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Synthesis of Poly(hydroxyurethane)s from Di(trimethylolpropane) and Their Application to Quaternary Ammonium Chloride-functionalized Films

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Poly(hydroxyurethane)s (PHUs) are synthesized by polyaddition of di(trimethylolpropane) carbonate (DTMPC) and a series of conventional aliphatic diamines and chemically modified through their side chains to design quaternary ammonium chloride (QAC)-functionalized PHU films. The reaction of DTMPC with a subtle excess of diamines affords PHUs with well-controlled molecular weights and polydispersities. The hydroxyl groups of these PHUs are modified with chloroacetyl chloride and then reacted with N,N-dimethyl-n-octylamine (DMOA) to easily give QAC-functionalized PHUs. On the other hand, the reaction of these PHUs with cross-linkable N,N,N',N'-tetramethyl-1,6-diaminohexane (TMDAH) undergoes quaternization and simultaneously forms networked structures, resulting in the formation of QAC-functionalized PHU network films. Especially, The usage of 20 mol% of TMDAH with respect to chloroacetyl groups of the PHU unit gives a self-supported film with well transparency and higher thermal stability. Furthermore, remaining chloroacetyl groups of the film can be modified with DMOA to afford PHU films with dually-structured QAC moieties. The resulting PHU film constructs the positively charged surfaces with a zeta potential of +8.3 mV.

Introduction

Poly(hydroxyurethane)s (PHUs) have been attracting a huge interest in the promising alternatives of widely-used polyurethanes because PHUs can be synthesized by ring-opening polyaddition of bifunctional cyclic carbonates and diamines without using toxic isocyanates.[1-20] Especially, five-membered cyclic carbonates can be derived from epoxides and CO_2 under mild conditions, therefore, the studies on PHUs are interested in the field of green chemistry. Numerous PHUs have been synthesized from bisphenol A[3-10] and bio-based polyols[11-15] as starting materials. PHUs are also interested in the introduction of functionalities by the usage of functional diamines or by chemical modifications via hydroxyl side chains. Nowadays it has been reported that silicone-conjugated PHUs show lower glass transition temperatures and well water repelling properties[3] and network gels of PHUs are obtainable by the reaction with aluminum or titanium alkoxides[10] or by the free-radical polymerization of PHUs bearing methacryl groups[5]. In addition, urethane linkages of PHUs can be degraded at alkaline conditions and further shows biodegradability, thus, PHUs are one of promising candidates for versatile materials based on biocompatibility and biodegradability. However, these PHUs are generally synthesized via five-membered cyclic carbonates and PHUs from six- or seven-membered cyclic carbonates are hardly reported except for a few case.[16-20] Especially, the ring-opening reaction of six-membered cyclic carbonates with amines requires the lower energy compared to five-membered carbonates[16-20] because ring strain energy of 6-membered cyclic carbonates are larger than that of 5-membered cyclic carbonates.[19] This implies that PHUs can be synthesized at milder conditions. Besides, differing from five- or seven-membered cyclic carbonates, six-membered cyclic carbonates generate only primary alcohols (hydroxymethyl groups) after the ring-opening reaction with amines, therefore, simple structured PHUs can be obtained.

Antimicrobial polymers are widely used for medical apparatus and implant materials and nowadays has attracting increasing attentions because of the spreading of infection diseases caused by multi-drug-resistant bacteria.[21,49] Since silver species especially silver nanoparticles are classically known for effective antimicrobial agents, Ag-conjugated polymer materials including polyurethanes are prepared.[21-26,39,40] The antimicrobial activity of Ag nanoparticles is depended on their particle sizes, therefore, control of the size and uniform spreading of them in the matrices are required. Furthermore, the leaching of high concentrated Ag ions are considered to be caused by cytotoxicity.[23,24] On the other hands, cationic polymers with amphiphilicity possibly show broad-spectrum antimicrobial properties through the membrane disrupting mechanism.[27,28,33-38,41-49] For the cationic moieties, quaternary ammonium salts (QAS)[27,28,33-38,41-46],

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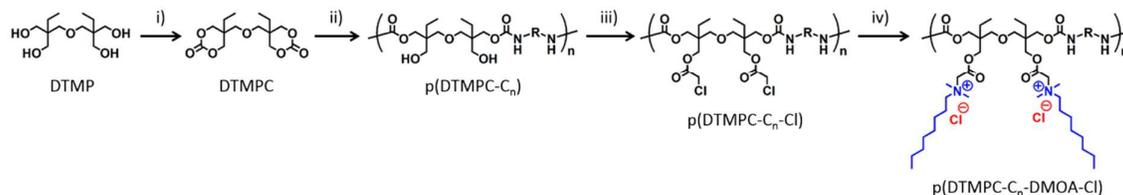
Scheme 1 Synthesis of quaternary ammonium chloride (QAC)-functionalized poly(hydroxyurethane) (PHU) from di(trimethylolpropane) (DTMP) by four steps: transesterification, polyaddition, chloroacetylation and quaternization. i) 4 equiv. of diphenyl carbonate (DPC), 140 °C, 48 h. ii) 1.0 or 1.1 equiv. of aliphatic diamines (n = 3, 6 or 12), DMF, 70 °C, 24 h. iii) 1.5 equiv. of chloroacetyl chloride, 1.1 equiv. of pyridine, 0 °C to ambient temperature, overnight, iv) 6 equiv. of *N,N*-dimethyl-*n*-octylamine (DMOA), DMF, 80 °C, 6 h.
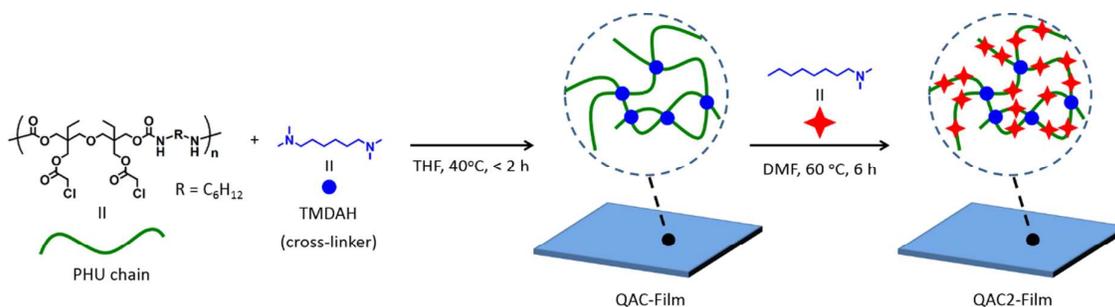
Scheme 2 Fabrication of QAC-functionalized PHU films (QAC-Films) via quaternization by cross-linkable *N,N,N',N'*-tetramethyl-1,6-diaminohexane (TMDAH) and subsequent modification with DMOA to form PHU films with dual QAC moieties (QAC2-Films).

quaternary phosphonium salts[46], protonated amine groups[47-49] effectively generate antimicrobial properties. Nowadays wide varieties of cationic polymers such as polyacrylates[22,40,45], polymethacrylate[41-43,46,49], polycarbonates[33-38], polypeptides[47], polyamines[48] are designed and characterized for their antimicrobial properties in many matrices including solution, films and gels. In contrast, the antimicrobial PHUs are rarely reported.[21] Furthermore, the film processing of antimicrobial polymers are of great importance for practical uses. However, antimicrobial polymer films reported generally require multi-step treatments: polymerizations, pre/post modifications of antimicrobial agents, formations of films by coating or casting and so on. Thus, it is fascinating theme for establishing the facile fabrication routes to antimicrobial polymer films.

