Preparation of Antibacterial Poly(methyl methacrylate) by Solution Blending with Water-Insoluble Antibacterial Agent Poly[(tert-buty1amino) ethyl methacrylate]

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ABSTRACT: A simple and effective way was developed to prepare antibacterial poly(methyl methacrylate) (PMMA) materials from commercial PMMA and synthesized poly[2-(*tert*-butylamino) ethyl methacrylate] (PTBAEMA) by solution blending and solvent evaporation methods. The chemical structure of as-synthesized PTBAEMA was characterized by FTIR and ^{1}H-NMR, and the molecular weight (M_w) and polydispersity index was determined by Gel Permeation Chromatograph. The two components, that is, PMMA and PTBAEMA, were partially miscible and of regular domain size and shape as revealed by SEM observation. Antibacterial assay revealed PMMA/PTBAEMA blends inherited the good antibacterial activity of PTBAEMA against both *Staphylococcus aureus* and *Escherichia coli*, no matter whether the bacteria were waterborne or airborne. Besides, the antibacterial performance of PMMA/PTBAEMA blends depended on the M_w and dosage of PTBAEMA, and type of bacteria strain. Furthermore, it was proved that PMMA/PTBAEMA blends killed bacteria on direct contact without releasing active component, which sufficiently met the demand of developing environment-friendly antibacterial materials.
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Key words: polymer synthesis and characterization; poly(vinyl ethers); polymer blends; biological applications of polymers

INTRODUCTION

In recent years, substantive effort has been devoted to developing new materials with antibacterial activity, so as to face up the increasing threaten to human health associated with bacteria infection.[1–3] Previous work to produce antibacterial materials is mainly concentrated on the incorporation of a leaching bioactive agent into materials, which is then released into the surrounding environment to exert the antibacterial action.[2,4–7] This kind of materials are easy to obtain[8] and often have superior antibacterial capabilities[9]; however, their applications are limited by some drawbacks, such as short-term effectiveness, potential threaten to environment, and inability to kill airborne bacteria.[10] Consequently, interest has been turned to materials based on contact-killing mechanism. They kill bacteria on direct contact, without the need to release active components. Therefore, the antibacterial activity is therefore retained throughout the process of using, and cause less damage to the environment.[11–14]

Cationic polymers are an important part of contact-killing materials.[15] It is widely accepted that their antibacterial action is based on the electrostatic and hydrophobic interaction between cationic polymers and bacteria cytoplasmic membrane.[11,16,17] Polymeric quaternary ammonium compounds (PQACs) are among the most often used cationic polymers. They have been successfully applied in the antibacterial modification of various materials, such as fiber,[18] filter paper,[19,20] glass,[21] stainless steel,[22] etc. However, since most of the PQACs are water-soluble, they have to be immobilized in materials properly to achieve a long-lasting antibacterial efficacy. Various methods have been developed for this purpose, including surface initiated atom transfer radical polymerization,[23,24] UV-induced graft polymerization,[18,25] reversible addition-fragmentation chain transfer

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polymerization,[15] coupling grafting,[26] etc. However, though these methods are effective and useful, the published examples often require tedious multistep surface modification.[27]

We report herein a simple and effective way to prepare antibacterial poly(methyl methacrylate) (PMMA) materials from commercial PMMA and synthesized poly[2-(*tert*-butylamino) ethyl methacrylate] (PTBAEMA) by solution blending and solvent evaporation methods. The as-synthesized PTBAEMA is biocidal against both *Escherichia coli* (*E. coli)* and *Staphylococcus aureus* (*S. aureus)*. PMMA/PTBAEMA blends inherit the good antibacterial activity of PTBAEMA, and kill both waterborne and airborne bacteria present on the surface. Furthermore, it is proved that the antibacterial action is based on contact-killing mechanism, rather than release-killing mechanism.

As highlighted here, since PTBAEMA is water-insoluble, it is possible to stabilize PTBAEMA in materials by simple physical entrapping and avoid the tedious multistep surface modification. Meanwhile, the similarity in the chemical structure may make PMMA and PTBAEMA compatible, and therefore helps to achieve an overall rather than local antibacterial activity. Therefore, this method combines the safety and durability of PQACs and the simple production technology of release-killing antibacterial materials. It is promising for developing antibacterial PMMA materials of high ratio of performance to price.

