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POLYMERS CONTAINING PENDENT INSECTICIDES

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INTRODUCTION

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The Fire Ant Problem

The fire ants Solenopsis invicta and Solenopsis richteri, were accidentally imported into the United States from South America through the port of Mobile, Alabama. Present evidence indicates that richteri was introduced about 1918, and its spread has been only moderately successful during the succeeding 62 years. At the present time, richteri infestation is limited to a small region of northern Alabama and Mississippi. In contrast to this, Solenopsis invicta has been extremely successful at establishing itself in the southeastern United States. Since its introduction in the mid 1940s, this species has expanded its range to nine southern states encompassing more than 50-million hectares of land. This phenomenal rate of spread is accounted for by two factors. The natural spread of the ants via mating flights is ideally suited to avoid inhibition by natural and man-made barriers. Mating takes place in swarms which have a minimum altitude of 500 feet above the ground. Following mating, a queen may alight miles from her home nest. A second major factor in the rapid spread of the ants has been the influence of transport by man. Commercial movements of nursery stock and sod during the 1940s and 1950s, prior

to the institution of quarantine procedures, greatly aided the introduction of the ants into uninfested regions.

The spread of the fire ant has been slowed somewhat by the natural limitations of its present environment. In those regions where the ants have met desert conditions or cold winters, extreme environmental conditions have clearly slowed their advance. However, considering how well the South American ant has adapted to the southern United States and the lack of competition from indigenous species, the ants may well overcome these limitations. Theoretical models derived from the present rate of spread of the ants across Texas have predicted that the ant could reach California in as little as six years.⁶ This model did not consider the potential for accidental introduction of the ant into the Pacific coast states.

At present, the northern movement of the ants has been mostly along the temperate regions of the Atlantic coast in the Carolinas, and no clear evidence of adaptations to colder climates has been presented. Failure to hibernate results in significant depletion of ant numbers during the winter months, and a cyclic pattern of expansion and contraction of ant numbers is observed even in Florida. This pattern correlates with the severity of the winter conditions in that state.⁷ However, modifying its behavior or mound structure or taking advantage of nesting sites near or within man-made structures could conceivably allow the ant to expand into colder regions.

Attempts to blunt the invasion of fire ants have taken two forms: eradication programs designed to eliminate the pest in infested areas and quarantine regulations directed at limiting the spread of fire ants beyond their present habitat. The eradication program has been fraught with problems since its inception. The primary obstacle to this effort has been in identifying an environmentally acceptable approach to fire ant control. At times this work has been near abandonment.⁸ Early approaches relied on heptachlor and dieldrin as the primary toxicants, but with the discovery of kepone and later mirex^{9,10} in the late 1950s, the eradication effort appeared promising. Several effective formulations employing mirex were tested.¹⁰⁻²⁰ Many of these employed a soybean oil bait to encourage ingestion by the ant.~~11-19,21~~ Ultimately, however, mirex and its analogs were found to be environmentally unacceptable.²²⁻³² The registration of mirex was revoked in 1971 with limited exceptions.³³ Since this time, the fire ant eradication efforts have been mainly limited to identifying and testing compounds to replace mirex in the program. To date, the USDA Gainesville laboratory (USDA-SEAAR) has assayed over 5000 formulations for potential use in the eradication effort with limited success. Only a few agents have shown acceptability in the laboratory tests, but with the exception of several now being field tested³⁴ all have been unacceptable for use in large-scale control programs.~~35-39~~

The fire ant quarantine was instituted in 1956. It basically consists of controls imposed on suppliers who ship soil, agricultural products, nursery stock, or sod from areas designated as infested to other regions of the country. Like the eradication program, the quarantine has experienced difficulty in the availability of effective toxicants. Dieldrin and aldrin have been used in the past as agents for this purpose. In recent years the quarantine has relied on the chlorinated cyclodienes, chlordane and heptachlor, with adequate success. However, since 1975, the EPA has sought to restrict the use of these compounds. The use of chlordane and heptachlor was terminated in December of 1979.

The efforts to control the spread of the fire ant arise mainly as a consequence of two considerations: the economic effect of fire ant infestations in crop land and the health hazard posed by the presence of the ant in populated regions.

Agricultural damage arising from fire ant infestation is difficult to assess due to the diverse nature of the losses. Fire ants are reported to feed on seedlings, germinating seed, and flowers, and they sting livestock and agricultural personnel. Particularly vulnerable to fire ant predation are ground-nesting birds, newborn livestock, and beneficial arthropods. Damage to farm machinery is encountered when the equipment strikes the mounds. This results in frequent cleaning and repairs as well as increasing the likelihood that workers will be stung while performing these operations. A significant loss of productivity of hay and grazing land is associated with heavy infestations. Farm laborers often demand higher wages to work heavily infested fields, and in some cases they refuse to enter the fields at all. Numerous other accounts of damage attributable to fire ants have been recorded without adequate substantiation.

