Polym. Bull. (2010) 65:215–226
DOI 10.1007/s00289-009-0196-y

ORIGINAL PAPER

Synthesis, characterization, and antibacterial activity of metal nanoparticles embedded into amphiphilic comb-type graft copolymers

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Received: 3 June 2009 / Revised: 13 October 2009 / Accepted: 15 October 2009 /
Published online: 27 October 2009

Abstract The synthesis, spectroscopic characterization, and antimicrobial efficiency of gold and silver nanoparticles embedded in novel amphiphilic comb-type graft copolymers having good film-forming properties have been described. Amphiphilic comb-type graft copolymers were synthesized by the reaction of chlorinated polypropylene (PP) ($M_w = 140{,}000$ Da) with polyethylene glycol (PEG) ($M_n = 2{,}000$ Da) at different molar ratios. Metal nanoparticles embedded graft copolymers were prepared by reducing solutions of the salts of silver or gold and the copolymer in tetrahydrofuran. The optical properties of the metal nanoparticle embedded copolymers were determined by using UV–visible spectroscopy. Surface plasmon resonance (SPR) of the gold and silver nanoparticle embedded copolymers in toluene was observed at a maximum wavelength (λ_{max}) of 428 and 551 nm in the UV–VIS absorption spectra, respectively. The average particle diameters of the gold and silver nanoparticles were found to be 50 nm from the high resolution scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). Amphiphilic polymer films containing silver and gold nanoparticles were found to be

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highly antimicrobial by virtue of their antiseptic properties to *Escherichia coli* and *Staphylococcus aureus.*

Keywords Gold nanoparticles · Silver nanoparticles · Comb-type amphiphilic polymer · Antimicrobial efficiency

Introduction

The interest in the synthesis and characterization of nanoparticles embedded amphiphilic block and graft copolymers has increased recently due to their possible applications in the fields of biology and material sciences. Nanoparticles show properties that are often different from those of their corresponding bulk materials. Size provides important control over many of the physical and chemical properties of nanoscale materials including luminescence, conductivity, and catalytic activity allowing application of these species in optical systems, catalysis, and biomedical technology [1]. With a practical application point of view, syntheses of polymer-stabilized nanoparticles and their patterning of the polymer-templated assembly is a very attractive research field compared with bare or small molecule-stabilized gold particles [2, 3]. Nanoparticles made from silver, gold, and copper have been the focus on research for many decades as a result of their intriguing optical properties and biological efficiency [4–10]. From a material point of view, it is advantageous to embed the metal nanoparticles in thin polymer films for optical and nonlinear applications [11]. When dispersed in liquid media, these nanoparticles usually display very intense colors due to surface plasmon resonance (SPR), a feature that can be attributed to the collective oscillation of conduction electrons as induced by an electromagnetic field [11]. The free-electrons in the metal (d electrons in silver and gold) are free to travel through the material. Light in resonance with the surface plasmon oscillation causes the free-electrons in the metal to oscillate. Metal nanoparticles and their brilliant colors due to SPR absorption constitute a large ongoing research field [12, 13]. The SPR frequency of nanosized metal particles is different from that of bulk material and has been shown to strongly depend on their size, shape, aggregation, and structure (solid vs. hollow) [14–17].

Metal nanoparticles have been typically produced in aqueous solutions in the presence of water-soluble polymers, where metal ions are reduced either by an added reductant or by the water-soluble polymers themselves. The polymers which have been used for the synthesis of gold nanoparticles include both neutral and charged polymers such as poly (*N*-vinyl pyrrolidone), poly (vinyl pyridine), polypyrrol, poly (ethylene glycol) (PEG), poly(vinyl alcohol), poly(vinyl methyl ether), and polyelectrolytes such as poly(acrylic acid), chitosan, poly(ethylene imine), cellulose, and poly (diallyl dimethylammonium) chloride [18–34]. Some of them such as poly (*N*-vinyl pyrrolidone), PEG, chitosan, and polyelectrolytes act not only as stabilizers, but also as reducing agents, that is, without addition of any other reductant [35]. In the case of PEG containing polymers, metal ions bind to the oxyethylene groups of PEG polymers when the coiled macromolecules form cavities similar to those of crown ethers [36]. Amphiphilic copolymers have a

unique molecular structure containing parts with both hydrophobic and hydrophilic character [37–40]. Comb-shaped graft polymers consist of a main polymer chain, the backbone, with side chains attached to it through covalent bonds.

