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SYNTHESIS AND BIOCIDAL ACTIVITIES OF POLYMER. II. BACTERICIDAL ACTIVITY OF HOMOPOLYMER OF AcDP AND COPOLYMER OF AcDP WITH MMA

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ABSTRACT

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, ^{1}H-NMR, and GC-MS spectra. The homopolymers of AcDP were obtained using benzoyl peroxide as a thermal initiator in toluene under different experimental conditions such as various initiator concentrations, polymerization temperatures, and polymerization times. The copolymer of AcDP and methyl methacrylate (MMA) was synthesized with a thermal initiator. Poly(AcDP) and poly(AcDP-*co*-MMA) were identified by IR and ^{1}H-NMR spectra. The maximum weight-average

molecular weights ($\overline{M}_w$) of poly(AcDP)s and poly(AcDP-*co*-MMA)s were 6,700 and 15,600, respectively. The monomer reactivity ratios, r_1 (AcDP) and r_2 (MMA), determined by the Kelen–Tüdös method, were 0.26 and 1.12, respectively. The glass transition temperature and the decomposition temperature of poly(AcDP) were 73.4 and 348°C, respectively. The bactericidal activities of AcDP, poly(AcDP), and poly(AcDP-*co*-MMA) were studied using the 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 such control polymers as poly(MMA) and poly(ethylene-*co*-vinyl acetate). The bactericidal activities decreased in the order DP > AcDP > poly(AcDP) > poly(AcDP-*co*-MMA) against *P aeruginosa*.

INTRODUCTION

Polymeric biocides have elicited considerable interest in recent years because of their long-lasting biocidal activities. A polymer-bound biocide may be slowly released from the polymer to serve its purpose or, alternatively, the polymer itself may exhibit biocidal properties. 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. Therefore, polymeric bactericides offer great promise for enhancing the efficacy of some existing bactericides as well as reducing the environmental problems associated with others. Many attempts have been made to create polymeric drugs utilizing characteristics like polymeric biocides, especially polymeric antitumors, but few works are reported on polymeric bactericides.

Pittman [1] synthesized copolymers of pentachlorophenyl 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 derivatives [2] 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.

J. R. Geigy A.G. [2] prepared a viscose film from a sodium hydroxide solution of a mixture of viscose containing cellulose with 2,4,4′-trichloro-2′-hydroxydiphenyl ether, which showed a clear bacteria-free zone against both *Staphylococcus aureus* SG 511 and *Escherichia coli* 92. He also prepared a mixture of polyamide 6 with 4,4′-dichloro-2′-hydroxydiphenyl ether and mixtures of 4,4′-dichloro-2′-hydroxydiphenyl ether with poly(vinyl chloride), dibutyl sebacate, and dibutyltin dilaurate. The specimens showed excellent biocidal activities as did that of a viscose containing 2,4,4′-trichloro-2′-hydroxydiphenyl ether.

For 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]. Apostolatos et al. [6] reported that the mixture of 2,4,4′-trichloro-2′-hydroxydiphenyl ether and 3,5,4′-

tribromosalicylanilide were effective against both Gram-positive and Gram-negative bacteria. Finzi et al. [7] studied the bactericidal power of DP against hospital-isolated bacteria. Carol et al. [8] reported the antimicrobial effect of a mixture of DP with soap and acyl isethionate salts having a cleaning composition. They found that the antimicrobial activity of DP-containing mixture was greater than that of soap itself.

AcDP was polymerized by a free radical initiator. The copolymer of AcDP with methyl methacrylate (MMA) was also synthesized. The copolymer compositions were analyzed quantitatively by UV spectroscopy. The monomer reactivity ratios, r_1(AcDP) and r_2(MMA), were determined by the Kelen–Tüdös method. The bactericidal activities of DP, AcDP, poly(AcDP), and poly(AcDP-*co*-MMA) were investigated against *P 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 and with KOH, and finally distilled. Methyl methacrylate (MMA; Junsei) was washed twice with 5% aq NaOH, 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 standard procedures. Poly(ethylene-*co*-vinyl acetate) (EVA) with 40% vinyl acetate (inherent viscosity, 0.70 $dL \cdot g^{-1}$; 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 by Pusan Urethane Co., Korea.

