APPLICATIONS OF FUNCTIONALIZED POLYMERS IN AGRICULTURE

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SUMMARY: A number of functionalized polymer containing pesticide active groups have been discussed for the purpose of developing ideal controlled release formulations for herbicides, molluscicides and wood preservation. These polymers have been prepared either by polymerization of active monomers or by chemical modification. The active groups are attached directly to the polymer backbone or through a spacer group via covalent or ironic bonds. The results obtained from the hydrolysis studies of these functionalized polymers, indicated that several factors appear to be major govering the rates of release of active moieties. These factors include the environmental conditions as well as the effects of polymers compositions, properties and chemical structures such as the degree of crosslinking, the type and ratio of comonomer, the hydrophilicity, the spacer group, the type of the pesticidepolymer chemical bonds, and the simulated conditions necessary to increase the duration of the activity such as pH and temperature.

Key Words: Polymeric biocides, polymeric pesticides, polymeric agrochemicals.

INTRODUCTION

Synthetic polymers play an important role in agricultural uses as structural materials for creating a climate beneficial to plant growth; e.g. mulches, shelters or greenhouses; for fumigation, and irrigation in transporting and controlling water distribution. However, the principle requirement in the polymers used in these applications is concerned with their physical properties; such as transmission, stability, permeability or weatherability; as inert materials rather than as active molecules. During the last few years, the science and technology of reactive functionalized polymers (1) have received considerable interest as one of the most exciting areas of polymer chemistry for the production of improved materials. They have found widespread applications as reactive materials based on the potential advantages of the specific active functional groups and the characteristic properties of the polymeric molecules. Their successful utilization's are quite broad including a variety of fields such as solid-phase synthesis (2-6), biologically active systems (7,8) and other various technological uses (9).

The aim of this article to illustrate our recent research currently being undertaken relating functionalized polymers to the important areas of International needs for agriculture to improve the undesirable side effect arising from the uses of agrochemicals and related biocides.

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Agriculture represents one of the important areas of international requirements for health, environmental pollution control, nutrition and economic developments. The rapidly growing demand for food is the main impetus behind the need for more efficient operation in both agriculture and industrial production to afford higher yields and better qualities. Agrochemicals are concerned with the utilization of chemicals to improve production of crops both in quality and quantity. Hence a great increase in the quantities of chemicals will be necessary for enhancing any substantial increase in farm production of foodstuffs. However, the potential hazards of the agrochemicals to public health and wildlife result in a great increase in limitations on their uses. Depending on the method of application and climatic conditions. As much as 90% of the applied agrochemicals never reach their objective and result in nonspecific and periodic applications. Both factors beside increasing the cost of the treatment produce undesirable side effects either to the plant or to the environment.

Controlled Release Formulations

Controlled release formulation has recently been emerged as new technique which designed to avoid or reduce the possible side effects accompanying the use of biologically active agents. The aims of this technique are: (I) to protect the supply of the agent, (ii) to allow the automatic release of the agent to the target at controlled rates, and (iii) to maintain its concentration within the optimum limits over a specified period of time, thereby producing great specificity and persistence. There are two different approaches in combining the biologically agents with polymeric materials: either by physical combination (encapsulation, or heterogeneous dispersion) to act as a rate controlling device, or by chemical combination to act as carrier for the agent. The choice of the best system to release the active agent is highly dependent on the biological and chemical properties of the agent and on its physicochemical interactions in the system. Although the design of the physical combinations is not Influenced by the chemical structure of the active agent molecule, i.e. there is no need for specific functional group, however, their applications in agrochemicals have drawbacks to their commercial production due to several considerable disadvantages accompanying their use and to the requirements within the used polymer.

In the chemical combination, the active material is released by a slow degradation of the polymer itself, or through cleavage of the active agent-polymer linkage by the environmental reactants. However, this system is not applicable for agrochemicals lacking reactive functional groups, which represents its main disadvantage. The rate of release of the active group from the polymer matrix and consequent duration of the effective action is Influenced by: (I) chemical characteristics of the active agent structure, (ii) nature of the active-agent-polymer bonds, i.e. stength and type such as esters, amides, ureas, urethanes, acetals, (iii) the distance of the active agent from the polymer backbone; for achieving an enhanced rate of release it is necessary to attach the active agent at some distance from the polymer backbone via a permanent spacer group to separate it from the steric hinderance of the backbone, (iv) rate of breakdown of the active group-polymer bonds by chemical, biological, or environmental agents such as sunlight, moisture and microorganisms, (v) chemical nature of the polymer backbone, (vi) chemical nature of the groups surrounding the active moieties, (vii) dimension and structure of the polymer molecule as governed by the degree of polymerization, comonomers, solubility, degree of crosslinking and the stereochemistry.

