

IR Spectroscopy Approach for the Study of Interactions Between an Oxidized Aluminium Surface and a Poly(Propylene-g-Acrylic Acid) Film

M. A. ROMERO,^{1,2} B. CHABERT,¹ and A. DOMARD^{1,*}

¹Laboratoire d'Etudes des Matériaux Plastiques et des Biomatériaux, URA CNRS 507, Université Claude Bernard Lyon I, 43 Boulevard du 11 Novembre 1918, 69622 Villeurbanne Cedex, France and ²Centre de Recherche de Voreppe S.A., BP 27, 38340 Voreppe, France

SYNOPSIS

In this paper, we report the study of the interactions between a poly(propylene-g-acrylic acid) and an oxidized aluminium surface by IR spectroscopy. A deposit of a pure poly(acrylic acid) on the same surface is used as a model. Under free acid form (COOH) we demonstrate the formation of hydrogen bondings between the acrylic carboxyl groups and OH functions located at the surface of alumina. This is characterized by an IR absorption [$\nu_{(C=O)}$] at 1733 or 1743 cm^{-1} when we observe the metal surface either after peeling of a PPg(OH) film initially pressed on it or after a deposit of PAA(OH). Under the carboxylate form (COO⁻), we observe two modes of interaction, the one purely ionic between COO⁻ and Al³⁺ with an absorption located near 1550 cm^{-1} and the other of complex form between COO⁻ and Al³⁺ giving a band near 1610 cm^{-1} . The water molecules can play a major part, in particular in the first case (COOH) where they destroy hydrogen bondings in favor of the formation of —COO⁻ groups, interacting with the metal surface according to ionic or complex modes as above. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Adhesion of a polymer to a metal surface is the result of various complex mechanisms. Therefore, several theories exist, each of them assuming one aspect of the phenomenon that can correspond to a mechanical, thermodynamic, or chemical approach.

Numerous authors were interested in chemical interactions that take place between metal oxides and various chemical structures, for example, Al₂O₃ hydrated or anhydrous with different organic acids. Two kinds of studies are reported. One, from a deposit of a monomer in solution,¹ in the liquid² or vapor³ state, on a metal surface; the second, with the polymer, from a deposit on a metal oxide⁴ or, from a mixture of oxide powder with a polymer solution.^{5,6}

The aim of our studies was to describe the interactions involved in the adhesion between a sheet of aluminium covered with Al₂O₃ and a film of polypropylene (PP) grafted with poly(acrylic acid) (PAA). For this purpose, various solutions of PAA were deposited on the metal surface, then analyzed by Fourier Transform infrared spectrometry (FT-IR) according to the reflection-absorption technique. The role of the structure of the carboxyl groups (—COOH or —COO⁻) was also investigated. A comparison was made with the results obtained from a grafted film of PP (PPg) pressed on a metal sheet then peeled.

EXPERIMENTAL

Materials

The poly(propylene) film used, 50 μm thick, was obtained from an extrusion process.

Size exclusion chromatography (SEC) measure-

* To whom correspondence should be addressed.

ments were performed with a Waters Associates Model 150-C instrument, with orthodichlorobenzene (ODCB) as eluent at 135°C and three columns packed with styragel of 10^3 , 10^4 , and 10^5 Å as pore sizes.

The instrument was calibrated with narrow distribution polystyrene standards. The relative (to polystyrene) weight-average molecular weight (M_w) of the PP film was 250,000 g mol⁻¹.

The degree of crystallinity (smectic form) of the PP film was near 58%. The crystallinity and the crystalline structures were determined by differential scanning calorimetry (DSC). The polymer contained 1025 ppm of antioxidants.

The aluminium sheet (Pechiney, France) used in the present study was covered with an anodised oxide layer.

The acrylic acid containing 200 ppm of stabilizer was from Coatex, France.

All the other reactives and solvents used were commercial products of reagent grade.

All the aqueous solutions were prepared with deionized water.

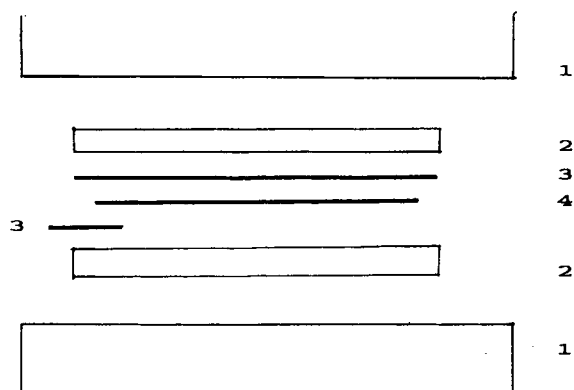
Methods

Grafting, Preparation of Poly(Propylene-g-Acrylic Acid)

The PP film was first irradiated in air by means of an electron beam accelerator with a total dose of 2 mrad, at ambient temperature. The film was then introduced into a Pyrex glass tube containing an aqueous solution of acrylic acid (AA) prepared at a given concentration within 10–30% (weight/weight). The solution was free of any kind of antihomopolymerizing agent. Nitrogen was bubbled into the tube for 15 min. The tube was then allowed to rotate into an oven thermostated at 99°C for 2 h by means of a planetary rotation. The irradiation was performed in the French Institute of Textile (Ecully, France).

The electron accelerator was a prototype of Irelec, France.

In order to remove the residual monomer (AA) and the homopolymer of acrylic acid (PAA), the grafted PP film was washed, first in running water, then in an aqueous solution of hydrochloric acid 1.25×10^{-2} N for 10 min, at ambient temperature, and, finally, in deionized water at 40°C, for 2.5 h with shaking and with several changes of water. The PAA grafted on PP chains was in the free acid form (PPg(OH)). The final yield of grafting was within 1–8% (weight/weight), depending on the concen-



- 1- press plates
- 2- aluminium sheet
- 3- untreated PP film
- 4- grafted PP film

Figure 1 Metalloplastic material preparation. 1, press plates; 2, aluminium sheets; 3, untreated PP film; 4, PPg film.

tration of the AA solution. In order to obtain the carboxylate form (PPg(O⁻)), the PPg film was soaked in an aqueous solution of sodium hydroxide 0.1 N for approximately 30 min, under stirring at ambient temperature. The excess of NaOH was removed by a washing with deionized water.

Metalloplastic Material Preparation

The metalloplastic material was obtained by pressing the PPg film onto the aluminium sheet at a pressure of 210 bar and a plate temperature of 120°C for 5 min (Fig. 1). The material was then rapidly cooled by pressing between two plates of copper in which cold water circulated.

