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Cationic polyesters with antibacterial properties: Facile and controllable synthesis and antibacterial study

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ABSTRACT

In this work, biodegradable antimicrobial cationic copolyesters were prepared via a simple two-step process. Firstly, brominated poly(butylene succinate) (BPBS) was prepared by addition of bromine to carbon–carbon double bonds on the backbone of poly(butylene succinate-*co*-butylene fumarate) (PBSF). Then, the quaternization of BPBS with series of *N*,*N*-dimethyl alkylamines afforded poly(butylene succinate) containing quaternary ammonium cations (QPBS) with various ion contents and alkyl chain lengths. The structures of BPBS and QPBS were systematically characterized by NMR, ATR-FTIR, GPC and XPS. The hydrophilicity and the antibacterial activity have been studied by water contact angle (WCA), inhibition zone method, optical density method and scanning electron microscope (SEM). WCA test indicates that the hydrophilicity of polyester is greatly improved after the introduction of quaternary ammonium cations. The antibacterial study reveals that cationic copolyesters exhibited excellent antibacterial performance for both *S. aureus* and *E. coli* when the alkyl chain length was greater than 8, as compared with the ion content and alkyl chain length is a more important factor for the antibacterial performance. Considering the biodegradation, good antibacterial activities and simple process, this kind of material may have great potential to be applied as biomaterials.

1. Introduction

Pathogenic microorganisms have serious impact on people's lives and property safety, especially in the field of biomedical and daily life applications, such as tissue engineering and regeneration, water treatment, wound dressings, blood purification and surgical sutures [1–12]. Every year, millions of people around the world die of bacterial infections. Therefore, antibacterial materials have attracted growing attentions from both academic researchers and industrial workers [13–17]. In fact, many antimicrobial articles have been reported recently, such as cationic compounds [18–20], chitosan and its derivatives [21,22], zwitterions [23], *N*-halamines [24] and guanidines [25]. The main class of antibacterial materials is antibacterial agent, which is a kind of functional material with antibacterial and bactericidal properties. The abuse of antibiotics makes bacteria resistant to antibacterial drugs. In addition, the organic small molecular antibacterial agent is chemically unstable, hard to process and volatile. Therefore, it is particularly important to develop new antibacterial materials to solve the problems mentioned above [26,27]. Cationic polymers are another important antibacterial material which includes synthetic polymers and natural polymers. But most of the synthetic cationic polymers reported are non-biodegradable. Although natural occurring chitosan has good biodegradability and biocompatibility, it only has antibacterial activity under acidic conditions [28]. Therefore, the synthesis of biodegradable polymers containing quaternary ammonium salt groups with antibacterial properties has important research significance.

In recent years, due to the lower price, good biocompatibility, biodegradability, and low toxicity, aliphatic polyesters, such as poly (lactic acid), polycaprolactone and poly(butylene succinate), have become an important direction for research and development of biodegradable synthetic biomaterials [29–32]. However, most of aliphatic polyesters and copolyesters lack functional groups and hydrophilicity,

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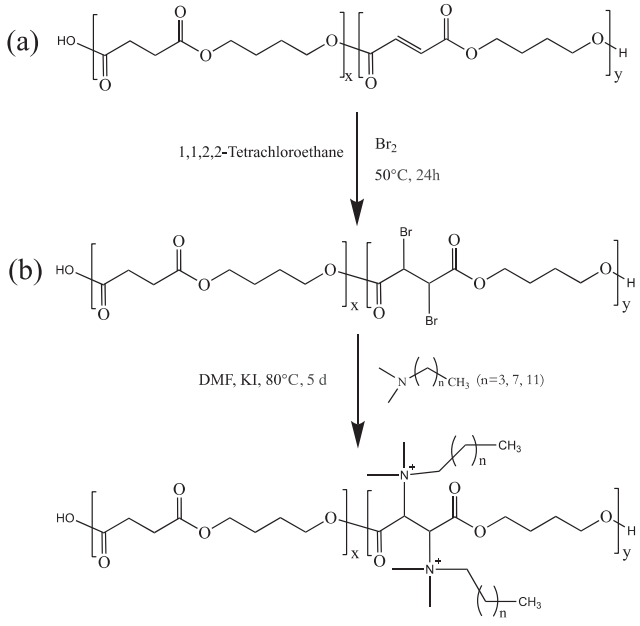
which greatly limit their widespread application [33]. Cationic groups can significantly improve the hydrophilicity and biodegradability of the aliphatic polyester because of their excellent hydrophilicity. Furthermore, they can endow certain antibacterial activity to the biodegradable polyester, which is significant to protect human health from disease attack [34].