MATERIALS AND METHODS

Materials

The 2-(*tert*-butylamino) ethyl methacrylate (TBAEMA, 97%) was purchased from ς-Aldrich, distilled under reduced pressure to remove the inhibitor, and used immediately. Nutrient agar, nutrient broth, peptone, and eosin methylene blue agar (EMB) were purchased from Guangdong Huankai Microbial Sci. and Tech. Co, and used according to the operation instruction. Poly (methyl methacrylate) (PMMA LX 040) was purchased from Heilongjiang Longxin Chemical. Other reagents were obtained from Guangzhou Chemical Reagent Factory, and used as received.

Synthesis of PTBAEMA

The polymerization was carried out as follows: 7.1 mL TBAEMA (0.04 mol), 60 mL tetrahydrofuran (THF), and AIBN were added into a two-necked round-bottom flask equipped with a condenser, a nitrogen inlet, and a magnetic stirrer. The amount of AIBN was varied in the range of 0.8–2.3% (molar ratio of AIBN/monomer). After purified nitrogen had been passed through the vessels for 0.5 h, the reaction systems were heated to 65°C, kept stirred at the temperature in nitrogen atmosphere for 20 h, and then stopped by cooling down to room temperature. The products were precipitated out in a large excess of deionized water, separated by filtration, purified by continuous extraction with soxhlet extractor, and finally dried in a vacuum oven at 60°C for 48 h.

Preparation of polymer films

To assess the biocidal activity, PTBAEMA films were prepared on microscope glass slides (25.4 $\times$ 76.2 mm^2) as follows: 2.5% w/v solutions of PTBAEMA were prepared in THF, and then twofold diluted by THF to obtain PTBAEMA solutions of different concentration. On the slides, 0.1 mL solution was spread evenly with a pipette, covering an area of about 25.4 $\times$ 50.0 mm^2. After solvent evaporation in fume hood for 24 h, the slides were dried in a vacuum oven at 60°C for 12 h. Samples of different molecular weights (M_w) were prepared in the same procedure.

PMMA/PTBAEMA blend films were prepared in a similar way, except that PTBAEMA solutions were diluted by 2.0% w/v PMMA THF solutions instead of THF.

Structure characterization

IR spectra were recorded on a FTIR (Perkin–Elmer Spectrum). ^{1}H-NMR spectra were recorded on a Mercury-Plus 300 Varian instrument. Average molecular weights (M_w) were measured using Gel Permeation Chromatograph (GPC) on a Waters Breeze equipped with a Waters 1515 Isocratic HPLC Pump, Waters 717-plus Autosampler, Viscotek 270 Dual Detector. SEM imaging was done on a Hitachi *S*-4800 electron microscope.

Determination of antibacterial activity

Bacterial culture

S. aureus ATCC 25932 and *E. coli ATCC* 25922 were chosen as testing bacteria. They were streaked out on nutrient agar plates and incubated at 37°C for 24 h. A representative colony was lifted off with a wire loop, placed in 50 mL of nutrient broth, and incubated with shaking at 37°C for 20 h. At this stage, the concentration of bacteria suspension reached $\sim 10^9$ colony-forming units per mL (CFU/mL). The required concentration was adjusted by nutrient broth.

Waterborne bacteria testing

One milliliter of bacterial suspension ($\sim 10^8$ CFU/mL) was placed on the surface of slides coated with

TABLE I
M_w and Yield of PTBAEMA with Different Amount of AIBN

Samples	Poly-1[a]	Poly-2	Poly-3	Poly-4
Amount of AIBN[b]	2.3%	1.7%	1.3%	0.8%
M_w/Daltons[c]	5867	7537	8303	10053
Polydispersity[c]	1.89	1.84	1.61	1.59
Yield/%	98.1	97.4	95.3	85.6