The polymeric biocide has several advantages and its potential benefits are: (i) prolongation of activity: it allows much lower amounts than conventional biocides to be used as it releases the required amount of active agent over a long period. (ii) Reduction of number of applications through achieving a long period of duration of activity by a single application. (iii) Reduction of cost: it eliminates the time and cost of repeated over applications because less active materials is needed. (iv) Reduction of mammalian toxicity. (v) Convenience: it converts liquids to solids, hence it results in easily handled transported materials with the reduction of their flammability. (vi) Reduction of environmental pollution: it eliminates the need for widespread distribution of large amount of biocides at one time, thereby it reduces the excess of toxic biocide levels in the surrounding environment. (vii) Reduction of evaporation and degradation losses by environmental forces or leaching by rain into the soil or waterways due to the macromolecular nature. (viii) Alternation or modification of the activity: it extends the duration of activity of less or non-persistent biocides which are unstable under an aquatic environment by protecting them from environmental degradation and hence enhances the practical applicability of these materials. (ix) Reduction of phytotoxicity by lowering the high mobility of the biocides in the soil and hence reduces its residues in the food web. (x) Extension of herbicide selectivity to additional crops by providing a continous amount of herbicide at a level sufficient to control weeds but without injuring the crop.

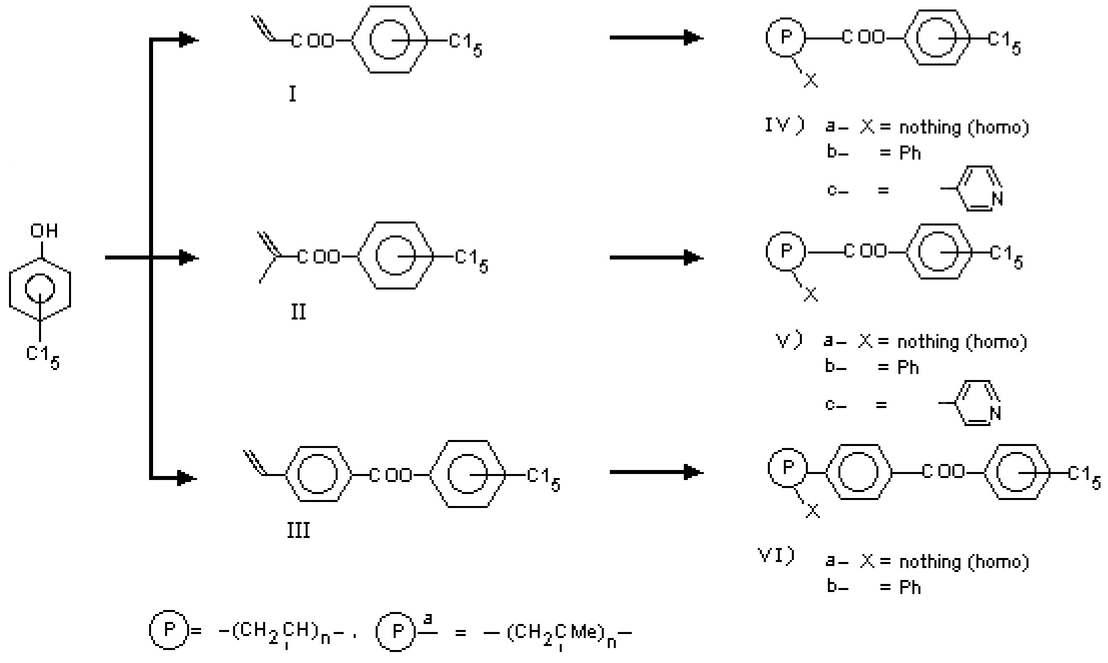
Polymeric Herbicides

The main problem with the use of less persistent conventional herbicides that have greater specificity, is the use of excess amounts than that actually required control the herb because they are unstable in an aquatic environment and of the need to compensate the amounts wasted by the environmental forces of photodecomposition, leaching and washing away by rain, evaporation, or biodegradation by microorganisms. They are also highly toxic to farm workers and expensive on multiple applications, which are required because of their lower persistence. On the other hand, the applications of large amounts of persistent herbicides are undesirable because of their frequent incorporation into the food chain. In addition, they result in a major contamination in the surrounding environment which result in a toxic hazard for humans. For these reasons many of these herbicides have been phased out.

In an attempt to make connection with the problems encountered in using conventional herbicides, some functionalized polymers containing pesticide moities as pendandt groups have been prepared by free radical polymerization of vinyl monomer type and their hydrolysis rates were studied under different conditions. As active pesticide group, pentrachorophenol (PCP) has been chosen because it is a major industrial chemical and represents one of the most widely used biocides in a variety of agrochemical applications, such as herbicide, molluscicide, fungicide, insecticide, algicide and bactericide. In addition, its hydroxyl group provides also a suitable mean for covalent bonding to a variety of polymerizable units.

