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Synthesis of mono functional carboxylic acid poly(methyl methacrylate) in aqueous medium using sur-iniferter. Application to the synthesis of graft copolymers polyethylene-*g*-poly(methyl methacrylate) and the compatibilization of LDPE/PVDF blends

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Abstract

Carboxylic acid mono functional poly(methyl methacrylate) was prepared by emulsion photopolymerization using 4-diethylthiocarbamoylsulfanylmethyl benzoic acid (DTBA) as sur-iniferter agent. DTBA is efficient to obtain mono functional polymers with a linear evolution of M_n vs. monomer conversion up to 60%. Beyond 60% monomer conversion, M_n decreases drastically and addition of a supplementary surfactant seems to disturb the effect of sur-iniferter. Secondly, an α-functional polymer presenting a $M_n = 43500$ g/mol, a polydispersity index $I_p = 2.67$ and a functionality $f_{COOH} = 98\%$ was grafted in the molten state onto a statistical copolymer of ethylene and glycidyl methacrylate and the amount of PMMA grafts was about 10 wt%. In a final step, the graft copolymer was used as emulsifier in LDPE/PVDF blends. Blends including the graft copolymer present a better interfacial adhesion and a reduction of the size of the dispersed phase in comparison with blends without additive.

Keywords: Polymer Synthesis; Sur-Iniferter; Emulsion

1. Introduction

The modification of commercially available polymers has been greatly developed these last years beside the synthesis of new polymeric engineering materials. This kind of chemistry permits to obtain polymers and copolymers presenting novel properties and applications. The peculiar case of polyolefins has been extensively studied by numerous authors and grafting maleic anhydride from polyethylene or polypropylene remains the most often encountered route in the literature [1–11]. These modified polyolefins are now commercialized since they permit the compatibilization of polypropylene with other polymers like polyamides or polyesters [12–14]. Acrylic and methacrylic monomers have also been very often grafted from polyolefins to give polymers presenting for example, polar groups or reactive functions such as epoxy groups or acid groups [15–22]. The most common way developed by workers consists in grafting monomers in molten state or in solution using initiators like peroxides. The presence of radicals in the medium is a real problem as polyethylene cross-links and polypropylene gives β-scission, modifying the properties of the starting polymers. The radical reaction can also be obtained by pre-activation of polymers by radiations (γ rays or electron beam) or reaction with ozone [23–25], but unfortunately, this activation also presents the disadvantage of polymer degradation. Other authors like Chung prepared graft copolymers using living radical reactions involving reactive pendant boranes [26–30]. Beside this way, Matyjaszewski et al. synthesized graft copolymers of polyvinyl chloride or polyethylene using Atom Transfer Radical Polymerization (ATRP) [31,32]. These last two ways of synthesis are interesting for the production of well-defined structures without any drastic

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Table 1
Polymer characteristics

Polymers	References	Supplier	M_w (g/mol)	M_n (g/mol)	Density (g/cm^3)	MFI (g/10 min)	T_m (°C)
LDPE	Stamylan LD	DMS	53,500	10,500	0.919	22 (190 °C, 2.16 kg)	104
PVDF	Solef 1010	Solvay	–	–	–	–	171
PMMA	18–223–0	Aldrich	120 000	–	–	–	114 (T_g)

modification of the starting polymers. Nevertheless, they require polymer presenting reactive sites towards boranes or ATRP.

So, researchers tried to develop new ways avoiding these lacks. One of them consists in preparing α-functional polymers that can be grafted onto polymers bearing reactive sites like succinic anhydride, glycidyl or oxazoline groups. This way is very interesting since the length and the number of grafts can be easily controlled. The synthesis of α-functional polymers can be achieved by telomerization [33,34] or by IniFerTer polymerization where iniferter means INItiator-transFER agent-TERminator) [35,36]. Iniferters are initiators, which have very high reactivities for the chain transfer reaction to the initiator and/or primary radical termination, i.e. ordinary bimolecular termination is strongly reduced. Additionally, the iniferter concept can be extended to living radical polymerization when the termination events (by chain transfer and/or primary radical termination) are reversible [37–39]. For instance, the photopolymerization of methyl methacrylate in the presence of benzyl *N*,*N*-diethyldithiocarbamate shows living characteristics (linear increase of the molecular weight with conversion and possibility to prepare block copolymers) [40]. Thus, a better control of the molecular weight can be achieved by using suitable iniferters.

In our effort to use environmentally friendly processes, poly(methyl methacrylate) was prepared by emulsion polymerization. In this respect, we developed a new concept of sur-iniferter (where the prefix sur- stands for SURfactant). Although surface active photoinitiators have already been used in microemulsion [41], to our knowledge, this is the first study using a surface active photoiniferter. Since the beginning of this work in 1996, new powerful living radical polymerization techniques, such as reversible addition-fragmentation chain transfer polymerization, have appeared and the design of reactive surfactants showing living properties is currently an emerging area of research [42]. In this paper, we prepared an α-functional PMMA using sur-iniferter emulsion photopolymerization and grafted it onto a polyolefine bearing reactive pendant functions.

2. Experimental part

2.1. Materials

α-bromo-*p*-toluic acid (98%, Aldrich), *N*,*N*-diethyldithiocarbamic acid sodium salt trihydrate (99%, Aldrich), benzyl *N*,*N*-dimethyldithiocarbamate (98%, Aldrich), and solvents (Aldrich) were used as received. Methyl methacrylate (99%, Aldrich) was purified by vacuum distillation.

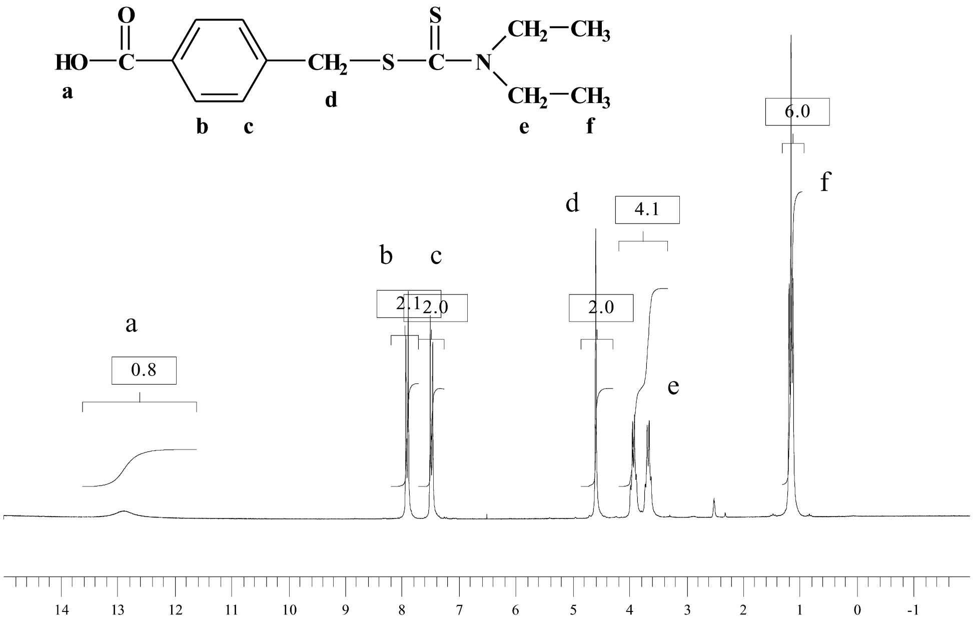


Fig. 1. ^{1}H NMR of DTBA in DMSO d^6.

