

Synthesis and Biocidal Activities of Polymer. III. Bactericidal Activity of Homopolymer of AcDP and Copolymer of AcDP with St

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SYNOPSIS

The bactericidal monomer 2,4,4'-trichloro-2'-acryloyloxydiphenyl ether (AcDP) was synthesized from 2,4,4'-trichloro-2'-hydroxydiphenyl ether (DP) and acryloyl chloride in the presence of triethylamine in dry THF at 20°C. The synthesized AcDP was identified by IR, ¹H-NMR, and GC-MS spectra. The homopolymer of AcDP was obtained using BPO as an initiator in toluene at 70°C. Copolymer of AcDP and styrene (St) was synthesized with a free radical initiator at 70°C. Poly(AcDP) and poly(AcDP-co-St) were identified by IR and ¹H-NMR spectra. The maximum weight average molecular weights (\bar{M}_w) of poly(AcDP) and poly(AcDP-co-St)s were 4100 and 11600, respectively. The monomer reactivity ratios, r_1 (AcDP) and r_2 (St), determined by the Kelen-Tüdös method, were 0.16 and 0.33, respectively. The glass transition temperature and decomposition temperature of poly(AcDP) were 73.4°C and 348°C, respectively. The bactericidal activities of AcDP, poly(AcDP), and poly(AcDP-co-St) were studied using agar dish test. The bactericidal activities of AcDP and its polymers as well as DP against *Pseudomonas aeruginosa* were very excellent compared to those of control polymers such as poly(St) and poly(ethylene-co-vinyl acetate). The bactericidal activities were decreased in the order DP > AcDP > poly(AcDP) > poly(AcDP-co-St) against *Pseudomonas aeruginosa*. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Polymeric bactericides offer great promise for enhancing the efficacy of some existing bactericides as well as reducing the environmental problems associated with others. 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. Many attempts have been made in polymeric drugs utilizing characteristics like polymeric biocides, especially, polymeric antitumors, but few works are reported on polymeric bactericides.

Pittman¹ synthesized copolymers of pentachlo-

rophenyl acrylate with ethyl acrylate or vinyl acetate as polymeric biocides and found that the copolymers exhibited excellent bactericidal activities against *Pseudomonas* sp. Some of the halogen-*o*-hydroxydiphenyl ether derivatives² have been used for protection of organic materials, such as synthetic resins, paper treatment liquors, printing thickeners, lacquers and paints, and cosmetic articles because of their remarkable biocidal activities.

Viscose film² containing cellulose mixed with 2,4,4'-trichloro-2'-hydroxydiphenyl ether and a sodium hydroxide solution was showed a clear bacteria-free zone against both *Staphylococcus aureus* SG 511 and *Escherichia coli* 92. Poly(vinylchloride) film mixed with dibutyl sebacate, dibutyl tin dilaurate, and 4,4'-dichloro-2'-hydroxy-diphenyl ether was showed excellent biocidal activities as that of viscose containing 2,4,4'-trichloro-2'-hydroxydiphenyl ether. The mixtures of 2,4,4'-trichloro-2'-hydroxy-

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diphenyl ether and 3,5,4'-tribromosalicylanilide were effective against both Gram-positive and Gram-negative bacteria.

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 *Pseudomonas aeruginosa*, existing in fiber, paper, latex, rubber, machine oil, leather, plastic, coatings, cosmetic articles, and packaging materials.³⁻⁵ AcDP was polymerized by a free radical initiator. Copolymer of AcDP with styrene (St) was also synthesized. The copolymer compositions were analyzed quantitatively by UV spectroscopy. The monomer reactivity ratios, r_1 (AcDP) and r_2 (St) were determined by the Kelen-Tüdös method. The bactericidal activities of DP, AcDP, poly(AcDP), and poly(AcDP-co-St) were investigated against *Pseudomonas aeruginosa*.

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, then distilled, refluxed with KOH and again distilled. Styrene (St; 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), THF (J. T. Baker), and other chemicals were purified by the standard procedures. Poly(ethylene-co-vinyl acetate) (EVA) having 40% of vinyl acetate (Inherent viscosity; 0.70 dl g^{-1} , Melt index; 57) was used as received from Aldrich. Beef extract (Difco), bacto-peptone (Difco), agar (Difco), and a bacteria, *Pseudomonas aeruginosa* ATCC 10145, were kindly supplied from PUSAN URETHANE Co., Korea.