Ionic functionalized aliphatic polyester can be synthesized from functional initiators, functional monomers, functional chain extenders or post modification of polymers. Although ionic groups can be introduced by the above methods, they have the drawbacks of low contents of ion groups, employment of toxic catalyst, and long reaction time arising from complex and multistep synthesis process [35–37]. The antibacterial polymers segment can be introduced to the side chain or the backbone of the aliphatic polyester by traditional radical reaction and atom transfer radical polymerization (ATRP) [38–40]. The introduced antimicrobial polymer segment endows the polymer with certain antibacterial properties, but it is not biodegradable because the antibacterial polymer segment is long. Jerome et al. [41] obtained fully biodegradable chlorinated polycaprolactone (PCL) by the ring opening polymerization of α-chlorocaprolactone and caprolactone, and then convert the chlorine atoms into azide group, which was further reacted with a quaternary ammonium salt group containing an alkenyl group by "click" type reaction to obtain an antimicrobial PCL. Although this click chemistry has the advantages of rapidity and good controllability, this "click" type azide-alkenyl requires the use of toxic copper as catalyst, which can form complexation with the triazole ring that is difficult to remove from the polymer. Thus, the biocompatibility of the material will be affected. Zhu et al. [42] synthesized propylene carbonate monomer containing bromine, which was subsequently ring-opened polymerized with caprolactone to afford a bromine-containing poly(ester-carbonate). Then antibacterial poly(ester-carbonate) was obtained by quaternization of bromine. However, the activity of propylene carbonate monomers containing bromine is low. The content of bromine containing carbonate monomer, the lower of polymer molecular weight obtained.

In this paper, we synthesized a series of random copolyesters of poly (butylene succinate-*co*-butylene fumarate) (PBSF) with different content of carbon–carbon double bonds [30,43]. Then cationic copolyesters were synthesized by addition of carbon-carbon double bonds on PBSF with bromine and subsequent quaternization, as shown in Scheme 1. Firstly, brominated poly(butylene succinate) (BPBS) was prepared by



Scheme 1. Synthesis routes of BPBS (a) and cationic copolyesters QPBS (b).

electrophilic addition of bromine to a carbon-carbon double bonds on the backbone of PBSF. Then, the quaternization reaction between BPBS and different tertiary amines gave cationic polyesters containing ammonium groups (QPBS) with various ion contents and alkyl chain lengths. The cationic contents on the side chain can be facilely adjusted by varying C=C content through controlling the feed ratio of fumaric acid to succinic acid. The chemical structures of unsaturated copolyesters and novel cationic polyesters were systematically characterized by FTIR, NMR and GPC. The film surface of unsaturated copolyesters and novel cationic polyesters were studied by water contact angle, X-ray photoelectron spectroscopy (XPS) and scanning electron microscope. The antibacterial capability of cationic copolyesters was studied using *Escherichia coli* and *Staphylococcus aureus*.

2. Experimental

2.1. Materials

Fumaric acid, 1,4-butanediol and succinic acid were purchased from Alfa Aesar (USA), BASF (German) and Anqinghexing Chemical Corp. (China), respectively. Tetra-*n*-butyl-titanate was bought from Nanjing Zunde technology Corp. (China) and distilled before use. *N,N*-dimethyldodecylamine and *N,N*-dimethyl-*n*-octylamine was obtained from TCI (Japan) and Aladdin (China), respectively. All the other reagents and solvents, analytical grade, were purchased from Beijing Chemical Reagents Corp. (China) and used without purification.

2.2. Synthesis of poly(butylene succinate-co-butylene fumarate) (PBSF)

PBSF was prepared as reported earlier [30,43]. Briefly, the random copolyesters of PBSF were synthesized from fumaric acid, succinic acid and 1,4-butanediol with different feed ratios by a two-step esterification and polycondensation. Tetra-*n*-butyl-titanate and hydroquinone were used as catalyst and free radical inhibitor, respectively. The crude products were dissolved in chloroform and insolvable parts were removed by filtration. The chloroform soluble parts were precipitated in excess amount of anhydrous methanol. The precipitates were collected and dried in vacuum oven at 50 °C for 24 h before use.

2.3. Synthesis of brominated poly(butylene succinate) (BPBS)

PBSF20 (the number 20 designates the molar ratio of butylene fumarate repeat units in the copolyester), its brominate-functional polyester of BPBS20 and quaternization cationic polyester of QPBS were chosen as the representative for the synthesis and characterization. BPBS was prepared via addition of bromine to carbon–carbon double bonds. Typically, PBSF20 (5 g, 6.53 mmol of carbon–carbon double bonds) and 1,1,2,2-tetrachloroethane (22.5 mL) were added to a 50-mL flask. Then, bromine (0.97 mL, 19.6 mmol) was added after the solid completely dissolved. The reaction was magnetically stirred at 50 °C for 24 h. The mixture was precipitated in excess anhydrous methanol and filtered, then the precipitate was washed with anhydrous methanol for 3 times. The solid product was dried in vacuum oven at 40 °C for 24 h.

