Published in final edited form as:

J Bioact Compat Polym. 2017 ; 32(5): 542–554. doi:10.1177/0883911516689334.

Controlling bacterial fouling with polyurethane/*N*-halamine semi-interpenetrating polymer networks

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Abstract

N-halamine-based interpenetrating polymer networks were developed as a simple and effective strategy in the preparation of antimicrobial polymers. An *N*-halamine monomer, *N*-chloro-2, 2, 6, 6-tetramethyl-4-piperidyl methacrylate, was incorporated into polyurethane in the presence of a cross-linker and an initiator. Post-polymerization of the monomers led to the formation of polyurethane/*N*-halamine semi-interpenetrating polymer networks. The presence of *N*-halamines in the semi-interpenetrating polymer networks was confirmed by attenuated total reflectance infrared, water contact angle, and energy-dispersive X-ray spectroscopy analysis. The *N*-halamine contents in the semi-interpenetrating polymer networks could be readily controlled by changing reaction conditions. The distribution of active chlorines within the semi-interpenetrating polymer networks was characterized with energy-dispersive X-ray spectroscopy. Contact mode antimicrobial tests, zone of inhibition studies, and scanning electron microscopy observations showed that the semi-interpenetrating polymer networks had potent antimicrobial and antifouling effects against both Gram-positive and Gram-negative bacteria. Release tests demonstrated the outstanding stability of the *N*-halamine structures in the new semi-interpenetrating polymer networks.

Keywords

Interpenetrating polymer network; *N*-halamine; antimicrobial; fouling; polyurethane

Introduction

Microbial contamination and biofilm formation on polymer surfaces cause serious complications in medical, environmental, industrial, and hygienic applications.^{1–6} Antimicrobial polymers can be a potential solution to these problems.^{7–10} The research interest in this lab focuses on *N*-halamine-based antimicrobial polymers. *N*-halamines

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Declaration of conflicting interests

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

contain one or more nitrogen-halogen covalent bonds.¹⁰ With the similar biocidal efficacy as chlorine bleach, *N*-halamines are much more stable, less corrosive, and have no-documented resistant species, making them attractive candidates for the preparation of antimicrobial polymers.¹¹ To date, various methods, including copolymerization,^{12,13} surface grafting,^{14,15} functional group transformation,¹⁶ blending,^{17–19} and coating,^{20–22} have been developed to incorporate *N*-halamines into conventional polymers to achieve biocidal effects.

Polyurethane (PU) is one of the most widely used polymers in various applications because of its wide availability, low cost, and excellent physical and biological properties.^{23–26} The current methods in the preparation of PU-based polymeric *N*-halamines suffer from certain limitations. For example, copolymerization to produce antimicrobial PU may not be practical for many applications. Reactive sites should be created to graft or covalently attach *N*-halamine structures onto PU surfaces, which can be difficult due to the inert surface of the polymer. Blending can be easily performed, but it can be difficult to match the compatibility of *N*-halamines and PU to prevent leaching of *N*-halamines. Coating is a simple process, but the adhesion of the *N*-halamine on PU surface can be a concern, and it is not easy to coat odd/tiny internal surfaces (e.g. small-bore PU tubing inner surface).

In response to these challenges, we developed PU/*N*-halamine antimicrobial interpenetrating polymer networks (IPNs). IPNs are alloys of cross-linked polymer networks (at least one of them is cross-linked).^{27–29} In our approach, an *N*-halamine monomer *N*-chloro-2, 2, 6, 6-tetramethyl-4-piperidyl methacrylate (TMPMCl) was first synthesized by chlorinating 2, 2, 6, 6-tetramethyl-4-piperidyl methacrylate (TMPM) as described in our previous study²⁰ and then diffused into PU in the presence of an initiator and a cross-link agent. Thermal treatment at 95°C led to the polymerization of TMPMCl with the cross-linking agent, forming cross-linked poly (*N*-chloro-2, 2, 6, 6-tetramethyl-4-piperidyl methacrylate) (PTMPMCl) inside PU. The resulting semi-IPN demonstrated potent and durable antimicrobial and antifouling efficacy against both Gram-positive and Gram-negative bacteria, significantly simplifying the preparation process of antimicrobial PU and other related polymers for a wide range of applications.

