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EVALUATION OF POLYMERS FOR
CONTROLLED DELIVERY OF HERBICIDES
FOR AQUATIC PLANT CONTROL

by

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SUMMARY

The major goal of this research was to prepare and evaluate new polymers containing pendent herbicide substituents. These systems were to be designed so that herbicide release would occur by the slow, sequential hydrolysis of the herbicide-polymer chemical bonds. The specific objectives of this research were to: (a) copolymerize the 2-acryloyloxyethyl and 2-methacryloyloxyethyl esters of fenac (AOE Fenac and MOE Fenac) with various amounts of methacrylic acid (MA); (b) copolymerize the 2-acryloyloxyethyl ester of 2,4-dichlorophenoxyacetic acid (AOE 2,4-D) with various amounts of 2-hydroxyethyl methacrylate (HEMA); (c) determine the reactivity ratios of the two monomers in the copolymerization; (d) synthesize copolymers of AOE 2,4-D and HEMA with uniform compositions and to compare their hydrolysis rates with those of analogous copolymers with nonuniform compositions; (e) carry out the copolymerization of AOE 2,4-D and HEMA in the presence of multifunctional branching and cross-linking agents; (f) copolymerize the 2-methacryloyloxyethyl ester of 2,4-D (MOE 2,4-D) with glycidyl methacrylate (GMA) and glyceryl methacrylate (GEM); (g) prepare 2-hydroxy-3-methacryloyloxypropyl 2,4-dichlorophenoxy acetate (HMOP 2,4-D); (h) homopolymerize and copolymerize HMOP 2,4-D with HEMA and GEM; (i) homopolymerize and copolymerize GMA with hydrophilic comonomers such as HEMA, and treat the resulting prepolymers with 2,4-D; and (j) determine the release rates of all the polymers prepared.

Copolymerizations of AOE Fenac and MOE Fenac with various amounts of MA were carried out in refluxing methyl ethyl ketone (MEK) with azobisisobutyronitrile (AIBN) as the initiator. The copolymers, however, did not undergo hydrolysis under mildly alkaline conditions.

A series of copolymerizations of AOE 2,4-D with various amounts of HEMA was also carried out in refluxing MEK with AIBN as the initiator. The molar feed ratios of AOE 2,4-D to HEMA employed were 84:16, 60:40, 50:50, and 40:60. The first copolymer did not undergo hydrolysis in a buffer solution with a pH of 8 at 30 °C. Although the second hydrolyzed very slowly releasing 2,4-D at a rate of less than 0.2 mg/g of copolymer/day for approximately 300 days, the rate of hydrolysis gradually increased with time. At the end of this period, the rate began to increase dramatically. The third and fourth copolymers released 2,4-D at nearly constant rates of 1.5 and 1.6 mg/g of copolymer/day, respectively.

A series of branched copolymers was prepared by carrying out copolymer-

izations of AOE 2,4-D and HEMA in dilute solutions in the presence of small amounts of 2,2-dimethylpropanediol dimethacrylate (DPDM) and 2,4-divinylbenzene. These copolymers hydrolyzed slightly faster in reconstituted hard water than did linear copolymers with similar compositions.

A series of crosslinked copolymers was prepared by carrying out copolymerizations of AOE 2,4-D and HEMA in concentrated solutions in the presence of small amounts of DPDM and pentaerythritol triacrylate. The crosslinked systems released 2,4-D in slightly alkaline solutions at nearly constant rates that varied from 0.4 to 2.2 mg/g copolymer/day. The rate of hydrolysis was more dependent on the percentage of HEMA contained in the copolymer than on its degree of crosslinking.

The free-radical reactivity ratios of AOE 2,4-D and HEMA were determined by the method of Fineman and Ross (1950) to be 0.44 and 2.62, respectively. These values were used to design experiments that produced copolymers with uniform compositions. In a brief hydrolysis study, these copolymers released 2,4-D slightly faster than copolymers with similar HEMA contents but with nonuniform compositions.

MOE 2,4-D was copolymerized with various amounts of HEMA, GMA, and GEM in MEK at 70°C with AIBN as the initiator. The copolymers containing HEMA and GMA did not hydrolyze under mildly alkaline conditions. The GMA copolymers, however, underwent hydrolysis similarly to AOE 2,4-D/HEMA copolymers. A copolymer prepared from a 60:40 MOE 2,4-D/GEM feed released 2,4-D very slowly for approximately 150 days before displaying a dramatic increase in its rate of hydrolysis. A copolymer prepared from a 50:50 feed released 2,4-D at a nearly constant rate of 1.8 mg/g copolymer/day for over 200 days.

HMOP 2,4-D was prepared in 96-98 % yield by the reaction of 2,4-D with GMA in the presence of tetramethylammonium chloride. The monomer was polymerized in MEK at 70°C with AIBN as the initiator. The homopolymer did not hydrolyze in reconstituted hard water.

HMOP 2,4-D was copolymerized with various amounts of HEMA and GEM. Although the copolymers containing HEMA did not undergo hydrolysis, copolymers containing approximately 60 mole % GEM released 2,4-D at a rate of 1 mg/g copolymer/day.

Samples of Poly GMA with number average molecular weights (M_n) that ranged from 16,000 to 23,600 were prepared by carrying out the polymerization of GMA with different amounts of AIBN. The homopolymers were treated with various amounts of 2,4-D to yield a series of adducts that contained from 10 to

79 mole % 2,4-D. These adducts, however, hydrolyzed very slowly when immersed in reconstituted hard water.

GMA was copolymerized with HEMA, 2-hydroxyethyl acrylate (HEA), 2-hydroxypropyl methacrylate (HPMA), and 2-dimethylaminoethyl methacrylate (DMAEMA) to afford the corresponding copolymers, which were treated with 2,4-D. The 2,4-D/Copoly(GMA-HEMA) adducts hydrolyzed at nearly constant rates releasing 0.6 to 0.9 mg 2,4-D/g adduct/day. The adducts prepared from the HEA and HPMA copolymers hydrolyzed very slowly. A 2,4-D/Copoly(GMA-DMAEMA) adduct released 2,4-D at a rate of 5 mg/g copolymer/day.

The homopolymerization of GMA was carried out in the presence of various amounts of 2-mercaptoethanol (ME). The hydroxy-terminated homopolymers, which had M_n 's of 5,800 and 8,600, were treated with 2,4-D to afford adducts that contained 60 mole % of the herbicide. These adducts released 2,4-D at rates of 4.1 and 1.5 mg/g adduct/day, respectively. A similar homopolymerization of GMA in the presence of 1-propanethiol (PT) produced a polymer with an M_n of 5,300. An adduct of this polymer that contained 60 mole % 2,4-D also underwent hydrolysis in reconstituted hard water releasing 2,4-D at a rate of 5 mg/g adduct/day.

Copolymerizations of GMA with HEMA were carried out in the presence of ME. The molar feed ratios of GMA to HEMA employed were 90:10 and 80:20. The copolymers were treated with 60 mole % 2,4-D to afford adducts that released the herbicide at rates of 4.7 and 4.8 mg/g adduct/day, respectively.

2,4-D/Poly GMA adducts containing pendent glycol moieties were prepared by treating samples of Poly GMA with H_2SO_4 prior to their reaction with 2,4-D. Adducts obtained from Poly GMA with an M_n of 16,500 hydrolyzed slower than similar adducts that did not contain glycol groups. Adducts prepared from hydroxy-terminated Poly GMA samples with M_n 's less than 6,000, however, released approximately 5 mg 2,4-D/g adduct/day.

The dimethylamine salt of 2,4-D (DMA 2,4-D) was physically incorporated in crosslinked chitosan and carboxymethylcellulose (CMC) matrices. Both formulations released the majority of their DMA 2,4-D in a few days when immersed in a buffer solution with a pH of 8. DMA 2,4-D and dichlobenil were also incorporated in beeswax matrices. Although DMA 2,4-D was quickly released from the beeswax matrix, dichlobenil was slowly released over a 6 month period.

CMC and hydroxyethyl cellulose were treated with the acid chloride of 2,4-D to afford the corresponding adducts. Both of these adducts hydrolyzed very quickly in a buffer solution with a pH of 8.

The syntheses of AOE and MOE 2,4-D were scaled-up to kilogram levels. This was accomplished by carrying out the reactions of the acid chloride of 2,4-D with HEA and HEMA in presence of powdered molecular sieves. Both monomers were extremely difficult to purify in large quantities.

Several attempts were made to scale-up the syntheses of a 50:50 MOE 2,4-D/GEM copolymer and a 50:50 AOE 2,4-D/HEMA copolymer crosslinked with DPDM. This work was abandoned because the polymerizations could not be carried out in concentrated solutions without the formation of insoluble gels.

The reaction of 2,4-D with GMA was scaled-up to provide kilogram quantities of HMOP 2,4-D. Large-scale polymerizations of the monomer in concentrated solutions, however, resulted in branched and crosslinked systems.

The synthesis of one of the most promising controlled-release systems prepared and evaluated in this study, i.e., an hydroxy-terminated, low-molecular-weight 2,4-D/Poly GMA adduct, was successively scaled-up to commercial levels. However, the processing of the adduct solution as obtained from the reaction mixture was difficult. A method must be developed to remove the solvent before the procedure can be used to prepare material for field tests.

PREFACE

The study presented in this report was sponsored by the Department of the Army Office of the Chief of Engineers (OCE) Directorate of Civil Works (DAEN-CW) through the U.S. Army Corps of Engineers (CE) Aquatic Plant Control Research Program (APCRP). The OCE Technical Monitor is Mr. E. Carl Brown. Funds for the study were provided by DAEN-CW under Department of the Army Appropriation No. 96X3122, Construction General. The APCRP is managed by the U. S. Army Engineer Waterways Experiment Station (WES), Vicksburg, Miss.

This work was conducted to develop and evaluate new polymer compounds containing pendant herbicide substituents with the ultimate purpose of producing effective, economical, and environmentally safe controlled release aquatic herbicides. The work was conducted from 1 August 1976 through 30 June 1983 by Dr. Frank W. Harris as principal investigator assisted by A. Aulabaugh, J.W. Thompson, C.O. Arah, M.W. Whitlock, M. Talukder, C.J. Chou, and R. Gupta.

The study was conducted under the general supervision of Dr. John Harrison, Chief, Environmental Laboratory (EL), WES; Dr. R. L. Eley, former Chief, Ecosystem Research and Simulation Division (ERSD), EL; Mr. Donald L. Robey, Chief, ERSD; Dr. R.M. Engler, former Chief, Ecological Effects and Regulatory Criteria Group (EERCG), ERSD; Dr. Thomas L. Hart, Chief, Aquatic Processes and Effects Group (APEG); and under the direct supervision of Dr. Howard Westerdahl, APEG, contract monitor. Mr. J.L. Decell is Manager, APCRP, at WES.

Commanders and Directors of WES during the conduct of this study and preparation of the report were COL John L. Cannon, CE, COL Nelson P. Conover, CE, COL Tilford C. Creel, CE, and COL Robert C. Lee, CE. Technical Directors were Mr. F.R. Brown and Dr. Robert W. Whalin.

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EVALUATION OF POLYMERS FOR CONTROLLED DELIVERY
OF HERBICIDES FOR AQUATIC PLANT CONTROL

INTRODUCTION

1. One approach to preparing controlled-release formulations that contain a high percentage of herbicide has been the synthesis of polymers that contain pendant herbicide substituents. These systems have been designed so that herbicide release will occur by the slow, sequential hydrolysis of herbicide-polymer chemical bonds. In the initial phase of this work herbicides were converted to polymerizable ester derivatives, which were subsequently homopolymerized (Harris, Post, and Feld 1974; Harris, Feld, and Bowen 1975; Harris and Post 1975). In this manner a series of polymers was prepared in which the herbicide was attached to the backbone via different spacer groups. It was postulated that increasing the distance between the hydrolyzable linkage and the hydrophobic backbone would enhance the hydrolysis of the herbicide-polymer ester bonds. Thus, the vinyl, the 2-acryloyloxyethyl, the 2-methacryloyloxyethyl, the 4-acryloyloxybutyl, and the 4-methacryloyloxybutyl esters of 2,4-dichlorophenoxyacetic acid (2,4-D), 2-(2,4,5-trichlorophenoxy) propionic acid (silvex), and 2,3,6-trichlorophenylacetic acid (fenac) were prepared and polymerized by bulk- and solution-free-radical techniques. The polymerizations were enhanced by low initiator concentrations and mild conditions. Polymeric materials were obtained that exhibited inherent viscosities as high as 2.03. None of the homopolymers, however, underwent hydrolysis under mildly basic conditions at ambient temperature.

2. In an attempt to enhance herbicide hydrolysis, the 2-acryloyloxyethyl and 2-methacryloyloxyethyl esters of 2,4-D (AOE 2,4-D and MOE 2,4-D) were copolymerized with monomers containing carboxyl or aminimide groups (Harris et al. 1977 a,b). For example, AOE 2,4-D was copolymerized with methacrylic acid and with trimethylamine methacrylimide. These copolymers did hydrolyze under mildly alkaline conditions. The rate of hydrolysis was dependent upon the amount and type of hydrophilic comonomer used. Surprisingly, the copolymers prepared from MOE 2,4-D did not undergo hydrolysis under similar conditions.

3. In this phase of the work, fenac was to be incorporated in copolymer systems. The copolymerization of AOE 2,4-D and MOE 2,4-D with new hydrophilic monomers was to be extensively investigated. The effects of sequence distribution, branching, and crosslinking on the resulting copolymers' rates of

hydrolysis were to be determined. A new herbicidal monomer containing 2,4-D and a hydrophilic group was to be prepared and polymerized. An alternate route to polymeric herbicides in which functionalized prepolymers were to be prepared and then treated with herbicides was to be explored. The specific objectives of this research were to: (a) copolymerize the 2-acryloyloxyethyl and 2-methacryloyloxyethyl esters of fenac (AOE Fenac and MOE Fenac) with various amounts of methacrylic acid; (b) copolymerize AOE 2,4-D with various amounts of 2-hydroxyethyl methacrylate (HEMA); (c) determine the reactivity ratios of the two monomers in the copolymerization; (d) synthesize copolymers of AOE 2,4-D and HEMA with uniform compositions and compare their hydrolysis rates with those of analogous copolymers with nonuniform compositions; (e) carry out the copolymerization of AOE 2,4-D and HEMA in the presence of multifunctional branching and crosslinking agents; (f) copolymerize MOE 2,4-D with glycidyl methacrylate (GMA) and glyceryl methacrylate (GEM); (g) prepare 2-hydroxy-3-methacryloyloxypropyl 2,4-dichlorophenoxy acetate (HMOP 2,4-D); (h) homopolymerize and copolymerize HMOP 2,4-D with HEMA and GEM; (i) homopolymerize and copolymerize GMA with hydrophilic comonomers such as HEMA, and to treat the resulting prepolymers with 2,4-D; and (j) determine the release rates of all the polymers prepared.

RESULTS AND DISCUSSION

Preparation and hydrolysis of copolymers containing fenac (Aulabaugh 1977)

4. Copolymerizations of AOE Fenac (1a) and MOE Fenac (1b) with various amounts of methacrylic acid (MA) (2) were carried out in refluxing methyl ethyl ketone (MEK) with azobisisobutyronitrile (AIBN) as the initiator (Tables 1-4). The yields of the copolymers ranged from 40 to 79%. Chlorine analysis indicated that the copolymers actual compositions at these conversions were nearly identical to the composition of the monomer feed.

5. In an attempt to increase the yield of the copolymers, a copolymerization of a 90:10 molar ratio of 1a to 2 was carried out in MEK contained in a sealed tube. The tube was degassed and sealed under vacuum prior to the polymerization. The yield of copolymer and the polymer's inherent viscosity, however, were not increased.

6. The acid-containing copolymers were soluble in chlorinated hydrocarbons, tetrahydrofuran (THF), N,N-dimethylformamide (DMF), acetone, MEK, and partially soluble in benzene, but were insoluble in water, aliphatic hydrocarbons, and ethyl ether. The inherent viscosities ranged from 0.07 to 0.14 (0.50 g/dl in chlorobenzene at 30°C) (Tables 1 and 2). Gel permeation chromatography studies of the copolymers showed they had number average molecular weights (M_n 's) of approximately 60,000-80,000 based on polystyrene standards. The gel permeation chromatograms also showed broad molecular weight distributions. The copolymers' glass-transition temperatures (T_g 's) ranged from 39-40°C to 77-78°C (Tables 3 and 4). In both AOE Fenac/MA and MOE Fenac/MA copolymers, the T_g increased as the percentage of MA in the copolymer increased. The T_g 's of the MOE Fenac copolymers were higher than those of the AOE Fenac copolymers.

7. A study of the hydrolysis of the copolymers in an aqueous solution buffered to pH 8 at 30°C was carried out. Thus, representative samples were extracted with ether overnight and then sieved to a particle size of 125-420 . The hydrolysis solutions were slowly agitated to ensure mixing. The amount of herbicide released from three replicates of each polymer was measured periodically by ultraviolet spectroscopic analysis. (All of the release rate studies in this work were carried out with similar procedures.)

