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Synthesis of End-Functionalized Polystyrenes Using ATRP and Their Grafting onto Polyethylene Copolymers

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ABSTRACT

Functional polystyrenes bearing one or two carboxy groups per chain end have been synthesized using atom transfer radical polymerization (ATRP). Commercially available haloesters were used as initiators for ATRP of styrene and the polymerization products were transformed via hydrolysis reaction into α-carboxy polystyrenes with one carboxy group in every chain end. By proper selection of the initiator, efficiencies of above 0.7 were obtained. The end-functionalized PSs were further examined for their ability to form PS-g-PE copolymers by reactive blending with polyethylene–glycidylmethacrylate copolymer (PE-g-GMA). The copolymers formed were used as compatibilizers for the immiscible polyethylene–polystyrene (HDPE/PS) blend. The effectiveness of the compatibilization was checked by tensile testing and SEM.

Key Words: Polystyrenes; Atom transfer radical polymerization; End-functionalized polymers; Polyethylene copolymers.

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INTRODUCTION

End-functionalized polymers have attracted much interest because of their potential application in different technological areas like surface modification,[1] adhesion,[2] and compatibilization of polymer blends.[3,4] They combine the physical properties of the polymers with the chemical properties of the terminal groups. The presence of a defined number of functional groups per chain facilitates the understanding of fundamental aspects of the different processes in which the functional polymers are involved.[5]

There are different synthetic efforts to prepare end-functionalized polymers, mostly by using techniques like anionic polymerization[6–8] and controlled radical polymerization.[5,9–13] The use of atom transfer radical polymerization (ATRP)[14–16] provides easier experimental conditions than the anionic polymerization and "tolerance" to the different functional groups. This tolerance enables the incorporation of the desired functional group, in a protected form or not, into the initiator molecule.

Polymers bearing cross-reactive functional groups, such as amine-anhydride, amine-carboxylic acid, amine-epoxy, oxazoline-carboxylic acid, and epoxy-carboxylic acid groups,[17] can react with each other, thus making the reactive blending process an effective strategy for compatibilization of immiscible polymers.[18–21] Reactive blending involves an in situ coupling reaction of functionalized components to form a block or graft copolymer at their interface.[22–25] If the copolymer resides at the interface where it is formed, it acts as a polymeric emulsifier in that it causes reduction of the interfacial tension stabilizing the interface and preventing the phases from coalescing.[26–29]

Additionally, the formed copolymer increases the adhesive strength between the two phases leading to a mechanically compatible blend.[30,31] Besides a compatibilization strategy for immiscible polymer blends, reactive blending has proved to be an alternative method for solvent free preparation of block or graft copolymers.[9,20,21] In contrast to the compatibilization process, in this case the in situ formed copolymer should be able to escape from the interface as rapidly as it is produced, so that the interface is constantly available for new copolymer synthesis.[32,33]

The parameters which are affecting the morphology of the reactive blend are among others the in situ formed copolymer architecture,[33,34] the coupling reaction rate[32,35] and the molecular weight of the reactive components.[32,36] In the present work, well-defined polystyrenes with carboxylic acid termini and high functionality have been prepared via ATRP. In previous synthetic studies on carboxylic acid terminated polystyrenes[11,13] various compounds have been examined as initiators. The α-halocarboxylic acids used had low initiator efficiency, probably because of the intramolecular cyclization into a γ-butyrolactone after addition of one styrene unit.[13] The use of carboxylic acid initiators with remote halogens afforded relatively high initiation efficiencies, while the most effective initiators proved to be the compounds bearing carboxylic groups protected by trimethyl silyl, *tert*-butyl dimethylsilyl or *tert*-butyl groups.[13] In this study, the initiators used for styrene polymerization were simple haloesters commercially available, that lead to polystyrenes with relatively controlled MW and narrow MWD. These were easily transformed into α-carboxylic acid-polystyrenes (PS-COOH) by subsequent hydrolysis of the ester protective groups. In the second part of our study, the PS-COOH of various MWs obtained, were melt blended with polyethylene-glycidylmethacrylate copolymer (PE-g-GMA) in order to evaluate their grafting efficiency onto a GMA-functionalized PE matrix, since reaction between carboxylic acid and epoxy groups can easily occur during melt blending conditions.[18,36–38] Grounded on the fact that reactive blending may force two thermodynamically immiscible polymers to stay together through covalent bond formation, the proposed procedure seems an interesting approach towards producing new materials that may combine the mechanical properties of polyethylene with the aromatic character of polystyrene.

The morphology of the binary mixtures PS-COOH/PE-g-GMA observed with SEM implies that in some cases PS-g-PE copolymers were formed. These were added as premade copolymers to the immiscible HDPE/PS system, in order to test their compatibilization efficiency. The melt blending procedure was repeated using an α-dicarboxylic acid-polystyrene (PS(COOH)$_2$), previously synthesized in our laboratory,[39] and the product of blending PS(COOH)$_2$ with PE-g-GMA showed an improved compatibilization activity when added as a third component to a binary HDPE/PS system.