Modeling

The PAA layers deposited on the metal oxide surface as models were prepared as follows. Samples of aluminium were dipped in PAA solutions at given concentrations, under free acid (PAA(OH)) or carboxylate (PAA(O⁻)) forms. After three seconds, the samples were removed and dried under vacuum (10^{-2} bars) at approximately 25°C.

The free acid form was prepared by mixing PAA powder ($M_w = 250,000$ g mol⁻¹) in methanol; the carboxylate form was obtained by adding a sodium hydroxide solution (0.1 N) to an aqueous solution of PAA until the equivalent point was reached.

The analysis of the samples thus obtained was carried out approximately 4 h after preparation.

Analysis

The percent of grafting (weight/weight) was determined by weighing and deduced from the relation: $G = [(W_f - W_o) / W_o] \times 100$ with G , the percent of grafting, W_o and W_f , the initial and final weights of the PP film.

FT-IR measurements were carried out on a Perkin Elmer spectrophotometer; the resolution and the number of scans were 4 cm^{-1} and 2 respectively. The PP films were analyzed using the transmission and the attenuated total reflection techniques. The metal oxide surfaces were observed by means of the reflection-absorption technique; the angle of incidence was 80° and the analysis was carried out under a nitrogen purge.

The amount of PAA deposited on the metallic substrates was determined from the infrared spectrum and computed assuming a linear relation as follows:

$$q = \frac{A(1455 \text{ cm}^{-1})}{A(945 \text{ cm}^{-1})} \times \frac{q_o}{\frac{A_o(1455 \text{ cm}^{-1})}{A_o(945 \text{ cm}^{-1})}}$$

where q is the amount of polymer on the observed sample, $A(1455 \text{ cm}^{-1})$ and $A(945 \text{ cm}^{-1})$ the absorbances of the vibrations corresponding to $\delta(\text{CH}_2)$ of PAA and $\nu(\text{Al}-\text{O})$ of Al_2O_3 ; q_o , $A_o(1455 \text{ cm}^{-1})$, and $A_o(945 \text{ cm}^{-1})$ are the same characteristics as those described above, but for a known weight of PAA(OH) deposited on the Al_2O_3 surface. The low intensity of the bending vibration of $-\text{CH}_2-$ makes it difficult to evaluate the amount of polymer present on the alumina substrates.

RESULTS AND DISCUSSION

Study of the Interactions Between Alumina and PAA Chains Under Free Acid Form ($-\text{COOH}$)

With a PPg(OH) Film

The IR spectrum obtained by transmission on 3% (weight/weight) grafted film [Fig. 2(a)] exhibits the existence of a major peak located at 1710 cm^{-1} . The broadening observed near the lowest frequencies is probably due to the presence of water [$\delta(\text{H}-\text{O}-\text{H}) 1600 \text{ cm}^{-1}$]⁷ and also to an interference band. The spectrum obtained by attenuated total reflection (ATR) [Fig. 2(b)] shows a little ab-

sorption near 1550 cm^{-1} that is characteristic of the antisymmetric valence vibration (ν_a) of $-\text{COO}^-$. This is in agreement with the presence of water in the sample. In Figure 2(a), the antisymmetric and symmetric vibration bands of $-\text{COO}^-$ are presumably overlapped by the interference waves present everywhere in the spectrum and by peaks characteristic of PP.

After the PPg(OH) film has been pressed on a sheet of oxidized aluminium then peeled (PPg(OH)/ Al_2O_3), the reflection spectrum [Fig. 3(a)] of the metal surface reveals the presence of PAA, in significant amounts, by a band at 1733 cm^{-1} and a little absorption at 1541 cm^{-1} . The first can be only assigned to $\nu_{(\text{C}=\text{O})}$ of the acidic form of the carboxylic functions and the second to $\nu_{a(\text{C}=\text{O})}$ of $-\text{COO}^-$ under ionic interaction with H^+ , Al^{3+} , or other present cations.^{5,7,8} The background noise renders the exact determination of the peak position difficult and, therefore, the determination of the counter ion associated with $-\text{COO}^-$. The most important observation is that after peeling, at the surface of the metal, at the level of the alumina layer, the $\nu_{(\text{C}=\text{O})}$ band corresponding to the PAA carboxylic function interacting with Al_2O_3 is displaced from 1710 (transmission analysis) to 1733 cm^{-1} (reflection-absorption).

From a Deposit of PAA(OH)

When the thickness of the layer of a pure PAA(OH) deposited on the Al_2O_3 surface decreases, the intensity of the band at 1694 cm^{-1} , corresponding to $\nu_{(\text{C}=\text{O})}$ of COOH groups, decreases to the benefit of a band located near 1743 cm^{-1} . In the case of a thick layer of PAA(OH) [Fig. 4(a)], the spectrum reveals also the presence of the ionized form (near 1541 cm^{-1}). Conversely, in the case of a fine deposit [Fig. 4(b)], the carboxylate form (near 1541 cm^{-1}) cannot be observed.

The pure PAA(OH) simply deposited on the metal surface or, deposited, then pressed in the same conditions as for the grafted film, behave the same towards alumina and gives spectra that are quite superimposable [Figs. 4(b, c)]. This result could signify that mechanical anchorage plays a minor part in the mechanism of interaction studied but also that anchorage can be attained from a single deposit of a PAA(OH) solution.

The difference between the two techniques of analysis, the one by transmission [Fig. 2(a)] and the other by reflection [Figs. 3(a), 4(a)] cannot be considered alone to explain a displacement of 30 cm^{-1} (hypothesis confirmed thereafter). Then, we