8. All of the polymers released less than 2.5 mg of fenac over a 120-day period. The small amount of fenac that was released was probably due to residual monomers that were trapped in the polymer matrix. A 0.5-g sample of a

Table 1. Copolymerization of AOE Fenac and MA

Monomer Feed (mole ratio AOE Fenac:MA)	Copolymer Composition ^a (mole ratio AOE Fenac:MA)	Yield (%)	$[\eta]^b$
100:0	100:0	75	0.08
95:5	94:6	63	0.10
90:10	90:10	79	0.07
90:10 (vacuum)	88:12	65	0.09
85:15	89:11	40	0.08

a. Determined from chlorine analysis

b. Inherent viscosity (0.50 g/dl in chlorobenzene at 30°C)

Table 2. Copolymerization of MOE Fenac and MA

Monomer Feed (mole ratio MOE Fenac:MA)	Copolymer Composition ^a (mole ratio MOE Fenac:MA)	Yield (%)	$[\eta]^b$
100:0	100:0	93	0.14
95:5	97:3	73	0.11
90:10	91:9	70	0.08
80:10	83:17	70	0.07

a. Determined from chlorine analysis

b. Inherent viscosity (0.50 g/dl in chlorobenzene at 30°C)

Table 3. Physical and Spectral Data for AOE Fenac-MA Copolymers

Copolymer (Mole Ratio AOE Fenac:MA)	IR ₁ (cm ⁻¹)	Elemental Analysis ^a			T _g ^b (°C)
		C	H	Cl	
100:0	1740	46.25	3.28	31.51	25-27
		46.51	3.36	31.60	
84:6	1740	46.41	3.34	31.00	39-40
	2900	46.46	3.42	30.65	
90:10	1740	46.52	3.39	30.64	42-43
	2900	46.46	3.42	30.65	
90:10 (vacuum)	1740	46.57	3.38	30.44	44-45
	2900	46.81	3.48	30.41	
90:11	1740	46.54	3.40	30.54	54-56
	2900	46.52	3.46	30.52	

a. Calcd/Found

b. Determined from differential scanning calorimeter (DSC) data

Table 4. Physical and Spectral Data for MDE Fenac-MA Copolymers

Copolymer (Mole Ratio MDE Fenac:MA)	IR ₁ (cm ⁻¹)	Elemental Analysis ^a			T _g ^b (°C)
		C	H	Cl	
100:0	1735	47.82	3.73	30.25	59-60
		47.70	3.73	30.34	
97:3	1735	47.88	3.75	30.02	63-65
		47.84	3.75	30.04	
91:9	1735	48.01	3.80	29.53	66-68
	2900	48.24	3.73	29.53	
83:17	1725	48.20	3.88	28.80	77-78
	2900	48.23	3.93	28.86	

a. Calcd/Found

b. Determined from DSC data

MDE Fenac-MA copolymer containing 15 mole % acid was hydrolyzed for 10 days in the buffer heated to 47°C. Approximately 137 mg (0.572 mmol) of fenac was released. This corresponds to 42% of the fenac originally contained in the polymer. Ethylene glycol (75 mg (0.12 mmole)) was detected in the water with gas chromatography using a Porapak Q column and a flame ionization detector.

Preparation and hydrolysis of linear copolymers of AOE 2,4-D and HEMA (Thompson 1978)

9. A series of copolymerizations of AOE 2,4-D (4) with various amounts of HEMA (5) was carried out. The copolymerizations were conducted in MEK heated at reflux with AIBN as the initiator. The molar feed ratios of 4 to 5 employed were 84:16, 60:40, 50:50, and 40:60. The white copolymers (6a-d) were isolated by precipitation in hexane and then extracted overnight with ether in order to remove any unreacted monomer. The yields of the copolymers ranged from 64-78%.

10. The copolymers were soluble in several organic solvents, such as THF, DMF, and aliphatic ketones, but were insoluble in aliphatic hydrocarbons, ethyl ether, and water. The copolymers had M_n 's that ranged from 4,500 to 6,600 and Tg's that varied from 19-33°C (Tables 5 and 6). The Tg's increased as the percentage of HEMA in the copolymers increased. Gel permeation chromatograms of the copolymers showed relatively broad molecular-weight distributions.

11. The release rates of the copolymers were determined by the procedure described in paragraph 7 (Tables 7 and 8). Copolymers 6b-d slowly underwent hydrolysis under the mild conditions. Copolymer 6a, however, did not hydrolyze. Evidently, this polymer did not contain enough hydrophilic moieties to permit hydrolysis. Powdered samples of this material also fused together when immersed in the buffer, thereby greatly reducing the amount of surface area exposed to the medium. This behavior can be attributed to the polymer's low Tg (19-20°C). Copolymers 6b-d also slowly swelled and then gradually went into solution as the hydrolyses proceeded. The swelling was accompanied by an autoacceleration in the rate of hydrolysis. Since the spectroscopic method used to determine release rates did not differentiate between bound and unbound 2,4-D, it is possible that the actual increases in rate were not as large as indicated in the tables. All of the analytical samples were centrifuged prior to analysis in an attempt to remove any remaining copolymer.

12. Although all the copolymers had densities greater than water, ground particles of these materials tended to float when initially placed in the buffer. This was probably due to entrapped air and surface-tension effects. Since the copolymers also hydrolyzed very slowly initially, it was postulated

Table 5. Copolymerization of AOE 2,4-D with HEMA

Polymer No.	Monomer Feed (Mole Ratio AOE 2,4-D:HEMA)	Copolymer Composition ^a (Mole Ratio AOE 2,4-D:HEMA)	$[\eta]^b$	M_n^c
<u>6a</u>	84:16	84:16	0.08	
<u>6b</u>	60:40	51:49	0.19	4,500
<u>6c</u>	50:50	40:60	0.43	6,400
<u>6d</u>	40:60	30:70	0.43	6,600

a. Determined from chlorine analysis

b. Inherent viscosity (0.50 g/dl in DMF at 30°C)

c. Determined from vapor pressure osmometry

Table 6. Physical and Spectral Data for AOE Fenac-MA Copolymers

Polymer No.	IR (cm ⁻¹)	Elemental Analysis ^a			T _g ^b (°C)
		C	H	Cl	
<u>6a</u>	1720	49.37	4.04		19-20
	3400	50.24	4.54	20.68	
<u>6b</u>	1720	50.72	4.86		27-28
	3400	50.62	4.84	15.99	
<u>6c</u>	1720	51.36	5.25		30-31
	3400	50.98	5.30	13.88	
<u>6d</u>	1720	52.02	5.65		32-33
	3400	51.89	5.80	11.54	

a. Calcd/Found

b. Determined from DSC data

Table 7. Hydrolysis of Copolymers 6b and 6d

Copolymer <u>6b</u>			Copolymer <u>6d</u>		
Days	Mg 2,4-D ^a per g Polymer	% 2,4-D Released	Days	Mg 2,4-D ^b per g Polymer	% 2,4-D Released
1	0.9	0.1	2	1.1	0.3
5	2.0	0.4	6	4.8	1.3
7	2.9	0.6	9	9.3	2.5
11	4.5	0.9	14	25.5	7.0
18	6.4	1.3	20	32.7	9.0
25	7.0	1.4	28	39.9	11.1
29	9.5	1.9	31	45.4	12.6
46	10.7	2.2	37	53.9	14.9
54	11.5	2.3	42	67.7	18.8
64	13.0	2.6	48	83.7	23.2
74	14.1	2.8	55	114.0	31.6
92	17.3	3.5	66	139.0	38.6
109	20.4	4.1	73	200.6	55.7
124	22.0	4.5	115	218.5	60.7
141	24.8	5.0	157	258.1	71.7
200	42.7	8.7	175	279.3	77.6
230	51.2	10.4			
261	62.8	12.8			
294	80.9	16.5			
352	97.8	19.9			
396	120.5	24.6			

a. Average amount of 2,4-D released from three 1-g replicates in designated number of days

b. Average amount of 2,4-D released from three 0.5-g replicates in designated number of days

Table 8. Hydrolysis of Polymer 6c^a

Copolymer <u>6c</u>			Polymer <u>6c</u> (surfactant)		
Days	Mg 2,4-D per g Polymer	% 2,4-D Released	Days	Mg 2,4-D per g Polymer	% 2,4-D Released
2	4.3	0.9	6	5.2	1.2
7	8.0	1.8	10	6.4	1.4
13	13.4	3.1	21	14.7	3.4
20	17.5	4.0	30	15.5	3.5
31	29.1	6.7	65	50.3	11.6
38	39.9	9.2	72	85.4	19.7
45	43.5	10.0	80	86.4	20.0
52	51.7	11.9	91	147.7	34.2
63	79.5	18.4	99	158.6	36.7
70	107.3	24.8	105	180.0	41.6
80	161.9	37.5	135	218.5	50.6
91	196.4	45.4	154	246.5	57.1
118	224.7	52.0	183	278.1	64.4
161	238.2	55.1			
212	312.3	72.3			

a. Release rates expressed as the average amount of 2,4-D released from three 0.5-g replicates in designated number of days

that the physical wetting of the copolymer surface could be playing a role in the hydrolysis process.

13. In order to test this hypothesis, the rate of hydrolysis of polymer 6c was determined in a buffer solution containing a few drops of a commercial surfactant, i.e., Dupont's Zonyl FSN. Although the polymer particles immediately sank when placed in the treated buffer solution, their rate of hydrolysis was not significantly different from that in the absence of the wetting agent (Table 8).

14. As in the case of AOE 2,4-D/methacrylic acid copolymers, the rate of hydrolysis appeared to depend upon the percentage of hydrophilic monomer in the copolymer. However, it is interesting to note that, although polymers 6c and d hydrolyzed considerably faster than 6b, polymer 6d hydrolyzed only slightly faster than 6c. Polymer 6d dissolved completely in 205 days while 6c was not entirely dissolved in 390 days. It is possible that there is a limiting degree of hydrophilicity above which an autoacceleration in rate occurs. Polymers 6c and d were evidently hydrophilic enough to almost immediately undergo auto-accelerating hydrolyses. Polymer 6b, however, hydrolyzed slowly until it became hydrophilic enough for the autoacceleration in rate to occur. The data suggest that this point was reached after 294 days at which time 8 mole % of the AOE 2,4-D contained in the copolymer had undergone hydrolysis. Hence, 43 mole % of AOE 2,4-D was present in the copolymer at the start of the auto-accelerating process. This is comparable to the 40 mole % of AOE 2,4-D contained in polymer 6c initially.

Determination of the reactivity ratios of AOE 2,4-D and HEMA (Thompson 1978)

15. In order to learn more about the copolymers' compositions, the free-radical reactivity ratios of AOE 2,4-D and HEMA were determined by the method of Fineman and Ross (1950). Thus, a series of copolymerizations with varying monomer feed ratios were run in MEK heated at 70°C. The copolymerizations were carried out to low conversions, and the resulting copolymers' compositions were determined by chlorine analysis (Table 9). The data were then substituted in the following equation:

$$\left(\frac{f_1}{f_2}\right)\left(\frac{1-2F_1}{F_1}\right) = \left[\left(\frac{f_1^2}{f_2^2}\right)\left(\frac{F_1^{-1}}{F_1}\right)\right] r_1 + r_2 \quad (1)$$

where f_1 and f_2 are the respective mole fractions of AOE 2,4-D and HEMA in a given feed, F_1 is the mole fraction of AOE 2,4-D in the resulting copolymer, and r_1 and r_2 are the free radical reactivity ratios of AOE

Table 9. Copolymerization of AOE 2,4-D with HEMA for Reactivity Ratio Determinations

Monomer Feed (mole ratio AOE 2,4-D:HEMA)	Copolymer Composition ^a (mole ratio AOE 2,4-D:HEMA)	Yield (%)
94:6	87:13	12
90:10	80:20	9
80:20	64:36	7
60:40	37:63	5
40:60	20:80	9

a. Determined by chlorine analysis

Table 10. Calculated Molar Feed Ratios for Uniform Composition AOE 2,4-D/HEMA Copolymers

Desired Molar Composition AOE 2,4-D:HEMA	$\frac{[\text{HEMA}]}{[\text{AOE 2,4-D}]}$	Initial Molar Feed Ratio AOE 2,4-D:HEMA
2:1	0.21	83:17
1:1	0.41	71:29
1:2	0.80	56:44

2,4-D and HEMA, respectively. The term on the left side of the equation was then plotted against the coefficient of r_1 for each feed ratio used. The slope and intercept of the straight line obtained, i.e., r_1 and r_2 , were determined by least-squares analysis to be 0.44 and 2.62, respectively.

16. Since HEMA is considerably more reactive than AOE 2,4-D, the composition of copolymers of these two monomers is nonuniform. Material formed early in the polymerization contains more HEMA than present in the feed, while copolymer formed at higher conversions contains less.

Preparation and hydrolysis of linear copolymers of AOE 2,4-D and HEMA with uniform compositions (Whitlock 1980)

17. The molar ratios of AOE 2,4-D and HEMA needed to prepare uniform composition copolymers containing 2:1, 1:1, and 1:2 ratios of AOE 2,4-D to HEMA were calculated according to the method of Fineman and Ross (1950) using the values of 0.44 for r_1 and 2.62 for r_2 . The results are given in Table 10.

18. Due to the change in monomer composition that occurs as the copolymerization proceeds, the initial feed ratios will only afford the desired copolymer composition if the polymerization is carried out to low conversion. However, if the rate of copolymerization is known, the initial monomer composition may be maintained by making appropriate monomer additions as the polymerization proceeds. Hence, the next step in this study was to determine the rate of the monomer conversion to copolymer. A series of copolymerizations of 10 g AOE 2,4-D and 1.67 g HEMA (71:29 mole ratio) in 50 ml of MEK at 70°C was carried out for various periods of time. The polymerizations gave an average conversion of 20 % per hour. Thus, 10 % of each comonomer was consumed per hour.

19. Copolymerizations of AOE 2,4-D and HEMA were then carried out using initial molar feed ratios of 83:17, 71:29, and 56:44 (Table 11). The copolymerizations were run in MEK at 70°C with AIBN as the initiator. An appropriate amount of each monomer was added after 1 hr so as to restore the initial monomer ratios. The monomer additions were repeated every hour for the next 2 hr. After the last addition, the reaction mixture was heated one additional hour, allowed to cool, and then added dropwise to 1000 ml hexane to precipitate the product. The white polymers were extracted overnight with ethyl ether to remove any unreacted monomer or initiator residues and dried under reduced pressure. The yields ranged from 43-75%.

20. This procedure gave very good results. The initial molar feed ratios

Table 11. AOE 2,4-D/HEMA Copolymers with Uniform Compositions

Polymer No.	Desired Composition	Monomer ^a Feed	Reaction ^b Time (hr)	Yield (%)	% Cl	Tg ^c (°C)	{η} ^d	Copolymer ^e Composition
<u>7a</u>	50:50	80:20 ^f	4	52	15.65	19	0.26	49:51
<u>7b</u>	60:40	86:14	4	57	17.15	19	0.19	58:42
<u>7c</u>	70:30	90:10	4	42	18.21	14	0.18	65:35
<u>8a</u>	50:50	71:29 ^g	5	70	16.70	22	0.22	55:45
<u>8b</u>	34:66	56:44	4	43	13.70	25	0.33	39:61
<u>8c</u>	66:34	83:17	4	75	19.62	20	0.15	75:25
<u>9^h</u>		50:50	24	80	14.96	20	0.26	46:54

a. Molar ratio AOE 2,4-D:HEMA

b. One hour interval between programmed additions

c. Determined from DSC data

d. Inherent viscosity (0.50 g/dl in DMF at 30°C)

e. Determined from chlorine analysis

f. 25% of total HEMA added initially and at each interval

g. 10% of initial feed added at each interval

h. Prepared by batch procedures

should have given copolymer compositions of 66:34, 50:50, and 34:66, respectively. As determined by chlorine analysis, actual copolymer compositions of 75:25, 55:45, and 39:61 were obtained. In each case, the copolymer contained slightly less than the theoretical amount of HEMA.

21. A second procedure was also used to prepare copolymers with uniform compositions (Table 11). In this procedure only the more reactive monomer, i.e., HEMA, was added to the polymerization. Thus, 50:50, 60:40, and 70:30 molar feed ratios of AOE 2,4-D to HEMA were weighed out. In this case, however, only 25% of the HEMA was added to the initial polymerization mixtures. The remaining 75% was added in three equal portions at 1-hr intervals during the polymerization. After the polymerization had been allowed to proceed a total of 4 hr, the reaction mixture was worked up as described in the first procedure. The yields of the copolymers ranged from 42-57%.

22. This procedure also gave very good results. Actual copolymer compositions of 49:51, 58:42, and 65:35 were obtained. Although the copolymers contained slightly more than the theoretical amount of HEMA, their compositions were closer to the calculated values than those obtained with the first procedure.

23. The copolymers were soluble in several organic solvents such as THF, DMF, and aliphatic ketones, but were insoluble in aliphatic hydrocarbons, ethyl ether, and water. Their Tg's ranged from 14-25°C and increased as the percentage of HEMA in the copolymers increased (Table 11).

24. The release rates of the copolymers were obtained by a slight modification of the procedure found in paragraph 7. In this case, the samples were immersed in reconstituted hard water with a hardness of 160-180 mg/l and a pH of 8.0. The solutions were also stored at ambient temperature (Tables 12-14).

25. As shown in the tables, all the AOE 2,4-D/HEMA copolymers underwent hydrolysis. Although only a small percentage of the 2,4-D contained in the copolymers was released in this brief study, the effect of the programmed addition of the monomers on the resulting copolymers' release rates can be seen by comparing the release rates of the copolymers made by the two different procedures to that of copolymer 9 (Table 14), which was prepared by a standard batch technique (Table 11). For example, copolymer 8b, which contained only 7% more HEMA, released 2,4-D approximately three times faster than 9. Copolymer 8a had a release rate slightly faster than 9, even though it contained 9% less HEMA. The most dramatic example of the effect of composition is found when comparing copolymer 8c with 9. Although the former contained over 50% less

Table 12. Hydrolysis of Copolymers 7a-c^a

Days	Copolymer <u>7a</u>		Copolymer <u>7b</u>		Copolymer <u>7c</u>	
	Mg 2,4-D per g polymer	% 2,4-D Released	Mg 2,4-D per g polymer	% 2,4-D Released	Mg 2,4-D per g polymer	% 2,4-D Released
2	5.4	1.1	3.0	0.6	2.7	0.5
9	11.1	2.3	6.5	1.5	7.0	1.2
13	12.6	2.6	7.6	1.4	8.2	1.4
20	15.3	3.1	9.1	1.7	9.9	1.7
26	17.0	3.5	10.6	2.0	10.9	1.9
34	18.3	3.8	12.2	2.3	12.0	2.1
47	20.4	4.2	14.0	2.6	14.0	2.5
54	21.1	4.3	14.8	2.8	14.7	2.6
61	21.7	4.5	15.7	2.9	14.9	2.6
68	22.3	4.6	16.1	3.0	15.6	2.7
75	22.8	4.7	16.5	3.1	16.0	2.8
85	22.9	4.7	16.6	3.1	16.7	2.9

a. Release rate expressed as the average amount of 2,4-D released from three 0.5-g replicates in designated number of days

Table 13. Hydrolysis of Copolymers 8a and b ^a

Copolymer <u>8a</u>			Copolymer <u>8b</u>		
Days	Mg 2,4-D per g Polymer	% 2,4-D Released	Days	Mg 2,4-D per g Polymer	% 2,4-D Released
2	1.6	0.3	2	8.3	2.0
9	5.0	1.0	6	14.1	3.3
13	6.0	1.2	9	17.1	4.0
20	7.8	1.5	16	24.0	5.7
26	8.6	1.7	23	27.2	6.4
34	10.0	1.9	30	31.3	7.4
40	11.0	2.1	40	35.0	8.3
47	12.1	2.3			
54	12.5	2.4			
68	13.4	2.6			
75	13.8	2.7			
85	14.1	2.7			

a. Release rate expressed as the average amount of 2,4-D released from three 0.5-g replicates in designated number of days

Table 14. Hydrolysis of Copolymers 8c and 9^a

Copolymer <u>8c</u>			Copolymer <u>9</u>		
Days	Mg 2,4-D per g Polymer	% 2,4-D Released	Days	Mg 2,4-D per g Polymer	% 2,4-D Released
4	2.7	0.4	6	2.7	0.6
10	4.3	0.7	9	3.8	0.8
17	5.6	0.9	16	6.6	1.4
24	6.3	1.0	23	7.3	1.5
31	7.2	1.2	30	7.5	1.6
45	7.7	1.3	40	8.5	1.8

a. Release rate expressed as the average amount of 2,4-D released from three 0.5-g replicates in designated number of days

Table 15. Copolymerization of AOE 2,4-D with HEMA in the Presence of Multifunctional Monomers (MM)

Polymer No.	Wt % MM	Copolymer Composition ^a			$[\eta]$ ^b	M_n ^c
		Mole Ratios AOE 2,4-D:HEMA:MM				
<u>10a</u>	4	36.0	60.4	3.6	0.208	17,000
<u>10b</u>	8 ^d	44.5	48.6	6.9	0.190	12,000
<u>11</u>	4 ^e	27.5	65.9	6.6	0.262	15,800
<u>12</u>	4 ^f	31.6	65.5	2.9	insoluble gel	insoluble gel

a. Determined from chlorine analysis

b. Inherent viscosity (0.50 g/dl in DMF at 30°C)

c. Number-average molecular weight determined with vapor-pressure osmometry (VPO)

d. 2,2-Dimethylpropanediol dimethacrylate

e. Divinyl benzene

f. Pentaerythritol triacrylate

HEMA, it released 2,4-D at approximately the same rate as 9. All of these comparisons strongly suggest that copolymers with uniform compositions will undergo hydrolysis at faster rates than analogous copolymers with non-uniform compositions.