EXPERIMENTAL

Materials

Styrene (99%, Aldrich) was treated with finely powdered CaH$_2$ and vacuum distilled before polymerization. Diphenylether (DPE, >98%, Merck), used as solvent, was stored over molecular sieves and purged with argon for 30 min prior to use. Copper(I) bromide, 2,2′-bipyridine (bipy), *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA), and the initiators: methyl α-bromophenylacetate (MBPA), methyl 4-bromomethylbenzoate (MBMB), ethyl 2-bromoisobutyrate (EBIB), methyl 2-bromopropionate (MBP) were all commercial products of Aldrich and were used without further purification. The bifunctional initiator 4-[3,5-*bis*(methoxycarbonyl)phenoxymethyl]benzyl bromide was synthesized according to known procedure.[40] Polystyrene ($M_n = 100{,}000$) was obtained from BDH, while PE-g-GMA and HDPE from Atocem Co. All polymers were dried in a vacuum oven at 80°C for 48 h to remove sorbed water before processing.

Synthesis of End-Functionalized Polystyrenes by Atom Transfer Radical Polymerization

A round-bottom flask equipped with a U-tube, rubber septum, magnetic stirrer and a gas inlet/outlet was flamed under vacuum. The initiator was added to the flask containing CuBr and the complexing ligand (bipy or PMDETA). The system was degassed four times and flushed with argon. The solvent and the monomer were consequently transferred to the flask via a syringe through the rubber septum. The reaction mixture was then immersed in an oil bath and heated at 110°C for 20 h. After cooling the reaction mixture to room temperature, THF was added in order to dissolve the polymer. The solution was filtered to remove the catalyst and afterwards precipitated in a large excess of ethanol 95%. The polymers obtained were dried under vacuum at 60°C for 24 h. These polymers were hydrolyzed by overnight refluxing with 10 N aqueous KOH solution in acetone or THF and acidified with HCl (37%) in order to obtain the carboxy end-functionalized polystyrene.

Blend Preparation

The blends were prepared by melt mixing in a home-made batch mixer, consisting of a heating cylindrical beaker of 35 mm diameter and a cylindrical rotor, rotating with controlled speed, under an inert atmosphere (N_2). Optimum blending conditions were 10 min and 230°C.

Films of polymer blends were made by compression molding between Teflon sheets at 230°C, pressure release and quenching to 0°C. SEM specimens were 1.5 mm thick plates, prepared by compression molding, which after remaining for 4–5 min in liquid N_2, were instantaneously cryofractured. SEM observations were made (a) on the cryofractured surfaces and (b) on very thin films of the blends, after their etching with a selective solvent; CH_2Cl_2 or a solvent mixture cyclohexane/toluene 80/20 (v/v) which can extract selectively the polystyrene phase.

Measurements

The number-average (M_n) and weight-average (M_w) molecular weights of the polymers were determined by gel permeation chromatography apparatus (Polymer Lab, Series II Marathon), equipped with a Fasma 500 UV-VIS detector and two Ultrastyragel columns (10^4 and 500 Å pore size). Measurements were performed in chloroform at room temperature, prior to hydrolysis of the ester end-groups, to avoid grafting of carboxylic acid groups onto the chromatography columns. The calibration was based on polystyrene standards. ^{1}H-NMR spectra were recorded at room temperature with a Bruker Avance DPX spectrometer at 400 MHz. The solvent used was $CDCl_3$, with TMS as standard. FT-IR spectra were obtained using a Perkin Elmer 1600 spectrometer. SEM observation was carried out with a JEOL JSM-500 model, at 500–10,000× magnifications. Specimens were gold coated prior to use. Tensile tests were performed according to the ASTM D882 standard, at room temperature, using a J.J. Tensile Tester type 5001 and film strips with dimensions $3.00 \times 0.65 \times 0.0025\ \mathrm{cm}^3$. Data reported were obtained at a cross-head speed of 10 cm/min.

RESULTS AND DISCUSSION

Synthesis and Characterization of Carboxylic Acid Terminated Polystyrenes

In order to determine the most efficient initiating system for the ATRP of styrene, different initiators like MBPA, MBMB, EBIB, and MBP were used in a first series of polymerizations. The initiating systems consisted of the haloester and equimolar amount of CuBr, while two different metal complexing ligands were used, bipy (CuBr : bipy = 1 : 3) and PMDETA (CuBr : PMDETA = 1 : 1). These polymerizations proceeded in a 67% styrene solution in diphenyl ether. The molecular weights of the α-carboxylic acid methyl/ester polystyrenes obtained were determined using gel permeation chromatography. In the cases where bipy was used as complexing ligand of the metal catalyst, the polymers obtained had molecular weights not higher than 3300, although complete monomer conversion should have theoretically resulted in polymers with a molecular weight of 9000. When bipy was replaced by PMDETA, the catalytic system seemed to be active only when combined with the MBP initiator. However, the obtained α-carboxylic acid methyl ester polystyrene had a molecular weight of 13,700, which was higher than the expected one ($M_{\mathrm{n,theor}} = 8300$). The ^{1}H-NMR spectrum of this polymer, depicted in Fig. 1, can give additional information about its molecular weight. The molecular weight can be calculated using the integral ratio of the resonance peak at $\delta \sim 3.5$ ppm attributed to the protons (H^{α}) of carboxylic acid methyl ester, to the resonance peaks in the range $\delta = 6.3–7.3$ ppm, attributed to the aromatic protons of the polystyrene. Thus, the calculated molecular weight was found in excellent agreement with the molecular weight obtained by GPC, as seen in Table 1. This result constitutes evidence of the presence of one methyl ester group on every growing polymer chain; i.e., the formation of α-carboxylic acid methyl ester-polystyrene. The higher than expected MW of PS obtained by the MBP/CuBr/PMDETA catalytic system should then not be attributed to bimolecular termination reactions, but rather considered as the result of low initiator efficiency.

