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염소치환 디페닐 에테르를 포함하는 아크릴 고분자 항균제의 합성 및 특성

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Synthesis and Antibacterial Activity of Acrylic Polymer Containing Chloro-Substituted Diphenyl Ether

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요 약 : 항박테리아성 단량체인 2,4,4'-트리클로로-2'-아크릴로일옥시디페닐 에테르(AcDP)와 2-히드록시에틸메타크릴레이트(HEMA)를 cyclohexanone을 용매로 사용하여 70℃에서 라디칼 공중합하였다. 공중합체내의 단량체 조성은 공중합체의 UV 스펙트럼으로부터 정량분석하여 구하였다. Kelen-Tüdös법에 의해 구한 단량체 반응성비의 값은 r_1(AcDP)=0.26, r_2(HEMA)=1.75이었다. 얻어진 단량체 반응성비의 값들로부터 AcDP의 입체장애 효과가 큰 영향을 미치는 것을 알 수 있었다. 공중합체들의 intrinsic viscosity는 0.05~0.15이었다. AcDP, poly(AcDP) 및 poly(AcDP-*co*-HEMA)의 항박테리아성은 shake flask test법으로 확인하였다. DP뿐만 아니라 AcDP 및 그 중합체의 *Staphylococcus aureus*에 대한 항박테리아성은 poly(HEMA) 및 poly(ethylene-*co*-vinyl acetate)와 같은 기준물질에 비하여 매우 우수하였다. *Staphylococcus aureus*에 대한 항박테리아성의 크기는 DP>AcDP>poly(AcDP-*co*-HEMA)>poly(AcDP) 순서이었다. 이러한 크기순서는 poly(AcDP-*co*-HEMA) 및 poly(AcDP)와 같이 polymer에 결합된 DP보다는 DP 및 AcDP와 같은 단량체 형태가 시편에서 용출되기 쉬운 것을 의미한다. Poly(AcDP-*co*-HEMA)가 poly(AcPD)에 비하여 DP 함량이 낮고(AcDP 함량 : 53.8 mol%) poly(HEMA)가 박테리아의 증식을 촉진시킴에도 불구하고 poly(AcDP-*co*-HEMA)의 항박테리아성은 poly(AcDP)에 비하여 약간 우수하였다.

Abstract : The antibacterial monomer, 2,4,4'-trichloro-2'-acryloyloxydiphenyl ether(AcDP) was copolymerized with 2-hydroxyethyl methacrylate(HEMA) in cyclohexanone at 70℃. The copolymer compositions were determined by quantitative ultra-violet(UV) analysis. The monomer reactivity ratios, r_1(AcDP) and r_2(HEMA) determined by Kelen-Tüdös method were 0.26 and 1.75, respectively. These values imply that the reactivity of AcDP was affected by the steric hindrance in the copolymerization. Intrinsic viscosities of copolymers were in the range of 0.05~0.15. The antibacterial activities of AcDP, poly(AcDP), and poly(AcDP-*co*-HEMA) were studied by shake flask test. The antibacterial activities of AcDP and its polymers as well as DP against *Staphylococcus aureus* were very excellent compared to those of control polymers such as poly(HEMA) and poly(ethylene-*co*-vinyl acetate). The antibacterial activities were decreased in the order of DP>AcDP>poly(AcDP-*co*-HEMA)>poly(AcDP) against *Staphylococcus aureus*. This is probably attributed to the easiness of leach or migration of DP or AcDP from the sample films compared to the polymer-anchored DP such as poly(AcDP-*co*-HEMA) and poly(AcDP). Even though poly(AcDP-*co*-HEMA)(AcDP content ; 53.8 mol%) has lower

DP moiety than poly(AcDP) and poly(HEMA) accelerate the increase in the growth of bacteria, the antibacterial activity of poly(AcDP-*co*-HEMA) on the basis of DP concentration was slightly higher than that of poly(AcDP).

INTRODUCTION

Polymeric biocides prepared by chemically bonding the biocides on polymers have attracted much interest because of their long-lasting biocidal activity. Polymeric bactericides can significantly reduce losses associated with volatilization, photolytic decomposition, dissolution, and transport. Moreover, increased efficiency, selectivity, and handling safety are additional benefits which may be realized.