26. This conclusion can be further substantiated by comparing the release rates of copolymers 7a-c with that of 9. Copolymer 7a, with only 3% less HEMA, released 2,4-D approximately two times faster than 9. Although copolymer 7b contained 12% less HEMA than 9, it had a faster hydrolysis rate. Even more significantly, the release rate of 7c, which contained 20% less HEMA, was also faster.

Preparation and hydrolysis of branched copolymers of AOE 2,4-D and HEMA (Thompson 1978)

27. In order to determine the effects of molecular weight and branching on the copolymers' rates of hydrolysis, copolymerizations were conducted in the presence of multifunctional branching agents. Thus, the polymerization of a 50:50 molar feed ratio of AOE 2,4-D and HEMA in the presence of 4 and 8% 2,2-dimethylpropanediol dimethacrylate (DPDM) provided the corresponding branched copolymers (10a and b). An additional branched copolymer (11) was prepared by polymerizing a 50:50 molar feed ratio of AOE 2,4-D and HEMA in the presence of 4% m-divinylbenzene (Table 15).

28. Although the inherent viscosities of the branched copolymers were comparable to those of their linear analogs, their molecular weights were higher. The Tg's of copolymers 10a and b were similar to those of corresponding linear compositions (Table 16). The Tg of polymer 11, however, was considerably higher, due to the aromatic ring introduced into the system through the use of m-divinylbenzene. The branched copolymers underwent hydrolysis in reconstituted hard water at rates slightly faster than those of linear polymers with similar compositions (Tables 17-18). As with the linear systems, the rates increased as the hydrolysis proceeded. The branched systems also slowly swelled and gradually went into solution.

Preparation and hydrolysis of crosslinked copolymers of AOE 2,4-D and HEMA (Arah 1979)

29. In order to determine the effects of cross-linking on the copolymers' release rates, 4% (w/w) of pentaerythritol triacrylate (PETA) was added to a polymerization of a 50:50 molar feed ratio of AOE 2,4-D and HEMA (Table 15). The resulting copolymer (12) underwent hydrolysis at nearly a constant rate (Table 18). The polymer swelled as the hydrolysis proceeded, but did not go

Table 16. Physical and Spectral Data for Copolymers of AOE 2,4-D, HEMA, and Multifunctional Monomers

Copolymer No.	IR (cm ⁻¹)	Elemental Analysis ^a			T _g ^b (°C)
		C	H	Cl	
<u>10a</u>	1720	52.11	5.48		25-27
	3400	51.92	5.66	12.90	
<u>10b</u>	1720	51.96	5.22		23-25
	3400	51.81	5.40	14.75	
<u>11</u>	1720	53.98	5.80		50-51
	3400	54.89	6.05	10.72	
<u>12</u>	1720	52.07	5.58		33-35
	3400	52.29	5.63	11.82	

a. Calcd/Found

b. Determined from DSC data

Table 17. Hydrolysis of Copolymers 10a and b^a

Copolymer <u>10a</u>			Copolymer <u>10b</u>		
Days	Mg 2,4-D per g Polymer	% 2,4-D Released	Days	Mg 2,4-D per g Polymer	% 2,4-D Released
3	0.4	0.1	4	6.3	1.4
16	1.9	1.9	7	13.9	3.1
23	16.8	4.2	14	34.0	7.6
31	27.4	6.9	21	35.9	8.1
37	44.5	11.3	34	43.7	9.8
44	76.5	19.4	57	240.6	54.2
56	134.3	34.1	85	257.6	58.1
79	264.2	67.1	113	267.0	60.2
105	268.9	68.2	146	291.0	65.6
135	283.2	71.9	194	313.3	70.6
154	318.2	80.8			

a. Release rate expressed as the average amount of 2,4-D released from three 0.5-g replicates in designated number of days

Table 18. Hydrolysis of Copolymers 11 and 12 ^a

Copolymer <u>11</u>			Copolymer <u>12</u>		
Days	Mg 2,4-D per g Polymer	% 2,4-D Released	Days	Mg 2,4-D per g Polymer	% 2,4-D Released
7	3.0	0.9	2	4.9	1.3
20	9.2	2.7	9	26.6	7.4
27	18.8	5.6	16	41.7	11.6
43	35.7	10.7	23	56.4	15.7
56	49.8	14.9	27	68.1	18.9
65	62.2	18.6	38	98.3	27.4
77	70.9	21.2	50	120.5	33.6
93	143.4	42.9	65	155.4	43.3
104	242.3	72.6	87	217.8	60.7
136	327.1	98.0	119	260.3	72.5
			154	267.2	74.4

a. Release rates expressed as the average amount of 2,4-D released from three 0.5-g replicates in designated number of days

into solution. Since this is the type of release rate desired, more extensive research was conducted on the effects of crosslinking.

30. A series of copolymerizations of AOE 2,4-D and HEMA was carried out with equimolar amounts of the two monomers in the presence of 2, 4, and 8 % (w/w) PETA and DPLDM (Tables 19 and 20). The polymerizations, which were conducted in various amounts of MEK at 70°C, were run until gelation occurred. The white polymers were isolated by precipitation in hexane, extracted overnight with ether to remove any unreacted monomer and initiator residues, and dried. Yields of the polymers ranged from 26-91%.

31. The crosslinked products were insoluble in organic solvents. Their Tg's ranged from 45-50 C, with the Tg's of the trifunctionally crosslinked polymers being higher than their difunctionally crosslinked counterparts (Tables 19 and 20).

32. The release rates of the crosslinked copolymers, which were determined in a buffer solution (pH = 8) at 30°C, were dependent upon the systems' hydrophilicity (Tables 21-24). As with the corresponding linear copolymers, the rates increased as the degree of hydrophilicity increased. Although there was some evidence that an increase in the degree of crosslinking may result in a slight decrease in the rate of hydrolysis, the hydrophilicity, as determined by the copolymer's composition at the time of gelation, appeared to be the major factor governing the rate at which a given copolymer underwent hydrolysis. For example, copolymer 13a hydrolyzed more than twice as fast as 13b although it had a considerably higher degree of crosslinking. This can be attributed to its higher HEMA content, i.e., its higher HEMA/AOE 2,4-D ratio. Another contributing factor may have been the hydrophilicity of the crosslinking agent itself. Since PETA contains a free hydroxyl group, the incorporation of this molecule into a crosslinked network may result in an increase in hydrophilicity.

33. An additional example of the overriding effect of composition can be found by comparing polymers 13a, c, and e. These copolymers underwent hydrolysis at similar rates despite their large differences in degree of crosslinking. Their hydrophilicities, as determined by their HEMA and PETA contents, however, were very similar.

34. There was some evidence that the degree of crosslinking may be more important in less hydrophilic copolymers, i.e., copolymers containing lower HEMA/AOE 2,4-D ratios. For example, copolymers 13b, d, and f had similar compositions but slightly different release rates. In fact, the release rates

Table 19. Crosslinking Studies with PETA

Polymer No.	Wt. % PETA in feed	Reaction Time (hr)	Yield (%)	Tg ^e (°C)	% Cl	Copolymer Composition ^f AOE 2,4-D:HEMA:PETA	Release Rate ^g
<u>13a</u> ^a	2	3 ^c	28	48	10.77	29:66:5	1.9
<u>13b</u> ^b	2	23 ^d	91	47	14.64	45:53:2	0.8
<u>13c</u> ^a	4	2 ^c	27	49	11.09	33:58:9	1.6
<u>13d</u> ^b	4	23 ^d	85	49	13.84	42:54:4	0.7
<u>13e</u> ^a	8	1 ^c	32	50	9.00	26:58:16	1.6
<u>13f</u> ^b	8	23 ^c	86	49	13.24	41:53:6	0.4

a. Volume of solvent used was 25 ml

b. Volume of solvent used was 80 ml

c. Actual time of polymerization, i.e., the time at which gelation occurred

d. Actual time of polymerization, i.e., reaction was allowed to run overnight during which time gelation occurred

e. Determined from DSC data

f. Calculated from chlorine analysis assuming complete incorporation of the used PETA

g. Over a period of about 60 days

Table 20. Crosslinking Studies with DPDM

Polymer No.	Wt. % DPDM in feed	Reaction Time ^d (hr)	Yield (%)	T _g ^e (°C)	% Cl	Copolymer Composition ^f		Release Rate ^g
						AOE	2,4-D:HEMA:DPDM	
<u>14a</u> ^a	2	4	28	46	10.57	28:66:6	2.2	
<u>14b</u> ^b	2	44	84	45	15.35	49:49:2	1.0	
<u>14c</u> ^c	2	192	90	45	12.62	35:62:3	h	
<u>14d</u> ^a	4	3	44	47	12.96	39:48:13	0.9	
<u>14e</u> ^b	4	7	58	47	12.02	34:60:6	0.8	
<u>14f</u> ^c	4	120	89	46	10.39	27:70:3	h	
<u>14g</u> ^a	8	2	26	48	9.30	27:48:25	1.1	
<u>14h</u> ^b	8	19	53	47	11.92	36:52:12	0.7	
<u>14i</u> ^c	8	17	76	47	11.02	30:61:9	h	

a. Volume of solvent used was 25 ml

b. Volume of solvent used was 50 ml

c. Volume of solvent used was 75 ml

d. Actual time of polymerization, i.e., the time at which gelation occurred

e. Determined from DSC data

f. Calculated from chlorine analysis assuming complete incorporation of the used PETA

g. Over a period of about 60 days

h. No hydrolysis data were obtained

Table 21. Hydrolysis of Crosslinked Copolymers 13a, 13c, and 13e^a

Copolymer <u>13a</u>			Copolymer <u>13c</u>			Copolymer <u>13e</u>		
Days	Mg 2,4-D per g	% 2,4-D Released	Days	Mg 2,4-D per g	% 2,4-D Released	Days	Mg 2,4-D per g	% 2,4-D Released
2	2.8	0.8	7	12.1	3.5	2	2.0	0.7
7	9.9	3.0	13	23.7	6.9	7	7.7	2.7
15	20.4	6.1	18	29.1	8.4	15	15.9	5.7
22	32.1	9.6	23	45.3	13.1	22	26.4	9.4
28	42.9	12.8	28	54.4	15.8	28	35.0	12.5
36	65.7	19.6	43	75.4	21.8	36	52.7	18.8
42	68.1	20.3	57	90.2	26.1	42	63.1	22.5
50	89.5	26.7	63	102.9	29.8	49	49.7	28.4
53	95.9	28.7	71	113.6	32.9	55	85.7	30.5
57	103.3	30.8	88	120.3	34.8	62	90.9	32.4

a. 25 ml MEK used in polymerization: release rate data expressed as the average amount of 2,4-D (in mg) released from three 0.5-g replicates

Table 22. Hydrolysis of Crosslinked Copolymers 13b, 13d, and 13f^a

Copolymer <u>13b</u>			Copolymer <u>13d</u>			Copolymer <u>13f</u>		
Days	Mg 2,4-D per g	% 2,4-D Released	Days	Mg 2,4-D per g	% 2,4-D Released	Days	Mg 2,4-D per g	% 2,4-D Released
2	1.5	0.3	2	0.5	0.1	2	0.0	0.0
9	6.2	1.4	9	3.8	0.8	9	1.1	0.3
15	12.3	2.7	15	8.5	1.8	15	2.4	0.6
22	15.6	3.4	22	11.4	2.4	22	3.8	0.9
29	22.3	4.9	29	17.9	3.8	28	6.4	1.6
36	33.0	7.2	39	32.9	6.9	36	9.0	2.2
43	41.2	9.0	42	35.5	7.5	46	13.2	3.2
61	45.4	10.0	61	41.2	8.7	53	14.5	3.5
74	51.6	11.3	74	47.1	9.9	61	20.2	4.9
83	63.7	14.0	83	56.4	11.9	83	32.3	7.8
95	71.7	15.7	95	64.1	13.5	95	40.9	9.9

a. 80 ml MEK used in polymerization: release rate data expressed as the average amount of 2,4-D (in mg) released from three 0.5-g replicates

Table 23. Hydrolysis of Crosslinked Copolymers 14a, 14d, and 14g^a

Copolymer <u>14a</u>			Copolymer <u>14d</u>			Copolymer <u>14g</u>		
<u>Days</u>	<u>Mg 2,4-D per g</u>	<u>% 2,4-D Released</u>	<u>Days</u>	<u>Mg 2,4-D per g</u>	<u>% 2,4-D Released</u>	<u>Days</u>	<u>Mg 2,4-D per g</u>	<u>% 2,4-D Released</u>
2	2.7	0.8	7	5.3	1.3	4	2.4	0.8
7	9.9	3.0	13	11.7	2.9	9	6.3	2.2
15	20.0	6.3	18	14.4	3.6	14	12.0	4.2
22	34.2	10.4	23	24.0	5.9	22	19.2	6.6
28	45.5	13.8	28	27.6	6.8	29	25.1	8.7
30	56.8	17.2	43	38.5	9.0	35	31.9	11.0
36	70.6	21.4	57	51.0	12.6	43	44.7	15.4
42	84.7	25.7	63	56.8	14.1	49	53.0	18.3
51	104.0	31.6	71	64.7	16.0	57	57.1	19.2
55	118.8	36.1	76	71.6	17.7	62	69.8	24.0

a. 25 ml MEK used in polymerization; release rate data expressed as the average amount of 2,4-D (in mg) released from three 0.5-g replicates

Table 24. Hydrolysis of Crosslinked Copolymers 14b, 14e, and 14h^a

Copolymer <u>14b</u>			Copolymer <u>14e</u>			Copolymer <u>14h</u>		
Days	Mg 2,4-D per g	% 2,4-D Released	Days	Mg 2,4-D per g	% 2,4-D Released	Days	Mg 2,4-D per g	% 2,4-D Released
2	6.0	1.3	4	2.1	0.6	7	5.0	1.4
8	13.1	2.7	10	6.4	1.7	13	8.2	2.2
17	21.4	4.5	19	14.9	4.0	22	14.9	4.0
29	34.7	7.3	31	24.7	6.6	34	22.6	6.1
79	84.5	17.7	81	57.0	15.2	84	46.6	12.6

a. 50 ml MEK used in polymerization: release rate data expressed as the average amount of 2,4-D (in mg) released from three 0.5-g replicates

Table 25. Ethylene Glycol Determinations

Copolymer No.	Days	Moles of Ethylene Glycol Detected X10	% of Theoretical ^a
<u>6b</u>	310	1.4	30.2
<u>6c</u>	212	3.2	22.7
<u>6c</u> (surfactant)	185	1.4	10.8
<u>6d</u>	287	1.1	8.6
<u>10a</u>	168	2.7	18.6
<u>10b</u>	114	1.6	13.1
<u>11</u>	67	0.2	7.1
<u>12</u>	51	1.3	24.6

a. Based on amount of 2,4-D detected in solutions by spectrophotometric analysis

decreased as the degree of crosslinking increased.

35. Interesting examples of the effects of composition and crosslinking can also be found by examining the results of the crosslinking studies with DPDM (Table 20). Since DPDM contains two methyl groups, the incorporation of this molecule in a network should result in a decrease in hydrophilicity. This may partially explain why 14g released 2,4-D at one half the rate of 14a. Of course, the reduced rate may be due to 14g's significantly higher crosslink density. Considering the results of the PETA studies, however, it is more likely that the large difference in rates was due to the difference in composition.

36. All of the crosslinked systems released 2,4-D at nearly constant rates. This is in contrast to linear AOE 2,4-D/HEMA copolymers which undergo autoaccelerating hydrolysis. This difference in behavior may be related to the fact that the crosslinked systems do not dissolve as the hydrolysis proceeds.

Determination of ethylene glycol in hydrolysis solutions of AOE 2,4-D copolymers

37. In an earlier study it was found that copolymers of AOE 2,4-D and methacrylic acid undergo hydrolysis at both ester linkages in the pendent herbicide chain. Although 2-hydroxyethyl 2,4-dichlorophenoxyacetate was not detected in the hydrolysis solutions used in that study, a substantial amount of ethylene glycol was found. In order to determine if the copolymers of AOE 2,4-D prepared in this work behave similarly, the hydrolysis solutions were analyzed for ethylene glycol. Based on the amount of 2,4-D that was detected in the solutions by spectrophotometric analysis, approximately 7 to 30% of the theoretical amount of ethylene glycol was found (Table 25). This indicates that hydrolysis did occur at both ester linkages.

Linear MOE 2,4-D copolymers

38. Although all the previous copolymers of MOE 2,4-D had been found to be resistant to hydrolysis, these materials still offered promise as controlled release systems because of their high Tg's. The copolymers could be ground into hard, fine powders that were easy to handle. Hence, a search for new comonomers that would afford hydrolyzable systems was initiated with the copolymerization of MOE 2,4-D with HEMA and GEM. The MOE 2,4-D/comonomer molar feed ratios used were 70:30, 60:40, and 50:50. The copolymerizations were conducted in MEK at 70°C with AIBN (0.016 g) as the initiator. The products were isolated by precipitation in hexane and then extracted overnight with ether. The yields of the copolymers ranged from 50-95% (Table 26).