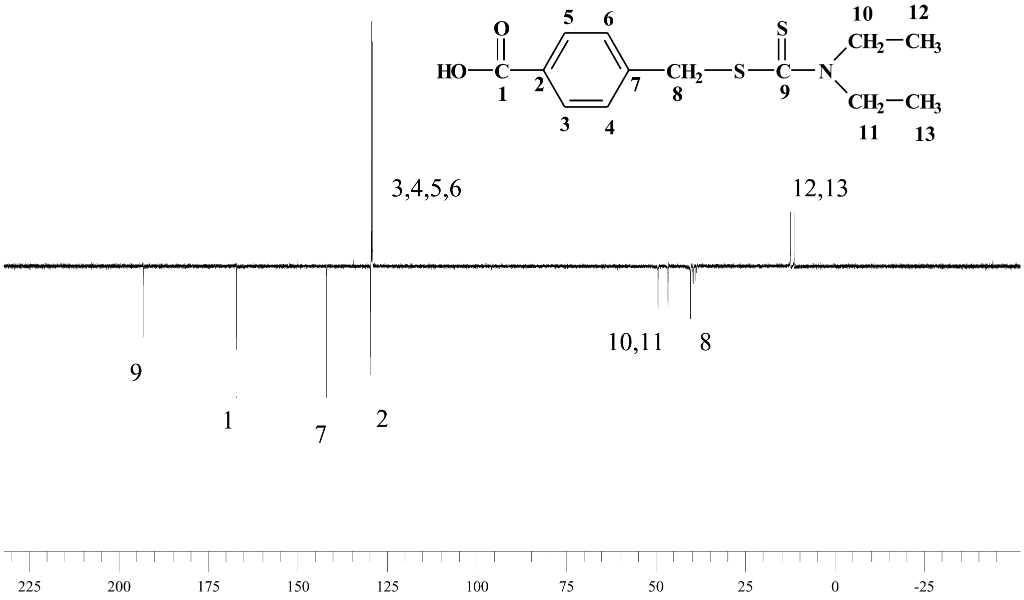


Fig. 2. ^{13}C NMR of DTBA in DMSO d^6.

The different polymers used in our experiments are listed in Table 1.

Lotader AX8840 was a statistical copolymer of ethylene/glycidyl methacrylate (92/8 wt%), produced by Atochem. This product, prepared by a high-pressure polymerization process, possesses the following characteristics: crystallinity inferior to 5%, softening temperature of 87°C, melt flow index (MFI) of 5 g/10 min (190 °C, 2.16 kg) and a number-average molecular weight (M_n) close to 20,000 g/mol.

PolyGMA was synthesized by polymerization of glycidyl methacrylate (GMA, purity 97% purchased from Aldrich). 1 mol of GMA was dissolved in 200 ml of tetrahydrofuran (THF) with 10^{-2} mol of 2,2′-azobisisobutyronitrile (AIBN). Nitrogen was bubbled for half an hour before heating at 60 °C during 8 h. Polymer was recovered by precipitation in methanol, filtered and dried. It had a number-average molecular weight (M_n) close to 25,000 g/mol and a polydispersity index of 5.20 (determined by size exclusion chromatography with PMMA standards).

2.2. Synthesis of 4-diethylthiocarbamoylsulfanylmethyl benzoic acid (DTBA)

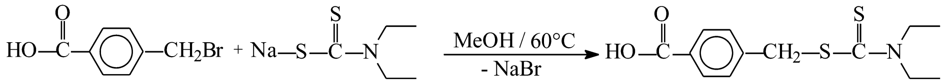
A 500 ml round bottom flask equipped with a condenser, in the absence of light, was filled with 21.50 g of α-bromo-*p*-toluic acid (0.1 mol), 22.53 g of *N*,*N*-diethyldithiocarbamic acid sodium salt trihydrate (0.1 mol), and 250 ml of methanol. The reaction mixture was left for 24 h at 60 °C under magnetic stirring, then cooled to 4 °C. The solvent was evaporated at room temperature under vacuum. The product was washed with water, dissolved in aqueous NaOH solution (0.1 N), filtered, precipitated in aqueous HCl solution (0.1 N), filtered and finally dried under vacuum (2×10^{-2} mm Hg) at 30 °C for 6 h. 23.80 g of a yellowish powder were recovered (84% yield). The product was stored in a cold and dark place. Elemental analysis: C 54.98%, H 6.46%, N 4.61%, O 11.30%, S 22.64% (Theoretical values: C 55.09%, H 6.05%, N 4.94%, O 11.29%, S 22.63%). ^{1}H and ^{13}C NMR (DMSO d^6) are given in Figs. 1 and 2. UV: 278 nm (C=S), 254 nm (aromatic ring).

2.3. Synthesis of carboxylic acid mono functional PMMA in aqueous medium

Typically, 150 ml of deionized water, 0.25 g of DTBA (0.8823×10^{-3} mol) and 26.5 g of MMA (0.265 mol) were introduced in a three necked round bottom flask, equipped with a mechanical stirrer. The stirring speed was kept at 450 rpm. The pH was adjusted at 8 by addition of NaOH (1 N). The reaction mixture was purged with nitrogen for 40 min. Then the emulsion polymerization took place under irradiation 15 cm away from a UV lamp (HPK 125, 125 W, 640 cd/cm^2) at room temperature during 24 h. The latex was precipitated in a large excess of methanol containing 0.01 vol.% hydrochloric acid, filtered, washed with methanol several times, and dried under vacuum.

2.4. Synthesis of Lotader-g-PMMA copolymer

Grafting procedure. Grafting in the molten state was carried out in a Rheocord Haake batch mixer (50 cm^3). 40 g of a carboxylic acid mono-functional PMMA ($M_n = 43,500$ g/mol, $I_p = 2.6$, $f_{COOH} = 0.98$) and 10 g of the copolymer of ethylene/glycidyl methacrylate (Lotader AX8840) were both introduced in the batch mixer preheated at 180 °C and mixed at 32 rpm for 30 min. After mixing, the sample was extracted from the mixer and quenched into liquid nitrogen in order to stop further reactions. The resulting products were dissolved in xylene at 110 °C,



Scheme 1. Synthesis of 4-diethylthiocarbamoyl sulfanyl methyl benzoic acid (DTBA).

precipitated into acetone at room temperature and dried. The purification of the product consisted in extracting the ungrafted PMMA. This was achieved by extraction of the latter with THF at 60 °C for 24 h. Then, the product was filtered and dried under vacuum at 60 °C for 6 h. This purification is necessary to determine the amount of PMMA grafted onto polyethylene. FTIR measurements indicates that a single purification step is sufficient to remove all the unreacted PMMA homopolymer.

