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CHARACTERIZATION AND EVALUATION OF POLYMERS CONTAINING HERBICIDES AS PENDENT SIDE CHAINS

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The syntheses of five vinyl monomers containing fenac, i.e., vinyl 2,3,6-trichlorophenylacetate, 2-acryloyloxyethyl 2,3,6-trichlorophenylacetate, 4-acryloyloxybutyl 2,3,6-trichlorophenylacetate, 4-vinyloxybutyl 2,3,6-trichlorophenylacetate, and 2-methacryloyloxyethyl 2,3,6-trichlorophenylacetate, were carried out. These monomers were polymerized by bulk- and solution-free-radical techniques to afford the corresponding polymers. A study of the hydrolysis of poly(vinyl 2,4-dichlorophenoxyacetate), poly(2-acryloyloxyethyl

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20. ABSTRACT (Continued)

2,4,-dichlorophenoxyacetate), an 87:13 copolymer of 2-acryloyloxyethyl 2,4-dichlorophenoxyacetate and trimethylamine methacrylimide, poly(1-methyl-2-acryloyloxyethyl 2,4-dichlorophenoxyacetate), and poly(4-acryloyloxybutyl 2,4-dichlorophenoxyacetate) at pH 7 was completed. The hydrolysis of poly(vinyl 2,3,6-trichlorophenylacetate), poly(vinyl 2,4-dichlorophenoxyacetate), poly(2-acryloyloxyethyl 2,4-dichlorophenoxyacetate), and a 75:25 copolymer of 2-acryloyloxyethyl 2,4-dichlorophenoxyacetate and trimethylamine methacrylimide at pH 8.08 was also investigated. The results of these studies showed that only copolymers containing hydrophilic residues will undergo hydrolysis. Hence, a detailed study of the copolymerization of the monomers containing 2,4-dichlorophenoxyacetic acid (2,4-D) with acrylic acid, methacrylic acid, N-vinyl-2-pyrrolidone, and trimethylamine methacrylimide was carried out. All of the resulting copolymers underwent hydrolysis in water with a pH of 8 at 30°C. The rate of hydrolysis depended on the type and amount of the hydrophilic comonomer used. Samples of three copolymers of 2-acryloyloxyethyl 2,4-dichlorophenoxyacetate containing 5% methacrylic acid, 10% methacrylic acid, and 35% trimethylamine methacrylimide, respectively, were prepared for preliminary field testing. Fenac was also physically incorporated in polyethylene pellets to provide an additional formulation for field evaluation.

SUMMARY

Our approach to preparing controlled-release formulations that contain a high percentage of herbicide has been the synthesis of polymers that contain pendent herbicide substituents. These systems have been designed so that herbicide release will occur by the slow, sequential hydrolysis of herbicide-polymer chemical bonds. The objectives of this research were: (1) to complete our study of the hydrolysis of polymers containing 2,4-dichlorophenoxyacetic acid (2,4-D) which was initiated under Contract No. DACW73-74-C-0001; (2) to determine the effects of pH on the polymers' rates of hydrolysis; (3) to synthesize a new series of polymers containing 2,3,6-trichlorophenylacetic acid (fenac); and (4) to determine the rates of hydrolysis of the polymers containing fenac under carefully controlled conditions.

The syntheses of five vinyl monomers containing fenac, i.e. vinyl 2,3,6-trichlorophenylacetate, 2-acryloyloxyethyl 2,3,6-trichlorophenylacetate, 4-acryloyloxybutyl 2,3,6-trichlorophenylacetate, 4-vinyloxybutyl 2,3,6-trichlorophenylacetate, and 2-methacryloyloxyethyl 2,3,6-trichlorophenylacetate, were carried out. These monomers were polymerized by bulk- and solution-free radical techniques to afford the corresponding polymers.

A study of the hydrolysis of poly(vinyl 2,4-dichlorophenoxyacetate), poly(2-acryloyloxyethyl 2,4-dichlorophenoxyacetate), an 87:13 copolymer of 2-acryloyloxyethyl 2,4-dichlorophenoxyacetate and trimethylamine methacrylimide, poly(1-methyl-2-acryloyloxyethyl 2,4-dichlorophenoxyacetate), and poly(4-acryloyloxybutyl 2,4-dichlorophenoxyacetate) at pH

7 was completed. The study was carried out for 340 days at which time the copolymer had released an average of 23 mg of 2,4-D per g of polymer. The homopolymers, however, failed to undergo hydrolysis.

The hydrolysis of poly(vinyl 2,3,6-trichlorophenylacetate), poly(vinyl 2,4-dichlorophenoxyacetate), poly(2-acryloyloxyethyl 2,4-dichlorophenoxyacetate), and a 75:25 copolymer of 2-acryloyloxyethyl 2,4-dichlorophenoxyacetate and trimethylamine methacrylimide at pH 8.08 was investigated. The results of this study show that only the copolymer which contains hydrophilic aminimide residues undergoes significant hydrolysis under these conditions.

Since the initial release rate studies indicated that in order for the polymers containing herbicides to undergo hydrolysis they must also contain hydrophilic substituents, a detailed study of the copolymerization of the previously prepared monomers was carried out. The hydrophilic comonomers used were acrylic acid, methacrylic acid, N-vinyl-2-pyrrolidone, and trimethylamine methacrylimide was carried out.

The hydrolysis of copolymers of 2-acryloyloxyethyl 2,4-dichlorophenoxyacetate with methacrylic acid and trimethylamine methacrylimide at pH 8.08 was investigated. A copolymer containing 20% methacrylic acid released 117 mg of 2,4-D per g of polymer in the first six days of this study. A copolymer containing 5% methacrylic acid released 13 mg 2,4-D per g of polymer in 78 days, while a copolymer containing 10% acid released 28.7 mg of 2,4-D per g of polymer in 76 days. A copolymer containing 25% of the aminimide residue released 5.1 mg of 2,4-D per g of polymer in 207 days, whereas, a copolymer containing

35% aminimide released 133.4 mg of 2,4-D per g of polymer in 123 days.

A study of the release rates of a copolymer of vinyl 2,4-dichlorophenoxyacetate containing 30% N-vinyl-2-pyrrolidone at pH 8.08 was also carried out. This copolymer released 3.3 mg of 2,4-D per g of polymer in 118 days.

The syntheses of three copolymers of 2-acryloyloxyethyl 2,4-dichlorophenoxyacetate containing 5% methacrylic acid, 10% methacrylic acid, and 35% trimethylamine methacrylimide, respectively, were scaled up to provide samples for preliminary field evaluation. Fenac acid was also physically incorporated in polyethylene pellets. The formulation, which contained 20% fenac acid, 8% ferrous oxide, and 72% high-density polyethylene,was sent along with the above samples to the University of Southwestern Louisiana for field testing.

The results of this research indicate that homopolymers containing 2,4-D or fenac as pendent substituents will not undergo hydrolysis in water with a pH of 7 or 8 at 30°C. Increasing the length of the pendent side chains does not result in the hydrolysis of the herbicide-polymer ester bonds.

Copolymers containing 2,4-D or fenac and hydrophilic residues will slowly hydrolyze in water at 30°C. Increasing the pH from 7 to 8 does not significantly enhance the rate of hydrolysis. The rate is dependent on the amount and type of the hydrophilic group used. Carboxylic acid groups serve as the most effective intramolecular catalyst for the hydrolysis.

PREFACE

This report was prepared under U.S. Contract No. DACW39-76-C-0016 (Neg.). The work was administered under the direction of the Department of the Army, USAE Waterways Experiment Station, Vicksburg, Mississippi, with Mr. William N. Rushing acting as the Contracting Officer's Representative.

This report covers work conducted from 1 August 1975 to 31 July 1976. The project personnel were M. Dykes, A. Aulabaugh, W. A. Feld, and R. D. Case, Jr.

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CHARACTERIZATION AND EVALUATION OF POLYMERS CONTAINING HERBICIDES AS PENDENT SIDE CHAINS

INTRODUCTION

1. Controlled-release, herbicide-polymer formulations that extend the control of equatic weeds have been developed.[1,2] Fenac-polyethylene and fenac-ethylcellulose formulations have been developed and studied in this laboratory.[3,4] In these formulations the herbicide is physically incorporated in a polymeric matrix and release occurs by diffusion. Although these formulations have considerable potential, a draw-back to their production and use is the large amount of inert polymer carrier (70-90% w/w) that must be employed. The development of new herbicide-polymer formulations that contain a high percentage of herbicide is highly desirable.