Table 26. Copolymerization of MOE 2,4-D with HEMA and GEM

Copolymer No.	Comonomer	Mole % MOE 2,4-D In Feed	Yield (%)	Mole % MOE 2,4-D ^a In Copolymer
<u>15a</u>	HEMA ^b	60	50	59
<u>15b</u>	HEMA	50	53	51
<u>16a</u>	GEM ^c	70	94	68
<u>16b</u>	GEM	60	94	56
<u>16c</u>	GEM	50	95	45

a. Determined from chlorine analysis

b. 35 ml MEK used in polymerization

c. 80 ml MEK used in polymerization

Table 27. Physical and Spectral Properties of Copolymers 15 and 16

Copolymer No.	Elemental Analysis			$\{\eta\}^a$	T _g ^b (°C)	IR (cm ⁻¹)
	C	H	Cl			
<u>15a</u>	51.35	5.14	16.77	0.79	60	3430 1720
<u>15b</u>	52.64	5.58	15.62	0.74	65	3400 1710
<u>16a</u>	51.73	5.28	17.43	0.16	50	3460 1730
<u>16b</u>	50.70	5.39	15.45	0.18	53	3440 1720
<u>16c</u>	50.75	5.68	13.49	0.25	68	3420 1720

a. Inherent viscosity (0.50 g/dl in DMF at 30°C)

b. Determined from DSC data

39. Copolymers 15 and 16 were soluble in several organic solvents, such as THF, DMF, and aliphatic ketones, but were insoluble in aliphatic hydrocarbons, ethyl ether, and water. The Tg's of these polymers ranged from 50-68°C (Table 27).

40. An attempt was also made to copolymerize MOE 2,4-D with crotonic acid. In this case, however, only MOE 2,4-D homopolymer could be isolated from the reaction mixture.

41. The MOE 2,4-D/HEMA copolymers did not undergo hydrolysis in a buffer solution (pH = 8) at 30°C. The MOE 2,4-D/GEM copolymers, however, slowly hydrolyzed under the mildly alkaline conditions (Table 28). Evidently, the extra hydroxyl group in GEM imparted enough hydrophilicity to the copolymers to permit hydrolysis to proceed. As with the AOE 2,4-D copolymers, the initial rate of hydrolysis depended on the amount of hydrophilic comonomer in the polymer. The copolymer prepared with a 60:40 feed displayed an autoacceleration in its hydrolysis rate after approximately 150 days of immersion. The copolymer prepared with a 50:50 feed hydrolyzed at a nearly constant rate for over 200 days. This is similar to the behavior of the crosslinked systems and may be related to the fact that the copolymer also did not go into solution as the hydrolysis proceeded.

42. A study was initiated to determine the reactivity ratios of MOE 2,4-D and GEM. Although small amounts of GEM were purified by chromatography on silica gel using an 80:20 mixture of methylene chloride and ether, not enough pure monomer could be obtained to complete this work. A short study was conducted to determine if the programmed addition of GEM to MOE 2,4-D would increase the hydrolysis rate of the resulting copolymer. Thus, two series of copolymerizations were carried out (Table 29). In the first, molar feed ratios of MOE 2,4-D to GEM of 50:50, 70:30, and 90:10 were copolymerized by the traditional batch technique. These copolymerizations were then repeated using a programmed addition procedure. Only 25% of the GEM feed was added to the initial polymerization. The remaining 75% was added in three equal portions at 1-hr intervals. (Since the reactivity ratios of these two monomers were not known, the initial molar feed ratios necessary to prepare copolymers with desired compositions could not be calculated.) All the reaction mixtures were then worked up by the method described for the AOE 2,4-D/HEMA copolymers. The yields of the copolymers ranged from 22-65%.

43. Copolymers 17a-c, made by the batch procedure, had MOE 2,4-D/GEM compositions of 48:52, 71:29, and 95:5. This close agreement between the initial

Table 28. Hydrolysis of MDE 2,4-D/GEM Copolymers 16a, 16b, and 16c^a

Copolymer <u>16a</u>			Copolymer <u>16b</u>			Copolymer <u>16c</u>		
Days	Mg 2,4-D per g	% 2,4-D Released	Days	Mg 2,4-D per g	% 2,4-D Released	Days	Mg 2,4-D per g	% 2,4-D Released
1	0.3	0.1	1	0.5	0.1	1	4.2	1.0
3	0.5	0.1	4	1.8	0.4	5	19.2	4.6
5	0.9	0.2	8	2.8	0.6	17	42.7	10.2
10	1.1	0.2	16	7.5	1.6	25	63.7	15.2
17	1.4	0.3	29	9.7	2.0	38	82.4	19.6
25	2.3	0.4	38	16.4	3.4	47	106.3	25.3
38	2.4	0.4	50	22.4	4.7	59	139.8	33.3
59	2.7	0.5	100	56.0	11.6	109	219.1	52.1
			215	170.0	35.2	225	425.0	100.0
			260	220.0	45.6			

a. 80 ml MEK used in polymerization: release rate data expressed as the average amount of 2,4-D (in mg) released from three 0.5-g replicates

Table 29. Copolymerization of MOE 2,4-D with GEM and GMA

Copolymer No.	Comonomer	Mole % MOE 2,4-D In Feed	Yield (%)	Mole % MOE 2,4-D ^a In Copolymer
<u>17a</u> ^b	GEM	50	65	48
<u>17b</u>	GEM	70	61	71
<u>17c</u>	GEM	90	43	95
<u>18a</u> ^c	GEM	80	22	48
<u>18b</u>	GEM	90	25	73
<u>18c</u>	GEM	97	37	86
<u>19a</u> ^b	GMA	50	91	50
<u>19b</u>	GMA	60	87	58

a. Determined from DSC data

b. Reaction time was 24 hr

c. 25% of total GEM added initially and at each 1-hr interval
(Total reaction time was 5 hr)

Table 30. Physical Properties of MOE 2,4-D Copolymers 17-19

Copolymer No.	% Cl	Tg ^a (°C)	η_{inh} ^b
<u>17a</u>	13.94	52	0.33
<u>17b</u>	17.85	42	0.16
<u>17c</u>	20.78	34	0.16
<u>18a</u>	13.99	54	0.21
<u>18b</u>	18.13	48	0.29
<u>18c</u>	19.69	30	0.17
<u>19a</u>	14.93	33	0.40

a. Determined from DSC data

b. Inherent viscosity (0.50 g/dl in DMF at 30 °C)

feed ratio and composition suggests that these two monomers have similar reactivity ratios. Copolymer compositions equal to the molar feed ratio occurs only when $r_1 = r_2 = 1$. (Copolymer systems are termed "ideal" when both comonomers show the same preference for adding one of the monomers over the other.) Thus, the two types of units, MOE 2,4-D and GEM, are arranged at random along the chain in relative amounts determined by the composition of the feed.

44. The programmed-addition procedure gave polymers (18a-c) with compositions of 48:52, 73:27, and 86:14, which were also approximately equal to the initial molar feed ratios. This further substantiates the premise that the monomers have similar reactivity ratios.

45. The MOE 2,4-D/GEM copolymers were soluble and insoluble in the same solvents as the AOE 2,4-D/HEMA copolymers. However, the Tg's of these copolymers were higher, ranging between 30-54°C (Table 30).

46. The release rates of MOE 2,4-D/GEM copolymers prepared by programmed-addition techniques were faster than those of analogous copolymers prepared by batch procedures (Tables 31 and 32). For example, copolymer 18a, which had the same composition as copolymer 17a, released 55.5 mg of 2,4-D in 23 days, whereas, 17a released only 33 mg in this same time period.

47. Finally, the copolymerization of MOE 2,4-D with a new monomer, i.e. GMA, was investigated. Since GEM is prepared from GMA, the synthetic route to copolymers prepared from this monomer involve one less step. Molar feed ratios of MOE 2,4-D to GMA of 50:50 and 60:40 were copolymerized in MEK at 70°C. The resulting copolymers (19a and b) were obtained in 91 and 87% yields, respectively (Table 29). The copolymers were soluble in THF, DMF, and aliphatic ketones, but insoluble in aliphatic hydrocarbons, ethyl ether, and water. The copolymers had Tg's of 33 and 52°C, which are similar to those of the MOE 2,4-D/GEM copolymers.

48. The MOE 2,4-D/GMA copolymers did not undergo hydrolysis in hard water solutions. Evidently, the epoxy ring contained in GMA did not impart enough hydrophilicity to permit hydrolysis. The ring also must not have undergone any appreciable amount of ring opening in the hydrolysis solutions.

Preparation of 2-hydroxy-3-methacryloyloxypropyl 2,4-dichlorophenoxyacetate (HMOP 2,4-D) (Talukder 1981)

49. A herbicidal monomer was sought that would contain its own hydrophilic group. Thus, HMOP 2,4-D (20) was prepared by the reaction of 2,4-D with GMA in the presence of the quarternary-ammonium-salt catalyst tetramethylammonium

Table 31. Hydrolysis of MOE 2,4-D/GEM Copolymers 17a-c^a

Copolymer <u>17a</u>			Copolymer <u>17b</u>			Copolymer <u>17c</u>		
Days	Mg 2,4-D per g	% 2,4-D Released	Days	Mg 2,4-D per g	% 2,4-D Released	Days	Mg 2,4-D per g	% 2,4-D Released
1	2.1	0.5	1	0.0	0.0	1	0.0	0.0
7	8.5	1.9	7	0.3	0.1	7	0.6	0.1
11	15.4	3.5	20	0.6	0.1	20	1.0	0.2
20	27.0	6.2	55	0.8	0.1	55	1.3	0.2
36	53.9	12.4	99	1.6	0.3	99	1.6	0.3
55	83.7	19.2	158	2.4	0.4	158	2.3	0.4
99	135.3	31.0						
106	149.8	34.4						
144	216.0	50.0						
165	219.0	50.2						

a. Release rate data expressed as the average amount of 2,4-D (in mg) released from three 0.5-g replicates

Table 32. Hydrolysis of MOE 2,4-D/GEM Copolymers 18a-c^a

Copolymer <u>18a</u>			Copolymer <u>18b</u>			Copolymer <u>18c</u>		
Days	Mg 2,4-D per g	% 2,4-D Released	Days	Mg 2,4-D per g	% 2,4-D Released	Days	Mg 2,4-D per g	% 2,4-D Released
2	13.1	2.8	2	1.4	0.3	2	0.0	0.0
6	20.4	4.3	6	2.1	0.4	6	0.3	0.1
16	44.5	9.4	9	2.2	0.4	16	0.7	0.1
23	55.5	11.7	16	3.5	0.6	23	0.9	0.2
30	60.1	12.7	23	3.6	0.6	30	1.0	0.2
40	69.4	14.7	30	3.8	0.7	40	1.2	0.2
			40	4.3	0.8			

a. Release rate data expressed as the average amount of 2,4-D (in mg) released from three 0.5-g replicates

chloride (TMC). After the reaction was allowed to proceed at 70°C for 3 hr, the percentage of unreacted epoxy groups in the GMA was determined by titration. The conversion of GMA to HMOP 2,4-D ranged from 96 to 98%. Although attempts to distill HMOP 2,4-D under reduced pressure were unsuccessful, the viscous, liquid monomer was purified by successive phase separations from acetone solutions with petroleum ether. High pressure liquid chromatography (HPLC) did indicate the presence of a small amount of a second compound, which was most likely the isomer 3-hydroxy-2-methacryloyloxypropyl 2,4-dichlorophenoxyacetate (20b). The monomer was used without purification in the majority of the polymerizations conducted in this study.

Homopolymerization of HMOP 2,4-D

50. The homopolymerization of HMOP 2,4-D was carried out in MEK at 70°C with AIBN as the initiator. Two different concentrations of the monomer were used, i.e., 60% w/w (21a) and 16.7% w/w (21b). The white polymer, which was isolated by precipitation in petroleum ether, was purified by reprecipitation from acetone with petroleum ether followed by extraction with ethyl ether. The yield of the polymer ranged from 45-65%. The homopolymer was soluble in several organic solvents such as THF, DMF, and aliphatic ketones, but was insoluble in aliphatic hydrocarbons, ethyl ether, and water. The homopolymer obtained from the concentrated polymerization mixture (21a) had a Tg of 42°C and an inherent viscosity of 0.21 (0.5 g/dl in DMF at 30°C), while the Tg of the polymer obtained from the more dilute polymerization mixture (21b) had a Tg of 46°C and an inherent viscosity of 0.18. It is very likely that some branching occurred in the former case, which would explain the lower Tg. Such branching could arise by free-radical abstractions of the hydrogens in pendent 2,4-D moieties, which would generate new polymerization sites along the backbone. Hydrogens located next to ether linkage are known to be extremely susceptible to free-radical abstraction.

51. The homopolymers did not release 2,4-D when immersed in reconstituted hard water with a pH = 8. Evidently, the free hydroxyl groups did not provide enough hydrophilicity to allow the hydrolysis to proceed.

Preparation of HMOP 2,4-D/HEMA copolymers

52. Copolymerizations of HMOP 2,4-D and HEMA were carried out using molar feed ratios of 76:24 (22a), 66:34 (22b-1), and 43:57 (22c). The copolymerizations were run in MEK at 70°C with AIBN as the initiator. The monomer mixtures were slowly added to the MEK solutions as the polymerizations proceeded. The final concentrations of the monomers in MEK were 60% (w/w).

The polymers, which were isolated by precipitation in petroleum ether, were reprecipitated from MEK with petroleum ether and then extracted overnight with ethyl ether. The yields of purified material ranged from 35-55%. The copolymers displayed the same solubility behavior as the HMOP 2,4-D homopolymers. Their Tg's ranged from 48-52°C and increased as the percentage of HEMA in the copolymers increased (Table 33).

53. A copolymerization with a molar feed ratio of HMOP 2,4-D to HEMA of 66:34 was also carried out with a total monomer concentration of 16.7% (w/w). The copolymer (22b-2) obtained in this case had a Tg of 60°C, which is considerably higher than the Tg of a similar copolymer (22b-1, Tg = 50°C) prepared in a more concentrated solution. This further substantiates the premise that the polymerization of HMOP 2,4-D in concentrated solutions results in branching.

54. The HMOP 2,4-D/HEMA copolymers immediately released a small amount of 2,4-D when immersed in the reconstituted hard water. Except in the case of copolymer (22c), the release rate decreased dramatically after approximately 50 days (Table 34). The former copolymer, which was prepared from a monomer feed containing 57 mole % HEMA, released 2,4-D very slowly but at a considerably faster rate than the other HEMA copolymers. The copolymer obtained from a dilute polymerization mixture (22b-2) showed a larger initial burst of 2,4-D than the copolymer obtained from a concentrated polymerization mixture (22b-1). However, the release rate of this copolymer also decreased dramatically after the initial burst of herbicide. The initial 2,4-D released from these copolymers most likely originated in unreacted monomer that was trapped in the polymer matrix.

Preparation and hydrolysis of HMOP 2,4-D/GEM copolymers

55. A series of copolymerizations of HMOP 2,4-D and GEM was carried out in MEK with two different concentrations of the reactants, i.e., 60% w/w (23a-c) and 16.7% w/w (24a-c). The molar feed ratios of HMOP 2,4-D to GEM used were 80:20, 64:36, and 51:49. The polymerization procedure and reaction work-up were identical to those described for the HMOP 2,4-D/HEMA copolymers. The yields of the copolymers ranged from 22-50% (Table 35).

56. The HMOP 2,4-D/GEM copolymers were soluble and insoluble in the same solvents as the HMOP 2,4-D/HEMA copolymers. However, the Tg's of these copolymers were higher, ranging between 50-55°C for 23a-c and between 56-65°C for 24a-c. The copolymers prepared in more dilute solutions had the highest Tg's (Table 36).

Table 33. Copolymerization of HMOP 2,4-D and HEMA

Copolymer No.	Molar Feed Ratio HMOP 2,4-D: HEMA	Yield (%)	T _g ^a (°C)	{η} ^b
<u>22a</u>	76:24	55	48	0.17
<u>22b-1</u>	66:34	45	50	0.18
<u>22b-2</u>	60:40	35	60	0.17
<u>22c</u>	43:57	35	52	0.19

a. Determined from DSC data

b. Inherent Viscosity (0.50 g/dl in DMF at 30°C)

Table 34. Hydrolysis of HMOP 2,4-D and HEMA Copolymers^a

Copolymer <u>22a</u>			Copolymer <u>22b-1</u>			Copolymer <u>22c</u>		
Days	Mg 2,4-D per g	% 2,4-D Released	Days	Mg 2,4-D per g	% 2,4-D Released	Days	Mg 2,4-D per g	% 2,4-D Released
2	2.3	0.4	2	2.0	0.4	2	2.1	0.5
7	6.5	1.2	7	6.0	1.2	7	7.7	1.8
12	13.6	2.5	12	13.5	2.8	14	20.5	4.8
17	15.4	2.8	17	16.5	3.4	17	22.0	5.2
24	16.0	3.0	24	18.0	3.7	24	24.0	5.6
50	23.0	4.2	50	30.0	6.2	50	28.0	6.6
170	33.0	6.2	170	41.0	8.4	170	51.6	12.6

a. Release rate data expressed as the average amount of 2,4-D (in mg) released from three 0.5-g replicates

Table 35. Copolymerization of HMOP 2,4-D and GEM

Polymer No.	Molar Feed Ratio HMOP 2,4-D: GEM	Yield (%)	Copolymer Composition ^a (Mole Ratio HMOP 2,4-D:GEM)
<u>23a</u> ^b	80:20	50	62:38
<u>23b</u>	64:36	37	55:45
<u>23c</u>	51:49	26	69:31
<u>24a</u> ^c	80:20	45	46:54
<u>24b</u>	64:36	33	41:59
<u>24c</u>	51:49	22	40:60

a. Determined from chlorine analysis

b. Copolymerization run in MEK with a reactant concentration of 60% (w/w)

c. Copolymerization run in MEK with a reactant concentration of 16.7% (w/w)

Table 36. Physical Properties of Copolymers of HMOP 2,4-D and GEM

Copolymer No.	% Cl	T _g ^a (°C)	{η} ^b
<u>23a</u>	15.35	50	0.46
<u>23b</u>	14.36	52	0.48
<u>23c</u>	16.38	55	0.49
<u>24a</u>	12.85	56	0.40
<u>24b</u>	11.88	60	0.41
<u>24c</u>	11.73	65	0.41

a. Determined from DSC data

b. Inherent Viscosity (0.50 g/dl in DMF at 30°C)

57. The HMOP 2,4-D/GEM copolymers obtained from concentrated polymerization mixtures (23a-c) released relatively large amounts of 2,4-D in the first 40 days following their immersion in hard water (Table 37). As with the HEMA copolymers, their release rates fell precipitously after this initial burst. The release rates of the HMOP 2,4-D/GEM copolymers obtained from dilute polymerization mixtures (24a-c), however, only decreased slightly over a 96-day period (Table 38). The release rates of all three polymers were nearly identical, i.e., 1 mg of 2,4-D per g of copolymer per day. This is not too surprising since chlorine analysis indicated that the compositions of all the copolymers were nearly identical (Table 36).