2.4. Synthesis of quaternized BPBS (QPBS)

BPBS20 (1 g, 1.08 mmol of theoretically fully addition bromine content) and KI (3.6 mg, 0.02 mmol) were dissolved in DMF (6 mL). Then, *N,N*-dimethyldodecylamine (2.34 mL, 8.64 mmol) were added to a 25-mL flask. The reaction was magnetically stirred at 80 °C for 5 days. The mixture was precipitated in an excess amount of anhydrous diethyl ether and filtered, then dissolved in dichloromethane and precipitated in anhydrous diethyl ether repeatedly to remove the residual tertiary amine. The final product was dried in vacuum oven at 40 °C for 24 h. 12C, 8C and 4C are abbreviation of *N,N*-dimethyldodecylamine, *N,N*-

dimethyl-*n*-octylamine and *N*,*N*-Dimethyl-butylamine, respectively. For example, QPBS20-12C represent NPBS quaternized with *N*,*N*-dimethyldodecylamine.

2.5. Film preparation

Spin-coating was performed on square coverslips ($1 \times 1\ cm^2$), which were cleaned by sonicating in ethanol for 10 min and acetone for another 10 min and dried in an oven. Cationic polymers were dissolved in $CHCl_3$ (50 mg/mL), and 200 μL of the polymer solution was spin coated on square coverslips at 300 rpm and 60 s, which was then dried and annealed at 50 °C in a vacuum oven.

2.6. Characterization

^1H NMR spectra were acquired with Bruker DMX-400 nuclear magnetic resonance (NMR) spectrometer at room temperature using tetramethylsilane and $CDCl_3$ as internal standard and solvent, respectively. The attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra were recorded on a Thermos Nicolet Avatar 6700 FT-IR equipped with an attenuated total reflectance device (Smart Orbit). The samples were scanned 32 times with a resolution of $4\ cm^{-1}$ from 500 to $4000\ cm^{-1}$ at room temperature. DSC analysis was measured on a DSC Q2000 (Perkin-Elmer instrument) equipped with a CryoFill liquid nitrogen cooling system under N_2 atmosphere. Samples were heated to 150 °C and maintained there for 3 min to eliminate thermal histories, and then quenched to −70 °C at 200 °C min^{-1} using liquid nitrogen as cooling agency and held there for 3 min. After that, the samples were reheated to 150 °C at 20 °C min^{-1} and held there for 3 min before they were cooled to −70 °C at the same rate. Both cooling and heating scans were recorded for analysis. The hydrophilicity of copolyesters were characterized on the basic of static contact angle measurements using a contact angle goniometer (DSA100, KRUSS, German) equipped with a video capture. The volume of the tested water droplet is 5 μL. The surface chemical components of the modified membranes were characterized through X-ray photoelectron spectroscopy (XPS, ESCALAB250XI, USA). The elemental composition of the modified polymer was quantitatively analyzed by elemental analysis (Flash EA 1112, Italy).

2.7. Antibacterial activity tests

Escherichia coli (*E. coli*, Gram-negative bacteria) and *Staphylococcus aureus* (*S. aureus*, Gram-positive bacteria) are used as model bacterial to evaluate the antibacterial characteristics and bactericidal efficacy of the membranes. *E. coli* (MG1655) and *S. aureus* (SA49521) were supplied by the Chinese Academy of Military Medical Sciences. The membrane was prepared on square coverslips with a size of $1 \times 1\ cm^2$. Before the microbiological experiment, all the membrane and the control coverslips were sterilized with ultraviolet light for 30 min. All the experiments were carried out with the initial bacterial concentration of 10^6 colonies forming units per mL (cfu mL^{-1}).

2.7.1. The inhibition zone method

Firstly, the antibacterial capability of functionalized polyester film was investigated by inhibition zone method [10,42]. The sterilized films were placed on the LB agar which was seeded with *E. coli* and *S. aureus* bacterial, respectively, and then incubated at 37 °C for 24 h. PBSF film was taken as control, and a digital camera was used to record inhibition zone.

2.7.2. Morphological observation of the bacteria

For evaluation the adhesion and antibacterial efficacy of the membranes, 0.1 mL of bacteria suspension was dripped onto polymer-coated glass coverslips and incubated at 37 °C for 3 h. Then the coverslips were immersed in 2.5 wt% glutaraldehyde solution at 4 °C for 2 h. For morphology observation, the fixed bacterial samples were subjected to a drying process by passing them through a series of graded alcohol solutions (30, 50, 70, 80, 90, 95 and 100%, 15 min for each time). Samples were dried overnight in a fume hood at room temperature. The samples were sputter-coated with a gold layer and observed under a scanning electron microscope (SU8020, HITACHI, Japan).

2.7.3. The optical density of bacterial count method

To evaluate the antibacterial activity of films in aqueous solution, a piece of sample coated coverslip was immersed in 2 mL of the bacterial suspension and incubated in a shaking incubator at 37 °C, 50 uL of bacteria solution added to 96-well plate at 2, 4, 6, 8 and 24 h, respectively. The optical density of bacterial suspension was measured at 600 nm using microplate reader (SpectraMax i3x).