Instruments

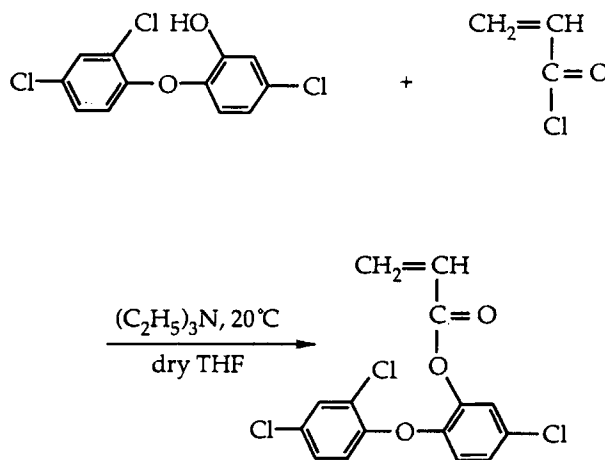
Infrared (IR) spectra were taken on a Nicolet 710 FT-IR spectrophotometer using KBr pellet. $^1\text{H-NMR}$ spectra were recorded on a Jeol JSM-PMX 60SI spectrophotometer. UV spectra were taken on a Shimadzu 2100 spectrophotometer. The purity of

a synthesized monomer was identified with a Waters (detector; 481, pump; 510, data module; 745B) liquid chromatograph (HPLC). Mass spectrum was determined on a Hewlett-Packard HP 5971 GC-MS spectrometer. Average molecular weight was determined by gel permeation chromatography (GPC; Waters, 150-C). Thermal properties were recorded on a du Pont 910 differential scanning calorimeter (DSC) and on a du Pont 951 thermogravimetric analyzer (TGA).

Synthesis of Monomer

2,4,4'-Trichloro-2'-acryloyloxydiphenyl Ether (AcDP)

AcDP was prepared by the reaction of 2,4,4'-trichloro-2'-hydroxydiphenyl ether (DP) and acryloyl chloride (Ac) in the presence of triethylamine as followings;



A mixture of 300 mL of tetrahydrofuran (THF), 23.5 g (8.12×10^{-2} mol) of DP, and 10.6 mL of triethylamine was put into 1 L of three-necked round-bottom flask equipped with a thermometer, a condenser, a dropping funnel, and a magnetic stirring bar. The flask was then maintained at 20°C , while 6.68 g (7.38×10^{-2} mol) of Ac dissolved in 50 ml of dry THF was added by dropping funnel for 1.5 h. The reaction mixture was stirred at 20°C for 6 h. After the flask was allowed to room temperature, the THF solution was filtered and the filtrate was removed by vacuum rotoevaporation. The remaining viscous liquid was poured into *n*-hexane and washed three times with 5% NaHCO_3 , then four times with water. The *n*-hexane layer was dried over 24 h with anhydrous Na_2SO_4 . After removing filtrate from the *n*-hexane solution by vacuum rotoevapor-

ation, the remaining slightly yellow liquid was re-crystallized twice from dry MeOH to yield 15.81 g (62.3%) AcDP as a transparent crystal, mp 49.2 ~ 50.5°C. The purity of synthesized AcDP was 99.3% by HPLC.

Syntheses of Polymers

Poly(2,4,4'-trichloro-2'-acryloyloxydiphenyl ether) [Poly(AcDP)]

A solution of 0.334 g (9.72×10^{-4} mol) AcDP and 4.95×10^{-6} mol of BPO in 10 mL dry toluene was introduced into a dry polymerization tube equipped with a magnetic stirring bar and a septa cap. The solution was deoxygenated by purging with purified N₂ gas. The tube was sealed and placed in a regulated thermostat bath at 70°C for 12 h. The resulting polymer was precipitated into MeOH. The precipitate was collected by filtration and dried under vacuum to constant weight.

Polystyrene [Poly(St)]

A solution of 0.909 g (8.73×10^{-3} mol) St and 4.42×10^{-5} mol of BPO in 10 ml dry toluene was introduced into a dry polymerization tube equipped with a magnetic stirring bar and a septa cap. The solution was deoxygenated by purging with purified N₂ gas. The tube was sealed and placed in a regulated thermostat bath at 70°C for 24 h. The polymer was precipitated in excess MeOH. The precipitate was collected by filtration and dried at room temperature under vacuum to constant weight.