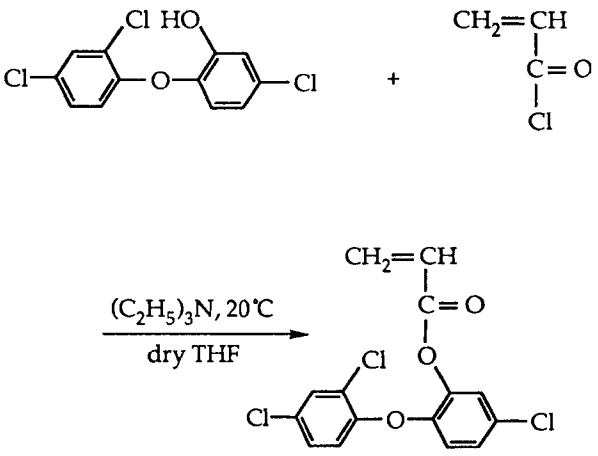
Instruments

IR spectra were taken on a Nicolet 710 FT-IR spectrophotometer by using a KBr pellet. ^{1}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-Mass spectrometer. Average molecular weight was determined by gel permeation chromatography (GPC; Waters, 150-C). Thermal properties were recorded on a DuPont 910 differential scanning calorimeter (DSC) and on a DuPont 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.



A mixture of 300 mL THF, 23.5 g (8.12×10^{-2} mol) DP, and 10.6 mL triethylamine was put into a 1-L three-necked round bottom flask equipped with a thermometer, a condenser, a dropping funnel, and a magnetic stirring bar. The flask was maintained at 20°C while 6.68 g (7.38×10^{-2} mol) Ac dissolved in 50 mL dry THF was added via the dropping funnel for 1.5 hours. The reaction mixture was stirred at 20°C for 6 hours. After the flask was allowed to reach 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 hours with anhydrous Na_2SO_4. After removing the filtrate from the *n*-hexane solution by vacuum rotoevaporation, the remaining slightly yellow liquid was recrystallized 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 the synthesized AcDP was 99.3% by HPLC.

Syntheses of Polymers

Poly(2,4,4′-Trichloro-2′-acryloyloxydiphenyl Ether) [Poly(AcDP)]

Homopolymerizations of AcDP were carried out using BPO as the initiator under several different experimental conditions, i.e., different BPO concentrations, polymerization temperatures, and reaction times (see Tables 1 and 2). In a typical example, a solution of 0.334 g (9.72×10^{-4} mol) AcDP and 4.95×10^{-6} mol 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 N_2 gas. The tube was sealed and placed in a regulated thermostat bath at 70°C for 12 hours. The resulting polymer was precipitated into MeOH. The precipitate was collected by filtration and dried under vacuum to constant weight.

Poly(Methyl Methacrylate) [Poly(MMA)]

A solution of 0.28 g (2.08×10^{-2} mol) MMA and 5.70×10^{-5} mol 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 N_2 gas and was sealed. Polymerization was carried out at 70°C for 48 hours, and then resulting polymer was precipitated into 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*-Methyl Methacrylate) [Poly(AcDP-*co*-MMA)]

Copolymerization of AcDP with MMA was carried out with BPO in toluene at 70°C. A series of copolymerizations, in which the feed ratios of AcDP (M_1) to MMA (M_2) were varied in the 0.33 to 3.00 range, yielded copolymers over a wide range of compositions. The copolymerizations were stopped before 10% conversion was reached. Taking one example as a typical copolymerization of $M_1/M_2 = 1$, both AcDP and MMA solutions were prepared to 9.72×10^{-2} mol/L in toluene, then 5 mL of each solution and 4.95×10^{-6} mol BPO 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 N_2 gas. The tube was sealed and placed in a regulated thermostat bath at 70°C for fixed periods of time. The polymer solution 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 [9]. For the analysis of poly(AcDP-*co*-MMA), 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 the UV spectrum. The composition of AcDP was determined by the characteristic absorption peak at 276.6 nm due to the π–π^* transition of the phenyl ring.