Pittman et al.[1,2] evaluated acrylic polymers containing pentachlorophenol as potential biocides. Akagane and Matsuura[3] synthesized poly(methyl methacrylate-*co*-pentachlorophenol)s containing high biocide compositions(80~85 mol%). These copolymers were formulated into chlorinated resin and tested as marine coatings. They reported that the pentachlorophenol-containing polymers exhibited better antifouling activity with superior slow-release characteristics than their corresponding monomeric biocides. Some of the halogen-o-hydroxydiphenyl ether derivatives[4] have been used for protection of organic materials, such as synthetic resins, paper treatment liquors, printing thickners, lacquers, paints, and cosmetic articles, because of their remarkable biocidal activities.

Recently, we reported the syntheses and biocidal activities of 2,4,4′-trichloro-2′-acryloyloxydiphenyl ether, N-acryloyl-2-(4′-thiazoly)benzimidazole, and their polymers.[5,6]

In this work, we synthesized 2,4,4′-trichloro-2′-acryloyloxydiphenyl ether(AcDP) by reacting acryloyl chloride(Ac) with 2,4,4′-trichloro-2′-hydroxydiphenyl ether(DP). DP was selected for its bactericidal activity against both *Pseudomonas aeruginosa* and *Staphylococcus aureus*, existing in fiber, paper, latex, rubber, machine oil, leather, plastic, cotings, cosmetic articles, and packaging materials.[7~9]

Copolymers of AcDP with 2-hydroxyethyl methacrylate(HEMA) were synthesized. The copolymer compositions were analyzed quantitatively by UV spectroscopy. The antibacterial activities of DP, AcDP, poly(AcDP), and poly(AcDP-*co*-HEMA) were investigated against *Staphylococcus aureus* by shake flask test.

EXPERIMENTAL

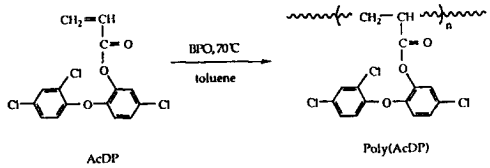
Materials. 2,4,4′-Trichloro-2′-hydroxydiphenyl ether(DP ; Ciba-Geigy) was recrystallized from n-hexane. Acryloyl chloride(Ac ; Aldrich) was used without further purification. Triethylamine(Junsei) was refluxed with acetic anhydride and with KOH, and finally distilled. 2-Hydroxyethyl methacrylate (HEMA ; Aldrich) was washed twice with 5% aq. NaOH and three times with water, then dried with Na_2SO_4 and distilled under nitrogen at reduced pressure. Benzoyl peroxide(BPO ; Junsei) was dissolved in $CHCl_3$ and precipitated by adding an equal volume of MeOH. Toluene(Junsei), cyclohexanone(Junsei), THF(J. T. Baker), and other chemicals were purified by the standard procedures. Poly(ethylene-*co*-vinyl acetate)(EVA) having 40% of vinyl acetate(Intrinsic viscosity ; 0.70 dlg^{-1}, Melt index ; 57) was used as received from Aldrich. Beef extract(Difco), bacto-peptone(Difco), agar (Difco), tryptone(Difco), dextrose(Aldrich), potassium phosphate(Aldrich), and the bacteria, *Staphylococcus aureus* ATCC 6538P, were kindly supplied from PUSAN URETHANE Co., Korea.

Instruments. IR spectra were taken on a Nicolet 710 FT-IR spectrophotometer using KBr pellet. UV spectra were taken on a Shimadzu 2100 spectrophotometer. Average molecular weight was determined by gel permeation chromatography(GPC ; Waters, 150C).

Synthesis of 2,4,4′-trichloro-2′-acryloyloxydiphenyl ether(AcDP). AcDP was prepared by the reac-

tion of 2,4,4′-trichloro-2′-hydroxydiphenyl ether (DP) and acryloyl chloride(Ac) in the presence of triethylamine. Details of synthesis and characterization procedure were reported in a previous paper.[5]

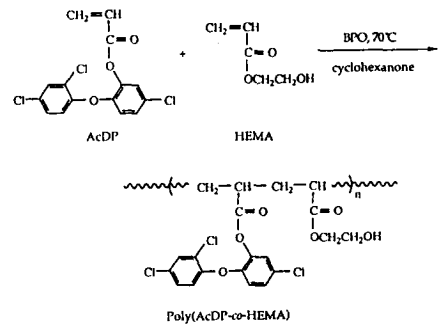
Synthesis of poly(2,2,4′-trichloro-2′-acryloyloxydiphenyl ether) poly[(AcDP)]. Poly(AcDP) was prepared by the radical polymerization of AcDP(82×10^{-3}mol) with BPO(2.97×10^{-5}mol) in 50 ml of toluene at 70℃(Scheme 1). Details of synthesis and characterization procedure were reported in a previous paper.[5]



Scheme 1.