Bactericidal polymers could be a promising coating material for general use [41]. Silver and silver-based compounds are highly antimicrobial by virtue of their antiseptic properties toward several kinds of bacterium including *Escherichia coli* and *Staphylococcus aureus*. Silver-based antimicrobial agents have received attention because of the low toxicity of the active silver ions to human cells, as well as it being a long-lasting biocide with high thermal stability and low volatility [42, 43]. PEG surfaces can also prevent bacterial adhesion [44]. This work refers to the synthesis, spectroscopic characterization, and antibacterial activity of metal nanoparticles embedded in amphiphilic comb-type graft copolymers. A series of the amphiphilic comb-type copolymers were synthesized by the reaction of chlorinated polypropylene (PP) (M_w = 140,000 Da) with PEG (M_n = 2,000 Da). Then, the organic–inorganic composites were prepared by reducing metal salts with $NaBH_4$ in the presence of the copolymer in tetrahydrofuran.

Experimental

Materials

Chlorinated polypropylene (PP-Cl, M_w 150,000 Da, three repeating units have 1 Cl in average), polyethylene glycol with M_n = 2,000 Da (PEG2000), NaH dispersed in oil (60 wt%), $AgNO_3$, and $HAuCl_4$ were supplied from Sigma–Aldrich and used as received. Tetrahydrofuran (THF) was supplied from Sigma–Aldrich and distilled from sodium flakes before use.

Synthesis of PP-g-PEG amphiphilic graft copolymers

The amphiphilic polymer was synthesized by modifying a previously reported procedure [37]. Typically, PP-Cl, 1.5 g (10 mmol Cl) was dissolved in 50 mL of freshly distilled THF. To this solution was added drop wise 20 mL of a THF solution containing PEG2000 (20 g, 10 mmol) and 2 mL of an aqueous NaOH solution (50 wt%), within 20 min (0.4 g of NaH was also used as a base instead of the aqueous NaOH solution). After stirring 3 days at room temperature, the reaction mixture was poured into 500 mL of water containing 1 mL of concentrated HCl. The polymer was filtered, washed with water and dried under vacuum overnight. For the purification, it was redissolved in THF and re-precipitated in 200 mL of distilled water and then dried under vacuum overnight at 50 °C.

Synthesis of gold (or silver) nanoparticles embedded PP-g-PEG amphiphilic graft copolymers

A series of gold (or silver) nanoparticles embedded PP-g-PEG amphiphilic graft copolymers were prepared by modifying a previously reported procedure developed

by Mirkin et al. [45]. A typical procedure is as follows. Aqueous solutions of metal salts ($AgNO_3$: 0.1 M, $HAuCl_4$: 0.1 M) and the reducing agent, $NaBH_4$ (0.1 M) were prepared separately. The PP-g-PEG2000 graft copolymer (0.2 g) was dissolved in 20 mL of THF. To this solution was added 0.01 mL of the $AgNO_3$ aqueous solution and vigorously stirred at room temperature for 10 min. Then the same volume of the reducing agent (0.01 mL of $NaBH_4$ aqueous solution) was added to this mixture, generating a pink yellow colloidal solution. (To prepare series of hybrid polymers containing different amount of metal nanoparticles, metal salt solutions ranging from 0.01 to 0.1 mL were used.) Over the next 30 min, the solution turned to a deep yellow color, due to the formation of silver nanoparticles. The solution was poured into a Petri dish ($\phi = 7$ cm) and the solvent was allowed to evaporate leaving a pink colored thin polymer film. The solvent cast film was washed with methanol and dried under vacuum. The colored film was redissolved in toluene (20 mL) to obtain a clear colored solution. A photograph of the colored solution was taken with a digital camera.