Poly(2,4,4'-trichloro-2'-acryloyloxydiphenyl ether-co-styrene) [Poly(AcDP-co-St)]

Copolymerization of AcDP with St was carried out with BPO in toluene at 70°C. A series of copolymerizations, in which the feed ratios of AcDP (M₁) to St (M₂) 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 M₁/M₂, both AcDP and St solutions were prepared to 9.72×10^{-2} mol/L in toluene, respectively then, 5 ml of each solutions and 4.95×10^{-6} mol of BPO were introduced into a dry polymerization tube equipped with a magnetic stirring bar and a septa cap. The solution was deoxygenated by purging with purified N₂ gas. The tube was sealed and placed in a regulated thermostat bath at 70°C for fixed periods of time. The polymer so-

lution obtained was precipitated in excess MeOH. The precipitate was collected by filtration and dried under vacuum to constant weight.

Analysis of Copolymer Compositions

The copolymer compositions were determined quantitatively by UV spectroscopy according to the literature.⁶ For the analysis of poly(AcDP-co-St), a definite amount of copolymer was dissolved in chloroform of spectroscopic grade. The solution was placed in a 1.0 cm quartz cell and quantitative analysis was performed on ultraviolet (UV) spectrum. The composition of AcDP was determined by a characteristic absorption peak at 276.4 nm due to π - π^* transition of phenyl ring.

Measurement of Molecular Weight

Average molecular weights of poly(AcDP), poly(AcDP-co-St), and poly(St) were determined by GPC using nonaqueous Microstyrigel column and monodisperse polystyrene as a standard at 40°C. The concentrations of polymers were 0.1% or less.

Thermal Properties

The glass transition temperature (T_g) was determined using a DSC on sample sizes averaging 10 mg under nitrogen at a heating rate of 10°C/min. Thermal stability was examined with a TGA at a scanning rate of 10°C/min under nitrogen atmosphere.

Accelerated Bacteria Growth Test

DP, AcDP, poly(AcDP), poly(AcDP-co-St), and poly(St) were blended individually with poly(ethylene-co-vinyl acetate) (EVA; VA content, 40%) at various concentrations (0.1 ~ 1.0 wt %) 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 were also prepared by casting from its THF solution. The Petri dishes containing test samples were dried over 24 h at room temperature and dried under vacuum at 30°C to constant weight. The nutrient agar (0.5% beef extract, 1.0% bacto-pepton, 0.5% NaCl, and 1.5% agar in distilled water) inoculated with *Pseudomonas aeruginosa* was poured into Petri dishes. The test specimens (circle-shaped, 16 mm diameter) were carefully pressed onto the centers of the plates to ensure good contact between the specimen and the agar surface, and the

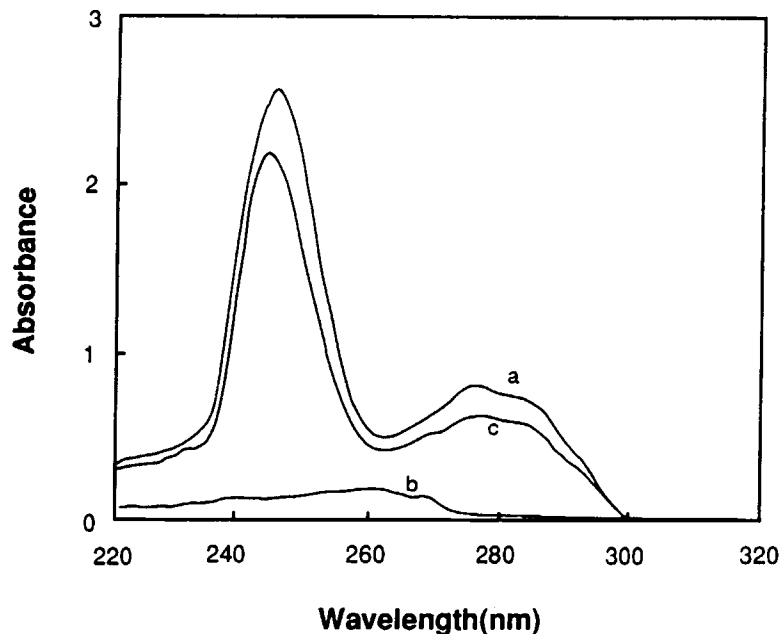


Figure 1 UV spectra of (a) Poly(AcDP), (b) Poly(St), and (c) Poly(AcDP-co-St) in Chloroform (12 mg/100 mL).

plates were incubated at 30°C for 24 h. After incubation, the plates were removed and examined.