A series of vinyl monomers containing PCP via an ester linkage have been prepared (10) an outlined in Scheme 1. These monomers have been homo-and copolymerized with styrene and 4-vinylpridine, which were

Scheme 1: Preparation of Pentachlorophenol Monomers and Their Polymers.



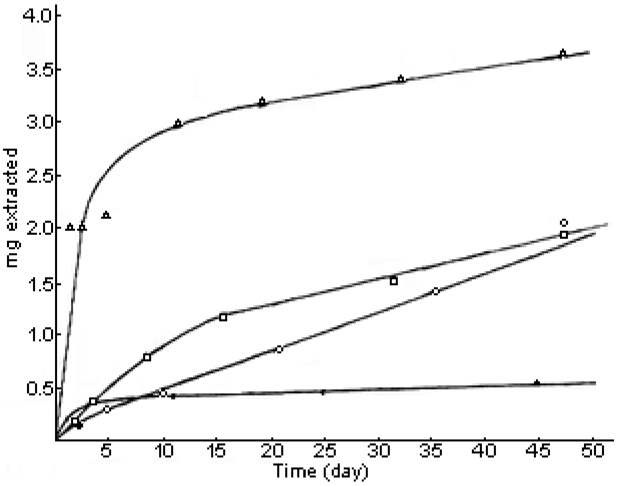


Figure 1: Pentachloraphenol relased from 0.1 of homopolymer, IV_a.

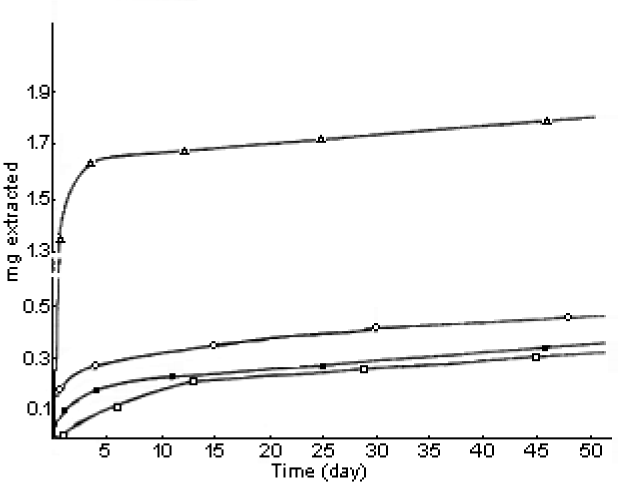


Figure 2: Pentachlorophenol relased from 0.1 g of copolymer, IV_b.

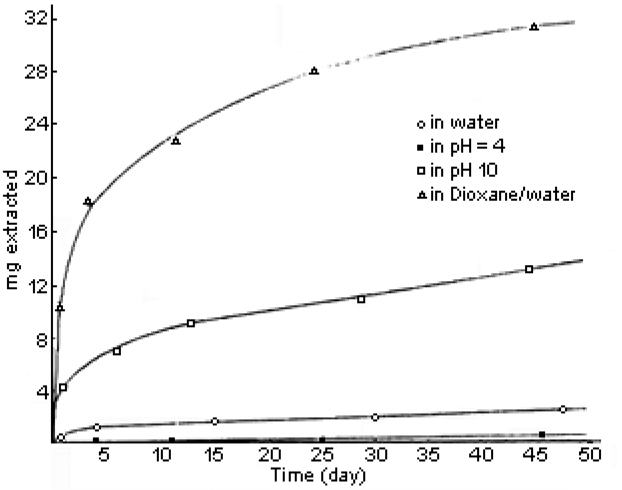


Figure 3: Pentachlorophenol relased from 0.1 g of copolymer, IV_c.

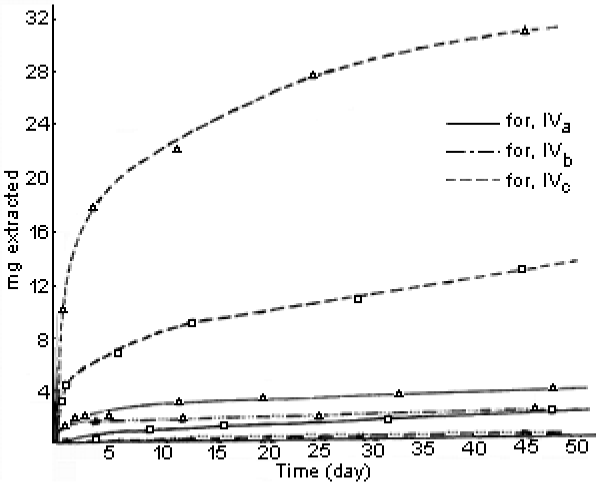


Figure 4: Pentachlorophenol relased from 0.1 of homopolymer, IV_a and copolymers, IV_b, and IV_c.