Measurement of Molecular Weight

Average molecular weights of poly(AcDP), poly(AcDP-*co*-MMA), and poly(MMA) were determined by GPC using a nonaqueous Microstyragel column and monodisperse polystyrene as the 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. The 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*-MMA), and poly(MMA) 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 dishes. Control films of pure EVA were also prepared by casting from its THF solution. The Petri dishes containing test samples were dried over 24 hours at room temperature and dried under vacuum at 30°C to constant weight. The nutrient agar (0.5% beef extract, 1.0% bacto-peptone, 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 plates were incubated at 30°C for 24 hours. 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, ^{1}H-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). The ^{1}H-NMR spectrum of AcDP (solvent, acetone-d_6) exhibited several peaks at 5.70–6.13 (m, =CH), 6.13–6.70 (m, $=CH_2$), 6.70–8.00 ppm (m, $C_{12}H_6$). From the UV spectrum, the wavelength and molar absortivity at maximum absorption were 246.6 nm and 6550, respectively. The mass spectrum exhibited characteristic isotope peaks for chlorine, and the mass (m/e) was 342 (M^+).

Characterization of Homopolymers

The homopolymerizations of AcDP were carried out with different initiator concentrations, reaction temperatures, and reaction times, as shown in Tables 1 and 2. The effects of initiator concentration and polymerization temperature, and reaction time on conversion percent are seen in Figs. 1 and 2, respectively.

It is seen that the conversion percent increases with increasing initiator concentration, polymerization temperature, and reaction time. Molecular weights of the poly(AcDP) obtained were low, being in the order of ca. 10^3, regardless of the initiator concentration. The number-average molecular weight was in the 1.7×10^3 to 3.1×10^3 range. This is attributed to the steric hindrance of the DP moiety attached to an acryloyl group.

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}. The ^{1}H-NMR spectrum of poly(AcDP) (solvent, $CDCl_3$) exhibited several peaks at 1.07–2.67 ($-CH_2-$), 2.67–3.43 ($-CH-$), and 6.03–8.03 ppm ($C_{12}H_6$). The glass transition and decomposition temperatures of poly(AcDP) were 73.4 and 348°C, respectively. The number- and weight-average molecular weights of poly(AcDP) were 2500 and 4100, respectively.

Poly(MMA) was also characterized by its IR and ^{1}H-NMR spectra. The glass transition and decomposition temperatures of poly(MMA) were 122.2 and 256°C, respectively. The number- and weight-average molecular weights were 10,600 and 19,100, respectively.

TABLE 1. Conversion Percent and Molecular Weight Data for Poly(2,4,4′-Trichloro-2′-acryloyloxydiphenyl Ether) Synthesized in Toluene with Various Concentrations of BPO and Polymerization Temperatures. Concentration of AcDP, 9.72×10^{-4} mol; solvent, toluene; time, 12 hours

Polymer	Temp, °C	BPO, mol	[I]/[AcDP], mol%	Conversion, %	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$
P-1	60	1.24×10^{-6}	0.13	7.5	—	—	—
P-2	60	2.48×10^{-6}	0.25	10.1	—	—	—
P-3	60	4.95×10^{-6}	0.51	13.9	4900	3100	1.58
P-4	60	9.91×10^{-6}	1.02	20.1	5100	3100	1.65
P-5	60	1.98×10^{-5}	2.03	27.4	4800	2900	1.66
P-6	60	4.95×10^{-5}	5.09	36.2	4300	2700	1.59
P-7	70	1.24×10^{-6}	0.13	11.2	5000	2800	1.79
P-8	70	2.48×10^{-6}	0.25	15.3	6700	2400	2.79
P-9	70	4.95×10^{-6}	0.51	18.8	4100	2500	1.64
P-10	70	9.91×10^{-6}	1.02	26.2	3500	2300	1.52
P-11	70	1.98×10^{-5}	2.03	39.6	3300	2300	1.43
P-12	70	4.95×10^{-5}	5.09	53.3	3100	2100	1.48
P-13	80	1.24×10^{-6}	0.13	—	—	—	—
P-14	80	2.48×10^{-6}	0.25	24.3	2800	2100	1.33
P-15	80	4.95×10^{-6}	0.51	28.8	2800	2100	1.33
P-16	80	9.91×10^{-6}	1.02	36.0	2700	2000	1.35
P-17	80	1.98×10^{-5}	2.03	48.5	2400	1900	1.26
P-18	80	4.95×10^{-5}	5.09	56.9	2300	1700	1.35

Copolymer Composition

The copolymer compositions were determined by quantitative UV analyses. The UV spectra of poly(AcDP), poly(MMA), and poly(AcDP-*co*-MMA) in chloroform are shown in Fig. 3, where 276.6 nm is selected as the characteristic wavelength for analyses of poly(AcDP-*co*-MMA), because poly(MMA) scarcely absorbs the light of that wavelength.