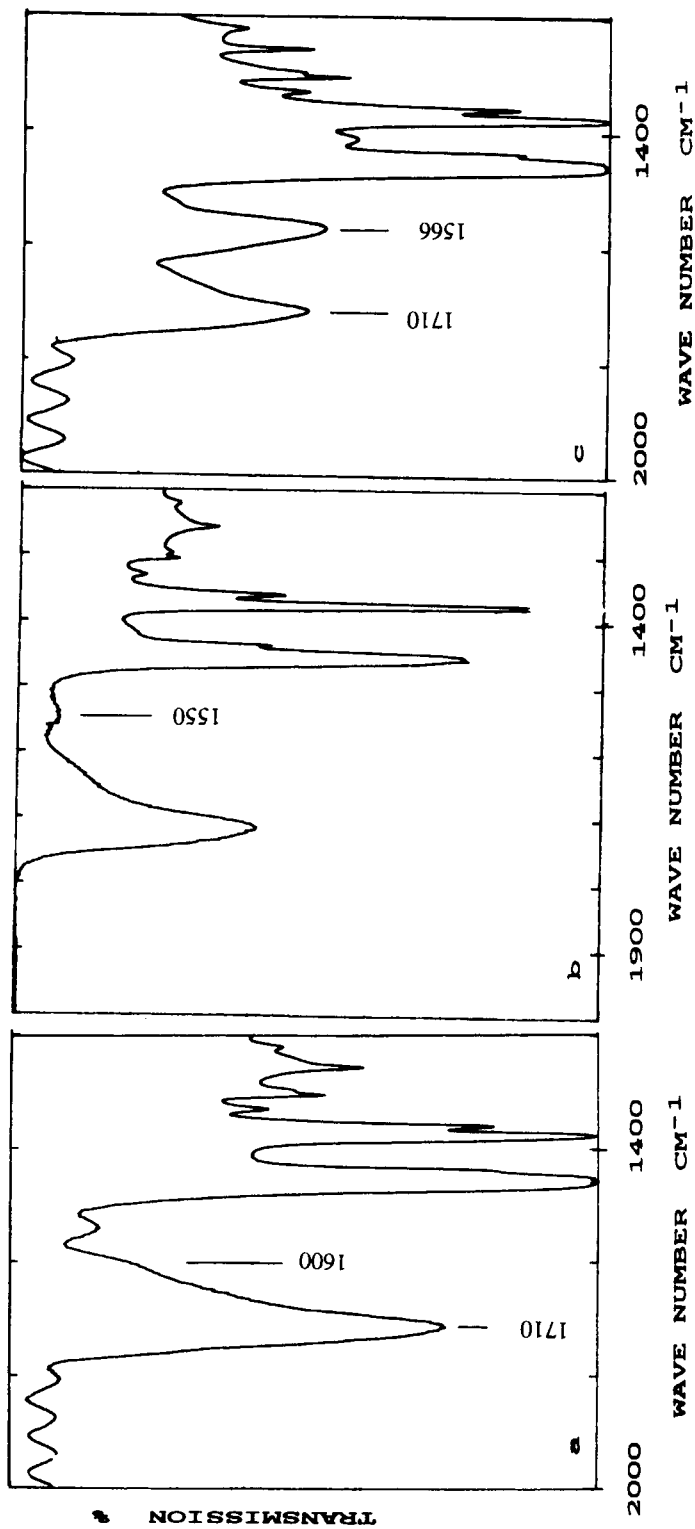


Figure 2 IR spectra of the PPg film: (a) under free acid form by the transmission technique; (b) by the A.T.R. technique; (c) under carboxylate form by the transmission technique.

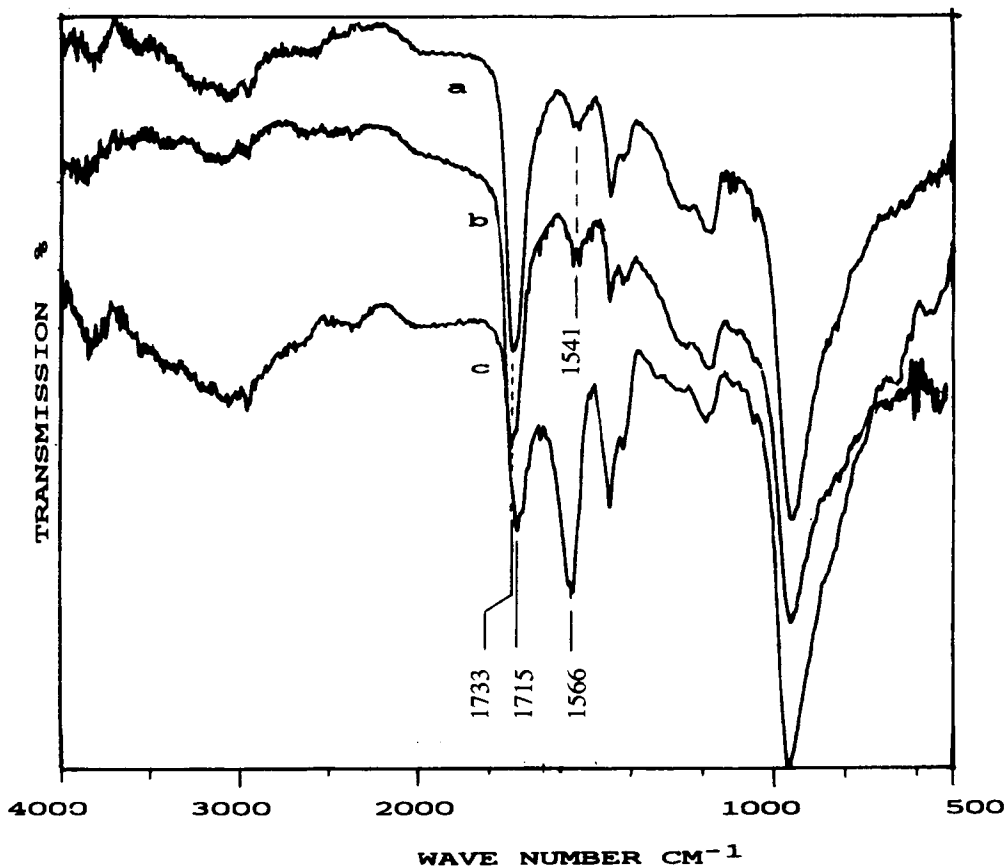


Figure 3 Reflection-absorption spectrum of the polymer remaining at the alumina surface after peeling of a PPg(OH) film initially pressed on the metal: (a) before washing; (b) after washings of 45 min; and (c) 7 h.

must assume a particular interaction between the COOH groups of PAA(OH) and the alumina layer.

In agreement with the works of Crisp⁵ and Rabie,⁶ the absence of $-\text{COO}^-$ at the surface of alumina in the case of a deposit of PAA(OH) of small thickness, shows the low reactivity or the absence of reactivity of $-\text{COOH}$ functions with Al_2O_3 .

