

Free-Radical Graft Copolymerization of Phosphonated Methacrylates onto Low-Density Polyethylene

Manuel Gaboyard, Jean-Jacques Robin, Yves Hervaud, Bernard Boutevin

Laboratoire de Chimie Macromoléculaire, UMR 5076-8, rue de l'Ecole Normale, Ecole Nationale Supérieure de Chimie de Montpellier, 34 296 Montpellier Cedex 5, France

Received 26 July 2001; accepted 14 February 2002

ABSTRACT: Dimethyl 2-methacryloxyethylphosphonate, its monosodium salt, and methyl 2-methacryloyloxyethylphosphonic acid were synthesized, characterized, and grafted onto low-density polyethylene (LDPE) powder under melt-processing conditions in a Rheocord batch mixer (Karlsruhe, Germany). We studied the graft copolymerization onto LDPE in the presence of free-radical initiators, benzoyl peroxide, and dicumyl peroxide, and we performed grafting onto ozone-pretreated LDPE without any free-radical initiator. Effects of reaction time, initiator concentration,

and reaction temperature were studied. The possibility of modifying LDPE in the molten state with phosphonated methacrylates was clearly demonstrated. Graft copolymers were characterized by Fourier transform infrared spectroscopy, differential scanning calorimetry, scanning electron microscopy, and water contact angles. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2011–2020, 2002

Key words: graft copolymers; initiators; melt

INTRODUCTION

Polymeric materials with desirable properties have gained widespread application in many fields during the past few decades. A large demand for new engineering materials has resulted in the development of different methods of polymer modification.

Most polymers in use today are fairly hydrophobic. Therefore, it is difficult to directly bond these polymers with other substances such as adhesion promoters, printing inks, and paints, which generally consist of polar components. To overcome this problem, many researchers have researched the grafting of reactive groups onto polymer backbones without changing the bulk properties of the materials. These studies have included plasma treatment;^{1,2} ozone treatment;^{3–5} flame treatment;^{6,7} corona discharge treatment;^{8,9} exposure to high-energy radiation such as γ rays,^{10–14} electron and ion beams, and ultraviolet sources;^{15–22} and free-radical initiation.^{23–27} The generated peroxides and hydroperoxides were able to initiate radical polymerization of unsaturated monomers, resulting in grafted polymer chains.

As for polyethylene (PE), most articles have described the graft copolymerization of vinylic monomers,²⁸ (meth)acrylates,^{3,17–20,25,27–31} maleates, and maleimides^{23,26,32} but also silanes²⁴ and allyl alcohol,¹⁴ for example. These graft copolymers are mainly used

as compatibilizers for polymer blends and adhesion promoters and as hot melt sealants.

To improve the adhesion of PE on metallic surfaces, we chose to introduce phosphonic structures, well known as adhesion promoters, along the polymer backbone. As Brondino et al. did with phosphonated acrylates onto poly(vinylidene fluoride) powders,³³ we investigated the free-radical graft copolymerization of phosphonated methacrylates onto low-density polyethylene (LDPE) powder, following two distinct processes: grafting in presence of free-radical initiators and thermally induced graft copolymerization onto ozone-pretreated LDPE.

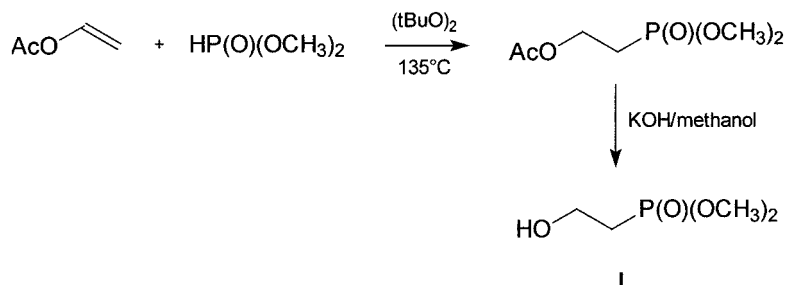
EXPERIMENTAL

Materials

PE was LDPE (Stamylan LD 1922Z) powder purchased from DSM (Paris, France) with a density of 0.92 g/cm³, a weight-average molecular weight of 53,500 g/mol, a number-average molecular weight of 10,500 g/mol, a melting point of 105°C, and a melt flow index (MFI; 190°C, 2.16 kg) of 22 g/10 min.

Benzoyl peroxide (BP), dicumyl peroxide (DCP), and others chemicals were purchased from Aldrich (Saint Quentin, France). BP was purified by recrystallization from a chloroform/methanol mixture. Dimethyl 2-methacryloxyethylphosphonate [MAPHO-S(OMe)₂] and its monosodium salt [MAPHO-S(OMe)(ONa)] were prepared according to a method described later.

Correspondence to: J.-J. Robin (jrobin@cit.ensm.fr).



Scheme 1

Monomer and copolymer analyses

NMR spectra were recorded on a Bruker AC 250 spectrometer (Wissembourg, France). CDCl_3 was used as an internal lock. Tetramethylsilane and orthophosphoric acid (H_3PO_4) were used as references for ^1H -NMR and ^{31}P -NMR spectroscopy, respectively. The letters *s*, *d*, *t*, *q*, and *m* designate singlet, doublet, triplet, quartet, and multiplet, respectively. Fourier transform infrared (FTIR) spectra were recorded with a Nicolet 510P spectrophotometer (Madison, WI). The position of the bands were given in cm^{-1} . Differential scanning calorimetry (DSC) analyses were recorded on a PerkinElmer DSC Pyris-1 apparatus (Courtaboeuf, France) under helium. Water contact angles were measured on a Krüss contact angle measuring system (G23) (Hamburg, Germany) with doubly distilled water. Scanning electron microscopy (SEM) analyses were carried out at the European Institute of Membranes (Montpellier, France) with a Leica S-260 (Wetzlar, Germany) or Hitachi S-4500 scanning electron microscope (Verriere-le-Buisson, France).