3. Results and discussion

3.1. Synthesis and characterization of BPBS and QPBS

Synthesis of PBSF is described by Wu et al [30]. The chemical structures of synthesized PBSF, BPBS and QPBS were confirmed by ^1H NMR spectra. Fig. 1a shows the ^1H NMR spectrum and corresponding assignments of PBSF20. Typical signals occurring at 6.85 ppm and 2.62 ppm belong to the unsaturated protons on $-CH{=}CH-$ (a) with *E*-conformation on fumarate and saturated protons of $-CH_2-CH_2-$ (e) on succinate, respectively. Cationic biodegradable polyesters were synthesized by addition of bromine to carbon-carbon double bonds on fumarate and subsequent quaternization with alkyl tertiary amines. As shown in Fig. 1b, the signal at 6.85 ppm, attributed to protons on carbon-carbon double bonds on fumarate, completely disappears in the spectrum of BPBS20. And new signals at 4.68 ppm, belonging to the proton of $>CH-Br$ (a) of brominated succinate moieties, appears on the spectrum of BPBS20. The ^1H NMR results confirm the successful synthesis of BPBS. The ^1H NMR spectrum of cationic copolyester and corresponding assignments are presented in Fig. 1c. Compared with ^1H NMR spectrum of BPBS20, new signals at 3.54–3.61 ppm, 3.47 ppm, 1.25–1.35 ppm and 0.85–0.88 ppm are attributed to the protons of $\equiv N-CH_2-$ (d), $\equiv N-CH_3$ (e), $-CH_2-CH_2-$ (i) and $-CH_3$ (j) of quaternary ammonium salt moieties on side chain. Therefore, it can be concluded that the cationic biodegradable polyesters have been successful synthesized.

The FT-IR spectra were further used to characterize the change of structure before and after ionic functionalization of PBSF (Fig. 2). The absorption peak at $1646.6\ cm^{-1}$ was a characteristic peak of the carbon-carbon double bond of PBSF. After the brominated reaction, this characteristic peak disappears in the BPBS spectrum, indicating that the brominated reaction has proceeded successfully. In the QPBS20-12C spectrum, the absorption peak at $2654.8\ cm^{-1}$ and $1578.8\ cm^{-1}$ are the characteristic peaks of the quaternary ammonium salt, and the absorption peak at $1410\ cm^{-1}$ is arising from C—N group. Therefore, it can reach a conclusion that the quaternary ammonium salt was successfully introduced into the molecular chain of PBSF copolyester.

The average molecular weight and molecular weight distribution of the copolyesters were determined by GPC, and the results were also summarized in Table 1. It can be found that the weight-average molecular weights of PBSF are higher than 9×10^4, which is high enough for application. However, molecular weight and molecular weight distribution of QPBS could not be determined by GPC due to the strong adsorption of quaternary cationic on column. As reported in an earlier literature [43,44], the melting point of PBSF is between the melting point of PBS and PBF homopolymer and approaches to the melting point of PBF homopolymer with the increase of BF content. As shown in Table 2, the contact angle of the pristine PBSF film was as high as 90 ± 1.3°. After cationic functional modification, the water contact angle of film decreased to around 20°, suggesting evident improved hydrophilicity. It is due to the introduction of hydrophilic quaternary