[a] PTBAEMA were abbreviated as Poly-n (n = 1, 2, 3, and 4) based on the difference in M_w.
[b] The unit was the molar ratio of initiator/monomer.
[c] Determined by GPC. Polymerization conditions: The concentration of TBAEMA was held constant at 0.5 mol/L. The reactants were kept stirred at 65°C in N2 atmosphere for 20 h.

polymer films, and spread with a disposable 10 μL inoculating loop. Each slide was placed in a sterile, covered Petri dish to protect the bacteria from drying out, and incubated at 37°C for 0.5 h. Then the slides were taken out, rinsed with 50 mL sterile 0.1% peptone water in 100 mL conical flasks, and treated by sonication (1 min at 100 W with vortexing) to recover the adherent cells on the slides. The number of bacteria was determined by viable cell counting method. Blank glass slide and glass slide coated with PMMA served as controls. The killing rate was calculated according to the following equation:

$$\text{Killing rate} = \frac{(A - B)}{A} \times 100\% \quad (1)$$

A, number of bacteria cells added on the surface of slides; B, number of surviving bacteria cells after incubating with polymer films.

Airborne bacteria testing

E. coli suspension (10^6 CFU/mL) was sprayed onto the surface of glass slide in a sterile bench. After drying for 2 min under air, the slide was placed in a Petri dish, and EMB agar (autoclaved and cooled to about 45°C) was then added in. The Petri dish was closed, sealed, and incubated at 37°C overnight.

Inhibition zone method

Polymer blend solutions were prepared as described above. Filter paper with a diameter of 9 mm was coated with 20 μL blend solution, and dried in fume hood for 24 h. Each Nutrient agar plate was inoculated with 400 μL bacteria suspension, containing 2.5×10^5 CFU/mL *E. coli* or 3.4×10^6 CFU/mL *S. aureus*. Filter papers were then placed on top of the agar plates and incubated overnight at 37°C. Colonies were visualized the next day, and digital images of the plates were captured.

RESULTS AND DISCUSSION

Synthesis of PTBAEMA

In previous studies, it was discovered that PTBAEMA exhibited good antibacterial activity, while the corresponding monomer was not active at all. This meant that M_w played an important role in the antibacterial action of PTBAEMA.[13,22,28] Therefore, in this study, PTBAEMA of different M_w was synthesized by free radical polymerization. As seen from Table I, the M_w of PTBAEMA decreased with the increase of AIBN, while the polydispersity index of M_w increased with it. This could be explained by the general features of free radical polymerization. With the increase of AIBN, the mole ratio of TBAEMA to AIBN decreased, which resulted in the decrease of M_w; but on the other hand, the termination rate of large molecular free radicals and chain transfer rate increased that hindered the steady propagation of polymer chain and therefore induced the increase of PDI.

High yield was obtained in our synthesis, all exceeding 85% (Table I), though it decreased slightly with the decrement of AIBN content. This was also in good accordance with the general features of free radical polymerization. With the increase of AIBN, more radical initiators were produced in the polymerization system, which was beneficial to the full polymerization of TBAEMA. According to the M_w of PTBAEMA, the polymers were termed as poly n (n = 1, 2, 3, and 4).

The chemical structures of TBAEMA and PTBAEMA were characterization by FTIR (shown in Figs. 1 and 2) and ^{1}H-NMR (shown in Fig. 3). As seen from Figure 2, both the spectra showed absorption bands at 1152 cm^{-1} (C—O—C asymmetrical stretching vibration), 3326 cm^{-1} (—NH stretching vibration), 1405 cm^{-1}, and 1126 cm^{-1} (C—N stretching vibration). The ^{1}H-NMR signal of —H(N) — (2.449 ppm) was also detected in their spectra. These data were in accordance with the structure. Moreover, the disappearance of C=C (FTIR) peak at 1640