2.5. Melt processing

LDPE/PMMA blends and LDPE/PGMA blends in known proportions (98/2, 95/5, 92/8 wt%) were prepared in a batch mixer Rheocord Polylab HAAKE during 15 min at 190 °C. These blends allow to prepare thin films (60 and 80 μm) by compression moulding at 190 °C for 2 min under a pressure of 12 MPa.

LDPE/PVDF blends (50/50 and 80/20 wt%) without or with compatibilizer (5 wt%) were prepared in a Rheocord Haake batch mixer (50 cm^3) in the molten state. The LDPE, the PVDF and the copolymer of Lotader-*g*-PMMA were introduced simultaneously in the batch mixer preheated at 180 °C and mixed at 64 rpm for 15 min. After mixing, the samples were taken from the mixer and then compression moulded into sheets (10 cm × 10 cm × 2 cm). The experimental conditions were as follows: $T = 180$ °C, $P = 100$ bars, $t = 2$ min.

2.6. Characterization

Number average molecular weight M_n, and polydispersity index I_p of the resulting polymers were measured at 30 °C by size exclusion chromatography SEC (Spectra Physics Instrument equipped with a SP8810 pump and a Shodex RISE-61 detector) with THF as eluent at 0.8 ml/min (columns: styragel HR5, phenogel 10 μ/10^4 Å, phenogel 10 μ/10^3 Å and phenogel 10 μ/500 Å). Calibration curve was performed with PMMA standards.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker 200 MHz spectrometer. Chemical shifts refer to tetramethylsilane.

UV spectra were recorded on a Shimadzu UV1205 spectrometer in 10 mm path length UV cell with THF as solvent.

Infrared spectroscopy measurements were performed in transmittance with a spectrometer NICOLET 510 P.

Measurements of the surface tension of aqueous solutions of DTBA sodium salt were realized with a tensiometer KRUSS K14 at 25 °C. A mixture containing 0.1 mol of DTBA, 0.1 mol of sodium hydroxide and 60 ml of water was prepared and filtered. DTBA sodium salt was recovered after evaporation of water under vacuum at 60 °C.

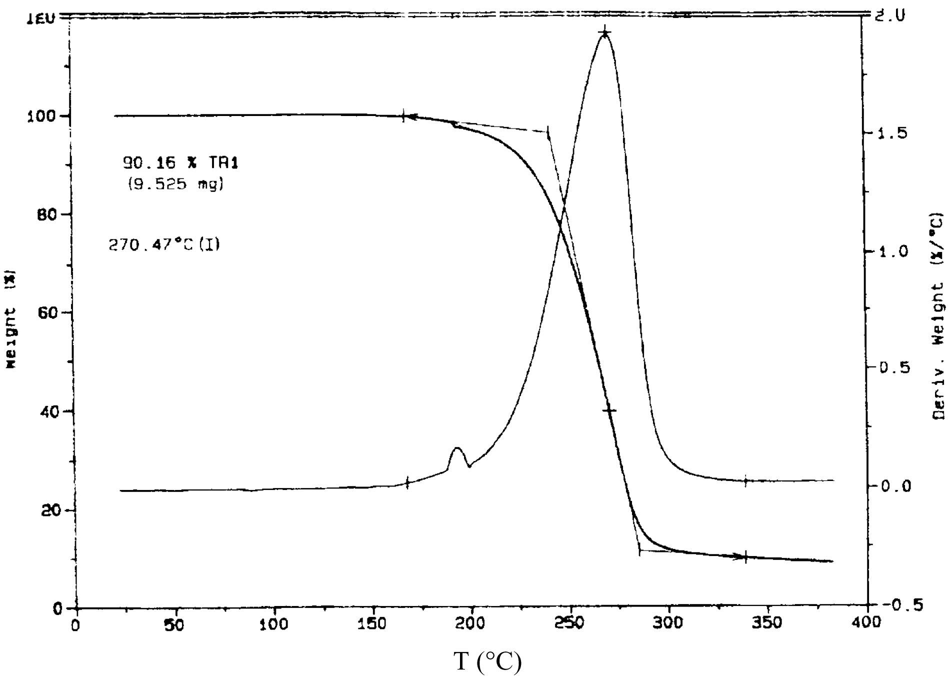


Fig. 3. Thermogravimetric analysis of DTBA (under nitrogen).

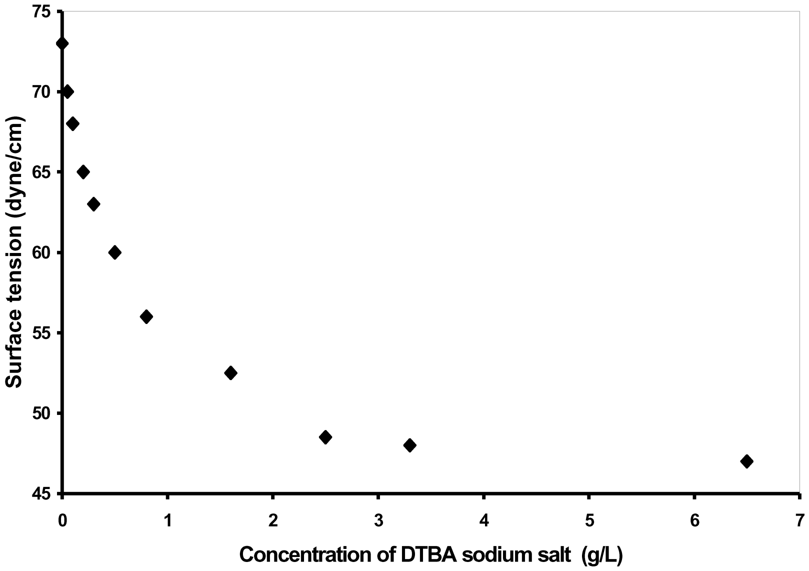


Fig. 4. Determination of the critical micellar concentration of DTBA sodium salt.

Different diluted solutions of DTBA sodium salt were prepared and their surface tension was measured.

To study the morphology of the blends, the samples were fractured in liquid nitrogen. The fractured surfaces were examined by Scanning Electron Microscopy (SEM), using a Cambridge Stereoscan 260, after they had been coated with a thin conductive layer of palladium alloy. The enlargement is specified in the legends.