Determination of antibacterial efficiency

A previously described method was used for determination of the antibacterial efficiency with some modifications [46]. Clean glass slides (2.5 × 7.5 cm) were coated by immersion into nanoparticles embedded polymer solutions and left to dry in air. The clinical isolates of *Escherichia coli* (Gram-negative) and *Staphylococcus aureus* (Gram-positive) were used. The isolates were subcultured on Blood Agar (Merck) plates. After incubation overnight at 37 °C, bacterial suspensions at McFarland 0.5 (10^8 cfu/mL) concentration were prepared in phosphate buffered saline (PBS) and the cell suspensions were sprayed onto the slides. After drying for 2 min in air, the slides was placed on Mueller–Hinton agar plates which have been cut to the size of slides and placed into sterile Petri dishes. The Petri dishes were sealed and incubated overnight at 37 °C. After the incubation period, the bacterial colonies grown between the slides and agar medium were counted under fluorescent light. Control slides were also prepared with uncoated slides. The tests were repeated three times and the average of the colony numbers was calculated by taking the mean of the colony numbers for the repeated tests.

Polymer characterization

^{1}H-NMR spectra were recorded in $CDCl_3$ with a tetramethylsilane internal standard using a Varian XL 200 device. FT-IR spectra were obtained using a Perkin Elmer Pyris 1 Spectrometer. UV–visible absorption spectra of the polymer solutions in toluene were recorded at room temperature using a Shimadzu 1700 Spectrometer with UV-quartz cuvettes (1 cm optical path) as the containers. A Perkin Elmer Atomic Absorption Spectrometer-Analyst 800 was used to determine the wt% of silver and gold in the graft copolymer samples. Scanning electron micrographs were taken on a JEOL JXA-6335 FS scanning electron microscope (SEM) with semi quantitative-Inca-energy dispersive X-ray spectroscopy (EDS) for elemental analysis. The specimens were frozen under liquid nitrogen then fractured, mounted,

and coated with palladium, gold, and carbon. The SEM was operated at 15 kV, and the electron images were recorded directly from the cathode ray tube on a Polaroid film.

