Copolymerization of Pentachlorophenyl Acrylate with Vinyl Acetate and Ethyl Acrylate. Polymer-Bound Fungicides

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Synopsis

Copolymers of pentachlorophenyl acrylate (M_1) with both vinyl acetate and ethyl acrylate were prepared (in benzene at 60°C initiated by *t*-butyl peroxypivalate) at a variety of M_1/M_2 ratios. The reactivity ratios for the vinyl acetate (M_2) copolymerizations were $r_1 = 1.44$ and $r_2 = 0.039$, while for ethyl acrylate copolymerizations $r_1 = 0.21$ and $r_2 = 0.88$. The glass transition temperatures were obtained as a function of the M_1/M_2 ratio. The values of T_g for the copolymers fell between those of poly(pentachlorophenyl acrylate) and either poly(vinyl acetate) or poly(ethyl acrylate). A series of bulk copolymers with low pentachlorophenyl acrylate content were studied as biocidal coatings using accelerated growth agar dish tests inoculated with *Aspergillus* sp., *Pseudomonas* sp., *Alternaria* sp., and *Aureobasidium pullulans*. The copolymers retarded or prevented growth but did not give a zone of inhibition around the coatings. Pentachlorophenol, when added to coating polymers, did exhibit a zone of inhibition due to migration of this biocide into the agar medium.

INTRODUCTION

The chemical anchoring of biocides to polymers represents an approach to the problem of preparing coatings with long-lasting biocidal activity.[1] For example, antifouling marine coatings have been prepared and tested where the active organotin antifouling biocidal agent is chemically bonded to the polymer by ester linkages.[2–4] Similar tin-containing systems have been tested as mildew resistant paint coatings.[5] It is possible that a polymer-bound biocide may be slowly released from the polymer to serve its purpose or, alternatively, the polymer itself may exhibit biocidal properties. Since pentachlorophenol is a known broad-spectrum biocide, we have wanted to evaluate acrylic polymers containing pentachlorophenol as potential biocides.[1,6] Thus, pentachlorophenol acrylate (PCPA) was prepared as a monomer, the copolymers of which would be tested for mildewcidal activity.

While copolymers of pentachlorophenyl acrylate have been described in the literature,[6,7] reactivity studies are not available for this monomer. A closely related monomer, pentachlorophenyl methacrylate, was prepared and its methyl methacrylate copolymers were prepared by Akagane and Matsuura.[7] These copolymers had high biocide compositions (80–95 mole %). These copolymers were formulated into chlorinated resin and resin-based marine coatings and tested as marine coatings versus similar coatings containing pentachlorophenol or the monomer. Slow release of pentachlorophenol from the polymer occurred, and this resulted in longer-term antifouling activity than that exhibited by

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coatings with the monomeric biocide.[7] However, the copolymer composition was important. The homopolymer was so hydrophobic that its hydrolysis was too slow to be a good antifouling candidate, but hydrolysis from the MMA copolymers was faster and effective. The elution of monomeric biocides from the films followed the expression $\ln L/L_0 = -Dt$, whereas the equation $L = K_0(e^{-kt} - e^{-Dt})$ described loss of toxicant from the polymeric biocides.[7]

Since we were interested in preparing copolymers of PCPA compatible with poly(vinyl acetate) or acrylic polymer coatings systems, detailed radical initiated copolymerizations were performed with both vinyl acetate and ethyl acrylate. The reactivity ratios were obtained and the glass transition temperatures, T_g, of these copolymers were also studied as a function of composition. Accelerated growth tests of the fungicidal activity of these polymers was carried out by agar dish screening tests.

EXPERIMENTAL

Materials

Commercially available vinyl acetate, ethyl acrylate (Eastman) and acryloyl chloride (Aldrich), were dried over Na_2SO_4 then vacuum distilled (1 torr) prior to use. Vinyl acetate was doubly distilled. Both monomers were stored in capped amber bottles at <0°C for no longer than two weeks before use. Pentachlorophenol (Dow Chemical Co., Dowcide EC-7) was checked for purity by ^{1}H-NMR and found to be about 95% pentachloro- and 5% tetrachlorophenol. This material was used as received in the preparation of pentachlorophenyl acrylate. The solvents were reagent grade (Fisher) and used as received. The polymerization initiator was *tert*-butyl peroxypivalate (Lupersol-11, Pennwalt Corp., 75% solution in mineral spirits, half-life 12 hr at 50°C).