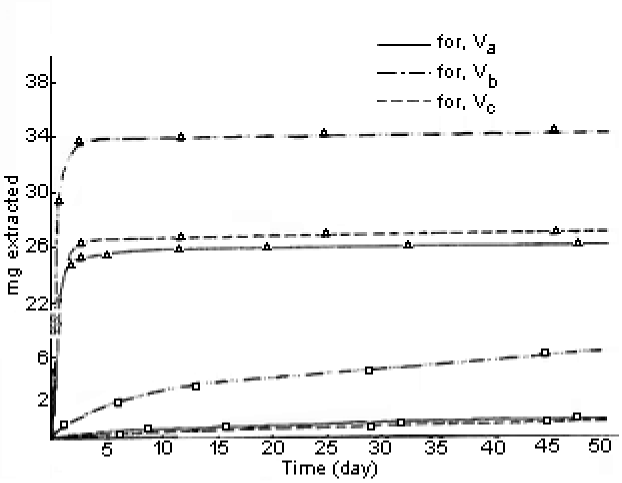


Figure 5: Pentachloraphenol relased from 0.1 of homopolymer, IV_a and copolymers, V_b, and V_c.

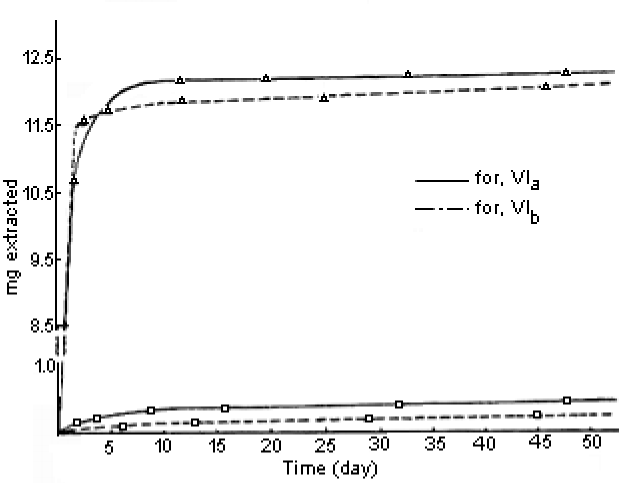
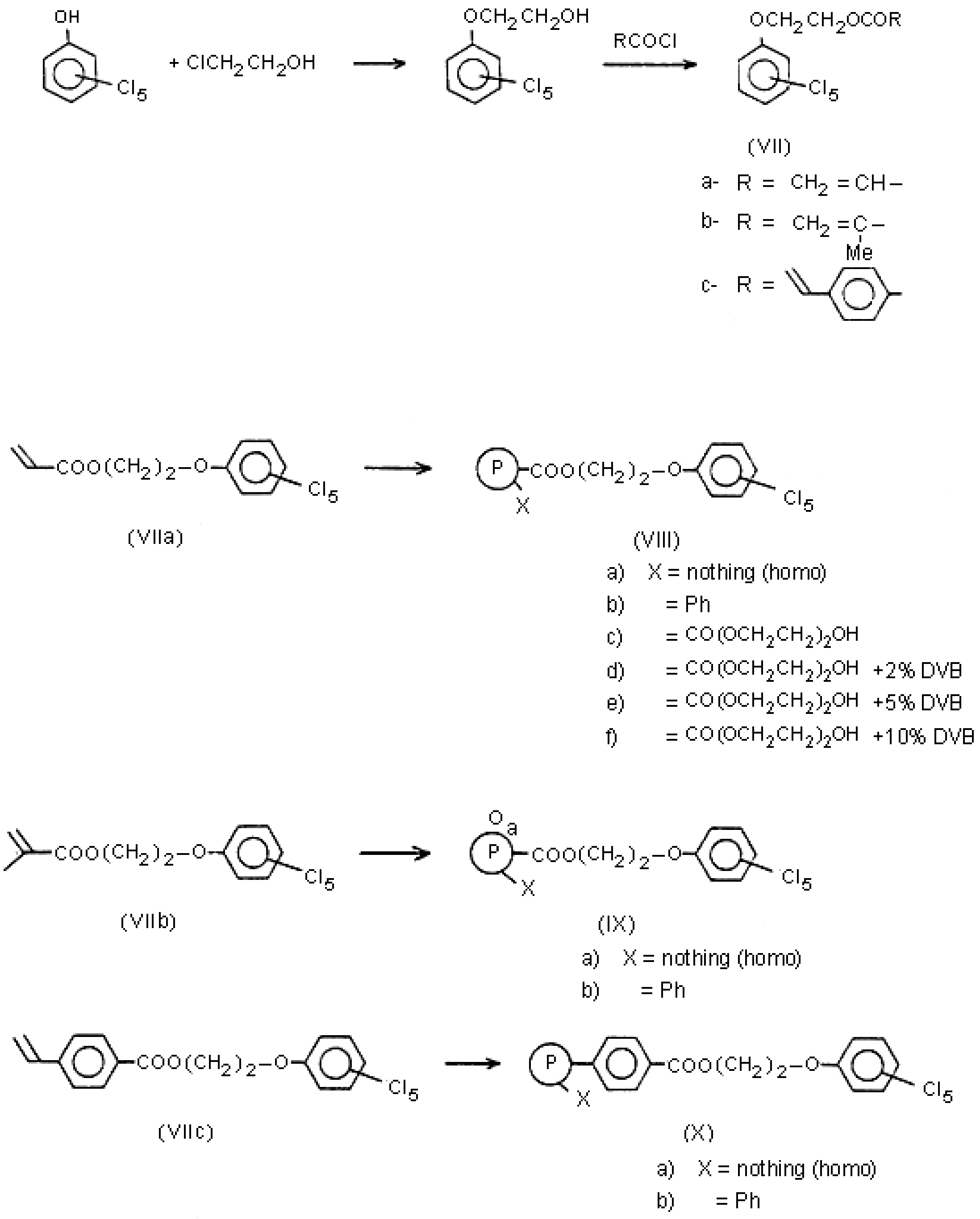