2. One approach to obtaining these formulations has been the synthesis of polymers that contain herbicides as pendent side chains. In the first part of this study polymers that contain 80-90% 2,4-dichlorophenoxyacetic acid (2,4-D) or 2-(2,4,5-trichlorophenoxy)propionic acid (silvex) were prepared from a series of vinyl monomers. The monomers, i.e. vinyl 2,4-dichlorophenoxyacetate (1a), vinyl 2-(2,4,5-trichlorophenoxy)propionate (1b), 2-acryloyloxyethyl 2,4-dichlorophenoxyacetate (2a), 2-acryloyloxyethyl 2-(2,4,5-trichlorophenoxy)propionate (2b), 2-methacryloyloxyethyl 2-(2,4,5-trichlorophenoxy)propionate (3b), 4-acryloyloxybutyl 2,4-dichlorophenoxyacetate (4a), and 4-acryloyloxybutyl

2-(2,4,5-trichlorophenoxy)propionate (4b), were polymerized by bulk-, solution-, and emulsion-free-radical techniques (Figure 1). The polymerizations were enhanced by low initiator concentrations and mild conditions. Polymers 5a-8b have intrinsic viscosities as high as 2.03 and can be cast into tough, transparent films.[5-7]

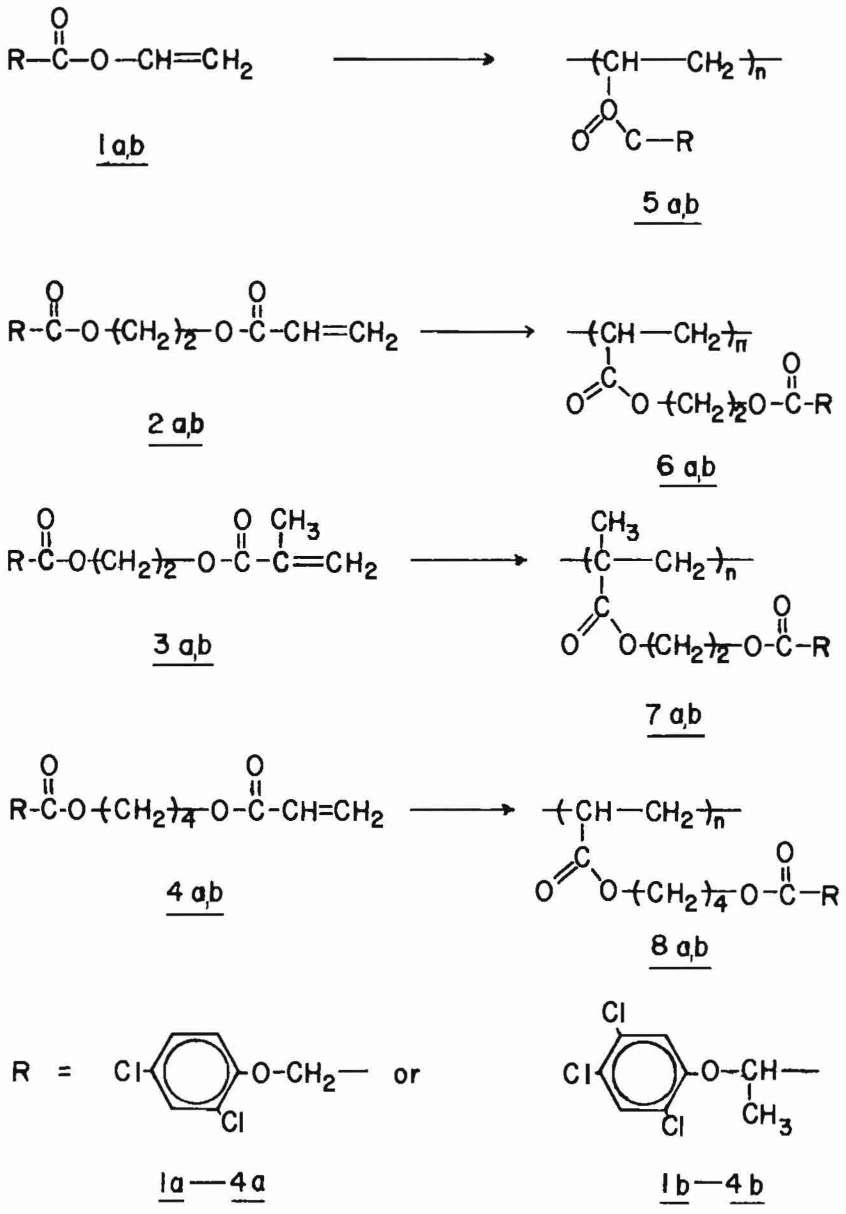


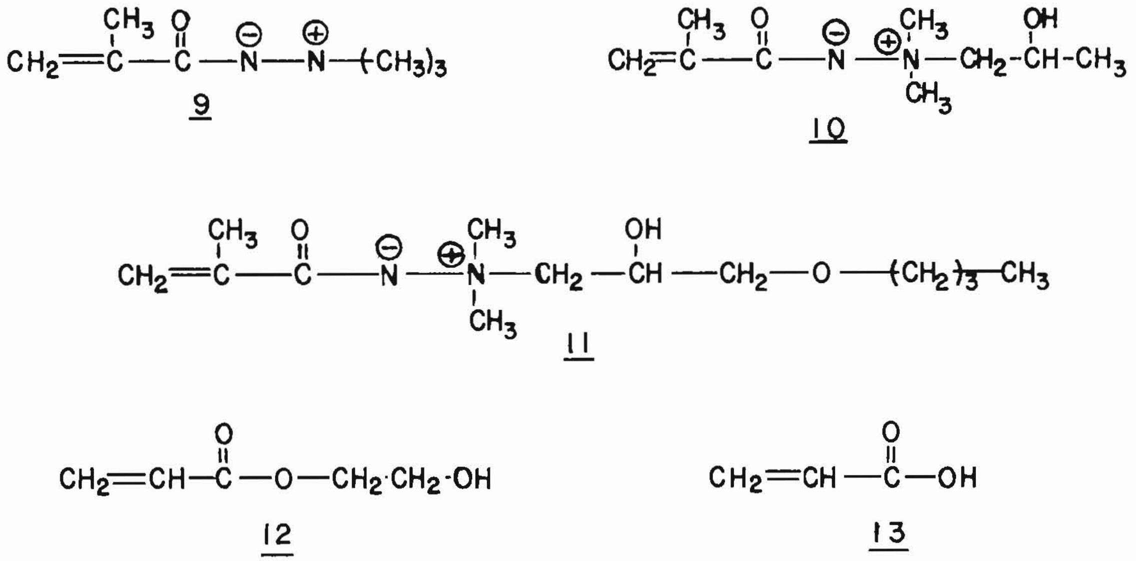
Figure 1. Polymerization of monomers containing 2,4-D and silvex.

3. The polymer systems were designed so that herbicide release would occur by the slow, sequential hydrolysis of the herbicide-polymer chemical bonds. In this first series of polymers the length of the linkage connecting the herbicide to the polymer backbone was varied. It was postulated that increasing the length of the pendent side chain would enhance the hydrolysis of the herbicide-polymer ester bond, since the bond would be removed from the hydrophobic backbone and less sterically hindered.

4. In another attempt to vary the rate of hydrolysis, copolymerizations of 2-acryloyloxyethyl 2,4-dichlorophenoxyacetate (2a) and 2-acryloyloxyethyl 2-(2,4,5-trichlorophenoxy)propionate (2b) with vinyl monomers that would vary the hydrophilicity of the resulting copolymer backbone were carried out. For example, the monomers 2a and 2b were copolymerized with trimethylamine methacrylimide (10) and 1,1-dimethyl-(2-hydroxypropyl)amine methacrylimide (11), hydroxyethyl acrylate (12), and acrylic acid (13) (Figure 2). These materials contain functional groups which give the corresponding copolymers greater hydrophilicity.

5. The major objectives of this research were: (1) to complete our study of the hydrolysis of polymers containing 2,4-D which was initiated under Contract DACW73-74-C-0001; (2) to determine the effects of pH on the polymers' rates of hydrolysis; (3) to synthesize and polymerize a new series of vinyl monomers containing 2,3,6-trichlorophenylacetic acid (fenac); and (4) to determine the rates of hydrolysis of the

polymers containing fenac under carefully controlled conditions.



$CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}\overset{\ominus}{N}{-}\overset{\oplus}{N}{-}(CH_3)_3$

9

$CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}\overset{\ominus}{N}{-}\underset{CH_3}{\overset{\oplus\,CH_3}{N}}{-}CH_2{-}\overset{OH}{\overset{|}{CH}}{-}CH_3$

10

$CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}\overset{\ominus}{N}{-}\underset{CH_3}{\overset{\oplus\,CH_3}{N}}{-}CH_2{-}\overset{OH}{\overset{|}{CH}}{-}CH_2{-}O{-}(CH_2)_3{-}CH_3$

11

$CH_2{=}CH{-}\overset{O}{\overset{\|}{C}}{-}O{-}CH_2{\cdot}CH_2{\cdot}OH$

12

$CH_2{=}CH{-}\overset{O}{\overset{\|}{C}}{-}OH$

13

Figure 2. Hydrophilic comonomers.