Here we report the facile fabrication of quaternary ammonium chloride (QAC)-functionalized PHU from bifunctional six-membered cyclic carbonates and conventional aliphatic diamines and their application to antimicrobial films. As a bifunctional carbonate, we selected di(trimethylolpropane) carbonate (DTMPC). DTMPC can be synthesized from commercially-obtainable di(trimetylolpropnae) (DTMP) through the reaction with diphenyl carbonates (DPCs).[50] DPC is less toxic and easier to handle than conventional phosgene and its derivatives and moreover is obtainable from ethylene carbonate through the reaction with methanol and phenol or from CO and phenol.[51-54] Therefore, in the overall reaction, it worth synthesizing PHUs from DTMPC in terms of green chemistry. The introduction of QAC moieties in PHUs is accomplished by OH groups of PHUs after suitable chemical modifications such as chloroacetylation, which allows us to expect that the reaction of chloroacetylated PHUs with di(tertiary amine)s is resulted in

the quaternization of the PHU chains and concomitant formation of cross-linked structures to afford easily QAC-functionalized PHU films. First, we synthesized PHUs from DTMPC and conventional aliphatic diamines with different methylene spacers (Scheme 1). Next, we modified the OH groups of the PHUs with chloroacetyl chloride to obtain chloroacetylated PHUs and finally reacted with *N,N*-dimethyl-*n*-octylamine (DMOA) to yield QAC-functionalized PHUs. As another approach, we reacted the chloroacetylated PHUs with a different amount of cross-linkable *N,N,N',N'*-tetramethyl-1,6-diaminohexane (TMDAH) to fabricate QAC-functionalized PHU films (Scheme 2). Furthermore, these films were modified with DMOA to obtain PHU films with dual QAC moieties. These QAC-functionalized PHUs and QAC-functionalized PHU films were characterized by ^{1}H nuclear magnetic resonance (NMR), Fourier transform-infrared (FT-IR) spectroscopy, size exclusion chromatography (SEC), thermogravimetric analysis (TGA), UV/vis.-near infra-red (NIR) absorption spectroscopy, elemental analysis (E. A.) and zeta potential measurements.

Experimental

Materials

Di(trimethylolpropane) (DTMP) was obtained from Aldrich Co., Ltd. Diphenyl carbonate (DPC) was supplied from Asahi Kasei Chemical Co., Ltd and purchased from Tokyo Chemical Industry Co., Ltd. Di(trimethylolpropane) carbonate (DTMPC) was synthesized from DTMP with an excess amount of DPC according to the procedure that we previously reported.[50] A series of aliphatic diamines was purchased from Tokyo Chemical Industry Co., Ltd. and Aldrich Co., Ltd. and used without any purification. Chloroacetyl chloride, anhydrous

pyridine, *N*,*N*-dimethyl-*n*-octylamine (DMOA) and *N*,*N*,*N'*,*N'*-tetramethyl-1,6-diaminohexane (TMDAH) were obtained from Tokyo Chemical Industry Co., Ltd. Other reagents and solvents were used without any purification.

Synthesis of PHUs (p(DTMPC-Cₙ))

General procedure.

DTMPC 604 mg (2.00 mmol) and aliphatic diamines (C_n) (2.20 mmol) were dissolved in DMF (4 mL) and the solution ($[C_n]_0/[DTMPC]_0 = 1.1$) was stirred at 70 °C for 24 h. The solution was added to water (200 mL) and allowed to stand at 4 °C overnight. Resulting precipitates were washed thoroughly with water and then dissolved in methanol. After drying by rotary evaporator, p(DTMPC-C_n) was obtained as white solids or colorless sticky liquid. PHUs obtained were characterized by SEC measurements, ^{1}H NMR and FT-IR spectroscopy. The results of SEC measurements are summarized in Table 1.

Synthesis of p(DTMPC-C₃)

p(DTMPC-C_3) was synthesized by the reaction of DTMPC and 1,3-diaminopropane (C_3). Yield: 40.0%. ^{1}H NMR (400 MHz, CD₃OD, δ): 4.05-3.90 (m, 4H, CH₂OC=O), 3.43 (s, 4H, CH_2OH), 3.32 (s, 0.6H, N*H*CO), 3.25 (s, 4H, CH₂OCH₂), 3.11 (t, 4H, *J* = 6.8 Hz, CH_2NHCOO), 2.66 (t, 0.4H, *J* = 7.2 Hz, CH_2NH₂), 1.63 (qui, 2.2H, *J* = 6.5 Hz, CH_2CH₂NHCOO), 1.37 (q, 4H, *J* = 7.3 Hz, CH₃CH_2), 0.86 (t, *J* = 6.6 Hz, 6H, CH₃). IR (ATR): ν = 3320 (w; ν(OH) and ν(NH)), 2958-2876 (w; ν(CH₂)), 1689 (s; ν(C=O)), 1530 (m; δ(N-H)), 1253 cm⁻¹ (s; ν(C-O)).

Synthesis of p(DTMPC-C₆)

p(DTMPC-C_6) was synthesized by the reaction of DTMPC and 1,6-diaminohexane (C_6). Yield: 85.9%. ^{1}H NMR (400 MHz, DMSO-d₆, δ): 4.05-3.93 (m, 4H, CH₂OC=O), 3.43 (s, 4H, CH_2OH), 3.25 (s, 4H, CH₂OCH₂), 3.06 (t, 4H, *J* = 7.0 Hz, CH_2NHCOO), 2.63 (t, 0.4H, ₁ = 7.2 Hz, CH_2NH₂), 1.47 (m, 4.4H, CH_2CH₂NHCOO), 1.37 (q, *J* = 7.2 Hz, 4H, CH₃CH_2), 1.32 (m, 4.4H, CH_2CH₂CH₂NH), 0.85 (t, *J* = 7.6 Hz, 6H, CH₃). IR (ATR): ν = 3305 (w; ν(OH) and ν(NH)), 2928-2957 (w; ν(CH₂)), 1665 (s; ν(C=O)), 1531 (m; δ(N-H)), 1242 cm⁻¹ (s; ν(C-O)).