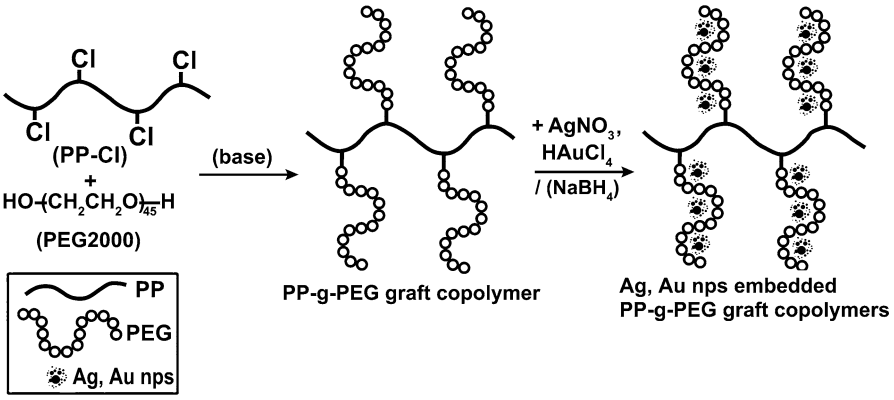
Results and discussion

Synthesis of amphiphilic polymers with good film properties

A series of the PP-g-PEG comb-type amphiphilic copolymers having good film properties (coded as Y-1, Y-2, and Y-3) were prepared by the reaction between chlorinated-PP and PEG2000 in the presence of a base catalyst. The reaction steps are shown in Scheme 1. The PEG content in the graft copolymer was proportional to the PEG feeding ratio. Amphiphilic graft copolymers were characterized by using ^{1}H-NMR and FTIR spectroscopy. Figure 1 shows a typical ^{1}H-NMR spectrum of a PP-g-PEG sample (Y-2). The PEG content (mol%) of the copolymers were calculated from the integral ratio of the PEG signal at 3.5 ppm to total integral value in the ^{1}H-NMR spectra and found to be 10 (Y-1), 14 (Y-2), and 17 (Y-3) (Table 1). FTIR spectra of the graft copolymers all exhibited the characteristic strong band of PEG at 1,102 cm^{-1} (spectrum not shown). Inorganic–organic hybrid polymers were obtained by reducing metal salts (Ag^{+} and Au^{3+}) to metal in the presence of the amphiphilic comb-type copolymer in solution. The concentration of the metal nanoparticles in the graft copolymers were analyzed by using an atomic absorption spectrometer and found to be from 0.046 to 1.64 wt%, which is proportional to the initial concentration of the metal salt. The concentration of the metal nanoparticles in the graft copolymers are also listed in Table 1.

Solution properties and UV–visible analysis

Polymer films containing silver and gold nanoparticles were redissolved in toluene. Figure 2 shows photographs of these colored solutions. Yellow, pink, red, and deep



Scheme 1 Synthesis of PP-g-PEG amphiphilic comb-type graft copolymers

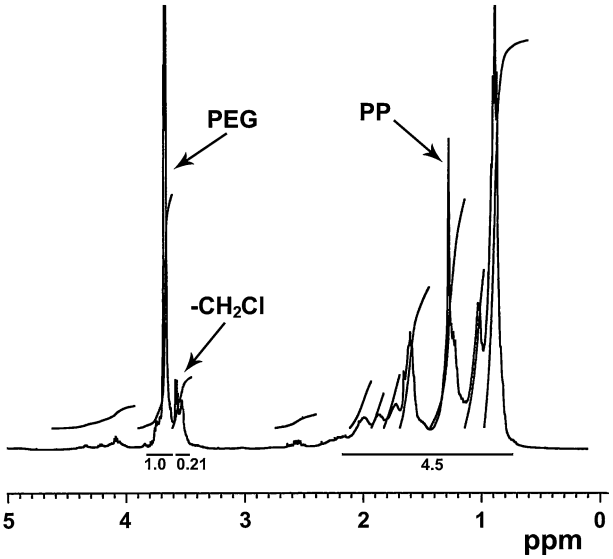


Fig. 1 ^{1}H-NMR spectrum of the PP-g-PEG (entry #Y-2)

Table 1 Preparation of the gold and silver nanoparticle embedded PP-g-PEG graft copolymers

Entry #	PEG content in PP-g-PEG (mol %)	Ag NPs in PP-g-PEG (wt%)	Au NPs in PP-g-PEG (wt%)
Ag11	10	0.046	–
Ag21	14	0.076	–
Ag31	17	0.104	–
Ag33	17	0.226	–
Ag34	17	0.264	–
Ag35	17	0.170	–
Au12	10	–	1.64
Au22	14	–	0.48
Au32	17	–	0.95
Au36	17	–	0.67

red colored solutions with characteristic maximum absorption peaks (λ_{max}) of the solutions were observed. The toluene solutions of the hybrid polymers had SPR bands [47, 48] at 428 nm (for silver nanoparticles) and at 551 nm (for gold nanoparticles) in their UV–visible absorption spectra (Fig. 3).

SEM and EDS analysis

SEM micrographs and semi-quantitative EDS analysis of the metal nanoparticles embedded graft copolymer samples (33 Ag, 34 Ag, and 12 Au) are shown in Fig. 4. The average size of the metal nanoparticles was 50 nm on the circular rows in SEM