RESULTS AND DISCUSSION

Synthesis of vinyl monomers containing fenac

6. The syntheses of five vinyl monomers containing fenac were carried out. Vinyl 2,3,6-trichlorophenylacetate (15) was prepared in high yield by the mercuric acetate-sulfuric acid catalyzed, vinyl-interchange reaction between vinyl acetate and fenac (14) (Figure 3). Four monomers were synthesized by the condensation of vinyl alcohols with fenac in the presence of the dehydrating agent dicyclohexylcarbodiimide (Figure 3). Thus, the reactions of fenac with 2-hydroxyethyl acrylate (12), 4-hydroxybutyl acrylate (16), 4-hydroxybutyl vinyl ether (17), and 2-hydroxyethyl methacrylate (18) gave 2-acryloyloxyethyl 2,3,6-trichlorophenylacetate (19), 4-acryloyloxybutyl 2,3,6-trichloro-

phenylacetate (20), 4-vinyloxybutyl 2,3,6-trichlorophenylacetate (21), and 2-methacryloyloxyethyl 2,3,6-trichlorophenylacetate (22), respectively. The purification of the monomers was difficult due to their tendency to undergo spontaneous polymerization.

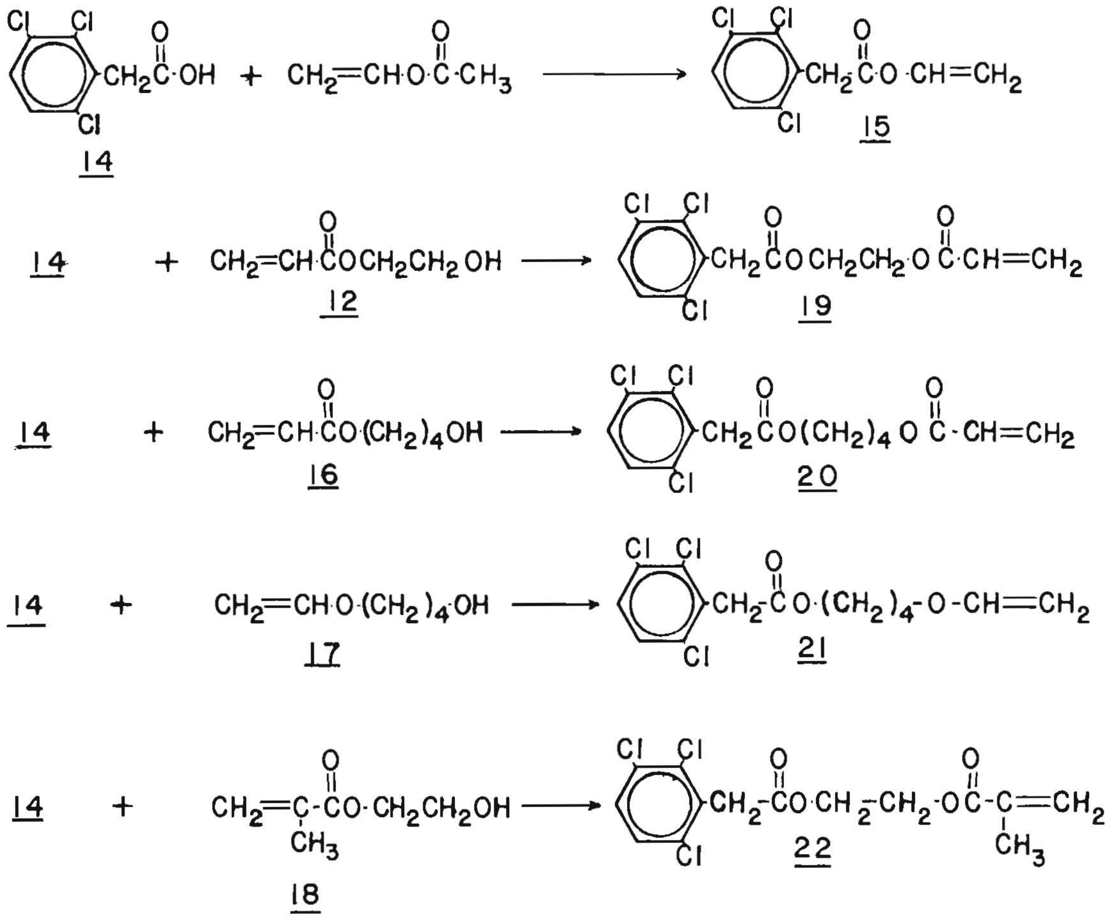


Figure 3. Synthesis of vinyl monomers containing fenac.

Polymerization of vinyl monomers containing fenac

7. The polymerization of vinyl 2,3,6-trichlorophenylacetate (14) was carried out by a bulk-free-radical technique (Figure 4). Polymer 23 is soluble in chlorinated hydrocarbon solvents and has an inherent

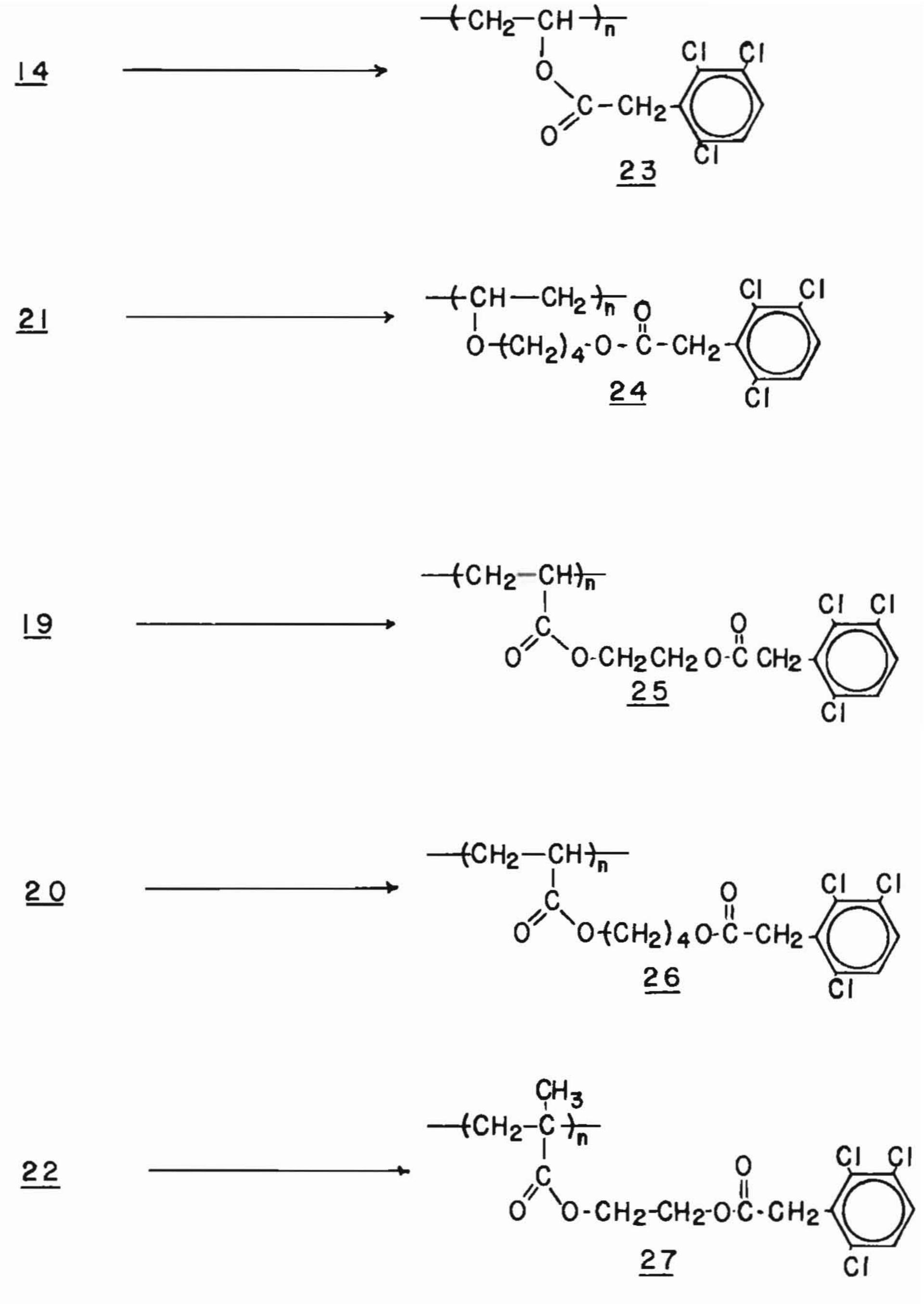


Figure 4. Polymerization of vinyl monomers containing fenac.

viscosity of 0.21.

8. The polymerization of 4-vinyloxybutyl 2,3,6-trichlorophenylacetate (21) was attempted by both solution- and bulk-free-radical techniques. No polymer, however, could be isolated from the solution polymerizations. The bulk polymerizations afforded very low yields (<5%) of polymer 24.

9. The polymerization of 2-acryloyloxyethyl 2,3,6-trichlorophenylacetate (19) was also carried out by bulk- and solution-free-radical methods. In this case, the bulk polymerizations resulted in chloroform-insoluble, crosslinked gels. The solution polymerizations also yielded a large amount of crosslinked material and a very low yield (<8%) of soluble polymer.