There have been instances reported in which fire ants are reputed to have beneficial effects such as their predation upon sugar cane borers, boll weevils, and lone star ticks. It is difficult to determine if the fire ants are filling a role that had not been performed by other predatory species prior to the introduction of the fire ant. Most of the data concern pest populations in infested areas with or without the application of pesticides employed to combat the fire ant. It is to be expected that many beneficial predators were already displaced from these regions by the fire ant. There is substantial evidence that this type of displacement occurs when fire ants enter a new region. While it is difficult to place a dollar figure on fire ant damage in the agricultural arena, at least one survey (commissioned by Allied Chemical) placed that figure at \$48 million in 1972 and further estimated the net loss in land value at that time to be \$500 million.¹

The difficulties encountered in controlling the imported fire ant stem from the social characteristics of the species coupled with its exceptionally high rate of spread. The primary social characteristic which contributes to the difficulty of chemical control is the method of food distribution found in the colony. All food encountered by the foraging members of the colony is distributed to the other members by trophylaxis. The food is passed by regurgitation through a chain of intermediates to the queen and brood. Ants showing abnormal behavior patterns or signs of toxicity are effectively excluded from the chain. Since rapid-acting pesticides never reach the queen, they cannot effectively destroy the reproductive capacity of the nest. Other factors contributing to the difficulty of control are the following:

- The mode and frequency of infestation by mating flights.
- The rapid development of the colonies.
- The absence of effective competitors.
- The omnivorous nature of the species.
- The ability of a solitary queen to regenerate a complete colony within a single season.
- The high mobility of the colonies (making it possible to reestablish if their immediate environment becomes unsuitable).

The magnitude and economics of the eradication program prevent the delivery of toxicant to the nonforaging members of the colony by direct means. The use of toxic baits which are efficiently incorporated into the food chain of the colonies by the foraging workers is the method of choice. Many researchers have shown that a complex pattern of food distribution exists within the fire ant colony. ~~14, 19, 21, 34, 35~~ The exact pattern of distribution, however, may depend on the physical and chemical nature of the nutrient (carbohydrate, protein, lipid, etc). ~~14, 19, 21, 34, 35~~ Lipid-containing baits, especially soybean oil, have been found to be extremely effective in promoting the entrance of chemicals into the food chain. ~~14, 19, 21, 34, 35~~ This finding is limited, of course, to the case where the formulation is neither repulsive nor immediately toxic to the ants. At present, soybean oil toxicants are most efficiently employed when incorporated onto the surface of corn cob grits prior to dispersal. ~~14~~

In consideration of these findings, the requirements for an effective bait toxicant have been summarized as follows:

- (1) The toxicant must be compatible with soybean oil.

- (2) The toxicant must display delayed toxicity such that no more than 15% of ants ingesting this material are killed in the first 24 hours.
- (3) The toxicant must display this delayed toxicity over a 10- to 100-fold concentration range.
- (4) The toxicant must be environmentally acceptable.

While many toxicants are compatible with soybean oil, only mirex and its analogs have been shown to fulfill requirements two and three; however, these toxicants have been judged environmentally unsafe. This is not unexpected since requirements two and three are often incompatible with the present definition of environmental acceptability. One common mechanism by which a toxicant can show delayed action is by requiring a slow metabolic alternation to yield the active agent as is the case with mirex. Such compounds are usually slowly degraded, if at all, in the environment, and they accumulate in nontarget organisms. This accumulation presents a potential environmental hazard.

At present, few compounds available have the potential for meeting the stringent requirements listed above. The application of controlled-release technology may offer one means of meeting this goal because this technique offers a means of obtaining delayed toxicity from environmentally acceptable toxicants. At least two controlled-release approaches are applicable to this problem: the encapsulation of toxicant within rate-controlling excipients and chemical attachment of toxicants to polymers by hydrolytically reversible linkages. While both approaches will yield toxicants with delayed action, preliminary findings with microcapsules suggested the polymeric approach to be more promising.

Previous Controlled-Release Approaches for Control of the Fire Ant

Controlled release and particularly microencapsulation are not new to the fire ant problem. In 1971 Markins and Hill⁵⁶⁻⁵⁸ reported the use of microencapsulated mirex-oil baits. The objective of that work was not to obtain delayed action, since this was inherent with mirex baits, but to extend the field life of the toxicant and limit its dissipation into the environment. The microcapsules were not designed to be ingested by the ants but rather to be carried to the nest and broken open. These and subsequent studies⁵⁹⁻⁶³ showed that the microcapsules prepared with gelatin and "plastic" wall materials did achieve the desired effect.

The use of microencapsulation to delay toxicity became more attractive when mirex was withdrawn from the eradication program. At that time the evidence suggested that microcapsules less than 10 microns in diameter could be ingested by the fire ants and regurgitated during trophylaxis. The slow release of toxicant from

the microcapsules was then expected to yield delayed toxicity. Several formulations based on this approach were tested by the USDA.

In general, all microcapsule preparations tested by the USDA have failed to delay the toxic effects of their incorporated toxicants. A further complication has arisen in subsequent studies of the feeding habits of the fire ant. ⁶² Researchers of the USDA have observed that while the ants are capable of ingesting 5-micron particles, they have been observed to separate dye-labeled microcapsules from the bait medium and direct them into the buccal pocket. The contents of this pocket are later discarded with the possible result that the microcapsules would not enter the food chain. The reason for this behavior may be obligatory for particles in the micron size range or may be determined either by the chemical nature of the wall material or by detection of the presence of toxicant through a taste mechanism. Contents of the buccal pocket have been observed to be discharged onto larvae with the ultimate consequence that they enter the food chain by this route. This has been shown to be the case with large dry protein particles. ⁶³

Thus, a microcapsule bait system cannot be completely ruled out; however, the likelihood of success remains in question. Such a system could not be adequately tested by the simple cup screening procedure, and whole-colony tests would be required. The application of microcapsules to a bait toxicant seem inappropriate until further basic studies have been completed.