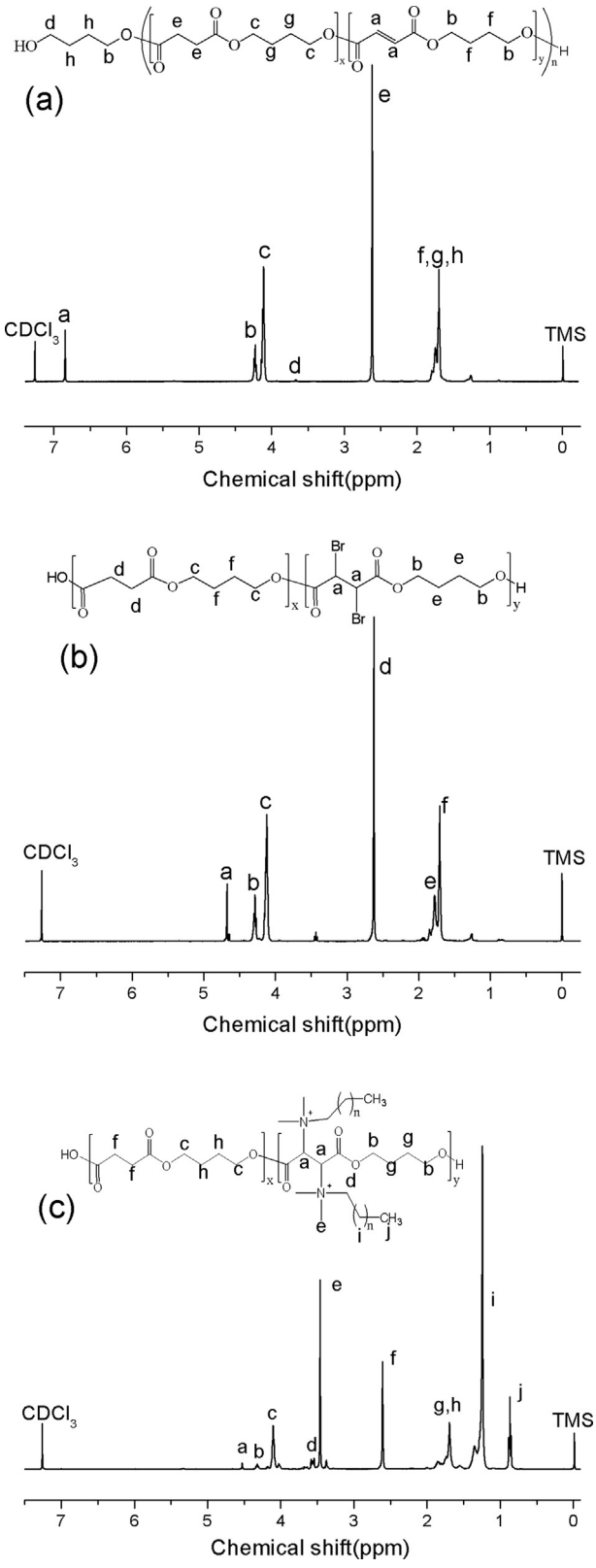


Fig. 1. ^{1}H NMR spectra of PBSF20 (a), BPBS20 (b) and QPBS20-12C (with *N*,*N*-dimethyldodecylamine) (c).

ammonium groups.

X-ray photoelectron spectroscopy (XPS) analysis was employed to determine chemical composition on the surface. At the same time, elemental analysis was used to quantitatively analyze the content of N

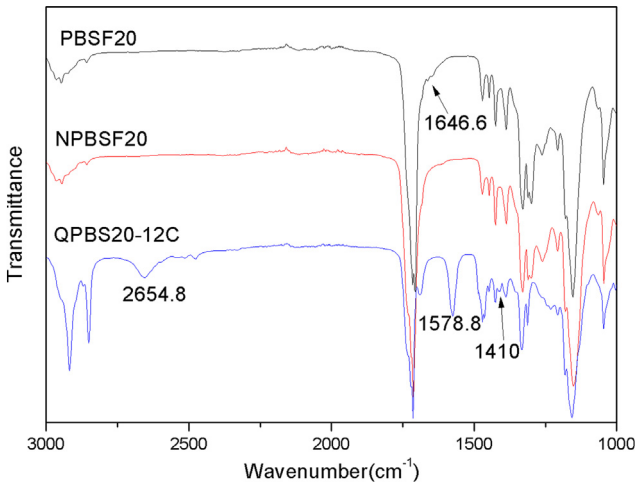


Fig. 2. FT-IR spectra of PBSF20, BPBS20 and QPBS20-12C.

Table 1
Composition, average molecular weight of the synthesized polyesters.

Sample	BS/BF molar ratio		$M_n \times 10^{-4}$ (g mol^{-1})[b]	$M_w \times 10^{-4}$ (g mol^{-1})[b]	M_w/M_n[b]	T_m (°C)
	Feed ratio	Found ratio (%)[a]				
PBSF10	90/10	9.4	4.92	9.02	1.83	114.85
PBSF15	85/15	15.5	4.78	9.31	1.95	116.81
PBSF20	80/20	21.3	5.23	11.75	2.25	117.23

[a] Molar fraction of PBF in copolymers, calculated from ^{1}H NMR.
[b] Measured by GPC.

Table 2
Contact angle measurement of deionized water on PBSF and QPBS coated coverslips film.

Samples	Water contact angle[a]/(deg)
PBSF20	90 ± 1.3
QPBS20-12C	21.4 ± 0.6
QPBS15-12C	22.3 ± 0.4
QPBS10-12C	23.7 ± 0.8
QPBS20-8C	20.3 ± 0.9
QPBS20-4C	19.2 ± 1.1

[a] The results were expressed as mean ± SD (n = 3).

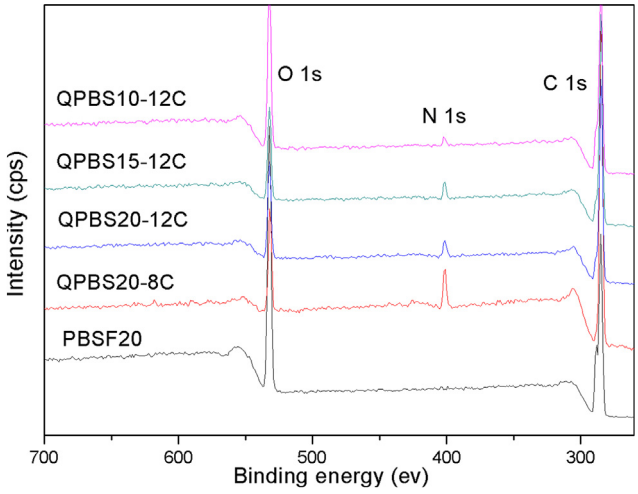


Fig. 3. XPS survey spectra of PBSF20, QPBS20-8C, QPBS20-12C, QPBS15-12C and QPBS10-12C.