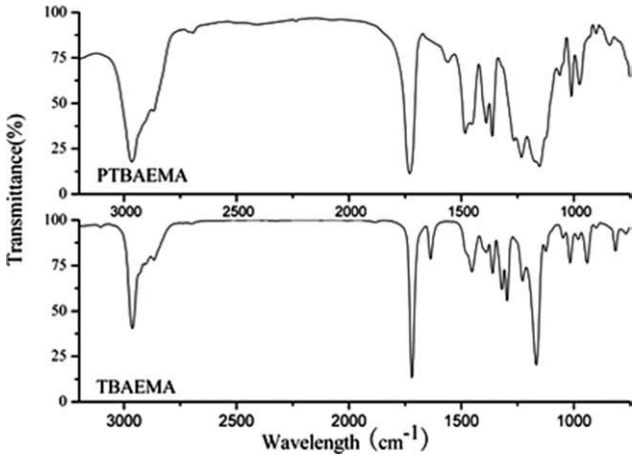

Figure 1 FTIR spectra of TBAEMA and PTBAEMA.

cm^{-1} and =CH (^{1}H-NMR) (shown in Fig. 2) at 6.012, 5.639 ppm (shown in Fig. 3) proved the successful polymerization of TBAEMA. Therefore, it could be concluded that the expected PTBAEMA was obtained in our synthesis.

Preparation of PMMA/PTBAEMA blends

The microstructure of PTBAEMA film, PMMA film, and PMMA/PTBAEMA blend films was observed by SEM, shown in Figure 3. The films were the same as those used in antibacterial assay. It was seen that PTBAEMA exhibited uniform and dense microstructure [Fig. 3(A)], while PMMA formed a consecutive network microstructure with many pores [Fig. 3(F)]. The micrographs of blend films were shown in Figure 3(B–E). The dark area in the photographs was composed of PMMA, and the light-dark part was PTBAEMA. With the addition of PMMA to PTBAEMA, the morphologies of the blended films changed dramatically. When the amount of PTBAEMA was over 50%, the PTBAEMA component formed a threadlike linear structure in the continuous network phase of PMMA. As the content of PTBAEMA decreased, the threadlike PTBAEMA shrink and finally became small ellipse particles that distributed in and around the pores of PMMA matrix. Interestingly, it was discovered that the pore diameters were in the range of 0.2–1 μm. These sizes were smaller than or close to those of bacterial cells, as *E. coli* cells were about 1–3 μm in length, 0.5–0.7 μm across, and *S. aureus* cells were about 0.8 μm in diameter. Therefore, it would not create an area that has no PTBAEMA component to contact with bacterial cells to exert the antibacterial activity. The particular microstructure might be even beneficial for enhancing the contact between blend films and bacterial cells. Meanwhile, the inspection of these micrographs indicated two phase of PTBAEMA and PMMA with regular domain size and shape. This meant that PMMA/PTBAEMA blends were partially miscible, which also supported the potential to blend PMMA with PTBAEMA to endow it with good and long-lasting antibacterial.

Waterborne bacteria testing of PTBAEMA

The antibacterial activity of PTBAEMA films against *E. coli* and *S. aureus* was summarized in Tables II and III. They were effective at killing waterborne *E. coli* and *S. aureus*. One milliliter 10^8 CFU/mL of both strains of bacteria was killed by the polymer films prepared from 1.25% w/v PTBAEMA solution. It corresponded to the dosage of 1.25 mg.

The antibacterial activity was influenced by the M_w and dosage of PTBAEMA and the type of bacteria. As for *E. coli*, the antibacterial activity increased with the M_w and amount of PTBAEMA. A killing rate of 65.23% was obtained at the concentration of 0.31% w/v when the M_w was 10,053, while the killing rate was only 22.82% at the M_w of 5867. When the concentration was as low as 0.16% w/v, poly-1 and poly-2 did not inhibit the growth of *E. coli*, as an increase in the number of surviving bacteria was observed; however, a good antibacterial activity was achieved in the same condition when M_w was more than 8303.