Another approach, structure modification, has been studied with regard to its application to toxicity delay for fire ant control. This technique is not fully controlled release and is best described as controlled activation. Toxicants are chemically modified to yield nontoxic products which are returned to their active state by digestive or metabolic processes. While these compounds are not stabilized to environmental degradation, they can display delayed toxicity since the time required to activate sufficient quantities of the protoxicant to yield a lethal dose may be several days. The majority of the work in this area has been performed by USDA researchers ⁶⁴ employing esters of either trichlorfon (Dylox) or the highly toxic monofluorinated two-carbon acids and alcohols. Some success has been obtained with the monofluorinated esters, but the trichlorfon esters show little toxicity at low concentration and insufficient delay at high concentration. The toxicity observed with high concentrations of trichlorfon esters is probably a property of the protoxicant form since no delay is observed; thus, the active concentration range of these compounds will be very small. The monofluoroesters are probably too toxic for general application.

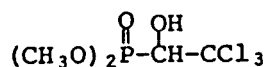
POLYMERS CONTAINING PENDENT INSECTICIDES

Polymeric toxicants are a combination of controlled release and the protoxicant approach. The significant difference is that the high-molecular-weight toxicant species cannot pass into the metabolic machinery due to the inability of the target insect to transport such materials across biological membranes. Only after the toxicant is released from the polymer does the compound display toxicity. In addition to delaying the activity of the toxicant, other properties may be advantageously altered such as solubility and taste. A proper choice of the polymer backbone can affect the solubility of the toxicant in a bait medium, and a high-molecular-weight polymeric form may be expected to elicit a diminished gustatory response.

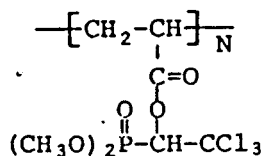
Unlike microencapsulated toxicants, polymeric insecticides would not be expected to show greatly enhanced stability to environmental conditions since the pendent toxicants are still exposed to chemical and photolytic degradation. Another advantage gained in addition to those cited above is the reduced mobility of the high-molecular-weight formulation. This would diminish the extent to which the toxicant is leached out of the area of application into the surrounding environment.

POLYMERS WITH PENDENT TRICHLORFON

The pesticide trichlorfon (Dylox) has long been known to be toxic to fire ants. However, due to its rapid action it is not effective as an agent for control of the species. The structure of trichlorfon is shown below:



It is one of the few approved insecticides which exhibits a functional group useful in forming covalent linkages which are hydrolytically unstable. The hydroxyl group of trichlorfon is useful for the formation of ester linkages to polymer carriers. An example of this type of compound is shown below as the ester of trichlorfon with poly(acrylic acid).



The preparation of esters of trichlorfon was explored using most of the conventional methods for ester formation. Among these methods were reaction with acyl chlorides and anhydrides, and the use of acyl activators such as carbodiimides, carbonyldiimidazole, and *n*-hydroxysuccinimide. All methods explored were ineffective when considering the economic constraints of industrial-scale synthesis. The use of acylation catalysts such as *N,N*-dimethylamino-pyridine was also ineffective. With the exception of reaction with anhydrides of fluorinated acids, such as trifluoroacetic acid and perfluorosuccinic anhydride, no simple ester synthesis seemed feasible. The problem was the reduced reactivity of the secondary hydroxyl of the trichlorfon molecule. This group is hindered by the presence of the nearby trichloromethyl moiety and is apparently hydrogen bonded to the nearby phosphoryl oxygen. Further complicating the chemistry was the inherent instability of the compound itself. Under basic conditions or at temperatures exceeding 40°C, trichlorfon exhibits a high propensity to dehydrohalogenate and rearrange to yield a compound with much diminished toxicity which is incapable of ester formation. Thus, all attempts to improve the yields of various synthesis resulted in significant degradation of the pesticide.

Dr. Melvin Look of the USDA reported the synthesis of esters of trichlorfon with lauric acid.⁶⁰ The method employed was the dehydration of the free acid in the presence of trichlorfon chlorosulfonic acid. He reported that good yields could be obtained by heating the reactants at 40°C for one hour. We repeated his work with similar success.

We at first attempted to employ Look's procedure with various acrylic monomers but were unsuccessful due to apparent sulfonation of the double bond under the reaction conditions employed. We then turned to direct coupling of trichlorfon to preformed polymers with pendent acid functionality. Although most such polymers were insoluble in chloroform, several were found to dissolve when sufficient chlorosulfonic acid was present. Using this procedure, we successfully prepared the acrylic product mentioned previously in satisfactory yield. However, the polymeric toxicant displayed limited toxicity in tests with the fire ant and showed only limited (15%) substitution.

Several lines of evidence suggested that the limited toxicity was a reflection of the limited loading and a too-slow hydrolysis of the pesticide from the polymer backbone. It was proposed that both of these problems could be eliminated by the use of a spacer group between the pesticide and the polymer backbone. Such a polymer is shown schematically in Figure 1.