Synthesis of p(DTMPC-C₁₂)

p(DTMPC-C_{12}) was synthesized by the reaction of DTMPC and 1,12-diaminododecane (C_{12}). Yield: 99.3%. ^{1}H NMR (400 MHz, CD₃OD, δ): 3.96-3.93 (m, 4H, CH_2OC=O), 3.43 (s, 4H, CH_2OH), 3.32 (s, 0.6H, NHCO), 3.24 (s, 4H, CH₂OCH2), 3.05 (t, 4H, *J* = 7.2 Hz, CH_2NHCOO), 2.65 (t, 0.4H, *J* = 7.2 Hz, CH_2NH₂), 1.46 (m, 4.4H, CH_2CH₂NHCOO), 1.37 (q, 4H, *J* = 7.5 Hz, CH₃CH_2), 1.28 (m, 17.6H, NHCH₂CH₂-(CH_2)₈), 0.85 (t, *J* = 7.4 Hz, 6H, CH₃). IR (ATR): ν = 3316 (w; ν(OH) and ν(NH)), 2924-2853 (w; ν(CH₂)), 1690 (s; ν(C=O)), 1534 (m; δ(N-H)), 1255 cm⁻¹ (s; ν(C-O)).

Synthesis of chloroacetylated PHUs (p(DTMPC-Cₙ-Cl))

General procedure.

To a DMF solution of p(DTMPC-C_n) (8 mL, 4 unit mmol) were added slowly chloroacetyl chloride 1276 mg (11.3 mmol) and pyridine 722 mg (9.13 mmol) at 0 °C. The mixture was stirred at ambient temperature overnight and then solvents were

evaporated. The pale yellow residues were dissolved in dichloromethane (250 mL) and washed three times with water (250 mL) and then dried over anhydrous sodium sulfate. After evaporation, p(DTMPC-C_n-Cl) was obtained as pale yellow sticky liquid. Chloroacetylated PHUs obtained were characterized by SEC measurements, ^{1}H NMR and FT-IR spectroscopy. M_n and M_w/M_n were calculated from SEC traces and the reaction efficiency of chloroacetylation was determined by ^{1}H NMR spectra. These results are listed in Table 1.

Synthesis of p(DTMPC-C₃-Cl)

Yield: 100.6%. ^{1}H NMR (400 MHz, CDCl₃, δ): 5.38 (br, 2H, NH), 4.14-4.00 (m, 12.4H, CH₂OC=O and ClCH₂), 3.40-3.36 (m, 0.4H, ClCH_2CONHCH₂), 3.29 (s, 4H, CH₂OCH₂), 3.22 (m, 4H, CH_2NHCOO), 1.72-1.65 (m, 2.2H, CH_2CH₂NHCOO), 1.43 (q, *J* = 7.2 Hz, 4H, CH₃CH_2), 0.87 (t, 6H, *J* = 7.6 Hz, CH₃). IR (ATR): ν = 3331 (w; ν(NH)), 2972-2880 (w; ν(CH₂)), 1700 (s; ν(C=O)), 1243 cm⁻¹ (s; ν(C-O)).

Synthesis of p(DTMPC-C₆-Cl)

Yield: 96.7%. ^{1}H NMR (400 MHz, CDCl₃, δ): 4.95 (br, 2H, NH), 4.10-3.99 (m, 12.4H, CH₂OC=O and ClCH₂), 3.28 (s, 4H, CH₂OCH₂), 3.15 (m, 4H, CH_2NHCOO), 1.50 (m, 4.4H, CH_2CH₂NHCOO), 1.42 (q, *J* = 7.6 Hz, 4H, CH₃CH_2), 1.33 (m, 4.4H, CH_2CH₂CH₂NH), 0.86 (t, 6H, *J* = 7.0 Hz, CH₃). IR (ATR): ν = 3342 (w; ν(NH)), 2969-2855 (w; ν(CH₂)), 1699 (s; ν(C=O)), 1240 cm⁻¹ (s; ν(C-O)).

Synthesis of p(DTMPC-C₁₂-Cl)

Yield: 99.2%. ^{1}H NMR (400 MHz, CDCl₃, δ): 4.87 (br, 1.6H, NH), 4.11-3.99 (m, 12.4H, CH₂OC=O and ClCH₂), 3.28 (s, 4H, CH₂OCH₂), 3.15 (q, *J* = 6.8 Hz, 4H, CH₂NHCOO), 1.49-1.40 (m, 8.4H, CH_2CH₂NHCOO and CH₃CH_2), 1.29-1.26 (m, 17.6H, NHCH₂CH₂-(CH_2)₈-CH₂CH₂NH), 0.86 (t, 6H, *J* = 7.4 Hz, CH₃). IR (ATR): ν = 3321 (w; ν(NH)), 2948-2851 (w; ν(CH₂)), 1742-1667 (s; ν(C=O)), 1240 cm⁻¹ (s; ν(C-O)).

Synthesis of QAC-functionalized PHUs (p(DTMPC-Cₙ-DMOA-Cl))

General procedure.

To a DMF solution (5 mL) of chloroacetylated PHUs (0.5 unit mmol) was added DMOA (3 mmol) at ambient temperature. After stirred at 80 °C for 6 h, the solution was added slowly to THF (200 mL) at ambient temperature. Resulting precipitates were washed with THF and then dissolved in dichloromethane and then precipitated from n-hexane. After washing with *n*-hexane and drying, QAC-functionalized PHUs (p(DTMPC-C_n-DMOA-Cl)) were obtained as pale yellow solids. QAC-functionalized PHUs obtained were characterized by SEC measurements, ^{1}H NMR and FT-IR spectroscopy. M_n and M_w/M_n were calculated from SEC traces and the reaction efficiency of quaternization was determined by ^{1}H NMR spectra. These results are listed in Table 1.

Synthesis of p(DTMPC-C₃-DMOA-Cl)

Yield: 80.4%. ^{1}H NMR (400 MHz, CD₃OD, δ): 4.48 (s, 3.2H, N⁺CH₂C=O), 4.18-3.97 (m, 7.9H, CH₂OC=O), 3.57 (m, 4.4H, CH_2N⁺CH₂C=O), 3.35-3.26 (m, CH₂OCH₂ and (CH₃)₂N⁺), 3.09 (m,

4H, CH_2NHCOO), 1.77 (m, 4.4H, CH_2CH$_2$N$^+$), 1.71-1.62 (m, 2.4H, CH_2CH$_2$NHCOO) 1.48 (q, J = 7.2 Hz, 4.0H, CH$_3$CH_2), 1.36-1.30 (m, 23.0H, CH$_3$-(CH_2)$_5$-CH$_2$CH$_2$N$^+$), 0.89 (t, 6H, J = 7.0 Hz, CH$_3$). IR (ATR): ν = 3361 (w; ν(OH)), 3220 (w; ν(NH)), 2940-2854 (w; ν(CH$_2$)), 1746 (s; ν(C=O of ester)), 1703 (s; ν(C=O of urethane)), 1244 cm^{-1} (s; ν(C-O)).