Preparation of 2,4-D/Poly GMA adducts (Chou 1982)

58. As mentioned in the INTRODUCTION, one of the objectives of this research was to investigate an alternate route to polymers containing pendent herbicide substituents. A prepolymer was to be prepared and then treated with herbicide. Thus, the homopolymerization of GMA was carried out in MEK containing ALN (1.5% by weight of GMA) at 68-70°C under a nitrogen atmosphere for 4 hr. A sample of the white polymer 25 was isolated by precipitation in water and then dried under vacuum overnight. The polymer was soluble in several organic solvents, such as THF, DMF, and aliphatic ketones, but was insoluble in aliphatic hydrocarbons, ethyl ether, and water. The polymer had a number average molecular weight of 23,600 and an inherent viscosity of 0.37 (0.5 g/dl in DMF at 30°C). The epoxy number of the polymer was 10.4, i.e., 97.2 % of the epoxide groups were intact.

59. The MEK solution of 25 was used directly in the preparation of the 2,4-D/Poly GMA adducts (26). Samples of this solution were mixed with various amounts of 2,4-D and TMC dissolved in cellosolve acetate (CA). The mixture was heated at 68-70°C under a nitrogen atmosphere for 4 hr. Adducts were prepared that contained 79, 51, 39, 20, and 10 mole % 2,4-D (Table 39). The products were isolated by the same procedure described for Poly GMA.

60. As shown in Table 40, all of the five adducts released a very small amount of 2,4-D in the hard water during their first 4 months of immersion. All of the release rates slowly accelerated as the hydrolysis proceeded. With the exception of the adduct containing 51 mole % 2,4-D (26b), all of the adducts released nearly equivalent percentages of their 2,4-D contents in 255 days. Thus, it appears that the degree of 2,4-D substitution did not significantly affect the adducts' hydrolysis rates. It is not readily apparent why 26b gave anomolous results.

Table 37. Hydrolysis of HMOP 2,4-D/GEM Copolymers 23a-c^a

Copolymer <u>23a</u>			Copolymer <u>23b</u>			Copolymer <u>23c</u>		
Days	Mg 2,4-D per g	% 2,4-D Released	Days	Mg 2,4-D per g	% 2,4-D Released	Days	Mg 2,4-D per g	% 2,4-D Released
3	10.0	1.8	3	9.8	1.9	3	8.0	1.9
8	73.0	13.9	8	36.0	7.5	8	26.0	6.1
20	109.0	19.9	20	42.0	9.0	20	40.0	9.4
35	141.0	25.8	35	56.0	11.5	35	55.0	12.9
43	156.0	29.5	43	74.0	15.0	43	60.0	14.1
130	163.0	30.0	130	77.0	15.8	130	72.0	16.9
250	163.0	30.0	250	77.0	15.8	130	72.0	16.9

a. Release rate data expressed as the average amount of 2,4-D (in mg) released from three 0.5-g replicates

Table 38. Hydrolysis of HMOP 2,4-D/GEM Copolymers 24a-c^a

Copolymer <u>24a</u>			Copolymer <u>24b</u>			Copolymer <u>24c</u>		
Days	Mg 2,4-D per g	% 2,4-D Released	Days	Mg 2,4-D per g	% 2,4-D Released	Days	Mg 2,4-D per g	% 2,4-D Released
1	5.4	1.3	1	5.0	1.4	1	5.6	1.5
5	13.0	3.3	5	10.0	2.7	5	12.0	3.3
10	21.0	5.3	10	18.0	4.9	10	22.0	6.0
25	33.0	8.3	25	41.0	11.1	25	42.0	11.5
34	39.0	9.8	34	45.6	13.3	34	46.0	14.0
49	57.0	14.3	49	58.0	15.7	49	63.0	17.9
64	80.0	20.0	64	75.0	19.7	64	82.0	22.5
96	106.0	26.5	96	100.0	27.0	96	104.0	28.6

a. Release rate data expressed as the average amount of 2,4-D (in mg) released from three 0.5-g replicates

Table 39. Preparation of 2,4-D/Poly GMA Adducts

Adduct No.	2,4-D Content ^a (Mole %)	E.N. ^b	$[\eta]$ ^c	Mg 2,4-D ^d per g per day	% 2,4-D ^d Released per day
<u>26a</u>	79	0.9	0.49	0.2	0.0
<u>26b</u>	51	3.0	0.61	0.1	0.0
<u>26c</u>	39	3.7	0.43	0.1	0.0
<u>26d</u>	20	5.9	0.40	0.1	0.0
<u>26e</u>	10	8.0	0.38	0.1	0.0

a. Calculated from epoxy number

b. Epoxy number determined by titration

c. Inherent viscosity (0.5 g/dl in DMF at 30°C)

d. 2,4-D release rate during the first four months

Table 40. Hydrolysis of 2,4-D/Poly GMA Adducts^a

Days	Mg 2,4-D per g Adduct Adduct No.					% 2,4-D Released Adduct No.				
	<u>26a</u>	<u>26b</u>	<u>26c</u>	<u>26d</u>	<u>26e</u>	<u>26a</u>	<u>26b</u>	<u>26c</u>	<u>26d</u>	<u>26e</u>
1	1.6	1.6	1.0	1.7	1.8	0.3	0.4	0.3	0.7	1.4
8	2.2	2.0	1.5	3.5	1.8	0.4	0.5	0.4	1.5	1.4
15	3.2	2.9	2.0	4.8	2.5	0.6	0.7	0.5	2.1	1.9
19	3.9	3.3	2.5	5.2	2.8	0.7	0.8	0.7	2.2	2.1
27	4.8	4.2	3.6	6.2	3.8	0.9	1.0	0.9	2.6	2.9
33	5.0	4.6	3.8	6.5	4.3	0.9	1.1	1.0	2.7	3.2
44	5.9	5.3	4.5	7.2	4.4	1.0	1.2	1.2	3.0	3.2
81	10.8	8.2	8.8	10.2	6.7	2.0	1.9	2.3	4.3	5.0
113	25.5	12.8	16.5	14.1	10.2	4.6	3.0	4.3	6.0	7.6
142	39.8	15.7	29.6	18.2	13.2	7.2	3.6	7.7	7.7	9.8
255	105.9	28.4	72.4	37.4	21.4	19.1	6.6	18.9	15.8	16.0

a. Release rates expressed as the average amount of 2,4-D released from three 0.5-g replicates in the designate number of days

61. In order to facilitate the hydrolysis of the 2,4-D/Poly GMA adducts, several attempts were made to introduce more hydrophilicity into the ester systems. These attempts included: (a) the introduction of hydrophilic groups along the precursor polymer backbone via the copolymerization of GMA with hydrophilic comonomers; (b) the preparation of hydroxy-terminated adducts with reduced molecular weights; and (c) the incorporation of glycol moieties in the system via the hydrolysis of pendent epoxy groups.

Preparation of 2,4-D/Copoly(GMA-HEMA) adducts

62. A series of copolymerizations of GMA with various amounts of HEMA and AIBN was carried out. The copolymerizations were conducted in MEK at 68-70°C under a nitrogen atmosphere for 4 hr. The molar feed ratios of GMA to HEMA employed were 60:40, which was run with 2.1% and 3.4% AIBN, and 50:50, which was run with 3.4% AIBN. In the latter case, the copolymer gelled during the polymerization. The 2,4-D/Copoly(GMA-HEMA) adducts 27a and b were prepared by treating the 60:40 copolymer solution with a solution of 2,4-D and TMC in CA (Table 41). The procedure followed was identical to that used in the preparation of the 2,4-D/Poly GMA adducts.

63. As shown in Table 42, the release rates of the 2,4-D/Copoly(GMA-HEMA) adducts in reconstituted hard water were considerably faster than those of the corresponding 2,4-D/Poly GMA adducts. The 60:40 copolymer prepared with 3.4% AIBN afforded an adduct which hydrolyzed faster than the analogous adduct based on the copolymer prepared with 2.1% AIBN. This may be due to differences in the copolymers' molecular weights. The copolymer prepared with the higher concentration of initiator should have a considerably lower molecular weight.

Preparation of 2,4-D/Copoly(GMA-HEA) adducts

64. Two copolymerizations of GMA with 2-hydroxyethyl acrylate (HEA) were carried out. The copolymerizations were conducted in MEK containing AIBN (3.4% by weight of comonomers) at 68-70°C under a nitrogen atmosphere for 4 hr. The molar feed ratios of GMA to HEA employed were 80:20 and 60:40. In the latter case, the copolymer gelled during the polymerization. The 2,4-D/Copoly (GMA-HEA) adduct 28 was prepared by treating the 80:20 copolymer solutions with a solution of 2,4-D and TMC in CA. The procedure followed was identical to that used in the preparation of the 2,4-D/Poly GMA adducts. The adduct did not dissolve completely in any solvent. Hence, some crosslinking must have occurred. The release rate of this adduct in reconstituted hard water was 0.2 mg per g of adduct per day (Table 43). Although this rate is faster than those of the corresponding 2,4-D/Poly GMA adducts, it is much slower than the desired

Table 41. Preparation of 2,4-D/Copoly(GMA-HEMA) Adducts

Adduct No.	E.N. ^a	Wt % AIBN	M _n ^b	E.N. ^c	2,4-D Content (mole %)	Mg 2,4-D ^d per g per day	% 2,4-D ^d Released per day
<u>27a</u>	6.0	2.1	--	1.6	37	0.6	0.1
<u>27b</u>	5.9	3.4	26,000	1.4	40	0.9	0.2

- a. Epoxy number of Copoly(GMA-HEMA) determined by titration
b. M_n of Copoly(GMA-HEMA) determined from vapor pressure osmometry (VPO)
c. Epoxy number of 2,4-D/Copoly(GMA-HEMA) adduct
d. 2,4-D release rate during 252 days

Table 42. Hydrolysis of 2,4-D/Copoly(GMA-HEMA) Adducts^a

Days	Adduct <u>27a</u>		Adduct <u>27b</u>	
	Mg 2,4-D per g	% 2,4-D Released	Mg 2,4-D per g	% 2,4-D Released
1	0.7	0.2	2.7	0.7
8	1.1	0.3	4.0	1.0
15	1.8	0.5	5.3	1.4
19	2.5	0.7	6.7	1.7
27	3.8	1.0	9.2	2.4
33	5.2	1.3	11.4	3.0
39	6.4	1.7	15.4	4.0
44	7.5	2.0	16.0	4.1
81	27.7	7.2	37.5	9.7
113	55.4	14.4	73.4	9.0
142	77.4	20.0	99.4	25.7
187	104.0	26.9	144.0	37.4
204	113.0	29.2	154.0	39.9
252	131.0	33.8	190.0	49.3

- a. Release rates expressed as the average amount of 2,4-D released from three 0.5-g replicates in the designated number of days

Table 43. Hydrolysis of 2,4-D/Copoly(GMA-HEA) Adduct 28^a

Days	Mg 2,4-D per g	% 2,4-D Released
1	1.2	0.2
6	2.4	0.5
42	5.8	1.2
75	10.7	2.1
107	22.1	4.4

a. Release rates expressed as the average amount of 2,4-D released from three 0.5-g replicates in the designated number of days

Table 44. Hydrolysis of 2,4-D/Copoly(GMA-HPMA) Adduct 29^a

Days	Mg 2,4-D per g	% 2,4-D Released
1	5.3	1.1
3	8.9	1.8
4	10.1	2.0
5	11.6	2.3
20	19.5	3.9
39	19.5	3.9
72	20.1	4.0
104	23.5	4.7

a. Release rates expressed as the average amount of 2,4-D released from three 0.5-g replicates in the designated number of days

release rate of 1 mg of 2,4-D per g of adduct per day.

Preparation of 2,4-D/Copoly(GMA-HPMA) adducts

65. A copolymerization of GMA with 2-hydroxypropyl methacrylate (HPMA) was conducted in MEK containing AIBN (3.4% by weight of comonomer) at 68-70°C under a nitrogen atmosphere for 4 hr. The molar feed ratio of GMA to HPMA employed was 60:40. The 2,4-D/Copoly (GMA-HPMA) adduct 29 was prepared by treating the 60:40 copolymer solution (E.N.= 3.7) with a solution of 2,4-D and TMC in CA. The procedure followed was identical to that used in the preparation of the 2,4-D/Poly GMA adducts. The adduct had an E.N. of 1.5 which corresponds to a 2,4-D content of 39%.

66. As shown in Table 44, after the adduct quickly released several mg of 2,4-D, the release rate decreased dramatically. The initial burst was probably due to the release of unreacted 2,4-D that was trapped in the polymer matrix.

Preparation of 2,4-D/Copoly(GMA-DMAEMA) adducts

67. Two copolymerizations of GMA with 2-dimethylaminoethyl methacrylate (DMAEMA) were also carried out. The copolymerizations were conducted in MEK containing AIBN (3.4% by weight of comonomers) at 68-70°C under a nitrogen atmosphere for 4 hr. The molar feed ratios of GMA to DMAEMA employed were 95:5 and 90:10. In the latter case, the copolymer gelled during the polymerization. The 2,4-D/Copoly(GMA-DMAEMA) adduct 30 was prepared by treating the 95:5 copolymer solution with a solution of 2,4-D and TMC in CA. The procedure followed was identical to that used in the preparation of the 2,4-D/Poly GMA adducts. The adduct did not dissolve completely in any solvent, indicating that some crosslinking occurred. The release rate of this adduct was 5.0 mg of 2,4-D per g of polymer. After approximately 172 mg of 2,4-D per g of polymer had been released, the release rate slowed considerably (Table 45). The pH of the solution had changed from 8.0 to 4.6, which may have affected the rate. It is more likely that the decrease in rate was due to a decrease in the diffusion of free 2,4-D out of the polymer particles. The concentration of 2,4-D in the solution at this point was approximately 36% of the saturation level (0.8 g/100 g).

Preparation of hydroxy-terminated 2,4-D/Poly GMA adducts with low molecular weights

68. It was postulated that the adducts' release rates could be enhanced by using an hydroxy-substituted chain transfer agent in the preparation of the Poly GMA prepolymer. This would result in hydroxy-terminated systems with reduced molecular weights that should be more hydrophilic and, hence, more

susceptible to hydrolysis. Thus, the homopolymerization of GMA was carried out in the presence of various amounts of the chain transfer agent 2-mercaptoethanol (ME) (Table 46). The polymerizations were conducted in MEK containing AIBN (2% by weight of GMA) at 68-70°C under a nitrogen atmosphere for 4 hr. The hydroxy-terminated prepolymers were treated with 2,4-D and tetraethylammonium bromide (TEB) in CA according to the earlier described procedure.

69. The release rates of these adducts (31a,b) were faster than those of the previously prepared 2,4-D/Poly(GMA) adducts 26 a-e (Table 47). As with the 2,4-D/Copoly(GMA-DMAEMA) adduct, the release rate of 31a appeared to slow considerably after approximately 175 mg of 2,4-D per g of adduct had been released. After 73 days the adduct was collected by filtration, washed with a litre of distilled water, dried under vacuum overnight, and then reimmersed in reconstituted hard water. The adduct immediately began to release 2,4-D very quickly. After 10 days, the rate had slowed to the same level displayed during the first 37 days of the study, i.e., approximately 4.0 mg per g of adduct per day.

Preparation of hydroxy-terminated 2,4-D/Copoly(GMA-HEMA) adducts with low molecular weights

70. The same approach to enhancing release rates described in the previous section was employed in the preparation of 2,4-D/Copoly(GMA-HEMA) adducts. Thus, the copolymerizations of GMA with various amounts of HEMA were carried out in the presence of ME. The copolymerizations were conducted in MEK containing AIBN (2% by weight of comonomers) and ME (3% by weight of comonomers) at 68-70°C under a nitrogen atmosphere for 4 hr. The molar feed ratios of GMA to HEMA employed were 90:10 and 80:20. The hydroxy-terminated prepolymers were treated with 2,4-D and TEB in CA according to the procedure described above to give adducts 32a and b (Table 48).