Synthesis of poly(2-hydroxyethyl methacrylate) [poly(HEMA)]. A solution of 9.72×10^{-4} mol of HEMA and 4.95×10^{-6}mol of BPO in 10 ml dry toluene was introduced into a glass ampoule equipped with a magnetic stirring bar and a septa cap. The solution was deoxygenated by purging with purified N_2 gas. The tube was sealed and placed in a regulated thermostat bath at 70℃ for 6 h. The solid precipitated during the polymerization was filtered off with a membrane filter[material ; poly (tetrafluoroethylene), mean pore size ; 0.5μm, diameter ; 45 mm]. Then it was dried under reduced pressure. The resulting solid was redissolved in EtOH, followed by precipitating in excess ether. The precipitate was collected by filtration and dried at room temperature under vacuum to constant weight. This poly(HEMA) was used as a control polymer for the accelerated bacteria growth test.

Synthesis of poly(2,4,4′-trichloro-2′-acryloyloxydiphenyl ether-*co*-2-hydroxyethyl methacrylate) [poly(AcDP-*co*-HEMA)]. Copolymerization of AcDP with HEMA was carried out with BPO in



Scheme 2.

cyclohexanone at 70℃(Scheme 2). A series of copolymerizations, in which the feed ratios of AcDP (M_1) to HMEA(M_2) were varied in the range of 0.33 to 3.00, yielded copolymers over a wide range of compositions. The copolymerizations were stopped less than 10% conversion. Taking one example as a typical copolymerization of M_1/M_2, both AcDP and HEMA solutions were prepared to 9.72×10^{-2}mol/L in cyclohexanone, respectively. Then, 5 ml of each solutions and 4.95×10^{-6}mol of BPO were introduced into a glass ampoule tube equipped with a magnetic stirring bar and a septa cap. The solution was deoxygenated by purging with purified N_2 gas. The tube was sealed and placed in a regulated thermostat bath at 70℃ for fixed periods of time. The polymer solution obtained was precipitated in excess n-hexane. The precipitate was collected by filtration and dried under vacuum to constant weight.

Characterization of Polymers. The details of quantitative UV analysis are found in the literature[10] but a brief explanation can be described as follows ; The absorbances of the mixed solutions of poly(AcDP) and poly(HEMA) in DMF with given weight fractions were recorded at 275.9 nm in order to calibrate the absorbance to the concentration of poly(AcDP)(concentrations of each homopolymers ; 12 mg/100 ml DMF). The absorbances of copolymers for analysis were then measured.

Average molecular weights of poly(AcDP) was determined by gel permeation chromatography using non aqueous Microstyragel column and mo-

nodisperse polystyrene as a standard at 40℃. The concentration of polymer was 0.1 wt%. The intrinsic viscosity of polymers([η]) was measured in N, N-dimethylformamide(DMF) at 30℃ with Cannon-Fenske viscometer.

Antibacterial Test(Shake Flask Test)

Preparation of specimen, buffer solution, nutrient broth, bacterial culture, and tryptone glucose extraxt agar : DP, AcDP, poly(AcDP), and poly(AcDP-*co*-HEMA) were blended individually with poly(ethylene-*co*-vinyl acetate)(EVA ; VA content, 40%) at 1 wt% concentration and dissolved in THF(5% solution). Then, test sample films of 0.1~0.13 mm thickness were prepared by casting the solutions on Petri dish. Control films of pure EVA and EVA containing 1 wt% of poly(HEMA) were also prepared by casting from their THF solution. In case of the latter, small amount of EtOH was added to THF solution to dissolve poly(HEMA) completely. The Petri dishes containing test samples were dried over 24 h at room temperature and dried under vaccum at 30℃ to constant weight. The specimens were prepared by cutting the film into square-shape(5 cm×5 cm).

Buffer solution was prepared by taking 1 ml from the mother solution, 34 g of potassium phosphate, 175 ml of 4% aq. NaOH solution and 325 ml of sterile distilled water, into 799 ml of sterile distilled water.