Synthesis of Pentachlorophenyl Acrylate (M_1)

Pentachlorophenyl acrylate was prepared by the reaction of pentachlorophenol and acryloyl chloride in the presence of triethylamine. A round-bottom flask (250 ml, equipped with a condenser and nitrogen blanket) was charged with previously dried benzene (100 ml), pentachlorophenol (13.3 g, 0.05 mole), and triethylamine (8.5 ml, 0.06 mole). The flask was then maintained at 20–25°C while acryloyl chloride (5.0 g, 0.06 mole) was added sequentially by pipet through the condenser. White triethylamine hydrochloride (mp 253°C) immediately precipitated. After 1 hr, the ice bath was removed and the flask was allowed to warm to room temperature. After warming, the benzene solution was filtered and washed three times with water (100 ml) to remove unreacted acryloyl chloride. The benzene layer was dried over the next 24 hr by repeated decantation over Na_2SO_4, then removed by vacuum rotoevaporation. The remaining brownish solid was recrystallized from ethyl ether to yield 10.1–12.4 g (63–77%) pentachlorophenyl acrylate as a while solid, mp 75°C, IR (KBr) 1765*s* (νC=O), 1630 (νC=C), 1380, 1360*s*, 1320, 1210, 1120*s*, (C—O—C), 1070, 1020, 980, 930, 870, 830, 790, 770, 720, and 650 (CCl) cm^{-1}; nmr ($CDCl_3$) δ5.10, 6.25 (M, 3, CH_2=CH).

ANAL. Calcd for $C_9H_3O_2Cl_5$: C, 33.74; H, 0.95. Found: C, 34.03; H, 0.99.

Copolymerizations and r_1, r_2 Determinations

The polymerizations used in determining the reactivity ratios were conducted in screw-cap bottles (30 ml) equipped with a Teflon Minninert valve for sample removal. The monomers in the appropriate molar ratios were charged to the bottle at about 5% total solids with benzene (20 ml), dodecane (0.50 g, an internal standard), and initiator (2% based on the monomers). The bottles were then heated at 60.0°C in a regulated oil bath. Samples (5 μl) were withdrawn at regular intervals and analyzed by gas chromatography.

A microprocessor-controlled Hewlett–Packard 5840A gas chromatograph was used to measure residual monomers (thus the percent monomer in the copolymer) in the polymerization liquor. The gas chromatograph was equipped with a 155 cm × 3 mm i.d. stainless steel column packed with 3% SE-30 on Chrom W-AWDMCS. All determinations were performed on 1-μl injections with column temperature programming from 75 to 240°C in 13 min. The reactivity ratios were subsequently calculated from these determinations by the nonlinear, least-squares method of Tidwell and Mortimer[8,9] using a computerized version already described.[10]

Glass Transition Temperatures

The values of T_g were determined by differential scanning calorimetry using a du Pont model 900 differential scanning calorimeter on sample sizes averaging 11 mg under nitrogen at a heating rate of 20°C/min.

General Bulk Polymerization Technique

The monomers and initiator were heated in a flask (50 ml equipped with condenser and blanketed with argon) to the desired temperature with a regulated oil bath (see Table I for amounts). The polymer was removed from the flask at the end of the desired reaction time and dissolved in acetone (150–200 ml). After complete dissolution, the polymer was reprecipitated, in a Waring blender, into petroleum ether. Each copolymer was reprecipitated from acetone into petroleum ether (30–60°) two more times followed by drying in vacuo.

Accelerated Growth Tests

Each of the copolymers listed in Table I was individually dissolved in acetone (2% solutions). Hard films of each were then cast on ceramic tile squares with wet film thicknesses of 0.003–0.005 in. Control films of pure poly(ethyl acrylate) and poly(vinyl acetate) were also prepared. Finally, samples containing blended pentachlorophenol or blended 2-(4′-thiazoyl)benzimidazole (into the control samples) were prepared for comparison. The tile squares were then placed into either a humidity chamber (30°C, 95% RH) or sterile Petri dishes containing malt extract agar. The agar was then added until it was adjacent to the tile surface. For each polymer, four such tile–agar dish samples were prepared. A fifth sample, for humidity chamber studies, was simultaneously inoculated with *Aspergillus* sp., *Alternaria* sp., *Auerobasidium pullulans*, and *Pseudomonas* sp. This multiple inoculation sample was called the "succession" sample. The four agar plates were each inoculated with one of the above four species, so that the

TABLE I
Copolymers of PCPA with Vinyl Acetate and Ethyl Acrylate for Use in Accelerated Growth Studies[a]