From the results above, it was discovered that the antibacterial activity of PTBAEMA was influenced significantly by M_w. This could be explained by the

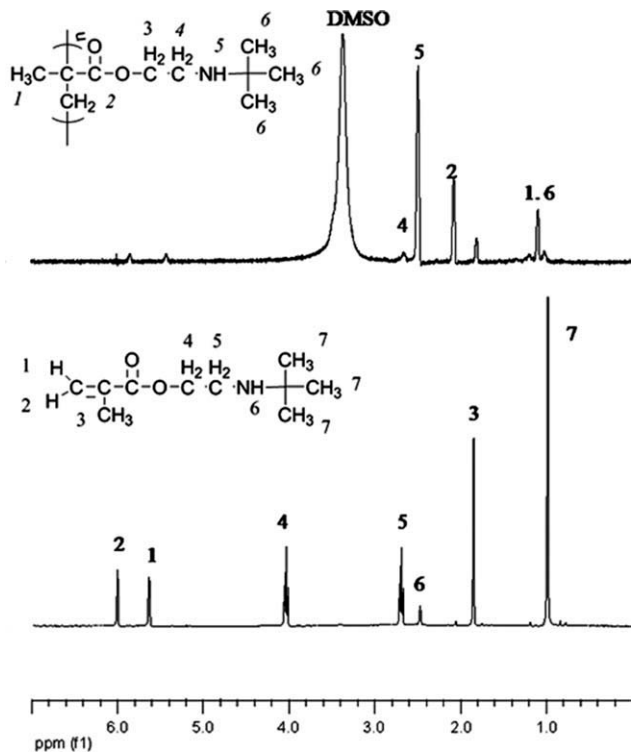

Figure 2 ^{1}H-NMR spectra of TBAEMA and PTBAEMA.