The details of quantitative UV analysis are found in the literature [9, 10], but a brief explanation follows. The UV spectra of copolymers of AcDP and MMA with several feed ratios were used to find absorbances of the π–π^* transition of the 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:

$$\varepsilon = 6.79X + 0.11(1 - X)$$

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

TABLE 2. Conversion Percent and Molecular Weight Data for Poly(2,4,4′-Trichloro-2′-acryloyloxydiphenyl Ether) Synthesized in Toluene with Different Polymerization Temperatures and Times at Constant Initiator Concentration. Solvent, toluene; [AcDP], 9.72×10^{-4} mol; [BPO], 4.95×10^{-6} mol

Polymer	Temp, °C	Time, h	Conversion, %	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$
P-19	60	3	—	—	—	—
P-20	60	6	6.8	—	—	—
P-3	60	12	13.9	4900	3100	1.58
P-21	60	24	24.5	4700	3000	1.57
P-22	70	3	6.8	5700	2900	1.97
P-23	70	6	11.8	4200	2700	1.56
P-9	70	12	18.8	4100	2500	1.64
P-24	70	24	32.3	3700	2300	1.61
P-25	80	3	15.3	2900	2200	1.32
P-26	80	6	17.8	3000	2300	1.30
P-15	80	12	28.8	2800	2100	1.33
P-27	80	24	36.9	2700	2000	1.35

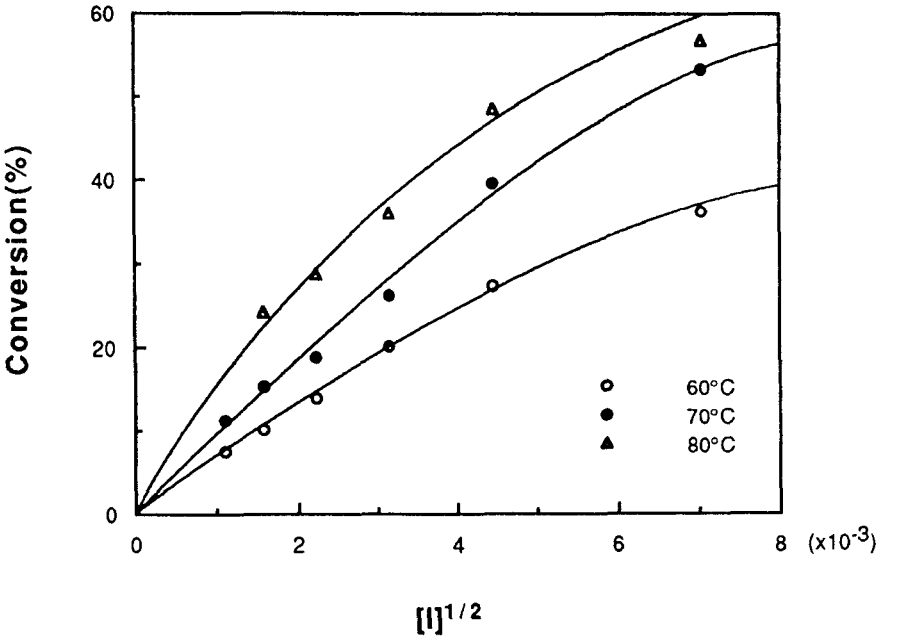


FIG. 1. Plot of conversion percent vs initiator concentration in the copolymerization of AcDP with MMA at various polymerization temperatures for 12 hours.

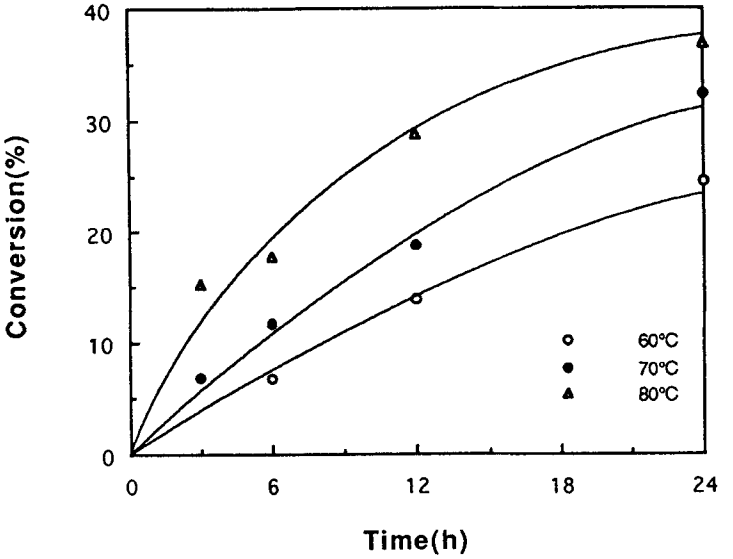


FIG. 2. Plot of conversion percent vs polymerization time in the copolymerization of AcDP with MMA at constant initiator concentration.