Materials and methods

Materials

TMPM, sodium dichloroisocyanurate (DCCNa), and di (ethylene glycol) dimethacrylate (DEGDMA) were purchased from Tokyo Chemical Industry (TCI). PU was provided by A-dec (Newberg, OR). Dicumyl peroxide was from Thermo SCI ACROS ORGANICS. The microorganisms, *Staphylococcus epidermidis* (*S. epidermidis* ATCC 35984) and *Acinetobacter calcoaceticus* (*A. calcoaceticus* ATCC 31926), were obtained from American Type Culture Collection (ATCC). All other reagents were analytical grade and used as received.

Instruments

A Nicolet iS10 Mid-IR spectrometer was used to record infrared (IR) spectra of the samples. ¹³C NMR studies were performed on a 500 MHz spectrometer (Bruker, Switzerland).

Scanning electron microscope (SEM) images and energy-dispersive X-ray spectroscopy (EDS) results were acquired from a JEOL JSM 7401 FE-SEM equipped with EDAX genesis XM2 imaging system. Water contact angles were measured on a VCA optima surface analysis system (AST, MA).

Synthesis of TMPMCI

TMPMCI was synthesized according to a method we reported previously as shown in Scheme 1.²⁰ Briefly, the mixture of TMPM (5.63 g) in chloroform (25 mL) and DCCNa (6.05 g) in water (25 mL) was stirred for 1 h at room temperature. The mixture was transferred into a separate funnel to collect the bottom layer. After evaporating chloroform, the raw product of TMPMCI was purified by recrystallization in water/ethanol. The final product was colorless oil at ambient temperature (yield: 92.4%).

Synthesis of PU/PTMPMCI semi-IPNs

A “sequential strategy”²⁹ was used to prepare the semi-IPN. PU disks (with a diameter of 7.76 mm and thickness of 5.52 mm) were immersed into a solution consisting of TMPMCI, dicumyl peroxide, and DEGDMA with a molar ratio of 100:8:5 for 4 h in 60 vol% of tetrahydrofuran (THF) and 40 vol% of toluene. The disks were put in a fume hood overnight to evaporate most of the solvent and then in vacuum oven at ambient temperature for 24 h. Afterward, the disks were heated at 95°C for 4 h to polymerize TMPMCI and DEGDMA, followed by washing with ethanol to remove soluble residues. The resulting semi-IPNs were insoluble in good solvents of PU such as THF. Percentage weight increase caused by the introduction of polymerized TMPMCI and DEGDMA was calculated according to the following equation

$$\text{WI \%} = \frac{(m_2 - m_1)}{m_1} \times 100$$

where m_1 and m_2 represent the weights of the original PU and the semi-IPN, respectively.

To determine the content of active chlorine, the semi-IPN disk was weighed, broken into small pieces, and immersed in 5 mL 0.01 mol/L sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) aqueous solution. Positive chlorine on the semi-IPN could oxidize $\text{Na}_2\text{S}_2\text{O}_3$, and the content of the unreacted sodium thiosulfate was titrated by 5×10^{-4} mol/L iodine solution. The untreated original PU disks were tested with the same procedures to serve as controls. The chlorine content (moles of Cl/g of semi-IPN) was calculated according to the equation

$$\left[\text{Cl} \right] \left(\frac{\text{mol}}{\text{g}} \right) = \frac{(v_0 - v_1) \times 5 \times 10^{-4} \div 10^3}{m}$$

in which v_1 and v_0 are the volumes (mL) of iodine solution consumed in the titration of the $\text{Na}_2\text{S}_2\text{O}_3$ solution with and without the semi-IPN treatment, respectively, and m is the weight of the semi-IPN. Each test was repeated three times.³⁰

The stability of the N–Cl bond in the *N*-halamine was also evaluated according to a reported method.²⁰ The semi-IPN disks were immersed individually in 10 mL distilled water, shaking (50 r/min) at ambient temperature. After a certain period of time (5, 24, 48, 72, and 96 h), 1 mL of solution was taken out and iodometrically titrated to determine the content of active chlorines.