Among the initiator-catalyst systems studied, MBP/CuBr/PMDETA was chosen as the most efficient for styrene polymerization. This was consequently applied in a series of experiments which were carried out using various $[\mathrm{St}]_0/[\mathrm{MBP}]$ ratios and a constant [MBP]/[CuBr]/[PMDETA] ratio of 1/1/1 in 67% styrene solution, where the brackets stand for molar concentrations. By varying the monomer to initiator molar ratio it is expected that polystyrenes of analogous variation in their molecular weights will be synthesized. The products were characterized by GPC and ^{1}H-NMR and the results are summarized in Table 1. The molecular weights of the obtained polymers follow the increase in the [monomer]/[initiator] ratio. However, only for the lower molecular weight polymers a coincidence between theoretical and experimental values can be observed. For higher molecular weights the initiator efficiency was between 0.60 and 0.86, showing that synthesis of polymers with MW higher than 20,000 is not possible.

The next step in optimizing the conditions for the ATRP of styrene initiated by the haloester compound chosen was to conduct polymerizations in bulk. The results of this series of polymerizations are summarized in Table 2. Increasing the monomer to initiator

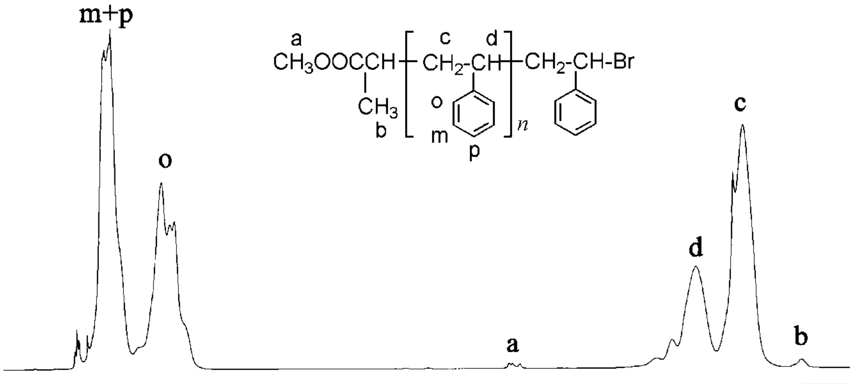

Figure 1. ^{1}H-NMR spectrum of α-methyl carboxylate-polystyrene with the assignment of peaks.

Table 1. Molecular weight characteristics of the synthesized polystyrenes, prepared from a 67% styrene solution in DPE.

$[St]_0/[MBP]^a$	$M_{n,theor}$	$M_{n,GPC}$	MWD	$M_{n,NMR}$	I_{eff}
42	4,400	4,300	1.24	4,400	1.02
80	8,300	13,700	1.29	12,700	0.60
87	9,100	14,500	1.30	14,550	0.63
146	15,200	17,600	1.40	—	0.86
218	22,700	—	—	—	—
273	28,400	—	—	—	—

[a] [MBP]/[CuBr]/[PMDETA] = 1/1/1. Polymerization at 110°C for 20 h.

molar ratio led to an analogous increasing trend in the molecular weight of the polymers obtained, reaching a value of 73,000. The polymers were further characterized by a narrow molecular weight distribution and a relatively steady initiator efficiency. As observed above, the initiator efficiency values were below 1, however they ranged between 0.67–0.77, which can be considered as a relatively steady level. This may lead to the conclusion that in the absence of solvent the polymerization system has a standard mechanism regarding the initiation and propagation processes. Independently of the amount of initiator added, a standard amount of it is activated towards free radical formation.

Figure 2 presents the experimentally obtained, as well as the theoretically expected, values of molecular weights against the molar ratios of monomer to initiator in the polymerization system. Both plots are linear, as a result of I_{eff} having a relatively narrow value range. What should also be stressed is the low MW distributions of all polystyrenes obtained, which can also be seen in their GPC chromatographs, depicted in Fig. 3.

Figure 4 shows the FT-IR spectra of the polystyrenes obtained. In support of the ^{1}H-NMR spectrum, FT-IR spectra testify to the presence of a methyl-ester group on the chain end of polystyrene. For comparison purposes the initiator's FT-IR spectrum is also

Table 2. Molecular weight characteristics of the synthesized polystyrenes, prepared in bulk.

mmol St/ mmol Init^a	$M_{n,theor}$	$M_{n,GPC}$	MWD	I_{eff}
121	12,600	18,500	1.28	0.68
132	13,700	21,400	1.27	0.64
200	20,800	29,800	1.31	0.70
209	21,700	28,000	1.24	0.77
300	31,200	46,800^b	1.29	0.67
382	39,700	59,000	1.37	0.67
476^c	49,500	73,000	1.34	0.68

[a] [MBP]/[CuBr]/[PMDETA] = 1/1/1. Polymerization at 110°C for 20 h.
[b] M_{NMR} = 41,700.
[c] 44 h Polymerization time.