Ozone pretreatment

The oxidization of LDPE was carried out in a double-jacketed reactor under a fluidized bed. Ozone was evolved with a silent discharge through an oxygen current (Trailgaz Minibloc 76 model (Garges les Gonesse, France)). LDPE was activated for 1 h through an air/ozone mixture current (750 L/h; $[\text{O}_3] = 18 \text{ g/h}$). The power of the ozone generator was fixed at 350 W. After this treatment, the LDPE powder was allowed to flow through air for 1 h to purge the residual ozone off. The ozone-pretreated LDPE was stored at 4°C before being submitted to the graft copolymerization.

Graft copolymerization and purification of copolymers

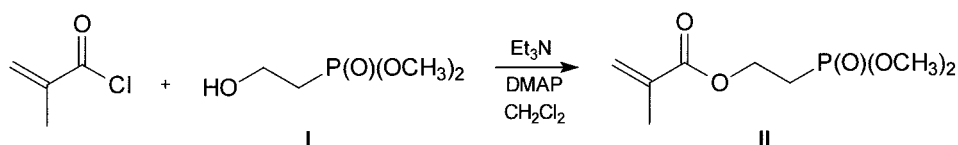
PE (45 g) was mixed homogeneously with the different monomers synthesized (5 g) (and eventually with free-radical initiators) at room temperature. Then, the mixture (LDPE/monomer/initiator or oxidized LDPE/monomer) was introduced in a batch mixer (Haake Rheocord Rheomix model, Karlsruhe, Germany) at 110°C with a rotating rate of 32 rpm in an air atmosphere for the prescribed time.

All the samples were purified with the same procedure. At the end of the reaction, the graft copolymer was cooled and ground at room temperature, and 5 g of the crude copolymer was dissolved in 50 mL of xylene and warmed under continuous stirring until it reached the boiling temperature of the solvent (135°C). The solution was kept under reflux for 1 h. Then, the warm solution was precipitated in methanol. The purified copolymers were filtered, washed with cold methanol, and dried under vacuum for 12 h at 80°C .

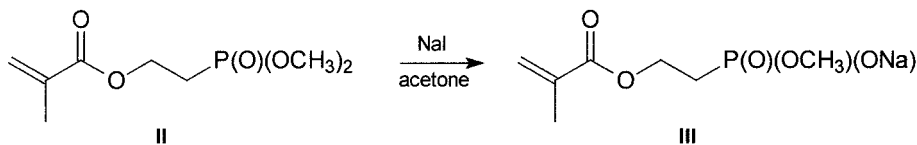
The determination of grafting rate (GR) by FTIR spectroscopy clearly provided evidence that monomers and their homopolymers were completely removed by precipitation, even in low concentration, because GRs were the same after two precipitations.

Determination of GR: poly(methyl methacrylate) (PMMA) calibration

To establish a PMMA IR calibration, we used several mechanical LDPE/PMMA mixtures in known proportions (2, 4, 6, and 8 wt %). From these mixtures, films of about 1 mm thick were made by compression molding in a laboratory press. The material was kept at 150 bars and 150°C for about 1 min.



Scheme 2



Scheme 3

DSC

Melting endotherms were measured with sample weights of about 8 ± 3 mg and a heating rate of $20^\circ\text{C}/\text{min}$. The instrument was calibrated with indium ($T_f = 158.9^\circ\text{C}$; $\Delta H_f = 26.81$ J/g, where ΔH_f is the value of the measured heat of fusion). The crystallinity values obtained were the averages of two measurements. Samples were preheated to 140°C and cooled at $20^\circ\text{C}/\text{min}$ to 60°C and kept at that temperature for 1 min before DSC measurements. The degree of crystallinity (X_c) was evaluated according to the baseline method proposed by Gray:³⁴

$$X_c = \frac{\Delta H_f}{\Delta H_{T_m}^\circ} \times 100$$

where $\Delta H_{T_m}^\circ$ is the heat of fusion for 100% crystalline PE. The value of $\Delta H_{T_m}^\circ$ (291.3 J/g) was obtained from Wunderlich and Baur.³⁵

MFI

The MFI of LDPE and selected grafted LDPE samples were measured as per ASTM D 1238 at 190°C and under a 2.16-kg load in a MFI apparatus from Dynisco (model D7054).

SEM

Morphological investigations were performed with a Leica S2000 or Hitachi S4500 scanning electron microscope coupled with a energy-dispersing X-ray spectroscopy (EDXS) apparatus (Kevex, Instruments, Boston). The samples were fractured at liquid nitrogen temperature.

RESULTS AND DISCUSSION

In this study, we examined the graft copolymerizations of phosphonated methacrylates onto LDPE in the molten state. Two different grafting techniques

were compared: copolymerization initiated by a free-radical initiator and thermally induced copolymerization onto ozone-pretreated LDPE. The grafting efficiencies of several phosphonated methacrylates were evaluated, and the graft copolymers were characterized.

Synthesis of phosphonated methacrylates monomers

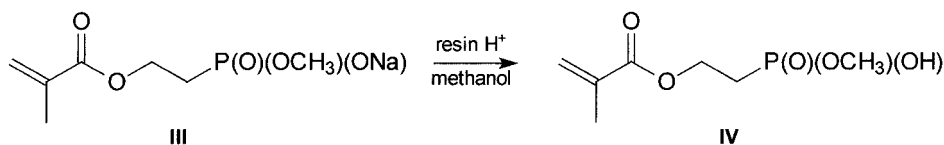
Monomers were synthesized according to the following procedure. First, the free-radical telomerization of vinyl acetate with dimethyl hydrogenphosphonate was performed in presence of di-*tert*-butyl peroxide at 135°C . The phosphonated monoacetate was isolated and saponified to obtain product I (dimethyl 2-hydroxyethylphosphonate; Scheme 1), the precursor of phosphonated methacrylates.