Figure 6: Pentachlorophenol relased from 0.1 g of homopolymer, VI_a and copolymers, VI_b.

introduced to induce hydrophobic and hydrophilic nature to the polymers. The rates of release of PCP from the polymers have been studied at four different media (water, pH=4, pH=10, and dioxane-water) and at 30°C, as show in Figures 1-3. The hydrolysis data of all the polymers showed increase in rates of release in dioxane-water and basic media and slightly lower rates in water and acidic media. A comparison between the rates of release from these polymers indicate that the rates increase with increasing the degree of hydrophilicity, i.e. copolymer IVc hydrolyzes faster than the homopolymer IVa which has higher rate than the hydrophobic copolymer IVb as shown

Scheme 2: Preparation of Polymerization of Pentachorophenol Monomers.



in Figure 4. Similarly, the results of the hydrolysis of polymethacrylate derivatives Va-c confrim the results obtained with the polyacrylate derviatives IVa-c as shown in Figure 5, which represents a comparison between their hydrolysis rates. An investigation of the hydrolysis of polystyrene derivatives VIa-b has also showed slightly faster release for a homopolymer VIa than the hydrophobic copolymer VIb as shown in Figure 6. The effect of the temperature on the release of PCP from the polymers Va-c, Figure 7, indicate that the rates of release are enhanced by increasing the temperature from 30° to 60°C.

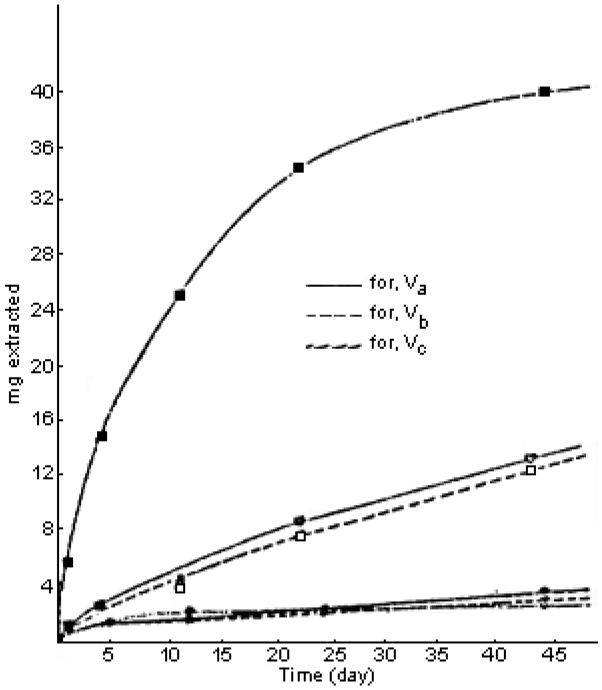
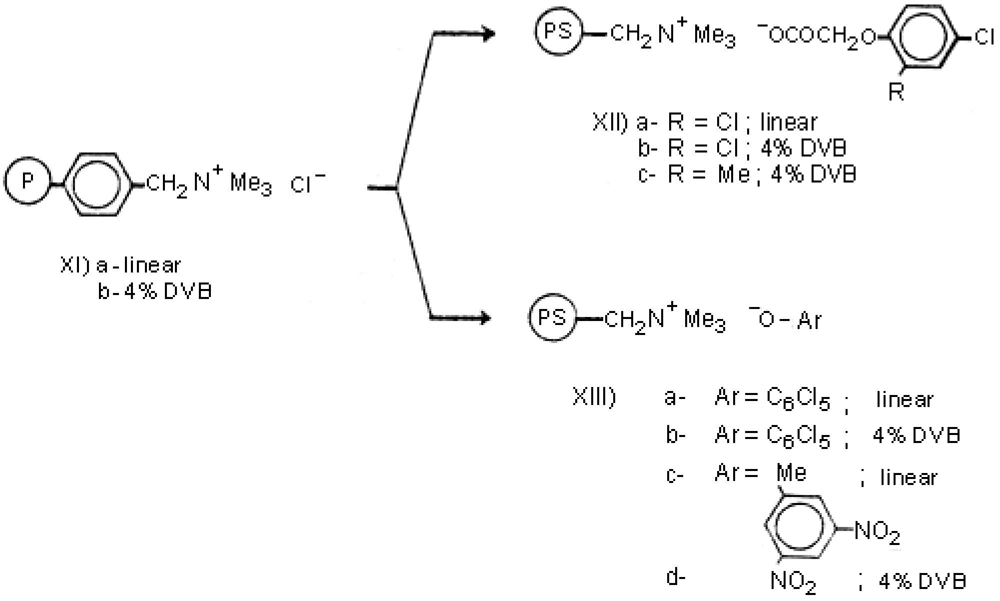