Synthesis of p(DTMPC-C$_6$-DMOA-Cl)

Yield: 78.9% . ^{1}H NMR (400 MHz, CD$_3$OD, δ): 4.47 (s, 1.6H, N$^+$CH$_2$C=O), 4.19-3.98 (m, 8H, CH$_2$OC=O), 3.58 (t, J = 8.4 Hz, 4.4H, CH$_2$N$^+$CH$_2$C=O), 3.31-3.30 (m, CH$_2$OCH$_2$ and (CH$_3$)$_2$N$^+$), 3.06 (m, 4H, CH_2NHCOO), 1.79 (br, 4.4H, CH_2CH$_2$N$^+$), 1.49-1.48 (m, 8.4H, CH_2CH$_2$NHCOO and CH$_3$CH_2), 1.38-1.32 (m, 26.4H, (CH_2)$_2$-CH$_2$CH$_2$NH and CH$_3$-(CH_2)$_5$-CH$_2$CH$_2$N$^+$), 0.91 (t, 6H, J = 6.8 Hz, CH$_3$). IR (ATR): ν = 3360 (w; ν(OH)), 3222 (w; ν(NH)), 2953-2855 (w; ν(CH$_2$)), 1746 (s; ν(C=O of ester)), 1700 (s; ν(C=O of urethane)), 1244 cm^{-1} (s; ν(C-O)).

Synthesis of p(DTMPC-C$_{12}$-DMOA-Cl)

Yield: 81.8%. ^{1}H NMR (400 MHz, CD$_3$OD, δ): 4.45 (s, 3.2H, N$^+$CH$_2$C=O), 4.16-3.96 (m, 12.4H, CH$_2$OC=O), 3.55 (t, J = 8.4 Hz, 4.2H, CH_2N$^+$CH$_2$C=O), 3.33-3.20 (m, CH$_2$OCH$_2$ and (CH$_3$)$_2$N$^+$), 3.03 (t, J = 6.8 Hz, 4H, CH_2NHCOO), 1.77 (br, 4.0H, CH_2CH$_2$N$^+$), 1.47-1.44 (m, 8.2H, CH_2CH$_2$NHCOO and CH$_3$CH_2), 1.36-1.28 (m, 38.6H, NHCH$_2$CH$_2$-(CH_2)$_8$-CH$_2$CH$_2$NH and CH$_3$-(CH_2)$_5$-CH$_2$CH$_2$N$^+$), 0.89 (t, 6H, J = 6.8 Hz, CH$_3$). IR (ATR): ν = 3348 (w; ν(OH)), 3215 (w; ν(NH)), 2917-2852 (w; ν(CH$_2$)), 1747 (s; ν(C=O of ester)), 1699 (s; ν(C=O of urethane)), 1246 cm^{-1} (s; ν(C-O)).

Fabrication of QAC-functionalized PHU films (QAC-Films)

To a THF (2 mL) dissolving chloroacetylated PHUs (p(DTMPC-C$_n$-Cl)) (2 unit mmol) was added TMDAH (0-4 mmol). The solutions with a different mole ratio of TMDAH to chloroacetyl group from 0 to 50 mol% were stirred for a few minutes at ambient temperature and moved to a glass Petri dish in 6 cm diameter. After dried at 40 °C within 2 h, the PHU films were formed.

Fabrication of dually-functionalized PHU film (QAC2-Film)

The QAC-Film prepared with 20 mol% of TMDAH was immersed in a DFM solution (50 mL) of DMOA 950 mg (6.00 mmol, ca. 5 equiv. with respect to chloroacetyl groups of PHU unit) and allowed to stand at 60 °C for 6 h. After the reaction, the film was rinsed three times by immersion in acetone and dried under an ambient atmosphere to yield dually-functionalized PHU film (QAS2-Film).

Characterization

^{1}H NMR spectroscopy were performed with a JEOL ECS-400 NMR spectrometer operating at 400 MHz using a tetramethylsilane as an internal reference. FT-IR spectroscopy was carried out with a Thermo Fisher Scientific Nicolet iS10 equipped with an ATR instrument. SEC was conducted with a Tosoh HLC-8320GPC equipped with an analytical column (6 mmØ x 150 mm) using DMF as an eluent operating a flow rate of 0.5 mL min^{-1} at 40 °C. Number averaged molecular weight
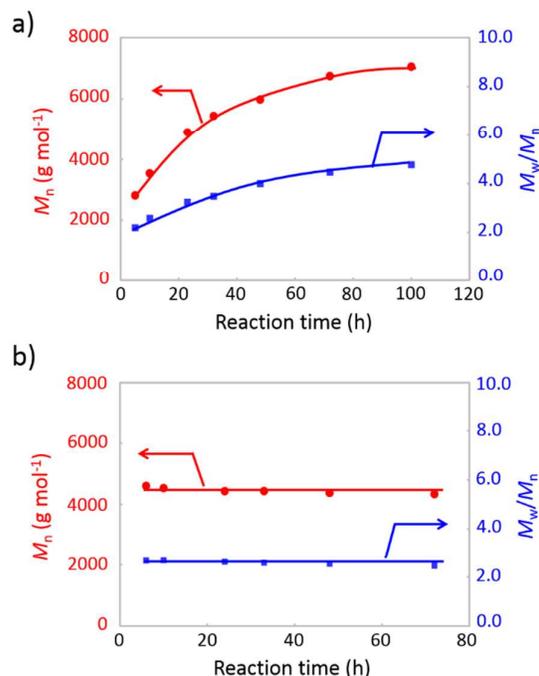
Figure 1 Time-course analysis of the polymerization of DTMPC and C$_6$ with different DTMPC/C$_6$ feed ratios in DMF at 70 °C. Initial C$_6$/DTMPC mole ratios ([C$_6$]$_0$/[DTMPC]$_0$) were a) 1.0 or b) 1.1. The M_n and M_w/M_n were calculated by SEC traces and plotted as a function of reaction time.

(M_n) and polydispersity index (M_w/M_n) were calculated from SEC traces using polystyrene standards. TGA was performed with a Seiko Instrument Inc. TG/DTA 6200 at a heating rate of 10 °C min^{-1} under nitrogen gas at a flow rate of 200 mL min^{-1}. UV/vis absorption spectra were recorded on a Jasco V570UV/Vis/NIR spectrophotometer. Zeta potential of film samples was measured with a Zeta-potential and Particle size analyser ELSZ-2 (Otuka Electronics Co., Ltd.) using a flat surface cell unit. The sample were measured in 10 mM NaCl solution at 26 °C and pH 7. The zeta potential values in volts were determined by the Smoluchowski method.