Then, as Bressy-Bronino et al. did,³⁶ we prepared phosphonated methacrylate [MAPHOS(OMe)₂, or II; Scheme 2] from methacryloyl chloride and I under Schautten-Baumann conditions and synthesized MAPHOS(OMe)(ONa) (III; Scheme 3) and methyl 2-methacryloyloxyethylphosphonic acid [MAPHOS(O)Me(OH), or IV; Scheme 4].³⁷

The structures of these products were checked by ¹H-NMR and ³¹P-NMR spectroscopy. The ¹H-NMR spectrum of IV (Fig. 1) showed a reduction by half of the doublet intensity at 3.7 ppm (³J_{HP} = 11.2 Hz), assigned to the —P(O)(OCH₃)(OH) function. The ³¹P-NMR spectrum exhibited one single peak at 25 ppm, confirming the monodealkylation.

Torque rheometry

We monitored the graft reaction by following torque-time behaviors for different polymer/monomer ratios. Graft copolymerizations usually induce a torque rise that stabilizes in a second step when the reaction ends. The reactive processing of PE in the presence of a free-radical initiator and a monomer led to the forma-



Scheme 4

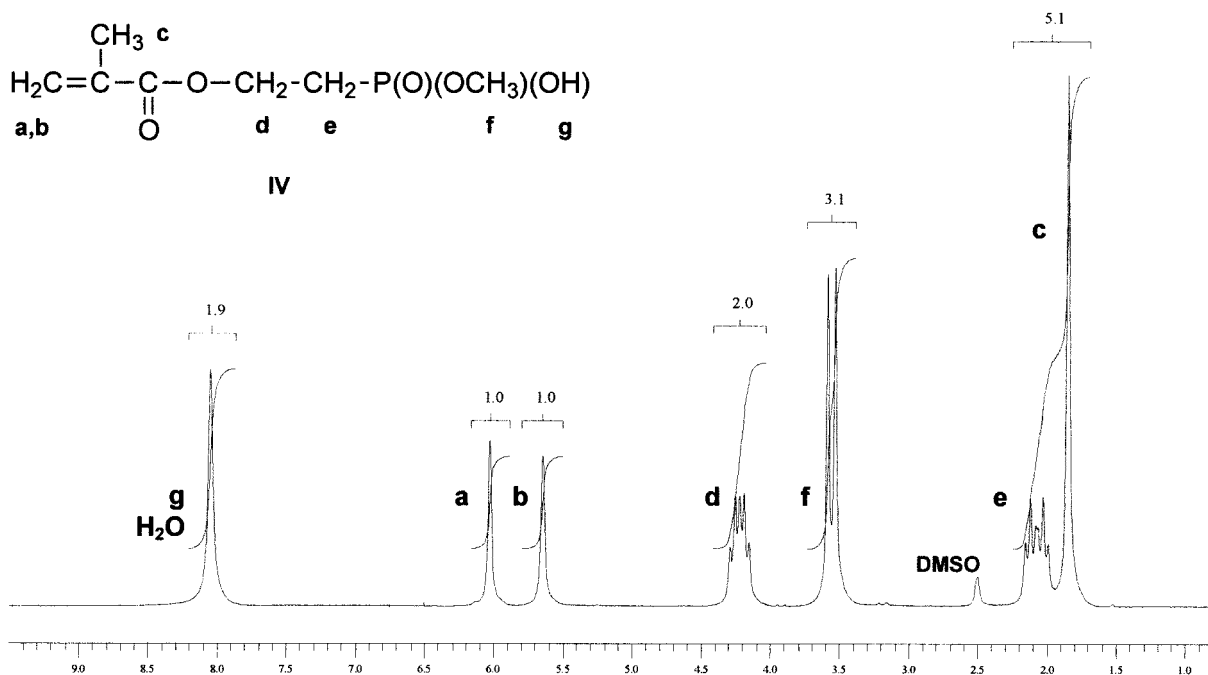


Figure 1 ^1H -NMR spectrum (DMSO- d_6) of IV.

tion of additional polymers; a major part of the polymer formed was grafted onto PE, causing a prominent increase in its molecular weight and, thus, contributing to a net enhancement in the melt viscosity of the material being processed and, hence, to a rise in the torque value as recorded in the mixer (as shown in Fig. 2). Partial and very limited crosslinking of PE may have occurred simultaneous to grafting, leading to microgel formation, and this might have also contributed to the observed torque rise.

With regard to ozone-pretreated LDPE, the decomposition of intramolecular dialkyl peroxides (coming from ozone treatment) mainly led to chain scissions and caused a decrease in molecular weight, which could be evaluated by viscosimetry as Brondino et al.³³ did with PVDF. Thus, the melt viscosity of the

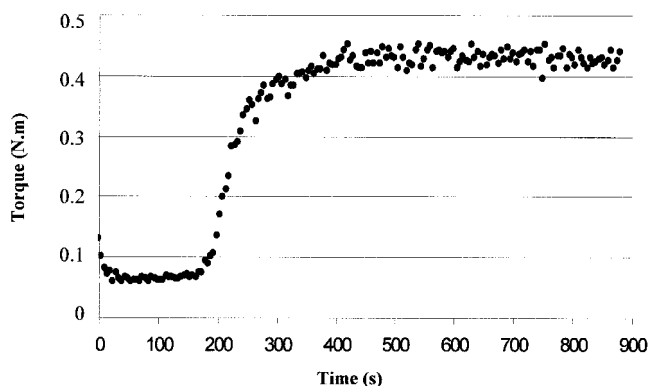


Figure 2 Torque versus time plots for the reactive melt processing of LDPE with free-radical initiators at 110°C.

grafted PE and, therefore, the observed torque value slightly decreased.

The nature and degree of the variations in torque with time during the reactive processing leading to significant grafting of PE were characteristically dependent on the nature of the monomer and the initial monomer and initiators ratios.

Characterization of grafted PE

As we mentioned in the Experimental section, our graft copolymers were purified by precipitation in methanol to eliminate the homopolymer. The GR was defined as the weight ratio of grafted monomer units to the graft copolymer. It was determined by FTIR with a calibration curve based on LDPE/PMMA blends.