Figure 7: Pentachlorophenol released from 0.1 g of homopolymer, V_a and copolymers, V_b, and V_c.

The study of the hydrolysis rates from the polymer IVa-c, Va-b and VIa-b has showed the effects of some factors, such as surrounding medium conditions, the temperature, and the nature of the groups surrounding the active moieties. However, for studying the effects of other factors as the spacer group and the dimensions of the polymer molecule, in addition to the above factors, a series of functionalized polymers containing PCP via oxyethylene spacer group have been prepared (11) as shown in Scheme 2. The homopolymer VIIIa with a spacer group has showed faster hydrolysis than the IVa because the ester linkage is removed from the hydrophobic backbone and is less sterically hindered, as shown in Figure 8. The results obtained with the hydrophobic copolymer VIIIb and the hydrophilic copolymer VIIIc confirm the structure picture provided by the hydrolytic release given in the first example, Figure 9.



Scheme 3: Preparation of Polymeriic herbicides.

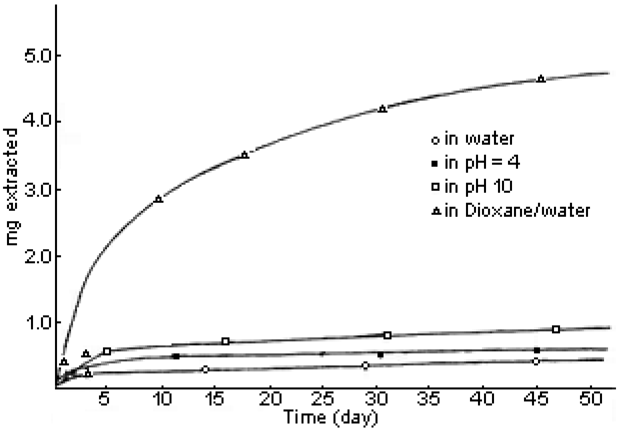


Figure 8: Pentachlorophenol released from 0.1 g of homopolymer, $VIII_a$.

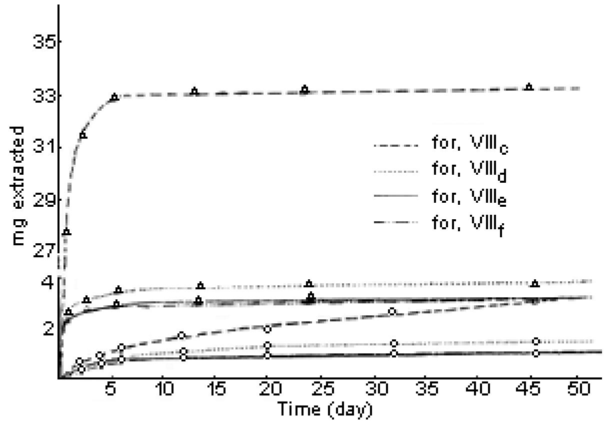


Figure 10: Pentachlorophenol released from 0.1 g of linear, $VIII_c$ and crosslinked, $VIII_e$, and $VIII_f$ polymers.