3. Results and discussion

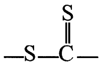
3.1. Synthesis of 4-diethylthiocarbamoylsulfanylmethyl benzoic acid (DTBA)

In the 1980's, Otsu et al. [35,36,40] described the synthesis of iniferter compounds such as benzyl *N*,*N*-diethyldithiocarbamate and their use in living radical photopolymerization of methyl methacrylate in solution. Upon UV irradiation, this asymmetric iniferter cleaves homolytically to give an efficient initiating benzyl radical and a dithiocarbamoyl radical, which preferentially reacts as a reversible terminator towards propagating radicals. Bertin et al. [43] have also successfully tested other dithiocarbamate derivatives for the bulk photopolymerization of methyl methacrylate. In this work, we prepared a ionizable iniferter, namely 4-diethylthiocarbamoylsulfanylmethyl benzoic acid (DTBA), showing surface active properties in aqueous medium. Accordingly, in reference to the terminology used in previous works on reactive surfactants (namely inisurfs, surfmers, and transurfs) [44], this new type of compounds was called sur-iniferter where the prefix sur- stands for SURfactant. Moreover, the carboxylic acid moiety in DTBA can be used for further chemical modification of the resulting polymer.

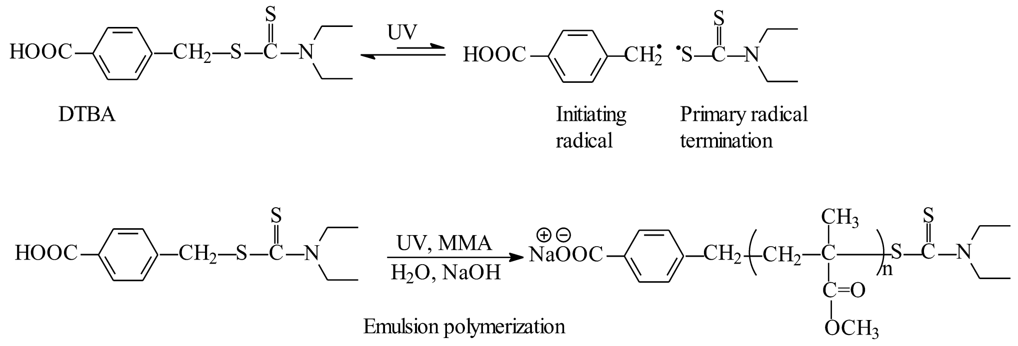
Table 2
CMC of some conventional surfactants

Surfactant	T (°C)	CMC (mmol/l)
Sodium palmitate $C_{15}H_{31}CO_2Na$	50–70	1.7
Sodium lauryl sulfate $C_{12}H_{25}OSO_3Na$	25–60	9.0
Sodium dodecyl benzene sulfonate $C_{12}H_{25}-C_6H_4-SO_3Na$	50–75	1.2

The new compound DTBA was synthesized in high yield by a conventional nucleophilic substitution reaction between *N*,*N*-diethyldithiocarbamic acid sodium salt and α-bromo-*p*-toluic acid as the primary alkyl halide (Scheme 1).

The product obtained was characterized by IR spectroscopy where the OH group of the acid functions is observed at 3427 cm^{-1}, the carbonyl at 1687 cm^{-1} and the  $-S-\overset{\overset{S}{\|}}{C}-$ group at 1251 cm^{-1}. The ^1H NMR (Fig. 1) and ^{13}C NMR (Fig. 2) are in good agreement with the expected structure of DTBA. At last, the UV spectroscopy permitted to confirm the attained structure with two main absorptions at 278 and 254 nm attributed to the C=S group and aromatic ring respectively. Thermal analysis (Fig. 3) showed that thermal degradation and vaporization of secondary products occurs above 160 °C and that the product is stable at ambient temperature.

DTBA presenting surfactant properties, its critical micellar concentration (CMC) was measured. This physical value was obtained by measuring the surface tension of DTBA sodium salt in water (Fig. 4). The CMC of DTBA sodium salt was found to be 2.7 g/l or 8.8×10^{-3} mol/l, what is similar to conventional surfactants (Table 2) [45].



Scheme 2. Emulsion photopolymerization of MMA with DTBA.

3.2. Synthesis of mono functional carboxylic acid PMMA in aqueous medium

Nowadays, the use of volatile organic compounds must be avoided due to environmental concerns. In this respect, emulsion polymerization [46] is a process of interest for polymer synthesis because the solvent is water. In this work, we took advantage of both the carboxylic acid functionality and the surface active properties of DTBA to prepare mono functional carboxylic acid PMMA by emulsion polymerization in aqueous medium, in the absence of any other co-surfactants (Scheme 2).

Sur-iniferters were shown to control both molecular weight and functionality of the formed macromolecules, and monodisperse polymeric nanoparticles were easily obtained by surfactant-free emulsion polymerization with sur-iniferters [47]. Block and graft copolymers were also prepared by this technique [48].

The ability of DTBA to cleave under UV irradiation was checked by using 4-hydroxy TEMPO as the radical trap. The decrease of the concentration of 4-hydroxy TEMPO vs. time, followed by high performance liquid chromatography, allowed us to estimate the dissociation rate constant k_d of DTBA sodium salt in water to be $2\times10^{-5}\ s^{-1}$ in our conditions of polymerization [47].

PMMA was prepared in high yield by emulsion photopolymerization with DTBA according to experimental conditions given in Table 3. Furthermore, molecular weights were determined by SEC vs. monomer conversion (Fig. 5). These results show that final molecular weight decreases when DTBA concentration increases. In a same way, polydispersity index I_p is greatly affected by DTBA concentration. Fig. 5 shows that M_n increases linearly up to monomer conversion of 60% and decreases drastically after. This last observation has not been explained up to now and would deserve further works. However, these experiments prove that DTBA acts as initiator, surfactant and reversible termination agent. At last, although DTBA is sufficient to stabilize effectively the latex particles, we have texted the effect of the addition of a conventional surfactant (Sodium dodecyl sulfate, SDS) on the obtained molecular weights. It appeared that this additive lead to a poor control of the polymerization as shown by a very high molecular weigh and f^* value. The high molecular weight obtained in the presence of SDS could be ascribed to the formation of micelles of SDS, which are nucleated by propagating radicals arising from DTBA. In these micelles, the concentration of terminators is possibly very low.

In the purpose of grafting these α functional polymers onto LDPE, it was necessary to measure their functionality in acidic group. This was done by UV titration of the benzylic ring at 254 nm. The dithiocarbamate group was studied (at 278 nm) to check the living character of the polymerization. Calibration curves were preliminarily obtained with different solutions of benzyl *N*,*N*-dimethyldithiocarbamate in tetrahydrofurane (Fig. 6). Functionality of PMMA was evaluated in THF solutions using Eq. 1 and knowing that each benzylic group implies one acidic function:

$$f_{COOH} = [-C_6H_5 - COOH]_{UV}\cdot(M_{n,SEC}\times V)/(1000\times m) \quad (1)$$

where $[-C_6H_5{-}COOH]_{UV}$ is the concentration of the

Table 3
Experimental conditions for emulsion photopolymerization of MMA with DTBA at pH = 8 ([MMA] = 1.77 mol/l)

Run	[DTBA] mmol/l	[DTBA]/[MMA] mol/mol ($\times10^{-3}$)	[SDS]/[MMA] mol/mol ($\times10^{-3}$)	Monomer conversion (%)	M_n	I_p	f^*
1	3.5	2.0	–	89	70,700	2.74	1.3
2	5.8	3.3	–	93	65,700	2.80	1.9
3	8.8	5.0	–	99	63,800	3.77	2.6
4	9.6	5.4	–	77	49,200	2.70	2.8
5	9.8	5.5	7.7	76	260,000	1.85	15.6

$f^* = M_{n,experimental}/M_{n,theoretical}$ with $M_{n,theoretical} = ([MMA]_o\times Conversion\times M_{MMA})/[DTBA]_t$ where $[DTBA]_t = [DTBA]_o\times(1-e^{-k_d t})$ and $k_d = 2\times10^{-5}\ s^{-1}$.