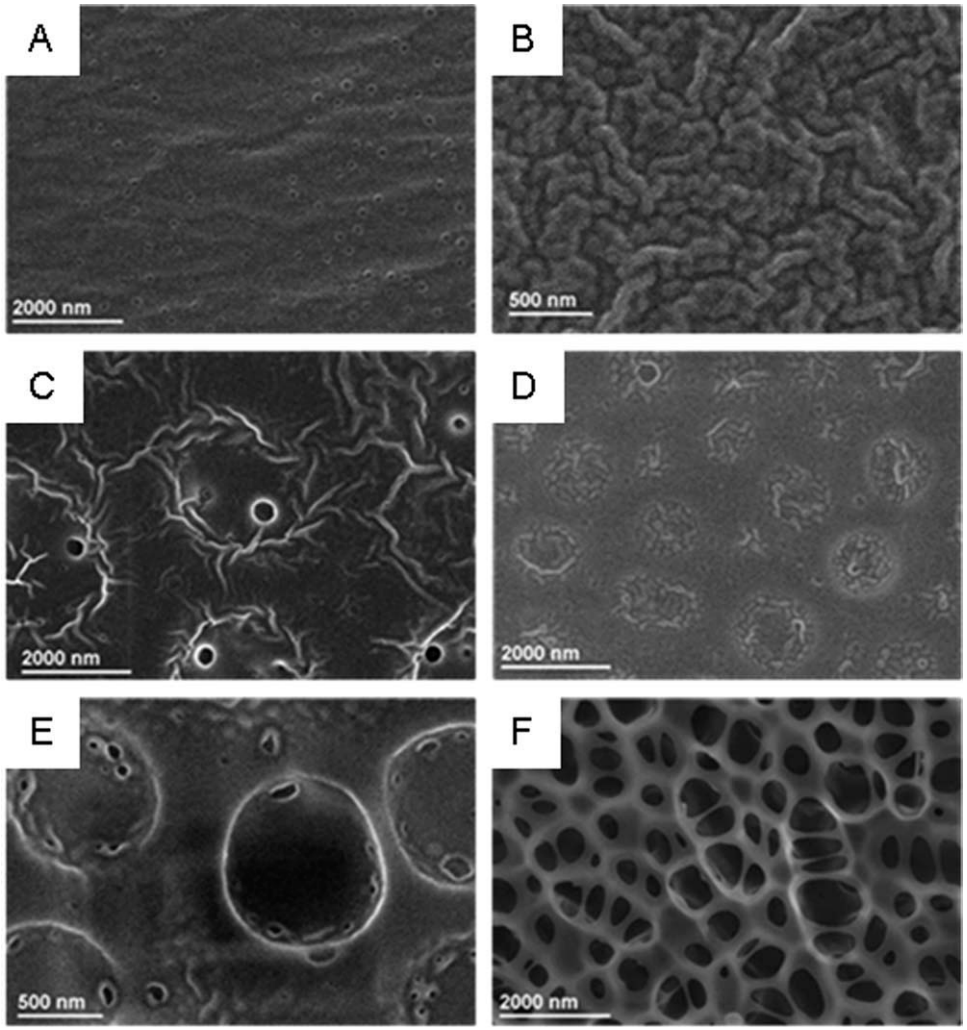

Figure 3 SEM photographs of polymer films prepared from pure PTBAEMA, pure PMMA, and Blend-3 with different composition. (A) Pure PTBAEMA; Blend-3 with PMMA to Poly-3*M* ratios of (B) 1 : 1; (C) 3 : 1; (D) 7 : 1; (E) 15 : 1; (F) pure PMMA.

antibacterial mechanism of cationic polymers, which was believed to be as follows: (1) adsorption onto the negatively charged bacterial cell surface; (2) penetration through the cell wall; (3) binding to the cytoplasmic membrane; (4) disruption of the cytoplasmic membrane; (5) release of intracellular constituents such as K^+, DNA, and RNA; and (6) death of bacteria cells. From this, it could be seen that the electrostatic attraction is the prerequisite of the antibacterial process, since the polymers has to be absorbed onto the bacterial cells to exert the antibacterial activity.[16,29–31] As the PTBAEMA films were prepared from polymer solutions by solvent evaporation method, the macromolecules with higher M_w might result in a local congregation of active groups so that cause the increase of regional charge density.

TABLE II
Killing Rate of PTBAEM Films Against *E. coli*

Content[a] (% w/v)	Killing rate (%)			
	Poly-1	Poly-2	Poly-3	Poly-4
0.16	−65.01	−78.33	72.41	50.60
0.31	11.78	16.67	67.38	33.41
0.63	22.82	56.25	58.05	65.23
1.25	100.00	99.30	99.92	99.24
2.50	100.00	100.00	100.00	100.00

[a] Content of PTBAEMA in the solution.

TABLE III
Killing Rate of PTBAEM Films Against *S. aureus*

Content[a] (% w/v)	Killing rate (%)			
	Poly-1	Poly-2	Poly-3	Poly-4
0.16	−27.39	−56.25	−32.72	−72.43
0.31	98.8	90.30	86.70	72.60
0.63	100.00	100.00	96.60	99.97
1.25	100.00	100.00	100.00	100.00
2.50	99.97	100.00	100.00	100.00

[a] Content of PTBAEMA in the solution.

TABLE IV
Killing Rate of Polymer Blend Films Against *E. coli*

Content[a] (% w/v)	Killing rate (%)			
	Blend-1	Blend-2	Blend-3	Blend-4
0.08	−17.39	−4.35	4.35	−8.7
0.16	−13.04	4.35	17.39	90.87
0.31	68.70	34.78	93.91	99.00
0.63	91.74	99.62	99.96	100.00
1.25	99.97	99.98	100.00	100.00

[a] Content of PTBAEMA in the blend solutions. Blends containing PMMA and Poly-1 was termed as Blend-1, and other blends were termed correspondingly.

TABLE V
Killing Rate of Polymer Blend Films Against *S. aureus*

Content[a] (% w/v)	Killing rate (%)			
	Blend-1	Blend-2	Blend-3	Blend-4
0.08	0	0	23.76	34.12
0.16	−3.57	4.35	59.06	33.41
0.31	21.83	56.52	42.59	62.12
0.63	96.59	99.30	99.92	99.24
1.25	100.00	100.00	100.00	100.00

[a] Content of PTBAEMA in the blend solutions. Blends containing PMMA and Poly-1 was abbreviated as Blend-1, and other blends were termed correspondingly.

Consequently, with the increase of M_w, PTBAEMA films formed a stronger electrostatic attraction with bacterial cells, and exerted the antibacterial activity to a greater degree.

