whatever the PPg film, the dark layer cannot be directly attributed to the whole grafted region. Moreover, dye molecules induce a swelling of the coloured region as shown by the comparison of the surface of the highly grafted unextracted film before (*Figure 2a*) and after colouring (*Figure 2c*).

In the case of the PP samples containing antioxidants, the thickness of the dark region increases with G_T

Table 2 I.r. microscopy analysis (with a 30 μm spatial resolution) of microtomic cuts performed on different PPg films[a]

Nature of the films		Extracted and irradiated at 2 Mrad		Unextracted and irradiated at 4 Mrad	
G_T value		4.0	0.9	3.0	0.9
Precise region of the film sheared edge:					
uppermost surface of face A	1	4.70	1.08	2.51	0.91
	2	3.35	0.97	2.26	0.54
	3	3.46	1.00	1.56	0.53
centre	4	3.52	0.90	1.58	0.71
	5	3.68	1.20	1.61	1.00
	6	–	1.30	2.81	
uppermost surface of face B	7			4.22	

[a] The spatial resolution used is always 30 μm while the film thickness varies from 50 to 80 μm depending on the pretreatment and the G_T value. Thus, the number of regions analysed varies from one sample to the other

(*Figures 2b* and *2c*) in relation with the surface acid enrichment previously evidenced (*Figure 1*). For high G_T values ($G_T \geqslant 3$), the coloured region becomes very irregular with the presence of bumps (*Figure 2c*) in agreement with Yamaguchi's results[14]. This area should correspond to the major part of the a.t.r. spectrum as well as to the insoluble fraction evidenced in part 1 of this series[9]. However, the G_T increase of the extracted film does not lead to a significant increase of the thickness of their dark region. This agrees with the variation of G_{ATR}, which becomes constant for the highest G_T values (*Figure 1*).

I.r. microspectrometry. The above techniques (a.t.r. and optical microscopy on coloured samples) allow only the analysis of the film surface. In order to reach the inner layers of the samples, i.r. microscopy is performed on microtomic cuts of uncoloured PPg samples. This technique leads to the following results. For all the films studied, an ungrafted layer, or at least a region with a very weak grafting ratio, cannot be observed due to the size of the spatial resolution (30 μm) compared to the film thickness (55 to 80 μm). The grafting ratio decreases from the surface to the centre (*Table 2*). For the same G_T value, this decrease is higher in the case of unextracted films. The highest grafted film ($G_T = 4$) is characterized by a local grafting ratio lower at one of the faces than in the film centre. This is probably due to a poor localization of the sample in the window. Nevertheless, whatever the case (extracted or unextracted films), an increase of G_T corresponds to a higher amount of PAA grafts both at the surface and in the bulk. Thus, an increase of the monomer concentration in the reaction medium allows the growth of the acidic chains at the surface as well as the propagation of the monomer molecules from the surface to the inner layers of the PPg samples. Unfortunately, the spatial resolution is too high, compared to the film thickness, for us to observe a surface layer constituted only of PAA.

All our results agree with those obtained in part 1 of this series, and allow us to specify the nature of the two kinds of copolymers present in the PPg film. One of them is extremely grafted, with a chemical structure very close to the PAA homopolymer; the other, much less grafted, is characterized by a large distribution of grafting ratios. According to i.r. analysis (a.t.r. and microscopy), the first copolymer should be formed on the film surface and should contain long PAA grafts. It should correspond essentially to the region revealed by the film colouring. The surface of highly grafted unextracted films shows a very irregular aspect. This could partly explain the important increase of their thickness compared to that of the extracted films. The distribution of the less grafted fractions should correspond to the chemical modification of the inner layers of the film, as shown by i.r. microspectrophotometry. These fractions could also correspond to the uncoloured layers. According to the optical microscopy analysis of the coloured samples, all the films should have a highly grafted surface layer. Nevertheless, this layer should be thicker for the unextracted samples owing to the growth of the PAA grafts from the film surface to the reaction medium. For all the samples, the chemical modification starts at the film surface and progressively propagates into the bulk. This propagation seems easier for the extracted films, whereas the presence of antioxidants favours surface grafting. A better grafting propagation could be explained by a better transport of the monomer molecules to the active sites, which depends on the diffusion and solubility parameters. In order to understand the reasons for such behaviour in the extracted films, it is important to know which of these two parameters plays the major part in the transport phenomenon. The permeation study of the films should allow us to answer this question.