Before studying GRs, we analyzed our copolymers by FTIR. Figure 3 shows the IR spectra of LDPE and LDPE-*g*-MAPHOS(OMe)₂. Characteristic absorption bands of MAPHOS(OMe)₂ were present at 1728 and 1035 cm^{-1} . They corresponded to C—O stretching vibrations of the carbonyl group and to P—OCH₃ stretching vibration of the phosphonate group, respectively.

Figure 4 shows the FTIR spectra of LDPE-*g*-MAPHOS(OMe)₂ initiated with BP. The intensity of characteristic absorption bands of MAPHOS(OMe)₂ increased (1730, 1256, and 1035 cm^{-1}), whereas the bands at 1464 and at 1377 cm^{-1} , characteristic of the LDPE main chain, did not change.

In the same way, Figure 5 shows the FTIR spectra of LDPE and LDPE-*g*-MAPHOS(OMe)(ONa) or LDPE-*g*-

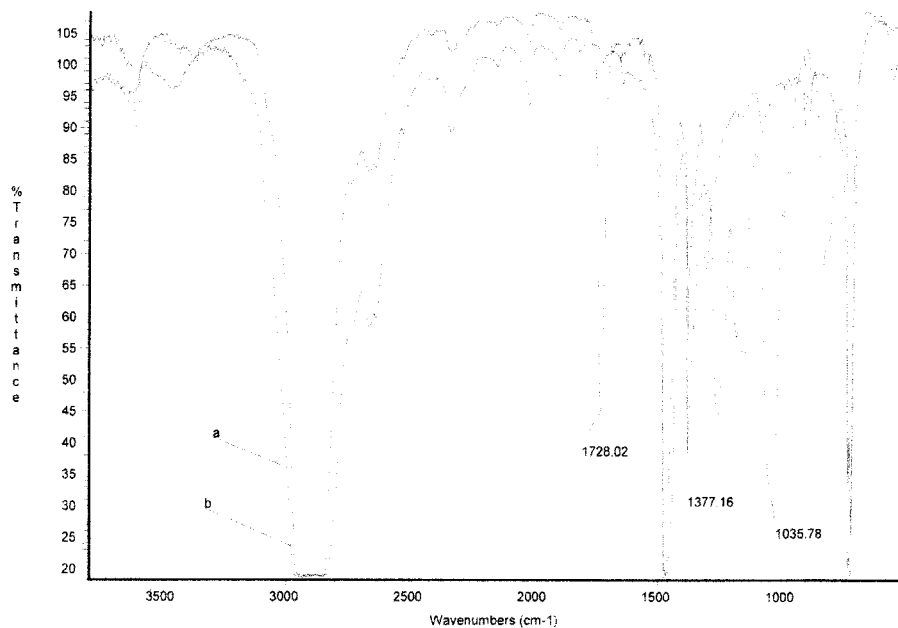


Figure 3 FTIR spectra of (a) LDPE and (b) LDPE-g-MAPHOS(OMe)₂.

MAPHOS(OMe)(OH), respectively, where characteristic absorption bands were 1714 and 1055 cm⁻¹ for MAPHOS(OMe)(ONa) and 1726 and 1055 cm⁻¹ for MAPHOS(OMe)(OH).

FTIR spectra of LDPE/PMMA films allowed us to calculate the intensity ratio of the C—O stretching of methacrylate at 1732 cm⁻¹ to the CH₃ symmetrical bending of LDPE at 1377 cm⁻¹. Thus, we established the calibration curve $I_{1732}/I_{1377} = f(\text{wt \% PMMA})$; Fig. 6).

Therefore, to determine the GR, we calculated the ratio I_{1732}/I_{1377} of each sample and reported it on the

calibration curve. This method was available because the IR absorption of poly(MAPHOS)(OMe)₂, poly(MAPHOS)(OMe)(OH), and poly(MAPHOS)(OMe)(ONa) were the same as that of PMMA.

The results of different graft copolymerizations are summarized in Table I.

Effect of free-radical initiator concentration

We chose to study two free-radical initiators with different half-lives. BP and DCP were evaluated for

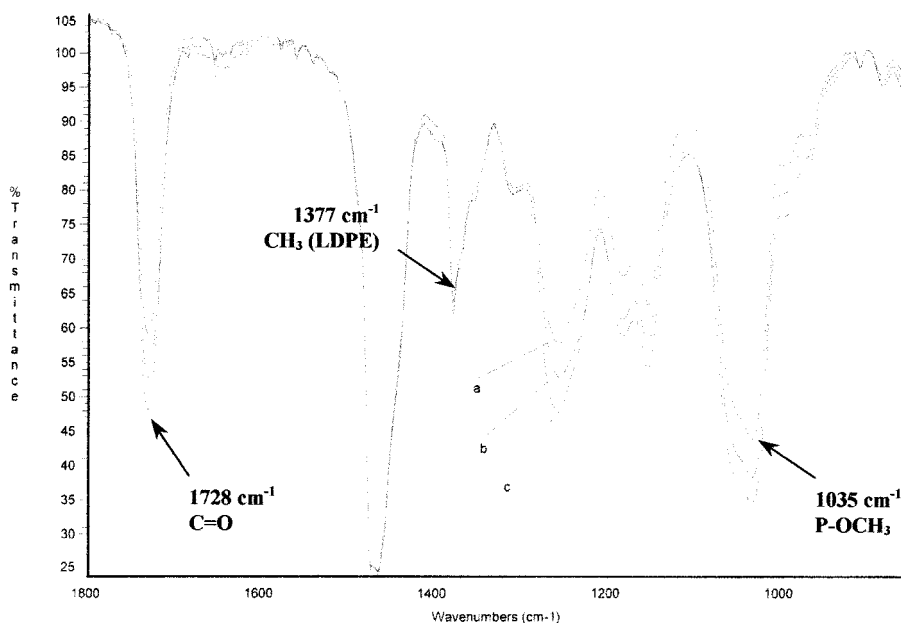


Figure 4 FTIR spectra of LDPE-g-MAPHOS(OMe)₂ initiated with (a) 0.1, (b) 0.25, and (c) 0.5 wt % BP at 110°C for 20 min.