POLYMERIC TOXICANT

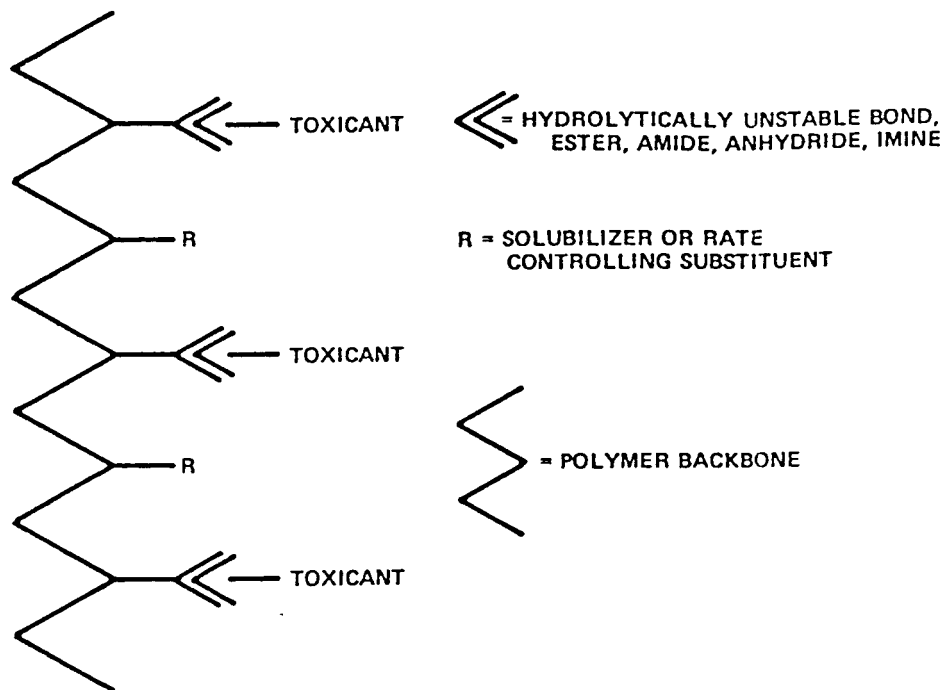


Figure 1. Polymeric pendent pesticide with a spacer group.

We chose to attempt the synthesis of several such polymers using a hydroxyl-containing polymer, a diacid spacer, and trichlorofon. The diacid spacers chosen were those shown below.

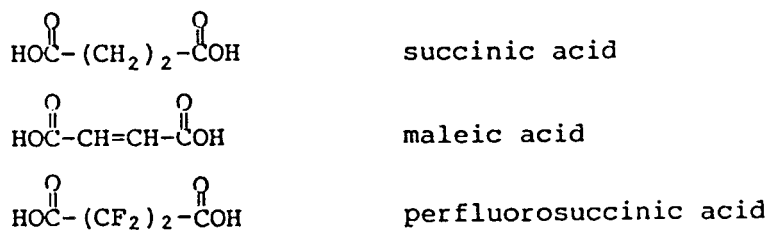


Figure 2 shows the various routes which can be employed to prepare a polymer of the type desired. The five possible routes begin with one of three starting points.

One synthesis begins with preparation of a polymer with pendent hydroxyl groups as shown at the far right of Figure 2. Onto this polymer one can attach the diacid spacer by treating the polymer with the cyclic anhydride of one of the diacids shown above.

when the remaining unsubstituted hydroxyls of the polymer formed esters with the pendent acid functions. Polymers produced by this approach were amorphous, insoluble masses.

The center scheme shown in Figure 2 may be completed by two alternative routes. The procedure begins with the coupling of the diacid spacer to the hydroxyl-containing pesticide. Preferably, this would be done by employing the cyclic anhydride. However, only perfluorosuccinic anhydride was reactive with trichlorfon. Monoester formation with straight-chain aliphatic diesters was attempted with adipic acid, but only the chlorosulfonic acid coupling was effective, and the cleanup and isolation proved economically unfeasible.

However, the highly reactive perfluorosuccinic acid ester of trichlorfon was carried to the second stage of this scheme. The right-hand branch of this scheme requires the coupling of the product monoester to a preformed hydroxyl-containing polymer. We studied dextran, poly(vinyl alcohol), and poly(2-hydroxyethyl methacrylate). Again, we employed the chlorosulfonic acid procedure for ester formation to avoid destruction of the trichlorfon. The result was unsatisfactory. The product polymers showed evidence by IR of ester formation but the presence of very little trichlorfon. Apparently, as soon as the pendent groups became coupled, a remaining free hydroxyl on the polymer would attack the labile trichlorfon-perfluorosuccinic acid linkage to release the trichlorfon and form an intramolecular crosslink.

The left-hand branch of this scheme, which employs the monomer instead of the preformed polymer, was attempted to avoid the problem just described. However, we were unable to implement the chlorosulfonic acid coupling procedure due to its propensity to sulfonate the acrylic moiety of the monomer. A carbodiimide coupling was partially successful, but we were unable to isolate a sufficient quantity of pure product to prepare polymer for testing. Use of an unpurified product yielded a polymer which apparently suffered the same limitations as the derivatives prepared with the preformed polymer.

The scheme at the left of Figure 2 was then studied. The acrylic monomer was prepared by reaction of the cyclic anhydrides of the three diacids employed, and the product was purified by recrystallization. The left-hand branch, wherein the monomer is reacted with trichlorfon prior to polymerization, was deemed unworkable since the chlorosulfonic acid coupling could not be employed in the presence of the acrylic function. No other coupling procedure seemed economically feasible. Thus, we were left with the right-hand branch of this scheme wherein the monomer is purified and polymerized, the polymer is purified, and this is followed by

coupling of the trichlorfon by chlorosulfonic acid dehydration. This procedure was successfully used in the preparation of the three desired polymers (Figure 3).

