Grafting of Poly[2-(*tert*-butylamino)ethyl methacrylate] onto Polypropylene by Reactive Blending and Antibacterial Activity of the Copolymer

Jean-Michel Thomassin, Sandrine Lenoir, Johan Riga, Robert Jérôme,* and Christophe Detrembleur

Center for Education and Research on Macromolecules (CERM), University of Liège, Sart-Tilman B6a, 4000 Liège, Belgium

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To combine low cost, good mechanical properties, and antibacterial activity in one material, a nonquaternized polymeric biocide, i.e., poly[2-(*tert*-butylamino)ethyl methacrylate] (PTBAEMA), was dispersed within a commodity plastic, i.e., polypropylene (PP). The high immiscibility of the two polymers was tackled by reactive compatibilization and thus by reaction of commercially available maleic anhydride grafted polypropylene with primary amine-end-capped PTBAEMA. This reactive polymethacrylate was synthesized by atom-transfer radical polymerization with an azide-containing initiator. The azide end group was converted into a primary amine by the Huisgen [3 + 2] cycloaddition of propargylamine. The accordingly formed PP-*g*-PTBAEMA copolymer was melt dispersed within neat PP and processed as fibers, whose antimicrobial properties were assessed by the viable cell counting method against *Escherichia coli*. The antibacterial activity was long-lasting as a result of the anchoring of the PTBAEMA chains onto PP, which prevented them from being released from the surface of the fibers.

Introduction

Microorganisms, such as bacteria and viruses, are present everywhere in the environment. Their infection remains one of the most serious complications associated with the use of indwelling medical devices. Any compound that inhibits the growth of microorganisms is referred to as a biocide. For the efficacy of low molecular weight biocides to be acceptable, they have to be combined with polymers. In a first strategy, they are either physically entrapped within a polymer or attached to it through a hydrolytically unstable bond. 2,4,4′-Trichloro-2-hydroxydiphenyl ether (Triclosan from CIBA) is a biocide commonly involved in this strategy.[1−4] The key issue is the control of the release of the biocide. Indeed, a too fast release results in an initially high concentration of the active compound in the environment, with high risks of toxicity and short-term biocidal activity. At the extreme opposite, the release is so slow that the antibacterial activity is negligible. In an alternative strategy, the active molecules are permanently attached to polymer chains, and the antibacterial action results from the contact of the microorganisms with the biocide, no release occurring. Typical examples are polymers substituted by quaternary ammonium,[5−11] phosphonium,[12−14] and pyridinium[15,16] cations. The reason for the antibacterial activity has to be found in the interaction of the cationic sites of the polymer with the negatively charged membrane of bacteria, which is ultimately disrupted. Poly[2-(*tert*-butylamino)ethyl methacrylate] (PTBAEMA) is a neutral polymer, which is inherently biocidal with potential application in antifouling paints and coatings.[17−23] The major role of PTBAEMA is thought to displace Ca^{2+} and/or Mg^{2+} ions from the outer membrane of the bacteria, which is accordingly disorganized and finally disrupted.[23] Apparently, this pendent bulky secondary amine does not need quaternization for being antibacterial.

Because of cost and poor mechanical properties, the aforementioned polymers are of a limited interest. Therefore, this study aims at dispersing the nonquaternized polymeric biocide, i.e., poly[2-(*tert*-butylamino)ethyl methacrylate], within a commodity plastic, i.e., polypropylene (PP), as a way to combine low cost, good mechanical properties, and antibacterial activity. The major concern is however to fight the deleterious effects of immiscibility, i.e., high interfacial tension and poor interfacial adhesion, which are expected to be strong when a polar polymer (PTBAEMA) is blended with a nonpolar one (PP). The possible consequences are thus that dispersion of PTBAEMA deteriorates the mechanical properties of PP and that the polymeric biocide is released, even though slowly, in the bacteria-containing liquid phases with a regular loss of antibacterial activity. The best way to overcome these drawbacks consists in grafting PTBAEMA onto PP by reactive blending,[24] followed by dispersion of the graft copolymer within PP, which might be carried out in the equipment used to process the final material as fibers, and thus with a high surface/volume ratio well suited to the envisioned application. Accordingly, polypropylene was grafted by poly[2-(*tert*-butylamino)ethyl methacrylate] (PP-*g*-PTBAEMA) by reactive blending of commercially available polypropylene-*g*-maleic anhydride (PP-*g*-MA), with a primary amine-end-capped poly[2-(*tert*-butylamino)ethyl methacrylate]. This end-functional polymer was prepared by atom-transfer radical polymerization (ATRP), because this technique is known to be effective toward methacrylates, including 2-(*tert*-butylamino)ethyl methacrylate,[23] and well-suited to the end functionalization of the polymer. This graft copolymer was dispersed within polypropylene, and the antibacterial activity of fibers of this binary blend was assessed by the viable cell counting method against *Escherichia coli*.[25]

Experimental Part

Materials. CuBr (Aldrich, 98%) was dispersed within glacial acetic acid under stirring for a few hours, filtered, washed with ethanol, dried under reduced pressure at 80 °C, and stored under nitrogen. 2-Bromoisobutyryl bromide (Aldrich, 98%), 1,4,7,10,10-hexamethyl-trieth-