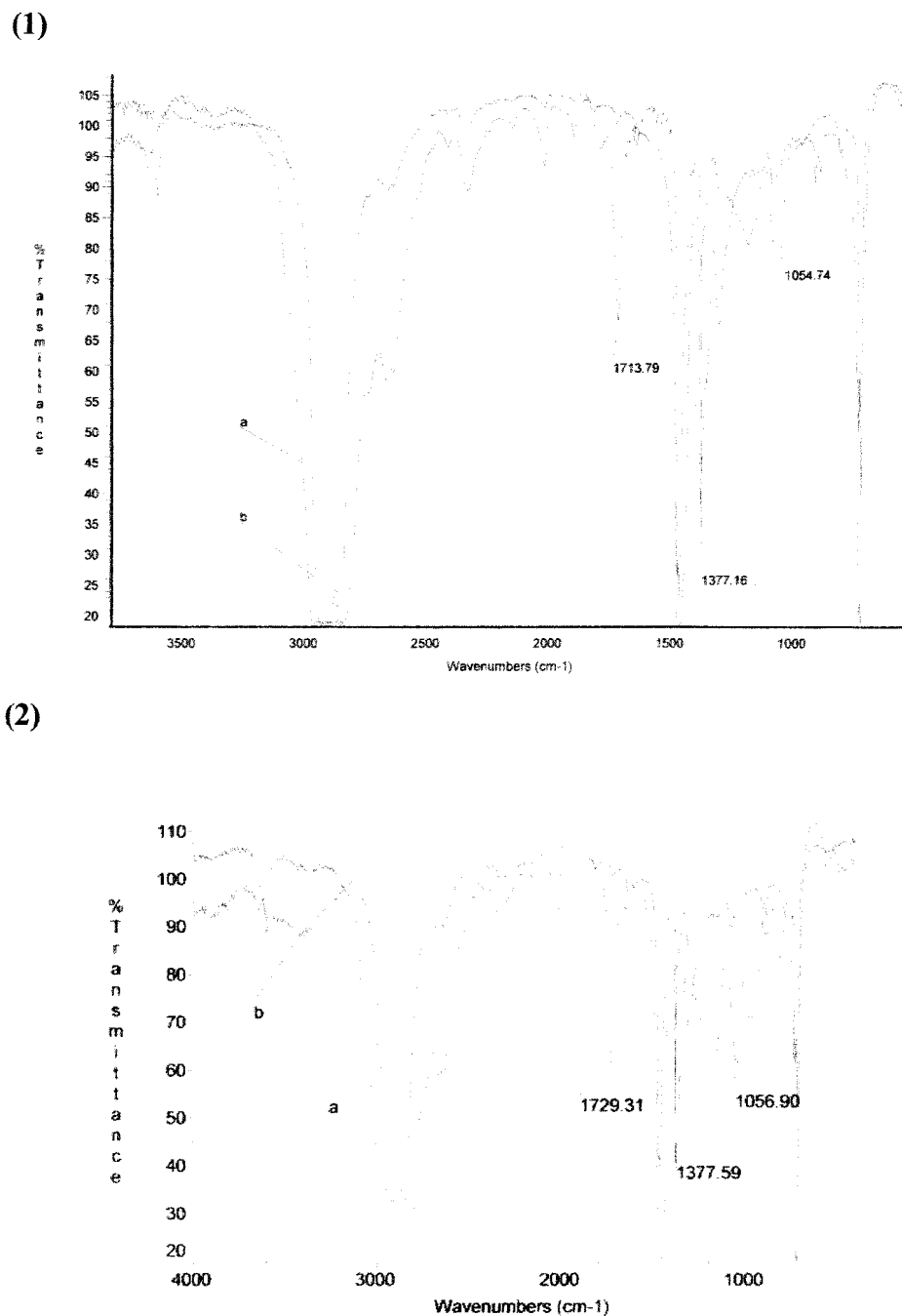


Figure 5 FTIR spectra of (1a) LDPE, (1b) LDPE-g-MAPHOS(OMe)(ONa), (2a) LDPE, and (2b) LDPE-g-MAPHOS(OMe)(OH).

their grafting efficiency in the field of reactive processing. BP was an excellent initiator for grafting, whereas DCP was quite ineffective in our processing conditions. Actually, at 110°C, the half-life of BP is 6 min, whereas the half-life of DCP is 10 h. Therefore, more radicals were quickly generated with BP, which led to better grafting. Also, BP melts at 104°C, which improves its dispersion in the molten polymer.

As shown in Table I, GR increased with the initial initiator concentration. Without peroxide, there was

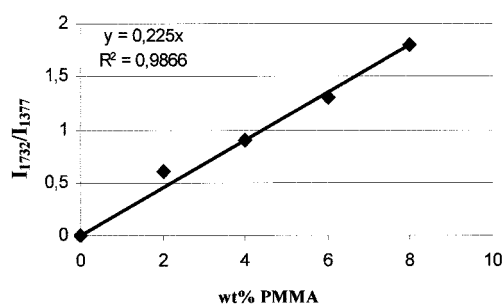


Figure 6 Calibration curve of LDPE/PMMA blends.

TABLE I
Graft Copolymerizations of Phosphonated Methacrylates onto LDPE

Number	Monomer wt %	Method	Initiator	Temperature (°C)	Time (min)	Grafting rate (%)	MFI (g/10 min)
MAPHOS (OMe) ₂							
1	2	—	—	110	20	0	20 ^a
2	10	A	0.50 wt % DCP	110	20	1.25	
3	10	A	0.50 wt % BP	110	20	5.8	10.5
4	10	A	0.25 wt % BP	110	20	5.2	17.0
5	10	A	0.10 wt % BP	110	20	4.5	19.5
6	10	B	—	110	20	5.5	60
7	10	B	—	150	20	5.9	>100 ^b
MAPHOS(OMe)(ONa)							
8	2	—	—	110	20	0	20 ^a
9	10	B	—	110	10	5.2	77
10	10	B	—	110	20	5.5	52
11	10	B	—	150	20	6.1	81
12	10	A	0.50 wt % BP	110	20	5.8	
MAPHOS(OMe)(OH)							
13	2	—	—	110	20	0	20 ^a
14	10	A	0.50 wt % BP	110	20	4.5	7.0
15	20	A	0.50 wt % BP	110	20	5.5	

Method A: graft copolymerization onto LDPE in the presence of the free-radical initiator; Method B: graft copolymerization onto ozone-pretreated LDPE.