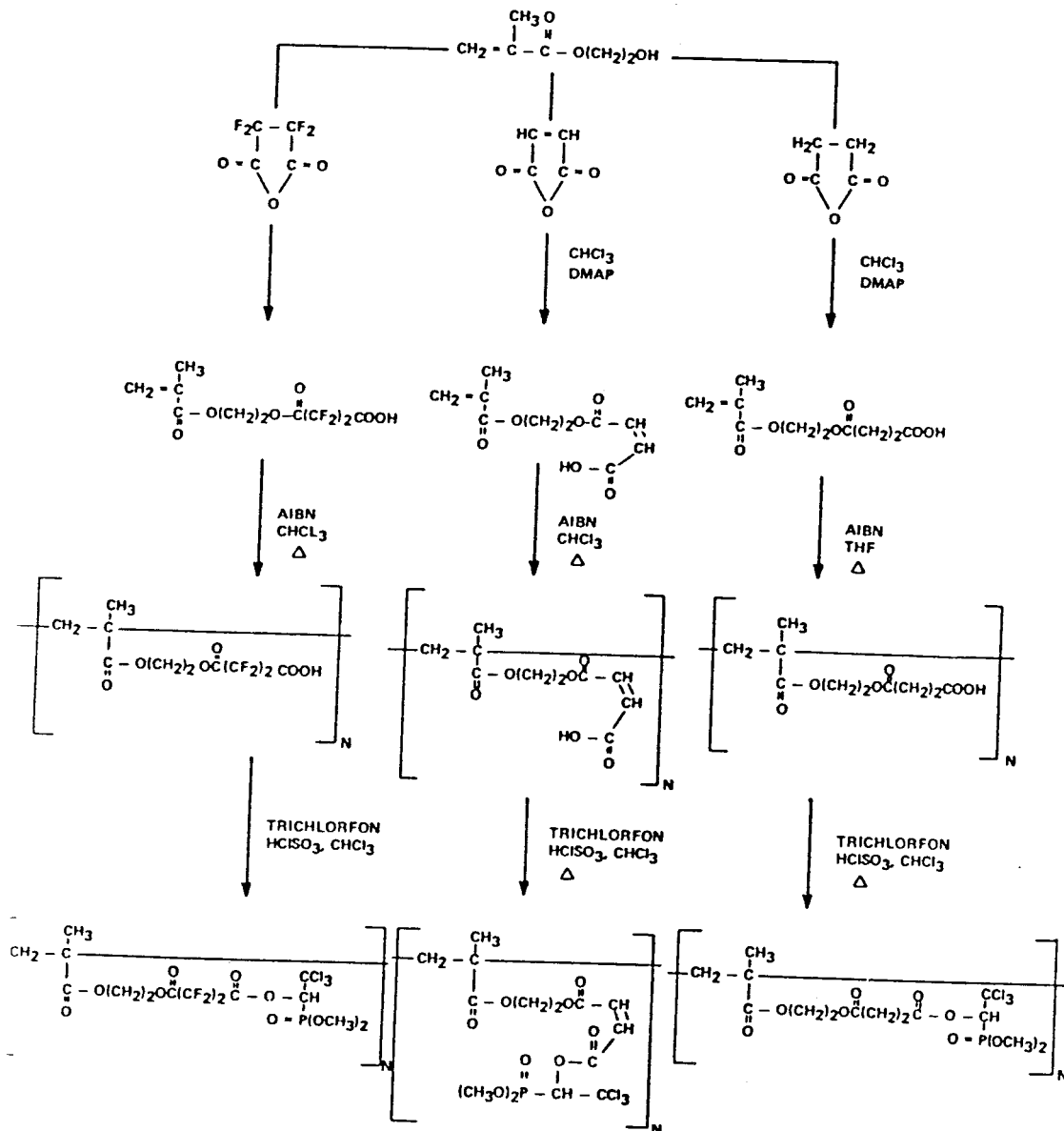


Figure 3. Synthesis of HEMA/trichlorfon polymers with diacid spacers.

PREPARATION AND TESTING OF POLYMERS WITH PENDENT TRICHLORFON

Figure 3 depicts the synthesis of the three polymers with diacid spacers. The hydroxyl-containing monomer employed was 2-hydroxyethyl methacrylate (HEMA) and was chosen more for convenience than for special properties desirable in the final product. This monomer, however, does offer the benefits of extended chain length and an additional ester linkage which would add slightly to the rate of release. The succinic and maleic condensation reactions were performed in chloroform and required dimethylaminopyridine as a catalyst. It was necessary to reflux the reaction mixture to achieve reaction, and we anticipated that the HEMA might polymerize during the refluxing step. We first employed a quinone inhibitor to avoid polymerization, but we later found it unnecessary and deleted it. An excess of HEMA was employed, and following the reaction, the unreacted monomer and solvent were removed under vacuum leaving a viscous oil which crystallized after several days at 4°C.

The reaction with perfluorosuccinic anhydride (PSA) was performed neat at room temperature without the need for a catalyst or radical scavenger. An excess of PSA was employed and was easily removed under vacuum.

Following the coupling of the diacid spacer to the monomer, each product was polymerized. Azobisisobutyronitrile (AIBN) was employed as a free-radical initiator in each case. The solvent for the PSA and maleic products was chloroform, and tetrahydrofuran was used with the succinic product. The choice of solvent was dictated by the desire that the polymer spontaneously separate from solution. Though the product polymers were insoluble in chloroform, adequate solubility was obtained when chlorosulfonic acid was added. A slight molar excess of trichlorfon was added to each reaction mixture, and the stirred solution was heated to 40°C. After 4 hours at 40°C, the polymers separated, and the solvent was decanted. The product polymers were dried under vacuum for 24 hours, and each appeared as a glassy amorphous film.