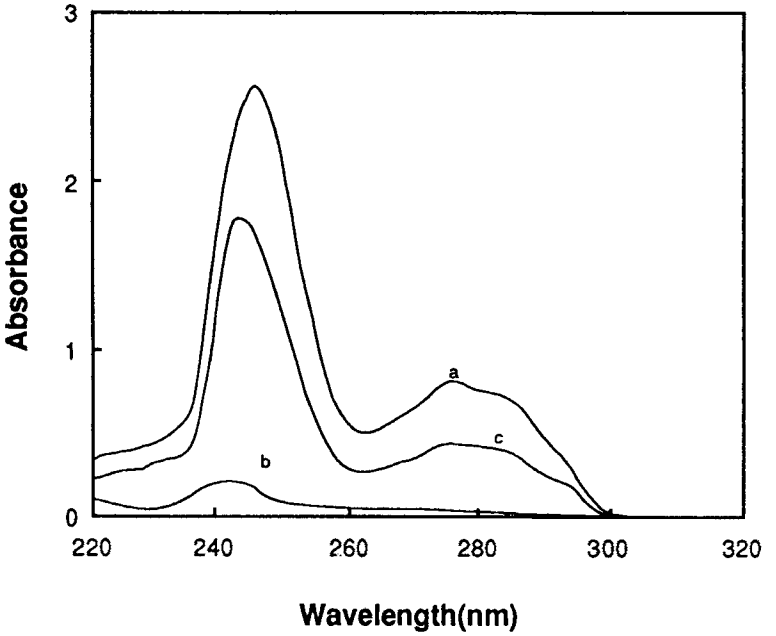


FIG. 3. UV spectra of (a) poly(AcDP), (b) poly(MMA), and (c) poly(AcDP-*co*-MMA) in chloroform (12 mg/100 mL).

TABLE 3. Reaction Parameters for the Copolymerization of AcDP (M_1) and MMA (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	Feed ratio (M_1:M_2)	Conversion, %	M_1 in copolymer by UV, mol%
M-1	7.5:2.5	10.3	57.5
M-2	7:3	9.6	51.1
M-3	6:4	8.7	44.2
M-4	5:5	9.0	37.0
M-5	4:6	10.1	30.5
M-6	3:7	9.6	24.1
M-7	2.5:7.5	8.5	19.6

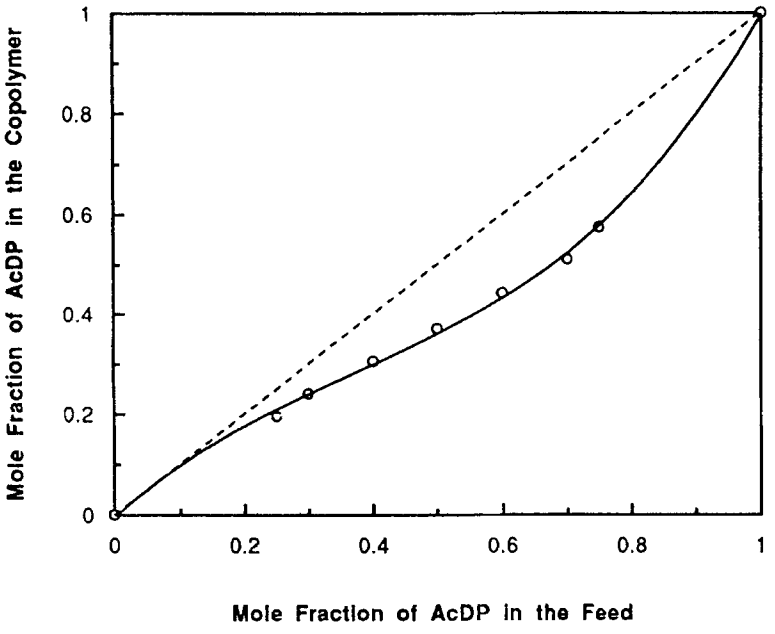


FIG. 4. Copolymer composition as a function of feed composition for the copolymerization of AcDP with MMA. The dashed line represents ideal random copolymerization.

