

Synthesis and Fungicidal Activities of Polymeric Biocides. I. TBZ-Containing Monomer and Polymers

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SYNOPSIS

The fungicidal monomer, *N*-acryloyl-2-(4'-thiazolyl)benzimidazole (AcTBZ) was synthesized from 2-(4'-thiazolyl)benzimidazole (TBZ) and acryloyl chloride in the presence of triethylamine in dry benzene at 30°C. The synthesized AcTBZ was identified by IR and ¹H-NMR spectra. The homopolymers of AcTBZ were obtained using BPO as a thermal initiator in benzene under different experimental conditions such as various initiator concentrations or polymerization temperatures. The homopolymer of AcTBZ was also prepared using benzophenone as a photo initiator in DMF at 20°C. The average molecular weights (\overline{M}_w) of those poly(AcTBZ)s obtained were very low, being in the order of ca. 10³. Copolymer of AcTBZ and acrylic acid (AA) was synthesized with thermal or photo initiators. Poly(AcTBZ) and poly(AcTBZ-*co*-AA) were identified by IR and ¹H-NMR spectra. The fungicidal activities of AcTBZ, poly(AcTBZ), and poly(AcTBZ-*co*-AA) were studied using agar dish test. The fungicidal activities of AcTBZ and its polymers as well as TBZ against *Aspergillus niger* and *Chaetomium globosum* were very excellent compared to those of control polymers such as poly(AA) and poly(ethylene-*co*-vinyl acetate). The fungicidal activities were decreased in the order TBZ > AcTBZ > poly(AcTBZ) > poly(AcTBZ-*co*-AA) against both *Aspergillus niger* and *Chaetomium globosum*. The fungicidal activities of TBZ, and the synthesized AcTBZ and polymers containing AcTBZ were better against *Chaetomium globosum* than against *Aspergillus niger*. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Polymeric biocides prepared by chemically bonding the biocides on polymers have attracted much interest because of their long-lasting biocidal activity.

A polymer-bound biocide may be slowly released from the polymer to serve its purpose or, alternatively, the polymer itself may exhibit biocidal properties. Therefore, polymeric fungicides offer great promise for enhancing the efficacy of some existing fungicides as well as reducing the environmental problems associated with others. Polymeric fungicides can significantly reduce losses associated with volatilization, photolytic decomposition, dissolution, and transport. Moreover, increased efficiency, selectivity, and handling safety are additional benefits

that 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 a polymeric fungicide.

Montemarano and Dyckman¹ reacted tributyltin oxide or tripropyltin oxide with poly(methyl vinyl ether-*co*-maleic acid) to produce a polymeric biocide. The polymer showed over 2 years of excellent antifouling performance. Fischer et al.² synthesized tin-containing analogues such as poly(tributyltin acrylate) and poly(triethyltin acrylate) as antifouling agents. Steele and Drisko³ studied similar tin-containing systems as mildew-resistant paint coatings. Pittman⁴⁻⁶ evaluated acrylic polymers containing pentachlorophenol as potential biocides. Akagane and Matsuura⁷ 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

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the pentachlorophenol-containing polymers exhibited better antifouling activity with superior slow-release characteristics than their corresponding monomeric biocides.

In this work, we synthesized *N*-Acryloyl-2-(4'-thiazolyl)benzimidazole (AcTBZ) by reacting acryloyl chloride with 2-(4'-thiazolyl)benzimidazole (TBZ) having fungicidal activity against *Chaetomium globosum* and *Apergillus niger*, which exist in fiber, paper, latex, rubber, machine oil, wood, leather, plastic, coatings, communication and electric instruments, and packaging materials. AcTBZ was polymerized by thermal or photo initiators. Copolymer of AcTBZ with acrylic acid was also synthesized. The fungicidal activities of TBZ, AcTBZ, and AcTBZ-containing polymers were investigated against *Chaetomium globosum* and *Apergillus niger* by agar dish test.