10. The bulk polymerization of 4-acryloyloxybutyl 2,3,6-trichlorophenylacetate (20) afforded a 52% yield of the gummy polymer 26. The white polymer has an inherent viscosity of 0.35.

11. The polymerization of 2-methacryloyloxyethyl 2,3,6-trichlorophenylacetate (22) was also carried out by a bulk-free-radical technique. However, the polymerization gave a very low yield (<10%) of polymer 27. A summary of the polymerization studies is given in Table 1.

Hydrolysis of polymers containing 2,4-D at pH 7

12. Our study of the hydrolysis of poly(vinyl 2,4-dichlorophenoxyacetate) (5a) poly(2-acryloyloxyethyl 2,4-dichlorophenoxyacetate) (6a), an 87:13 copolymer of 2-acryloyloxyethyl 2,4-dichlorophenoxyace-

Table 1. Polymerization Conditions for Vinyl Monomers Containing Fenac

Monomer	Method	Reaction Temp. (°C)	Reaction Time (hr)	[Monomer][b]	[AIBN][c]	Results
21	Solution[a]	80°	1.5	25%	0.025%	No polymer formed
21	Solution	80°	3.0	25%	0.025%	No polymer formed
21	Bulk	80°	2.0	---	0.1%	<10% soluble polymer
19	Bulk	75°	3.0	---	0.1%	Crosslinked gel
19	Bulk	75°	1.0	---	0.1%	Crosslinked gel
19	Solution	75°	0.08	25%	0.025%	<8% soluble polymer
20	Bulk	75°	2.0	---	0.1%	52% yield polymer
22	Bulk	75°	0.16	---	0.1%	<10% soluble polymer

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[a] Benzene solvent. [b] Weight-to-volume % where applicable. [c] Azobisisobutyronitrile; concentration weight-to-volume % for solution method and weight-to-weight % for bulk method.

tate and trimethylamine methacrylimide, poly(1-methyl-2-acryloyloxyethyl 2,4-dichlorophenoxyacetate), and poly(4-acryloyloxybutyl 2,4-dichlorophenoxyacetate) (8a), which was initiated under Contract DACW73-74-C-0001, was completed. The study was carried out with polymer samples that were extracted with ethanol to remove unreacted monomer and then ground and sieved to a particle size of 125-400 μ. One-gram replicates were immersed in 300 ml of distilled water (pH 7.0) at 30°C, and the amount of herbicide released from each was determined periodically by spectrophotometric analysis. The amounts shown in Figure 5 are the averages of three replicates. The study was continued for 340 days at which time the copolymer samples had released an average of 23 mg of 2,4-D. The homopolymers, however, failed to undergo hydrolysis. These results indicate that in order for a polymer containing pendent herbicide substituents to undergo hydrolysis at 30°C and pH 7, it must also contain pendent hydrophilic residues, such as aminimide groups.

Hydrolysis of polymers containing 2,4-D and fenac at pH 8

13. A study of the hydrolysis of poly(vinyl 2,3,6-trichlorophenylacetate) (23), poly(vinyl 2,4-dichlorophenoxyacetate) (5a), poly(2-acryloyloxyethyl 2,4-dichlorophenoxyacetate) (6a), and an 75:25 copolymer of 2-acryloyloxyethyl 2,4-dichlorophenoxyacetate and trimethylamine methacrylimide at pH 8.08 was carried out. The polymers were immersed in a buffer solution containing boric acid and sodium hydroxide at 30°C. The amount of herbicide released was determined periodic-

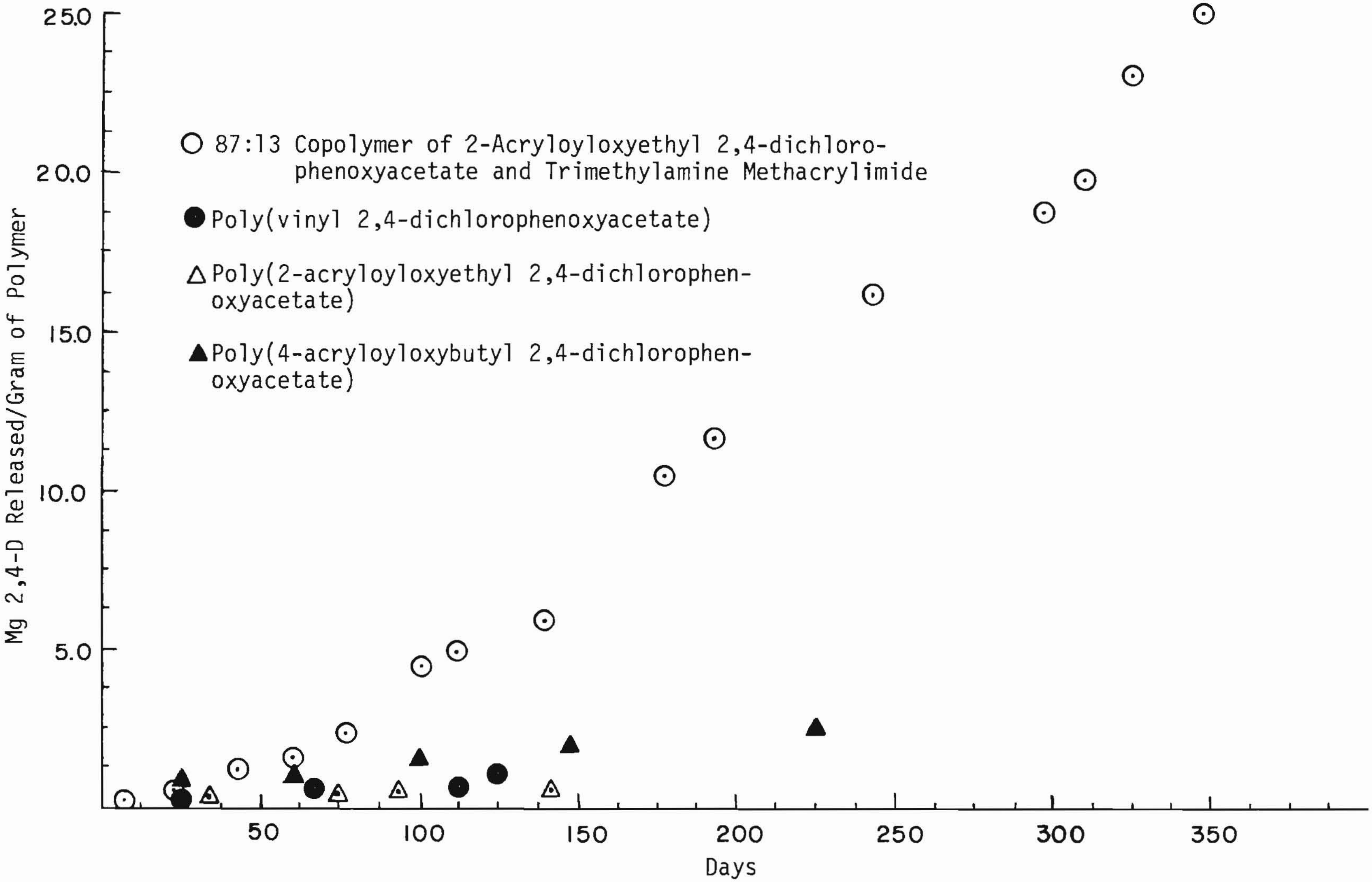

Figure 5. Hydrolysis of polymers containing 2,4-D at pH 7

ally by spectrophotometric analysis. The data shows that only the copolymer which contains hydrophilic aminimide residues undergoes significant hydrolysis under these conditions (Figure 6). In fact, even the rate of hydrolysis for this copolymer is not significantly different than that observed at pH 7.

Copolymerization studies

14. Since the initial release rate studies indicated that in order for the polymers containing herbicides to undergo hydrolysis they must also contain hydrophilic substituents, a detailed study of the copolymerization of the previously prepared monomers was carried out (Figure 7, Tables 2,3). The hydrophilic comonomers used were acrylic acid, methacrylic acid, N-vinyl-2-pyrrolidone, and trimethylamine methacrylimide.

15. The copolymerization of vinyl 2,4-dichlorophenoxyacetate (1a) with acrylic acid (13) using a mole ratio of 1a:13 of 80:20 was carried out by both solution- and bulk-free-radical techniques. The solution copolymerizations resulted in crosslinked, insoluble gels. The bulk-free-radical method afforded crosslinked polymer and a low yield (<10%) of chloroform-soluble polymer (Table 2).