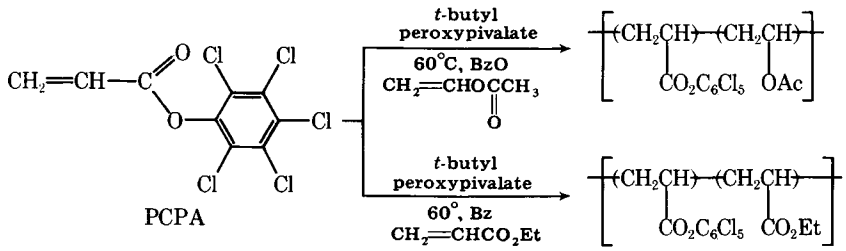
Polymer no.	PCPA, g	Vinyl Acetate, g	Ethyl Acrylate, g	Time, hr	Conv., %	PCPA in copolymer, mole % b	c	Tg, °C	$[\eta]_{THF}^{30°}$, dl/g	$Mn \times 10^{-4}$ [d]
1	1.0	19.0		3	60	5.43	5.50	38	0.34	8.9
2	0.3	19.7		3	59	2.44	2.60	37	0.33	7.4
3	0.2	19.8		3	59	1.07	1.15	33	0.33	7.5
4	0.1	19.9		4	61	0.43	0.55	32	0.32	11.0
5	0.02	20.0		4	60	0.10	0.20	30	0.32	7.7
6	0.4		19.6	2.5	58	0.80	0.93	−3	0.42	6.6
7	0.3		19.7	2.5	58	0.68	0.60	−3	0.42	6.9
8	0.2		19.8	2.5	57	0.56	0.60	−6	0.41	6.8
9	0.1		19.9	2.5	56	0.19	0.20	−11	0.40	6.9
10	0.02		20.0	2	58	0.06	0.10	−18	0.42	7.4

[a] Polymerizations were conducted in bulk. Each reaction was initiated with 0.04 g AIBN.
[b] Calculated from chlorine analyses (average of duplicate analyses).
[c] Calculated from pyrolysis gas chromatography studies.
[d] Determined by gel permeation chromatography using THF elution through 16 ft columns of Styragel and employing the Universal Calibration technique.

growth of each separate species could be ascertained. The agar dishes were then incubated at 24°C for a period of eight weeks. *Aureobasidium pullulans* became the dominant organism on the succession coating incubated for eight weeks in the humidity chamber. After eight weeks, the plates were removed and examined. 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.

RESULTS AND DISCUSSION

PCPA was copolymerized in various ratios with both vinyl acetate and ethyl acrylate in benzene at 60°C (Fig. 1). Several different M_1^0/M_2^0 ratios were employed, and for each ratio the copolymer composition was determined at several different conversions. The results for vinyl acetate are summarized in Table II, while those of ethyl acrylate are listed in Table III. All the data were then computer-fitted to the integrated form of the copolymer equation using the nonlinear least-squares method of Tidwell and Mortimer,[8,9] which had been adapted previously[10] to a computerized format.



The calculated reactivity ratios for the PCPA (M_1) copolymerization with vinyl acetate were $r_1 = 1.44 \pm 0.17$, $r_2 = 0.039 \pm 0.01$. For ethyl acrylate copolymer-

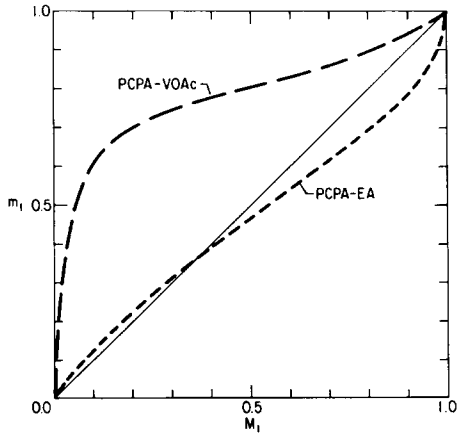


Fig. 1. Relationship of the molar fraction of PCPA in the feed (M_1) and the molar fraction in the copolymer (m_1) when PCPA is copolymerized at 60°C with (A) vinyl acetate and (B) ethyl acrylate.