The presence of $-\text{COO}^-$ functions, in the case of PPg(OH)/ Al_2O_3 , results from a partial ionization state of the grafted PAA, probably due to water molecules always present in the media. They can solvate some $-\text{COOH}$ functions and then act on the equilibrium $-\text{COOH} + \text{H}_2\text{O} \rightleftharpoons -\text{COO}^- + \text{H}_3\text{O}^+$. This must be related to the method of grafting and washing of the PP film that consists of soaking it in an aqueous media for long periods. Thus the modified layer of the film is likely to contain an amount of water that varies according to the quality of the dryings. The DSC spectrum (Fig. 5) demonstrates this phenomenon. This residual water cannot go through the unmodified PP layer, thus,

the evaporation of the solvent can take place only at the modified surface. It is then possible to generate an enrichment of H_2O at the interface PPg(OH)/ Al_2O_3 during the pressing.

In the case of a fine deposit of PAA(OH) from a solution in methanol, the water content of the material is limited in two ways. The first is that the solvent used contains only 0.1% of H_2O and the second is that water is more easily eliminated from such a thin layer.

Thus, we show the very important part that water can play in the mechanism of interaction between a metal oxide and the superficial layer of a polymer film in contact with it.

Influence of a Washing at the Interface Polymer/Metal

In the Case of a Deposit of PAA(OH). A dipping in water, under stirring, of aluminium samples on

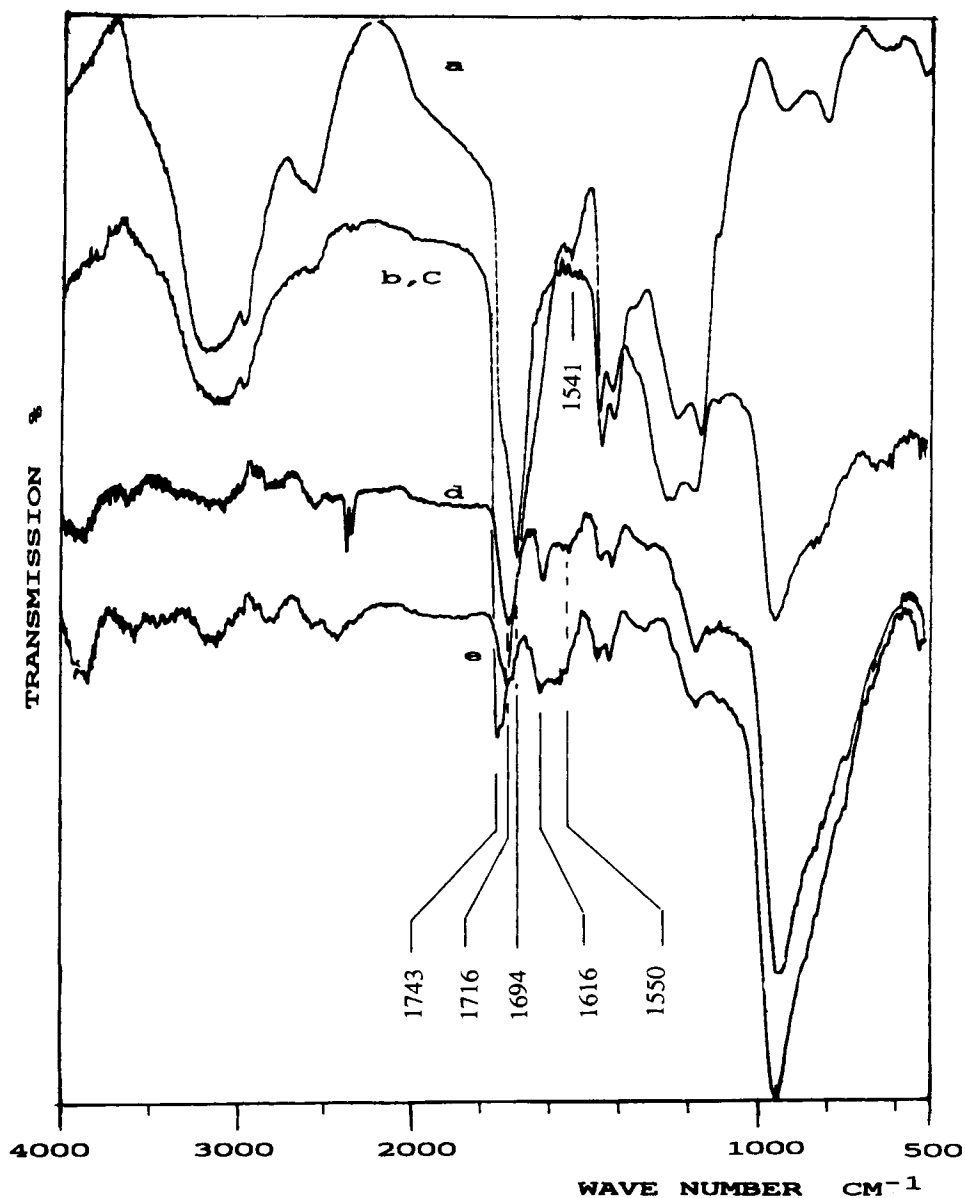


Figure 4 Reflection-absorption spectrum of (a) thick and (b, c, d, e) thin layers of PAA under free acid form deposited on the alumina surface: (b) simply deposited; (d) the same after a washing of 45 minutes; and (e) 7 hours in water. (c) Reflection-absorption spectrum of a thin layer of PAA deposited and then pressed on the metal (210 bars, 120°C, 5 min).

which was previously deposited PAA(OH), leads to a progressive solubilization of the latter. It is interesting to note that this removal of product tends towards a plateau of which the limiting value is the same, whatever the initial amount deposited (Table I^{a,b}). The system behaves as if an external layer of polymer was highly retained on the alumina and the rest of the polymer ignored by the metal surface. This particular behaviour can be attributed to a chemical interaction between the materials, to a

mechanical anchorage of PAA chains in alumina pores, or both. During this treatment, the band at 1743 cm^{-1} disappears to give rise to a band at 1716 cm^{-1} [Fig. 4 (b, d, e)]. The absorbance of the latter decreases with washing to the benefit of two others located near 1616 and 1550 cm^{-1} . The first (1616 cm^{-1}) could be assigned to the presence of water due to washing, in agreement with the deformation band of water observed by Nakamoto⁷ in the range within 1600–1630 cm^{-1} ; but, in that case, the symmetric