EXPERIMENTAL

Materials

2-(4'-Thiazolyl)benzimidazole (TBZ; Aldrich), 2,2'-azobisisobutyronitrile (AIBN; Junsei), and potassium persulfate (PPS; Junsei) were recrystallized from acetone. Acryloyl chloride (Ac; Aldrich) was used without further purification. Triethylamine (Junsei) was refluxed with acetic anhydride, then distilled, refluxed with KOH, and again distilled. Benzoyl peroxide (BPO; Junsei) was dissolved in CHCl_3 and precipitated by adding an equal volume of MeOH. Benzophenone (BP; Janssen) was recrystallized from MeOH. Acrylic acid (AA; Junsei) was distilled from copper powder under reduced pressure. Benzene (Junsei) and other chemicals were purified by the standard procedures. Poly(ethylene-co-vinyl acetate) (EVA) having 40% of vinyl acetate (inherent viscosity; 0.70 dLg^{-1} , Melt index; 57) was used as received from Aldrich. Potato dextrose agar (Difco) and two kinds of fungi, *Aspergillus niger* (ATCC 2118) and *Chaetomium globosum* (ATCC 2121), were kindly supplied from Pusan Urethane Co., Korea.

Instruments

IR spectra were taken on a Nicolet 710 FT-IR spectrophotometer using KBr pellet. $^1\text{H-NMR}$ spectrum was recorded on a Jeol JSM-PMX 60SI spectrophotometer. The purity of a synthesized monomer was identified with a Waters 150 HPLC. Average molecular weight was determined by gel permeation

chromatography (GPC; Waters, 150-C). Canrad-Hanovia equipped with a mercury-vapor lamp of medium pressure and a quartz sleeve (Ace Glass) was used as a photochemical equipment.

Synthesis of Monomer

N-Acryloyl-2-(4'-thiazolyl)benzimidazole (AcTBZ) was prepared by the reaction of 2-(4'-thiazolyl)benzimidazole (TBZ) and acryloyl chloride (Ac) in the presence of triethylamine. A mixture of 250 mL of benzene, 8.0 g (3.98×10^{-2} mol) of TBZ, and 6.0 mL of triethylamine was put into 500 mL 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 2.67 g (2.95×10^{-2} mol) of Ac dissolved in 50 mL of dry benzene was added by a dropping funnel for 30 min. The reaction mixture was stirred at 30°C for 20 h. After the bath was removed and the flask was allowed to return to room temperature. The benzene solution was filtered and washed three times with 5% NaHCO_3 , then four times with water. The benzene layer was dried over 24 h with anhydrous Na_2SO_4 . The benzene solution was filtered and the filtrate was removed by vacuum rotoevaporation. The remaining brown solid was recrystallized from dry ethyl acetate to yield 4.19 g (55.6%) AcTBZ as a yellow solid, mp $139.5\text{--}140.5^\circ\text{C}$. The purity of synthesized AcTBZ was 99% by HPLC.

Syntheses of Homopolymers

Thermal Polymerization of AcTBZ

Thermal polymerizations of AcTBZ were carried out using BPO as a thermal initiator under several different experimental conditions, i.e., different BPO concentration and polymerization temperatures (see Table I). For example, a solution of 0.22 g (8.62×10^{-4} mol) AcTBZ and 2.06×10^{-6} mol of BPO in 10 mL dry benzene 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 80°C for 12 h. The precipitates during polymerization was filtered off with a membrane filter. Then it was dried under reduced pressure. The resulting solid was redissolved in DMF, followed by precipitating in excess ether. The precipitate was collected by filtration and dried under vacuum to constant weight. The polymer obtained was identified by IR spectrum.

This poly(AcTBZ) was used for the accelerated fungi growth test, which will be mentioned later.

Photo Polymerization of AcTBZ

A solution of 0.22 g (8.62×10^{-4} mol) AcTBZ and 1.65×10^{-5} mol of benzophenone in 10 mL dry DMF was introduced into a dry polymerization tube equipped with a septa cap. The solution was deoxygenated by purging with purified N₂ gas. The tube was sealed and placed in a photochemical apparatus equipped with a quartz absorption sleeve and a mercury-vapor lamp (200 W) of medium pressure at 20°C for 2 h. The polymer was precipitated in excess ether. The precipitate was collected by filtration and dried at room temperature under vacuum to constant weight.

Thermal Polymerization of AA

A solution of 1.05 g (1.46×10^{-2} mol) acrylic acid (AA) and 4.69×10^{-5} mol of AIBN in 10 mL dry benzene 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 1 h. The solid precipitated during polymerization was filtered off with a membrane filter. Then, it was dried under reduced pressure. After redissolving in ethanol, the polymer was precipitated in excess ether. The precipitate was collected by filtration and dried under vacuum to constant weight.