^a Virgin LDPE:MFI = 20 g/10⁻².

^b Value out of range.

no graft copolymerization. So, radicals induced by mechanical shearing of the molten polymer were not sufficient to lead to graft copolymerization.

Ozone pretreatment dependence on GR

We performed graft copolymerizations at two temperatures to evaluate the effect of temperature on GR. For both monomers, GR was larger at 150°C than at 110°C, but the crude copolymers became slightly brown, which could be explained by the starting decomposition of the monomer and homopolymer.

As mentioned previously, we did not observe a torque rise during the grafting reaction, but instead we observed a decreasing torque that finally reached a nearly steady value after 20 min. Actually, ozone pretreatment generates very few radicals. Boutevin and colleagues^{28,38} studied the oxidation of LDPE by ozone. Peroxides and hydroperoxides were titrated by a colorimetric method. In our experimental conditions, they showed that the concentration of peroxides was close to 10⁻⁴ eq/g. The activated polymer did not contain more than one macroinitiator by chain. In these conditions, crosslinking was limited, and the graft copolymerization was characterized by a decreasing melt viscosity.

GRs were similar to the ones obtained by direct graft copolymerization initiated by BP.

Effect of monomers

The graft copolymerization of MAPHOS(OMe)(ONa) (III) onto LDPE initiated by BP led to the same result

as for MAPHOS(OMe)₂ (II; see Table I). Although MAPHOS(OMe)(ONa) was a solid monomer and did not melt before its degradation temperature (320°C), grafting onto LDPE occurred in the molten state. Actually, it seemed to be soluble in the molten polymer because the molten mixture was homogeneous (no solid dispersion was observed when mixing). This may explain its ability to copolymerize in these conditions. GR remained the same after two precipitations. This confirmed that MAPHOS(OMe)(ONa) was really grafted onto the LDPE backbone.

GRs with MAPHOS(OMe)(OH) (IV) were lower (Table I). In the same conditions, with MAPHOS(OMe)₂, the GR was 5.8%, whereas it was 4.5% with IV. Even when we increased the initial monomer weight percentage, the GR did not reach the value of the other copolymerizations. MAPHOS(OMe)(OH) is a very polar monomer. When it is mixed in the hydrophobic molten PE, it may form micelles. This may have prevented the polymerization of our polar monomer by limiting its diffusion toward the reactive sites. When the initial amount of IV was increased, this phenomenon was amplified because the GR did not increase a lot. Besides, the purification of these graft copolymers was more difficult. Two precipitations were indispensable to eliminate the homopolymer.

Melt rheology

Various degrees of crosslinking of PE were likely to occur as side reactions during graft copolymerization. The torque rise with time observed in the mixer (Fig. 2) as the graft copolymerization progressed may be

TABLE II
Calorimetric Results of LDPE-g-MAPHOS

Number	Grafted monomer	T_f (°C)	X_c (%)	GR (%)
	—	105.5	25.1	0
3	MAPHOS(OMe) ₂	105.8	23.2	5.8
4	MAPHOS(OMe) ₂	104.5	23.0	5.2
5	MAPHOS(OMe) ₂	103.8	23.3	4.5
6	MAPHOS(OMe) ₂	104.6	24.7	5.5
7	MAPHOS(OMe) ₂	105.1	25.2	5.9
10	MAPHOS(OMe)(ONa)	104.5	24.8	5.5
11	MAPHOS(OMe)(ONa)	105.1	24.1	6.1
12	MAPHOS(OMe)(ONa)	105.5	23.2	5.8
14	MAPHOS(OMe)(OH)	104.8	22.9	4.5
15	MAPHOS(OMe)(OH)	104.8	20.4	5.5

partly due to grafting and partly due to limited crosslinking. In our experimental conditions, the gel content (the hot xylene insoluble part) of the products was nil. Thus, if the crosslinking reaction was carried out in the mixer onto the molten polymer, the crosslinked fractions tended to be dispersed in a non-crosslinked matrix.

When a free-radical initiator was used, the MFI of LDPE-g-MAPHOS(OMe)₂ gradually decreased from a value of 20.0 (virgin LDPE) to 10.5 g/10 min under the given set of conditions (Table I). The trends of change in MFI were directly linked to the initial initiator ratio and GR. When the amount of BP was increased, the grafting efficiency was improved, and chain extension was promoted, leading to a rise in molecular weight. For the grafting of MAPHOS(OMe)(OH), the MFI value dropped sharply to 6.7 g/10 min, although the GR value was only 4.5. In this case, the intermolecular interactions (mainly hydrogen bonds) may have contributed to a net enhancement in the melt viscosity.

As for ozone-pretreated LDPE, the MFI values increased from 20.0 up to 100 g/10 min (Table I). The high values of MFI evidenced a lowering of molecular weight due to chain scission reactions. The decomposition of intramolecular dialkyl peroxides depends on temperature and reaction times; as a consequence, the highest values of MFI were observed at 150°C.

Crystallinity dependence on GR

The crystallinity data for LDPE in the grafted samples are gathered in Table II. The melting temperature of graft copolymers was similar to the that of virgin LDPE (about 105°C). For all monomers, the grafting copolymerization led to a light loss of crystallinity, which may have been attributed to the presence of branched chains on the LDPE backbone, which disturbed crystallization.