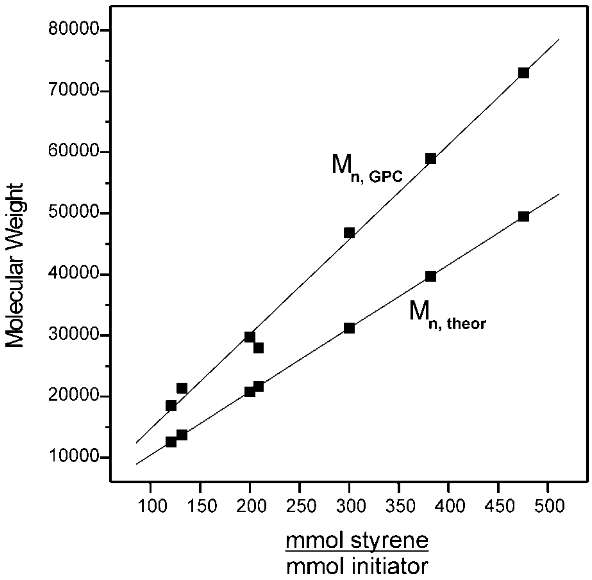

Figure 2. Molecular weights of synthesized polystyrenes and theoretically expected MW against monomer to initiator molar ratio.

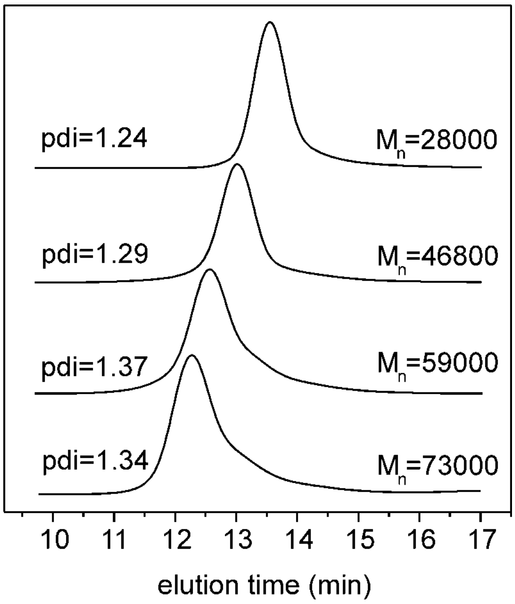

Figure 3. GPC traces of the synthesized polystyrenes.

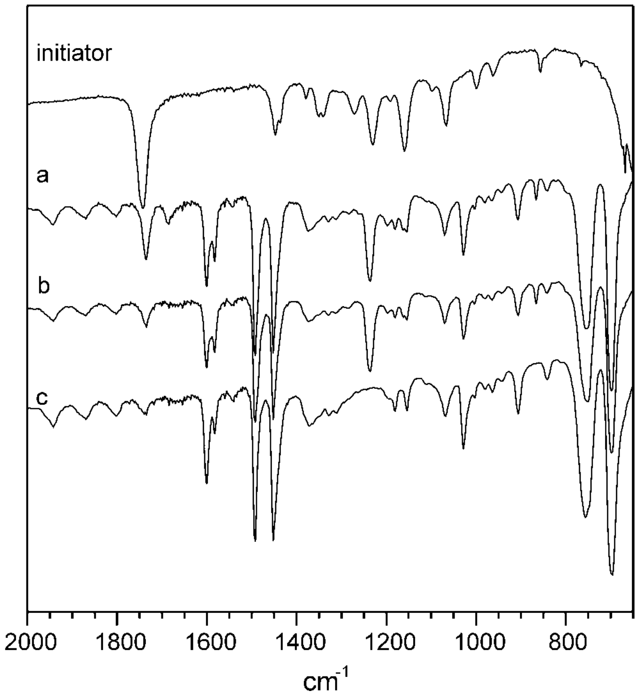

Figure 4. FT-IR spectra of the MBP initiator and the obtained α-methyl carboxylate-polystyrenes of different molecular weights $M_{n,GPC}$ (a) 4300, (b) 13,700, and (c) 46,800.

included in the figure. Thus it can be easily observed that several peaks (at 866, 1236, and 1734 cm^{-1}) attributed to the initiator compound are also present in the polystyrenes' spectra obtained. However, these are not to be seen in the spectrum of higher molecular weight polystyrenes, due to the decrease of the end groups concentration. Hydrolysis of the ester group resulted in the α-carboxy polystyrene as proven by ^{1}H-NMR.

The same technique for synthesizing α-carboxy-terminated polystyrenes was utilized for the synthesis of α-di-carboxy-PS, which has been the subject of previous work in our laboratory.[39]

Reactive Blending of Carboxylic Acid Terminated Polystyrenes with Polyethylene-Glycidylmethacrylate Copolymer

The α-carboxy-polystyrenes prepared were melt blended with an epoxy functionalized polyethylene (PE-g-GMA), in order to examine their grafting efficiency. For convenience, the polystyrenes used will be referred to according to their molecular weight, as listed in Table 3.