To compare the release rates of these polymeric pesticides with the ester prepared with poly(acrylic acid), we synthesized the PAA compound by direct reaction of poly(acrylic acid) (molecular weight 50,000) with trichlorfon using chlorosulfonic acid in chloroform. Again, the unsubstituted polymer was insoluble in chloroform, but it dissolved after the addition of chlorosulfonic acid. The product remained soluble. The chlorosulfonic acid was neutralized with sodium bicarbonate, and the sodium sulfate was removed by filtration. The polymer remained in solution in chloroform and was precipitated by the addition of diethyl ether. The polymer was reprecipitated three times from chloroform with ether.

Figure 4 shows schematically the method employed to determine the rate of hydrolysis of these polymers. Ten milliliters of distilled water was placed in a 12-ml, screw-cap tube. Each polymer (100 mg) was weighed under dry conditions into a small-diameter dialysis bag sealed at one end. Approximately 2 ml of water from the screw-cap tubes was transferred into the dialysis bag, and the other end was quickly sealed. After the bags were dropped into their respective tubes, the tubes were closed and placed in a device which rotated them end over end at 25°C.

At selected intervals a 5-ml sample was removed from each tube and stored for analysis. The 5-ml of water was replaced, and the rotation was continued. At the end of the experiment, the entire sample from the tube was removed. The volume external to the bag was separated and stored, and the contents of each bag were removed and stored for analysis. Prior to the analysis, the water was removed with heating under a gentle stream of nitrogen. The polymer carriers were still observable in the samples extracted from the dialysis bags. Control samples were also run including: free trichlorfon, each polymer treated with chlorosulfonic acid but without trichlorfon, and dialysis bags containing only water.

Analysis was by the modified Fisk-Subbarow colorimetric procedure.⁶² This analysis is sensitive to total phosphate rather than trichlorfon. While insufficient sample was available to employ chromatographic separation, all previously examined polymeric

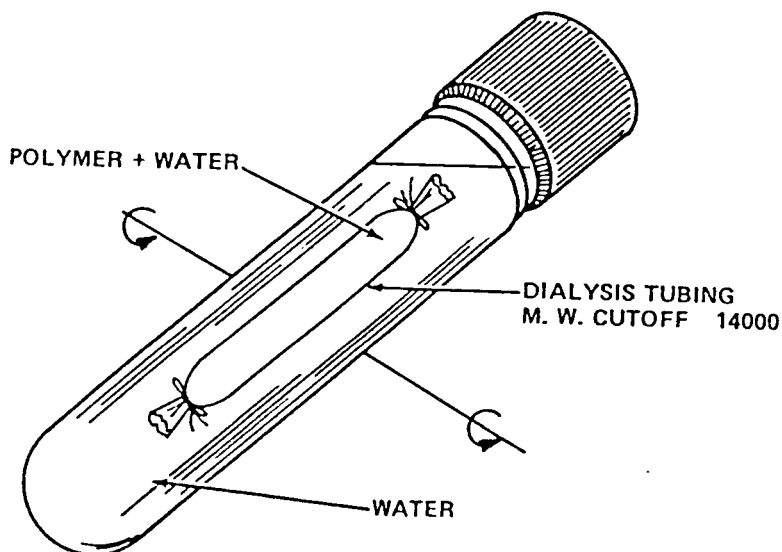


Figure 4. Apparatus for determining release rates for pendent-polymeric toxicants.

derivatives showed only trichlorfon as a discernable hydrolysis product by TLC. While it is not inconceivable that some of the product from the polymers with diacid spacers may have been the diacid monoester of trichlorfon, the spacers were originally chosen such that under conditions of the ant's digestive tract the monoesters would be autocatalytically cleaved to yield free trichlorfon.

RESULTS AND DISCUSSION

Figure 5 shows the early-time release of trichlorfon from the poly(acrylic acid) product. The half-life for release was approximately 14 hours. This result was substantially less than the half-life expected. This finding has forced us to re-examine our rationale for the lack of toxicity for the PAA polymer. It appears likely that the ants are able to rapidly detoxify or eliminate trichlorfon, and dosages administered slowly over a period as short as 14 hours cannot be considered cumulative. It would still be expected that faster releasing polymers would be more toxic, but half-lives shorter than 14 hours could never be expected to yield delayed toxicities of 24 hours or greater.