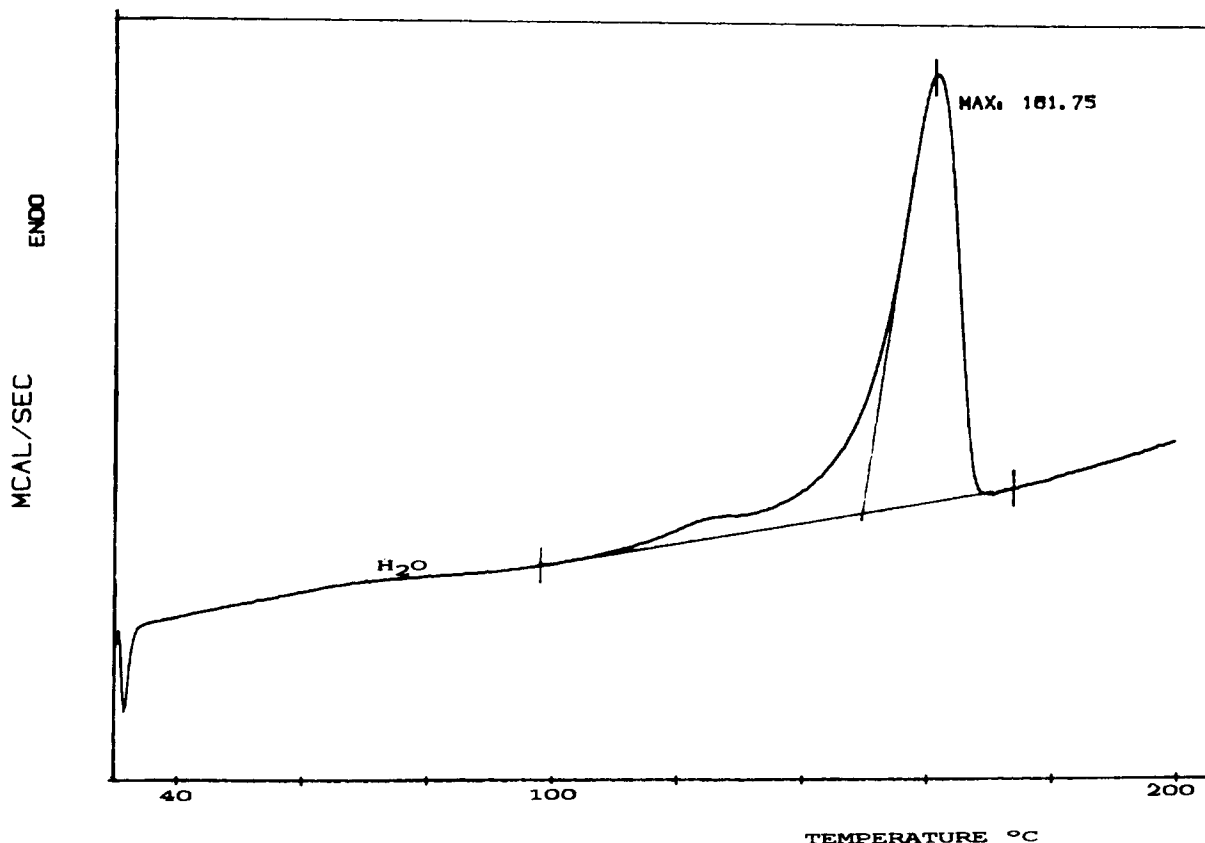


Figure 5 DSC spectrum of the PPg(OH) film.

and antisymmetric valence vibration of H_2O would appear, with a great absorbance in the range⁸ 3200–3550 cm^{-1} that is not the case [Fig. 4(d)].

Table I Amount of Polymer Present at the Alumina Surface Before and After Washing

Observed Sample	Amount of Polymer (mg/cm^2)		
	Initially	Washing of	
		45 Min	7 H
PAA(OH)/ $\text{Al}_2\text{O}_3^{\text{a}}$ thick layer	0.66	0.01	0.01
PAA(OH)/ $\text{Al}_2\text{O}_3^{\text{b}}$ thin layer	0.08	0.01	0.01
PPg(OH)/ $\text{Al}_2\text{O}_3^{\text{c}}$	0.03	0.03	0.04
PAA(O ⁻)/ $\text{Al}_2\text{O}_3^{\text{d}}$ thick layer	0.20	0.01	0.01
PAA(O ⁻)/ $\text{Al}_2\text{O}_3^{\text{d}}$ thin layer	0.01	0.01	0.01
PPg(O ⁻)/ $\text{Al}_2\text{O}_3^{\text{f}}$	0.06	0.03	0.03

^{a,b,d,e} Poly(acrylic acid) under ^{a,b} free acid and ^{d,e} carboxylate form deposited on the metal oxide surface.

^{c,f} Polymer remaining at the alumina surface after peeling of a film grafted under ^d free acid or ^f carboxylate form, and initially pressed on the metal.

In the Case of a PPg(OH) Film. A dipping of 45', after peeling, of a piece of oxidized aluminium on which was pressed a PPg(OH) film gives no change in the IR spectra of the metal surface. After 7 h in water, we observe no removal of product (Table I^c) but, in this case, the $\nu_{(\text{C}=\text{O})}$ is displaced from 1733 to 1715 cm^{-1} [Fig. 3(c)]. This displacement corresponds to two alumina surfaces observed by the same technique (reflection-absorption). Thus, when results obtained by transmission and reflection are compared, the displacement of wavelength observed cannot be attributed to an experimental shift, as Allara proposed it.⁴ The absorbance of this band decreases to the benefit of another peak located at 1566 cm^{-1} . This band that base covers the range 1500–1650 cm^{-1} could be the result of the convolution of the two bands at 1616 and 1550 cm^{-1} previously evidenced.

As a conclusion, a dipping in water, whatever the case studied, after peeling of a PPg(OH) film or after a deposit of PAA(OH), leads to the destruction of the interaction that gives the bands at 1733 and 1743 cm^{-1} , respectively. Thus, the band near 1710 cm^{-1} is regenerated. In contact with water, the acid groups are partially dissociated [$\text{pK}_{\text{a}}(\text{PAA}) = 4.3$] into

—COO⁻ and H⁺, and then react with alumina according to ionic or complex interactions. In the case of PAA(OH) after washing, there remains only a small amount of product in an ionic or a complex interaction with the metal surface, which could concern various sites present at the surface of Al₂O₃.

The bands at 1733–1743 cm⁻¹ appearing on the alumina surface only for PPg(OH) after peeling or for a deposit of PAA(OH) (of low depth) reflects particular situations for the COOH directly in contact with the metal.