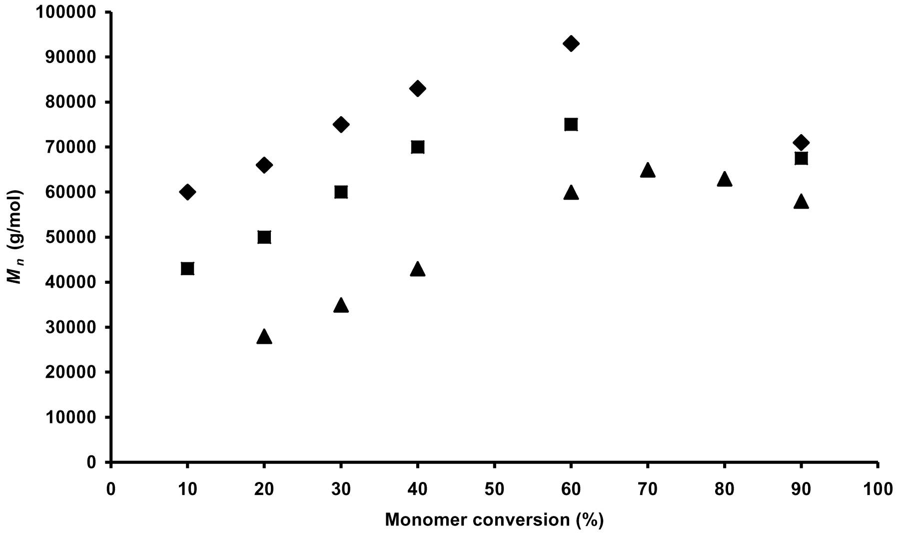


Fig. 5. Evolution of molecular weight versus monomer conversion in emulsion photopolymerization of MMA (1.77 mol/l) at pH = 8 in the presence of DTBA: 3.5 mmol/l (◆), 5.8 mmol/l (■), 8.8 mmol/l (▲) (runs 1–3 in Table 3).

initiator moiety (mol/l) given by Fig. 6 and determined by UV titration of *m* grams of polymer in *V* ml of THF. M_n is the molecular weight of the polymer determined by size exclusion chromatography.

Fig. 7 gives an example of the evolution of the benzylic groups (and so, of acidic functions) and CS_2 groups during polymerization of MMA with DTBA in experiment 4 (Table 3). It shows that benzylic absorbancy is constant as a function of time, indicating that the polymers obtained are monofunctional ones.

The decrease in CS_2 absorbancy (i.e. decrease of the living properties) is due to a slight decomposition of the functional PMMA dithiocarbamate moiety under UV irradiation, as previously noticed by OTSU with benzyl *N*,*N*-diethyldithiocarbamate [37,38].

So, mono functional carboxylic acid PMMA is easily prepared by this method. The use of sur-iniferter is a very convenient and environmentally friendly route to prepare mono functional polymers. It efficiently competes with other traditional methods such as the use of functional transfer agents in telomerization where functionality of high molecular weight polymers is not well controlled [33,34].

In order to obtain the graft copolymer, we decided to use an α functional polymer obtained at a monomer conversion of 40% using a molar ratio DTBA/monomer of 5×10^{-3} (similar conditions as experiment N°3), leading to a molecular weight of 43500 g/mol and $I_p = 2.67$. The functionality by UV titration gives $f_{COOH} = 0.98$.

3.3. Synthesis of PE-g-PMMA copolymer

The Lotader-*g*-PMMA copolymer was synthesized from the monofunctional carboxylic acid poly(methyl methacrylate) and the poly(ethylene-*co*-glycidyl methacrylate)

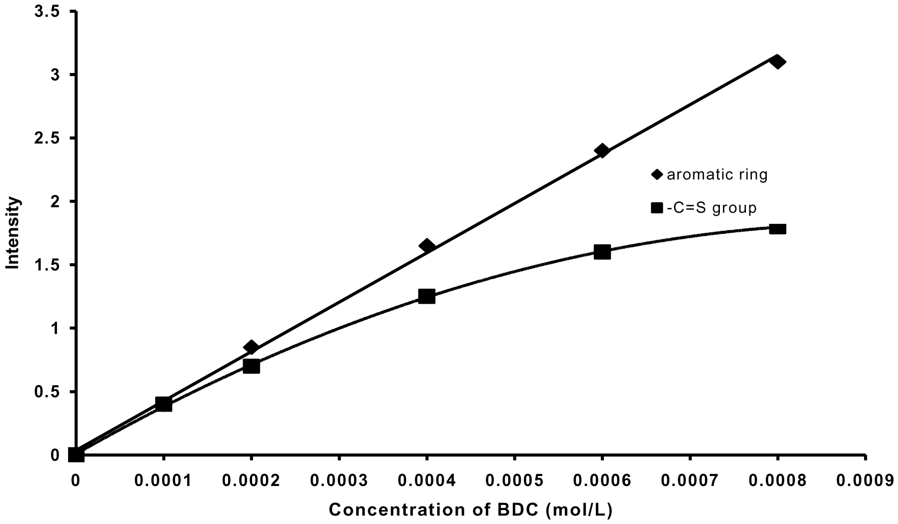


Fig. 6. Calibration curves for aromatic and C=S group determination in polymers (benzyl *N*,*N*-dimethyldithiocarbamate).