Nutrient broth was prepared from 3 g of beef extract, 5 g of peptone, and 1000 ml of sterile distilled water.

Bacterial culture was prepared as follows : Freeze-dried ampoule of *Staphylococcus aureus* (ATCC 6538P) was opened, and the bacteria was smeared with a wire loop to give single colonies on nutrient agar and incubated at 37℃ for 24 h. A representative colony was picked off with a wire loop and placed in a 10 ml of nutrient broth, which was then incubated with shaking at 37℃ for 18 h. At this stage, the concentration of *Staphylococcus aureus* was about 10^8 cells/ml. By diluting with buffer solution, a culture a *Staphylococcus aureus* containing about 10^5 cells/ml was prepared.

Tryptone glucose extract agar was prepared from 3 g of beef extract, 5 g of trypton, 1 g of dextrose, 15 g of agar, and 1000 ml of sterile distilled water.

Antibacterial Assessment : Exposure of bacterial cells to specimen was started when 5 ml of the bacterial culture containing about 10^5 cells/ml was added to 200 ml of erlenmeyer flask equipped with screw cap containing 70 ml of buffer solution and specimen, which was preequilibrated at 37℃. After shaking the above solution at 37℃ for 1 h, 1 ml of solution was diluted with 9 ml of sterile distilled water, and then decimal serial dilution was performed twice. 1 ml portions were removed and quickly mixed with 15 ml of tryptone glucose extract agar in Petri dish. At this stage, the concentration of *Staphylococcus aureus* was about 10^1 cells/ml. After incubation at 37℃ for 24 h, the colonies which were present on the surface of tryptone glucose extract agar in Petri dish were counted. The percent reduction of bacteria was calculated as follows :

$$\text{Percent reduction of bacteria} = \frac{B-A}{B} \times 100$$

where A is the number of bacteria recovered from the inculated solution which contains the specimen in the flask and B(blank) is the number of bacteria recovered from the inoculated solution which does not contain the specimen in the flask.

RESULTS AND DISCUSSION

Characterization. The copolymer compositions were determined by quantitative UV analyses,[10] where 275.9 nm is selected as the characteristic wavelength for analyses of poly(AcDP-*co*-HEMA), because poly(HEMA) scarcely absorb at that wavelength. A straight-line calibration plot was obtained for the absorbance values by using the Beer-Lambert Law versus the mole ratio of the two monomer units in the polymer mixtures. From the calibration curve, the following equation was derived.

$$\varepsilon = 6.44X + 0.10(1-X)$$

where ε is the specific extinction coefficient of the copolymer and X is the weight fraction of AcDP unit in the copolymer.

The compositions of the copolymers were calculated from the above equation using the specific extinction coefficient of each copolymer, and were listed in Table 1.

IR spectrum(Fig. 1) of poly(AcDP-*co*-HEMA) indicated absorptions at 3436 cm^{-1}(O-H, HEMA), 3091 cm^{-1}(phenyl ring, AcDP), 1765 cm^{-1}(C=O, AcDP), and 1724 cm^{-1}(C=O, HEMA) with disappearance of vinyl absorptions at 1633 cm^{-1}(AcDP) and 1637 cm^{-1}(HEMA).

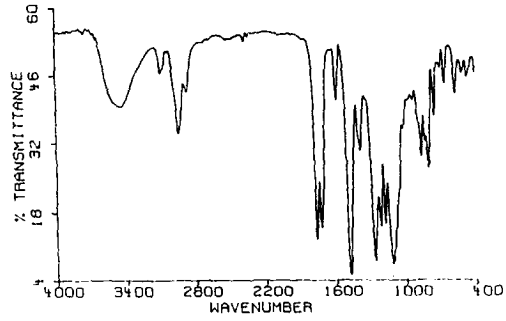


Fig. 1. FT-IR spectrum of poly(2,4,4'-trichloro-2'-acryloyloxydiphenyl ether-*co*-2-hydroxyethyl methacrylate).(KBr disk)

Table 1. Reaction Parameters for the Copolymerization of AcDP(M_1) and HEMA(M_2) with BPO in Toluene at 70℃, Copolymer Composition, and Intrinsic Viscosity.[M] ; 9.72×10^{-2}mol/l, [BPO] ; 4.90×10^{-4} mol/l