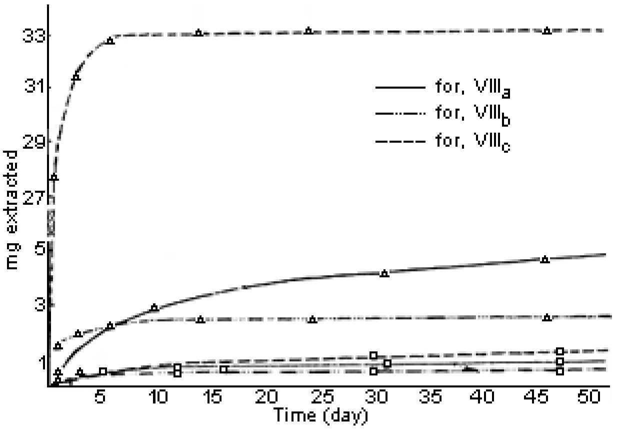


Figure 9: Pentachlorophenol released from 0.1 g of homopolymer, $VIII_a$, and copolymers, $VIII_b$ and $VIII_c$.

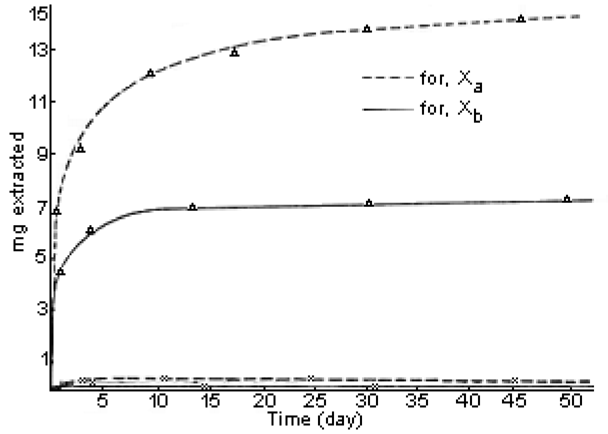
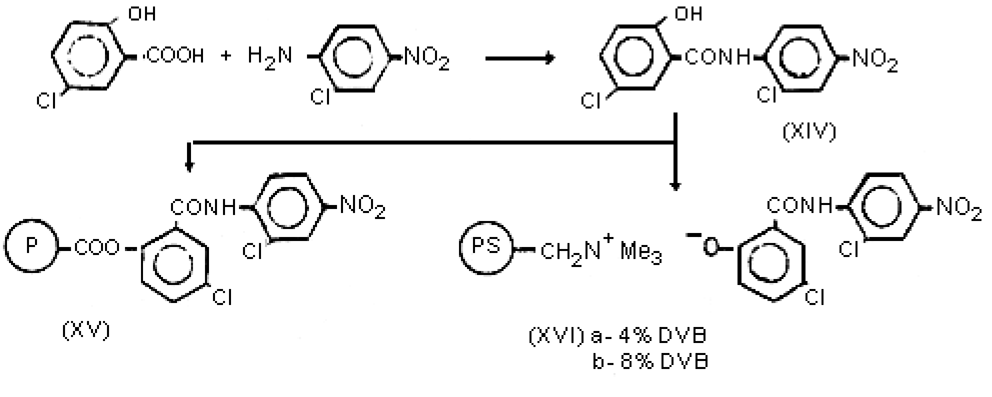