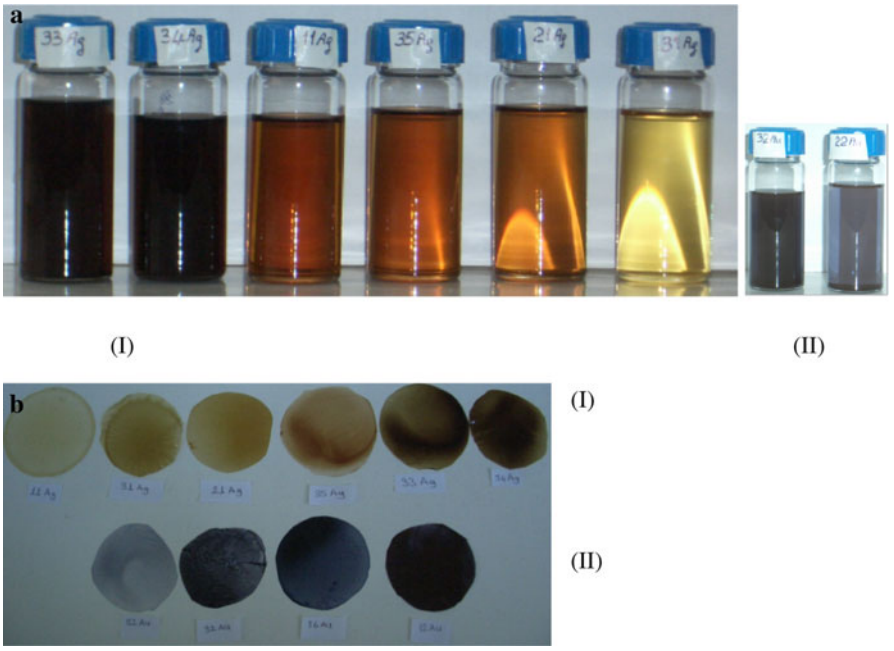


Fig. 2 **a** Photographs of toluene solutions of amphiphilic copolymers stabilize colloidal dispersion of silver (I) and gold (II) nanoparticles; **b** cast film sheets from these toluene solutions

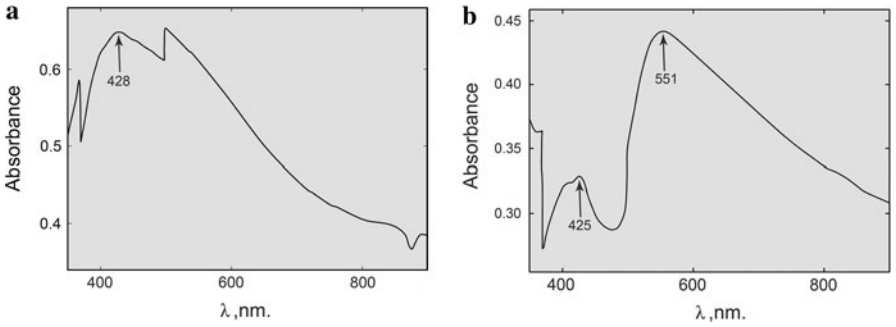


Fig. 3 UV–visible curves of **a** silver nanoparticle embedded amphiphilic graft copolymers (33 Ag) and **b** gold nanoparticle embedded amphiphilic graft copolymers (12 Au)

micrographs (Fig. 4a). Even though the rough surface of the sample may be caused by the sample preparation technique described in the experimental section, these circular rows of the silver nanoparticles in Fig. 4a may also indicate that the salts of the metal infiltrates the PEG brushes and the metal nanoparticles are formed in between these PEG brushes. In other words, the reduction of the metal cation complexed with a PEG brush [36] may cause this circular row observed in the SEM micrographs.

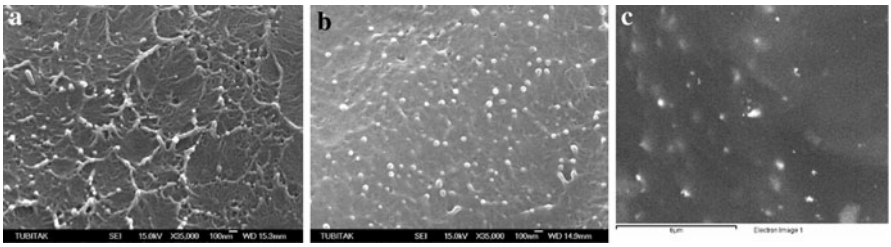


Fig. 4 SEM micrograph of **a** silver nanoparticle embedded amphiphilic graft copolymers (33 Ag) and **b** 34 Ag, and **c** Au embedded amphiphilic graft copolymers (12 Au)