71. The release rates of these hydroxy-terminated copolymer adducts were considerably faster than those of the 2,4-D/Copoly(GMA-HEMA) adducts 27a and b even though much less HEMA was employed (Table 49). They were also slightly faster than that of the corresponding hydroxy-terminated 2,4-D/Poly GMA adduct 31a. As with 31a the release rates did slow dramatically after approximately 171 mg per g of adduct was released after 58 days. Adduct 32a was isolated by the procedure described for 31a and reimmersed in reconstituted hard water. The adduct quickly began to release 2,4-D at almost the same rate displayed during its first month of immersion. This rate was maintained until the adduct had released approximately 170 additional mg of 2,4-D per g of adduct. At this

Table 45. Hydrolysis of 2,4-D/Copoly(GMA-DMAEMA) Adduct 30^a

Days	Mg 2,4-D per g	% 2,4-D Released
2	13.6	2.9
7	53.7	11.4
8	59.0	12.6
9	74.4	15.8
24	152	32.4
26	157	33.5
33	172	36.6
76	186	39.6
108	191	40.6

a. Release rates expressed as the average amount of 2,4-D released from three 0.5-g replicates in the designated number of days

Table 46. Preparation of 2,4-D/Poly GMA Adducts

Adduct No.	E.N. ^a	Wt. % ME ^d	M _n ^b	E.N. ^c	2,4-D Content (mole %)	Mg 2,4-D per g per day	% 2,4-D Released per day
<u>31a</u>	10.5	3.0	5,800	2.4	60	4.1 ^e	0.9 ^e
<u>31b</u>	10.7	1.5	8,600	2.4	61	1.5 ^f	0.3 ^f

a. Epoxy number of GMA

b. M_n of Poly GMA determined from VPO

c. Epoxy number of 2,4-D/Poly GMA adduct

d. % ME by weight of GMA

e. 2,4-D release rate during 41 days

f. 2,4-D release rate during 80 days

Table 47. Hydrolysis of Hydroxy-Terminated 2,4-D/Poly GMA Adducts^a

Adduct 31a			Adduct 31b		
Days	Mg 2,4-D per g	% 2,4-D Released	Days	Mg 2,4-D per g	% 2,4-D Released
4	21.5	4.7	3	6.9	1.5
12	62.4	13.5	4	7.8	1.7
16	74.9	16.2	5	8.4	1.8
19	86.6	18.8	10	13.8	3.0
22	103	22.4	12	15.0	3.3
27	124	27.0	19	22.5	4.9
31	139	30.2	24	29.7	6.5
37	157	34.1	27	34.5	7.5
41	176	38.3	31	40.5	8.8
49	185	40.3	36	48.9	10.6
61	191	41.6	40	57.4	12.8
73	192	41.7	54	82.9	18.0
75	238	51.8	64	99.3	21.6
76	260	56.6	80	124	26.9
83	297	64.6			
88	318	69.0			
110	351	76.4			

a. Release rates expressed as the average amount of 2,4-D released from three 0.5-g replicates in the designated number of days

Table 48. Preparation of Hydroxy-Terminated
2,4-D/Copoly(GMA-HEMA) Adducts

Adduct No.	Molar Feed Ratio of 1:13	E.N. ^a	E.N. ^b	2,4-D Content (mole %)	M _n ^c	Mg 2,4-D ^d per g per day	% 2,4-D ^d Released per day
<u>32a</u>	90:10	9.3	2.4	60	5,200	4.7	0.94
<u>32b</u>	80:20	8.5	2.1	58	8,200	4.8	0.95

a. Epoxy number of hydroxy-terminated copoly(GMA-HEMA)

b. Epoxy number of 2,4-D adduct

c. M_n of copoly(GMA-HEMA) determined from VPO

d. 2,4-D release rate during the first month

Table 49. Hydrolysis of Hydroxy-Terminated
2,4-D/Copoly(GMA-HEMA) Adducts^a

Adduct <u>32a</u>			Adduct <u>32b</u>		
Days	Mg 2,4-D per g	% 2,4-D Released	Days	Mg 2,4-D per g	% 2,4-D Released
2	23.7	4.8	3	48.4	9.7
6	31.5	6.3	6	60.4	12.1
9	43.5	8.7	9	81.6	16.3
12	62.2	12.4	14	112	22.6
17	97.1	19.4	18	128	25.6
21	115	23.1	24	153	30.7
27	145	29.0	28	168	33.5
31	160	32.1	36	181	36.2
39	171	34.2	48	185	37.0
51	179	35.8	55	185	37.0
58	182	36.4			
66	217	43.5			
70	281	56.2			
75	315	63.0			
79	334	67.0			
97	347	69.4			
98	390	78.0			
99	404	80.8			
104	433	86.6			
110	456	91.2			

a. Release rates expressed as the average amount of 2,4-D released from three 0.5-g replicates in the designated number of days

point the rate again rapidly decreased. The pH of the hydrolysis solution had also decreased to 5.8. After 97 days, the adduct was isolated by filtration and washed with 2 l of water. After drying overnight under vacuum, the replicates were reimmersed in fresh reconstituted hard water. Once again, the adduct quickly began to release 2,4-D at essentially the same rate displayed during its first month of immersion.

Preparation of 2,4-D/Poly GMA adducts containing pendent glycol moieties

72. The next attempt at increasing the adducts' hydrophilicities involved the generation of glycol moieties along the polymer backbone. It was postulated that the systems' hydrophilicities could be increased dramatically by hydrolyzing several of the pendent epoxide groups. Two different approaches were investigated. In the first, the Poly GMA prepolymer was partially hydrolyzed prior to its treatment with 2,4-D. In the second, a 2,4-D/Poly GMA adduct was prepared that contained unreacted epoxide groups. The epoxide groups were then converted to glycol moieties. Both approaches were also used with the hydroxy-terminated systems described earlier.

Reaction of 2,4-D with partially hydrolyzed Poly GMA

73. The homopolymerization of GMA was carried out in MEK containing AIBN (3% by weight of GMA) at 68-70°C under a nitrogen atmosphere for 4 hr. Concentrated sulfuric acid was diluted with CA and then added dropwise to the polymerization mixture. The mixture was stirred and heated at 68-70°C under a nitrogen atmosphere for 2 hr. The hydrolysis was carried out with 0.7 wt % and 0.28 wt % sulfuric acid (Table 50). The partially hydrolyzed prepolymers were treated with 2,4-D and TMC in CA according to the earlier described procedure to give adducts 33a and b.

74. The release rates of these adducts were even slower than those of the corresponding 2,4-D/Poly GMA adducts (Table 51). This was totally unexpected since the adducts should be considerably more hydrophilic than adducts 26a-e.

75. A series of homopolymerizations of GMA was carried out in the presence of various amounts of the chain transfer agent ME. The polymerizations were conducted in MEK containing AIBN (2% by weight of GMA) at 68-70°C under a nitrogen atmosphere for 4 hr. The hydrolysis reactions were carried out with 0.37 wt % sulfuric acid according to the procedure described in the previous sections. The partially hydrolyzed hydroxy-terminated prepolymers were treated with 2,4-D and TMC in CA by the procedure described earlier (Table 52).

76. As shown in Tables 53 and 54, the release rates of these adducts were

Table 50. Reaction of 2,4-D With Partially Hydrolyzed Poly GMA

Adduct No.	Wt % ^a H ₂ SO ₄	E.N. ^b	E.N. ^c	Epoxide opened (mole %)	E.N. ^d	M _n ^e	2,4-D Content (mole %)	Mg 2,4-D ^f Released per day
<u>33a</u>	0.70	11.0	8.2	25	1.3	16,500	51	0.04
<u>33b</u>	0.28	11.0	10.1	8	2.5	--	50	0.03

a. % H₂SO₄ by weight of GMA

b. Epoxy number of Poly GMA before hydrolysis with H₂SO₄

c. Epoxy number of partially hydrolyzed Poly GMA

d. Epoxy number of 2,4-D adduct

e. M_n of partially hydrolyzed Poly GMA determined from VPO

f. 2,4-D release rate during the first month

Table 51. Hydrolysis of 2,4-D/Partially Hydrolyzed Poly GMA Adducts^a

Days	Adduct <u>33a</u>		Adduct <u>33b</u>	
	Mg 2,4-D per g	% 2,4-D Released	Mg 2,4-D per g	% 2,4-D Released
2	0.3	0.1	0.3	0.1
3	0.8	0.2	0.6	0.2
8	0.9	0.2	0.6	0.2
17	1.2	0.3	1.1	0.3
24	1.5	0.4	1.2	0.3
31	1.5	0.4	1.2	0.3

a. Release rates expressed as the average amount of 2,4-D released from three 0.5-g replicates in the designated number of days

Table 52. Reaction of 2,4-D With Partially Hydrolyzed Poly GMA

Adduct No.	Wt % ^a ME	E.N. ^b	E.N. ^c	Epoxyde opened (mole %)	E.N. ^d	M _n ^e	2,4-D Content (mole %)	Mg 2,4-D ^f Released per day
<u>34a</u>	1.0	11.4	10.0	10.0	1.7	8,300	62	2.0
<u>34b</u>	3.0	10.4	--	--	2.5	5,600	45	5.3
<u>34c</u>	4.0	9.9	--	--	2.4	4,200	40	5.2
<u>34d</u>	5.0	10.6	--	--	1.8	3,000	53	5.1

a. % ME by weight of GMA

b. Epoxy number of hydroxy-terminated Poly GMA before being hydrolyzed

c. Epoxy number of partially hydrolyzed, hydroxy-terminated Poly GMA

d. Epoxy number of 2,4-D adduct

e. M_n of Poly GMA determined from VPO

f. 2,4-D release rate during the first month

Table 53. Hydrolysis of Adduct 34a^a

Days	Mg 2,4-D per g	% 2,4-D Released
4	37.0	7.9
5	41.0	8.7
6	43.9	9.3
7	42.2	9.4
10	48.9	10.4
15	55.4	11.8
24	73.4	15.6
29	81.5	17.3
32	91.4	19.4
36	98.4	20.9
39	102	21.7
42	112	23.8
47	122	25.9
51	130	27.6
57	141	30.0
61	148	31.5
69	157	33.4
81	166	35.3
88	169	35.9
93	174	37.0
100	179	38.1
127	180	38.3

a. Release rates expressed as the average amount of 2,4-D released from three 0.5-g replicates in the designated number of days

Table 54. Hydrolysis of Adducts 34b, c, and d ^a

Days	Mg 2,4-D per g Adduct No.			% 2,4-D Released Adduct No.		
	<u>34b</u>	<u>34c</u>	<u>34d</u>	<u>34b</u>	<u>34c</u>	<u>34d</u>
6	51.0	55.7	54.7	10.8	11.9	11.6
10	78.1	92.9	91.1	16.6	19.8	19.4
17	130	144	140	27.6	30.6	29.7
20	160	159	160	34.1	33.9	34.0
27	173	177	176	36.8	37.7	37.5
31	184	186	182	39.2	39.5	38.7
35	184	189	190	39.2	40.2	40.4
45	202	200	202	42.9	42.6	42.9
52	204	201	202	43.4	42.9	42.9
69	204	202	202	43.4	42.9	42.9
73	277	283	---	58.9	60.4	---
79	312	318	---	66.4	67.7	---
101	342	357	---	72.8	76.0	---

a. Release rates expressed as the average amount of 2,4-D released from three 0.5-g replicates in the designated number of days

slightly faster than those of adducts 31a and b, which did not contain any glycol moieties. Surprisingly, adducts 34b, c, and d all displayed similar release rates. Once again, the adducts' release rates decreased markedly after approximately 170 mg of 2,4-D per g of adduct was released. Adducts 34b and c were isolated by the procedure described for 31a and reimmersed in reconstituted hard water. Both adducts quickly began to release 2,4-D at very accelerated rates.

Hydrolysis of the residual epoxy groups in a 2,4-D/Poly GMA adduct

77. A 2,4-D/poly GMA adduct (E.N.= 2.6) containing 57 mole % 2,4-D was prepared from a Poly GMA sample with an M_n of 20,000 according to the procedure described for adduct 26. Concentrated sulfuric acid was diluted with CA and then added to the adduct mixture, which was stirred and heated at 68-70°C under a nitrogen atmosphere for 42 hr. The hydrolysis was carried out with 0.015 wt % sulfuric acid. The partially hydrolyzed adduct had an E.N.= 0.2 which suggests that 38 mole % of the epoxide groups were opened.

78. It appears that the adduct's hydrophilicity was increased, as adduct 35a released 2,4-D much faster than adducts 26 a-e (Table 55). Its release rate of 0.9 mg of 2,4-D per g of per day was remarkably constant over a 5-month period.

Hydrolysis of the residual epoxy groups in hydroxy-terminated 2,4-D/Poly GMA adducts

79. A sample of adduct 31a in MEK was treated with various amounts of sulfuric acid in CA at 68-70°C for 3 hr to afford 36a and b (Table 56). Surprisingly, the release rate of 36b was slightly slower than that of 36a even though 36b contained more glycol moieties (Table 57). In fact, both of the adducts released 2,4-D slower than 31a, which does not contain any glycol functions. It is possible that some of the pendent 2,4-D ester linkages also underwent hydrolysis during the sulfuric acid treatment. The release rates of both adducts slowed considerably after approximately 170 mg of 2,4-D per g of adduct was released. As in previous cases, when the adducts were reimmersed in reconstituted hard water, they immediately began to release 2,4-D at greatly accelerated rates.

Effect of the molecular weight of Poly GMA on the hydrolysis of 2,4-D/Poly GMA adducts

80. The results of the hydrophilicity studies reported in the previous sections suggested that the molecular weight of the polymer precursor might also play a major role in determining an adduct's release rate. In order to

Table 55. Hydrolysis of 2,4-D/Poly GMA Adduct 35a^a

Days	Mg 2,4-D per g	% 2,4-D Released
6	11.6	2.5
7	13.3	2.8
8	14.0	3.0
10	16.5	3.5
17	23.2	4.9
23	28.5	6.1
30	34.5	7.3
39	45.0	9.6
46	53.4	11.4
53	56.4	12.0
56	57.3	12.2
63	68.4	14.6
77	84.6	18.0
98	95.4	20.3
115	111	23.6
134	128	27.1
163	144	30.7
220	180	38.3
251	190	40.4

a. Release rates expressed as the average amount of 2,4-D released from three 0.5-g replicates in the designated number of days

Table 56. Preparation of Partially Hydrolyzed,
Hydroxy-Terminated 2,4-D/Poly GMA Adducts

Adduct No.	Wt % ^a H ₂ SO ₄	M _n ^b	E.N. ^c	2,4-D Content (mole %)	E.N. ^d	Epoxy opened (mole %)	Mg 2,4-D ^e per g per day	% 2,4-D ^e Released per day
<u>36a</u>	0.58	5,800	2.4	60	2.2	3.0	3.6	0.8
<u>36b</u>	2.30	5,800	2.4	60	2.1	5.5	2.6	0.6

a. % H₂SO₄ by weight of GMA

b. M_n of Poly GMA determined from VPO

c. Epoxy number of 2,4-D adduct before hydrolysis

d. Epoxy number of 2,4-D adduct after hydrolysis with sulfuric acid

e. 2,4-D release rate during 40 days

Table 57. Hydrolysis of Adducts 36a and b ^a

Days	Adduct <u>36a</u>		Adduct <u>36b</u>	
	Mg 2,4-D per g	% 2,4-D Released	Mg 2,4-D per g	% 2,4-D Released
4	22.2	5.9	18.7	4.1
12	64.2	14.9	44.2	9.6
16	79.9	17.4	48.9	10.6
19	88.9	19.3	57.9	12.6
22	103	22.4	66.9	14.6
27	120	26.2	85.4	18.6
31	131	28.4	94.6	20.6
37	146	31.8	106	23.0
41	163	35.4	121	26.4
49	172	37.3	131	28.4
61	182	39.5	152	33.1
68	182	39.5	163	35.4
76	212	46.2	190	41.4
80	271	58.9	222	48.2
85	305	66.4	256	55.7
107	339	73.8	314	68.4

a. Released rates expressed as the average amount of 2,4-D released from three 0.5-g replicates in the designated number of days

further investigate the effect of molecular weight, an attempt was made to reduce the molecular weight of the Poly GMA prepolymer without increasing its hydrophilicity. Two approaches were investigated. In the first, the molecular weight was decreased by using increased amounts of the initiator AIBN. In the second, the homopolymerization of GMA was carried out in the presence of a chain transfer agent that does not contain any hydrophilic functionality, i.e., 1-propanethiol (PT).

Preparation of low-molecular-weight 2,4-D/Poly(GMA) adducts via the use of increased amounts of AIBN

81. Homopolymerizations of GMA were carried out in MEK containing 3.4 wt % and 4.0 wt % AIBN at 68-70°C under a nitrogen atmosphere for 4 hr. In the latter case, the polymer gelled during the polymerization. The polymer prepared with 3.4 wt % AIBN had a number-average molecular weight of 17,000. This is approximately 6,600 amu less than the molecular weight of the Poly GMA prepared previously with 1.5 wt % AIBN. The epoxy number of the polymer was 10.4, i.e., 97% of the epoxide groups remained intact. Several 2,4-D/Poly GMA adducts(37a-d) were prepared by treating the polymer solution with various amounts of 2,4-D and TMA in CA. The procedure followed was identical to that described earlier. The adducts contained 51, 40, 31, and 19 mole % 2,4-D (Table 58).

82. As shown in Table 59, the release rates of these adducts were very slow. In fact, they were very similar to those of adducts 26a-e, which were prepared from the Poly GMA with a molecular weight of 23,600.

Preparation of low-molecular-weight 2,4-D/Poly GMA adducts via the use of the chain transfer agent 1-propanethiol

83. A homopolymerization of GMA was carried out in MEK containing AIBN (2% by weight of GMA) and PT (3% by weight of GMA) at 68-70°C under a nitrogen atmosphere for 4 hr. The polymer had an epoxy number of 10.8 and a number-average molecular weight of 5,300. A 2,4-D/Poly GMA adduct 38 containing 60 mole % of 2,4-D (E.N.= 2.34) was prepared by treating the polymer solution with 2,4-D and TEB in CA. The procedure was identical to that described earlier. As shown in Table 60, the release rate of this adduct was 5 mg per g of adduct per day, which was forty times faster than those of the corresponding adducts 26 and 37. In fact, the release rate was even slightly faster than that of the hydroxy-terminated 31a, which had a comparable molecular weight. The adduct's release rate did decrease after approximately 170 mg of 2,4-D per g of adduct had been released.

Table 58. Preparation of 2,4-D/Poly GMA Adducts
With Reduced Molecular Weights

Adduct No.	E.N. ^a	2,4-D Content (mole %)	Mg 2,4-D ^b per g per day	% 2,4-D ^b Released per day
<u>37a</u>	2.8	51	0.20	0.04
<u>37b</u>	3.8	40	0.07	0.02
<u>37c</u>	4.9	31	0.04	0.02
<u>37d</u>	6.5	19	0.05	0.03

a. Epoxy number of 2,4-D/Poly GMA adduct

b. 2,4-D release rate during 229 days

Table 59. Hydrolysis of 2,4-D/Poly GMA Adducts^a
With Reduced Molecular Weights

Days	Mg 2,4-D per g Adduct No.				% 2,4-D Released Adduct No.			
	<u>37a</u>	<u>37b</u>	<u>37c</u>	<u>37d</u>	<u>37a</u>	<u>37b</u>	<u>37c</u>	<u>37d</u>
1	2.7	3.5	3.3	1.4	0.6	0.9	1.0	0.6
7	4.5	5.9	5.1	2.6	1.0	1.5	1.6	1.1
11	4.9	6.9	5.3	3.1	1.1	1.8	1.7	1.4
18	5.1	7.1	5.7	3.7	1.2	1.9	1.8	1.6
72	11.3	9.0	6.8	6.0	2.6	2.4	2.1	2.6
119	23.2	17.0	14.0	11.0	5.3	4.4	4.4	4.8
229	48.4	19.0	17.5	12.4	11.1	5.0	5.5	5.5

a. Release rates expressed as the average amount of 2,4-D released
from three 0.5-g replicates in the designated number of days

Table 60. Hydrolysis of 2,4-D/Poly GMA Adduct 38^a

Days	Mg 2,4-D per g	%2,4-D Released
4	33.5	6.7
6	40.0	8.0
8	53.7	10.7
13	77.1	15.4
18	106	21.2
21	122	24.5
25	146	29.2
31	173	34.6
53	211	42.1
83	211	42.1

a. Release rates expressed as the average amount of 2,4-D released from three 0.5-g replicates in the designated number of days

84. The effect of the molecular weight of the prepolymer on the 2,4-D adduct's release rate is illustrated in Table 61. In all three types of adducts, dramatic increases in release rates were achieved when the molecular weight was reduced to less than approximately 8,000. Apparently, these low-molecular-weight adducts are considerably more susceptible to hydrolysis than their high polymer analogs. In fact, it appears that most of the large increases in release rate attained in this study can be attributed to molecular weight reductions.