Results and discussion

Synthesis of PHUs from DTMPC and a series of conventional aliphatic diamines

DTMPC was synthesized from DTMP and an excess amount of DPC according to the procedure we previously reported[50]. The reaction of DTMPC and 1,6-diaminohexane (C$_6$) was performed in DMF at 70 °C at different C$_6$/DTMPC feed ratios without any catalysts. The reaction mixtures were characterized by SEC measurements (Figure S1) and M_n and M_w/M_n were calculated by their SEC traces. The results obtained were plotted as functions of reaction time in Figure 1. When the mixture at a C$_6$/DTMPC feed ratio of 1.0 was reacted for 5 h, M_n and M_w/M_n were 2,800 g mol^{-1} and 2.20, respectively. These values gradually increased with an increase in reaction time and at 100 h reached up to 7,000 g mol^{-1} and 4.0, respectively.
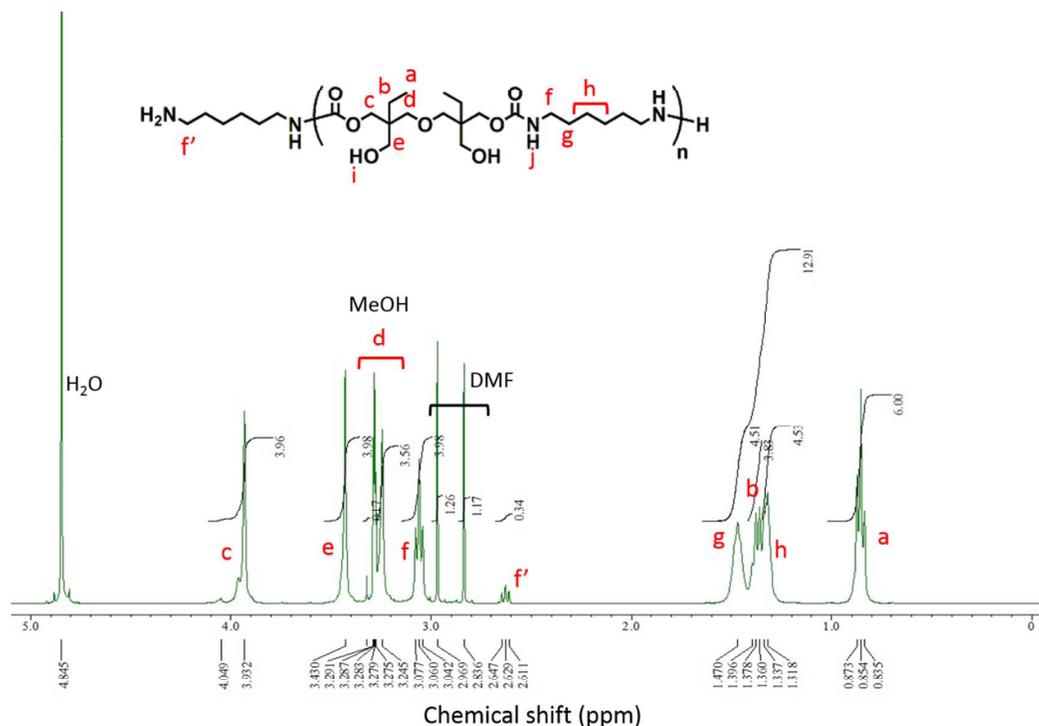
Figure 2 ^{1}H NMR spectrum of p(DTMPC-C$_6$) in CD$_3$OD. p(DTMPC-C$_6$) was synthesized from DMF solution of DTMPC and C$_6$ ([C$_6$]$_0$/[DTMPC]$_0$ = 1.1) and purified by precipitation. The attribution of these signals is shown in the figure.

Table 1 Characterization of PHUs synthesized from DTMPC and aliphatic diamines with different numbers of methylene spacers ([C$_n$]$_0$/[DTMPC]$_0$ = 1.1, n = 3, 6, 12) before/after successive modification with chloroacetyl chloride and *N,N*-dimethyl-*n*-octylamine (DMOA).

R	p(DTMPC-C$_n$)			p(DTMPC-C$_n$-Cl)				p(DTMPC-C$_n$-DMOA-Cl)	
	Yield (%)	M_n (g mol^{-1})^a	M_w/M_n^{a}	Yield (%)	f(Cl) (%)^b	M_n (g mol^{-1})^a	M_w/M_n^{a}	Yield (%)	f(N) (%)^c
C$_3$H$_6$	40.0	3,800	2.11	89.2	100.6	4,100	2.15	80.4	99.1
C$_6$H$_{12}$	85.9	5,300	2.56	96.7	98.5	5,800	2.46	78.9	98.9
C$_{12}$H$_{24}$	99.3	6,300	2.61	99.2	99.3	8,800	2.25	81.8	90.0

^{a}Determined by SEC measurements with polystyrene standards. ^{b}Fractions of the modification of chloroacetyl groups calculated from ^{1}H NMR spectra. ^{c}Fractions of the modification of DMOA calculated from ^{1}H NMR spectra.

Meanwhile, at a C$_6$/DTMPC ratio of 1.1 in which C$_6$ is slightly greater than DTMPC, M_n and M_w/M_n were determined to be 4,500 g mol^{-1} and 2.5, respectively at 6 h. The M_n value is closely related to that calculated theoretically (M_n = M. W. of PHU unit x n + M. W. of both chain ends = 418.52 x 10 + 115.20 + 1.01 = 4,301 g mol^{-1}). At this ratio, these values did not change in longer reaction time, indicating that the reaction was almost completed within 6 h. On the other hand, PHUs with well-controlled M_n and M_w/M_n were obtained from the solution at the C$_6$/DTMPC ratio of 0.91 (Date are not shown).

After the mixture of DTMPC and C$_6$ at a C$_6$/DTMPC ratio of 1.1 was reacted for 24 h, the resulting p(DTMPC-C$_6$) was purified by precipitation from water and obtained as sticky liquids with a yield of 85.9%. The ^{1}H NMR spectrum of the p(DTMPC-C$_6$) in CD$_3$OD is shown in Figure 2. The signal ascribed to the methylene groups adjusting to N-H bonds (f) appears at ca. 3.1 ppm. In addition, the peaks of methylene