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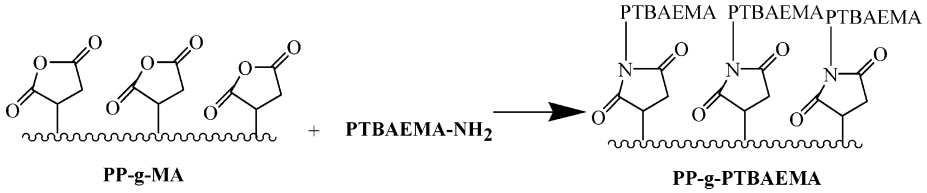
Scheme 1. Coupling Reaction of PP-*g*-MA and PTBAEMA−NH_2



ylenetetramine (HMTETA) (Aldrich, 97%), CuI (Aldrich, 98%), diethyl ether (Aldrich), anhydride sodium sulfate (Aldrich), triethylamine (Janssens, 99%), 3-chloropropanol (Aldrich, 98%), propargylamine (Aldrich, 98%), tributyltin hydride (Aldrich, 97%), sodium azide (Sigma, >97%), tetrabutylammonium hydroxide (Aldrich, 40 wt % in water), polypropylene-*g*-maleic anhydride (Priex 20097, 0.5 wt % maleic anhydride) from Solvay, and polypropylene (BP 110-GA12) from BP were used as received. 2-(*tert*-Butylamino)ethyl methacrylate (TBAEMA) (Aldrich, 97%) was dried over CaH_2, distilled under reduced pressure, and stored under N_2 at −20 °C. Methylene chloride (CH_2Cl_2) was refluxed over CaH_2 and degassed by nitrogen bubbling for 20 min. Toluene was refluxed over the Na/benzophenone complex, distilled, and degassed by nitrogen bubbling for 20 min. Dimethylformamide (DMF) (Acros) was dried over phosphorus pentoxide (Aldrich) for a week, distilled, and degassed by nitrogen bubbling for 20 min.

Synthesis of 3-Azidopropanol.[26] 3-Chloropropanol (19 g, 0.2 mol) was added to a mixture of water (19 mL), sodium azide (26.4 g, 0.4 mol), and tetrabutylammonium hydroxide (1,5 mL). The mixture was stirred at 80 °C for 72 h. The product was extracted with ether (3 × 50 mL), the solution was dried over sodium sulfate, before the solvent was removed, and 3-azidopropanol was distilled in vacuo with all the precautions against explosion risks. The yield was 80%. ^{1}H NMR (250 MHz, $CDCl_3$): δ_a = 3.80 ppm (1H, $CH_2O\mathit{H}$); δ_b = 3.51 ppm (t, J = 6.3 Hz, 2H, $\mathit{CH_2}$OH); δ_c = 3.23 ppm (t, J = 6.3 Hz, 2H, $\mathit{CH_2}N_3$); δ_d = 1.63 ppm (quintuplet, J = 6.3 Hz, 2H, $CH_2\mathit{CH_2}CH_2$). No unreacted 3-chloropropanol was detected by ^{1}H NMR.

Synthesis of 3-Azidopropyl bromoisobutyrate (BIPAP). A solution of bromoisobutyryl bromide (20.93 g, 0.09 mol), triethylamine (12.5 mL, 0.09 mol), and methylene chloride (45 mL) was cooled in an ice−water bath. 3-Azidopropanol (9.09 g, 0.09 mol) was added dropwise over a period of 20 min, and the mixture was stirred in the cooling bath for 1 h followed by 14 h at room temperature. Methylene chloride (50 mL) was added, and the mixture was extracted with an aqueous solution of hydrochloric acid (1/10, v/v, 2 × 50 mL), water (2 × 50 mL), 10 wt % aqueous NaOH (2 × 50 mL) and water again (2 × 50 mL). The organic solvent was removed in vacuo, and 3-azidopropyl bromosiobutyrate was collected (yield 60%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.85 ppm (8H, BrC($\mathit{CH_3}$)$_2$ and $CH_2\mathit{CH_2}CH_2$); δ = 4.15 ppm (t, J = 6.5 Hz, 2H, $\mathit{CH_2}$OC═O); δ = 3.33 ppm (t, J = 6.3 Hz 2H, $\mathit{CH_2}N_3$). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 28.8 ppm ($CH_2\mathit{CH_2}$-CH_2); δ = 31.5 ppm (2C, BrC($\mathit{CH_3}$)$_2$); δ = 48.8 ppm ($\mathit{CH_2}N_3$); δ = 56.7 ppm (BrC(CH_3)$_2$); δ = 63.6 ppm ($\mathit{CH_2}$OC═O); δ = 172.1 ppm ($CH_2O\mathit{C}$═O).

Synthesis of NH_2-Terminated PTBAEMA. 3-Azidopropyl bromoisobutyrate (0.61 g, 2.44 × 10^{-3} mol), CuBr (0.35 g, 2.4 × 10^{-3} mol), HMTETA (0.57 g, 2.4 × 10^{-3} mol), toluene (8 mL), and a magnetic stirrer were added to a glass flask that was closed by a three-way stopcock. This solution was degassed by bubbling of nitrogen for 20 min. The monomer was added with a syringe, and the reactor was heated in an oil bath thermostated at 70 °C. Progress of polymerization was followed by picking up samples that were analyzed in the Sartorius MA50 analyzer (infrared heater, "standard desiccation" at 150 °C) for the gravimetric determination of the monomer conversion and by size exclusion chromatography (SEC) after the catalyst was extracted by elution of the polymer solution in THF through an Al_2O_3-filled column. When a conversion of 80% was reached, 3 equiv of tributyltin hydride was added to the solution, and the reaction mixture was maintained at 70 °C for 12 h. It was then diluted with THF and eluted through Al_2O_3. After solvent elimination, the polymer was dried in vacuo at 40 °C overnight.