Antimicrobial efficiency

PP-g-PEG graft copolymers have some antibacterial efficiency because of the reduced biofilm formation on the PEG units. Silver ions have long been known to have strong inhibitor and bactericidal effects on a broad spectrum of bacteria [43]. When gold and silver nanoparticles are added to a polymer the antimicrobial efficiency of the polymer increased. Slides coated with silver or gold nanoparticles embedded copolymers had significantly decreased bacterial colony numbers of *E. coli* and *S. aureus* when compared with the slides coated with copolymers without silver or gold nanoparticles. Figures 5, 6 shows photographs of coated glass slides

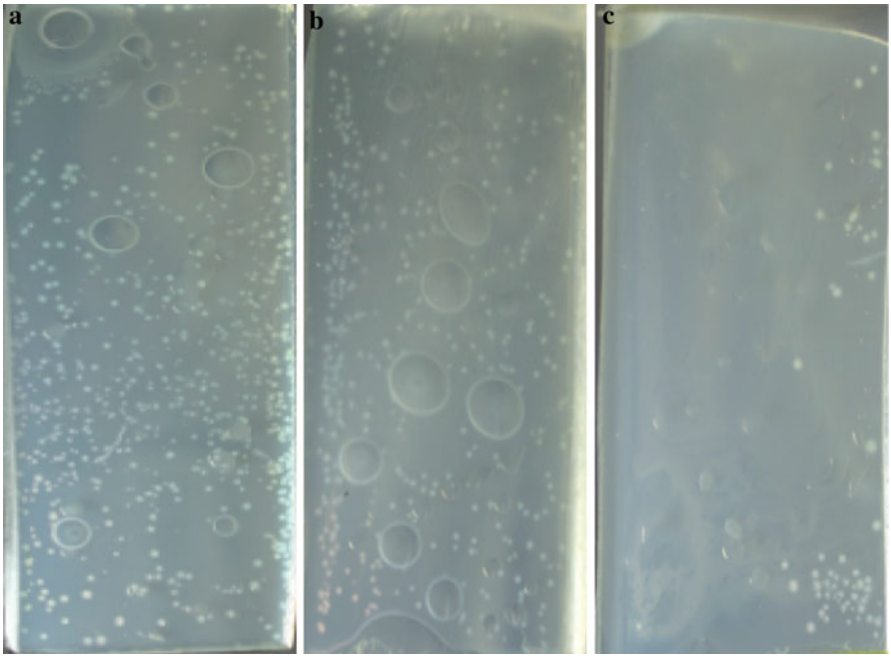


Fig. 5 *Escherichia coli* bacteria photographs of glass slide sample coated **a** control (K5), **b** PP-Cl, and **c** silver nanoparticle embedded amphiphilic graft copolymer (33 Ag)