Table 3
N content of PBSF20 and QPBS and its film surface.

Samples		PBSF20	QPBS20-8C	QPBS20-12C	QPBS15-12C	QPBS10-12C
N content (%)	Surface value[a]	0	3.11	3.51	3.33	2.05
	Theoretical value[b]	0	2.50	2.27	1.83	1.24
	Bulk value[c]	0	2.48	2.11	1.62	1.23

[a] Determined by XPS.
[b] Calculated by ^{1}H NMR.
[c] Measured by elemental analysis.

in our cationic polymer. It gives the present element peaks on the surface of the pristine PBSF, QPBS coatings (Fig. 3). It can be seen that QPBS-12C film surface exhibited a visible nitrogen atomic peak at 401 eV, which represented the presence of nitrogen element (N 1s peak) arising from the quaternary ammonium group, whereas no nitrogen peak can be found from the spectrum of pristine PBSF. This result confirmed the presence of nitrogen elements on the membrane surface of QPBS. It can be observed from Table 3 that all these surface nitrogen values are greater than the theoretical and bulk nitrogen content. It suggests that quaternary ammonium ions enrich on the membrane surface, which will be favorable to the antibacterial properties of cationic copolyesters. By comparing the N content of bulk value to that of theoretical value, the conversion yield of the quaternary amines can be obtained (QPBS20-8C, 99.2%; QPBS20-12C, 93.0%; QPBS15-12C, 88.5%; QPBS10-8C, 99.2%).

3.2. Antibacterial properties

Antibacterial properties are an important property for antibacterial materials. *E. coli* (Gram-negative bacteria) and *S. aureus* (Gram-positive bacteria) bacteria are used as model bacterial to evaluate the antibacterial characteristics and antibacterial efficacy of biomaterial for biomedical and healthcare application [45]. In this work, the antibacterial activity of the films of cationic copolyester is evaluated by bacterial inhibition zone toward *E. coli* and *S. aureus* bacteria, respectively. Meanwhile, the pristine PBSF membrane is used as control. As predicted, PBSF reveals no inhibition zone for both *E. coli* and *S. aureus*, while cationic copolyesters show great inhibition effect on *E. coli* and *S. aureus* bacteria (Fig. 4), except QPBS20-4C, which has no inhibition zone against for *E. coli* and *S. aureus* bacteria. The sizes of inhibition zones of QPBS20-12C, QPBS15-12C, QPBS10-12C and QPBS20-8C for *E. coli* bacterial are about 8.4 mm, 6.1 mm, 4.9 mm and 1.4 mm, respectively. The sizes of the inhibition zones of QPBS20-12C, QPBS15-12C, QPBS10-12C and QPBS20-8C for *S. aureus* bacteria are about 13 mm, 12.2 mm, 5.9 mm and 4.1 mm, respectively. The results indicate that the quaternary ammonium cationic copolyesters had poor antibacterial activity when the chain length of quaternary ammonium is less than 8 carbons, and cationic copolyesters with longer chain lengths has a larger inhibition zone when the ionic content at the same, implying a greater antibacterial activity. Moreover, the results show that the chain length has a greater effect on the antibacterial activity of the cationic copolyester than the ionic content. Polymers with long-chain alkyl quaternary ammonium salts have been found to have good antibacterial ability in the last century, but the antibacterial mechanism of quaternary ammonium salt polymers is not very clear, and it is generally accepted that it is similar to that of small molecule long-chain alkyl quaternary ammonium salts [46,47]. Long-chain quaternary ammonium salt has antibacterial activity against Gram-positive bacteria and Gram-negative bacteria, and it may be explained as that longer cationic chains has a strong adsorption capacity to bacteria, thereby penetrating the bacterial cytoderm and causing the death of bacteria [16,48,49]. The antibacterial property of quaternary ammonium salt is strongly affected by its hydrophobic group [50]. The cell membrane of bacterial has somewhat hydrophobicity, and the polymer needs some hydrophobicity to better penetrate into the cell membrane through diffusion. The quaternary ammonium salt of longer alkyl chain has higher hydrophobicity and can enter the interior of the cell more easily. Furthermore, when the chain length of alkyl quaternary ammonium is the same, cationic copolyester with a higher cationic content has a larger inhibition zone, indicating higher antibacterial activity towards both *E. coli* and *S. aureus* bacteria. This is consistent with the results of XPS. The results of XPS indicate that cations enrich on the film surface of the cationic copolyester. In particular, when the alkyl chain length is 12, higher cationic content of quaternary ammonium salt polyester has greater antibacterial activity.