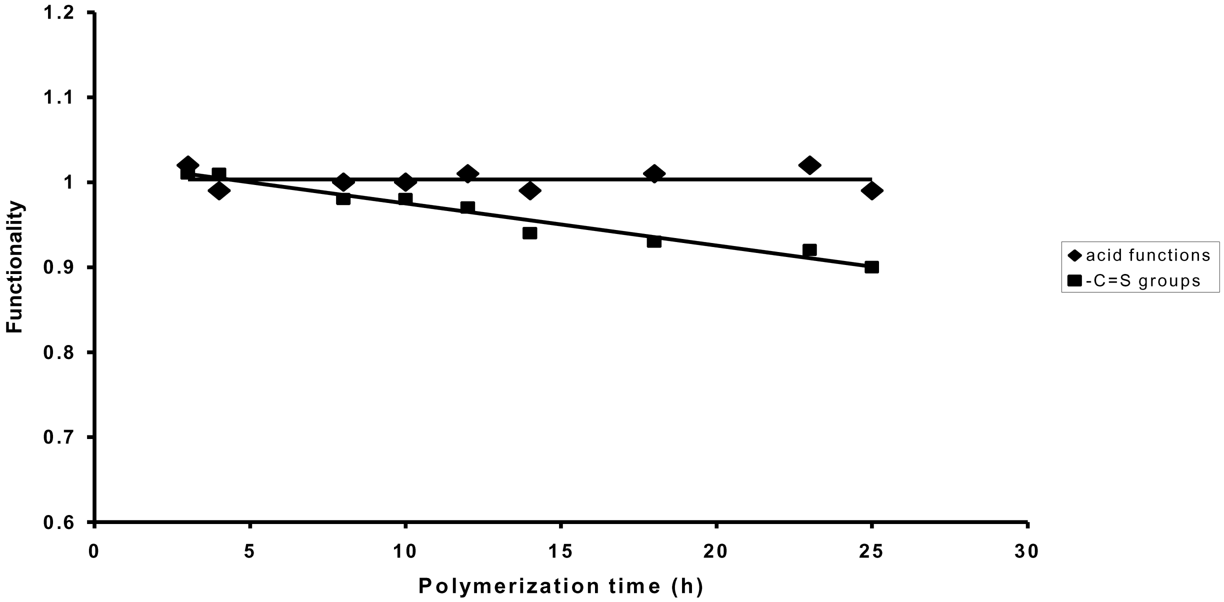


Fig. 7. Evolution of the polymer content in carboxylic acid function and C=S group versus polymerization time.

(Lotader AX8840). This reaction was carried out in the molten state and without catalyst. The resulting products were dissolved in hot xylene at 110 °C, precipitated into acetone at room temperature and dried. The purification of the product consisted in extracting the ungrafted PMMA. The mechanism of grafting is based on the reaction of carboxyl with epoxy groups. The reaction mechanism is given in Scheme 3.

The grafting yield of PE-*g*-PMMA copolymer was determined by FTIR.

The calculation of grafting yields of PE-*g*-PMMA copolymer synthesized in molten state was achieved using a calibration curve established with mechanical LDPE/PMMA blends in known proportions (98/2, 96/4, 95/5, 92/8 wt%). The ratio I_{1732}/I_{1380} (I_{1732} : intensity corresponding to the absorption frequency of the carbonyl group of PMMA, I_{1380} : intensity corresponding to the symmetrical deformation of methyl groups in LDPE) of different samples were reported on a graph. These results enabled us to establish the calibration curve $I_{1732}/I_{1380} = f$ (wt% PMMA) (Fig. 8). Then, the value of intensity ratio (I_{1732}/I_{1380}) measured on the spectra of the purified copolymer PE-*g*-PMMA (Fig. 9) is considered. However, purified copolymer contained carbonyl groups coming both from PMMA grafts and glycidyl methacrylate units of LOTADER. So, we used Eq. 2 to determine the grafting yield of PMMA in the purified copolymer:

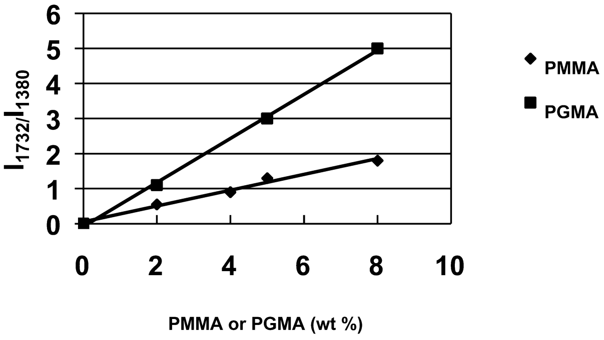


Fig. 8. PMMA calibration curve (from LDPE/PMMA blends) for the determination of the amount of PMMA grafts in the purified copolymer by F.T.I.R and PGMA calibration curve (from LDPE/PGMA blends) for the determination of the content of GMA in LOTADER by F.T.I.R.

$$(I_{1732}/I_{1380})_{\text{PMMA}} = (I_{1732}/I_{1380})_{\text{Purified copolymer}} - (I_{1732}/I_{1380})_{\text{Poly(ethylene-}co\text{-glycidyl methacrylate)}} \quad (2)$$

The statistical copolymer (Lotader AX8840 purchased from Atochem) possesses an average content of GMA of 8 wt%. To validate the method to determine the grafting yield by FTIR analysis, we applied it to Lotader AX8840. Samples of this statistical copolymer were pressed into thin films at 190 °C for 2 min under a pressure of 12 MPa between two Teflon® sheets. To determine the GMA content in the copolymer, we calculated the ratio (I_{1732}/I_{1380}) for this sample (Fig. 10) and we reported it on the calibration curve established with mechanical blends from LDPE/PGMA, in known proportions (98/2, 95/5, 92/8 wt%) (Fig. 8). We found that the statistical copolymer contained 7.5% in weight of GMA, this result being in agreement with the value given by Atochem and proving the validity of the method.

From the ratio I_{1732}/I_{1380} measured on the spectrum of the purified copolymer (Fig. 9) and the ratio I_{1732}/I_{1380} measured on the spectrum of poly(ethylene-*co*-glycidyl methacrylate) (Fig. 10), we can calculate the value of the ratio I_{1732}/I_{1380} relative to carbonyl groups belonging to