Physical formulations of herbicides entrapped in biodegradable matrices

85. The dimethylamine salt of 2,4-D (DMA 2,4-D) was physically incorporated in crosslinked chitosan and carboxymethylcellulose (CMC) matrices. This was accomplished by adding a crosslinking agent, e.g., glutaraldehyde, to a stirred aqueous solution of chitosan or CMC containing DMA 2,4-D. In both cases, the addition of the crosslinking agent resulted in the immediate formation of an insoluble gel. The gels were filtered, dried in a vacuum oven, and ground to a uniform particle size. Unfortunately, the gel particles released most of their DMA 2,4-D in a few days when immersed in a pH = 8 buffer solution. In an attempt to slow down the release of 2,4-D from crosslinked chitosan formulations, the matrix was coated with a crosslinked chitosan film. This formulation, however, still released the water-soluble salt very quickly with the majority of the active ingredient being lost in a few days.

86. DMA 2,4-D and dichlobenil were also incorporated in beeswax matrices by the following procedure. Solid slabs of beeswax were frozen to -78°C and then ground to a fine powder. The powder was mixed with 20% (w/w) of herbicide and 6% (w/w) iron oxide. The resulting mixture was melted in a hot water bath, stirred, and then poured into a brass pellet mold. The mold was cooled rapidly in a dry ice/acetone bath to afford cylindrical pellets that weighed 0.25 g and were 6 mm in length and 5 mm in diameter. Upon immersion in the pH = 8 buffer, DMA 2,4-D was quickly released from the beeswax matrix. Dichlobenil, however, was slowly released over the 6-month test period at a rate of 0.10-0.15 mg per pellet per day.

Chemical attachment of herbicides to biodegradable polymers

87. The reaction of the acid chloride of 2,4-D with CMC was carried out under several different sets of reaction conditions. The best yield of acylated product was obtained in refluxing pyridine. This formulation, however, hydrolyzed quickly in the pH = 8 buffer. Evidently, the anhydride linkages that joined the 2,4-D to the CMC backbone were very susceptible to basic

Table 61. Effect of Molecular Weight of Preformed Polymer on the Hydrolysis of 2,4-D/Poly GMA Adducts

Adduct Type	Adduct No.	M _n of Polymer	Mg 2,4-D per g per day
2,4-D/Poly GMA Adducts	<u>26a-e</u>	23,600	less than 0.2
	<u>37a-d</u>	17,000	less than 0.2
	<u>31b</u> *	8,600	1.5
	<u>31a</u> *	5,800	4.1
	<u>38</u>	5,300	5.2
2,4-D/Copoly (GMA-HEMA) Adducts	<u>27b</u>	26,000	0.9
	<u>32b</u> *	8,200	4.8
	<u>32a</u> *	5,200	5.2
2,4-D/Poly GMA Adducts Containing Glycol Moieties	<u>35a</u>	20,000	0.9
	<u>34a</u> *	8,300	2.0
	<u>34b</u> *	5,600	5.3
	<u>34c</u> *	4,200	5.2
	<u>34d</u> *	3,000	5.1

* Hydroxy-Terminated Adduct

hydrolysis.

88. Hydroxyethyl cellulose (HEC) was also treated with the acid chloride of 2,4-D in a DMF/pyridine mixture. The reaction afforded a 70-80% yield of product. Chlorine analysis indicated that the degree of substitution was approximately 2. This formulation also released the majority of its 2,4-D content in a few days.

Scale-up of monomer syntheses

89. The scale-up work described in this and the following sections was carried out simultaneously and in conjunction with much of the research described earlier.

90. In order to develop procedures for producing large amounts of material for field tests, a study of the scale-up of the syntheses of the most promising copolymers was begun in the last quarter of 1979. This work was initially focused on the scale-up of the syntheses of the monomers AOE and MOE 2,4-D and GMA. Since both of the herbicide monomers are prepared from the acid chloride of 2,4-D, approximately 90 kg of 2,4-D acid was treated with thionyl chloride to afford over 70 kg of the reactive intermediate. The reactions of the acid chloride with HEA and HEMA were initially carried out in the presence of N,N-dimethylaniline, which was used to neutralize the liberated HCl. Since the yields of AOE and MOE 2,4-D at the 1-2 kg level were less than 30%, the use of other bases was investigated. This led to the discovery that the yields could be increased to approximately 40-50% by employing 3,5-lutidine. Several problems, however, were still encountered in carrying out the syntheses on a large scale. For example, after the reaction between the acid chloride of 2,4-D and HEA or HEMA was stopped, the reaction mixture had to be extracted several times to remove unreacted starting material. During these extractions, relatively stable emulsions formed, thereby greatly delaying the extraction process. The reactions were carried out under several different sets of reaction conditions in an attempt to alleviate these problems. The extraction emulsions were avoided and the yields increased to approximately 70% by decreasing the concentration of reactants and increasing the time of reaction. Apparently, the increase in the amount of solvent permitted more of the intermediate 2,4-D/lutidine salt to remain in solution.

91. Since this procedure was still time-consuming, several modifications were investigated in order to simplify and improve the process. This work led to the replacement of the tertiary amine base with molecular sieves. (Powdered 3A sieves had been reported to effectively adsorb HCl.) Thus, the reaction of

the acid chloride of 2,4-D with HEMA was carried out over powdered molecular sieves in carbon tetrachloride, ether, and ethylene chloride. The yield of MOE 2,4-D ranged from 50 to 75%. This procedure was considerably simpler because the reaction mixture did not have to be extracted to remove the amine. However, the yield of product decreased to less than 30% when large amounts of the sieves were used. This was because they were partially deactivated by water adsorption during handling and storage. The problem was solved by drying the sieves under vacuum immediately prior to use.

92. Regardless of the procedure used, the monomers were obtained in impure states. Although small amounts of either monomer could be purified, the purification of large amounts in a reasonable period of time proved difficult. For example, several attempts were made to recrystallize large amounts of MOE 2,4-D from organic solvents. However, the monomer either completely failed to crystallize or crystallized very slowly (1-2 weeks). Although small amounts of pure materials were obtained, attempts to distill the monomer under high vacuum resulted in considerable decomposition. A copolymerization of the impure MOE 2,4-D with GEM was carried out to determine if purification could be avoided. The polymerization, however, gave only a small amount of low molecular weight material.

93. The preparation of large amounts of the comonomer GEM was also extremely time-consuming. This was because the hydrolysis of GMA had to be carried out in dilute solution in order to avoid side reactions.

94. Due to the many problems experienced with the preparation and purification of AOE and MOE 2,4-D, a search for a more easily prepared herbicidal monomer was initiated. Thus, 2,4-D acid was treated with GMA in the presence of a quaternary ammonium salt catalyst to afford a quantitative yield of HMOE 2,4-D. Although HPLC analysis showed that the crude product contained at least two isomers, the material could be successfully polymerized without purification. No major problems were encountered in preparing approximately 2 kg of HMOE 2,4-D by this procedure.

Scale-up of polymer syntheses

95. The first two syntheses selected for scale-up were that of a 50:50 MOE 2,4-D/GEM copolymer and a 50:50 AOE 2,4-D/HEMA copolymer crosslinked with 2 wt % DPDM. The MOE 2,4-D/GEM copolymer was prepared in 100-500 g lots in MEK with a monomer concentration of 20-25 wt %. However, attempts to increase the monomer concentration resulted in the formation of insoluble gels. This was attributed to an increase in chain transfer to polymer as the concentration

increased. The increase in concentration was necessary in order to make the commercial production of the copolymer economically feasible.

96. Attempts to scale-up the synthesis of the crosslinked AOE 2,4-D/HEMA copolymer were also unsuccessful. This was due to the fact that it was impossible to control and predict the degree of crosslinking when the concentration of reactants was increased.

97. As soon as the preparation of HMOE 2,4-D described in paragraph 94 was developed, work was begun on the scale-up of the monomer's polymerization. Although several runs gelled, successful homopolymerizations were carried out in xylene and MEK with monomer concentrations as high as 50-60%. The homopolymer, however, did not undergo hydrolysis in reconstituted hard water. Work was then initiated on the scale-up of the copolymerization of HMOE 2,4-D with HEMA and with GEM. All attempts to run these copolymerizations with monomer concentrations above 50% resulted in the formation of insoluble gels.

Scale-up of the preparation of 2,4-D/Poly GMA adducts

98. In order to avoid chain transfer problems, a new synthetic route to the desired polymers was devised. Glycidyl methacrylate (GMA) was homopolymerized to afford an epoxy-containing prepolymer with a number-average molecular weight of approximately 24,000. The polymer was then treated with 60 mole % 2,4-D to yield the corresponding 2,4-D/Poly GMA adduct. Despite the fact that only preliminary release rate data were available on this formulation, its preparation was immediately scaled-up due to the pressing needs of the Corps for material for field tests. Due to the lack of suitable production facilities on campus, this work was conducted by Daychem Laboratories. Approximately 90 kg (200 lbs) was prepared in March 1981 by Daychem and sold to Wright State University. The material was hand delivered to Mid-Florida Mining where it was incorporated in clay pellets with great difficulty. Unfortunately, the process of coating the clay with a methyl ethyl ketone solution of the polymer resulted in a very tacky formulation that plugged the pellet dies.

99. In June 1981 another 180 kg (400 lbs) of the 2,4-D/Poly GMA adduct was prepared by Daychem Laboratories and sold to Wright State. This material was also incorporated in clay pellets by Mid-Florida Mining. The same processing problems mentioned above were experienced during the pelletization process.

100. During the course of the scale-up work, careful release rate studies were run on the 2,4-D adduct. These studies revealed that the formulation released 2,4-D at a very slow rate (0.2 mg of 2,4-D/g of adduct/day). The ini-

tial burst of 2,4-D observed in the subsequent field tests was probably due to unreacted herbicide that was trapped in the resin. Because of the adhesive nature of adduct when applied from solution, the clay pellets did not disintegrate when immersed in water. This further reduced the amount of herbicide released from the copolymer.

101. These results led to the following conclusions:

- a. The preparation of large amounts of 2,4-D/Poly GMA adduct was feasible.
- b. The release rate of the initial adduct was too slow and had to be increased.
- c. The clay pelletizing procedure using a solution of adduct had to be improved or else abandoned.

102. During the next 18 months considerable research was carried out to increase the adduct's release rate and to improve the processability of the resin. This led to the discovery that the release rate could be increased dramatically by decreasing the molecular weight of the Poly GMA prepolymer. In fact, the release rate could be increased from 1 to 5 mg 2,4-D/g adduct/day by decreasing the molecular weight from 9,000 to 5,000. Several kilograms of two different adducts were then prepared and isolated by precipitation in water. Although the precipitation process was tedious due to the tendency of the resins to become tacky and aggregate, assurances were given by several industrial pilot-plant operators that the process was feasible with their equipment. Powdered samples of each adduct were incorporated in clay pellets by the Agriculture Warehouse Co. No significant problems were encountered in processing the dry powders. The release rates of pellets of the two adducts were determined at the U.S. Department of Agriculture (USDA) Laboratory in Fort Lauderdale. They were approximately 1.5 mg 2,4-D/g adduct/day and 5 mg 2,4-D/g adduct/day, respectively. After consultation with Corps and USDA personnel, it was decided to scale-up the preparation of an adduct that would release 2,4-D at a rate intermediate between these two.

103. During April 1983, approximately 455 kg (1000 lbs) of the desired adduct was prepared at SBS Chemical's pilot plant. The adduct met all of the material specifications. However, several attempts to precipitate the adduct in water were unsuccessful. The adduct formed a sticky, fibrous mat that aggregated along the bottom and sides of the precipitation vessels.

104. During the next several weeks, many different approaches to precipitating the adduct were investigated. This work led to a procedure in which the

adduct solution was first diluted with an equal volume of methanol and then added to ice water to afford an off-white powder. Because of the many material losses suffered during the unsuccessful precipitation attempts, the total amount of material obtained was 227 kg (500 lbs). This was incorporated in clay pellets by the Agricultural Warehouse.

105. Two attempts were made in July 1983 to prepare an additional 227 kg (500 lbs) of adduct. Unfortunately, the monomer holding tanks were extremely warm during the first run due to the hot weather. The heat resulted in the premature polymerization and gellation of the GMA monomer. In the second attempt, due to a malfunctioning pump, the 2,4-D was added too quickly. This resulted in the gellation of the entire batch.

106. During July it was also discovered that the pellets prepared by the Agriculture Warehouse released all of their 2,4-D content in a few days. In fact, a high percentage of the 2,4-D was released as the methyl ester. Evidently, the methanol used to dilute the adduct solution reacted with the resin. It is also likely that the adduct underwent considerable hydrolysis in the methanol-water precipitation mixture.

CONCLUSIONS AND RECOMMENDATIONS

107. AOE and MOE Fenac can be copolymerized with MA to afford copolymers with M_n 's of 60,000 to 80,000. These materials, however, do not undergo hydrolysis under mildly alkaline conditions.

108. Copolymers with M_n 's of 4,500 to 6,600 can be obtained from the copolymerization of AOE 2,4-D with HEMA. Upon immersion in a buffer solution (pH = 8), the copolymers hydrolyze very slowly until a sufficient percentage of the polymer's repeat units have been converted to hydrophilic moieties. At this point, i.e., when the AOE 2,4-D content has been reduced to approximately 60 mole %, the rate of hydrolysis dramatically increases and then remains relatively constant for a period of 6-8 months. The length of the inhibition period prior to the autoacceleration in rate is dependent upon the amount of HEMA initially incorporated in the copolymer. Polymers containing over 40 mole % HEMA are hydrophilic enough to almost immediately undergo autoaccelerating hydrolyses.

109. The reactivity ratios of AOE 2,4-D and HEMA in their copolymerizations are 0.44 and 2.62 respectively. Since HEMA is considerably more reactive than AOE 2,4-D, the composition of their copolymers is nonuniform. Material formed early in the polymerization contains more HEMA than present in the feed, while copolymer formed at higher conversions contains less.

110. Copolymers of AOE 2,4-D and HEMA with uniform compositions can be prepared by making appropriate monomer additions as the polymerization proceeds. Such copolymers will undergo hydrolysis at faster rates than copolymers with similar HEMA contents and nonuniform compositions.

111. Branched copolymers of AOE 2,4-D and HEMA can be prepared by carrying out their copolymerizations in dilute solutions containing small amounts of multifunctional monomers, such as DPDM. The branched systems hydrolyzed slightly faster than linear copolymers with similar compositions.

112. The copolymerization of AOE 2,4-D and HEMA in concentrated solutions containing small amounts of DPDM and PETA results in crosslinked systems. These materials undergo hydrolysis at nearly constant rates. The material's hydrophilicity, as determined by the copolymer's composition at the time of gellation, is more important in determining the system's rate of hydrolysis than its degree of crosslinking. A given system's rate can be varied by varying the crosslink density, providing the degree of hydrophilicity remains the same.

113. MOE 2,4-D can be copolymerized with HEMA, GMA, and GEM to afford copolymers with Tg's near 50°C. The copolymers containing HEMA and GMA do not hydrolyze under mildly alkaline conditions. The MOE 2,4-D/GEM copolymers, however, undergo hydrolysis similarly to AOE 2,4-D/HEMA copolymers, i.e., they hydrolyze slowly until approximately 50 mole % of their repeat units consist of hydrophilic moieties. At this point, the rate dramatically increases and then remains relatively constant for 6-8 months. Copolymers containing over 50 mole % of GEM begin to hydrolyze at a constant rate almost immediately upon immersion.

114. The reaction of 2,4-D with GMA in the presence of TMC affords a nearly quantitative yield of HMOP 2,4-D. The monomer as obtained is sufficiently pure to undergo successful homopolymerization and copolymerization. The homopolymer and copolymers containing HEMA do not hydrolyze under mildly alkaline conditions. HMOP 2,4-D/GEM copolymers containing greater than 50 mole % GEM hydrolyze at nearly constant rates.

115. GMA can be homopolymerized in MEK with AIBN as the initiator to afford polymers with M_n 's of greater than 20,000. The homopolymer will react with 2,4-D in the presence of quaternary ammonium salts to give ester adducts. The degree of substitution of 2,4-D in such adducts does not significantly affect the very slow rate at which they undergo hydrolysis in reconstituted hard water.

116. GMA can be copolymerized with hydrophilic comonomers, such as HEMA, HEA, HPMA, and DMAEMA. The amount of comonomer that can be used, however, is limited as the use of excessive amounts will result in crosslinking. Some 2,4-D/GMA copolymer adducts can be prepared that hydrolyze 30 to 40 times faster than similar homopolymer adducts.

117. Glycol moieties can be incorporated in 2,4-D/Poly GMA adducts by treating their free epoxy groups with very dilute H_2SO_4 . Adducts treated in this manner undergo hydrolysis at greatly accelerated rates.

118. Hydroxy-terminated polymers with M_n 's of less than 10,000 can be prepared by the homopolymerization and copolymerization of GMA in the presence of ME. The 2,4-D adducts prepared from these polymers are considerably more susceptible to hydrolysis than their higher molecular weight analogs. The molecular weight of the prepolymer is more important than its relative degree of hydrophilicity in determining the corresponding adduct's rate of hydrolysis.

119. Low-molecular weight Poly GMA can also be prepared by carrying out the polymerization of GMA in the presence of PE. The 2,4-D adducts prepared

from Poly GMA with an M_n of approximately 5,000 hydrolyze 30 to 40 times as fast as those prepared from Poly GMA with an M_n of 24,000. The most effective method for increasing the rate of hydrolysis of systems of this type appears to lower their molecular weights.

120. DMA 2,4-D can be physically entrapped in beeswax and in crosslinked chitosan and CMC matrices. The water-soluble salt, however, is released quickly from these formulations upon immersion in water. Dichlobenil can also be physically dispersed in beeswax matrices. These formulations slowly release the herbicide, which is only slightly water soluble, for at least 6 months following immersion.

121. The 2,4-D can be chemically attached to CMC and HEC. The resulting 2,4-D/polymer adducts rapidly undergo hydrolysis under slightly alkaline conditions.