Antimicrobial activity of the PU/*N*-halamine semi-IPN

Gram-positive bacteria *S. epidermidis* (*Staphylococcus epidermidis*, ATCC 35984) and Gram-negative bacteria *A. calcoaceticus* (*Acinetobacter calcoaceticus*, ATCC 31926) were used as model microorganisms to evaluate the antimicrobial activity of the *N*-halamine semi-IPN¹⁷ due to their biofilm formation capability and their important roles in inducing biofilms on medical devices and dental tubing. The bacteria were cultured following the instruction provided by ATCC. Briefly, the bacteria were placed into broth solution and incubated for 24 h (*S. epidermidis* at 37°C and *A. calcoaceticus* at 30°C according to ATCC's recommendation). After centrifugation, the harvested bacteria were resuspended in sterile phosphate-buffered saline (PBS) to concentrations of 10^8 to 10^9 colony forming units per milliliter (CFU/mL), and 2 μL of the bacteria PBS suspensions were placed onto the surface of a semi-IPN disk. The disk was “sandwiched” using another identical disk.²⁰ After different periods of contact time, the “sandwich” was immersed into sterile PBS, vortexed to separate the “sandwich,” and then sonicated¹⁷ for 10 min to transfer the adherent bacteria into the solution, which was vortexed and then serially diluted. A total of 100 μL of each dilution was placed onto agar plates and after 24 h of incubation, CFUs on the plates were counted. The same procedures were applied to the original PU disks to serve as controls. Each test was repeated three times.

Zone of inhibition test

Inhibition zone test was carried out following the previous reported procedures.³¹ Briefly, the surface of agar plates was covered by 1 mL of 10^8 – 10^9 CFU/mL of *A. calcoaceticus* (ATCC 31926). The plates were then incubated at 30°C for 2 h to form a thin bacterial layer on top of nutrient agar. Semi-IPN disks were put on the surface of the agar plates covered by bacteria and were gently pressed to ensure full contact between the disk and agar. PU disks were processed in the same way as control. After incubation at 30°C for 24 h, the inhibition zone surrounding each disk was measured.

Antifouling activity of the *N*-halamine semi-IPN

The bacteria *S. epidermidis* and *A. calcoaceticus* were cultured, harvested, and resuspended in sterile PBS with a final concentration of 10^5 – 10^6 CFU/mL, as described above. The *N*-halamine semi-IPN disks were immersed individually in 5 mL bacterial suspension for 30 min with constant shaking in a water bath (at 37°C for *S. epidermidis* and 30°C for *A. calcoaceticus*) to allow bacteria initial adhesion.^{31,32} The disks were rinsed gently with PBS three times to remove loosely attached bacteria and then incubated in 5 mL fresh broth

solution for 24 h for bacterial colonization. The disks were taken out and washed gently with non-flow sterile PBS to remove planktonic bacteria and immersed in 3% glutaraldehyde in 0.1 M sodium cacodylate buffer (SCB) at 4°C for 24 h. After washing with SCB, the disks were dehydrated sequentially with 30%, 50%, 75%, 90%, and 100% ethanol (30 min at each concentration). Thereafter, the disks were mounted onto sample holder, sputter coated with gold, and observed under SEM to check for the presence of adherent bacteria. Pure PU disks were processed with the same procedures to serve as controls.

Results and discussion

Preparation and characterization of the PU/N-halamine IPNs

The THF solution of TMPMCl²⁰ was used to swell PU in the presence of dicumyl peroxide (initiator) and DEGDMA (cross-linking agent) to prepare the PU/N-halamine IPN. Although both PU and the polymer of TMPMCl (PTMPMCl) were soluble in organic solvent such as THF, the IPNs were not. The solvents could only swell, but could not dissolve, the IPNs. After the evaporation of the solvents, the IPNs returned to their original shapes. These results suggested that the semi-IPNs were not physical mixtures of PU and PTMPMCl. Instead, PU and the polymer of TMPMCl with DEGDMA could have covalently bonded together. The bonding between PU and PTMPMCl could be because that the initiator, dicumyl peroxide, could generate macro-free radicals on PU polymers, which could initiate the grafting of TMPMCl and DEGDMA onto PU, covalently linking PU with the cross-linked polymer of TMPMCl and DEGDMA, forming “grafted semi-IPN.”^{33,34}

The effects of TMPMCl concentrations in the swelling solution on the preparation of the IPNs were shown in Figure 1. As expected, with the increase in TMPMCl/DEGDMA concentration, the contents of the cross-linked TMPMCl/DEGDMA and the active chlorines in the resulting IPNs gradually increased. With the TMPMCl/DEGDMA concentrations in the swelling solution of 6.75%, 17.80%, and 26.60% (w/w %), the cross-linked TMPMCl/DEGDMA in the IPNs were 7.57% (IPN1), 12.24% (IPN2), and 21.35% (IPN3) (w/w %), and the titratable positive chlorines were 5.19 ± 1.17 , 9.56 ± 0.61 , and 16.02 ± 3.04 (mol Cl⁺/g IPN), respectively.