Wettability of grafted LDPE films

The contact angle data are collected in Table III. Contact angles were measured for grafted LDPE films

realized from purified copolymers. Because the contact angle of a water droplet depends on the surface energy, grafting polar monomer onto the LDPE backbone should have lowered the surface energy and increased the wettability. The increase in grafting correlated with a decrease in contact angles from 103 to 92°. The low decrease of contact angles did not really reflect the importance of the GR. There was no particular orientation of grafted polar groups toward the outermost layer of the surface. Nevertheless, these measurements confirmed that polar groups were grafted onto LDPE.

Morphological investigations of grafted LDPE films

To examine the innermost structure of the grafted LDPE, we performed SEM by the secondary electron (SE) and retrodiffused electron (RE) methods. SE micrographs give a representation by topographic contrast, whereas RE micrographs give a representation by chemical contrast. Thus, it was possible to distinguish the phase containing phosphonated polymer, which is rich in phosphorus, versus the PE matrix, which is rich in carbon, by RE SEM.

As shown in Figure 7, RE SEM micrographs revealed heterogeneity of the films as expected. White nodules were dispersed in a dark matrix. EDXS analyses indicated that the dark matrix was essentially composed of carbon, whereas the white nodules contained oxygen, phosphorus, and sodium (for LDPE-g-MAPHOS(OMe)(ONa)). These films were prepared from twice-purified copolymers. Therefore, these nodules could not be inclusions of homo(MAPHOS).

Comparison of Figure 7(a) with Figures 7(c) and 7(e) revealed that the phosphonated phase was more homogeneously distributed in the case of MAPHOS(OMe)₂ than in the cases of MAPHOS(OMe)(ONa) and MAPHOS(OMe)(OH). This could be explained by

TABLE III
Water Contact Angle Measurements on Grafted LDPE Films

Graft copolymer Number	GR (%)	Contact angle (°)
	0	103
2	1.25	102
5	4.5	99
4	5.2	97
6	5.5	96
3	5.8	95
7	5.9	95
10	5.5	103
12	5.8	102
11	6.1	102
14	4.5	96
15	5.5	92

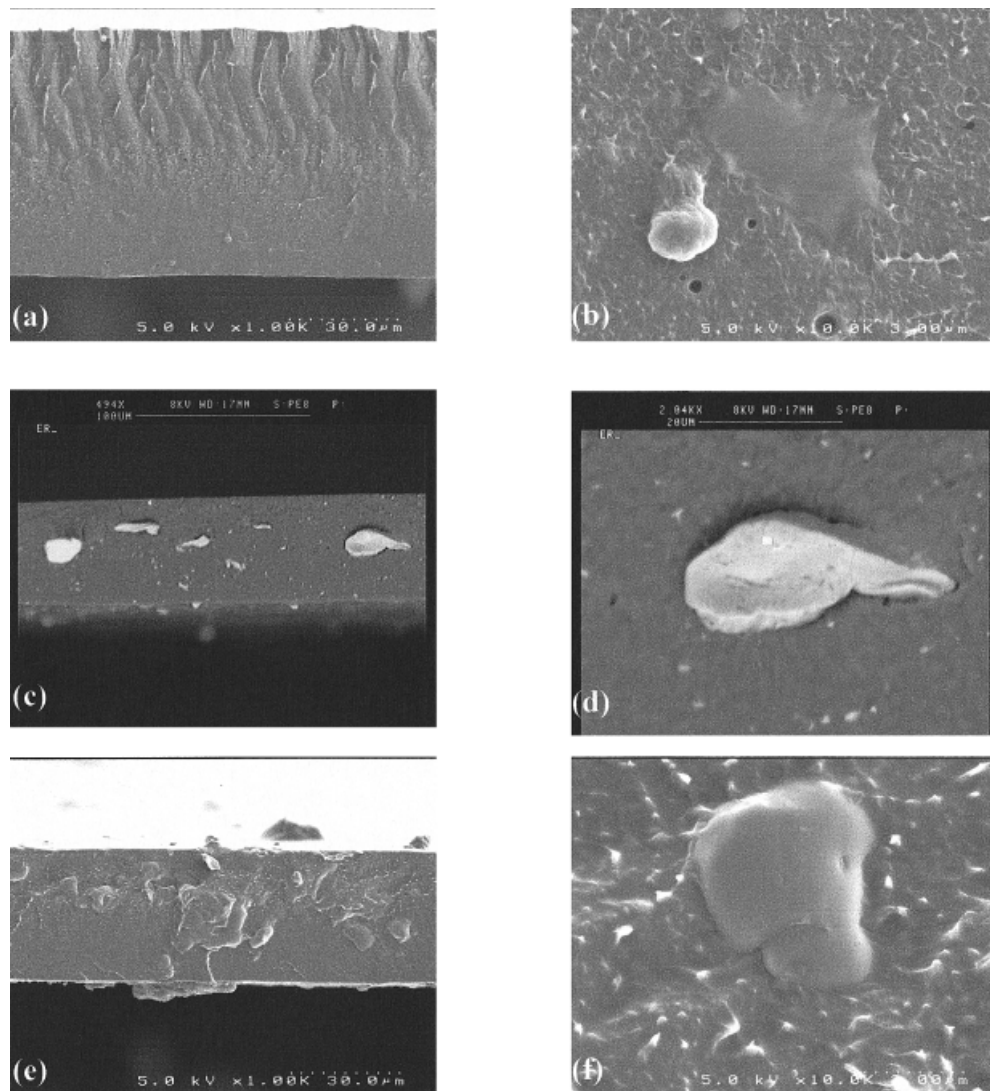


Figure 7 SEM micrographs of (a,b) LDPE-g-MAPHOS(OMe), (c,d) LDPE-g-MAPHOS(OMe)(ONa), and (e,f) LDPE-g-MAPHOS(OMe)(OH).

the polarity of the grafted chains and their more or less pronounced incompatibility versus the PE matrix. MAPHOS(OMe)(OX) ($X = \text{Na}$ or H) graft units were obviously incompatible with PE, and big clusters were observed, as shown in Figure 7(d,e).