16. The solution-free radical copolymerization of 2-acryloyloxyethyl 2,4-dichlorophenoxyacetate (2a) with 13 using a mole ratio of 2a:13 of 80:20 afforded the copolymer 29 in 63% yield. The polymer is soluble in chlorinated hydrocarbon solvents and has an inherent viscosity of 0.70. Infrared and elemental analyses indicate that the co-

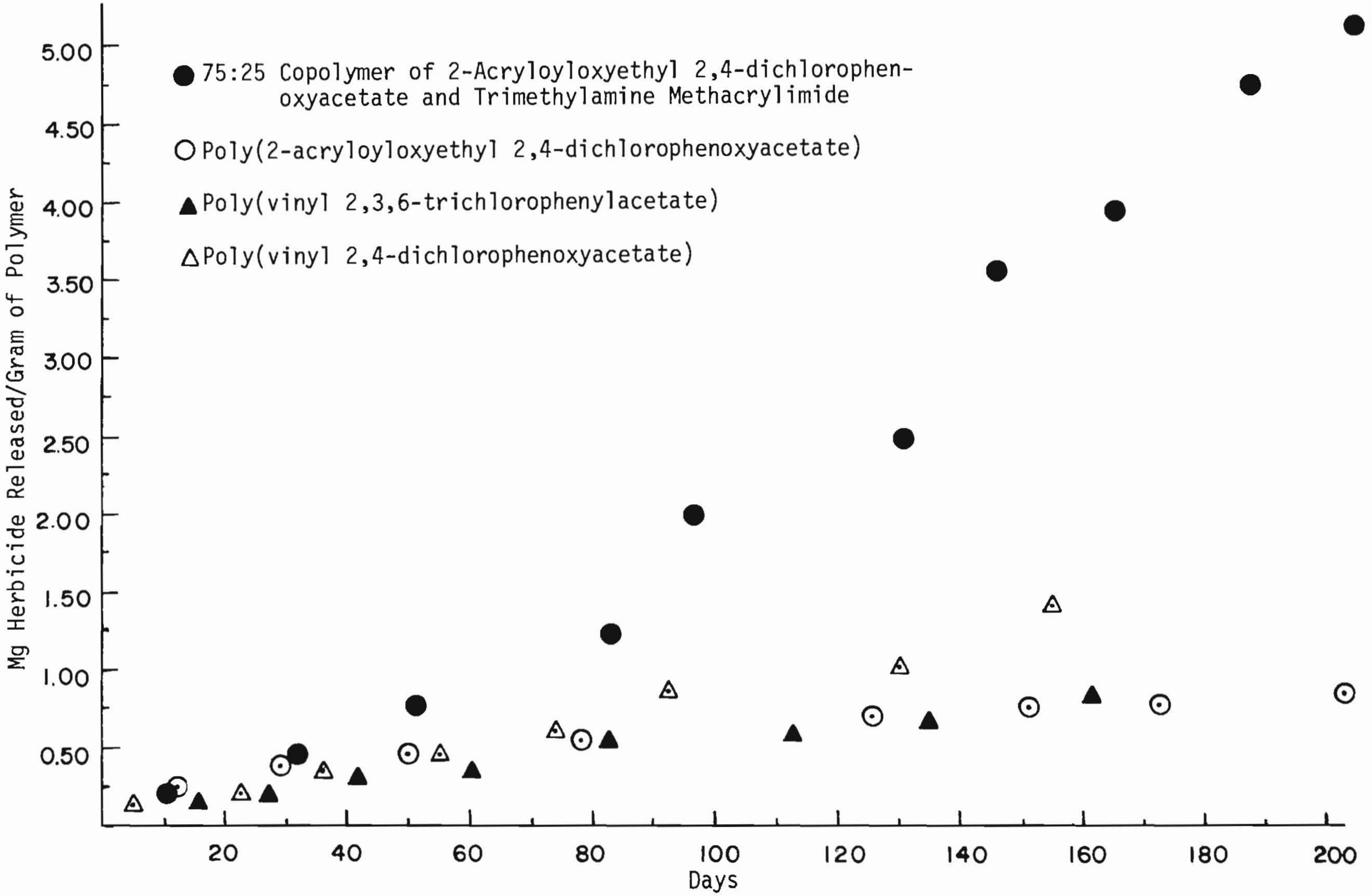

Figure 6. Hydrolysis of polymers containing 2,4-D and fenac at pH 8

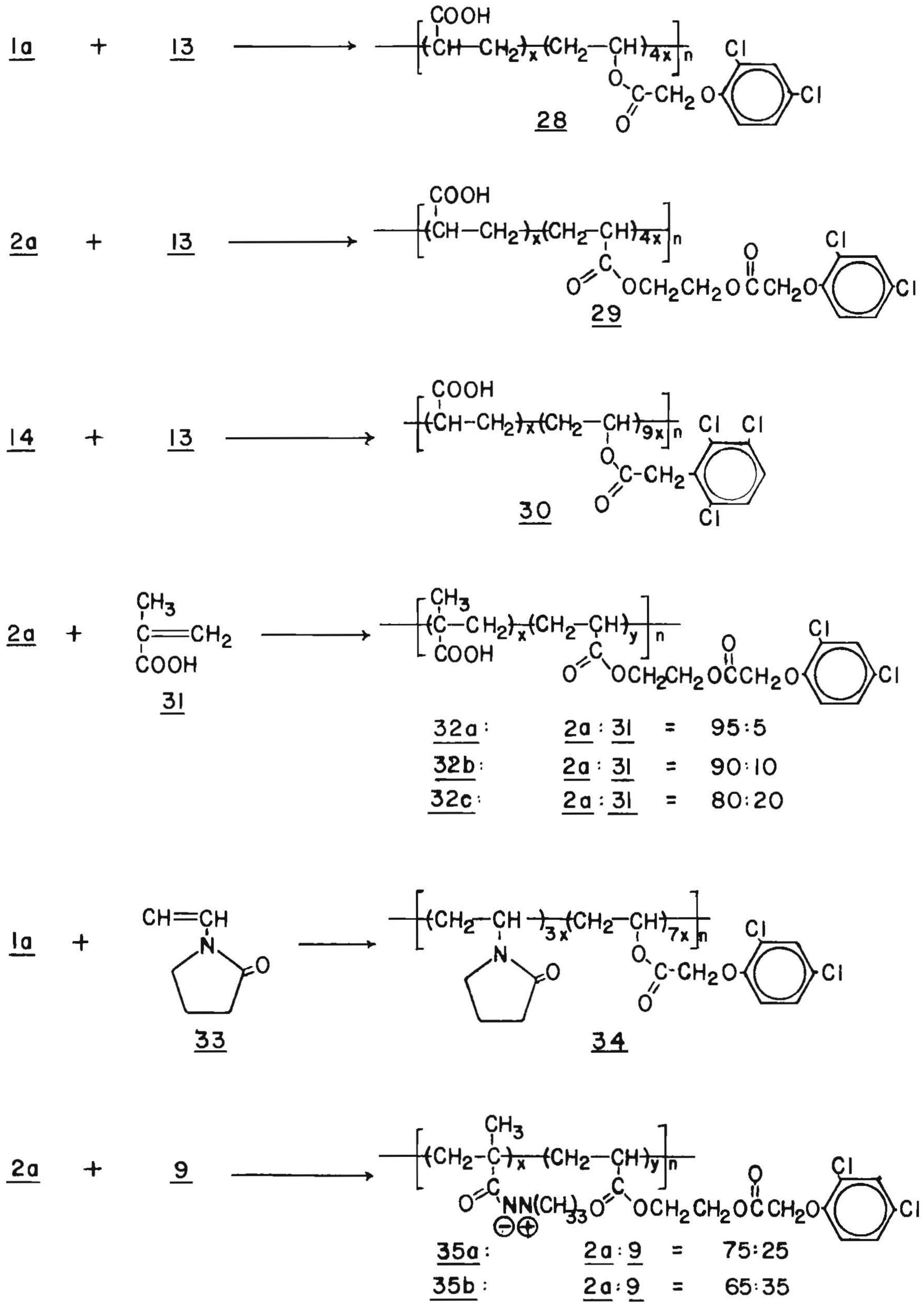

Figure 7. Copolymerization of vinyl monomers

Table 2. Summary of 2,4-Dichlorophenoxyacetate Copolymers: Methods and Results

Monomers (Mole Ratio In Feed)	Method (Solvent)[a]	Reaction Temp. (°C)	Reaction Time (hr)	[Monomer][b]	[AIBN][c]	Results
1a (80) + 13 (20)	Solution (Benzene)	75°	0.08	25%	0.025%	Crosslinked gel
2a (80) + 13 (20)	Solution (Benzene)	75°	0.25	25%	0.01%	63% Yield
2a (95) + 31 (5)	Solution (2-Butanone)	78°	3.0	25%	0.013%	Quant. Yield
2a (90) + 31 (10)	Solution (2-Butanone)	78°	3.0	25%	0.013%	88% Yield
2a (80) + 31 (20)	Solution (2-Butanone)	78°	3.0	25%	0.013%	81% Yield
1a (80) + 33 (20)	Solution (Benzene)	60°	38.0	25%	0.05%	46% Yield
2a (80) + 9 (20)	Bulk	72°	4.0	---	0.05%	49% Yield
2a (50) + 9 (50)	Bulk	76°	3.0	---	0.05%	60% Yield
1a (80) + 31 (20)	Solution (Benzene)	60°	1.0	25%	0.01%	Low Yield

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[a] Where applicable. [b] Weight-to-volume % where applicable. [c] Azobisisobutyronitrile; concentration weight-to-volume % for solution method and weight-to-weight % for bulk method.