RESULTS AND DISCUSSION

Identification of 2,4,4'-Trichloro-2'-acryloyloxydiphenyl Ether

Synthesized AcDP was identified from its IR, ¹H-NMR, UV, and GC-MS spectra. The IR spectrum shows characteristic absorption bands at 1633, 980, and 920 cm⁻¹ (vinyl) and 1750 cm⁻¹ (C=O). ¹H-NMR spectrum of AcDP (solvent; Acetone-d₆) exhibited several peaks at 5.70 ~ 6.13 (m, =CH), 6.13 ~ 6.70 (m, =CH₂), 6.70 ~ 8.00 ppm (m, C₁₂H₆). From UV spectrum, the wavelength and molar absorptivity at maximum absorption were 246.6 nm and 6550, respectively. The mass spectrum exhibited characteristic isotope peaks for chlorine and mass (m/e) was 342 (M⁺).

Characterization of Homopolymers

Poly(AcDP) was identified from its IR spectrum indicating absorptions at 2930 cm⁻¹, characteristics of the vinyl polymer backbone, with disappearance of vinyl absorptions of monomeric AcDP at 1633, 980, and 920 cm⁻¹. ¹H-NMR spectrum of

poly(AcDP) (solvent; CDCl₃) exhibited several peaks at 1.07 ~ 2.67 (—CH₂—), 2.67 ~ 3.43 (—CH—), and 6.03 ~ 8.03 ppm (C₁₂H₆). The glass transition temperature and decomposition temperature of poly(AcDP) were 73.4°C and 348°C, respectively. The number and weight average molecular weights of poly(AcDP) were 2500 and 4100, respectively.

IR spectrum of poly(St) indicated absorptions at 2921 and 2849 cm⁻¹ characteristic of the vinyl polymer backbone, with disappearance of vinyl absorptions at 3084, 1630, 990, and 909 cm⁻¹. From ¹H-NMR spectrum of poly(St) (solvent; CDCl₃), two peaks were observed at 0.83 ~ 2.43 (—CHCH₂—) and 5.73 ~ 7.53 ppm (C₆H₅—). The glass transition temperature and decomposition temperature were 100.5°C and 381°C, respectively. The number and weight average molecular weights were 6300 and 14800, respectively.

Copolymer Composition

The copolymer compositions were determined by quantitative UV analyses. The UV spectra of poly(AcDP), poly(St), and poly(AcDP-co-St) in chloroform are shown in Figure 1, the 276.4 nm is selected as the characteristic wavelength for analyses of poly(AcDP-co-St), because poly(St) scarcely absorb the light of wavelength.

Table I Reaction Parameters for the Copolymerization of AcDP (M_1) and St (M_2) with BPO in Toluene at 70°C and Copolymer Composition. $[M]$; 9.72×10^{-2} mol/L, $[BPO]$; 2.46×10^{-4} mol/L

Polymer No.	Feed Ratio ($M_1 : M_2$)	Conversion (%)	M_1 in Copolymer by UV (mol %)
S-1	7.5 : 2.5	9.7	56.6
S-2	7 : 3	8.8	55.2
S-3	6 : 4	8.3	49.1
S-4	5 : 5	9.4	46.4
S-5	4 : 6	9.3	42.2
S-6	3 : 7	7.9	37.5
S-7	2.5 : 7.5	9.6	34.9

The details of quantitative UV analysis are found in the literatures^{6,7} but a brief explanation can be described as follows; The UV spectra of copolymers of AcDP and St with several feed ratios were used to find absorbances of π - π^* transition of phenyl ring in AcDP. A straight-line calibration plot was obtained for the absorbance values by using the Beer-Lambert law against the mole ratio of the two monomer units in the polymer mixtures. From the calibration curve, the following equation was derived

$$\epsilon = 6.72X + 0.28(1-X)$$

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 I and Figure 2.