Exp. No.	Feed ratio (M_1 : M_2)	Conversion (%)	M_1 in copolymer by UV (mol%)	[η] (dlg^{-1})
H-1	7.5 : 2.5	9.5	50.5	0.05
H-2	7 : 3	10.1	49.2	0.06
H-3	6 : 4	8.8	40.5	0.08
H-4	5 : 5	9.1	32.3	0.09
H-5	4 : 6	9.6	23.6	0.11
H-6	3 : 7	8.2	18.3	0.12
H-7	2.5 : 7.5	8.8	14.5	0.15

The intrinsic viscosities of poly(AcDP-*co*-HEMA)s were listed in Table 1. As can be seen in Table 1, the intrinsic viscosities of copolymers were increased with increasing the content of HEMA unit in copolymers.

The number and weight average molecular weights of poly(AcDP) were 2700 and 4600, respectively. The intrinsic viscosity of poly(HEMA) was 0.24 dlg^{-1}.

Poly(AcDP-*co*-HEMA) used for the estimation of antibacterial activity contained 53.8 mol% of AcDP as calculated from UV method and its intrinsic viscosity was 0.10 dlg^{-1}.

Monomer Reactivity. The reactivity ratio of each monomer was estimated by the Kelen-Tüdös me-

Table 2. Kelen-Tüdös Parameters for Determination of Monomer Reactivity Ratios for the Copolymerization of AcDP(M_1) and HEMA(M_2). α=2.39, r_1(AcDP)=0.26 and r_2(HEMA)=1.75

Exp. No.	$X=\frac{M_1}{M_2}$	$Y=\frac{m_1}{m_2}$	X^2	Y−1	$F=\frac{X^2}{Y}$	$G=\frac{X(Y-1)}{Y}$	α+F	$\eta=\frac{G}{\alpha+F}$	$\xi=\frac{F}{\alpha+F}$
H-1	3.00	1.02	9.00	0.02	8.82	0.06	11.21	0.01	0.79
H-2	2.33	0.97	5.43	−0.03	5.60	−0.07	7.99	−0.01	0.70
H-3	1.50	0.68	2.25	−0.32	3.31	−0.71	5.70	−0.12	0.58
H-4	1.00	0.48	1.00	−0.52	2.08	−1.08	4.47	−0.24	0.47
H-5	0.67	0.31	0.45	−0.69	1.45	−1.49	3.84	−0.39	0.38
H-6	0.43	0.22	0.18	−0.78	0.82	−1.52	3.21	−0.47	0.26
H-7	0.33	0.17	0.11	−0.83	0.65	−1.61	3.04	−0.54	0.21

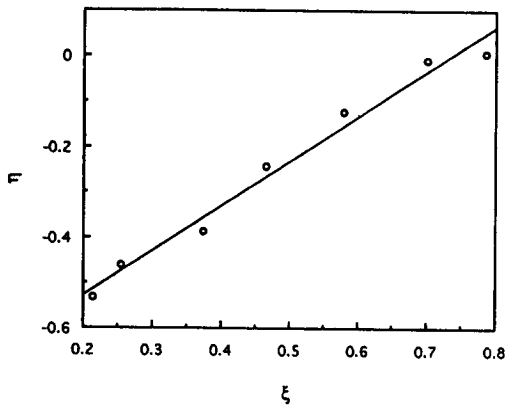


Fig. 2. Kelen-Tüdös plot for the copolymerization of AcDP and HEMA : r_1(AcDP) = 0.26, r_2(HEMA) = 1.75.

Table 3. Results of Antibacterial Activity Test on DP, AcDP, Poly(AcDP), Poly(AcDP-*co*-HEMA), and Control Polymers

Sample[a]	Concentration of bactericidal agent (wt%)	Number of bacteria (*Staphylococcus aureus* ATCC 6538P)	Reduction of bacteria (%)
Blank[b]	none	53± 7	−
EVA[c]	none	58± 5	−9
Poly(HEMA)	none	77± 6	−45
DP	1	11± 3	79
AcDP	1	22± 4	59
Poly(AcDP)	1	44± 5	17
Poly(AcDP-*co*-HEMA)[d]	1	42± 5	21

[a] Poly(HEMA), DP, AcDP, poly(AcDP) and poly(AcDP-*co*-HEMA) are blended individually with 99 wt% of EVA.
[b] Blank is the innoculated solution which does not contain the specimen in the flask.
[c] Poly(ethylene-*co*-vinyl acetate) without bactericide, (vinyl acetate content ; 40%).
[d] The content of AcDP in copolymer is 53.8 mol%.

thod.[11] Fig. 2 shows a typical Kelen-Tüdös plot to determine monomer reactivity ratios, in which the ordinate η and the abscissa ξ are explained in Table 2 along with other several parameters.