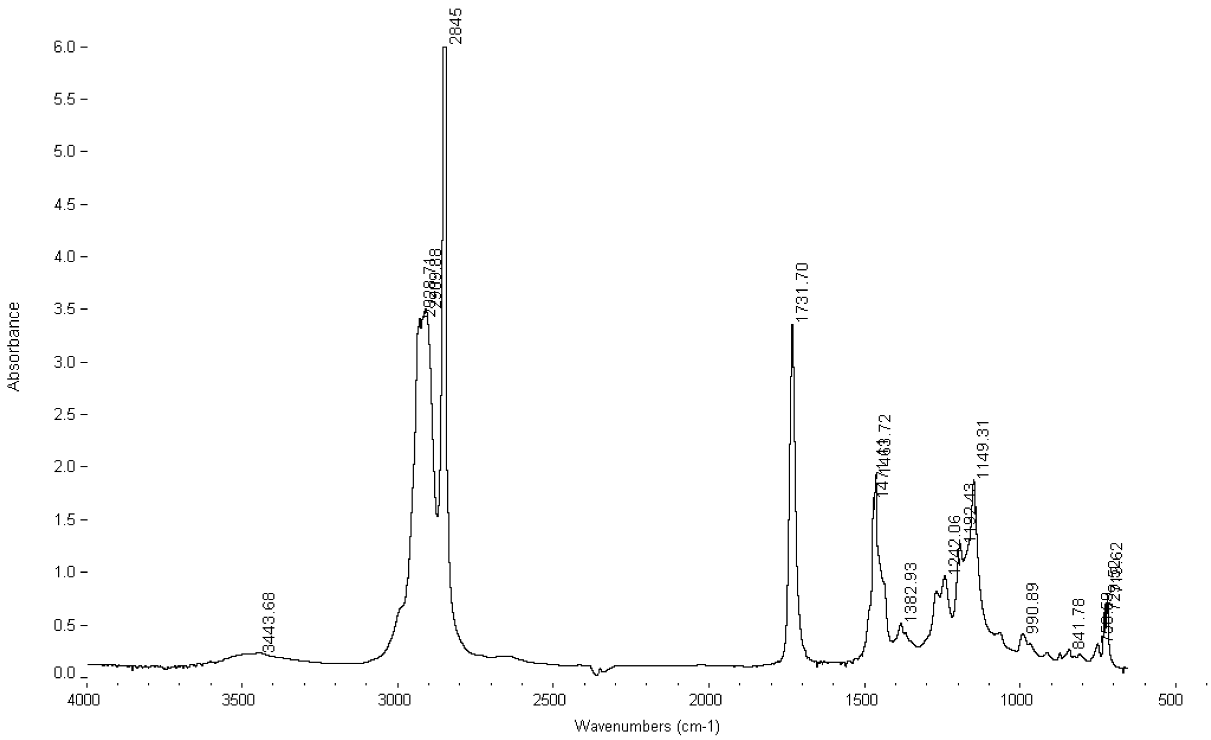


Fig. 9. F.T.I.R. spectrum of the purified copolymer.

PMMA (Eq. (2)). This value is reported in Eq. (3) given by LDPE/PMMA blends calibration curve (Fig. 8). The amount of PMMA grafts in the purified copolymer is about 10 wt%.

$$I_{1732}/I_{1380} = 0.225 \times \text{PMMA (wt\%)} \quad (3)$$

Knowing the initial blend of poly(ethylene-*co*-glycidyl methacrylate) (10 g that is to say 5.6×10^{-3} mol of GMA) and monofunctional carboxylic acid poly(methyl methacrylate) (40 g that is to say 9.2×10^{-4} mol, corresponding to 16 mol% relative to GMA reactive sites of

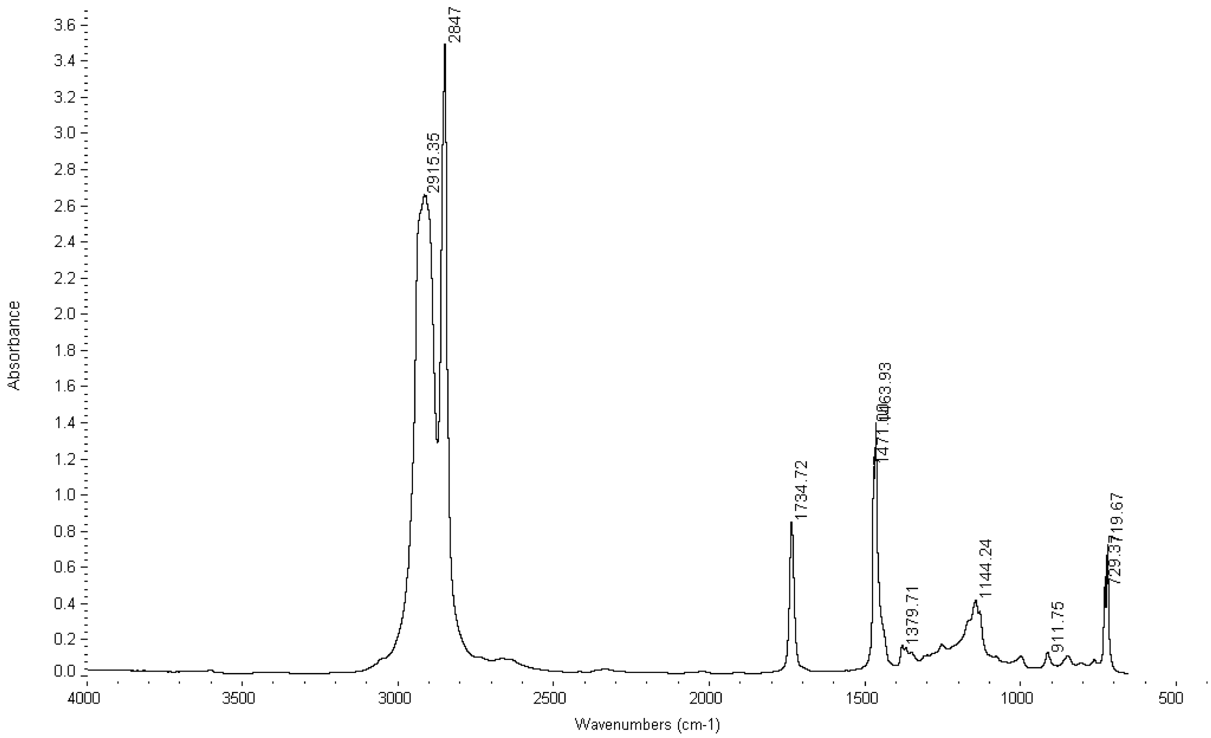


Fig. 10. F.T.I.R. spectrum of Lotader AX8840.

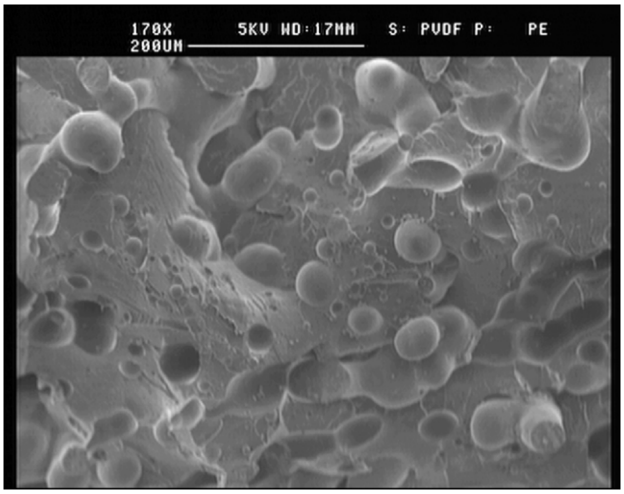


Fig. 11. SEM micrograph of LDPE/PVDF (50/50 wt%) blends without PE-*g*-PMMA (× 170).

LOTADER), we can calculate that 3% of the PMMA chains have reacted on LOTADER. This low yield of grafting can be ascribed to the rather high molecular weight of the reactive PMMA chains and also to the low concentration of PMMA chains in the initial blend.

3.4. Compatibilization of LDPE-PVDF blends

We studied the morphologies of compatibilized LDPE/PVDF (50/50 and 80/20 wt%) blends with PE-*g*-PMMA copolymer (10 wt% PMMA grafts) as compatibilizer.

The LDPE/PVDF (50/50 and 80/20 wt%) blends without compatibilizer possess a coarse morphology (Figs. 11 and 12) with larger-size domains, as compared to compatibilized blends (Figs. 13 and 14). In the absence of compatibilizer, the large size of particles (average diameter of 10 μm), with no evidence of adhesion between the matrix and dispersed phase, confirms the incompatibility between the two components.