Monomer Reactivity

The reactivity ratio of each monomer was estimated by the Kelen-Tüdös method.⁸ Figure 3 shows a typical Kelen-Tüdös plot to determine monomer reactivity ratios, in which the ordinate η and the abscissa ξ are explained in Table II along with other several parameters.

The Kelen-Tüdös plot gives r_1 value of 0.16 (AcDP) and r_2 value of 0.33 (St). Since $r_1 (k_{11}/k_{12})$ is less than unity for the copolymerization of AcDP and St, AcDP radical addition to St monomer occurs more readily than addition of AcDP radical to AcDP monomer. This is probably attributed to the steric hindrance of AcDP.

Characterization of Copolymers

IR spectrum of poly(AcDP-co-St) indicated absorptions at 2929 and 2851 cm^{-1} , characteristics of the vinyl polymer backbone, 1763 cm^{-1} ($\text{C}=\text{O}$,

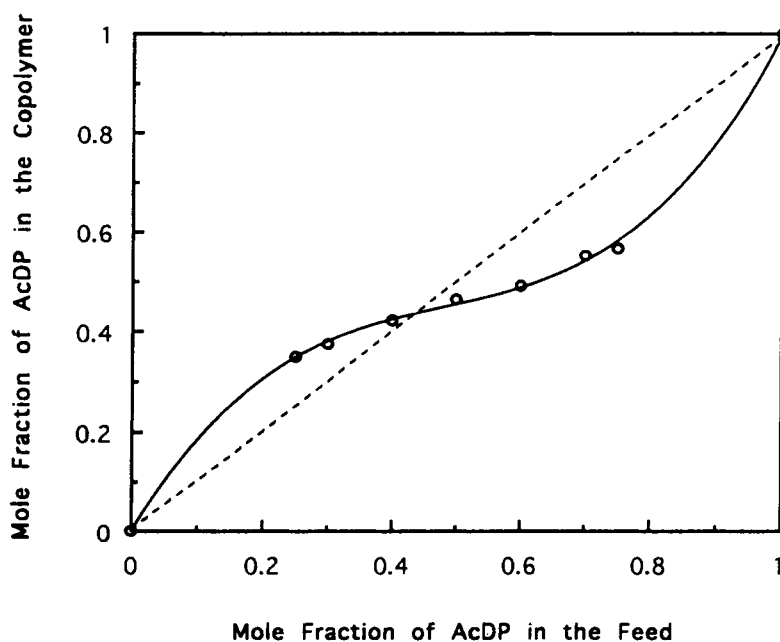


Figure 2 Copolymer composition as a function of feed composition for the copolymerization of AcDP with MMA. The dotted line represent ideal random copolymerization.

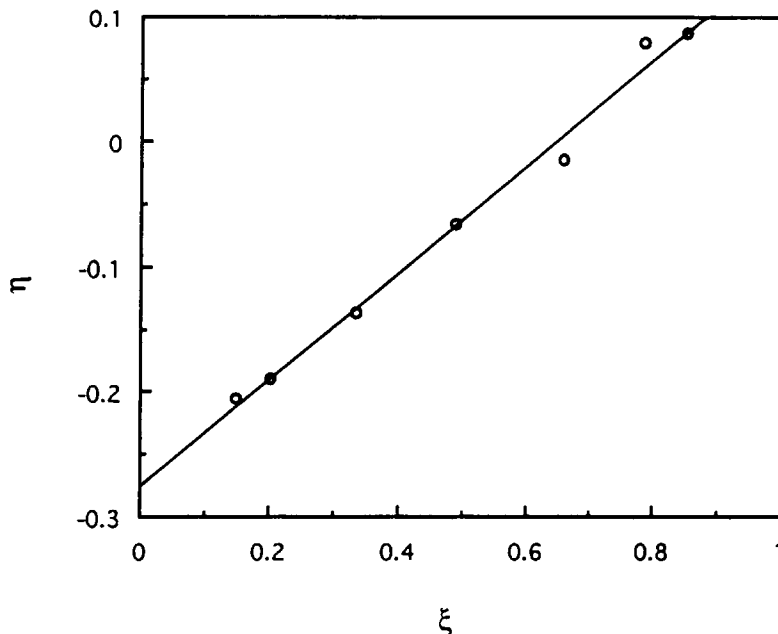


Figure 3 Kelen-Tüdös plot for the copolymerization of AcDP and St: r_1 (AcDP) = 0.16, r_2 (St) = 0.33.