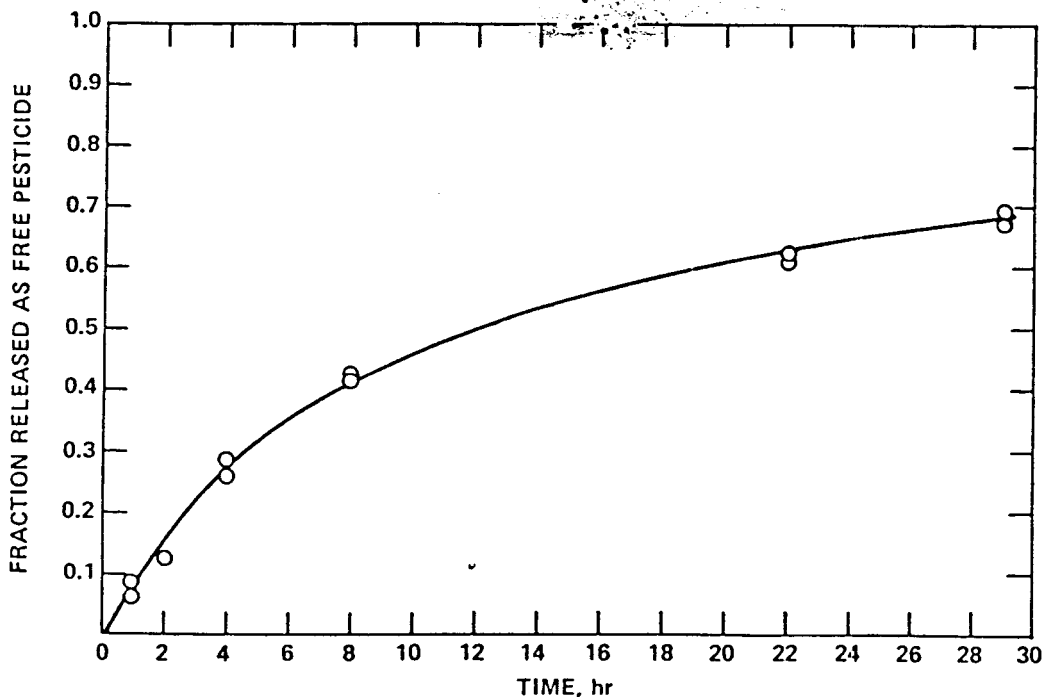


Figure 5. Release of trichlorfon from poly(acryloyl trichlorofon).

Figure 6 shows the release data for all of the polymers tested. The hydrolysis of trichlorfon from the three polymers with diacid spacers was significantly more rapid than that from the poly(acrylic acid) product. Little difference can be seen among the diacid-containing polymers when compared to the poly(acrylic acid) product. However, the order of these three is in opposition to the rates that would be expected based on the stability of the ester formed with each diacid. On these grounds, we would have expected that the polymer containing perfluorosuccinic acid would have been the fastest, followed by the polymer containing maleic acid. In fact, the maleic acid polymer was fastest, and the perfluorosuccinic polymer was slightly slower even than the succinic product. It is possible that despite the lability of the bond, the fluorocarbon nature of the bridging diacid was sufficient to exclude water from the region of the ester linkage.

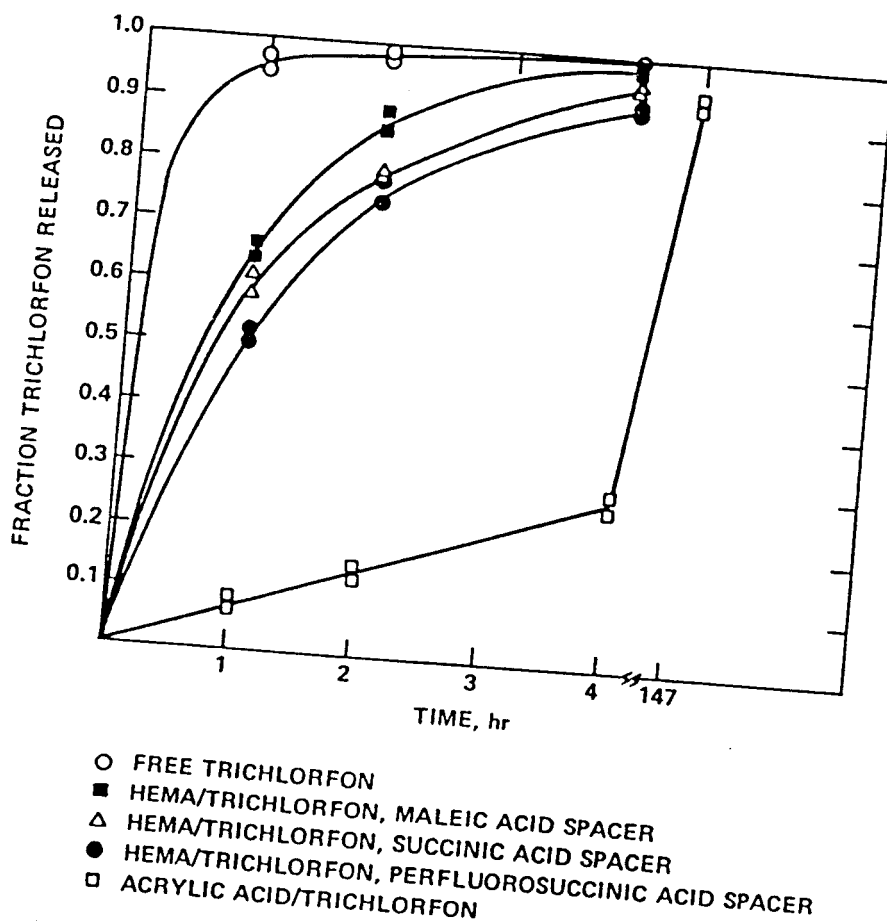


Figure 6. Release rates for trichlorfon-containing polymers.

This figure also shows the observed release of free trichlorofon from the dialysis bag. Clearly, the observed delay of release for the polymeric forms cannot be accounted for as simply the time required for trichlorofon to diffuse through the dialysis membrane. A break in the time axis was employed to show that the poly(acrylic acid) product did indeed release all of its active content.

Table I shows the pertinent data for each of the polymers. The percent of substitution represents the percent of available polymer sites that had trichlorofon attached. There was significant improvement with the polymers having diacid spacers. This was probably due to reduced steric hinderance for attachment at a greater distance from the polymer backbone. When the mass of the bridging diacid is considered, however, the increased loading becomes less significant. The percent by weight of trichlorofon for each polymer is nearly equivalent for all preparations. The observed half-life of each polymer is also shown in Table I.