PTBAEMA−N_3 (3.5 g, M_n = 15000 g/mol, 2.33 × 10^{-4} mol), CuI (0.133 g, 7 × 10^{-4} mol), and propargylamine (0.128 g, 2.33 × 10^{-3} mol) were dissolved in THF (15 mL), and the solution was heated to 40 °C for 16 h. The solution was eluted through Al_2O_3, and the functional polymer was collected after solvent elimination.

Extrusion. Melt-blending was carried out in a 5 cm^3 DSM microextruder in a two-step method. The PP-*g*-PTBAEMA copolymer was first prepared by melt-blending PP-*g*-MA and PTBAEMA−NH_2 at 160 °C for 5 min. The same blend was prepared with unreactive PTBAEMA for the sake of comparison. In a second step, the blends were dispersed within PP at 180 °C for 5 min and extruded as fibers with a diameter in the 120−200 μm range.

Antimicrobial Assessment (Shake Flask Method). A freeze-dried ampule of *E. coli* (DH5α) was opened, and the culture was picked up with a micropipet and placed in 2 mL of nutrient broth (composition for 1 L of nutrient broth (Luria−Bertani, LB): 10 g of bactotryptone, 5 g of an extract of yeast, sodium chloride), followed by incubation (incubator shaker model G25, New Brunswick Scientific Co., Inc., Edison, NJ) at 37 °C overnight. Then 200 μL of the culture was placed in 100 mL of nutrient broth, and the bacterial culture was incubated at 37 °C for 4 h. This culture of *E. coli* that contained ca. 10^8 cells/mL (absorbance at 600 nm, 0.6) was used for the antibacterial test. A 0.5 g sample of the prepared fibers was dispersed in 9 mL of a sterile saline water mixture (prepared by dissolving 8.5 g of sodium chloride in 1 L of distilled deionized water in a "Schott" bottle followed by sterilization at 121 °C for 20 min) and inoculated with 1 mL of the bacterial culture that contained about 10^8 cells/mL. At regular time intervals, 100 μL samples were picked out and diluted (decimal serial dilutions until 10^5) by mixing 100 μL with 900 μL of sterile saline water. The surviving bacteria were counted by the spread plate method (100 μL samples of the decimal dilutions were spread on a Petri dish that contained LB agar). The Petri dishes were incubated at 37 °C overnight. After incubation, the colonies were counted.

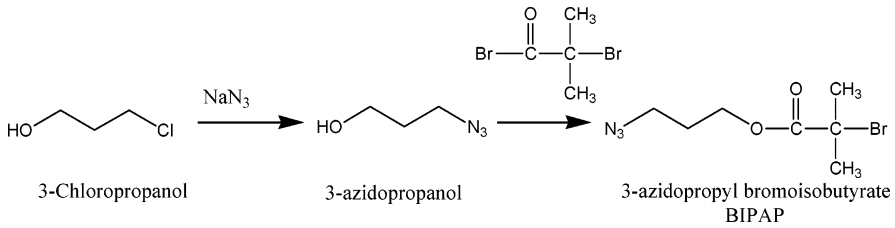
Characterization. SEC was performed in DMF at 40 °C, with a Waters 600 liquid chromatograph equipped with a Waters 410 refractive index detector and Styragel HR columns effective in the 100−5000 (HR 1), 500−20000 (HR 2), and 5000−600000 (HR 4) molecular weight range. The Styragel columns were calibrated with PMMA standards. ^{1}H NMR spectra were recorded with a Bruker AN 400 (400 MHZ) in $CDCl_3$ at 25 °C using Me_4Si as a reference. The morphology of the blends was observed with a Philips CM100 transmission electron microscope. A Reichter-Jung ultracryomicrotome equipped with a diamond knife was used to prepare ultrathin samples at −78 °C.

Results and Discussion

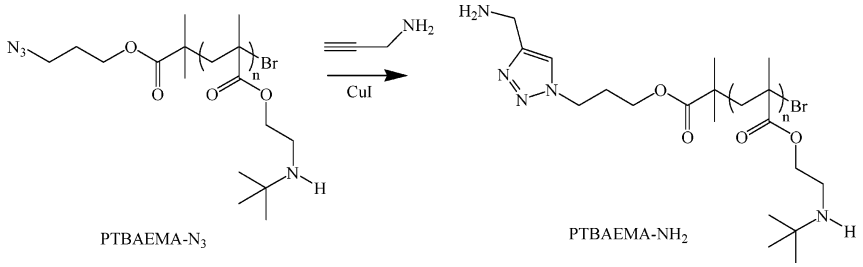
The commercial availability of PP-*g*-MA makes the access to graft copolymers straightforward and very convenient by reactive blending. For grafting PTBAEMA onto this reactive polyolefin, PTBAEMA should be ideally end-capped by a primary amine highly reactive toward anhydride, as shown in Scheme 1.