AcDP) and 701 cm^{-1} (= C—H, monosubstituted ring, St) with disappearance of vinyl absorptions at 1633 cm^{-1} (AcDP) and 1630 cm^{-1} (St). The copolymer was also characterized by $^1\text{H-NMR}$ spectrum, exhibiting very similar characteristic peaks as poly(St).

Molecular weights and glass transition temperatures of poly(AcDP-co-St)s were listed in Table III. As can be seen in Table III, the number average molecular weights of copolymers were in the range of $3.6 \times 10^3 \sim 6.6 \times 10^3$ and were larger than that of poly(AcDP).

To estimate bactericidal activities of polymers, several poly(AcDP-co-St)s were synthesized and

the characterization results were summarized in Table IV.

Accelerated Growth Studies of Bactericidal Activity

The biocidal properties of AcDP and its polymers were studied in agar dish tests. Films cast on Petri dish were individually inoculated with *Pseudomonas aeruginosa*. The samples inoculated with a single organism were used for the agar dish tests at 30°C . A scale of growth was then set up as follows: 5, no growth on film, zone of inhibition present; 4, no growth on film, growth occurs on agar up to the edge

Table II Kelen-Tüdös Parameters for Determination of Monomer Reactivity Ratios for the Copolymerization of AcDP (M_1) and St (M_2). $\alpha = 1.18$, r_1 (AcDP) = 0.16 and r_2 (St) = 0.33.

Polymer No.	$X = \frac{M_1}{M_2}$	$Y = \frac{m_1}{m_2}$	X^2	$Y - 1$	$F = \frac{X^2}{Y}$	$G = \frac{X(Y - 1)}{Y}$	$\alpha + F$	$\eta = \frac{G}{\alpha + F}$	$\xi = \frac{F}{\alpha + F}$
S-1	3.00	1.30	9.00	0.30	6.90	0.69	8.10	0.09	0.85
S-2	2.33	1.23	5.43	0.23	4.41	0.44	5.60	0.08	0.79
S-3	1.50	0.97	2.25	-0.03	2.32	-0.05	3.50	-0.01	0.66
S-4	1.00	0.87	1.00	-0.13	1.15	-0.15	2.33	-0.06	0.49
S-5	0.67	0.73	0.45	-0.27	0.61	-0.25	1.80	-0.14	0.34
S-6	0.43	0.60	0.18	-0.40	0.31	-0.29	1.49	-0.19	0.21
S-7	0.33	0.54	0.11	-0.46	0.20	-0.28	1.38	-0.20	0.15

Table III Molecular Weights and Glass Transition Temperatures of Poly (AcDP-co-St).

Polymer No.	\overline{M}_w	\overline{M}_n	$\overline{M}_w/\overline{M}_n$	T _g (°C)
S-1	9100	5100	1.78	79.0
S-2	8800	5100	1.73	80.7
S-3	10500	5400	1.94	82.1
S-4	9000	4700	1.91	82.9
S-5	11600	6600	1.76	83.8
S-6	7700	3600	2.14	85.0
S-7	9500	5900	1.61	87.0

of film (no zone of inhibition); 3.5, very very sparse growth detected in places on film; 3, sparse growth on film; 2, moderate growth on film; 1, heavy growth on film.

In Table V, it is seen that the inhibition area increases with rising concentration regardless of the kinds of those monomers and polymers. The specimens of AcDP and poly(AcDP), prepared by blending with EVA, exhibited excellent bactericidal activities without growth on film at the concentration of 1 wt % bactericidal agent, but exhibited sparse or moderate growth of *Pseudomonas aeruginosa* at the concentration of 0.1 wt %. In case of poly(AcDP-co-St), the bactericidal activity was very different from those of AcDP and poly(AcDP), depending on the differences in the copolymer composition of AcDP from 19.2 to 73.2 mole %, as seen in Table IV. The bactericidal activities against *Pseudomonas aeruginosa* were decreased in the order DP > AcDP > poly(AcDP) > poly(AcDP-co-St). 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-St). This result is in agreement with the study of Pittman¹ stating that the blended pentachlorophenol can leach or migrate

Table V Results of Agar Dish Accelerated Growth Test on Dp, AcDP, Poly(AcDP), Poly(AcDP-co-St), and Control Polymers.