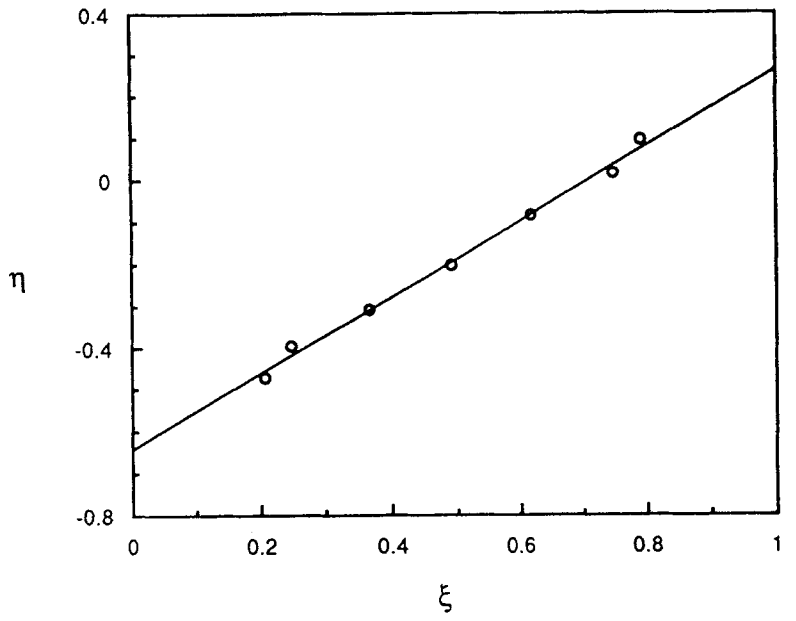


FIG. 5. Kelen-Tüdös plot for the copolymerization of AcDP and MMA: r_1(AcDP) = 0.26, r_2(MMA) = 1.12.

The compositions of the copolymers were calculated from the above equation by using the specific extinction coefficient of each copolymer. They are listed in Table 3 and shown in Fig. 4.

Monomer Reactivity

The reactivity ratio of each monomer was estimated by the Kelen-Tüdös method [11]. Figure 5 shows a typical Kelen-Tüdös plot to determine monomer reactivity ratios, in which the ordinate η and the abscissa ξ are explained in Table 4 along with several other parameters.

The Kelen-Tüdös plot gives an r_1 value of 0.26 (AcDP) and an r_2 value of 1.12 (MMA). Since r_1 (k_{11}/k_{12}) is less than unity for the copolymerization of AcDP and MMA, AcDP radical addition to MMA monomer occurs more readily than addition of AcDP radical to AcDP monomer. This can be attributed to the steric hindrance of AcDP.

Characterization of Copolymers

The IR spectrum of poly(AcDP-*co*-MMA) indicated absorptions at 3095 cm^{-1} (phenyl ring of AcDP), 1765 cm^{-1} (C=O, AcDP), and 1729 cm^{-1} (C=O, MMA) with the disappearance of vinyl absorptions at 1633 (AcDP) and 1637 cm^{-1} (MMA). Poly(AcDP-*co*-MMA) (solvent, $CDCl_3$) was also identified by several peaks on its ^{1}H-NMR spectrum: 0.53-1.37 (α-CH_3), 1.37-2.77 (—CH_2—), 2.77-2.90 (—CH—), 3.03-3.93 (—O—CH_3), 6.33-7.57 ppm ($C_{12}H_6$).