Morphological and physical modification of PP

Differential scanning calorimetry. The initial PP samples (with or without antioxidants) have a melting temperature (T_f) near 164°C (*Table 3*). After irradiation, the T_f value is lowered to 161°C, in agreement with scissions of the PP chains at the surface of the crystalline regions[15,16]. After 2 h at 99°C in water saturated with N_2, the T_f remains constant for the films containing antioxidants and decreases very slightly for the others. Thus, the heating necessary for the chemical modification does not seem to produce further degradation of the PP samples. As a consequence, we can conclude that the free radicals trapped in the crystalline regions contribute neither to the grafting nor to further chain scissions. If we consider the variations of the crystallinity ratio listed in *Table 3* for the different samples studied, they are insignificant (compared to the experimental error).

Thermogravimetric analysis. Two parameters can be measured: the loss of matter (Q) occurring between 30 and 395°C and the temperature where the degradation

Table 3 Melting temperature (T_f) and crystallinity (X) of various PP samples at the different stages of the chemical modification

Nature of the films	T_f (°C)	X (%)
Initial PP	164.0±0.5	58.5±0.9
Extracted PP	164.6±0.8	51.5±0.5
Unextracted PP irradiated at 4 Mrad	160.7±0.5	53.0±1.0
Extracted PP irradiated at 12 Mrad	161.0±0.5	56.7±0.5
PP+Δ[a]	162.7±0.5	54.5±0.8
Unextracted PP irradiated at 4 Mrad+Δ	160.5±0.5	58±2
Extracted PP irradiated at 2 Mrad+Δ	163.7±0.5	56±1

[a] Δ corresponds to a heating of 2 h at 99°C in water saturated with nitrogen

Table 4 Thermogravimetric analysis of various PP films performed in a helium atmosphere with a 10°C min^{-1} ramp temperature: Q corresponds to the loss of material occurring between 30 and 395°C and T_d to the temperature at which 2% of the matter is lost

Nature of the PP samples	Initial	Irradiated at 4 Mrad	Irradiated at 4 Mrad $+\Delta^a$	Extracted	Extracted and irradiated at 2 Mrad	Extracted and irradiated at 2 Mrad $+\Delta$
Q (%)	22.0	28.0	23.3	37.3	43.2	35.7
T_d (°C)	326.5	310.3	320.2	310.3	295.0	305.5

[a] Δ corresponds to a heating of 2 h at 99°C in water saturated with nitrogen

begins (T_d), corresponding to a loss of matter of 2% (w/w) of the original sample. It is important to note that the samples studied here are of approximately the same thickness. Thus, this parameter cannot be considered as playing an important part in any differences observed in the results[17].

Before irradiation, Q is lower and T_d is higher for the unextracted films than for the others (*Table 4*). Thus, it appears that the thermal behaviour of the polymer depends on the presence of antioxidants, although the analysis is performed in a helium atmosphere. The ionizing beam makes the PP more sensitive to thermal degradation whether or not the antioxidants are extracted. Indeed, after irradiation, the loss of matter is higher and degradation occurs at lower temperatures (*Table 4*). According to the results obtained for unirradiated films, the thermal degradation is higher in the extracted samples. Nevertheless, if we compare the absolute values of Q and T_d, the role of irradiation on the thermal behaviour of the PP samples seems to be of the same order whether or not the films contain antioxidants. Whatever the case, heating for 2 h at 99°C in water saturated with N_2 leads to a weak thermal stabilization of the irradiated PP (*Table 4*) for Q decreases and T_d increases. This phenomenon seems as important in the extracted sample as in the unextracted ones.

The calorimetric and thermogravimetric analyses give us a better understanding of the phenomena occurring in the polymer after irradiation and during chemical modification. It is well known that irradiation produces free radicals throughout the material. In the amorphous phase, these radicals are labile enough to crosslink together, while, in the crystalline parts, they remain trapped and only able to react with the oxygen initially present or with the nearest PP chains. Thus, irradiation may be responsible for the destruction of the crystalline regions. This phenomenon should be weaker in the case of a sample containing antioxidants. During the thermal treatment, the free radicals trapped in the crystalline regions should not induce further degradation, while the radicals present in the amorphous parts should crosslink together owing to a higher mobility. These two phenomena (scission and crosslinking) seem to be as important in the extracted films as in the others. Polymer samples without antioxidants submitted to an ionizing beam should contain a greater amount of radicals compared to stabilized PP samples. Thus, we would presume that crosslinking and chain scission are more extensive in the extracted films. This is not the case. If we consider the phenomena involved during grafting, the radicals present in the amorphous phase should preferably react with the acrylic acid molecules; those trapped in the crystalline parts that are inaccessible to the monomer molecules should react with the oxygen initially present and thus lead to chain scissions.