Sample	Concentration of Bactericidal Agent (wt %)	<i>Pseudomonas aeruginosa</i> (ATCC 10145)
EVA ^a	none	1
Poly(St) ^b	none	1
DP	0.1	3.5
	0.5	3.5
	1.0	4
	1.0	4
AcDP	0.1	3
	0.5	3.5
	1.0	4
Poly(AcDP)	0.1	2
	0.5	3
	1.0	4
Poly(AcDP-co-St) (S-8)	0.1	2
	0.5	3
	1.0	3
Poly(AcDP-co-St) (S-9)	0.1	2
	0.5	2
	1.0	3
Poly(AcDP-co-St) (S-10)	0.1	1
	0.5	2
	1.0	3
Poly(AcDP-co-St) (S-11)	0.1	1
	0.5	1
	1.0	2

^a poly(ethylene-co-vinyl acetate) without bactericide, (vinyl acetate content, 40%).

^b poly(styrene) without bactericide.

from sample films, whereas polymer-anchored pentachlorophenol cannot. Therefore, bactericidal activities of polymers are plausibly due to the release of DP bound to the polymer chain via ester linkage or to the bactericidal action of polymer itself. It is also noted that the bactericidal activity of

Table IV Reaction Parameters for the Copolymerization of AcDP (M₁) and St (M₂) with BPO in Toluene at 70°C, Copolymer Composition, Molecular Weight Data, Glass Transition Temperature, and Decomposition Temperature.

Polymer No.	M ₁ (mol)	M ₂ (mol)	BPO (mol)	Feed Ratio (M ₁ : M ₂)	M ₁ in Copolymer by UV (mol %)	Molecular Weights			T _g (°C)	Decomposition Temp. (°C)
						\overline{M}_w	\overline{M}_n	$\overline{M}_w/\overline{M}_n$		
S-8	3.71×10^{-3}	3.49×10^{-4}	2.06×10^{-5}	9.14 : 0.86	73.2	6600	3000	2.20	77.8	382
S-9	3.62×10^{-3}	8.73×10^{-4}	2.31×10^{-5}	8.06 : 1.94	56.9	7700	2600	2.96	79.9	351
S-10	2.73×10^{-3}	1.75×10^{-3}	2.27×10^{-5}	6.10 : 3.90	47.8	16200	5000	3.24	82.2	370
S-11	2.96×10^{-3}	1.75×10^{-2}	1.03×10^{-4}	1.45 : 8.55	19.2	28900	8000	3.61	90.5	374

poly(AcDP-co-St) was not better than that of poly(AcDP), probably due to the effect of poly(St) having no bactericidal activity.

Pseudomonas aeruginosa showed, however, abundant growth on the control polymers such as EVA and poly(St), meaning that this bacteria was excellent test organism to evaluate the biocidal effects of chemically anchored biocides and blended biocides.

The results of the agar dish accelerated bacteria growth test are summarized in Table V.

CONCLUSIONS

In this work, the bactericidal monomer, 2,4,4'-trichloro-2'-acryloyloxydiphenyl ether (AcDP), was synthesized. The yield and purity were 62.3 and 99.3%, respectively. Poly(2,4,4'-trichloro-2'-acryloyloxydiphenyl ether) [(poly(AcDP)] was synthesized by a free radical initiator. Its number and weight average molecular weights were 2500 and 4100, respectively. Poly(2,4,4'-trichloro-2'-acryloyloxydiphenyl ether-co-styrene)s [poly(AcDP-co-St)]s were also synthesized, whose 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) = 0.16 and r_2 (St) = 0.33. These values imply that the copolymerization was affected by the steric hindrance of the monomer containing 2,4,4'-trichloro-2'-hydrox-

ydiphenyl ether (DP). The bactericidal activities of 2,4,4'-trichloro-2'-acryloyloxydiphenyl ether, poly(2,4,4'-trichloro-2'-acryloyloxydiphenyl ether), and poly(2,4,4'-trichloro-2'-acryloyloxydiphenyl ether-co-styrene) against *Pseudomonas aeruginosa* were excellent compared to those of poly(styrene) and poly(ethylene-co-vinyl acetate). It was found that the bactericidal activity against *Pseudomonas aeruginosa* was decreased in the order DP > AcDP > poly(AcDP) > poly(AcDP-co-St).

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