After a first series of blending experiments and according to the literature, the optimum blending conditions were defined to be 230°C and 12 min mixing time. PE-g-GMA/PS-COOH blends of different weight ratios (90/10, 80/20, 70/30, 60/40 wt/wt)

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Table 3. Molecular weights of α-carboxylic acid polystyrenes used for melt blending with PE-g-GMA.

PS-COOH	$M_{n,GPC}$	PS-COOH	$M_{n,GPC}$
PS13	13,700	PS48nf[a]	48,500
PS14	14,500	PS55	55,000
PS30	30,000	PS73	73,000
PS47	47,000	PS200[b]	2,00,000

[a] Nonfunctional polystyrene, prepared by ATRP by use of 1-phenylethylbromide as initiator.

[b] Commercial product of Aldrich.

were consequently prepared and the SEM micrographs of the blends' cryofractured surfaces, after extraction of the non-grafted PS (Fig. 5), show that the PE-g-GMA/PS-COOH 80/20 blend displays the best phase dispersion. In this case, polyethylene forms a continuous matrix and polystyrene is dispersed in it in the form of spherical particles, though having a wide particle size distribution.

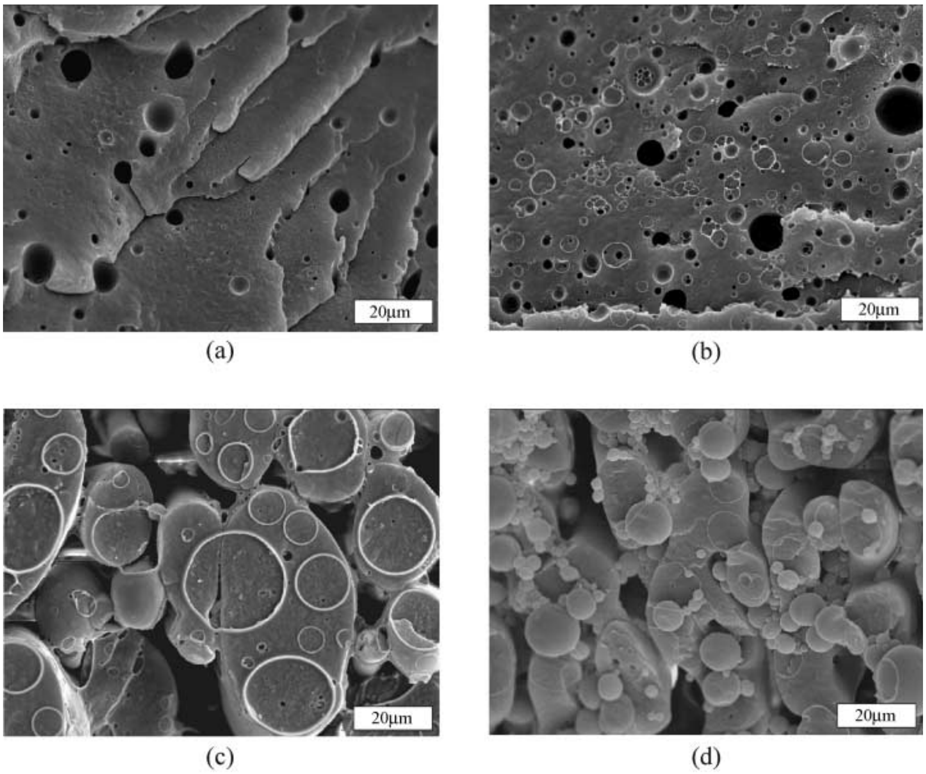

Figure 5. SEM micrographs of cryofractured and etched with selective solvents at room temperature PE-g-GMA/PS-COOH blends of various compositions: (a) 90/10; (b) 80/20; (c) 70/30; and (d) 60/40. (White stripes equal to 20 μm.)

Our study continued with examination of the effect of the α-functional polystyrenes' molecular weight on their grafting efficiency. Thus, a series of PE-g-GMA/PS-COOH 80/20 blends were prepared, with PS-COOHs of various molecular weights, ranging between 14,000 and 200,000. For comparison reasons, blends with nonfunctional polystyrene (prepared via ATRP and commercial) were also made. SEM micrographs of these blends' cryofractured surfaces after etching are depicted in Fig. 6. An increase of the polystyrene molecular weight from 14,000 to 47,000 does not seem to cause a differentiation in the way the PS phase is dispersed in the PE matrix. However, a further increase in the molecular weight up to 73,000 leads to a very fine dispersion, as polystyrene forms small spherical droplets with shape and size homogeneity. Comparison of the PS droplet size in Fig. 6(c)–(f), where the commercial non-functional polystyrene is used, shows that in the case of the PS73/PE-g-GMA blend grafting reaction between the epoxy-carboxylic acid coupling pair must have taken place. The in situ formed graft copolymer PS-g-PE may then act as a polymeric emulsifier, that stabilizes the fine morphology through decreasing the interfacial tension of the dispersed particles, prevents them from coalescing and stabilizes them at a micron scale. Indeed, particles observed with SEM had an approximate diameter of ca 0.5 μm. In the absence of this grafting procedure, the commercial polystyrene blend had a coarse phase morphology, with big PS domains.