TABLE II
Result of the Copolymerization of Pentachlorophenyl Acrylate (M_1) and Vinyl Acetate (M_2) in Benzene at 60°C

Polymer no.	M_1, mole %	M_2, mole %	m_2, mole %	Conversion, %
1	67.5	32.5	14.3	14.1
2	67.5	32.5	27.5	27.2
3	67.5	32.5	25.8	41.8
4	67.5	32.5	22.1	60.1
5	67.5	32.5	25.3	68.3
6	7.2	92.8	56.2	16.8
7	7.2	92.8	51.7	22.4
8	66.4	33.6	17.6	12.8
9	66.4	33.6	17.7	25.6
10	66.4	33.6	19.0	35.2
11	66.4	33.6	21.5	40.8
12	66.4	33.6	20.6	53.6
13	3.9	96.1	80.4	6.2
14	3.9	96.1	77.9	9.2
15	3.9	96.1	78.1	15.1
16	3.9	96.1	68.4	18.9
17	56.9	43.1	28.4	13.8
18	56.9	43.1	28.7	16.5
19	2.6	97.4	78.1	16.5
20	2.6	97.4	78.6	20.3
21	2.2	97.8	78.2	14.9
22	2.2	97.8	78.3	18.7
23	2.2	97.8	78.7	22.9
24	56.0	44.0	28.0	10.0
25	56.0	44.0	28.0	13.6
26	56.0	44.0	28.9	15.9
27	2.0	98.0	78.5	15.0
28	2.0	98.0	78.9	17.8
29	55.5	44.5	28.2	8.8
30	55.5	44.5	28.6	10.8
31	55.5	44.5	29.0	15.2

izations, $r_1 = 0.21 \pm 0.06$ and $r_2 = 0.88 \pm 0.19$. Figure 2 plots the 95% joint confidence limits for the r_1,r_2 determinations.

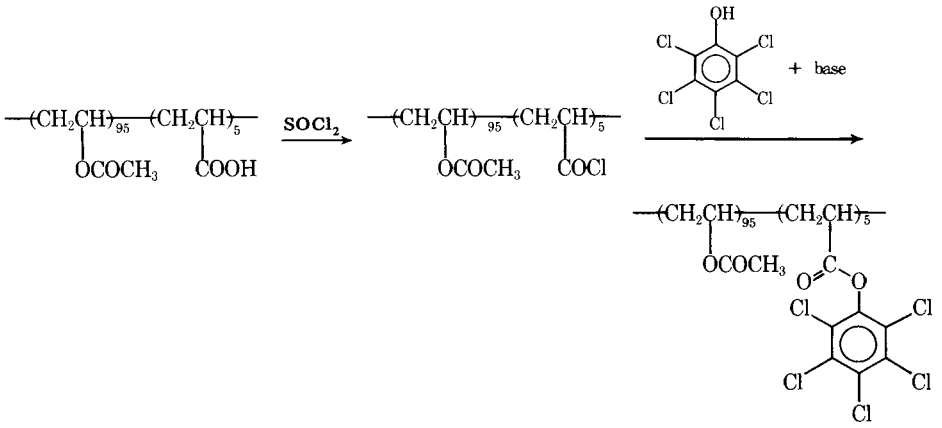
A series of PCPA copolymers was also prepared in bulk, containing small amounts of this monomer for use in accelerated growth tests of fungicidal activity. These are listed in Table I. These copolymers have low T_g values (−18 to −3°C for the ethyl acrylate series and 30 to 38°C for the vinyl acetate series) because of their low PCPA content. The molecular weight distributions were quite broad in all cases ($M_w/M_n > 3.5$).

Other synthetic routes were explored briefly to bind these fungicidal structures into polymers. The first involved direct reaction of the fungicide with the preformed coating polymer containing a suitable functional group. For example, a vinyl acetate/acrylic acid (95:5) copolymer was prepared and the carboxylic acid units were converted to acid chloride groups with excess thionyl chloride. Reaction of the polymeric acid chlorides with the —OH group of pentachlorophenol could lead to an anchored fungicide. This technique, however, was less than satisfactory. The polymeric acid chlorides were very sensitive to hydrolysis,

TABLE III
Results of the Copolymerization of Pentachlorophenyl Acrylate (M_1) and Ethyl Acrylate (M_2) in Benzene at 60°C