Table 3. Physical and Spectral Data for 2,4-Dichlorophenoxyacetate Copolymers

Copolymer	ir (cm^{-1})	η (solvent)	Elemental Analysis[b] C	H	Cl	N
29	1730 (C=0) 2990 (COOH)	0.70 (TCE)[c]	48.98 48.68	3.88 3.95	21.03 21.03	
32a	1730 (C=0)	0.26 (MEK)[d]				
32b	1730 (C=0) 3000 (COOH)	0.14 (MEK)				
32c	1740 (C=0) 3020 (COOH)	0.38 (MEK)	49.36 49.42	3.99 4.11	20.81 20.81	
34	1750 (C=0)	0.20 (BzCl)[e]	51.23 50.87	4.05 4.14	24.06 24.04	2.04 2.12
35a	1750 (C=0) 1580 (N-H)	0.44 (BzCl)	49.95 49.82	4.40 4.59	19.99 19.45	1.97 2.54
35b	1750 (C=0) 1580 (N-H)	0.20 (BzCl)	50.89 50.48	4.97 4.98	17.91 17.75	3.81 3.62
1a + 31	1720 (C=0) 3000 (COOH)					

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[a] Inherent viscosity (dl/g) at 30° and 0.5 g/dl. [b] Calcd/Found. [c] TCE=*sym*-tetrachloroethane. [d] MEK=2-butanone. [e] BzCl=chlorobenzene.

polymer contains 20% acrylic acid.

17. Vinyl 2,3,6-trichlorophenylacetate (14) was copolymerized with 13 using a mole ratio of 14:13 of 90:10. The bulk-free-radical polymerizations gave a large amount of crosslinked material and a low yield (<10%) of chloroform-soluble polymer.

18. The solution-free-radical copolymerization of 2-acryloyloxyethyl 2,4-dichlorophenoxyacetate (2a) with methacrylic acid (31) was carried out using mole ratios of 2a:31 of 95:5, 90:10, and 80:20. The copolymers 32a, 32b, and 32c, which were obtained in greater than 80% yields, are soluble in chlorinated hydrocarbons, acetone, and 2-butanone. The copolymers have inherent viscosities of 0.26, 0.14, and 0.38 dl/g, respectively. Infrared and elemental analysis of 32c indicate that the copolymer contains 20% methacrylic acid. Elemental analyses of 32a and 32b were not obtained due to the fact that the calculated values are nearly identical to those expected for the homopolymer of 2a and, therefore, are of little analytical value.

19. The solution-free-radical copolymerization of vinyl 2,4-dichlorophenoxyacetate (1a) and N-vinyl-2-pyrrolidone (33) with a feed mole ratio of 1a:33 of 80:20 afforded the copolymer 34. The copolymer is soluble in chlorinated hydrocarbons and hot benzene and has an inherent viscosity of 0.20 dl/g. Infrared and elemental analyses indicate that the polymer contains 30% 1a.

20. Two bulk-free-radical copolymerizations of 2a and trimethylamine methacrylimide (9) using mole ratios of 2a:9 of 80:20 and 50:50

were carried out to afford the copolymers 35a and 35b in 49 and 60% yields, respectively. The copolymers are soluble in chlorinated hydrocarbons and acetone and have inherent viscosities of 0.44 and 0.20 dl/g, respectively. Infrared and elemental analyses indicate that 35a contains 25% 9 and 35b contains 35% 9.

Hydrolysis of copolymers at pH 8

21. A study of the release rates of the 95:5, 90:10, and 80:20 copolymers of 2-acryloyloxyethyl 2,4-dichlorophenoxyacetate and methacrylic acid (32a-c) at pH 8.08 was carried out. The polymers were immersed in a boric acid-sodium hydroxide buffer solution at 30°C, and the amount of herbicide released was determined periodically by spectrophotometric analysis. The copolymer 32c containing 20% methacrylic acid released 117 mg of 2,4-D in the first six days of the study. This rapid hydrolysis was accompanied by considerable swelling of the polymer particles which prevented further spectroscopic analysis of the sample solutions. The copolymer 32a containing 5% of the hydrophilic acid residue released 13.0 mg of herbicide in 78 days, while the copolymer 32b containing 10% acid released 28.7 mg of 2,4-D in 76 days. These accelerated release rates are in sharp contrast to that of poly-(2-acryloyloxyethyl 2,4-dichlorophenoxyacetate) which released less than 0.9 mg of 2,4-D in 206 days under the same conditions (Figure 8).

22. A study of the release rates of the 70:30 copolymer of vinyl 2,4-dichlorophenoxyacetate and N-vinyl-2-pyrrolidone (34) at pH 8.08 was also carried out. The data shown in Figure 9 was obtained by