Although SEM observations can give various information, they cannot ascertain grafting reactions. Extraction experiments can reveal more in that direction. Thus, blends of PE-g-GMA/PS-COOH and PE-g-GMA/PS-$(COOH)_2$ were treated with different selective solvents for PS to remove any polystyrene that is not chemically bound on the PE matrix. However, in this case extraction experiments were proven inadequate for quantitative analysis of the grafted chains, since it was impossible to extract the whole PS amount from the PE matrix, although the specimens tested were very thin films. This was attributed to the fact that during melt, mixing part of PS was enclosed in PE structures, which were impenetrable by the solvent. So, the extraction results were used only as a qualitative hint. Comparison between mono- and bifunctional polystyrenes showed that blends of PE-g-GMA with bifunctional polystyrene had a lower weight loss than the respective blends with monofunctional polystyrene.

Use of PS-COOH/PE-g-GMA and PS-$(COOH)_2$/PE-g-GMA Blends as Premade Compatibilizers in HDPE/PS Incompatible Systems

Since there was strong evidence that during blending of PE-g-GMA with PS-COOH a graft copolymer (PS-g-PE) is formed, we assumed that these binary blends could be added in the incompatible HDPE/PS system to examine any compatibilizing efficiency, i.e., their ability to act as premade compatibilizers as previously reported.[41–43] Thus, a series of ternary blends HDPE/PS/PS-g-PE were prepared, using various PS-g-PE copolymers obtained after reactive blending of PE-g-GMA with PS-COOH. The mechanical properties of the obtained ternary blends were studied by tensile testing. Table 4 lists the molecular characteristics of the premade copolymers and Table 5, the ultimate properties of the ternary systems tested.

The results in Table 5 on the blends' ultimate elongation ε_b, which presents a sensitive indicator of component adhesion, suggest that both monofunctional and bifunctional