Table I Conversion Percent and Molecular Weight Data of Poly[*N*-Acryloyl-2-(4'-thiazolyl)benzimidazole] [Poly(AcTBZ)] Synthesized in Benzene for 12 h at Different Initiator Concentrations and Polymerization Temperatures

Initiator (mol)	Temp. (°C)	Conversion (%)	\overline{M}_w	\overline{M}_n
BPO, 4.13×10^{-6}	60	6	—	—
BPO, 4.13×10^{-6}	70	11	—	—
BPO, 4.13×10^{-6}	80	25	900	600
BPO, 2.06×10^{-6} ^a	80	16	3000	800
BPO, 8.26×10^{-6}	80	30	1100	600
BPO, 1.65×10^{-5}	80	33	1400	900
BP, 1.65×10^{-5} ^b	20	10	1700	1200

Concentration of AcTBZ: 8.62×10^{-4} mol.

^a Homopolymer used for the accelerated fungi growth test.

^b Photopolymerization: solvent; DMF, polymerization time; 2 h.

Syntheses of Copolymers

Copolymerization of AcTBZ and AA

The poly[*N*-acryloyl-2-(4'-thiazolyl)benzimidazole-*co*-acrylic acid] was prepared by the copolymerization of AcTBZ and AA with BPO under various different experimental conditions by similar methods as the thermal polymerization of AcTBZ. Taking one example as a typical copolymerizations of AcTBZ with AA, a solution of 0.373 g (1.46×10^{-3} mol) AcTBZ, 0.105 g (1.46×10^{-3} mol) AA, and 4.13×10^{-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 90°C for 24 h. The poly(AcTBZ-*co*-AA) obtained in this way was used for further accelerated fungi growth test.

Photo Copolymerization of AcTBZ and AA

The poly(AcTBZ-*co*-AA) was also prepared by the copolymerization of AcTBZ and AA with benzophenone. The procedure used was the same as that of the photo polymerization of AcTBZ.

Measurement of Molecular Weight

Average molecular weights of poly(AcTBZ)s were determined by gel permeation chromatography using nonaqueous Microstyrigel column and monodisperse polystyrene as a standard at 40°C. The concentrations of polymers were 0.1% or less. For poly(AcTBZ-*co*-AA), the inherent viscosity was measured in DMF at 30°C using the Cannon-Fenske viscometer.

Accelerated Fungi Growth Test

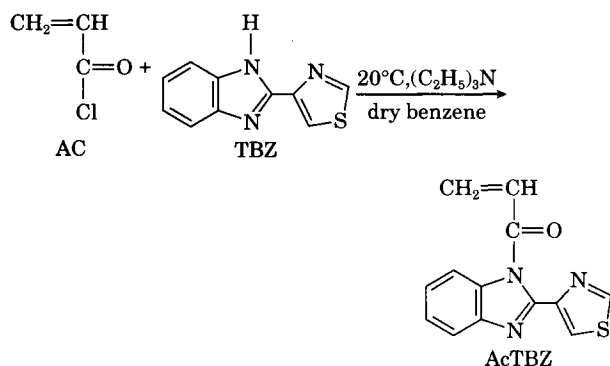
TBZ, AcTBZ, poly(AcTBZ), and poly(AcTBZ-*co*-AA) were blended individually with poly(ethylene-*co*-vinyl acetate) (EVA; VA content, 40%) at various concentrations (0.01–0.50 wt %) and dissolved in THF (5% solution). Then, test sample films of 0.1–0.13 mm thickness were prepared by casting the solutions on Petri dish. Control films of pure EVA were also prepared by casting from its THF solution. In case of poly(AA), the polymer was dissolved in water (5% solution) and the sample specimen was prepared by permeating the solution to a filter paper. 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 circle-shaped

specimens of 16 mm diameter were placed into sterile Petri dishes containing malt extract agar. The agar was then added until it was adjacent to the specimen surface. For each specimen, two agar plates were inoculated with *Aspergillus niger* or *Chaetomium globosum*, so that the growth of each separate species could be ascertained. The agar dishes were then incubated at 24°C. After 1 week, the plates were removed and examined.

RESULTS AND DISCUSSION

Identification of *N*-Acryloyl-2-(4'-thiazolyl)benzimidazole

AcTBZ was prepared according to the following scheme:



Synthesized AcTBZ was identified from its IR and $^1\text{H-NMR}$ spectra. The IR spectrum shows characteristic absorption bands at 3087, 1610, 994, and 910 cm^{-1} ($=\text{C}-\text{H}$) and 1701 cm^{-1} ($\text{C}=\text{O}$). From $^1\text{H-NMR}$ spectrum (solvent; CDCl_3) of AcTBZ, the monomer was identified with characteristic peaks at 5.63–6.03 (m, 1, $=\text{CH}$), 6.03–6.60 (m, 2, $=\text{CH}_2$), 7.20–7.60 (m, 2, benzene ring), 7.60–8.03 (m, 2, benzene ring), 8.15 (d, 1, thiazole ring), and 8.83 ppm (d, 1, thiazole ring).