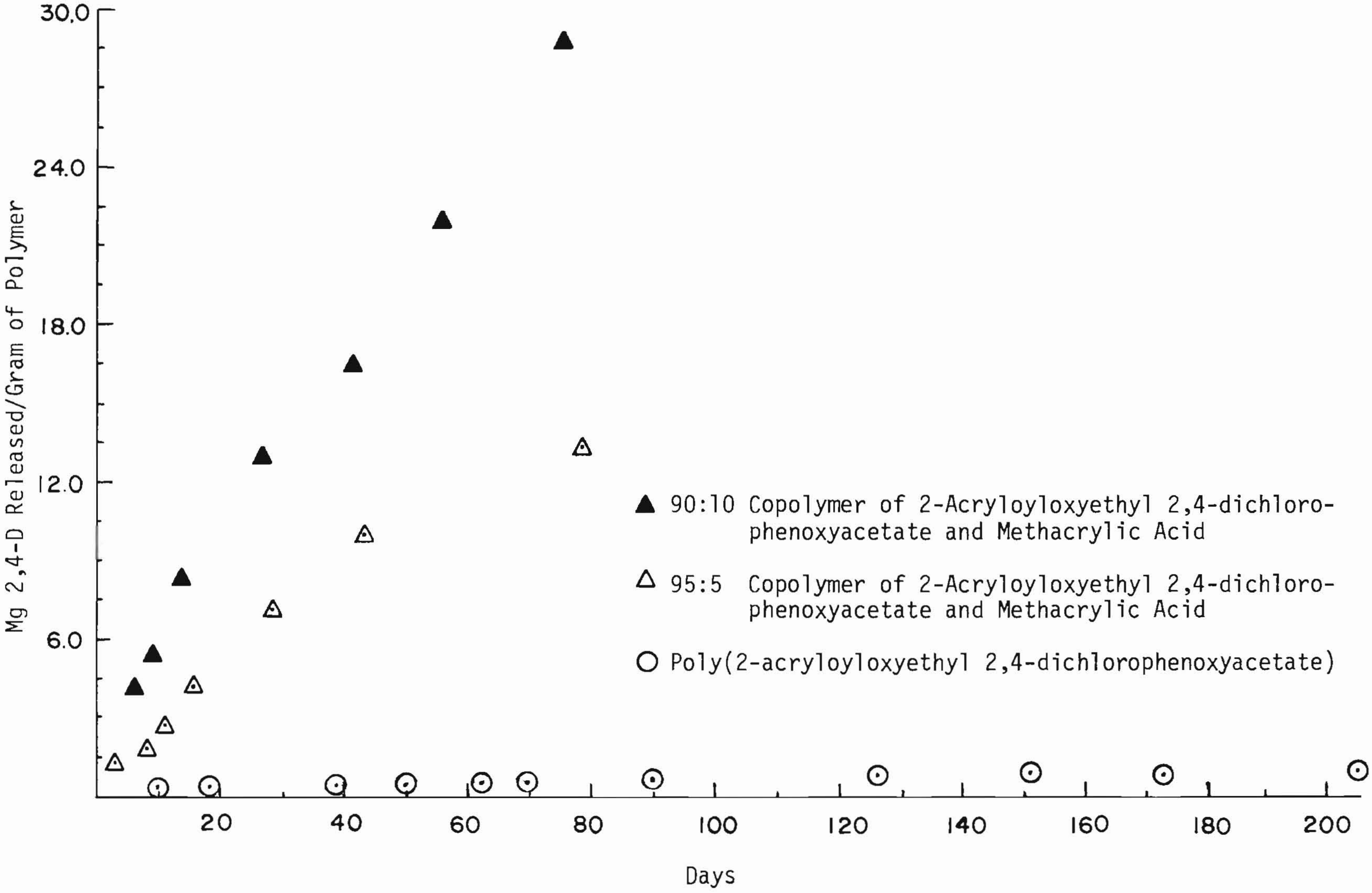

Figure 8. Hydrolysis of methacrylic acid copolymers

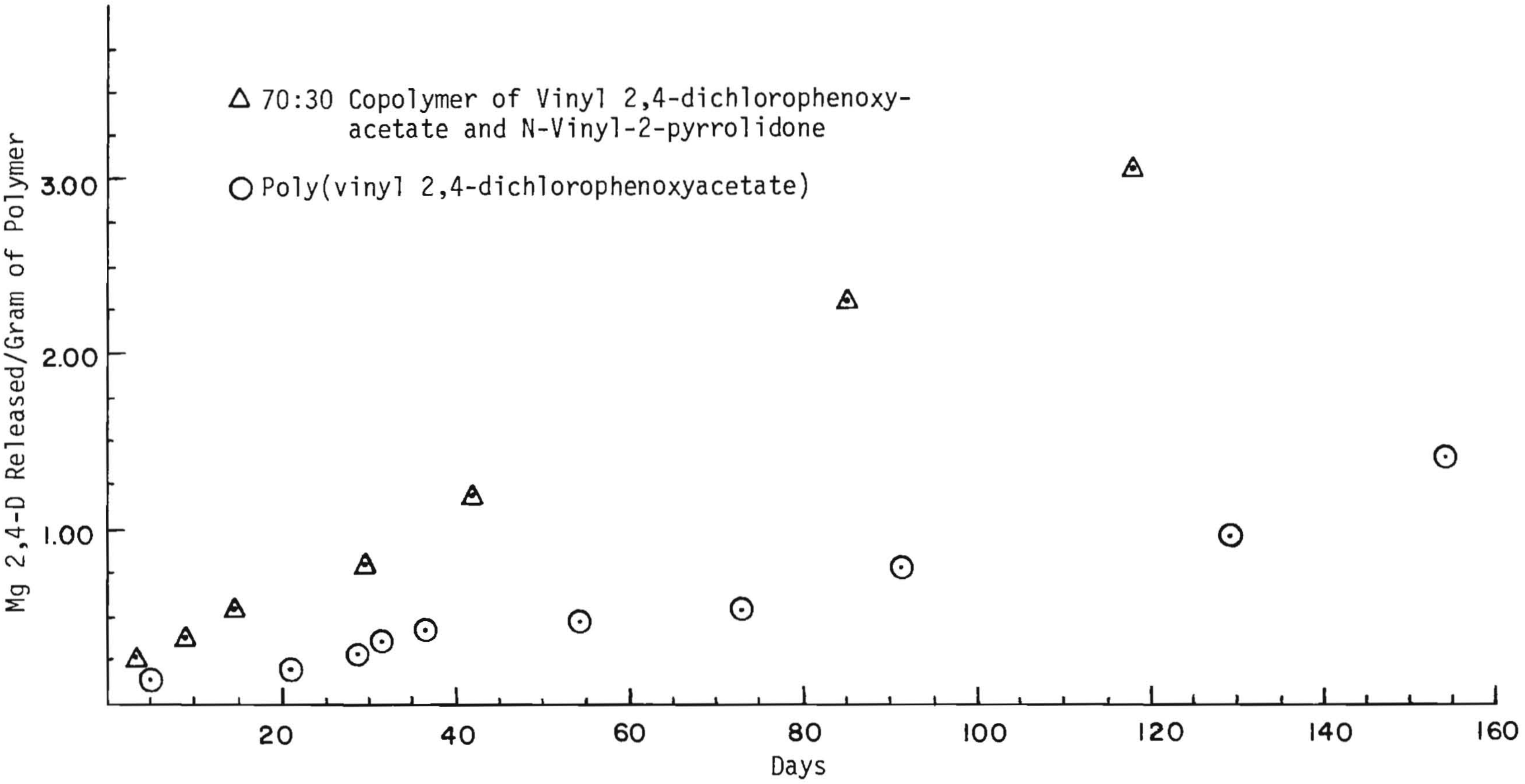

Figure 9. Hydrolysis of N-vinyl-2-pyrrolidone copolymers

employing the procedure described above. The copolymer released 3.3 mg of 2,4-D in 118 days. (The homopolymer, poly(vinyl 2,4-dichlorophenoxyacetate), released approximately 1.4 mg of herbicide in 154 days.)

23. The results of a study of the hydrolysis of the 75:25 and 65:35 copolymers of 2-acryloyloxyethyl 2,4-dichlorophenoxyacetate and trimethylamine methacrylimide at pH 8.08 are shown in Figure 10. The copolymer 35a containing 25% of the hydrophilic aminimide residue released 5.1 mg of herbicide in 207 days. The rate of hydrolysis of this copolymer is not significantly different than that observed for the copolymer containing 13% 9. However, the copolymer 35b containing 35% of the aminimide released 133.4 mg of 2,4-D in 123 days.

Preparation of samples for preliminary field evaluation

24. The syntheses of copolymers 32a, 32b, and 35b were scaled up to provide 10-g samples for evaluation in 8-ℓ containers. An additional 770 g of copolymer 32b were prepared for field testing in pools.

25. Fenac acid was also physically incorporated in a polyethylene matrix. The formulation, which contained 20% fenac acid, 8% ferrous oxide, and 72% high-density polyethylene, was prepared in the form of 0.5-g pellets. Approximately 900 g (1800 pellets) were sent along with the above samples to the University of Southwestern Louisiana for evaluation.

CONCLUSIONS AND RECOMMENDATIONS

26. Vinyl monomers containing fenac can be prepared in reasonable yields. These monomers can be polymerized by free-radical techniques

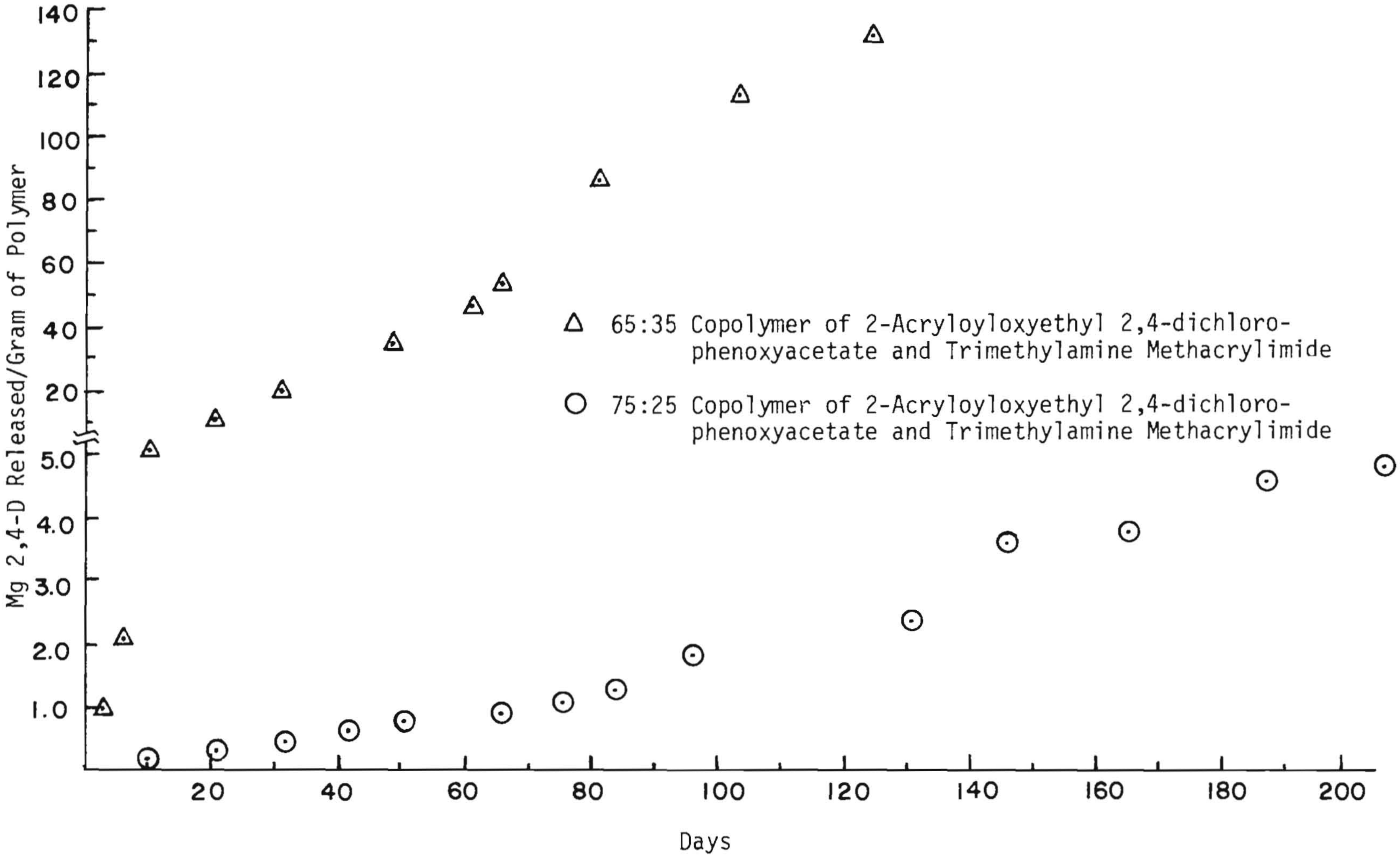

Figure 10. Hydrolysis of trimethylamine methacrylimide copolymers

to afford the corresponding polymers. The polymers' viscosities are not as high as those of polymers prepared from vinyl monomers containing 2,4-D.