Assignment of Bands at 1743 and 1733 cm⁻¹

We can assume that all of the spectra modifications we observed correspond only to changes between various possibilities of hydrogen bondings between —COOH of PAA chains (grafted or not), H₂O molecules or OH of the alumina surface. Two situations corresponding to a PPg(OH) or PAA(OH) alone or after being contacted onto alumina surfaces must be considered and are represented in Figure 6. Carboxylic acid functions of acrylic repeating units, whatever the case, before a contact with the metal, give a unique band centered near 1710 cm⁻¹. As shown in Figure 6(I₁) this absorption would correspond to the “dimer” form⁸⁻¹⁰ obtained mainly by the antiparallel association of two carboxyl groups of two chains or of two segments of the same macromolecule. After a contact with the surface of the metal, this band disappears entirely to the benefit of a band centered at 1743 cm⁻¹ for a deposit of PAA(OH) and at 1733 cm⁻¹ for a PPg(OH) after peeling. Figure 6 allows us to assign the first to an interaction of monomer type between —COOH and OH located at the metal surface [Fig. 6(II₃)], and the second to a system of a sideways hydrogen bonding chains formed along the polymer backbone and the OH groups of the metal surface [Fig. 6(II₂)] as proposed by Davies and Yarwood.¹¹ In fact, in the latter case, the location of the band, due to the technique, can vary with the depth of the remaining material. In particular, a decrease of the frequencies is observed when the depth decreases.¹² Thus, these two bands could correspond to the same interaction, i.e., a monomer type hydrogen bonding [Fig. 6(II₃)].

After washing, this structure is destroyed, certainly because water molecules act as raptors of the metal —OH···O=C—OH hydrogen bondings that leads to a new formation of the dimer form [Fig. 6(I₁,II₁)] but also, for the major part, to the formation of carboxylates. These are then the groups

that give ionic or complex interactions with the alumina surface and provide their retention.

Nature of the Polymer Remaining at the Metal Surface

If we consider the nature of the polymer remaining at the surface of alumina after pressing and peeling of a PPg(OH) film, various hypotheses are possible among which the most probable are the following: a homopolymer of PAA(OH), a PPg(OH), a mixture of PPg(OH) and PP, a mixture of PAA(OH) and PP, a mixture of PAA(OH) and PPg(OH), and a ternary assembly of PAA(OH), PP and PPg(OH). The first and the last three hypotheses could be rejected since in all these cases, a removal of product would be observed as for the case of a pure PAA(OH) deposited on alumina. The second and the third hypotheses suppose the presence of two polymers at the surface of the metal oxide. The IR analysis is incapable of distinguishing between these two hypotheses. In fact, the small amount of polymer present at the metal surface after peeling leads us to suppose that the cohesion concerns only a layer of macromolecules of low thickness (approximately 0.5 μm). During the electron beam treatment, all the PP chains in the film can be considered as equally irradiated. Therefore, it is difficult to imagine that some PP chains could be completely ignored by the irradiation and grafting while others would be modified. Moreover, an experiment consisting of placing the grafted film in the conditions of solubilization of a pure PP (ODCB at 135°C) leads to the extraction of an insoluble fraction. The IR analysis of this part reveals a spectrum quite similar to that of a pure PAA. Nevertheless, this fraction is insoluble in water whatever the pH.

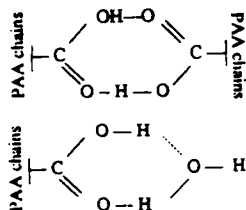
As a conclusion, the layer observed at the surface of the alumina can be considered as only constituted of PP chains highly grafted with PAA.

Study of the Interaction Between Alumina and PAA Under Carboxylate Form (—COO⁻)

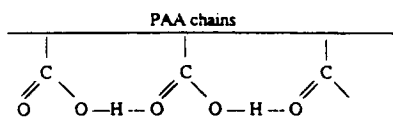
With a PPg(O⁻) Film

The PPg(O⁻) film [Fig. 2(c)], before pressing, shows the existence of —COO⁻ functions by the presence of a ν_{a(COO⁻)} band at 1566 cm⁻¹, but also of —COOH functions by an absorption band at 1710 cm⁻¹. Thus, despite the excess of NaOH used to dissociate the COOH groups, they are not all ionized. We can attribute this behaviour to a limited diffusion of OH⁻ ions in the modified PP layers

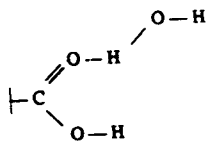
(1) dimers 1700-1710 cm^{-1} (8,9,10)



(2) sideways chains 1730 cm^{-1} (10)

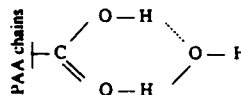


(3) monomers 1740 cm^{-1}

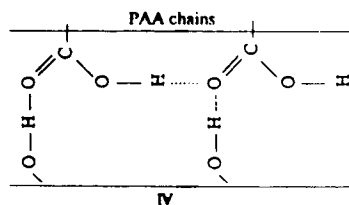


I

(1) dimers 1700-1710 cm^{-1} (11)

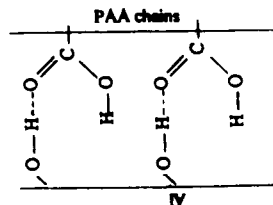


(2) sideways chains 1730 cm^{-1} (11)



IV

(3) monomers 1740 cm^{-1} (11)



IV

II

Figure 6 Various possible hydrogen bonding arrangements for PAA carboxylic functions under acidic form and the corresponding IR absorption frequencies ($\nu_{\text{C=O}}$): (I) PAA chains (grafted or not) alone; (II) after a contact with the surface of the metal (alumina).

caused, in particular, by an increase of hydrophobicity for the deep layers where the grafting ratio is lower. Thus, only the carboxylic functions at the film surface could be easily ionized.

After pressing against the aluminium sheet then peeling, a layer of graft copolymer remains also at the metal surface under acrylate form [Fig. 7(a)], but with a $\nu_{\text{a}(\text{COO}^-)}$ that is displaced from 1566

(transmission analysis) to 1600 cm^{-1} (reflection-absorption analysis), accompanied by a broadening of the peak near the lowest frequencies.