TABLE 4. Kelen-Tüdös Parameters for Determination of Monomer Reactivity Ratios for the Copolymerization of AcDP (M_1) and MMA (M_2). $\alpha = 1.74$, r_1(AcDP) = 0.26 and r_2(MMA) = 1.12

Polymer	$X = \frac{M_1}{M_2}$	$Y = \frac{m_1}{m_2}$	X^2	$Y - 1$	$F = \frac{X^2}{Y}$	$G = \frac{X(Y-1)}{Y}$	$\alpha + F$	$\eta = \frac{G}{\alpha + F}$	$\xi = \frac{F}{\alpha + F}$
M-1	3.00	1.36	9.00	0.36	6.64	0.79	8.38	0.09	0.79
M-2	2.33	1.04	5.44	0.04	5.22	0.10	6.96	0.02	0.75
M-3	1.50	0.79	2.25	−0.21	2.84	−0.39	4.58	−0.09	0.62
M-4	1.00	0.59	1.00	−0.41	1.70	−0.70	3.44	−0.20	0.49
M-5	0.67	0.44	0.44	−0.56	1.01	−0.85	2.75	−0.31	0.37
M-6	0.43	0.32	0.18	−0.68	0.58	−0.92	2.32	−0.40	0.25
M-7	0.33	0.24	0.11	−0.76	0.46	−1.04	2.20	−0.47	0.21

TABLE 5. Molecular Weights and Glass Transition Temperatures of Poly(AcDP-*co*-MMA)

Polymer	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$	T_g, °C
M-1	7,700	4,300	1.79	78.9
M-2	7,800	4,300	1.81	80.6
M-3	8,900	5,000	1.78	82.3
M-4	11,000	5,600	1.96	83.6
M-5	13,000	6,800	1.91	87.6
M-6	15,600	7,800	2.00	89.6
M-7	15,300	8,600	1.78	92.4

Molecular weights and glass transition temperatures of poly(AcDP-*co*-MMA)s are listed in Table 5. As can be seen in Table 5, the number-average molecular weights of copolymers were in the 4.3×10^3 to 8.6×10^3 range and were larger than those of homopolymers. Molecular weights increased with decreasing feed ratio, M_1/M_2, implying that the lower molecular weight was caused by steric hindrance of the DP moiety attached to an acryloyl group.

To estimate the bactericidal activities of polymers, several poly(AcDP-*co*-MMA)s were synthesized, and the characterization results are summarized in Table 6.

Accelerated Growth Studies of Bactericidal Activity

The biocidal properties of AcDP and its polymers were studied in agar dish tests. Films cast on Petri dishes were individually inoculated with *Pseudomonas aeruginosa*. 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 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 7 it is seen that the inhibition area increases with rising concentration regardless of the kinds of monomers and polymers. The specimens of AcDP, poly(AcDP), prepared by blending with EVA, exhibited excellent bactericidal activities without growth on film at a concentration of 1 wt% bactericidal agent, but exhibited sparse or moderate growth of *P aeruginosa* at a concentration of 0.1 wt%. The bactericidal activity was slightly affected by the molecular weight of poly(AcDP). The bactericidal activity of a lower molecular weight of poly(AcDP) was slightly higher than that of a higher molecular weight of poly(AcDP). This may be attributed to the ease of migration of lower molecular weight of poly(AcDP) from the sample films. In the case of poly(AcDP-*co*-MMA), the bactericidal activity was very different from those of AcDP and poly(AcDP), depending on the differences in the copolymer composition of AcDP from 17.1 to 72.1 mol%, as seen in Table 6. The decreasing bactericidal activities against *P aeruginosa* were in the order DP > AcDP > poly(AcDP) > poly(AcDP-*co*-MMA). This can probably be attributed

TABLE 6. Reaction Parameters for the Copolymerization of AcDP (M_1) and MMA (M_2) with BPO in Toluene at 70°C, Copolymer Composition, Molecular Weight Data, Glass Transition Temperature (T_g), and Decomposition Temperature (T_d)

Polymer	M_1, mol	M_2, mol	BPO, mol	Feed ratio (M_1:M_2)	M_1 in Copolymer by UV, mol%	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$	T_g, °C	T_d, °C
M-8	5.41×10^{-3}	5.61×10^{-4}	3.01×10^{-5}	9.06:0.94	72.1	9,200	3,100	2.97	78.1	386
M-9	5.94×10^{-3}	2.80×10^{-3}	4.46×10^{-5}	6.79:3.21	58.0	16,800	3,100	5.42	80.7	380
M-10	5.39×10^{-3}	5.61×10^{-3}	5.61×10^{-5}	4.90:5.10	42.6	24,600	3,000	8.20	84.7	368
M-11	2.22×10^{-3}	9.35×10^{-3}	5.90×10^{-5}	1.92:8.08	17.1	32,800	10,000	3.28	96.3	341