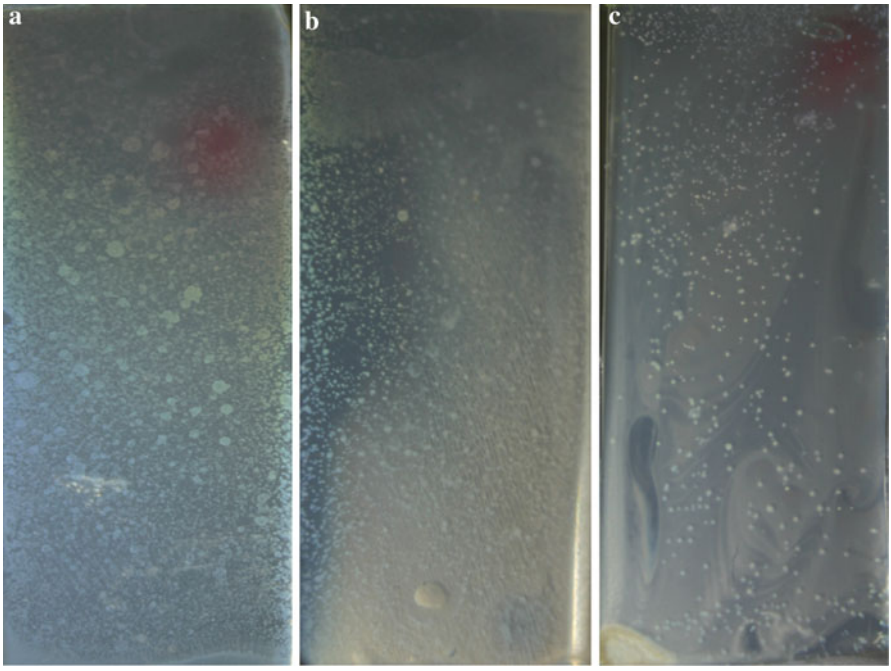


Fig. 6 *Staphylococcus aureus* bacteria photographs of glass slide sample coated **a** control (K5), **b** PP-Cl, and **c** silver nanoparticle embedded amphiphilic graft copolymers (33 Ag)

Table 2 *Escherichia coli* and *S. aureus* bacteria numbers on the silver or gold embedded amphiphilic copolymer films

	E. coli (cfu/mL)	*S. aureus* (cfu/mL)
K	380	4,800
PP	340	5,500
PPCl	160	2,800
Y-1	320	3,300
Y-2	180	3,600
Y-3	270	3,400
33 Ag	35	280
34 Ag	45	700
12 Au	22	130
32 Au	120	250
36 Au	40	70

on which *E. coli* and *S. aureus* cell suspensions were sprayed, respectively. In addition, the number of the bacteria colony forming units (cfu) per mL that were observed with these glass slides are listed in Table 2. Cfu values of the *E. coli* and *S. aureus* are high for the control glass slides (K), slides coated with polypropylene film (PP), and slides coated with chlorinated polypropylene film (PP-Cl).

It has been known that grafting of PEG on the polymer surfaces reduces biofilm formation [49]. In case of the PP-g-PEG graft copolymer samples without metal nanoparticles obtained in this work, the similar effect of PEG units has also been observed. It can be seen that the bacterial colony numbers on the samples Y-1, Y-2, and Y-3 in Table 2 have been found to be less than those of controls (K, PP, and PP-Cl). A dramatic decrease in the colony numbers on the hybrid polymer series with silver or gold nanoparticles (33Ag, 34Ag, 12Au, 32Au, and 36Au) has been observed. Likewise, the numbers of bacteria, on all the polymer samples with various amounts of silver or gold nanoparticles were dramatically lower than those on the K-, PP-, and PP-Cl-control slides. However, interpretation of the significance of variations in the numbers of bacterial colonies resulting from the slight differences in silver or gold nanoparticles concentrations in the polymers was difficult. We conclude that further studies with more variation of the concentration of the nanoparticles in the polymers and with higher numbers of polymer samples should be carried out since physical conditions, such as inhomogeneous coating of the slides, may alter the interpretation of the results when the colony numbers are low.

Conclusion

PP is an inexpensive, hydrophobic thermoplastic with very good film properties. PP must be chemically modified to produce a water-soluble PP (amphiphilic polymer) to be used in a wide range medically relevant applications requiring water solubility. This work describes a simple way to prepare a series of comb-type amphiphilic copolymer of polypropylene and poly (ethylene glycol). Metal nanoparticles stabilization in toluene solution of this amphiphilic copolymer was also observed. These PP-g-PEG sheets having embedded metal nanoparticles synthesized in this work showed antibacterial efficiency. In conclusion, these organic–inorganic hybrid polymers can be promising materials for the fabrication of antibacterial coatings.

Acknowledgments We acknowledge funding from TÜBİTAK-Ankara (grant# 108T423) and from the Commission of Zonguldak Karaelmas University Scientific Research Projects (grant# 2008-70-01-01 and grant# 2008-13-03-01).

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