Characterization of Polymers

The thermal homopolymerizations of AcTBZ were carried out with different initiator concentrations and reaction temperatures (see Table I). The effect of initiator concentration on conversion percent is seen in Figure 1.

It is seen that the conversion percent increases with increasing initiator concentrations. The conversion percent also increases with increasing polymerization temperatures, as shown in Table I.

Molecular weights of poly(AcTBZ) obtained in this way were very low, being in the order of ca. 10^3 , regardless of the initiator concentrations. The weight average molecular weight was in the range of 0.9×10^3 – 3.0×10^3 . This is probably attributed to the steric hindrance of TBZ moiety attached to an acryloyl group. The photopolymerized poly(AcTBZ) had also lower molecular weight of oligomer scale.

The homopolymer was characterized by the disappearance of the stretching and bending absorption bands caused by terminal vinyl, such as at 1610, 994, and 910 cm^{-1} on its IR spectrum. And it was also characterized from $^1\text{H-NMR}$ spectrum (solvent; DMSO-d_6) with peaks at 2.03–3.10 (m, 2, $-\text{CH}_2-$), 4.73–5.37 (m, 1, $-\text{CH}-$), 7.03–7.50 (m, 2, benzene ring), 7.50–8.07 (m, 2, benzene ring), 8.50 (d, 1, thiazole ring), and 9.37 ppm (d, 1, thiazole ring).

The copolymerizations of AcTBZ and AA were also carried out with thermal initiators such as AIBN or BPO. As shown in Table II, the conversion percent was varied depending on the kinds of initiator and concentration of initiator and the copolymer was not obtained when PPS was used as an initiator. Inherent viscosity of poly(AcTBZ-co-AA) in DMF (0.25 g/dL) was 0.17 dLg^{-1} at 30°C.

The copolymer was identified by the characteristic absorption bands at 3600–3100 ($-\text{OH}$), 1722 ($\text{C}=\text{O}$), 1210 ($\text{C}-\text{O}$), and 750 cm^{-1} (benzene ring) and by the disappearance of the stretching absorption bands caused by terminal vinyl, such as at 1610, 994, and 910 cm^{-1} on its IR spectrum. The copolymer was also characterized by $^1\text{H-NMR}$ spectrum, exhibiting very similar characteristic peaks as poly(AcTBZ).

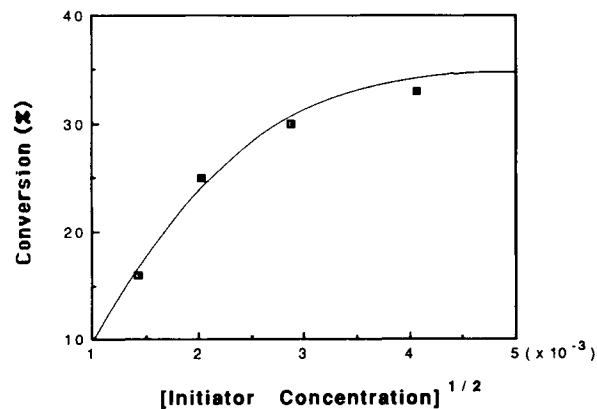


Figure 1 Plot of conversion percent vs. initiator concentration in thermal homopolymerization of *N*-acryloyl-2-(4'-thiazolyl)benzimidazole at 80°C.

Table II Conversion Percent for the Copolymerization of *N*-Acryloyl-2-(4'-Thiazolyl) Benzimidazole with Acrylic Acid

Comonomer	Initiator (mol)	Temp. (°C)	Solvent	Conversion (%)	Polymer Formation ^a
AA	PPS, 2.37×10^{-5}	40	DMSO	—	N
AA	BPO, 4.13×10^{-6}	90	toluene	48	Y
AA ^b	BPO, 4.13×10^{-5}	90	toluene	66	Y
AA ^c	BP, 4.13×10^{-5}	20	DMF	28	Y
AA	AIBN, 4.13×10^{-5}	70	toluene	38	Y

Concentration of AcTBZ and AA: 1.46×10^{-3} mol.

^a Y and N are denoted as yes or no copolymerization, respectively.

^b Copolymer used for the accelerated fungi growth test.

^c Photo polymerization time; 2 h.