Polymer no.	M_1, mole %	M_2, mole %	m_2, mole %	Conversion, %
1	34.9	65.1	66.5	6.9
2	34.9	65.1	66.5	13.1
3	34.9	65.1	66.4	18.3
4	34.9	65.1	66.8	24.2
5	77.8	22.2	28.1	7.1
6	77.8	22.2	28.3	10.0
7	77.8	22.2	29.6	15.2
8	77.8	22.2	29.7	19.9
9	28.0	72.1	78.1	7.2
10	28.0	72.1	77.7	10.7
11	28.0	72.1	76.2	21.1
12	28.0	72.1	76.1	27.0
13	79.4	20.7	44.9	3.3
14	79.4	20.7	45.9	8.8
15	79.4	20.7	47.2	13.9
16	79.4	20.7	49.5	18.8
17	27.1	72.9	80.1	6.6
18	27.1	72.9	78.8	12.8
19	79.7	20.3	45.9	7.7
20	79.7	20.3	48.1	10.3

and polymer degradation occurred, presumably because of the presence of HCl. This decomposition was reflected by a decrease in viscosity during this reaction sequence. Furthermore, the final polymers exhibited strong, broad hydroxyl stretching bands in their infrared spectra.



Transesterification was also attempted unsuccessfully. Poly(ethyl acrylate) was reacted with pentachlorophenol in the presence of *p*-toluenesulfonic acid in benzene. Very little ethanol was isolated, and upon precipitation of the polymer in petroleum ether, only oily material remained.

The glass transition temperatures were studied as a function of copolymer composition. Poly(pentachlorophenyl acrylate) has a high transition temperature (T_g = 143°C), and all the copolymer T_g values fell between 143°C and the

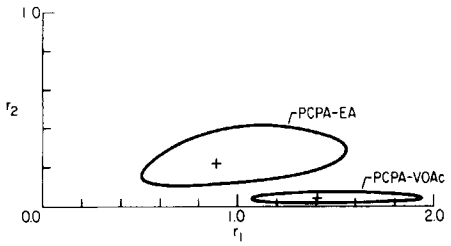


Fig. 2. Estimated 95% joint confidence limits of r_1 and r_2 for the copolymerization of PCPA (r_1), and vinyl acetate and ethyl acrylate (r_2).

T_g values of the homopolymer of vinyl acetate (28°C) or of ethyl acrylate (−24°C). Thus, any addition of PCPA to the copolymer increases T_g. Figure 3 plots T_g versus copolymer composition. The pentachlorophenol substituent causes a chain stiffening, but the curve shape is unusual and is not explained by common T_g/composition models. Very small PCPA incorporations, however, produce marked changes on T_g.

The glass transition temperatures for the copolymers with higher PCPA contents depend on their thermal history. T_g increases after heating to the T_g the first time. For example, the PCPA (67 parts)/PVOA (33 parts) copolymer exhibited a T_g of 77°C (several separate experiments). If the T_g is remeasured after heating to above 77°C, however, a new value for T_g (99°C) is noticed. After the second heating cycle, the T_g further increased to 103°C. Vinyl acetate units decarboxylate at about 165–175°C accompanied by darkening of the polymer. The original T_g values listed in Tables IV and V are reproducible after the first heating.

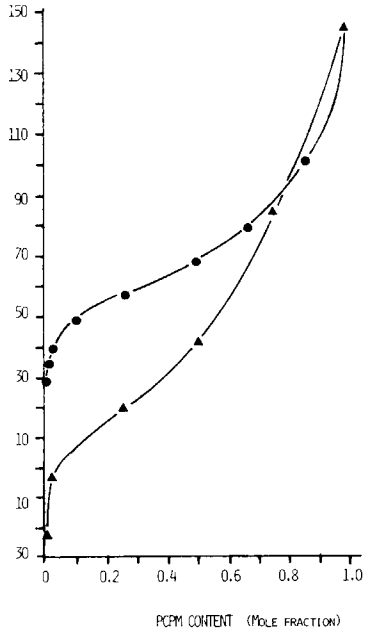


Fig. 3. Glass transition temperatures of PCPA/vinyl acetate and PCPA/ethyl acrylate (M_1 = PCPA) copolymers as function of composition: (●) PCPA/VA; (▲) PCPA/EA.

TABLE IV
Glass Transition Temperature (T_g) of Pentachlorophenyl Acrylate (M_1)–Vinyl Acetate (M_2) Copolymers

Mole % M_1 in copolymer	Weight % M_1 in copolymer	T_g, °C
0	0	28
0.002	0.006	32
0.016	0.050	38
0.10	0.20	48
0.25	0.52	56
0.50	0.76	67
0.67	0.87	77
0.85	0.95	101
1.00	1.00	143

Accelerated Growth Studies of Fungicidal Activity

The biocidal properties of PCPA copolymers 1–10 in Table I (low PCPA contents) were studied in humidity chamber and agar dish tests. Films of each, cast on tile squares, were individually inoculated with *Aspergillus* sp., *Alternaria* sp., and *Aureobasidium pullulans*. Also, films of each were inoculated with all four of these organisms as previously described.[11] These mixed inoculations will be called "succession" studies. Agar dish tests (at 24°C using malt extract agar) used the samples inoculated with a single organism, and humidity chamber tests used the succession inoculations. They were carried out for eight weeks.