The Kelen-Tüdös plot gives r_1 value of 0.26 (AcDP) and r_2 value of 1.75(HEMA). Since $r_1(k_{11}/k_{12})$ is less than unity for the copolymerization of AcDP and HEMA, AcDP radical addition to HEMA monomer occurs more readily than addition of AcDP radical to AcDP monomer. This is probably attributed to the steric hindrance of AcDP.

Antibacterial Activity. The antibacterial activities of DP, AcDP, poly(AcDP), and poly(AcDP-*co*-HEMA) against *Staphylococcus aureus* were studied in shake flask test. The results are summarized in Table 3. In Table 3, it is seen that the number of bacteria which was recovered from the innoculated solution containing DP, AcDP poly (AcDP), and poly(AcDP-*co*-HEMA) was decreased. Whereas the number of bacteria was increased in poly(HEMA) and EVA compared to blank. The antibacterial activities against *Staphylococcus aureus* were decreased in the order of DP>AcDP >poly(AcDP-*co*-HEMA)>poly(AcDP)>EVA>poly (HEMA). The antibacterial activity of monomeric compounds such as DP and AcDP was larger than that of polymers such as poly(AcDP) and poly (AcDP-*co*-HEMA). This is probably attributed to the easiness of leach or migration of DP or AcDP from the sample films compared to the polymer-anchored DP such as poly(AcDP) and poly(AcDP-*co*-HEMA). This result is in agreement with the study previously reported by Pittman.[1] He suggested that the blended pentachlorophenol can leach or migrate from sample films, whereas polymer-anchored pentachlorophenol cannot. Even though poly(AcDP-*co*-HEMA)(AcDP content ; 53.8 mol%) has lower DP moiety than poly(AcDP) and poly (HEMA) accelerate the increase in the growth of bacteria, the antibacterial activity of poly(AcDP-*co*-HEMA) on the basis of DP concentration was slightly higher than that of poly(AcDP). This phenomenon is plausibly due to the difference of hydrophilicity between poly(AcDP-*co*-HEMA) and poly (AcDP).

CONCLUSIONS

In this work, poly(2,4,4′-trichloro-2′-acryloyloxydiphenyl ether-*co*-2-hydroxyethyl methacrylate) [poly(AcDP-*co*-HEMA)] was synthesized. The copolymer compositions were analyzed by UV spectroscopy. The monomer reactivity ratios, r_1 and r_2 were determined by the Kelen-Tüdös method ; r_1 (AcDP) = 0.26 and r_2(HEMA) = 1.75. These values imply that the reactivity of AcDP was affected by the steric hindrance in the copolymerization. Intrinsic viscosities of copolymers were in the range of 0.05~0.15. The antibacterial activities of 2,4,4′-trichloro-2′-hydroxydiphenyl ether(DP), 2,4,4′-trichloro-2′-acryloyloxydiphenyl ether(AcDP), poly(2,4,4′-trichloro-2′-acryloyloxydiphenyl ether)[poly(AcDP)], and poly(2,4,4′-trichloro-2′-acryloyloxydiphenyl ether-*co*-2-hydroxyethyl methacrylate) [poly(AcDP-*co*-HEMA)] against *Staphylococcus aureus* were excellent compared to those of poly(HEMA) and poly(ethylene-*co*-vinyl acetate). It was found that the antibacterial activity against *Staphylococcus aureus* decreased in the order of DP>AcDP>poly(AcDP-*co*-HEMA)>poly(AcDP). This is probably attributed to the easiness of leach or migration of DP or AcDP from the sample films compared to the polymer-anchored DP such as poly(AcDP) and poly(AcDP-*co*-HEMA). Even though poly(AcDP-*co*-HEMA)(AcDP content ; 53.8 mol%) has lower DP moiety than poly(AcDP) and poly(HEMA) accelerate the increase in the growth of bacteria, the antibacterial activity of poly(AcDP-*co*-HEMA) on the basis of DP concentration was slightly higher than that of poly(AcDP).

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