The distribution of the active chlorines in the semi-IPNs was investigated. Figure 2 shows the SEM-EDS spectrum of semi-IPN3. In addition to the C, N, and O peaks, the spectrum of semi-IPN3 displayed strong peaks of Cl (2.63 keV), which could be used to quantify active chlorine in the samples. In pure PU, the detected surface and cross section chlorine could be caused by the noise from the baseline.

In the semi-IPNs, with the increase in the cross-linked TMPMCl/DEGDMA content, the levels of active chlorine in the cross section gradually increased, in good agreement with the trend of the titration results (Figure 1). The surface chlorine content, however, reached the maximum content around 1%. After a certain limit, further increase in the cross-linked TMPMCl/DEGDMA content had little effects on the surface chlorine level, suggesting that instead of accumulating on the surface, the cross-linked TMPMCl/DEGDMA presented both on the surface and in the bulk of PU, and there was a saturation value of active chlorine on the surface.

The semi-IPNs were characterized with attenuated total reflectance infrared (ATR-IR) spectra, as shown in Figure 3. Because of the strong absorptions of the urethane band at 1699 cm^{-1} , no significant difference could be found between the PU spectrum and the semi-IPN3 spectrum. However, after subtracting the PU spectrum from the semi-IPN3 spectrum, signals at 1720 cm^{-1} (ester carbonyl stretching vibration) and 1169 cm^{-1} (ester C–O vibration) could be observed, suggesting the presence of PTMPMCI in the resulting semi-IPN.

Figure 4 shows the effects of the semi-IPN on water contact angle. The original PU had a rather hydrophobic surface, with a contact angle of 111° . With the increase in the cross-linked TMPMCI/ DEGDMA content, the contact angle gradually decreased. These results indicated that the copolymer of TMPMCI and DEGDMA presented on the sample surface, and the ethylene glycol groups in DEGDMA led to a more hydrophilic surface.

Antimicrobial and antifouling efficacy of the PU/N-halamine semi-IPNs

The active chlorines in the semi-IPNs provided potent antimicrobial effects against both Gram-negative bacteria *A. calcoaceticus* and Gram-positive bacteria *S. epidermidis*.

In the contact mode antimicrobial tests, the original PU did not provide any detectable antimicrobial functions. On the other hand, the semi-IPNs provide 80%–99% of reduction of the testing bacteria within 1 h. As a general trend, higher chlorine content led to higher antimicrobial potency. After 4 h of contact, all the semi-IPNs provided a total kill of *A. calcoaceticus* and *S. epidermidis* (Figure 5).

In zone of inhibition tests (Figure 6), while the original PU disk did not provide any inhibition zone against *A. calcoaceticus*, all the semi-IPNs provided a small, yet clear zone against the bacteria.

Similar results were obtained in the testing of *S. epidermidis* (pictures not shown). The zone could be caused by the oxidative positive chlorine generated through the following equation²⁰

The Cl^+ could diffuse into the surrounding environments to inhibit the growth of bacteria. Apparently, the release rate of Cl^+ is of great importance to the antimicrobial activity and stability of the semi-IPNs. In releasing tests (Figure 7), after 4 days of immersion in distilled water, semi-IPN1, semi-IPN2, and semi-IPN3 released 0.005, 0.015, and 0.021 ppm of chlorine, which was far less than the Environmental Protection Agency's (EPA) maximum residual disinfectant limits of 4.0 ppm.²⁰ These results were reasonable because four methyl groups connected to the neighboring carbons of the N–Cl groups in the semi-IPNs. The electron donating effect could destabilize any developing negative charge on N as Cl^+ left the polymer, leading to stable N-halamine structure and very low positive chlorines released.

The antimicrobial efficacy of the semi-IPNs resulted in powerful antifouling effects. As shown in Figure 8, after 24 h of growth, a large amount of *S. epidermidis* and *A. calcoaceticus* colonized on the original PU. On the other hand, the semi-IPNs had much cleaner surface with only scattered bacteria; higher *N*-halamine contents led to lower level of adherent bacteria with abnormal morphologies, suggesting less healthy state of the adherent bacteria.