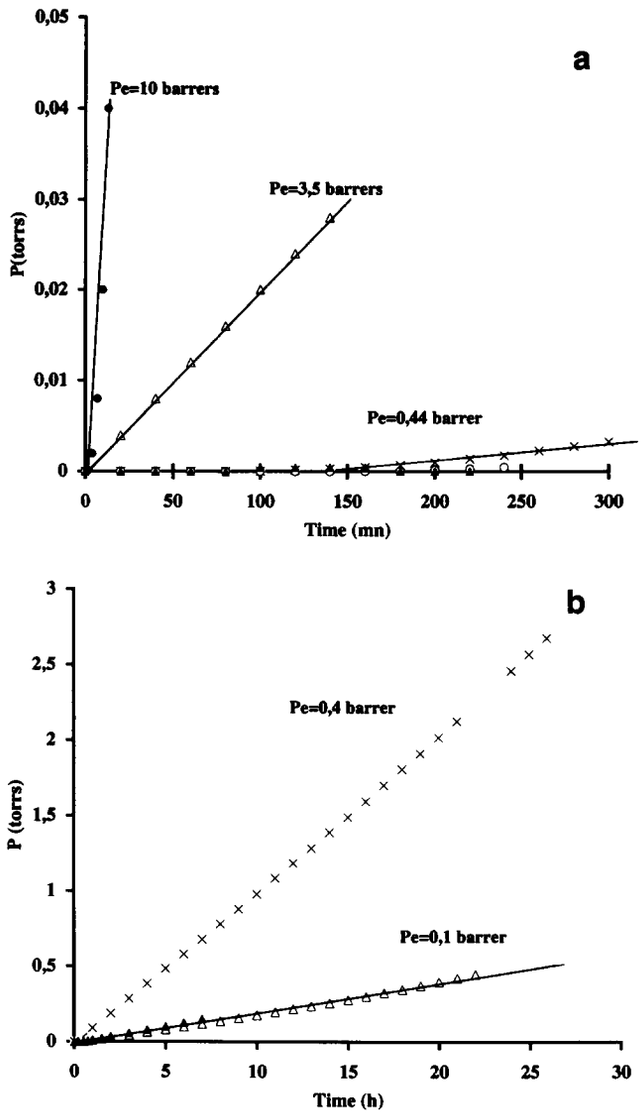

Figure 3 Permeation analysis of various PP films at 23°C in water vapour (a) and nitrogen (b): initial (×); grafted with a G_T value of 1.5 with (▲) and without (△) prior extraction of the antioxidants; extracted, irradiated and stored one month (○) and two months (●)

As a conclusion, the crystalline and amorphous phases seem to play an important role in the locus of the chemical modification and we can presume that they play a major part in the mechanism of grafting propagation. The permeation study of the films should allow us to demonstrate it.

Permeation. The permeability of the initial PP to water vapour (*Figure 3*) is very low: 0.4 Barrer only. For an unextracted film, irradiated at 2 Mrad and stored in air at ambient temperature for one month, it is very

close to the limit of this technique's sensitivity, i.e. 0.1 Barrer (*Figure 3*). After two months under the same conditions, the water permeability of this film increases by 10 Barrers. The sample becomes brittle while, in the same conditions of irradiation and ageing, a PP film containing antioxidants remains ductile.

The grafted films, extracted or not, have a lower permeability to N_2 than the initial PP: 0.1 and 0.4 Barrer respectively. N_2 molecules do not interact with the carboxylic acid functions; thus, the transport of these molecules through the polymer can only occur by diffusion. This phenomenon should be less pronounced in the grafted films than in the initial ones. This could result from the partial crosslinking of the surface PAA grafts, but especially from the low mobility of the PAA chains at ambient temperature, their glass transition temperature being equal to 106°C. The unextracted grafted film shows a very weak permeability to water vapour (0.1 Barrer) although it is highly grafted, while water propagates more easily through the extracted PPg film ($Pe = 3.5$ Barrers). As the diffusion parameter does not play an important part in the permeation behaviour of the PPg samples, this result can only be explained by a better solubility of extracted film in water, in comparison to a continuous grafting in bulk.