End functionalization of polymers by a primary amine was reported in the scientific literature, by either living anionic[27,28]

Scheme 2. Synthesis of the BIPAP Initiator



Scheme 3. Huisgen [3 + 2] Cycloaddition of Propargylamine to PTBAEMA−N_3



or controlled radical[29,30] polymerization, followed by end group derivatization. For instance, bromide-end-capped polystyrene was prepared by ATRP, and the α-bromide end group was converted into a primary amine by reaction with sodium azide followed by reduction of the azide end group by $LiAlH_4$.[31] Although quite efficient, this multistep functionalization was not quantitative. Indeed, a small fraction of the PS chains (∼5 mol %) were not end-capped by a bromide as a result of unavoidable irreversible termination during ATRP and non-quantitative substitution of bromide by azide. As a whole, 90% of the chains were amino-terminated.

An alternative strategy was used in this work that consists in initiating the ATRP of TBAEMA by an azido-containing compound, e.g., BIPAP (Scheme 2). As a result, most of the chains were capped by an α-azido group (PTBAEMA−N_3) that was ultimately reacted with propargylamine according to the Huisgen [3 + 2] cycloaddition, known as a "click" reaction because of high selectivity and quantitativeness.[32]

The azido-containing ATRP initiator (BIPAP) was synthesized by a two-step method: (i) 3-azidopropanol was prepared by reaction of 3-chloropropanol with sodium azide in an aqueous solution of tetrabutylammonium hydroxide at 80 °C for 72 h (80% yield),[25] followed by (ii) reaction of azidopropanol with bromoisobutyryl bromide in the presence of triethylamine in dichloromethane at room temperature (60% yield). No residual bromoisobutyryl bromide or bromoisobutyric acid was observed by ^{1}H NMR, which means that ATRP will be initiated selectively by the azido-containing bromide. Polymerization of TBAEMA was initiated by BIPAP with CuBr as a catalyst ligated by HMTETA in toluene at 70 °C. The composition of the polymerization medium was as follows: [TBAEMA]/[BIPAP]/[CuBr]/[HMTETA] = 117/1/1/1. Figures 1 and 2 show that the polymerization of TBAEMA was under control under these conditions. Indeed, the concentration of the active species was constant all along the polymerization, as supported by the linearity of $\ln([M]_0/[M])$ vs time (Figure 1). Moreover, the molecular weight increased linearly with the monomer conversion (Figure 2), and the polydispersity remained narrow (M_w/M_n = 1.1−1.2, Figure 2). The α-amino-functional PTBAEMA (PTBAEMA−NH_2) was prepared by reaction of PTBAEMA−N_3 with an excess (10 equiv) of propargylamine in the presence of CuI (3 equiv) in THF at 40 °C (Scheme 3). This reaction was complete, at least within the limits of resolution of infrared (IR) spectroscopy. Indeed, the characteristic absorption of the azido group of PTBAEMA−N_3 disappeared at 2100 cm^{-1} (Figure 3). Nevertheless, SEC of PTBAEMA−N_3 before and after reaction with propargylamine showed a bimodal distribution for the reaction product (Figure 4). The shoulder on the high molar mass side results from a coupling reaction, as

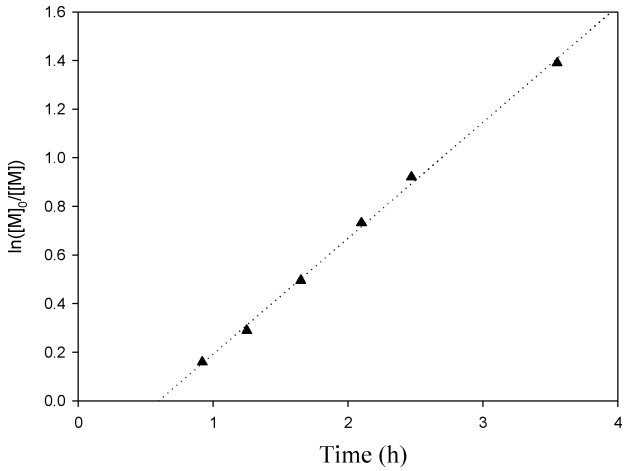


Figure 1. Time dependence of $\ln([M]_0/[M])$ for the ATRP of TBAEMA initiated by BIPAP and catalyzed by CuBr/HMTETA at 70 °C in toluene: $[TBAEMA]_0$ = 4 M; $[BIPAP]_0 = [HMTETA]_0 = [CuBr]_0$ = 50 mM.

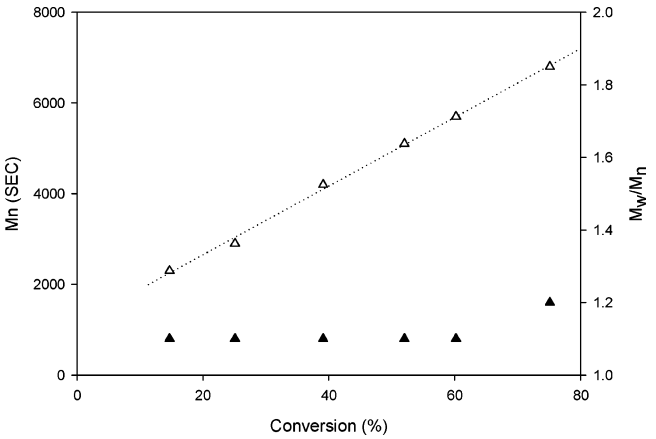


Figure 2. Conversion dependence of M_n and M_w/M_n for the ATRP of TBAEMA initiated by BIPAP and catalyzed by CuBr/HMTETA at 70 °C in toluene: △, M_n, SEC; ▲, M_w/M_n. $[TBAEMA]_0$ = 4 M; $[BIPAP]_0 = [HMTETA]_0 = [CuBr]_0$ = 50 mM.