Accelerated Growth Studies of Fungicidal Activity

The biocidal properties of AcTBZ and its polymers were studied in agar dish tests.⁶ Films cast on Petri dish were individually inoculated with *Aspergillus niger* and *Chaetomium globosum*. The samples inoculated with a single organism were used for the agar dish tests (at 24°C using malt extract agar). Tests were made for 1 week. Fungicidal activity was evaluated using a scale of fungi growth set up from the calculated inhibition area (cm²) as follows: above 2.01, no growth on film, zone of inhibition present; 2.00–1.91, no growth on film, growth occurs on agar up to the edge of film (no zone of inhibition); 1.90–1.72, very sparse growth detected in places on film; 1.41–0.01, moderate growth on film; below 1.00, heavy growth on film.

In Figure 2, the inhibition area (cm²) against *Aspergillus niger* is plotted against the concentration of TBZ, AcTBZ, and its polymers. It is seen that

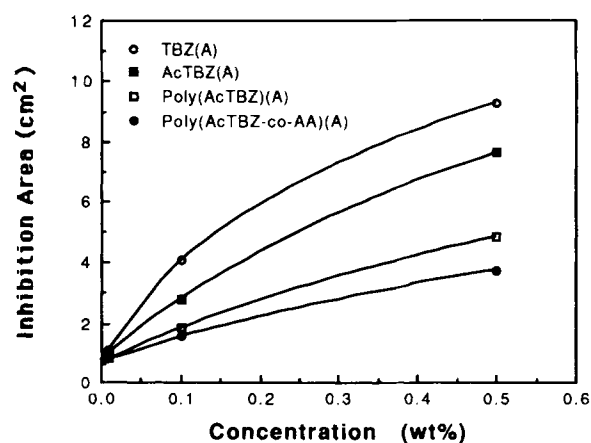


Figure 2 Plot of inhibition area against *Aspergillus niger* vs. concentration (wt %) for various fungicidal agents.

the inhibition area increases with rising concentration, regardless of the kinds of those monomers and polymers. The specimens of AcTBZ, poly(AcTBZ), or poly(AcTBZ-co-AA), prepared by blending with EVA, exhibited excellent fungicidal activities, having inhibition zone at the concentrations above 0.2 wt % of fungicidal agent, but exhibited moderate or heavy growth of *Aspergillus niger* at the concentrations below 0.01 wt % of fungicidal agent. TBZ and AcTBZ showed good fungicidal activities even at the concentrations below 0.1 wt % of fungicidal moiety. The fungicidal activities against *Aspergillus niger* were decreased in the order TBZ > AcTBZ > poly(AcTBZ) > poly(AcTBZ-co-AA). This is probably attributed to the easiness of leach or migration of TBZ or AcTBZ from the sample films compared to the polymer-anchored TBZ such as poly(AcTBZ) or poly(AcTBZ-co-AA). This result

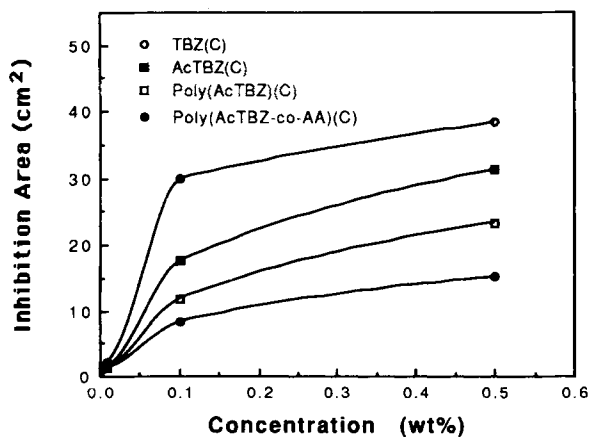


Figure 3 Plot of inhibition area against *Chaetomium globosum* vs. concentration (wt %) for various fungicidal agents.

is in agreement with the study of Pittman,⁶ stating that the blended pentachlorophenol can leach or migrate from sample films, whereas polymer-anchored pentachlorophenol cannot. It is also noted that the fungicidal activity of poly(AcTBZ-co-AA) was not better than that of poly(AcTBZ), probably due to the effect of poly(AA) having no fungicidal activity.