Further work with the trichlorofon polymer does not appear to be justified at this point for two primary reasons: (1) the apparent detoxification capacity of the fire ant toward trichlorofon greatly diminishes the likelihood of success, and (2) trichlorofon is now suspected of being a possible pollution hazard by the EPA. This should not be construed to mean that research on the use of polymeric pesticides should be abandoned however. In fact, our success in this preparation evidences the potential for this approach when employed with other pesticides.

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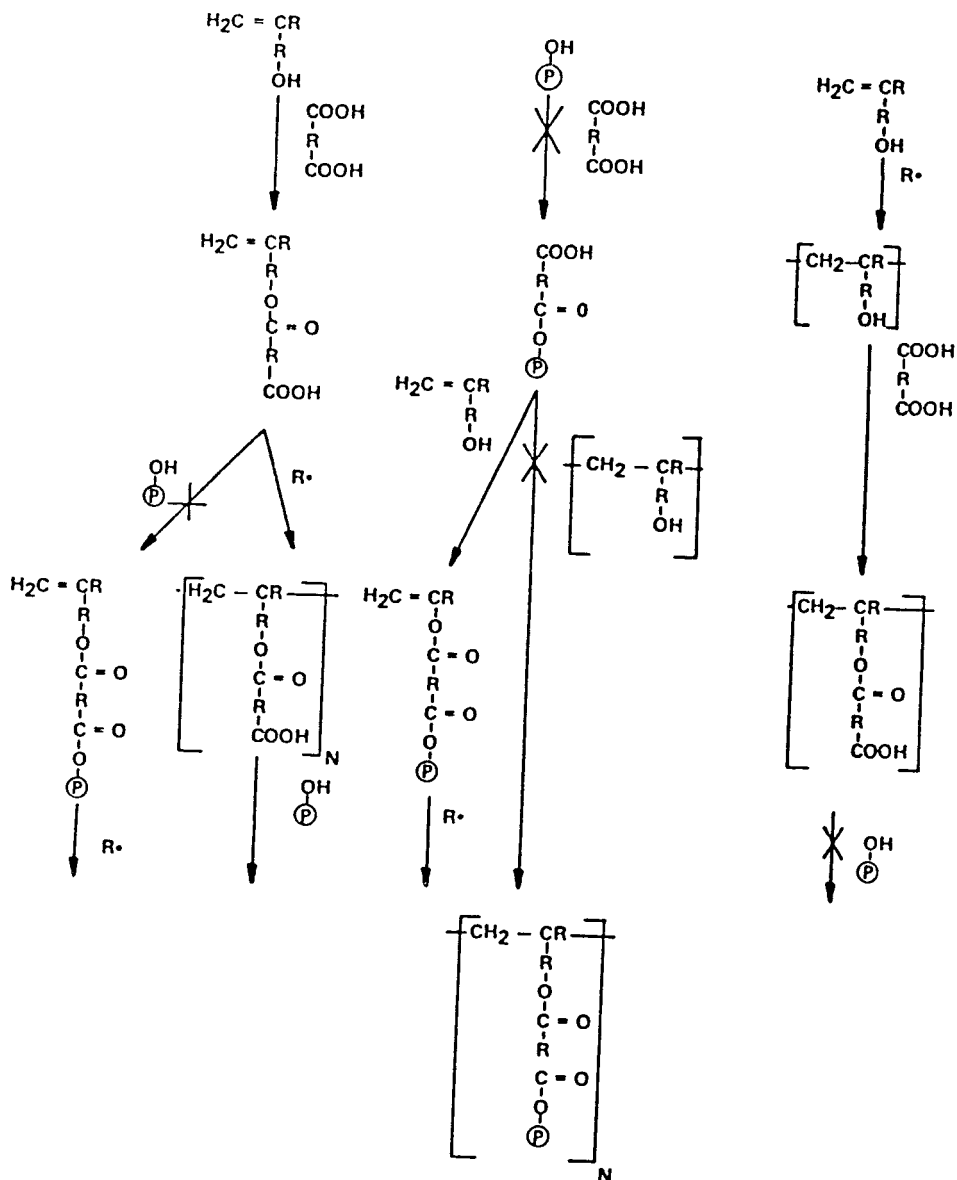


Figure 2. Synthetic routes to polymers with pendent trichlorfon.

The use of cyclic anhydrides is necessitated by the importance of avoiding polymer crosslinking during this step. However, substitution of diacids onto a preformed polymer is never 100% efficient, and our greatest success was 80% of substitution. This is not of itself a problem, but it led to significant difficulties during the subsequent step. The dehydration to attach trichlorfon also resulted in substantial crosslinking of the polymer which arose

TABLE I. PROPERTIES OF POLYMERS WITH PENDENT TRICHLORFON

Sample number	Polymer	Group	Substitution, %	Weight Percent Toxicant	Half Life in H ₂ O, hr
6-70-3	Poly(Acrylic Acid)	--	15.8	37.4	14.00
6-72-1	Poly(Hydroxyethyl methacrylate)	Succinic acid	52.6	40.7	0.85
6-70-5	Poly(Hydroxyethyl methacrylate)	Maleic acid	51.1	41.2	0.77
6-72-3	Poly(Hydroxyethyl methacrylate)	Perfluoro-Succinic acid	73.9	46.5	0.95

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