groups adjusting to the oxygen atom of urethane bonds (c) or hydroxyl groups (e) are observed at 3.9 or 3.5 ppm, respectively. Their FT-IR spectrum also represents the formation of urethane bonds and hydroxyl groups (Figure S2). Furthermore, the signal ascribed to the protons of methylene groups adjusting to the non-reacted amine groups at end chains (f') is confirmed at 2.7 ppm. These results clearly indicate the formation of urethane bonds and isolation of p(DTMPC-C$_6$). The SEC trace of the p(DTMPC-C$_6$) is same as that before purification (Figure S3). Similarly, 1,3-propanediamine (C$_3$) and 1,12-dodecanediamine (C$_{12}$) were reacted with DTMPC and p(DTMPC-C$_3$) and p(DTMPC-C$_{12}$) were obtained, respectively and characterized by SEC measurements, FT-IR and ^{1}H NMR spectroscopy (Figure S2-4). The yield, M_n, M_w/M_n of these PHUs are summarized in Table 1. These PHUs can be also obtained at relatively high yields and the M_n and M_w/M_n are effectively controlled.
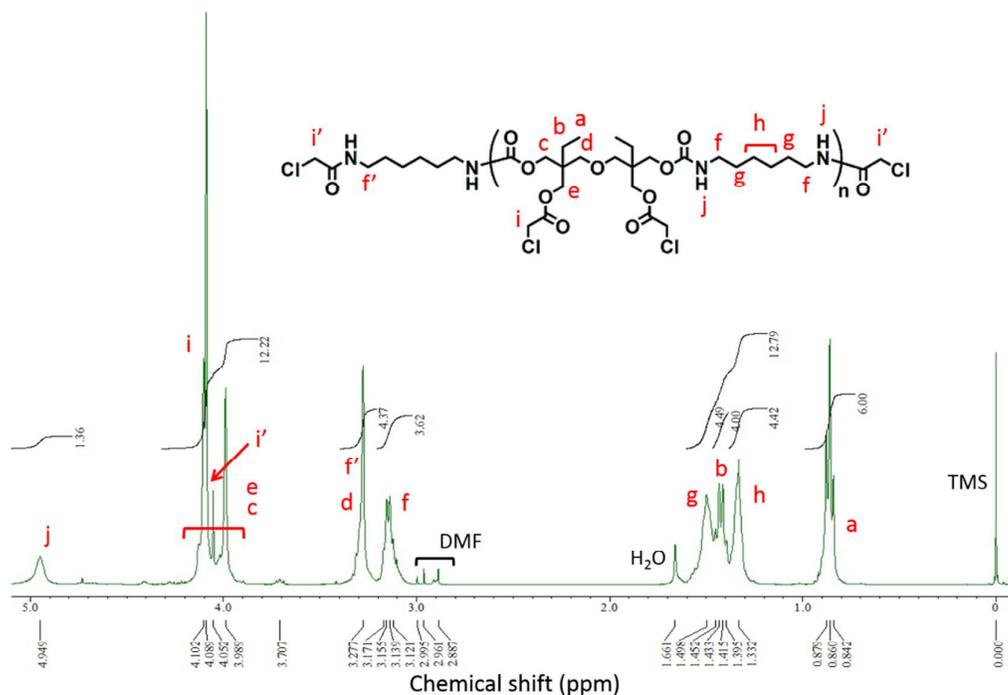
Figure 3 ^{1}H NMR spectrum of p(DTMPC-C_6-Cl) in $CDCl_3$ with 0.1 v/v% of TMS. p(DTMPC-C_6) was synthesized from DMF solution of DTMPC and C_6 ([$C_6]_0$/[DTMPC]$_0$ = 1.1) and then subsequently chloroacetylated. The attribution of these signals is shown in the figure.

Figure 4 ^{1}H NMR spectrum of p(DTMPC-C_6-DMOA-Cl) in CD_3OD. p(DTMPC-C_6) was synthesized from DMF solution of DTMPC and C_6 ([$C_6]_0$/[DTMPC]$_0$ = 1.1) and then
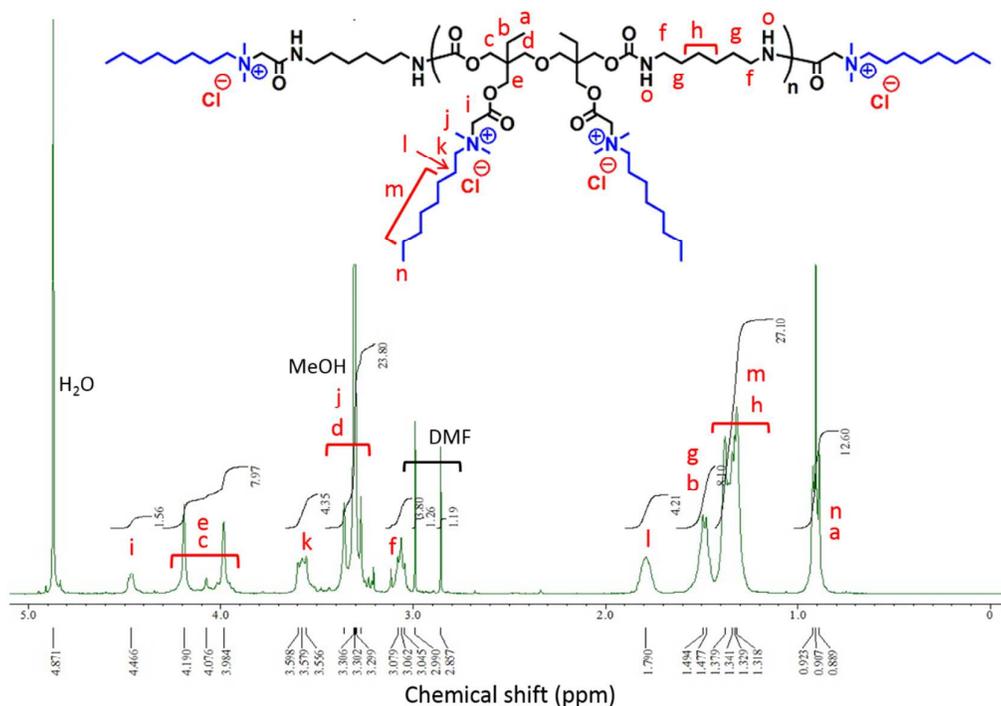
subsequently chloroacetylated followed by reacted with DMOA. The attribution of each signal is shown in the figure.