27. Homopolymers containing 2,4-D or fenac as pendent substituents will not undergo hydrolysis in water with a pH of 7 or 8 at 30°C. Increasing the length of the pendent side chains does not result in the hydrolysis of the herbicide-polymer ester bonds.

28. Copolymers containing 2,4-D or fenac and hydrophilic residues will slowly hydrolyze in water at 30°C. Increasing the pH from 7 to 8 does not significantly enhance the rate of hydrolysis. The rate is dependent on the amount and type of the hydrophilic group used. Carboxylic acid groups serve as the most effective intramolecular catalyst for the hydrolysis.

29. Future research should be directed towards the development and evaluation of copolymers containing herbicides and hydrophilic residues, since they appear to have considerable potential as controlled-release agents. The results of this study indicate that copolymers can be prepared with release rates that vary from several weeks to several years.

EXPERIMENTAL

Instrumentation

30. Ultraviolet spectroscopic analyses were obtained with

a Cary Model 14 Recording Spectrophotometer. Viscosities were determined in a Cannon Number 75 viscometer. Nuclear magnetic resonance (nmr) spectra were recorded with a Varian HA-60 spectrometer. Infrared spectra were obtained on a Perkin-Elmer 457 Spectrophotometer. Elemental analyses were performed by Midwest Microlab, Indianapolis, Indiana.

Reagents

31. Methacrylic acid was obtained from Eastman Organic Chemicals. The aminimide comonomers were provided by Ashland Chemicals. Fenac and 2,4-D were provided by AmChem Products, Inc. N-Vinyl-2-pyrrolidone, acrylic acid, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 4-hydroxybutyl acrylate, and 4-hydroxybutyl vinyl ether were purchased from Polysciences, Inc. Vinyl acetate was obtained from Aldrich Chemicals. All the reagents were distilled or recrystallized immediately prior to use.

Vinyl 2,3,6-trichlorophenylacetate (15)

32. A mixture of 21.5 g (0.09 mol) of 2,3,6-trichlorophenylacetic acid, 0.4 g (0.0012 mol) of mercuric acetate and 62.0 g (65 ml, 0.72 mol) of vinyl acetate was stirred under nitrogen for 0.5 hr. Three drops (0.04 ml) of 100% sulfuric acid were added and the mixture was maintained at 95°C for 3 hr. The solution was cooled and 7.0 g of sodium acetate trihydrate was added. The solution was filtered and vacuum distilled to yield 14.5 g (69%) of a colorless liquid that solidified on cooling: nmr ($CDCl_3$) δ 4.10 (s,2, $-CH_2-$), 4.70 (m,2,

CH_2) and 7.25 ppm (m,3, -O-CH=, aromatic); ir (neat) 1760 (C=O) and 1650 cm^{-1} (-CH=CH_2).

<u>Anal</u>. Calcd for $C_{10}H_7Cl_3O_2$: C, 45.23; H, 2.66

Found: C, 45.43; H, 2.75

<u>General procedure for the preparation of vinyl monomers 19-22</u>

33. Equimolar portions of 2,3,6-trichlorophenylacetic acid, the appropriate alcohol, and dicyclohexylcarbodiimide were mixed in anhydrous ether. After stirring for 18 hr, the solution was filtered. The filtrate was washed with four portions of 2% acetic acid, four portions of water, four portions of 5% sodium bicarbonate, and finally with four portions of water. The ethereal layer was dried with sodium sulfate, filtered and evaporated. The residue was taken up in hexane and filtered to remove a small amount of dicyclohexylurea. The hexane was evaporated, and the residue was chromatographed on a 1 by 6-in. silica gel column with benzene as the eluent.

<u>2-Acryloyloxyethyl 2,3,6-trichlorophenylacetate (19)</u>

34. The benzene solution was evaporated to give a 40% yield of a pale yellow oil: nmr ($CDCl_3$) δ 4.00 (s,2, -CH_2-), 4.31 (s,4, -CH_2-CH_2-), 5.80 (s,1, vinyl), 6.10 (s,1, vinyl), 6.25 (s,1, vinyl), and 7.22 ppm (s,2, aromatic); ir (neat) 1730 (C=O) and 1630 cm^{-1} (-CH=CH_2).

<u>Anal</u>. Calcd for $C_{13}H_{11}Cl_3O_4$: C, 46.25; H, 3.28; Cl, 31.51

Found: C, 46.04; H, 3.41; Cl, 31.84

<u>4-Acryloyloxybutyl 2,3,6-trichlorophenylacetate (20)</u>

35. The benzene solution was evaporated under vacuum to give a 44%

yield of a pale yellow oil: nmr ($CDCl_3$) δ 1.67 (m,4,- CH_2-CH_2-), 4.00 (s,2, $-CH_2-\overset{O}{C}-$), 4.13 (m,4, -O-CH_2-), 5.95 (m,3, -CH=CH_2), and 7.22 ppm (m,2, aromatic); ir (neat) 1735 (C=O) and 1635 cm^{-1} (-CH=CH_2).

<u>Anal</u>. Calcd for $C_{15}H_{15}Cl_3O_4$: C, 49.27; H, 4.14

Found: C, 49.04; H, 4.34

<u>4-Vinyloxybutyl 2,3,6-trichlorophenylacetate (21)</u>

36. The benzene solution was evaporated under vacuum to give a 59% yield of a yellow oil: nmr ($CDCl_3$) δ 1.68 (m,4, -CH_2CH_2-), 3.95 (m,6, -CH_2-O- and =CH_2), 4.00 (s,2, $-CH_2-\overset{O}{\overset{\parallel}{C}}-$), 6.40 (m,1, -O-CH=), and 7.28 ppm (m,2, aromatic); ir (neat) 1740 (C=O) and 1615 cm^{-1} (-CH=CH_2).

<u>Anal</u>. Calcd for $C_{14}H_{15}Cl_3O_3$: C, 49.80; H, 4.48

Found: C, 50.08; H, 4.72

<u>2-Methacryloyloxyethyl 2,3,6-trichlorophenylacetate (22)</u>

37. The benzene solution was evaporated under vacuum to give a 50% yield of a viscous yellow oil: nmr ($CDCl_3$) δ 1.88 (s,3, -CH_3), 4.01 (s,2, -CH_2-), 4.30 (s,4, -CH_2-CH_2-), 5.45 (m,1, vinyl), 6.00 (s,1, vinyl), and 7.25 ppm (m,2, aromatic); ir (neat) 1740 (C=O) and 1615 cm^{-1} (-CH=CH_2).

<u>Anal</u>. Calcd for $C_{14}H_{13}O_4Cl_3$: C, 47.82; H, 3.72; Cl, 30.25

Found: C, 47.96; H, 3.93; Cl, 30.48

<u>General bulk polymerization procedure</u>

38. The monomer(s) and azobisisobutyronitrile (AIBN) were thoroughly mixed and slowly heated to the desired temperature. After heating for the specified time, the reaction mixture was cooled to

afford a polymeric residue. The product was dissolved in chloroform and then precipitated in hexane. The polymer was collected by filtration, extracted with ether or ethanol overnight, and dried under vacuum at 64°C for 24 hr.

General solution polymerization procedure

39. The monomer(s), AIBN, and benzene (4 ml/g of monomer) were stirred and slowly heated to the reaction temperature. After heating for the specified time, the viscous solution was diluted with chloroform and poured into hexane. The polymer that precipitated was collected by filtration and extracted with ether or ethanol overnight. The polymer was then dried under vacuum at 64°C for 24 hr.

Preparation of pH 8 buffer

40. A solution of 23.19 g (0.375 mol) boric acid in approximately 800 ml of glass-distilled water was titrated with a 0.7N aqueous solution of sodium hydroxide to a pH of 8.08. The mixture was then diluted with water to a volume of 1.00 ℓ.

General procedure for hydrolysis studies

41. Powdered samples of the polymers were sieved to a particle size of 420 to 125 μ. Three 1.0-g replicates of each polymer were placed in individual 500-ml flasks containing 300 ml of the pH 8.08 buffer and a sintered glass sampling tube. The amount of herbicide released was determined periodically by withdrawing a sample and subjecting it to ultraviolet spectroscopic analysis at 198 nm for 2,4-D and 203 nm for fenac.

Preparation of polyethylene pellets containing fenac

42. Fenac was thoroughly ground and sieved to a particle size of 420-125 μ. Powdered high-density polyethylene (72%) and ferrous oxide (8%) were then mixed with the fenac (20%). Pellets 1.6 cm in diameter were made by compressing 0.500 g of the uniform mixture in a brass die at 2000 psi for 6 min at 135°C.

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References: p. 35-36.

1. Herbicides. 2. Hydrolysis. 3. Polymers. I. U. S. Army. Corps of Engineers. II. Wright State University. (Series: U. S. Waterways Experiment Station, Vicksburg, Miss. Contract report A-77-1)
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