This gathering of polar chains created big phosphonated clusters in the PE matrix. This morphology could be correlated with the lower GR observed with MAPHOS(OMe)(OH). As mentioned previously, the monomer should have been dispersed in the molten LDPE as micelles that limited its diffusion toward growing macroradicals. This arrangement led to the structures observed in Figure(d,f).

CONCLUSIONS

In this study, the grafting of phosphonated methacrylates onto LDPE powders was investigated. On one

hand, we performed graft copolymerization onto LDPE in the presence of free-radical initiators. On the other hand, ozone-pretreated LDPE was subjected to further modification via thermally induced graft copolymerization. Both processes gave graft copolymers with a similar GR.

Morphological, calorimetric, and spectroscopic analyses confirmed the grafting of MAPHOS monomers. We showed that the grafting of phosphonic moieties enhanced the hydrophilicity of LDPE. In a later study, we will investigate the adhesion properties of such graft copolymers on steel plates.

References

1. Chan, C. M.; Ko, T. M.; Hirakoa H. Surf Sci Rep 1996, 24, 1.
2. Strobel, M.; Lyous, C. S.; Mittal, K. L., Eds. Plasma Surface Modification of Polymers: Relevance to Adhesion; VSP: Zeist, The Netherlands, 1994.

3. Shi, J. L.; Kang, E. T.; Neoh, K. G.; Tan, K. L.; Liaw, D. J. *Eur Polym J* 1998, 34, 1429.
4. Mathieson, I.; Bradley, R. H. *Int J Adhes Adhes* 1996, 16, 29.
5. Chtourou, H.; Riedl, B.; Kokta, B. V. *Polym Degrad Stab* 1994, 43, 149.
6. Sutherland, I.; Brewis, D. M.; Heath, R. J.; Sheng, E. *Surf Interface Anal* 1991, 17, 507.
7. Briggs, D.; Brewis, D. M.; Koniecko, M. B. *J Mater Sci* 1979, 14, 1344.
8. Iwata, H.; Kishida, A.; Suzuki, M.; Hata, Y.; Ikada, Y. *J Appl Polym Sci* 1988, 26, 3309.
9. Briggs, D.; Kendall, C. R. *Int J Adhes* 1982, 2, 13.
10. Hoffman, A. S. *Adv Polym Sci* 1984, 57, 141.
11. Klein, P. G.; Woods, D. W.; Ward, I. M. *J Polym Sci Part B: Polym Phys* 1987, 25, 3315.
12. Hassanpour, S. *Radiat Phys Chem* 1999, 55, 41.
13. Lacoste, J.; Deslandes, Y.; Black, P.; Carlsson, D. J. *Polym Degrad Stab* 1995, 49, 21.
14. Austin, M. E.; Busfield, W. K.; Pomery, P. J. *Eur Polym J* 1995, 31, 683.
15. Owens, D. K. *J Appl Polym Sci* 1975, 19, 3315.
16. Kunz, C. O.; Long, P. C.; Wright, A. N. *Polym Eng Sci* 1972, 12, 209.
17. Ishihara, K.; Iwasaki, Y.; Ebihara, S.; Shindo, Y.; Nakabayashi, N. *Colloid Surf B* 2000, 18, 325.
18. Wirsén, A.; Lindberg, K. T.; Albertsson, A. C. *Polymer* 1996, 37, 761.
19. Liqun, Z.; Irwan, G. S.; Kondo, T.; Kubota, H. *Eur Polym J* 2000, 36, 1591.
20. Kojima, M.; Kondo, T.; Kubota, H.; Katakai, R. *Polym Degrad Stab* 1999, 63, 147.
21. Svorcik, V.; Rykba, V.; Stibor, I.; Hnatowicz, V.; Vacik, J.; Stopka, P. *Polym Degrad Stab* 1997, 58, 143.
22. Fink, D.; Klett, R.; Muller, M.; Omichi, H.; Hosoi, F.; Vacik, J.; Hnatowicz, V.; Chadderton, L. T. *Appl Phys A: Mater Sci Process* 1996, 63, 441.
23. Kelar, K.; Jurbowski, B. *Polymer* 2000, 41, 1055.
24. Shieh, Y.; Liu, C. *J Appl Polym Sci* 1999, 74, 3404.
25. Park, S. H.; Lee, J. S.; Suh, K. D. *J Mater Sci* 1998, 33, 5145.
26. Boutevin, B.; Lusinchi, J. M.; Pietrasanta, Y.; Robin, J.-J. *J Fluorine Chem* 1995, 73, 79.
27. Naqvi, M. K.; Reddy, R. *Polym Plast Technol Eng* 1997, 36, 585.
28. Boutevin, B.; Pietrasanta, Y.; Taha, M.; Sarraf, T. *Eur Polym J* 1984, 20, 1131.
29. Boutevin, B.; Pietrasanta, Y.; Sarraf, T. *Angew Makromol Chem* 1988, 162, 175.
30. Valenza, A.; Geuskens, G.; Spadaro, G. *Eur Polym J* 1997, 33, 957.
31. Ghosh, P.; Chattopadhyay, B.; Sen, A. K. *Polymer* 1998, 39, 193.
32. de Vito, G.; Lanzetta, N.; Maglio, G.; Malinconico, P.; Musto, P.; Palumbo, R. *J Polym Sci Polym Chem Ed* 1984, 22, 1335.
33. Brondino, C.; Boutevin, B.; Parisi, J.-P.; Schrynmackers, J. *J Appl Polym Sci* 1999, 72, 611.
34. Gray, A. P. *Thermochim Acta* 1970, 1, 563.
35. Wunderlich, B.; Baur, H. *Adv Polym Sci* 1970, 7, 151.
36. Bressy-Brondino, C.; Boutevin, B.; Hervaud, Y.; Gaboyard, M. *J Appl Polym Sci* 2002, 83, 2277.
37. Paul, J. M.; Pirri, R.; Hervaud, Y.; Brondino-Bressy, M. C. *Atofina*, 2001; *Fr. Pat. Appl.* 0110815.
38. Boutevin, B.; Pietrasanta, Y.; Taha, M.; Sarraf, T. *Eur Polym J* 1984, 20, 875.