Conclusion

PU/*N*-halamine semi-IPNs were prepared through the diffusion of TMPMCl, DEGDMA, and an initiator into the PU polymer, followed by post-polymerization of the monomers. The contents of the *N*-halamines in the semi-IPNs could be readily controlled by changing reaction conditions. ATR spectra, water contact angle, and SEM-EDS studies suggested that the *N*-halamines presented both on the surface and in the bulk of PU. The new semi-IPNs demonstrated powerful antimicrobial and antifouling efficacy against both Gram-negative and Gram-positive bacteria. Higher *N*-halamine contents resulted in higher antimicrobial potency. The ease and the wide applicability of the preparation pathway as well as the promising properties of the resulting semi-IPNs make the new strategy an attractive candidate for the antimicrobial treatment of PU and other related polymers to control microbial fouling, the root cause of biofilm formation, for a wide range of applications.

Acknowledgments

Funding

This study was sponsored by NIH, NIDCR (Grant number R01DE018707).

References

1. Hall-Stoodley L, Costerton JW, Stoodley P. Bacterial biofilms: from the natural environment to infectious diseases. *Nat Rev Microbiol.* 2004; 2:95–108. [PubMed: 15040259]
2. Gu H, Hou S, Yongyat C, et al. Patterned biofilm formation reveals a mechanism for structural heterogeneity in bacterial biofilms. *Langmuir.* 2013; 29:11145–11153. [PubMed: 23919925]
3. Seale AC, Blencowe H, Manu AA, et al. Estimates of possible severe bacterial infection in neonates in sub-Saharan Africa, south Asia, and Latin America for 2012: a systematic review and meta-analysis. *Lancet Infect Dis.* 2014; 14:731–741. [PubMed: 24974250]
4. Wu H, Moser C, Wang H-Z, et al. Strategies for combating bacterial biofilm infections. *Int J Oral Sci.* 2015; 7:1–7. [PubMed: 25504208]
5. Kregiel D. Advances in biofilm control for food and beverage industry using organo-silane technology: a review. *Food Control.* 2014; 40:32–40.
6. Bott TR. *Industrial biofouling: occurrence and control* New York: Elsevier; 2011
7. Gyawali R, Ibrahim SA. Natural products as antimicrobial agents. *Food Control.* 2014; 46:412–429.
8. Siedenbiedel F, Tiller JC. Antimicrobial polymers in solution and on surfaces: overview and functional principles. *Polymers.* 2012; 4:46–71.
9. Penesyan A, Gillings M, Paulsen I. Antibiotic discovery: combatting bacterial resistance in cells and in biofilm communities. *Molecules.* 2015; 20:5286–5298. [PubMed: 25812150]
10. Eknoian MW, Putman JH, Worley SD. Monomeric and polymeric *N*-halamine disinfectants. *Ind Eng Chem Res.* 1998; 37:2873–2877.