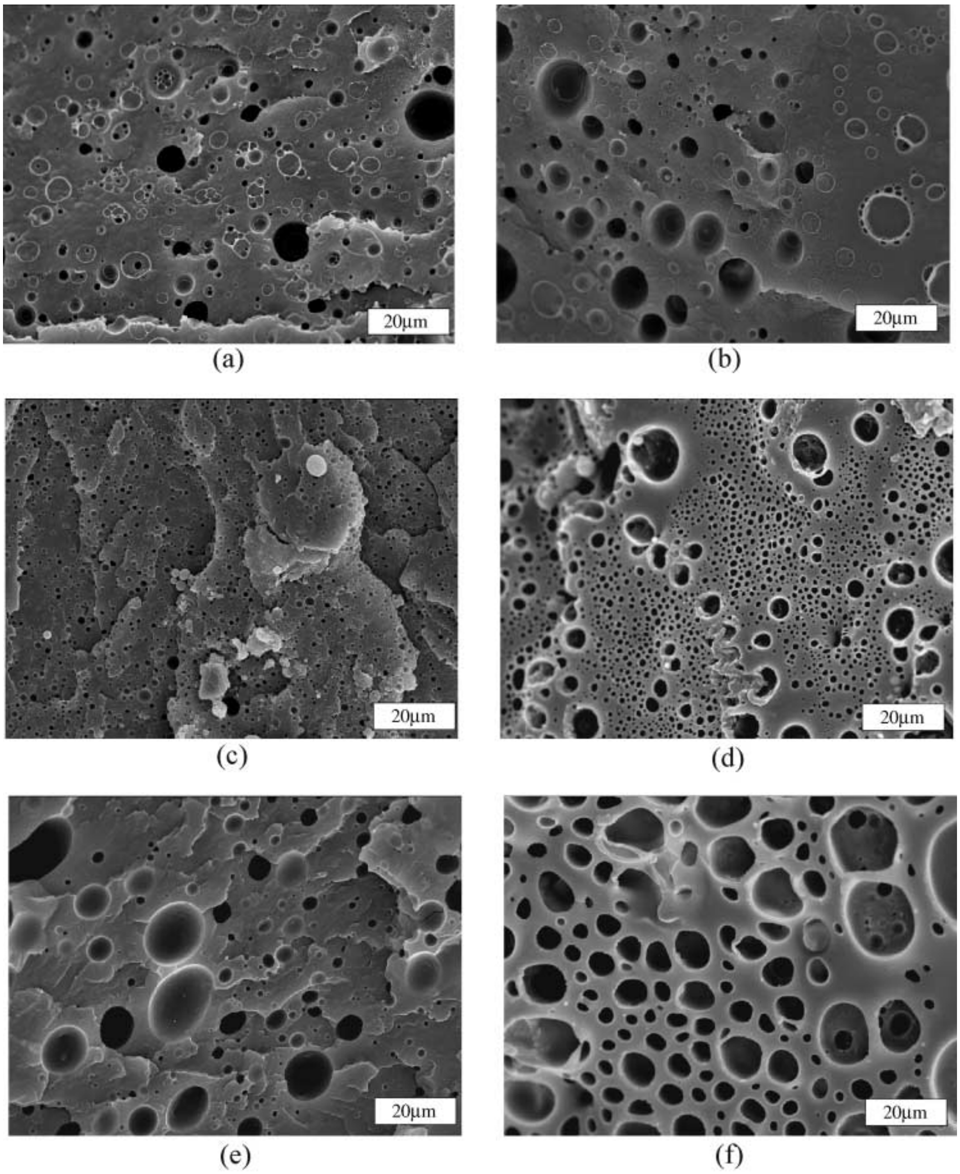

Figure 6. SEM micrographs of cryofractured and etched with dichlormethan at R.T. surfaces of PE-g-GMA/PS-COOH 80/20 blends, with PS-COOH of different molecular weights: (a) PS14; (b) PS47; (c) PS73; (d) PS200; (e) PS48nf; and (f) PS commercial. (White stripes equal to 20 μm.)

PS-containing copolymers may promote compatibilization of HDPE/PS blends. The intrinsically brittle behavior of the PS component and the stresses developed at the interface of the two hard thermoplastics can be responsible for the generally observed low ε_b values.[44] Reproducibility was not very good and this can be attributed to the low efficiency of the mixing conditions plus the fact that these products were obtained in a

Table 4. Copolymer molecular characteristics, MW of the α-functional polystyrene and PE/PS blend composition (wt/wt) of the pre-made PS-g-PE copolymer.

PS-g-PE copolymer	$MW_{PS\text{-}COOH}$	PE/PS composition of the PS-g-PE copolymer (wt/wt)
cop55	55,000	70/30
cop73	73,000	80/20
cop200	200,000	80/20
cop51	51,000[a]	66/33[a]

[a] Bifunctional PS-$(COOH)_2$.

two-step process. Best results indicating compatibilization were obtained for samples 3 and 7, though in both cases reproducibility was also poor. The increased ε_b values of samples 3 and 7 can be explained by referring to the SEM micrographs, where the insoluble HDPE/PS/PE-g-PS blend seems to form a load supporting network.

The compatibilization efficiency of the copolymer obtained from the monofunctional polystyrene was further examined using SEM and the results for the cryofractured and etched specimens are presented in Fig. 7.

The ternary blends of HDPE/PS/copolymer (80/10/10) using the copolymer 55 and copolymer 73 show a fine dispersion of the PS into the polyethylene matrix compared to the incompatible binary blend HDPE/PS 80/20. The formation of an interpenetrating network is also evidenced since the grafted PS cannot be removed by the etching process. The presence of the grafted PS in the boundaries between the etched and not etched phases supports the view that a significant amount of the copolymer is located at the interface.

Table 5. Ultimate properties of ternary HDPE/PS/PS-g-PE blends obtained with addition of various pre-made copolymers (cop).[a]

Sample	Composition	Weight ratio	σ_y (MPa)	σ_b (MPa)	ε_b (%)
1	HDPE		21 ± 0	19 ± 0	>1,100
2	HDPE/PS	85/15	—	21 ± 0	10 ± 3
3	HDPE/PS/cop55	80/10/10	—	19 ± 2	37 ± 7
4	HDPE/PS/cop73	80/10/10	—	18 ± 2	22 ± 13
5	HDPE/PS/cop200	80/10/10	—	17 ± 1	14 ± 4
6	HDPE/PS/cop51	80/15/5	—	21 ± 1	10 ± 3
7	HDPE/PS/cop51	80/10/10	20 ± 0	14 ± 2	112 ± 49
8	HDPE/PS/cop51	80/10/10[b]	19 ± 1	13 ± 3	86 ± 54
9	HDPE/PS	75/25[c]	—	18 ± 5	4 ± 2
10	HDPE/PS/cop51	70/20/10	—	23 ± 2	9 ± 3

[a] See Table 4.
[b] Blending at 250°C.
[c] 10 min mixing.

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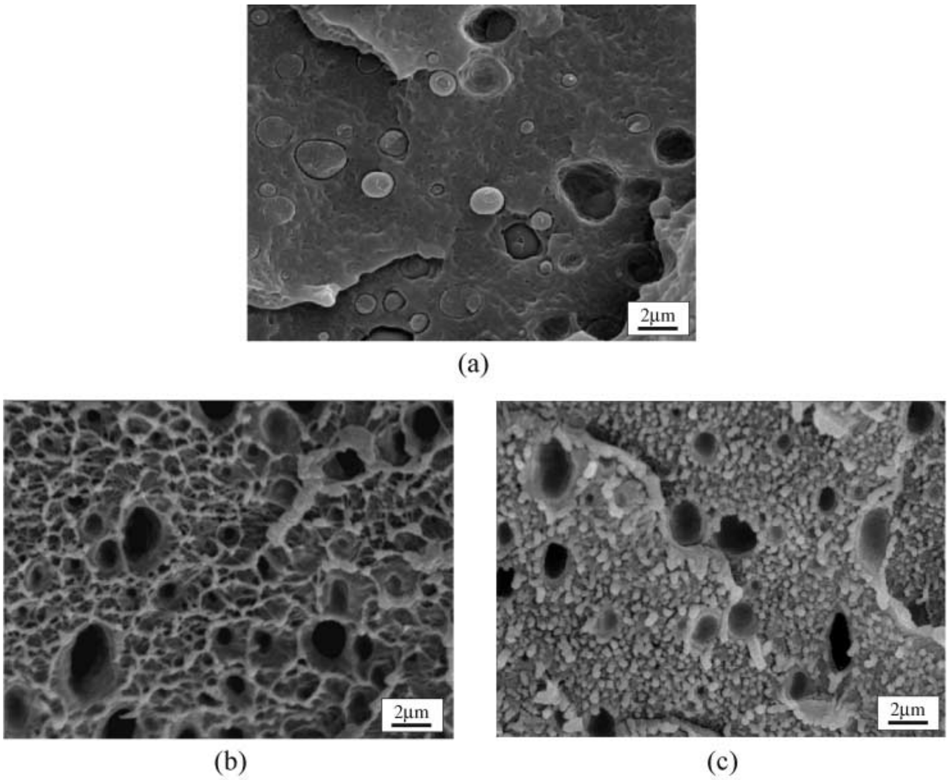