In order to test the antibacterial ability of the cationic copolyester membrane in aqueous solution. A series of cationic copolyester membranes were immersed in bacterial suspension with a concentration of 10^6 cfu mL^{-1}, then the optical density of co-culture solutions at 600 nm (OD 600) was detected at 2, 4, 6, 8 and 24 h, respectively. Fig. 5 showed that the OD600 curves of cationic copolyester films in the presence of *E. coli* or *S. aureus*. A control experiment was also carried out with bacterial broth on pristine PBSF film. High OD600 value represents high concentration of bacterial and poor antibacterial property. In our study, the OD value of *N*,*N*-dimethyldodecylamine quaternized polyesters changes little after 24 h of culture compare to 3 h of culture, which suggests that QPBS20-12C showed good inhibitory effect against *E. coli* and *S. aureus*. For non-quaternized polyester or with the alkyl chain length of the quaternary ammonium salt less than 8 carbons, their OD values were higher or even close to the OD value of the blank group, which implies poor inhibition effect or no inhibition effect. Comparing three cationic copolyesters quaternized with *N*,*N*-dimethyldodecylamine, it can be found that even the molar content of quaternary ammonium salt is only 10%, it has a good antibacterial property. Moreover, quaternized copolyester containing a dodecyl chain show a better inhibition of bacterial growth in this work. This result is consistent with that of inhibition zone. As discusses before, it is due to the stronger adsorption capacity and higher hydrophobicity of longer cationic chains.

We further investigated the morphology of *S. aureus* and *E. coli* bacteria after incubation with PBSF and QPBS20-12C film for 3 h by SEM. A large amount of bacterial adhered on the PBSF film surface, and most of the adhered bacteria aggregate into clusters and almost cover the whole membrane surface. In contrast, only a few bacterial could be found on QPBS20-12C film surface, suggesting that the existing quaternary ammonium salt segment on these coatings effectively prevented bacterial adhesion. Generally, hydrophobic PBSF membrane surface can easily adsorb biomolecules and enhance microorganism adhesion. Therefore, it can be concluded that the bacterial adhesion was directly affected by the quaternary ammonium groups on the surface of cationic copolyester and cationic copolyester has a certain antibacterial ability and its film has anti-adhesion properties to bacteria (Fig. 6).

4. Conclusions

In this study, quaternary ammonium cationic copolyesters were successfully prepared facilely via a two-step process of bromine and subsequent quaternization at low cost. The ionic content and the alkyl

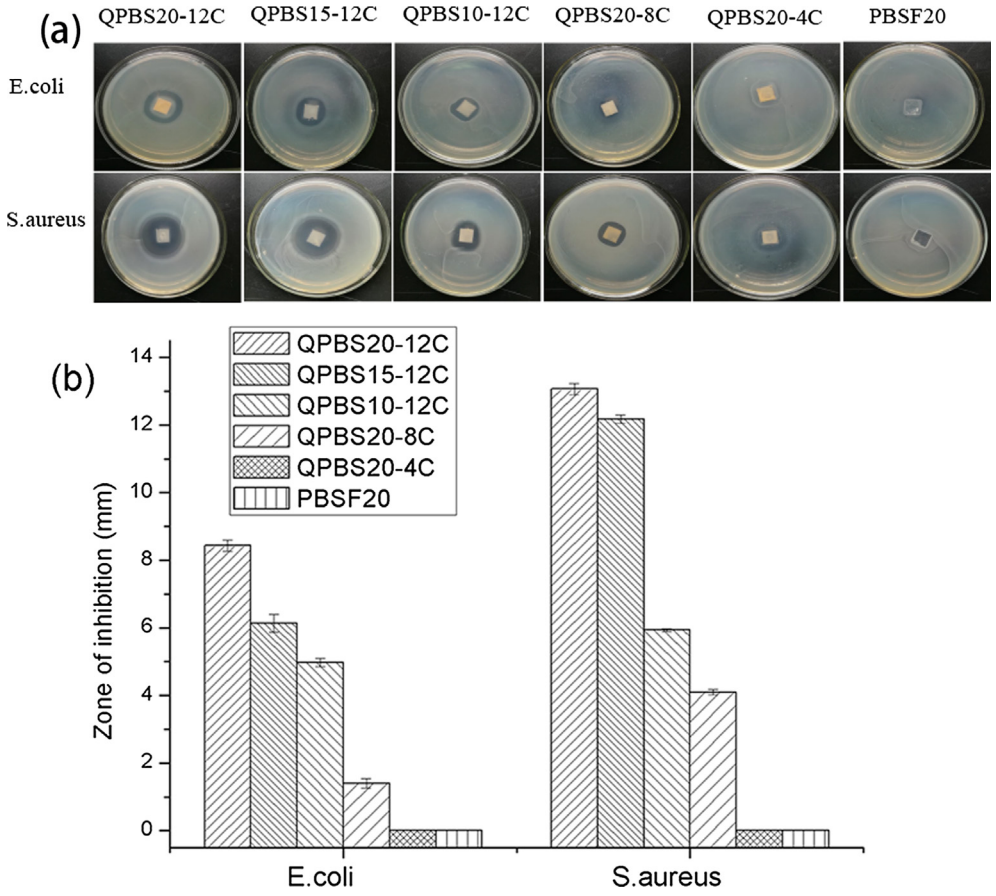


Fig. 4. The inhibition zone photographs of PBSF and QPBS contact against *E. coli* and *S. aureus* bacteria (a). The sizes of inhibition zone of PBSF and QPBS contact against *E. coli* and *S. aureus* bacteria (b). The results were expressed as mean ± SD (n = 3).