11. Barnes K, Liang J, Wu R, et al. Synthesis and antimicrobial applications of 5,5'-ethylenebis[5-methyl-3-(3-triethoxysilylpropyl)hydantoin]. *Biomaterials*. 2006; 27:4825–4830. [PubMed: 16757023]
12. Sun Y, Sun G. Novel regenerable N-halamine polymeric biocides. I. Synthesis, characterization, and antibacterial activity of hydantoin-containing polymers. *J Appl Polym Sci*. 2001; 80:2460–2467.
13. Sun Y, Sun G. Durable and refreshable polymeric N-halamine biocides containing 3-(4'-vinylbenzyl)-5,5-dimethylhydantoin. *J Polym Sci Part A*. 2001; 39:3348–3355.
14. Badrossamay MR, Sun G. A study on melt grafting of N-halamine moieties onto polyethylene and their antibacterial activities. *Macromolecules*. 2009; 42:1948–1954.
15. Aumsuwan N, Heinhorst S, Urban MW. Antibacterial surfaces on expanded polytetrafluoroethylene; penicillin attachment. *Biomacromolecules*. 2007; 8:713–718. [PubMed: 17291097]
16. Sun X, Zhang L, Cao Z, et al. Electrospun composite nanofiber fabrics containing uniformly dispersed antimicrobial agents as an innovative type of polymeric materials with superior antimicrobial efficacy. *ACS Appl Mater Interfaces*. 2010; 2:952–956. [PubMed: 20380426]
17. Lin J, Jiang F, Wen J, et al. Fluorinated and un-fluorinated N-halamines as antimicrobial and biofilm-controlling additives for polymers. *Polymer*. 2015; 68:92–100. [PubMed: 26166903]
18. Chyli ska M, Kaczmarek H, Burkowska-But A, et al. Novel biocidal N-halamine plastic based on poly(vinyl chloride): preparation and characteristics. *J Ind Eng Chem*. 2015; 28:124–130.
19. Sun X, Cao Z, Porteous N, et al. Amine, melamine, and amide N-halamines as antimicrobial additives for polymers. *Ind Eng Chem Res*. 2010; 49:11206–11213. [PubMed: 21088762]
20. Cao Z, Sun Y. Polymeric N-halamine latex emulsions for use in antimicrobial paints. *ACS Appl Mater Interfaces*. 2009; 1:494–504. [PubMed: 20353242]
21. Cerkez I, Kocer HB, Worley SD, et al. N-halamine biocidal coatings via a layer-by-layer assembly technique. *Langmuir*. 2011; 27:4091–4097. [PubMed: 21348478]
22. Denis-Rohr A, Bastarrachea LJ, Goddard JM. Antimicrobial efficacy of N-halamine coatings prepared via dip and spray layer-by-layer deposition. *Food Bioprod Process*. 2015; 6:12–19.
23. Szycher M. Biostability of polyurethane elastomers: a critical review. *J Biomater Appl*. 1988; 3:297–402. [PubMed: 3060587]
24. Lamba NM, Woodhouse KA, Cooper SL. *Polyurethanes in biomedical applications* Boca Raton, FL: CRC Press; 1997
25. Griesser HJ. Degradation of polyurethanes in biomedical applications—a review. *Polym Degrad Stab*. 1991; 33:329–354.
26. Planck H, Syre I, Dauner M, et al. Polyurethane in biomedical engineering: II. *Prog Biomed Eng*. 1987; 3:213.
27. Zhao N, Liu S. Thermoplastic semi-IPN of polypropylene (PP) and polymeric N-halamine for efficient and durable antibacterial activity. *Eur Polym J*. 2011; 47:1654–1663.
28. Liu S, Zhao N, Rudenja S. Surface interpenetrating networks of poly(ethylene terephthalate) and polyamides for effective biocidal properties. *Macromol Chem Phys*. 2010; 211:286–296.
29. Dragan ES. Design and applications of interpenetrating polymer network hydrogels: a review. *Chem Eng J*. 2014; 243:572–590.
30. Cao Z, Sun Y. N-Halamine-based chitosan: preparation, characterization, and antimicrobial function. *J Biomed Mater Res A*. 2008; 85:99–107. [PubMed: 17688258]
31. Chen Z, Luo J, Sun Y. Biocidal efficacy, biofilm-controlling function, and controlled release effect of chloromelamine-based biore-sponsive fibrous materials. *Biomaterials*. 2007; 28:1597–1609. [PubMed: 17184837]
32. Chen Z, Sun Y. N-Halamine-based antimicrobial additives for polymers: preparation, characterization, and antimicrobial activity. *Ind Eng Chem Res*. 2006; 45:2634–2640. [PubMed: 18714370]
33. Gitsov I, Zhu C. Novel functionally grafted pseudo-semi-interpenetrating networks constructed by reactive linear-dendritic copolymers. *J Am Chem Soc*. 2003; 125:11228–11234. [PubMed: 16220941]

34. Karabanova LV, Lloyd AW, Mikhlovsky SV, et al. Polyurethane/poly(hydroxyethyl meth-acrylate) semi-interpenetrating polymer networks for biomedical applications. *J Mater Sci Mater Med*. 2006; 17:1283–1296. [PubMed: 17143760]

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Figure 1. Effects of TMPMCl concentration in the swelling solution on weight increase and titratable active chlorine content of the semi-IPNs.

Figure 2.
SEM-EDS spectrum of semi-IPN3 and summary of chlorine contents.

Figure 3.
ATR spectra of semi-IPN3, PU, difference spectrum of the semi-IPN3 and PU and TPMCI.

Figure 4.
Water contact angles (degree) of the original PU and the semi-IPNs.

Figure 5. Recoverable CFU and corresponding percentage reduction of *A. calcoaceticus* and *S. epidermidis* in direct contact mode antimicrobial study.

Figure 6. Inhibition zones of (a) PU, (b) semi-IPN1, (c) semi-IPN2, and (d) semi-IPN3, against *A. calcoaceticus*.

Figure 7.
Positive chlorine content in the releasing solution.

Figure 8.
Representative SEM images of bacterial fouling on the original PU and the semi-IPNs after 24 h of culturing.

Scheme 1.
Synthesis of TMPMCl by chlorination reaction.