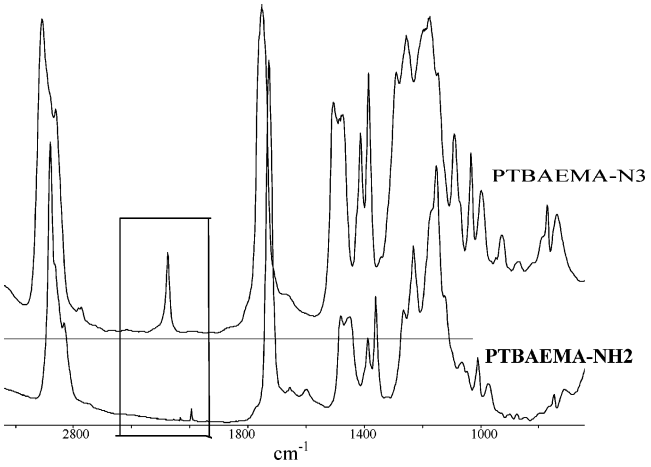


Figure 3. FTIR spectra of PTBAEMA−N_3 and PTBAEMA−NH_2.

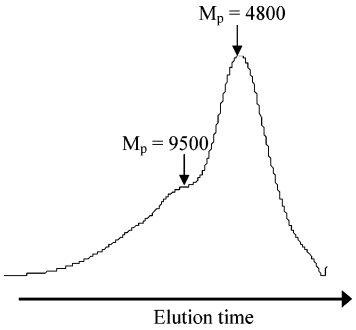


Figure 4. SEC chromatogram after the click reaction (PTBAEMA−NH_2).

supported by the deconvolution of the elution chromatogram that showed that the molar mass of the longer chain population was twice that of the main peak. A parasitic coupling reaction is not surprising because the PTBAEMA chains are end-capped not only by a primary amine but also by a bromide, which can lead to a nucleophilic substitution as illustrated in Scheme 4. To prevent this side reaction from occurring, the ω-bromide end group of the chains was reacted with tributyltin hydride and converted into a hydrogen at the end of the ATRP of

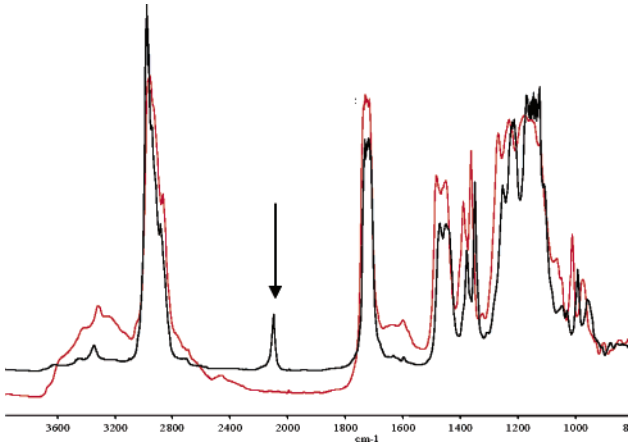
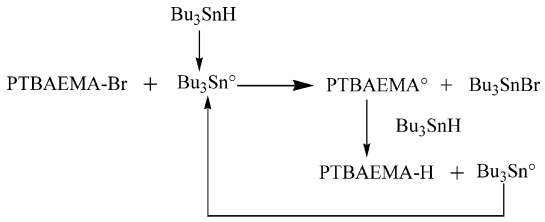


Figure 5. FTIR spectra (black) before (PTBAEMA−N_3) and (red) after (PTBAEMA−NH_2) the click reaction with propargylamine.

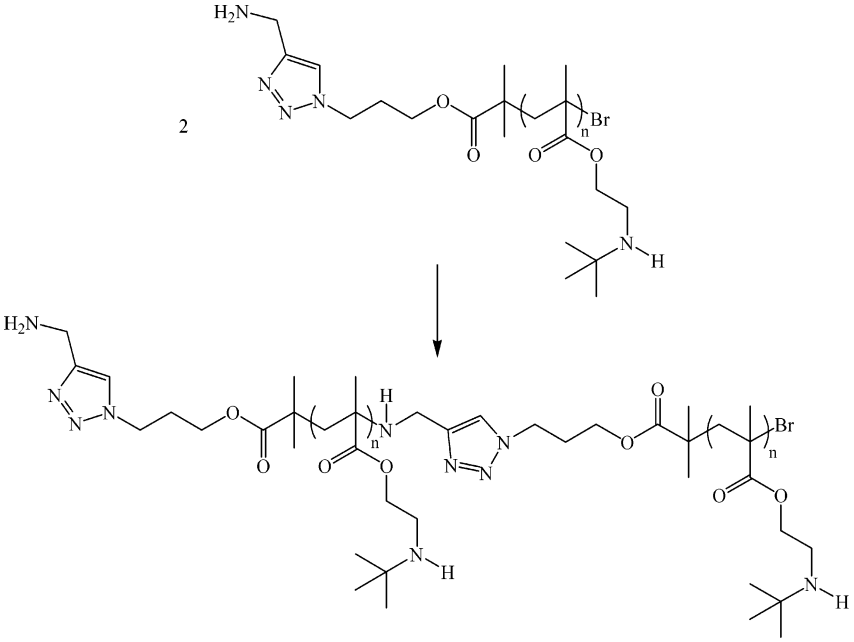
Scheme 5. Deactivation of the Bromide End Group by Tributyltin Hydride