Representative results are summarized in Table VI. Neither *Aspergillus* sp. nor *Pseudomonas* sp. effectively utilized either of the control films [i.e., pure poly(vinyl acetate) or poly(ethyl acrylate)] during the duration of these tests. Therefore, it is not clear how much control the anchored fungicides actually imparted to the films for these two species. *A. pullulans*, likewise, showed very little growth when inoculated alone or either poly(vinyl acetate) or poly(ethyl acrylate). *Alternaria* sp., however, showed abundant growth on the two polymers. Therefore, it was an excellent test organism to evaluate the biocidal effects of chemically anchored biocides and blended biocides. Finally, *A. pullulans* did grow as the dominant organism on both poly(vinyl acetate) and poly(ethyl acrylate) controls in the succession studies. It was subsequently shown that *A.*

TABLE V
Glass Transition Temperatures (T_g) of Pentachlorophenyl Acrylate (M_1)–Ethyl Acrylate (M_2) Copolymers

Mole % M_1 in copolymer	Weight % M_1 in copolymer	T_g, °C
0	0	−24
0.007	0.019	−4
0.25	0.48	18
0.50	0.73	40
0.75	0.89	83
1.00	1.00	143

TABLE VI
Results of Agar Dish and Humidity Chamber Accelerated Growth Tests on Film-Forming Copolymers Containing Bound Pentachlorophenol

Polymer No. (Table I)	Fungicidal monomer present, mole %	Coating monomer present in polymer[a]	*Pseudomonas* sp.	*Aspergillus* sp.	*Alternaria* sp.	*Auerobasidium pullulans*	Succession[b]
Control PVA[a]	None	VA	3	3	1.5–2	3.0–3.5	2
Control PEA[a]	None	EA	3	3	1.5	3	1.5
1 PCPA	(0.85)	EA			4	3	3
2 PCPA	(0.65)	EA			3.5	3	3
4 PCPA	(0.20)	EA	3	3	3	3	2.5
5 PCPA	(0.07)	EA	3	3	2–2.5	3	2
9 PCPA	(0.47)	VA	3.5	3.5–4	3.5	3.5	4
10 PCPA	(0.07)	VA	3.5	4	3.5	3.5	3.5
PVA pentachlorophenol[c]	blended[c]	VA	5	3.5	5	3–5[d]	3–5[d]

[a] PVA = Pure poly(vinyl acetate); PEA = pure poly(ethyl acrylate); VA = vinyl acetate; EA = ethyl acrylate.

[b] The succession studies were carried out in a humidity chamber whereas individual inoculation tests were agar dish tests (see experimental section). Scale of growth: 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 detection in places on film; 3 = sparse growth on film; 2 = moderate growth on film; 1 = heavy growth on film.

[c] In this case 0.3 wt % pentachlorophenol was blended into the control poly(vinyl acetate).

[d] Very slight growth detected on films, and zones of inhibition was clearly observed.

pullulans would grow on the controls as long as *Alternaria* sp. was present in the inoculum.

Several very important findings should be pointed out. Copolymers of ethyl acrylate and PCPA exert control on *Alternaria* sp. and succession growth at all levels studied (from 0.85 to 0.07 mole %). When 0.85 mole % of PCPA was present, no growth of *Alternaria* sp. was detected on the film. Also, no zone of inhibition existed when polymer-anchored pentachlorophenol was used. When 0.3 wt % of pentachlorophenol was blended into poly(vinyl acetate), however, a large zone of inhibition occurred with *Pseudomonas* sp. and *Alternaria* sp. Clearly, blended pentachlorophenol can leach or migrate from the film, whereas polymer-anchored pentachlorophenol (to the level at which microbiologic growth is a sensitive detector) cannot.

As the mole % of PCPA in ethyl acrylate copolymers drops from 0.85 to 0.07, the degree of resistance to *Alternaria* sp. or succession growth also decreases. Copolymers of vinyl acetate and PCPA control growth in a similar manner. Even 0.07 mole % of PCPA is very effective in controlling *Alternaria* sp. in vinyl acetate copolymers.

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