chain length of this cationic polyester can be easily controlled. Hydrophilicity of cationic functionalized copolyester was greatly improved after the introduction of quaternary groups. The antibacterial results show that cationic polyesters possess good antibacterial activities when the side chain length of quaternary ammonium on cationic copolyester is higher than 8 carbons and the antibacterial activities increases with content of cationic.

5. Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical or time limitations. The data will be made available upon request.

Acknowledgments

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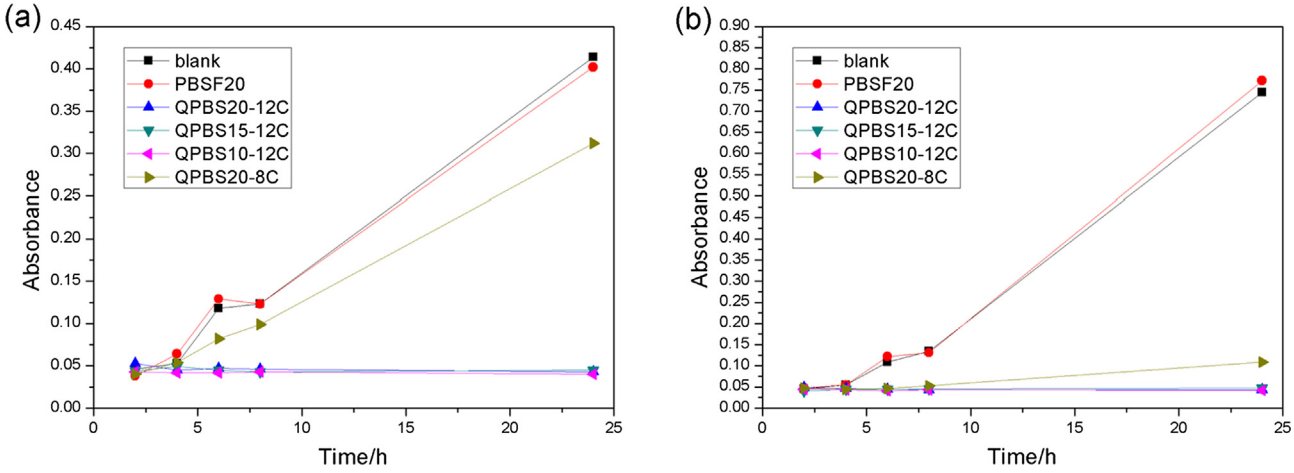

Fig. 5. Antibacterial evaluations of QPBS against *E. coli* (a) and *S. aureus* (b) bacteria by optical density method.

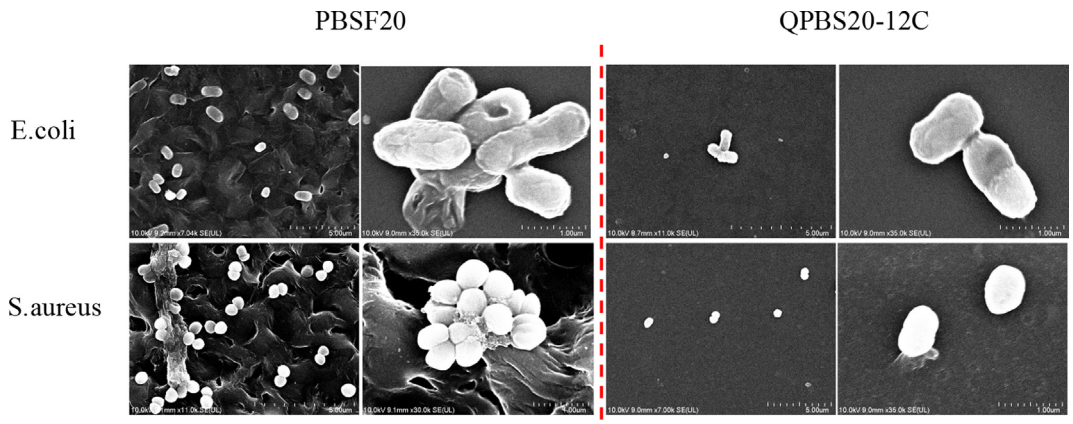

Fig. 6. SEM images of the morphologies of *E. coli* and *S. aureus* cultured on PBSF and QPBS20-12C film surfaces for 3 h.

acknowledged.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.eurpolymj.2018.11.009.

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