TBAEMA[33] (Scheme 5). The Huisgen cycloaddition of propargylamine onto PTBAEMA−N_3 was successfully carried out in the presence of copper(I) iodide. IR spectroscopy confirmed the complete disappearance of the azido group at the end of the reaction (Figure 5), and no coupling reaction was observed by SEC (Figure 6). However, the amino end group could not be observed by ^{1}H NMR because of the overlapping of the resonances characteristic of the chain end protons and the protons of the main chain. MALDI-TOF analysis also failed in observing the amino end group.

A two-step process was used to disperse PTBAEMA−NH_2 within PP. PTBAEMA−NH_2 (M_n = 20000 g/mol) was first melt-blended with PP-*g*-MA (0.5 wt % MA, equivalent molec-

Scheme 4. Coupling Reaction Occurring during the Huisgen [3 + 2] Cycloaddition



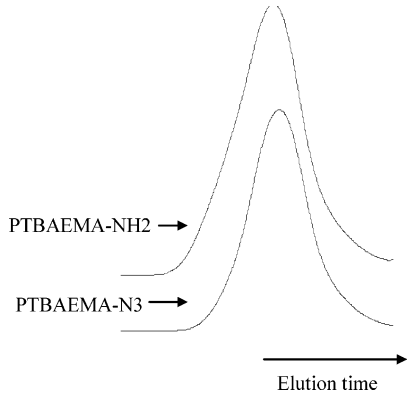


Figure 6. SEC chromatograms before (PTBAEMA−N_3) and after (PTBAEMA−NH_2) the click reaction of propargylamine.

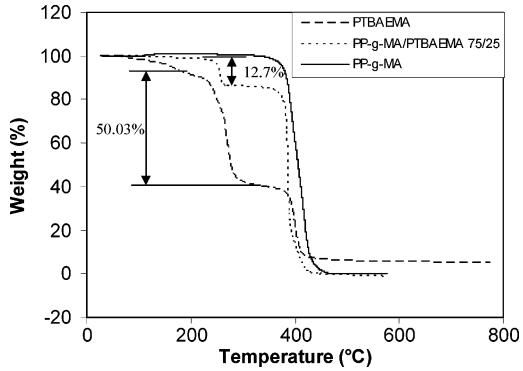


Figure 7. TGA curves for PP-*g*-MA, PTBAEMA, and the PP-*g*-MA/PTABAEMA (75/25) blend.

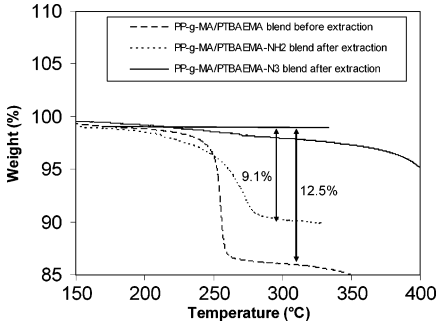


Figure 8. TGA curves for the PP-*g*-MA/PTABAEMA (75/25) blend before and after elimination of the ungrafted PTBAEMA.

ular weight 19800) in a 5 cm^3 microextruder at 160 °C for 5 min. The purpose being to synthesize the PP-*g*-PTBAEMA graft copolymer (Scheme 1), stoichiometric amounts of primary amine and maleic anhydride were used, which corresponded to a 50/50 (w/w) blend of PP-*g*-MA and PTBAEMA−NH_2. For the sake of comparison, the PTBAEMA−N_3 precursor was also dispersed within PP-*g*-MA under the same conditions. Later on, a PP-*g*-MA/PTBAEMA−NH_2 blend with a 75/25 (w/w) composition was prepared to minimize the amount of unreacted PTBAEMA−NH_2 in the final blend. This nongrafted PTBAEMA−NH_2 was removed by pouring a *p*-xylene solution of the blend in methanol. PP-*g*-MA and PP-*g*-PTBAEMA were insoluble and precipitated in methanol, whereas the ungrafted PTBAEMA remained in solution. This treatment was repeated three times, until the separation was complete. The content of PTBAEMA in the purified PP-*g*-PTBAEMA graft copolymer was determined by thermogravimetric analysis (TGA). Indeed, PP-*g*-MA degraded in a single step at approximately 400 °C, in contrast to a three-step degradation (150, 270 (total weight loss 50%), and 400 °C) for PTBAEMA (Figure 7). The first two degradation steps, until 300 °C, were thus observed independently of PP and used to determine the content of PTBAEMA in the graft copolymer. As expected, a 12.5 wt % weight loss was observed at 300 °C in the 75/25 PP-*g*-MA/PTBAEMA−NH_2 blend before purification (Figure 8). After elimination of the ungrafted PTBAEMA, the weight loss at 300 °C was 9.1 wt %, consistent with the grafting of ∼73 wt % PTBAEMA−NH_2 and thus very close to completion (Figure