Synthesis of QAC-functionalized PHUs

PHUs possess two hydroxyl groups in their unit, which can be chemically modified to give functionalities. PHUs synthesized from 5-membered cyclic carbonates have been modified with functional substrates such as methacryl isocyanate and acyl chloride to give functional polymers.[5,6,8,10] In this study, to employ the quaternization reaction of tertiary amines with alkyl halides, we selected commercially-obtainable chloroacetyl chloride. Chloroacetylated PHUs p(DTMPC-C_n-Cl) were obtained by one-pot synthesis; p(DTMPC-C_n) synthesized from DTMPC and different diamines in DMF were not purified and reacted with chloroacetyl chloride. Figure 3 shows the ^{1}H NMR spectrum of p(DTMPC-C_6-Cl) in $CDCl_3$ after purification. The signal at 3.4 ppm assigned to the methylene protons adjusting to the OH groups completely disappears and strong singlet signal newly appears at 4.1 ppm. The total value of these signals (c + e + i) is 12.22, indicating that 98.5% of the OH groups were converted to the chloroacetyl groups. The chloroacetylation was also supported by FT-IR spectroscopy showing that the strong stretching vibration at ca. 3400 cm^{-1} based on hydroxyl groups disappeared and the stretching vibration assigned to carbonyl bonds of ester groups appears as a shoulder peak at ca. 1740 cm^{-1} (Figure S5). The SEC curve of p(DTMPC-C_6-Cl) gave a broad peak and M_n and M_w/M_n were determinedto be 5,800 g mol^{-1} and 2.41, respectively (Figure S6 and Table 1). The M_n value is well corresponded to theoretical value (M. W. = M. W. of chloroacetylated PHU unit x n + M. W. of both chloroacetylated chain ends = 571.49 x 10 + 191.68 + 77.49 = 5984.07 g mol^{-1}) and the M_w/M_n value was not changed, indicating that the chloroacetylation was performed with neither the cleavage nor the cross-linking of PHU chains. For other two PHUs (p(DTMPC-C_3) and p(DTMPC-C_{12})), chloroacetylation was performed by the same way and corresponding chloroacetylated PHUs were obtained in high yields (Figure S5-7).

The chloroacetylated PHUs p(DTMPC-C_6-Cl) were reacted with DMOA in DMF at 80 °C for 6 h. After the solution was added to THF, pale orange insoluble oils were formed. Since p(DTMPC-C_6-Cl) is soluble in THF, the precipitation suggests that the reaction proceeded. The precipitates were purified by successive precipitation from THF followed by *n*-hexane and finally yielded as pale orange solids. The FT-IR spectrum of the solids shows an increase in the stretching vibration peaks based on methylene groups, which implies the modification of DMOA (Figure S8). Figure 4 is the ^{1}H NMR spectrum of the solids in which characteristic signals ascribed to methyl (j, n) and methylene groups (k-m) adjusting to quaternary ammonium ions appear at 3.5 and 1.8 ppm. Judging from their proton ratios, it is clear that chloroacetyl groups are quantitatively reacted with DMOA to give p(DTMPC-C_6-DMOA-Cl). The PHU can be soluble in water and from the ^{1}H NMR spectrum in D_2O it proved to be to some extent aggregated in aqueous media (data are not shown). Although we do not characterize by SEC measurement, judging from the ^{1}H NMR spectrum, the cleavage of main and side chains of the PHUs does not occur. Similarly, two chloroacetylated PHUs
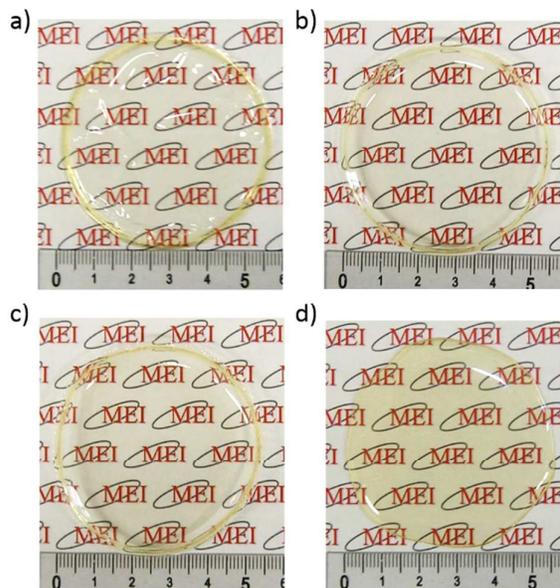
Figure 5 a-c) Photographs of PHU films prepared from p(DTMPC-C_6-Cl) and a different amount of TMDAH as cross-linkers. The mole factions of TMDAH were a) 10, b) 20 or c) 30 mol% with respect to the chloroacetyl group of PHU unit. d) Photograph of QAC2-Film prepared by the reaction of QAC-Film with DMOA in DMF at 60 °C for 6 h. The QAC-Film was prepared at 20 mol% of TMDAH.
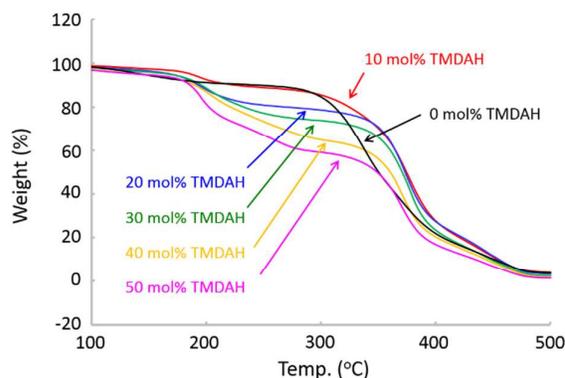
Figure 6 TGA profiles of QAC-functionalized PHU films prepared from p(DTMPC-C_6-Cl) with different amounts of TMDAH. The mole fraction of TMDAH were 0 (black line), 10 (red line), 20 (blue line), 30 (green line), 40 (orange line) or 50 mol% (purple line) with respect to chloroacetyl groups of PHU unit.

p(DTMPC-C_3-Cl) and p(DTMPC-C_{12}-Cl) were converted into p(DTMPC-C_3-DMOA-Cl) and p(DTMPC- C_{12}- DMOA-Cl), respectively and confirmed that their modification were quantitatively conducted (Figure S8, S9).

Fabrication of QAC-functionalized PHU films

PHU films were prepared by the aging of a THF solution of p(DTMPC-C_6-Cl) with a different amount of cross-linkable TMDAH at 40 °C within 2 h in a glass Petri dish. During this process, solvents are removed and simultaneously the reaction of chloroacetyl groups with tertiary amines proceeds. Using more than 10 mol% of TMDAH with respect to chloroacetyl groups of PHU unit, a stable film with well-transparency was

Table 2 E. A. results of the PHU film prepared with 20 mol% of TMDAH (QAC-Film) and the PHU film after modification of DMA (QAC2-Film).

		C (%)	H (%)	N (%)	Cl (%)	C/N	Cl/N
QAC-Film	found	50.83	7.65	5.92	11.28	8.59	1.91
	calcd[a]	53.31	8.24	6.43	11.94	8.29	1.86
QAC2-Film	found	53.97	9.44	6.45	8.58	8.37	1.33
	calcd[b]	59.12	9.88	7.05	8.93	8.39	1.27

[a]Determined as the p(DTMPC-C$_6$-Cl)/TMDAH ratio of 1/4 (C$_{290}$H$_{534}$N$_{30}$O$_{82}$Cl$_{22}$). [b]Determined as the p(DTMPC-C$_6$-Cl)/TMDAH/DMOA ratio of 1/4/14 (C$_{430}$H$_{856}$N$_{44}$O$_{82}$Cl$_{22}$).

obtained. As the solution without TMDAH led to only sticky liquids after the same treatment, the film formation is obviously caused by the cross-linking with TMDAH. Especially, when more than 20 mol% of TMDAH was used, resulting films became less sticky and were easier to be detached from glass Petri dishes to obtain self-supported films. Figure 5 exhibits photographs of the resulting films prepared with 10-30 mol% of TMDAH. Although these films are colored to be slightly yellow, more than 80% of transmittance are shown at a broad range from 420 to 2000 nm and transparency is not depended on the amount of TMDAH used (Figure S10). Further increase in the amount of TMDAH also gave films but these films have the large amounts of opaque domains (Figure S11). Finally, when 50 mol% of TMDAH were used, resulting films showed less than 30% of transmittance.