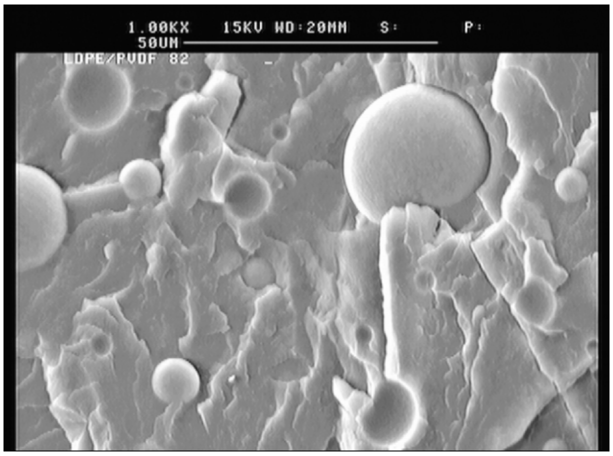


Fig. 12. SEM micrograph of LDPE/PVDF (80/20 wt%) blends without PE-*g*-PMMA (× 170).

Fig. 13. SEM micrograph of LDPE/PVDF blends (50/50 wt%) with 5 wt% PE-*g*-PMMA (× 225).

In comparison, the addition of 5 wt% of PE-*g*-PMMA in these blends (Figs. 13 and 14) improves the interfacial adhesion and reduces the size of the dispersed phase. The phase boundaries become less clear when 5 wt% of PE-*g*-PMMA are added to LDPE/PVDF 80/20 wt% blends (Fig. 14) in comparison with LDPE/PVDF 50/50 wt% blends (Fig. 13). Figs. 13 and 14 show the typical behavior of compatibilized blends with improved phase cohesion. The PE-*g*-PMMA copolymer is efficient as compatibilizer for LDPE/PVDF blends because PMMA grafts are compatible with PVDF while the statistical copolymer LOTADER backbone is compatible with polyethylene.

4. Conclusion

Carboxylic acid monofunctional PMMA was synthesized by emulsion photopolymerization with DTBA which acts as sur-iniferter, leading to a linear evolution of M_n vs. monomer conversion up to 60%. The polymers

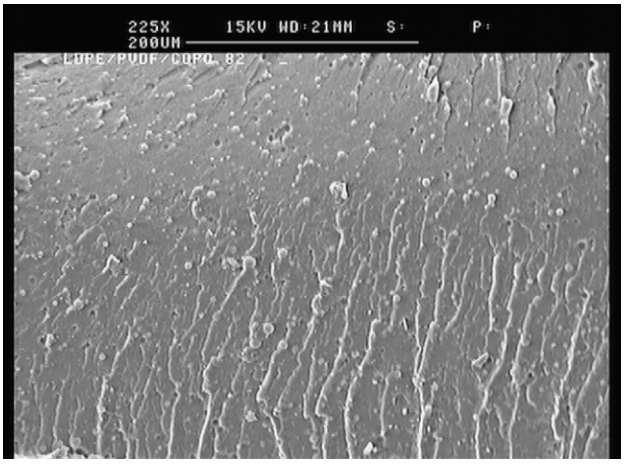
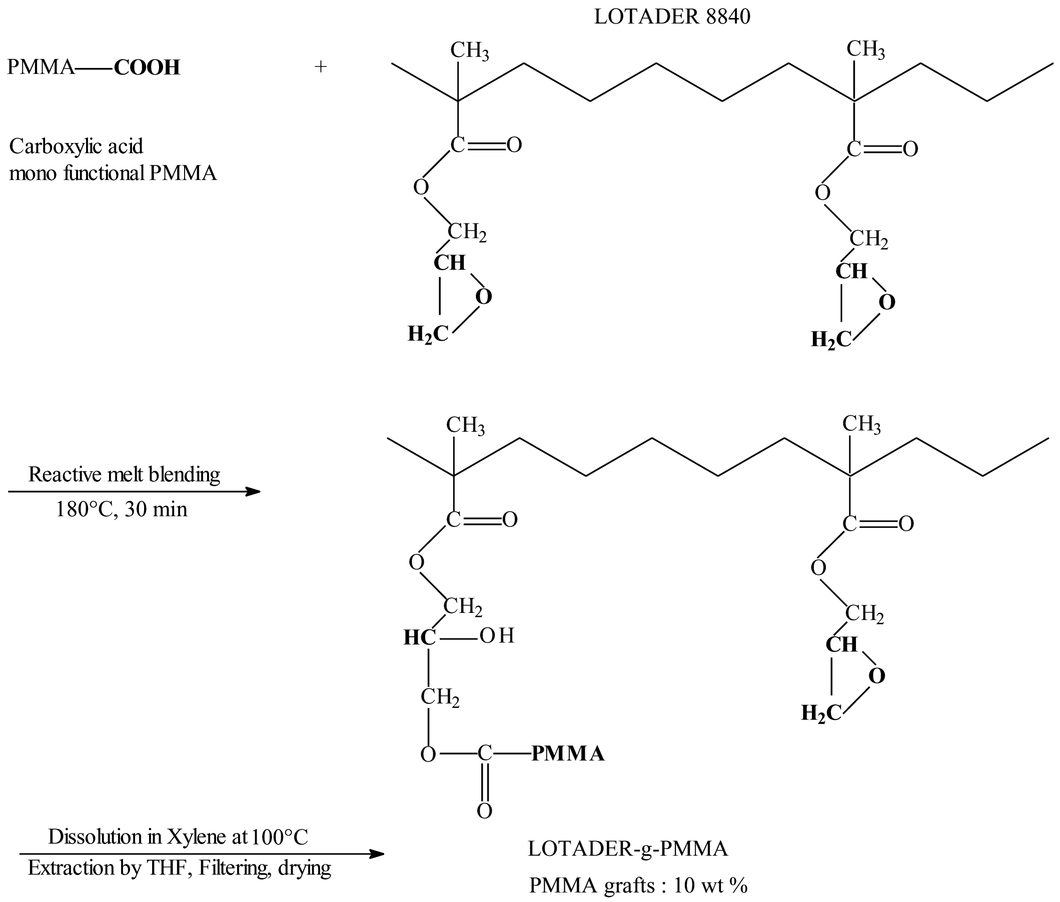


Fig. 14. SEM micrograph of LDPE/PVDF blends (80/20 wt%) with 5 wt% PE-*g*-PMMA (× 225).



Scheme 3. Grafting of carboxylic acid monofunctional PMMA onto poly(ethylene-*co*-glycidyl methacrylate).

present a functionality in carboxylic acid group close to 1 that proves the efficiency of the sur-iniferter agent. This carboxylic acid monofunctional polymer was reacted in the molten state with poly(ethylene-*co*-glycidyl methacrylate) and gave polyethylene-*g*-PMMA with about 10 wt% of PMMA grafts. This copolymer acted as compatibilizer in LDPE/PVDF/PE-*g*-PMMA blends (50/50/5 or 80/20/5 weight compositions) and decreased surface tensions leading to blends presenting improved homogeneity.

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