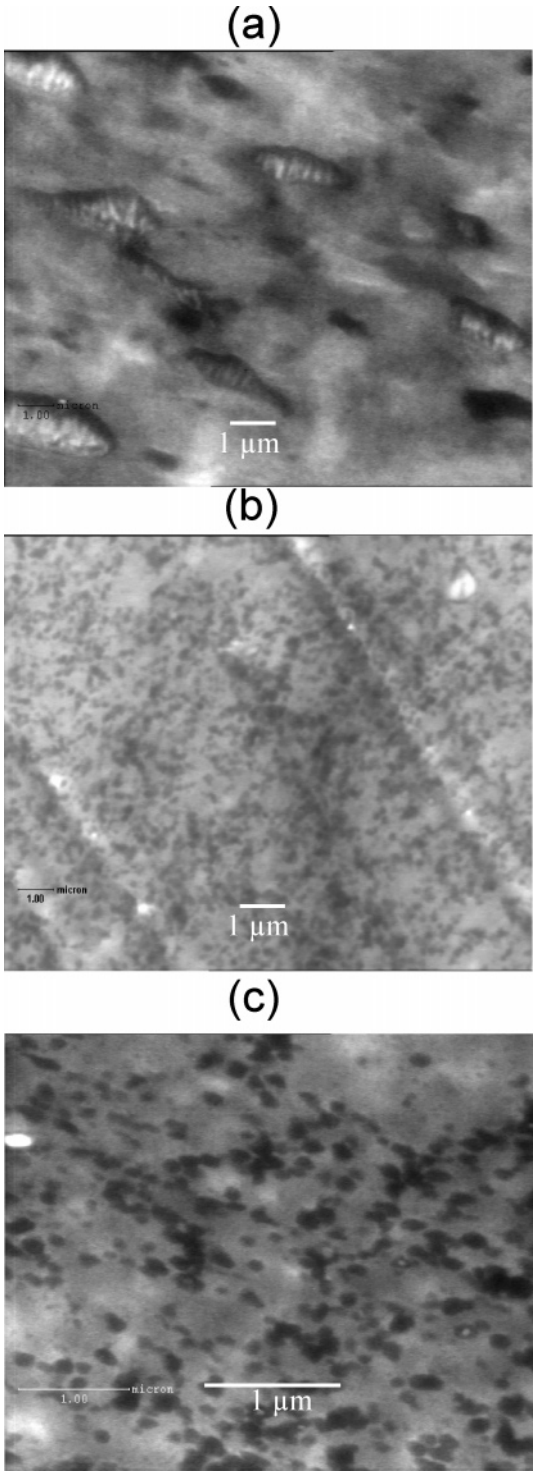


Figure 9. TEM micrographs of (a) the PP (50 wt %)/PP-*g*-MA (12.5 wt %)/PTBAEMA−N_3 (12.5 wt %) blend (magnification 1950×) and (b, c) the PP (50 wt %)/PP-*g*-MA (12.5 wt %)/PTBAEMA−NH_2 (12.5 wt %) blend (magnification (b) 1950× and (c) 5000×).

Table 1. Composition of the Blends Prepared in This Work

biocide	blend no.	[PP], %	[PP-*g*-MA], %	[PTBAEMA], %
PTBAEMA−N_3	1	50	37.5	12.5
	2	50	25	25
PTBAEMA−NH_2	3	50	37.5	12.5
	4	50	25	25

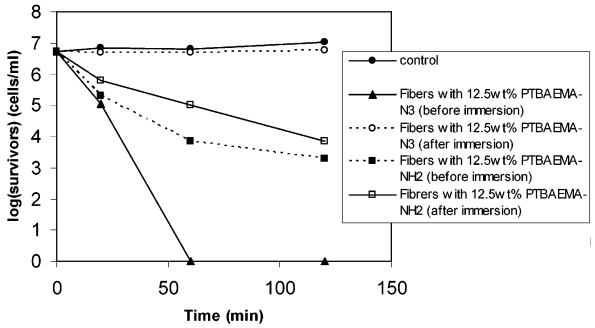


Figure 10. log(number of survivors) versus exposure time for fibers containing 12.5 wt % PTBAEMA−N_3 and PTBAEMA−NH_2 before and after immersion in THF for 1 week.

8). The grafting was slightly lower (66 wt %) in the case of the 50/50 PP-*g*-MA/PTBAEMA blend. When PTBAEMA−N_3 was used instead of PTBAEMA−NH_2, PTBAEMA−N_3 was quantitatively removed by precipitation in methanol, in line with the absence of grafting and efficacy of the purification method.

Finally, the crude graft copolymers (75/25 and 50/50) were dispersed within a PP matrix in the 5 cm^3 microextruder at 180 °C for 5 min and processed as fibers to maximize the surface available to bacteria. Dispersion of PTBAEMA within PP was observed by transmission electron microscopy (TEM). When the PP-*g*-MA/PTBAEMA−N_3 premixture was dispersed in PP, PTBAEMA domains larger than 1 μm were observed (Figure 9a), in agreement with the immiscibility and poor dispersion of PTBAEMA and PP. In contrast, when the dispersion of the PP-*g*-MA/PTBAEMA−NH_2 premixture (mainly PP-*g*-PTBAEMA) was concerned, PTBAEMA was homogeneously dispersed, and the average size of the PTBAEMA domains was less than 200 nm (Figure 9b,c), which was the signature of the effective compatibilization of the binary blend.