These films were also characterized for their thermal stability by TGA and TGA curves are shown in Figure 6. Pure chloroacetylated PHUs without TMDAH showed a slight weight loss by 250 °C and thermal decomposition gradually proceeded from 250-500 °C, which is similar to that of conventional PU.[55] PHU film prepared with 10 mol% of TMDAH gave two-step weight loss in which the first thermal decomposition began at 160 °C and ended at 250 °C and the second occurred at 250-500 °C. As the second weight loss is ascribed to the decomposition of urethane linkages, the first is obviously caused by the TMDAH linkers. Notice that for the PHU film with 10 mol% TMDAH, the temperature at which the urethane linkages are decomposed was higher than that for the pure PHUs without TMDAH. This result strongly indicates the contribution of the formation of networked structures. For the PHU films with 20 or 30 mol% of TMDAH, the weight loss based on the TMDAH linkers were increased but the decomposition temperature of urethane linkages remained unchanged. However, further increase in TMDAH up to 40 or 50 mol% gave lower decomposition temperature of urethane linkages. This could be due to a decrease in the hydrogen bonding among urethane linkages and an increase in unreacted tertiary amines of TMDAH. From these results, it is found that the reaction of p(DTMPC-C$_6$-Cl) with 20 or 30 mol% of TMDAH affords to self-supported films with well transparency and thermal stability. In addition, Table 2 exhibits the E. A. of the QAC-Film prepared at 20 mol% of TMDAH. The C/N and Cl/N values calculated are well equalled to those theoretically evaluated.

The PHU films prepared with less than 50 mol% of TMDAH remain chloroacetyl groups, which can be further reacted with tertiary amines to prepare PHU films with different QAC moieties. In this paper, as a preliminary experiment, we added the PHU films prepared with 20 mol% of TMDAH in a DMF solution of DMOA to prepare QAC2-Films (Scheme 2). The resulting film became slightly swollen and colored yellow (Figure 5d). Compared to the QAC-Film, the QAC2-Film gave a larger decrease in the weight at 160-250 °C based on the thermal decomposition of quaternized moieties (Figure S12 and Figure 6). Besides, FT-IR spectrum of the film showed an increase in the characteristic signals at 2900-2800 cm^{-1} assigned to the methylene groups (Figure S13), which implies the secondary quaternization with DMOA. From E. A., the C/N and Cl/N values are calculated to be 8.37 and 1.33, respectively. These values are well corresponded to those founded as the p(DTMPC-C$_6$-Cl)/TMDAH/DMOA ratio of 1/4/14, indicating that remaining chloroacetyl groups were quantitatively reacted with DMOA (Table 2).

Zeta potential measurements give valuable information of the charges of the film surfaces by characterization of the electrochemical double layer at the solid-liquid interfaces.[56] Our films were analyzed for their surface charges and the effects of the amounts of QAC moieties loaded in our films were evaluated. In spite of the existence of quaternary ammonium groups, the zeta potential of QAC-Film fabricated using 20 mol% of TMDAH was calculated to be -15.1 mV. Although we cannot explain clearly the reason why the surface possesses the negative charge, the surface might be form the environment in which negatively charged OH$^-$ and/or Cl$^-$ are preferentially adsorbed via urethane bonds.[56,57] In addition, QAC moieties serve as cross-linking points and thus would be distributed mainly in the inner side of the film and the net charge of the QAC structures is effectively neutralized. As other reason, a subtle amount of ester bonds might be hydrolyzed to form carboxylic acids, which are contributed to the formation of negative charged surfaces. When the amounts of TMDAH increased to 30 mol%, the resulting QAC-Film showed a zeta potential of +1.1 mV. This inversion of the surface charge is due to an increase in the QAC moieties in the film. On the other hand, after remaining chloroacetyl groups of QAC-Film prepared using 20 mol% of TMDAH were completely converted to QAC structures, the zeta potential of the resulting QAC2-Film was +8.3 mV. The difference of the surface charge is +23.4 mV before/after the modification with

DMOA, which is clearly ascribed to an increase in the amounts of QAC moieties. In the literatures, film materials containing tertiary amines or quaternary ammonium salts have shown a zeta potential of ca. +50 mV at neutral conditions,[57,58] which are quite greater than that of our films. We consider that the weak positive charge of QAC2-Film is caused by the neutralization of the net charge of QAC moieties covered with hydrophobic *n*-octyl groups. From these results, we found that to some extent, positive-charged surfaces can be constructed by the control in the amounts of QAC moieties through the reactions with TMDAH and DMOA.

Conclusions

In this paper, we describe the synthesis of QAS-functionalized PHUs using DTMPC and aliphatic diamines as starting materials and facile fabrication of PHU films bearing dual QAS moieties. The reaction of DTMPC with a slight excess of diamines leads to PHUs with well-controlled molecular weights and polydispersities. The resulting PHUs possess two OH groups in their repeating unit, which can be chemically modified with functional groups. In facts, we successfully synthesized QAC-functionalized PHUs in high yields from these PHUs via chloroacetylation by chloroacetyl chloride followed by quaternization by DMOA. During these reactions, neither cleavage nor cross-linking of PHU chains occurred and more than 90% of QAC moieties were introduced. On the other hand, the simple reaction of chloroacetylated PHUs with bifunctional tertiary amine TMDAH underwent both quaternization and formation of networked structures, resulting in QAC-functionalized PHU films. Especially, the reaction with 20 mol% of TMDAH gave self-supported films with excellent transparency and flexibility. In addition, different structured QAC moieties were successfully introduced in the film by the secondary quaternization reaction of DMOA. The film with dual QAC moieties possessed weak positively-charged surfaces, which implies that the film effectively interacts with microbes with negative charges and is possibly applied as an antimicrobial film.

Since DTMPC can be synthesized through non-phosgene and green sustainable routes, the studies on the DTMPC-based PHUs are worth in green chemistry. To the best of our knowledge, the studies on QAC-functionalized PHU films have not been reported yet and our report is first example. Furthermore, the fabrication route to PHU films we described here simultaneously accomplished quaternization and film formation, which expects that this method will be regarded as a fundamental technique to designing and fabricating antimicrobial PHU films. The characterization of antimicrobial activity of these PHUs and PHU films are in progress.

Acknowledgements

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