TABLE 7. Results of Agar Dish Accelerated Growth Test on DP, AcDP, Poly(AcDP), Poly(AcDP-*co*-MMA), and Control Polymers

Sample	Weight percent of bactericidal agent, mol[a]	*Pseudomonas aeruginosa* (ATCC 10145)
EVA[b]	None	1
Poly(MMA)[c]	None	1
DP	0.1 (6.91×10^{-6})	3.5
	0.5 (3.45×10^{-5})	3.5
	1.0 (6.91×10^{-5})	4
AcDP	0.1 (5.82×10^{-6})	3
	0.5 (2.91×10^{-5})	3.5
	1.0 (5.82×10^{-5})	4
Poly(AcDP) (P-3)	0.1 (5.82×10^{-6})	2
	0.5 (2.91×10^{-5})	3
	1.0 (5.82×10^{-5})	3.5
Poly(AcDP) (P-9)	0.1 (5.82×10^{-6})	2
	0.5 (2.91×10^{-5})	3
	1.0 (5.82×10^{-5})	4
Poly(AcDP) (P-18)	0.1 (5.82×10^{-6})	2
	0.5 (2.91×10^{-5})	3.5
	1.0 (5.82×10^{-5})	4
Poly(AcDP-*co*-MMA) (M-8)	0.1 (5.23×10^{-6})	2
	0.5 (2.62×10^{-5})	3
	1.0 (5.23×10^{-5})	3
Poly(AcDP-*co*-MMA) (M-9)	0.1 (4.81×10^{-6})	2
	0.5 (2.40×10^{-5})	2
	1.0 (4.81×10^{-5})	3
Poly(AcDP-*co*-MMA) (M-10)	0.1 (4.18×10^{-6})	1
	0.5 (2.09×10^{-5})	2
	1.0 (4.18×10^{-5})	3
Poly(AcDP-*co*-MMA) (M-11)	0.1 (2.41×10^{-6})	1
	0.5 (1.21×10^{-5})	1
	1.0 (2.41×10^{-5})	2

[a]The value of parenthesis denotes the mole of DP or DP moiety present in film.

[b]Poly(ethylene-*co*-vinyl acetate) without bactericide (vinyl acetate content, 40%).

[c]Poly(methyl methacrylate) without bactericide.

to the ease 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*-MMA). This result is in agreement with the study of Pittman [1] who stated that blended pentachlorophenol can leach or migrate 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 the polymer itself. It is also noted that the bactericidal activity of poly(AcDP-*co*-MMA) was not better than that of poly(AcDP), probably due to the fact that poly(MMA) has no bactericidal activity.

However, *P aeruginosa* showed abundant growth on the control polymers such as EVA and poly(MMA), meaning that this bacteria is an excellent test organism to evaluate the biocidal effects of chemically anchored biocides and blended biocides.

The bactericidal activity tests for each samples were performed at least three times and showed good reproducibility. The results of the agar dish accelerated bacteria growth test are summarized in Table 7.

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)s [(poly(AcDP)]s were synthesized by a free radical initiator under various experimental conditions such as initiator concentrations, polymerization temperatures, and polymerization times. Their molecular weights were observed to be low, being in the order of ca. 10^3. The weight-average molecular weight was in the 2.3×10^3 to 6.7×10^3 range. Poly(2,4,4′-trichloro-2′-acryloyloxydiphenyl ether-*co*-methyl methacrylate)s [poly-(AcDP-*co*-MMA)]s were also synthesized, and their 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(MMA) = 1.12. These values imply that the copolymerization was affected by the steric hindrance of the monomer containing 2,4,4′-trichloro-2′-hydroxydiphenyl ether (DP). The bactericidal activities of 2,4,4′-trichloro-2′-acryloyloxydiphenyl ether, poly(2,4,4′-trichloro-2′-acryloyloxy-diphenyl ether), and poly(2,4,4′-trichloro-2′-acryloyloxy-diphenyl ether-*co*-methyl methacrylate) against *Pseudomonas aeruginosa* were excellent compared to those of poly(methyl methacrylate) and poly(ethylene-*co*-vinyl acetate). It was found that the bactericidal activity against *P aeruginosa* decreased in the order DP > AcDP > poly(AcDP) > poly(AcDP-*co*-MAA). Finally, it was concluded that the bactericidal activity of poly(AcDP) became slightly higher as its molecular weight decreased.

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