(a)

(b)

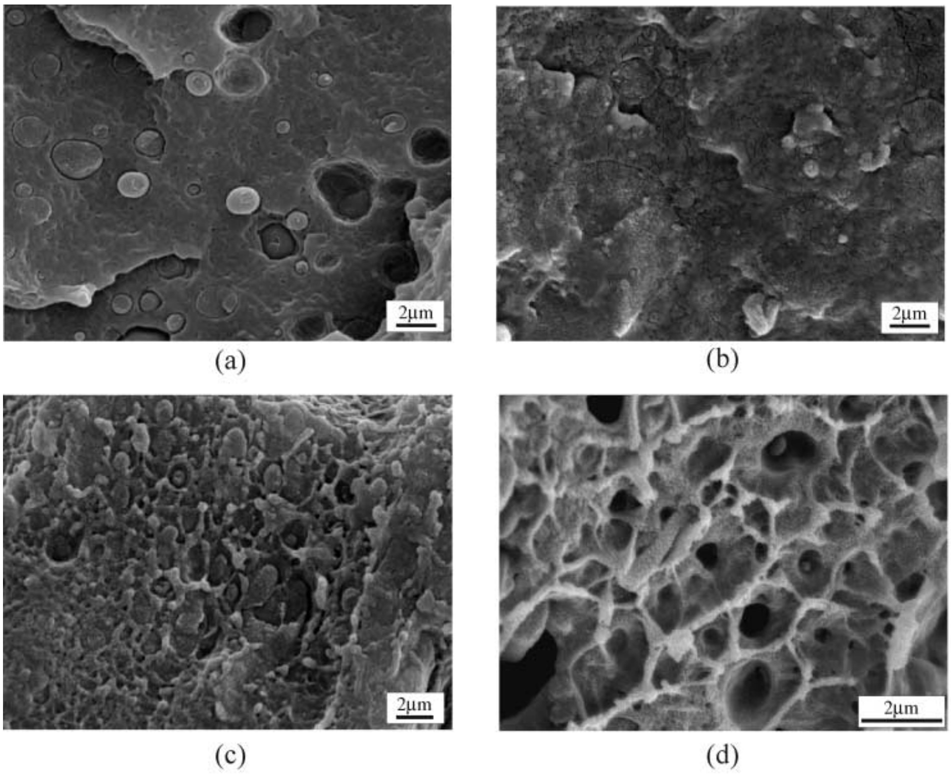
(c)

Figure 7. SEM micrographs of cryofractured and etched surfaces of (a) binary blend HDPE/PS 80/20 and of ternary blends; (b) HDPE/PS/cop55 80/10/10; and (c) HDPE/PS/cop73 80/10/10. (Bars are equal to 2 μm.)

SEM examination of the ternary blends HDPE/PS/copolymer (80/10/10 and 80/15/5) with the bifunctional copolymer (copolymer 51), is depicted in Fig. 8. It is evident that with 5% copolymer there are only minor changes in the morphology compared to the immiscible HDPE/PS blend, while with 10% copolymer the morphology changes drastically and fine dispersion in a submicron scale can be observed. The presence of the interpenetrating network with the copolymer located at the interface was observed using higher magnification, as shown in Fig. 8(d).

CONCLUSION

New end-functionalized polystyrenes, bearing one carboxy group per chain end using commercially available haloesters as initiators for ATRP of styrene were synthesized. The reaction conditions were studied in order to ensure high initiating efficiency and overall control of the polymerization. The efficiency of the functionalization was proved by size exclusion chromatography and ^{1}H-NMR.



(a) (b) (c) (d)

Figure 8. SEM micrographs of cryofractured and etched surfaces of blends: (a) HDPE/PS (×5000); (b) HDPE/PS/cop51 80/15/5 (×5000); (c) HDPE/PS/cop51 80/10/10 (×5000); and (d) HDPE/PS/cop51 80/10/10 (×10,000). (Bars are equal to 2 μm.)

Reactive grafting of the end functionalized polystyrenes onto PE-g-GMA resulted in polyethylene-polystyrene copolymers which were successfully used for the compatibilization of the immiscible polyethylene-polystyrene blend.

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