Table III revealed the results of waterborne bacteria testing against *S. aureus*. When the concentration reached 0.16% w/v, the number of surviving bacteria decreased after bacterial testing, and the decrease scope increased with the content of PTBAEMA in the polymer films. Meanwhile, it was found that *S. aureus* was more susceptive to PTBAEMA than *E. coli*, as 0.31% w/v of poly-1 killed 98.80% of *S. aureus* and only 11.78% of *E. coli* in the same condition. This is most likely caused by the difference in the cell envelope structure of the two bacteria. Compared to *S. aureus* (gram-positive bacterium), *E. coli* (gram-negative bacterium) possess an extra outer membrane composed of phospholipids, proteins, and lipopolysaccharides, which makes it more resistant to the attack of antibacterial agents.[32]

However, different from *E. coli*, the PTBAEMA films with lower M_w was more biocidal against *S. aureus*, as poly-1 was more biocidal poly-4 at the concentration of 0.16% w/v. This might be relevant to the sensitivity difference and influence of M_w. Since *S. aureus* was more susceptive to PTBAEMA than *E. coli*, the PTBAEMA films could kill *S. aureus* at comparatively lower local concentration of active groups, namely lower M_w. However, as the local congregation of active groups decrease with the decrease of M_w, the contact area between PTBAEMA and *S. aureus* might increase with the decrease of M_w, causing the enhancement of antibacterial activity.

Waterborne bacteria testing of PTBAEMA/PMMA blends

From Tables IV and V, it was found that the good antibacterial activity was retained after PTBAEMA had been blended in PMMA by solvent blending, and the antibacterial activity of polymer blend films increased with the increase of content of PTBAEMA in the polymer films. However, different from PTBAEMA films, polymer blend films tended to be more biocidal against both *E. coli* and *S. aureus* at higher M_w of PTBAEMA. Perhaps after being blended with PMMA, the concentration of active groups was diluted, and it became a decisive factor of the antibacterial performance. Therefore, the increase of M_w was beneficial to enhancing the antibacterial activity of blend films, as it promoted the increase of local concentration of active groups.

Moreover, although the overall antibacterial activity decreased with the decrease of content of PTBAEMA in the blends, it should be point out that the number of bacteria killed by per unit amount of PTBAEMA increased. As PMMA added took a part of surface area that originally covered by PTBAEMA to attack bacteria, the antibacterial

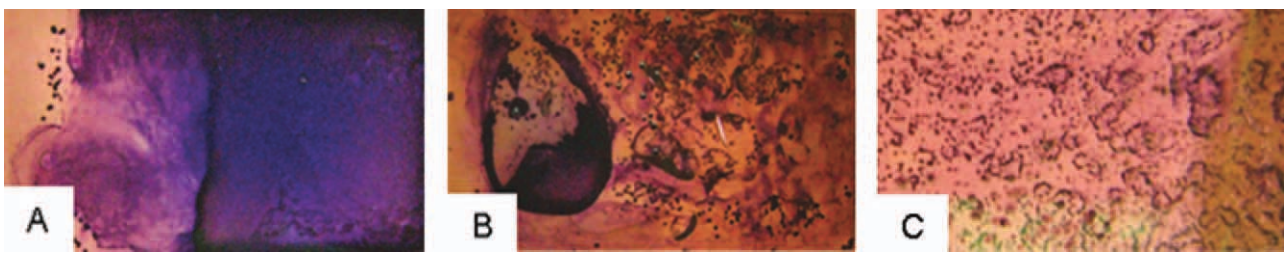

Figure 4 Airborne bacteria testing of polymer films prepared from PMMA/PTBAEMA blends. Blend-1 with PMMA to Poly-1 mol ratios of (A) 1 : 1; (B) 2 : 1; (C) control experiment using blank glass slide. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