Similarly, Figure 3 shows the plot of inhibition area against *Chaetomium globusum* vs. concentration for various fungicidal moieties such as TBZ, AcTBZ, and its polymers. The fungicidal activities against *Chaetomium globusum* were also decreased in the order TBZ > AcTBZ > poly(AcTBZ) > poly(AcTBZ-co-AA). TBZ showed excellent fungicidal activity having inhibition zone even at very low concentration (0.01 wt %) of fungicidal agent. In case of poly(AcTBZ) and poly(AcTBZ-co-AA), a larger zone of inhibition was exhibited at the concentrations above 0.03 wt %.

It should be noted that fungicidal properties of poly(AcTBZ) and the AA copolymer are clearly inferior to those of unsubstituted TBZ, plausibly due to the fact that TBZ is too firmly bound for controlled release to the polymer chain. It is recommended to bind the TBZ unit to the main chain via urethane or urea links, for example, by use of isocyanate or chloroformate chemistry, because urea groups incorporating a ring N atom of the benzimidazole system are known to hydrolyze with greater

ease than amide groups. It is expected that TBZ groups so tied to the polymer chain would probably undergo hydrolytic release at a rate sufficient for biological action in the free state of the agent. Further works on this subject are now undertaking and will be reported elsewhere.

Comparison of Figure 2 and Figure 3 indicates that the magnitudes of inhibition area showing the fungicidal activities of AcTBZ and its polymers are much larger, at the same concentration, against *Chaetomium globusum* than those against *Aspergillus niger* over the entire concentration ranges. The result implies that the fungicidal activities of TBZ, AcTBZ, poly(AcTBZ), and poly(AcTBZ-co-AA) were better against *Chaetomium globusum* rather than against *Aspergillus niger*.

Aspergillus niger and *Chaetomium globusum* showed, however, abundant growth on the control polymers such as EVA and poly(AA), meaning that these fungi were excellent test organisms to evaluate the biocidal effects of chemically anchored biocides and blended biocides.

The results of the agar dish accelerated fungi growth test are summarized in Table III.

CONCLUSIONS

In this work, the fungicidal monomer, *N*-acryloyl-2-(4'-thiazolyl)benzimidazole (AcTBZ), was syn-

Table III Results of Agar Dish Accelerated Growth Test on TBZ, AcTBZ, Poly(AcTBZ-co-AA), and Control Polymers

Sample	Concentration of Fungicidal Agent (wt %)	<i>Aspergillus niger</i> (ATCC 2118)	<i>Chaetomium globusum</i> (ATCC 2121)
EVA ^a	none	0.75	0.98
P(AA) ^b	none	0.00	0.00
TBZ	0.01	1.12	2.12
	0.10	4.08	29.95
	0.50	9.25	38.34
AcTBZ	0.01	1.01	1.51
	0.10	2.81	17.53
	0.50	7.62	31.18
poly(AcTBZ)	0.01	0.83	1.40
	0.10	1.85	11.76
	0.50	4.83	23.28
poly(AcTBZ-co-AA)	0.01	0.81	1.25
	0.10	1.55	8.27
	0.50	3.75	15.14

^a Poly(ethylene-co-vinyl acetate) without fungicide, (vinyl acetate content, 40%).

^b Poly(acrylic acid) without fungicide.

thesized. The yield and purity were 55.6 and 99%, respectively. Poly [*N*-acryloyl-2-(4'-thiazolyl)benzimidazole]s [(poly(AcTBZ)]s were synthesized by thermal and photo initiators and its molecular weights were observed to be very low, being in the order of ca. 10^3 . The weight average molecular weight (\overline{M}_w) was in the range of 0.9×10^3 – 3.0×10^3 . Poly [*N*-acryloyl-2-(4'-thiazolyl)benzimidazole-*co*-acrylic acid] [poly(AcTBZ-*co*-AA)] was also synthesized. The fungicidal activities of *N*-acryloyl-2-(4'-thiazolyl)benzimidazole, poly [*N*-acryloyl-2-(4'-thiazolyl)benzimidazole], and poly [*N*-acryloyl-2-(4'-thiazolyl)benzimidazole-*co*-acrylic acid] against *Aspergillus niger* and *Chaetomium globosum* were excellent compared to those of poly(acrylic acid) and poly(ethylene-*co*-vinyl acetate). It was found that the fungicidal activities against both *Aspergillus niger* and *Chaetomium globosum* were decreased in the order TBZ > AcTBZ > poly(AcTBZ) > poly(AcTBZ-*co*-AA). Finally, it was concluded that the fungicidal activities of TBZ, AcTBZ, poly(AcTBZ), and poly(AcTBZ-*co*-AA) were better

against *Chaetomium globosum* rather than against *Aspergillus niger*.

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