The dynamic shake flask method was used to assess the ability of the blends to kill bacteria. For this purpose, 0.5 g samples of the fibers with the compositions listed in Table 1 were shaken in 10 mL of a bacterial suspension (10^8 cells/mL) at 37 °C for 20, 60, and 120 min. The number of viable cells in the suspension was counted after incubation and dilution of the samples, followed by overnight incubation on agar plates. Figures 10 and 11 show plots of log(number of survivors) against the exposure time when the same amount of *E. coli* (10^8 cells/mL of bacteria) was exposed to the fibers. For the noncompatibilized blend containing 12.5 wt % PTBAEMA (PP/PP-*g*-MA/PTBAEMA−N_3), all the bacteria were killed within 60 min (Figure 10). In contrast, the bacterial activity of the compatibilized blend was lower as shown by the number of bacteria that decreased slowly, suggesting that a lower amount of PTBAEMA was available at the fiber surface. The ability of the fibers to preserve their antibacterial properties after contact with the solution of bacteria is a key issue. Indeed, although the solubility of PTBAEMA in water is very low, the antibacterial activity of the fibers might decrease as a result of the leaching of ungrafted PTBAEMA. To know whether this

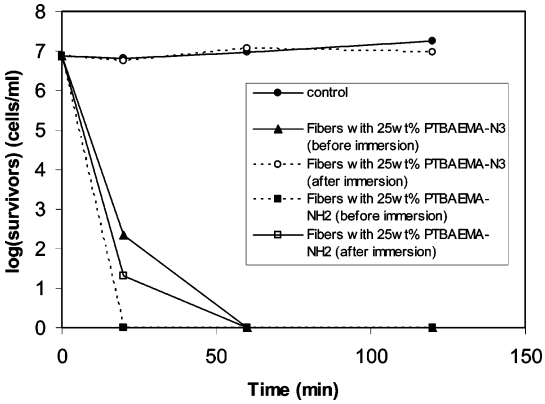


Figure 11. log(number of survivors) versus exposure time for fibers containing 25 wt % PTBAEMA−N_3 and PTBAEMA−NH_2 before and after immersion in THF for 1 week.

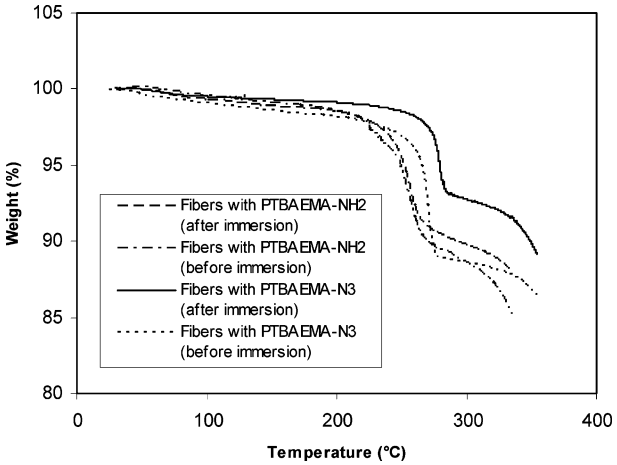


Figure 12. TGA curves of fibers containing 25 wt % PTBAEMA−N_3 and PTBAEMA−NH_2 before and after immersion in THF for 1 week.

leaching can occur and whether the antibacterial activity would decrease in such a case, this activity was measured for fibers consisting of compatibilized and noncompatibilized blends before and after immersion in THF (a good solvent for TBAEMA and a poor solvent for PP) for 1 week. Importantly, the compatibilized blend retained its activity after immersion in THF in contrast to the noncompatibilized one (Figure 10). These results were confirmed by the antibacterial tests applied to the blends containing 25 wt % PTBAEMA (Figure 11). Although the blends killed all the bacteria within 60 min independently of the compatibilization, only the antibacterial activity of the compatibilized blend (PP/PP-*g*-MA/PTBAEMA−NH_2) was maintained after the immersion in THF. The leaching of ungrafted PTBAEMA in THF was confirmed by the quantitative analysis of PTBAEMA in the blends by TGA (cf. supra) before and after immersion for 1 week (Figure 12). Approximately 35% of the initial amount of PTBAEMA was lost after immersion of the PP/PP-*g*-MA/PTBAEMA−N_3 blend in THF. The loss of the antibacterial activity after this treatment was evidence that the extracted PTBAEMA was localized at the surface of the fibers. Only about 10% of the PTBAEMA was extracted from the PP/PP-*g*-MA/PTBAEMA−NH_2 blend, while the antibacterial activity was basically maintained (Figure 11), so assessing that a sufficient amount of PTBAEMA grafted to PP was available at the surface of the fibers and provided them with a long-lasting antibacterial activity.

Conclusions

In this paper, a strategy for providing PP with a long-lasting antibacterial activity was proposed. A biocidal poly(methacrylate) end-capped by an α-primary amine, i.e., PTBAEMA−NH_2, was first grafted onto PP by reactive blending, thus by reaction with the maleic anhydride groups of PP-*g*-MA in the melt. PTBAEMA−NH_2 was prepared by ATRP initiated by an azide-containing activated bromide, followed by the Huisgen [3 + 2] cycloaddition of propargylamine to the azides. The PP-*g*-PTBAEMA copolymer was melt dispersed within neat PP and processed as fibers endowed with a long-lasting antibacterial activity. Indeed, the anchoring of the PTBAEMA biocide onto PP chains prevented it from being released from the surface of the fibers.

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