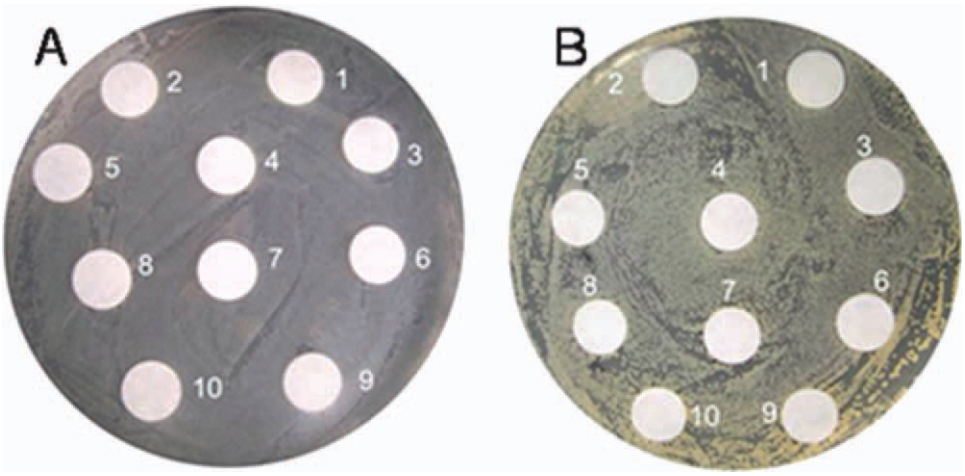

Figure 5 Representative images of inhibition zone test of PMMA/PTBAEMA blends. (A), *E. coli*; (B), *S. aureus*., (1), (2), (3), and (4) were prepared from Blend-1, Blend-2, Blend-3, and Blend-4 with the molar ratio of 1 : 1, respectively, (5), (6), (7), and (8) were prepared from Blend-1, Blend-2, Blend-3, and Blend-4 with the molar ratio of 2 : 1, respectively, (9) and (10) were prepared from Blend-1 and Blend-2 with the molar ratio of 4 : 1, respectively.

activity was somewhat lower than films containing only PTBAEMA. However, considering the dosage of PTBAEMA needed to kill bacteria, it was still attractive to endow the materials of PMMA with antibacterial activity by the addition of PTBAEMA.

Airborne bacteria testing of PMMA/PTBAEMA blends

The ability of PMMA/PTBAEMA films to kill airborne *E. coli* was tested, and the results were shown in Figure 4. The test was first carried out using nutrient agar, but it was not easy to distinguish the lemon yellow *E. coli* colony from the polymer films. Therefore, EMB agar was employed, as it enabled *E. coli* colony to show obvious black color. As seen from Figure 5(C), after spraying the bacterial suspension onto the surface of blank glass slide, numerous colonies of *E. coli* grown were well distinguishable. In Figure 5(A), the blue color was caused by the interaction between PTBAEMA and methyl blue present in EMB agar, and no black bacteria colony existed in the blue area. A few black bacteria spread on the edge of the blue area, which was not covered by the polymer films. It meant that polymer blend films containing 1.25% w/v of poly-1 killed airborne *E. coli* completely. When the content of PTBAEMA was reduced to 0.63% w/v, the reduction of bacteria colony was also observed. Airborne bacteria test was also carried out against *S. aureus* and achieved satisfactory result (results not shown here).

Inhibition zone test

Since the appearance of clear inhibition zone indicates the release of active components, the inhibition zone method was employed to investigate the antibacterial action of PMMA/PTBAEMA blends.[31,32] The test was carried out against both *E. coli* and *S. aureus*. As shown in Figure 5, no obvious inhibition zone was observed, which meant that the active component was not released from the filter paper and stabilized in polymer blends. This proved that the antibacterial action of polymer blends was based on contact-killing mechanism, and the active components were not released into the surrounding environment. Therefore, PMMA/PTBAEMA blends caused less damage to environment, and had the potential to be used in long-term application.

CONCLUSIONS

In conclusion, we have successfully and simply prepared antibacterial PMMA materials by solution blending with water-insoluble antibacterial agent PTBAMA. The polymer blends were partially miscible, which enabled the uniform distribution of PTBAEMA in PMMA materials. Moreover, it was proved that PTBAEMA had good antibacterial activity against both *E. coli* and *S. aureus*, and that the good antibacterial activity was maintained in PMMA/PTBAEMA blends. The as-prepared blends were effective at killing both waterborne and airborne bacteria. Furthermore, it was revealed that the antibacterial action was based on the direct contact between materials and bacteria cells, without the need to release active component to the surrounding environment. Therefore, this rout had combined the safety and durability of contact-killing materials and simple production technology of release-killing antibacterial materials, and obtained antibacterial PMMA materials of high price/performance ratio. We hope that the simple and efficient rout

introduced in this study can be further extended to prepare other antibacterial materials.

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