With a Deposit of PAA(O⁻)

The IR analysis [Fig. 8(a)] of an oxidized metal surface covered by a layer of PAA under acrylate

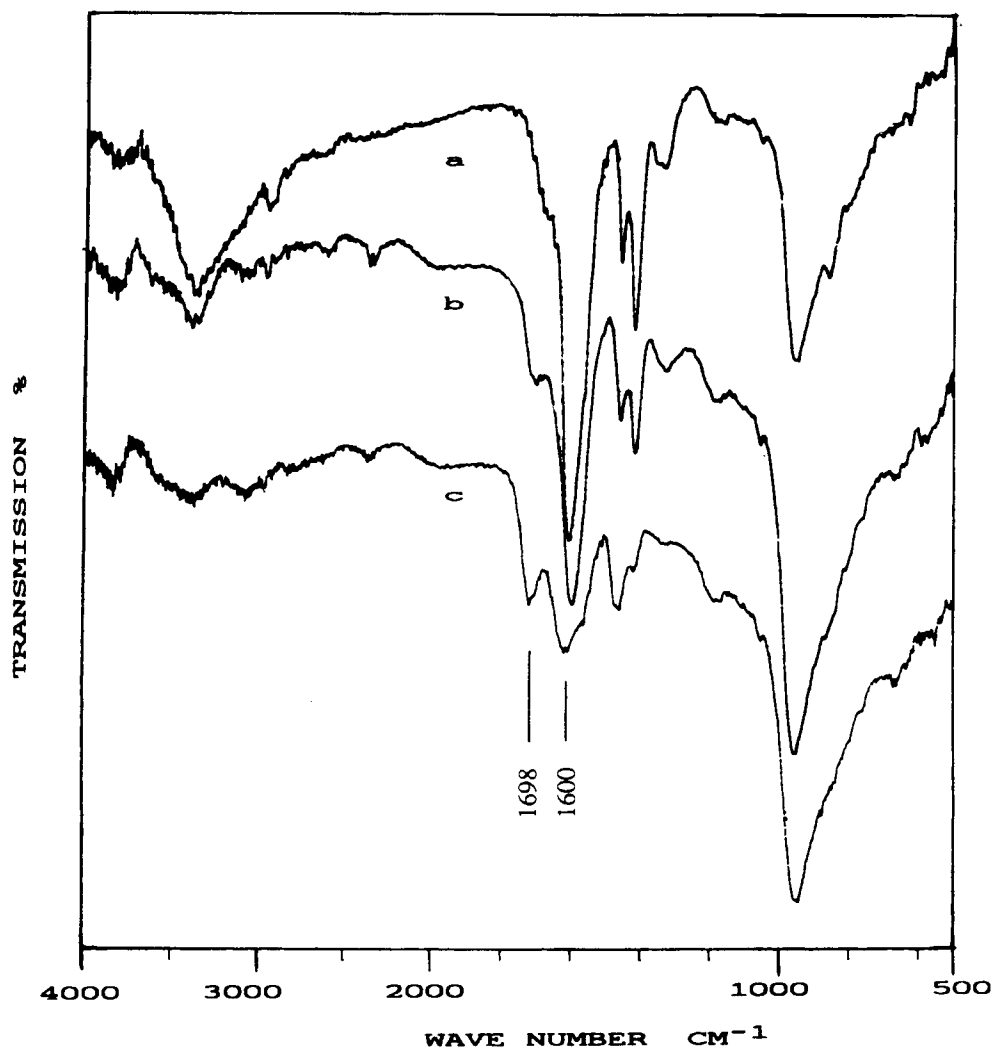


Figure 7 Reflection-absorption spectrum of the polymer remaining at the alumina surface after peeling of a $PPg(O^-)$ film initially pressed on the metal (a) before washing; (b) after a washing of 45 min; and (c) 7 h.

form reveals the presence of a peak at 1610 cm^{-1} and a shoulder near 1570 cm^{-1} . These bands can only be assigned to $\nu_a(\text{COO}^-)$ corresponding to carboxylate functions that are under complex interactions with aluminium⁵ (1610 cm^{-1}) and, to a small part of them, that are under ion pairs form, principally with Na^+ (1570 cm^{-1}). The band at 1610 cm^{-1} observed for the two cases above could also be attributed to $\delta_{(\text{H}-\text{O}-\text{H})}$ of water molecules adsorbed by $PAA(O^-)$, grafted or not. In both cases, the presence of water is obvious and is revealed by heavy absorption bands near 3400 cm^{-1} [Figs. 7(a), 8(a)].

We can remember that the bands corresponding to water are generally large. This could explain the broadening of the base of the peak at 1610 cm^{-1} .

But water cannot be considered as the main origin of this peak. Thus, the peak at 1610 cm^{-1} corresponds quite well to the interaction between COO^- and Al^{3+} .

These results lead to an interesting conclusion. In both cases studied, corresponding to a $PPg(O^-)$ or a $PAA(O^-)$ in contact with Al_2O_3 , the simple ionic interaction between COO^- and Na^+ or Al^{3+} appears largely disfavored to the benefit of a complex interaction with Al^{3+} ions.

Role of Washing

In the Case of $PPg(O^-)$. A dipping in water of pieces of oxidized aluminium sheets, after pressing then