It is difficult to propose a mechanism that would take into account all the results presented in this work. It is obvious that the irradiated extracted film had been submitted to an important degradation due to chain scission. This should explain its permeability to water vapour. In part 1 of this series[9], we proposed that grafting in the bulk of the extracted PPg films was partially due to degradation, allowing the preferential migration of the monomer molecules to the active sites. This hypothesis can be eliminated; indeed calorimetric and thermogravimetric analyses show that heating the irradiated films, for 2 h at 99°C in water saturated with N_2, does not make the extracted samples more thermally sensitive than the unextracted ones. Thus, the better propagation of the monomer molecules through the polymer can be explained by the solubility parameter relating to the balance between hydrophilic and hydrophobic parts in the irradiated films and also to the evolution of the balance localization as the grafting evolves. Nevertheless, we can expect that the heating involved in the chemical modification favours the transport of the monomer molecules. Unfortunately, the permeation analysis cannot be performed at such a temperature.

CONCLUSION

This work allows us to have a better understanding of the localization of grafting. The chemical modification remains heterogeneous and only affects the amorphous parts of PP. Indeed, these are the only regions easily accessible to the monomer molecules. The semicrystalline character of the PP used and the localization of antioxidants in the amorphous parts makes the polymer locally anisotropic. Thus, the peroxide radicals produced in the amorphous parts of the PP are much more abundant for the extracted films than for the others. This particular localization of grafting can then explain the better permeability to water vapour due to the solubility effect.

ACKNOWLEDGEMENTS

We acknowledge Dr M. Escoubes and Dr J. Y. Dolveck (University of Lyon) for their fruitful help and discussion on permeation experiments, and Dr Petit (C R V Pechiney, Grenoble) for fruitful discussions.

REFERENCES

1 Geleji, F. and Odor, L. *J. Polym. Sci.* (*C*) 1963, **4**, 1223
2 Bhardwaj, I. S. and Heusinger, H. *Colloid Polym. Sci.* 1978, **256**, 663
3 Sundardi, F. *J. Appl. Polym. Sci.* 1978, **22**, 3163
4 Rao, M. H. and Rao, K. N. *Polym. Bull.* 1979, **1**, 727
5 Pugh, C. and Hsieh, Y. L. *J. Appl. Polym. Sci.* 1984, **29**, 3641
6 Gawish, S. M., Gavet, L. and Chabert, B. *Am. Dyestuff Reporter* Dec. 1989, p. 54
7 Yao, Z. P. and Ranby, B. *J. Appl. Polym. Sci.* 1990, **41**, 1459
8 Mehta, I. K., Kumer, S., Chauhan, G. S. and Misra, B. N. *J. Appl. Polym. Sci.* 1990, **41**, 1171
9 Romero, M. A., Domard, A. and Petit, D. *Polymer* 1993, **34** (14), 3004
10 Bellamy, L. M. 'The IR Spectra of Complex Molecules', Chapman and Hall, London, 1975, pp. 13 and 183
11 Rebattet, L., Genies, E., Pineri, M. and Escoubes, M. Proc. 3rd Int. Conf. on Effective Membrane Processes — New Perspectives, BHR Gr. Conf. Ser. No. 3 (Ed. R. Paterson), London, 1993, p. 323
12 Audoin, L. and Verdu, M. 'Radiation Effects on Polymers' *ACS Symp. Ser.* 1991, **475**, 473
13 Williams, J. L. 'Radiation Processing of Polymers' (Eds. A. Singh and J. Silverman), Hanser, New York, 1992, p. 255
14 Yamaguchi, T., Nakao, S. I. and Kimura, S. *Macromolecules* 1991, **24**, 5522
15 Busfield, W. K. and O'Donnell, J. H. *Eur. Polym. J.* 1978, **15**, 379
16 Krestev, V., Dobreva, B., Kresteva, M., Minkova, L. and Nedkov, E. *Bulg. J. Phys.* 1988, **15** (3), 265
17 Cohen, A., Carriere, C. J. and Pasztor, A. J. *Polym. Eng. Sci.* 1993, **33** (6), 317