122. AOE and MOE 2,4-D can be prepared in kilogram quantities by the reaction of the acid chloride of 2,4-D with HEA and HEMA, respectively. Although the reactions are facilitated by the use of molecular sieves that adsorb the liberated hydrochloric acid, the average yields are only 50%. The monomers must be purified prior to polymerization. MOE 2,4-D is very difficult to purify in large quantities. The preparation of large amounts of GEM is also extremely time-consuming because the hydrolysis of GMA must be carried out in very dilute solutions.

123. HMOP 2,4-D can be prepared in kilogram quantities by the reaction of 2,4-D with GMA. The monomer is obtained in quantitative yield and can be polymerized without purification.

124. Polymerizations involving AOE and MOE 2,4-D are very difficult to scale-up because they cannot be carried out in solutions containing high concentrations of the monomers. Such conditions result in the formation of insoluble gels. The polymerization of HMOP 2,4-D in concentrated solutions also often results in gellation.

125. The most promising controlled-release systems prepared and evaluated in this study, i.e., the low-molecular-weight 2,4-D/Poly GMA adducts, can be prepared in commercial quantities. However, the processing of the adduct solution as obtained from the reaction mixture is difficult. A method must be developed to remove the solvent before the adduct can be used in field tests.

126. Solvent removal and the subsequent processing of the resin would be greatly facilitated if the adduct did not contain unreacted epoxy groups. For example, the adduct solution cannot be heated to remove solvent because these

groups readily undergo thermal polymerization. It is recommended that research be carried out to eliminate these groups from the system. This could be accomplished by reducing the amount of epoxy groups contained in the prepolymer. Approximately 40 mole % of these groups are not needed because they do not react with 2,4-D (probably due to steric hindrance). Hence, their replacement with an inert monomer, such as styrene or methyl methacrylate, would not reduce the adducts' 2,4-D content. Solvent could be readily removed from such a system at elevated temperatures, and the product could be processed similarly to thermoplastics in conventional equipment.

REFERENCES

- Arah, C.O. 1978. "Synthesis and Hydrolysis of Hydrogels Containing Pendent Herbicide Substituents," M.S. Thesis, Wright State University, Dayton, Ohio.
- Aulabaugh, A.E. 1977. "Synthesis and Polymerization of Unsaturated Esters of 2,3,6-Trichlorophenylacetic Acid," M.S. Thesis, Wright State University, Dayton, Ohio.
- Chou, C.J. 1982. "Preparation and Hydrolysis of 2,4-Dichlorophenoxyacetic Acid/Poly(glycidyl methacrylate) Adducts," M.S. Thesis, Wright State University, Dayton, Ohio.
- Fineman, M., and Ross, S.D. 1950. "Linear Method For Determining Monomer Reactivity Ratios in Copolymerization," Journal of Polymer Science, Vol 5, pp 259-265.
- Harris, F.W., Post, L.K., and Feld, W.A. 1974. "Investigation of Factors Influencing Release of Herbicides from Polymers Containing Herbicides as Pendent Side Chains," Final Report, Part I, Contract No. DACW73-74-C-0001, Dayton, Ohio.
- Harris, F.W., Feld, W.A., and Bowen, B. 1975. "Investigation of Factors Influencing Release of Herbicides from Polymers Containing Herbicides as Pendent Side Chains," Final Report, Part II, Contract No. DACW73-74-0001, Dayton, Ohio.
- Harris, F.W., and Post, L.K. 1975. "Synthesis and Polymerization of the Vinyl and Acryloyloxyethyl Esters of 2,4-Dichlorophenoxyacetic Acid and 2-(2,4,5-Trichlorophenoxy)propionic Acid," Journal of Polymer Science, Vol 13, pp 225-229.
- Harris, F.W., Dykes, M., Aulabaugh, A., Feld, W.A., and Case, R.D. 1977a. "Characterization and Evaluation of Polymers Containing Herbicides as Pendent Side Chains," Final Report, Contract No. DACW39-76-0016, Dayton, Ohio.
- Harris, F.W., Aulabaugh, A.E., Case, R.D., Dykes, M., and Feld, W.A. 1977b. "Polymers Containing Pendent Herbicide Substituents: Preliminary Hydrolysis Studies," Controlled Release Polymeric Formulations, Paul, D.R., and Harris, F.W., Eds., ACS Symposium Series, No. 53, pp 222-226.
- Marking, L.L., and Dawson, V.K. 1976. "Toxicity of Quinaldine Sulfate to Fish," Investigations in Fish Control, No. 48, U.S. Fish and Wildlife Service, Washington, D.C., pp 8-10.
- Refofo, M.F. 1965. "Glyceryl Methacrylate Hydrogels," Journal of Applied Polymer Science, Vol 9, pp 3161-3166.
- Scoggins, M. W. 1977. "Spectroscopic Determination of Ethylene Glycol in Motor Oil," Analytical Chemistry, Vol 49, No. 4, pp 582-585.
- Talukder, M.A. 1981. "Synthesis and Hydrolysis of Homopolymers and Copolymers of 2-Hydroxy-3-methacryloyloxypropyl 2,4-Dichlorophenoxyacetate," M.S. Thesis, Wright State University, Dayton, Ohio.

Thompson, J.W. 1978. "Synthesis and Characterization of 2-Acryloyloxyethyl 2,4-Dichlorophenoxyacetate/2-Hydroxyethyl Methacrylate Copolymers," M.S. Thesis, Wright State University, Dayton, Ohio.

Whitlock, M.W. 1980. "Synthesis and Hydrolysis of Uniform-Composition Copolymers Containing Pendent Herbicide Substituents," M.S. Thesis, Wright State University, Dayton, Ohio.

APPENDIX A: EXPERIMENTAL METHODS

General procedure for the copolymerization of AOE Fenac, MOE Fenac, and AOE 2,4-D

1. Herbicide monomer, the comonomer, deoxygenated 2-butanone (4 ml/g of monomers), and 0.05% (w/v) AIBN were stirred and slowly heated to 78°C. The solution was heated at reflux for 3 hr under nitrogen, diluted with 2-butanone, and poured into hexane. The polymer that precipitated was collected by filtration and extracted overnight with ether to remove unreacted monomer. The copolymer was reprecipitated from chloroform with hexane. The copolymer was then dried under vacuum at 64°C.

Preparation of buffer solution

2. A solution of 0.375 mol boric acid in approximately 800 ml glass-distilled water was titrated with a 0.7 N aqueous solution of sodium hydroxide to a pH of 8.00. The volume of the mixture was then diluted with water to 1 l.

Preparation of reconstituted hard water (Marking and Dawson 1976)

3. The reconstituted hard water that was prepared by the known procedure contained 192 mg/l NaHCO_3 , 120 mg/l $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, 120 mg/l MgSO_4 , and 8 mg/l KCl .

Hydrolysis studies

4. The homopolymers and copolymers were ground and sieved to obtain a uniform particle size of 125-420 μ . Three 0.5-g replicates of each sample were placed in individual 500-ml flasks containing 300 ml of buffer solution or reconstituted hard water. The flasks were equipped with sintered-glass sampling tubes which allowed analytical samples to be removed free of any polymer particles. In some cases, the flasks were placed in a constant temperature air bath maintained at $30^\circ \pm 1.0^\circ\text{C}$. The bath was attached to a laboratory rotator that provided slight agitation. Some flasks were stored at ambient temperature without agitation. The amount of fenac or 2,4-D released was determined periodically by spectrophotometric analysis at 203 and 230 nm, respectively.

Determination of reactivity ratios of AOE 2,4-D and HEMA (Thompson 1978)

5. Several copolymerizations with different feed ratios were carried out by the following procedure: AOE 2,4-D, HEMA, 2-butanone, and AIBN were deoxygenated and sealed in a glass ampule under vacuum. After the ampule was rotated and heated to 80°C for 1 hr, it was opened and the contents poured into hexane. The copolymer that precipitated was collected by filtration, extracted overnight with ether to remove unreacted monomer, and dried under vacuum at

64°C. The percentage of AOE 2,4-D in the copolymer was determined by chlorine analysis.

Determination of ethylene glycol in hydrolysis solutions of AOE 2,4-D copolymers (Scoggins 1977)

6. The amount of ethylene glycol present in the hydrolysis solutions was determined by the following colorimetric procedure. To 1 ml of the solution was added 4 ml of 0.003 M trisodium paraperiodate, 1 ml of 0.03 M 3-methyl-2-benzothiazolinone hydrazone hydrochloride monohydrate (MBH), and 30 ml of 0.007 M ferric chloride. The mixture was then diluted with water to 100 ml. The solution, which was dark blue indicating the presence of ethylene glycol, was then subjected to spectrophotometric analysis at 630 nm.

Preparation of linear copolymers of AOE 2,4-D and HEMA with uniform compositions (Whitlock 1980)

7. The following is a description of a typical copolymerization procedure. Copolymerizations were conducted in an Ace Glassware polymerization vessel. MEK (50 ml) was placed in the polymerization vessel and purged with nitrogen for 30 min. After the solvent was heated to 70°C, 10 g of AOE 2,4-D, 1.67 g of HEMA, and 0.016 g of AIBN were added under nitrogen. The polymerization mixture was maintained at 70°C and stirred for 1 hr. An additional 1.0 g of AOE 2,4-D and 0.167 g of HEMA were then added and the polymerization was allowed to proceed at 70°C. This addition of monomers was repeated two more times at 1-hr intervals. After the last addition, the polymerization mixture was heated at 70°C for an hour, cooled, and then added dropwise to 1 l of hexane. The polymer that precipitated was collected by filtration, extracted overnight with anhydrous ethyl ether, and dried under reduced pressure.

Preparation of branched and crosslinked copolymers of AOE 2,4-D and HEMA (Arah 1978)

8. Copolymerizations were conducted in an Ace glassware polymerization vessel equipped with a hollow trubore stirrer that permitted nitrogen to be introduced below the surface of the reaction mixture. The copolymerizations were carried out in MEK at 70°C for the designated time period (Tables 15, 19, and 20). AIBN (0.016 g) was used as the initiator. Crosslinked systems were run until gelation occurred. The reaction mixtures were added to hexane, and the resulting suspensions agitated in a Waring blender. The polymers were collected by filtration, extracted overnight with anhydrous ethyl ether to remove unreacted monomer and initiator residues, and then dried under vacuum at 34°C.

2-Hydroxy 3-methacryloyloxypropyl 2,4-dichlorophenoxyacetate (HMOP 2,4-D)

9. The following procedure was carried out with equimolar amounts of 2,4-D and GMA. A stirred slurry of 2,4-D in MEK (15% w/w) and TMC (1.5% w/w) was heated to 70 °C under a nitrogen atmosphere. A mixture of GMA and p-methoxyphenol (0.15% w/w) was then slowly added to the reaction vessel with constant stirring. The reaction mixture was maintained at 70 °C for 3 hr, cooled, and then stored in the refrigerator. Determination of the epoxy content of several different reaction mixtures indicated that 96-98% of the GMA underwent reaction under these conditions. All attempts to distill the product under reduced pressure resulted in considerable decomposition. The light yellow oil was purified by the following procedure. Low-boiling petroleum ether was slowly added to a stirred clear solution of the crude product in acetone. The heavy, highly viscous oil that slowly separated at the bottom of the container was removed using a separatory funnel. After the process was repeated several times, the monomer was dried under reduced pressure overnight in order to remove residual acetone, MEK, and petroleum ether. The yield of purified monomer was 75%. IR(neat) 3500-3200 (-OH), 1740-1680 (C=O ketone), and 1620 cm^{-1} (C=C alkene, aromatic); NMR (chloroform- D_1) 7.0 (q, 15H, C_6H_3), 5.6 (d, 10 H, = CH_2), 4.5 (q, 10H, -O- CH_2), 3.5 (m, 5H, -CH), 4.8 (s, 5H, -OH), 2.5 (q, 10H, -O- CH_2), 2.1 (s, 15H, - CH_3), and 3.2 ppm (s, 10H, -O- CH_2 -C-), Anal. Calcd. for $\text{C}_{15}\text{H}_{16}\text{Cl}_2\text{O}_6$: C, 49.60; H, 4.44; Cl, 19.51 Found: C, 49.45; H, 4.66; Cl, 19.77

Glyceryl methacrylate (GEM) (Ref. 1965)

10. To a suspension of GMA in water (60% v/v) was added concentrated H_2SO_4 (0.1 v/v). The mixture was stirred for 5 days at 0 °C, during which time the GMA went into solution. The solution was neutralized with NaOH and extracted several times with anhydrous ether. The ether extract was saturated with NaCl and stored for 1 hr. After the water that separated was removed, the ether layer was diluted with methylene chloride and dried over anhydrous MgSO_4 . The solvents were then removed under reduced pressure and the residual products stored in the refrigerator.

Homopolymerization of HMOP 2,4-D (Talukder 1981)

11. Homopolymerizations were conducted in an Ace glassware polymerization vessel. A typical homopolymerization procedure follows: MEK (50 ml) was placed in the polymerization vessel and heated to 70 °C under nitrogen. A mixture of 10 g of HMOP 2,4-D and 0.1 g of AIBN was then slowly added over 0.5 hr with constant stirring. After the stirred polymerization mixture was main-

tained at 70°C for an additional 2 hr, it was cooled and then added dropwise to 1 l of petroleum ether. The polymer that precipitated was collected by filtration, extracted overnight with anhydrous ethyl ether to remove unreacted monomer and initiator residues, and then dried under vacuum.

Preparation of HMOP 2,4-D copolymers

12. Copolymerizations were conducted in an Ace glassware polymerization vessel. The following is a description of a typical copolymerization procedure: MEK (75 ml) was placed in the polymerization vessel under a continuous stream of nitrogen. After the solvent was heated to 70°C, a mixture of 22.5 g of HMOP 2,4-D (0.06 mol), 2.5 g of GEM (0.015 mol), and 0.25 g of AIBN was slowly added over 1 hr with constant stirring. The stirred polymerization mixture was heated at 70°C for an additional 2 hr, cooled, and then added dropwise to 2 l of petroleum ether. The polymer that precipitated was collected by filtration, extracted with anhydrous ethyl ether, and dried under reduced pressure.

Preparation of 2,4-D/Poly GMA adducts (Chou 1982)

13. All of the 2,4-D/Poly GMA adducts were prepared by the same general procedure. The following is a typical example. MEK (135 g) was placed in a 1-l Ace polymerization vessel under a nitrogen atmosphere. After the solvent was heated to 65°C, a mixture of 250 g of GMA, 5.0 g of AIBN, and 2.5 g of ME was slowly added over a 3-hr period with constant stirring. After the addition was complete, the polymerization mixture was maintained at 70°C for 1 hr. A mixture of 0.5 g of AIBN in 10 g of MEK was added, and the polymerization mixture was maintained at 70°C for another hour. A mixture of 60 g of 2,4-D, 33 g of cellosolve acetate, and 2.5 g of TEAB was then added, and the reaction allowed to proceed at 70°C for 1 hr. The addition of the above mixture was repeated three more times at 2-hr intervals. After the last addition, the reaction mixture was maintained at 70°C for 2 hr, and then cooled to room temperature. The polymer solution was diluted with twice the amount of acetone, and added dropwise to stirred distilled water. The resulting precipitate was agitated in a Waring blender containing a 1:5 mixture of ethyl alcohol and water. The polymer was collected by filtration and dried under vacuum overnight.

Preparation of 2,4-D/copolymer adducts

14. Copolymerizations were conducted in an Ace glassware polymerization vessel. The following is a description of a typical copolymerization procedure. MEK (135 g) was placed in the polymerization vessel under a continuous

stream of nitrogen. After the solvent was heated to 65°C, a mixture of 200 g of GMA, 45 g of HEMA, 5.0 g of AIBN, and 2.5 g of ME was slowly added over a 3-hr period with constant stirring. After the addition was complete, the polymerization mixture was maintained at 70°C for 1 hr. A mixture of 0.5 g of AIBN in 10 g of MEK was added, and the polymer solution was maintained at 70°C for another hour. A mixture of 26 g of 2,4-D, 25 g cellosolve acetate, and 1 g of TEAB was then added and the reaction allowed to proceed at 70°C for 1 hr. The addition of the above mixture was repeated three more times at 2-hr intervals. After the last addition, the reaction mixture was maintained at 70°C for 2 hr. The product was isolated by the procedure described for the homopolymer adducts.

General procedure for the hydrolysis of residual epoxy groups

15. Polymer hydrolysis reactions were also conducted in an Ace glassware polymerization vessel. The following is a description of a typical hydrolysis procedure. The Poly GMA solution (100 g), which was prepared according to the procedure described earlier, and 30 g of CA were placed in the reacting vessel under a continuous stream of nitrogen. The polymer solution was then heated with constant stirring. A dilute acid solution was prepared by adding 10 ml of a mixture of 1.0 ml of concentrated H₂SO₄ and 100 ml of CA to 40 ml of CA. When the temperature of the polymer solution reached 65°C, the acid solution was slowly added over a period of 1.5 hr. After the addition was complete, the mixture was maintained at 70°C for 0.5 hr.

Determination of epoxy (oxirane) and 2,4-D content in 2,4-D/Poly GMA adducts (Personal Communication with Glidden-Durkee 1982)

16. The following solutions were prepared for the determination of epoxy content: 0.1 N perchloric acid (HClO₄); 25% w/v tetraethylammonium bromide in glacial acetic acid, and 0.5% w/v crystal violet in glacial acetic acid. The 0.1 N perchloric acid solution was prepared by adding 20 ml of acetic anhydride to a mixture of 8.5 ml of 72% HClO₄ in 300 ml of glacial acetic acid. After the mixture was allowed to stand overnight, it was standardized with potassium hydrogen phthalate (KHP). Approximately 0.15 g KHP in 10 ml glacial acetic acid was used. The normality of the solution was calculated using the following equation:

$$\text{Normality} = \frac{\text{g of KHP} \times 1000}{204.2 \times \text{ml of HClO}_4}$$

The tetraethylammonium bromide solution was prepared by dissolving 100 g in 400 ml of glacial acetic acid.

17. To between 0.2 and 0.3 g of the sample contained in a 125-ml conical flask was added 10 ml of acetone. The tetraethylammonium bromide solution (10 ml) and one or two drops of the crystal violet indicator were then added. The mixture was titrated with the HClO_4 solution until the color changed from violet blue to green. The epoxy content was calculated using the following equation:

$$\% \text{ oxirane (O)} = \frac{1.6 (\text{normality of } \text{HClO}_4)(\text{titration ml of } \text{HClO}_4)}{\text{wt. of the sample}}$$

A sample calculation of 2,4-D content is given below:

$$\% \text{ oxirane (O)} = \frac{16 (1-x)}{142 (1-x) + 363x + \text{g of AIBN} + \text{g of ME}}$$

where x is the percentage of 2,4-D in the adduct.