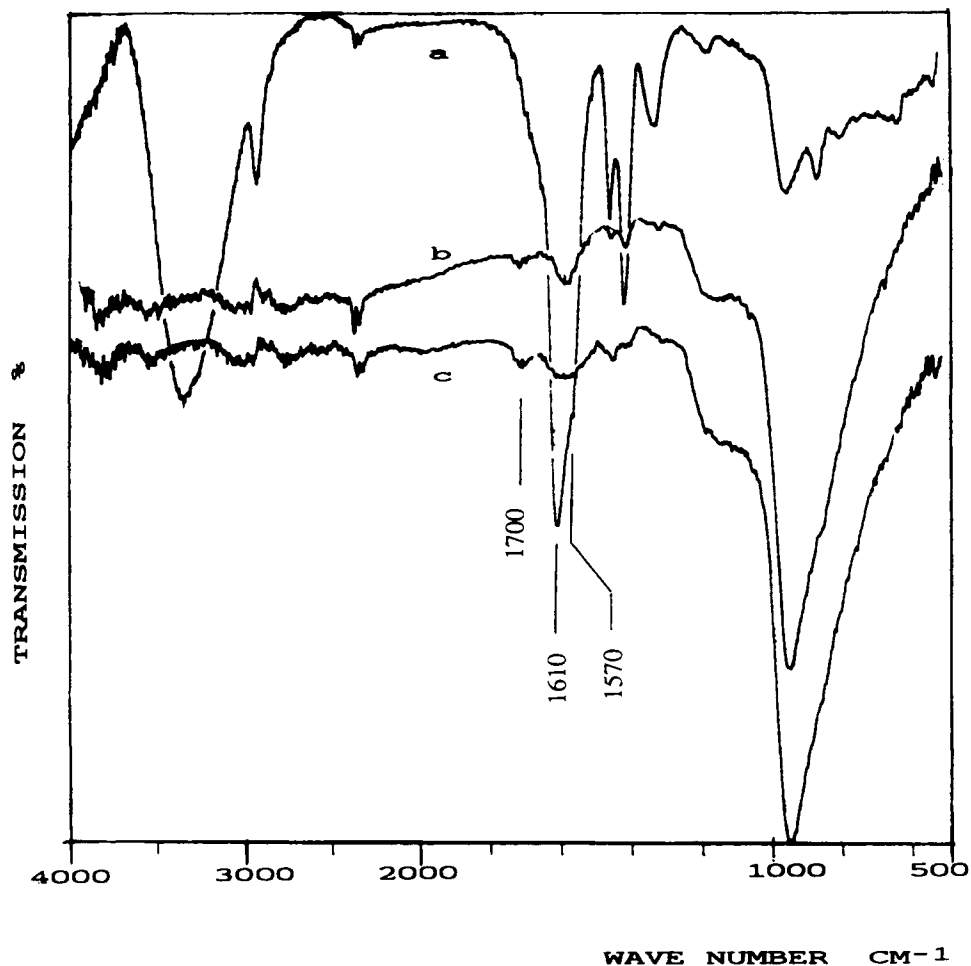


Figure 8 Reflection-absorption spectrum of a layer of PAA under carboxylate form deposited on the alumina surface: (a) before washing; (b) after washings of 45 min; and (c) 7 h.

peeling of a $\text{PPg}(\text{O}^-)$ film leads to the IR spectra shown in Figures 7(b,c). The analysis of the metal surface reveals the presence of carboxylate groups initially in complex interaction with Al^{3+} . A weak absorption at 1698 cm^{-1} can be also observed. It corresponds to a $\nu_{(\text{C}=\text{O})}$ of $-\text{COOH}$ in the dimer form.

We also observe a loss of matter that is time dependent, but that tends to a constant value. This value (Table I^f) is the same as for a $\text{PPg}(\text{OH})$ film, in the same condition (grafting ratio, washing time). Thus we assume that a greater number of PPg layers are extracted after peeling under $\text{PPg}(\text{O}^-)$ form than under $\text{PPg}(\text{OH})$ form, in relation with a lower cohesion of $\text{PPg}(\text{O}^-)$. Finally, only the layers that interact with the metal surface can be retained.

In the Case of $\text{PAA}(\text{O}^-)$. The washing of a metal surface on which was previously deposited $\text{PAA}(\text{O}^-)$

leads to a progressive loss of product by dissolution. As for the equivalent situation corresponding to a deposit of $\text{PAA}(\text{OH})$ on alumina, the removal of matter tends towards a plateau whatever the amount of polymer initially deposited (Table I^{d,e}). As shown by the IR analysis [Fig. 8(b,c)], this dissolution generates a modification of the polymer at the polymer/metal interface (increase of the COOH/COO^- ratio).

As we demonstrated, the polymer that remains at the surface of the metal after peeling of a PPg film can only be a PPg . If the interaction between a ligand (COO^-) (L) and a metal (M) leads to the formation of a complex (C), we can consider an equilibrium that conditional constant K corresponds to $K = (\text{L})(\text{C})/(\text{M})$. The decrease of (L) must induce a decrease of (C). Conversely, since the grafted PP is insoluble in water, the concentration of ligand

(COO⁻) at the interface remains unchanged. Thus, in these conditions, the complexation reaction is not displaced and the complex form is preserved even after washings.

PAA is water soluble in particular when it is in carboxylate form. Therefore, the concentration of ligand at the interface PAA(O⁻)/Al₂O₃ decreases during dipping in water of a sample covered with this homopolymer. This is accompanied by a disappearance of the complexed form. Water favours also the dissociation of COOH groups, always present at the interface.

Whatever the form, free acid or carboxylate, PAA is soluble in water. Thus, dipping of metal samples covered with this polymer leads to a similar loss of matter in both cases. Despite the prolonged washings, the presence of polymer at the Al₂O₃ surface can result from ionic or complex interactions between Al₂O₃ and —COO⁻ formed during dipping in water or to mechanical anchorage of PAA chains in the pores of the metal oxide.

CONCLUSION

In this work we showed that after peeling of a PP grafted film (with PAA under free acidic form) pressed on an alumina surface, there remains primarily a copolymer PPg(OH). At the interface polymer/metal, the COOH groups are typically interacting with OH groups located at the Al₂O₃ surface by means of hydrogen bondings. The parts of water as well as the ionic form of the carboxyl groups were demonstrated. A better understanding of the mechanism that is responsible for the linkage between the metal and the polymer chains of the sur-

face will lead us to a better interpretation of the adhesion between the metal and the modified polymer film.

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REFERENCES

1. F. J. Boerio, J. P. Boerio, and R. C. Bozian, *Appl. Surf. Sci.*, **31**, 42 (1988).
2. J. T. Hall and P. K. Hansma, *Surf. Sci.*, **76**, 61 (1978).
3. I. Kusaka and W. Suetaka, *Spectro. Acta*, **36A**, 647 (1980).
4. D. L. Allara, *Polym. Sci. Tech.*, **12B**, 751 (1980).
5. S. Crisp, H. J. Prosser, and A. D. Wilson, *J. Mat. Sci.*, **11**, 36 (1976).
6. S. M. Rabie, A. Sawaby, M. A. Moharam, A. M. Nas-sar, and K. H. Tahon, *J. Appl. Polym. Sci.*, **41**, 445 (1990).
7. K. Nakamoto, *Infrared Spectra of Inorganic and Co-ordination Compounds*, Wiley-Interscience, New York (1970).
8. L. J. Bellamy, *The IR Spectra of Complex Molecules*, Chapman and Hall, London, **1**, 1975.
9. K. Nakanishi, *Infrared Adsorption Spectroscopy—Practical*, Holden-Day Inc., San Francisco and Nankodo Company Limited, Tokyo, 1962.
10. J. Yarwood, *Coll. Surf.*, **52**, 35 (1991).
11. G. H. Davies and J. Yarwood, *Spectro. Acta*, **43A**, 1619 (1987).
12. D. L. Allara and R. G. Nuzzo, *Langmuir*, **1**, 52 (1985).

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