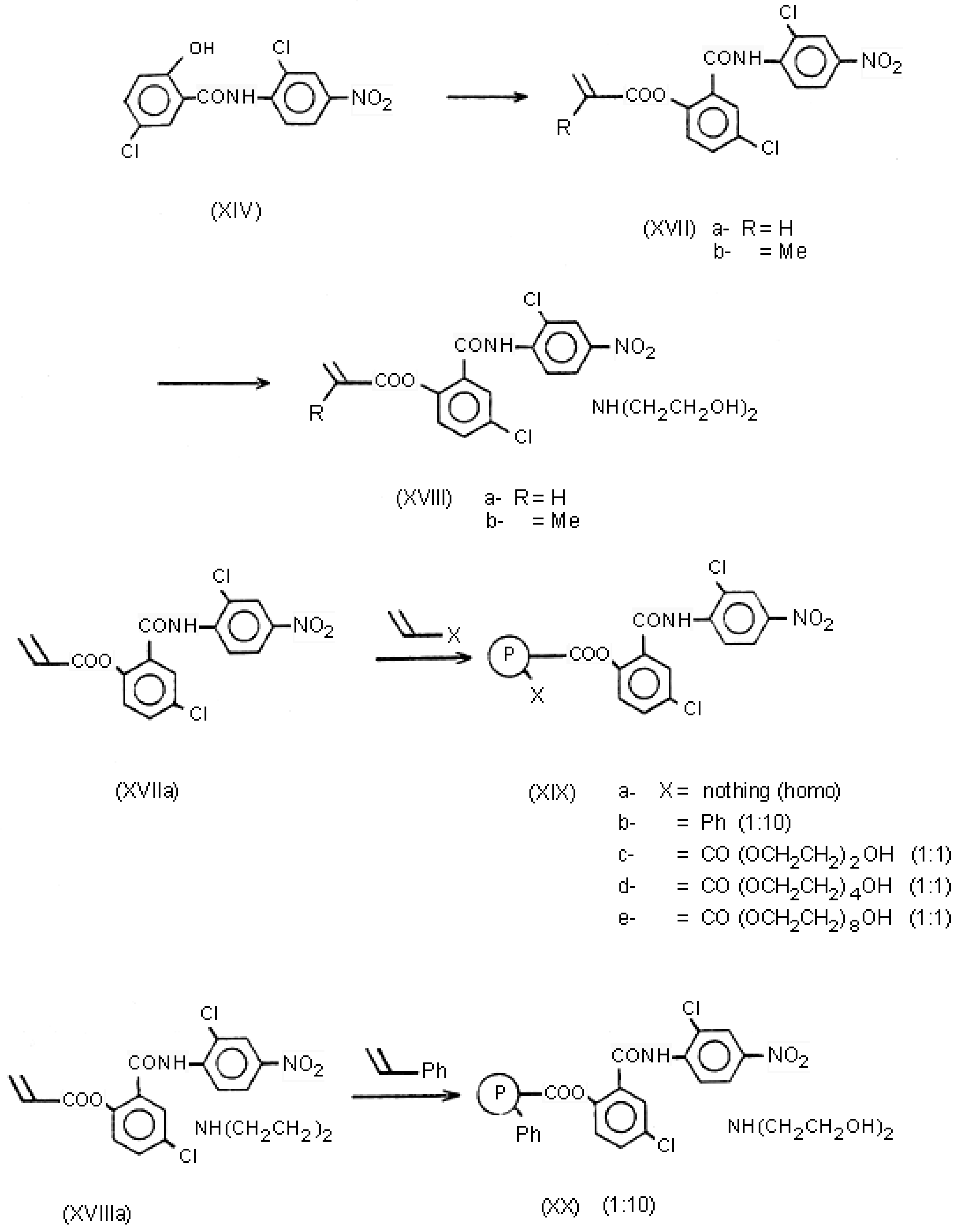
Figure 11: Pentachlorophenol released from 0.1 g of homopolymer, X_a and copolymer, X_b.



Scheme 4: Preparation of Niclosamide Polymers.

Crosslinked copolymers with different ratios of divinylbenzene (DVB), VIId-f, have showed much lower release rates than the linear polymer VIIIc, as shown in Figure 10. The hydrolysis data for the polymers IXa-b and for the polymers Xa-b, Figure 11, indicate that the homopolymers IXa and Xa have released PCP faster than the copolymers IXb and Xb.

In another example, polymeric herbicides containing active moieties ionically bound to ammonium salt groups have been investigated (12) to demonstrate the reactivity displayed by the polymers through changing the chemical nature of linkage bond and the chemical characteristics of the active agent structure, in addition to the polyelectrolyte character and the crosslinking ratio. As active herbicide agents, in addition to PCP, the herbicides of general use and that contain functional group for bonding to the polymer matrix have been chosen, such as 2,4-dichlorophenoxyacetic acid, 2-methyl-4-chlorophenoxyacetic acid and 2,4-dinitro-6-methylphenol. The polymeric herbicides have been prepared by the chemical modification tech-



Scheme 5: Preparation and Polymerization of Niclosamide Monomers.

nique as shown in Scheme 3. Plots of the amounts of herbicides released vs. time, Figures 12-15, indicate that : (i) the linear polyherbicides release the active agents much more rapidly than the crosslinked systems, (ii) although there is some evidence that an increase in the degree of crosslinking may result in a slight decrease in the rate of hydrolysis, the hdrophilicity of the ammonium salt groups appears to be the major factor govering the rate of release. This can be attributed to an intramolecular interaction of neighbouring ammonium salt groups generated by the hydrolysis, (iii) the effect of the surrounding medium is also a major factor in which all systems showed significantly faster release in the basic media.

However, the major drawback to the economical use of these polymeric herbicides is the large amount of inert polymers that must be employed as a carier for the herbicide and hence the left residual materials once the herbicide group has been exhausted which are harmful for the soil and the plant. Some attempts have been made to reduce this problem, which mainly based on the concept of attaching the pesticides to biodegradable carriers of similar structures to agricultural residues consisting of polysaccharides such as bark, sawdust, cellulose and other cellulosic wastes. However, the main disadvantages with the use of such naturally occurring polymers are the difficulties encountered with their chemical modification and the extremely low concentration of herbicide attached to them due to their insolubility in solvents suitable for modification. Hence, the use of excessive amounts of such bioactive polymers usually necessary for herb con-

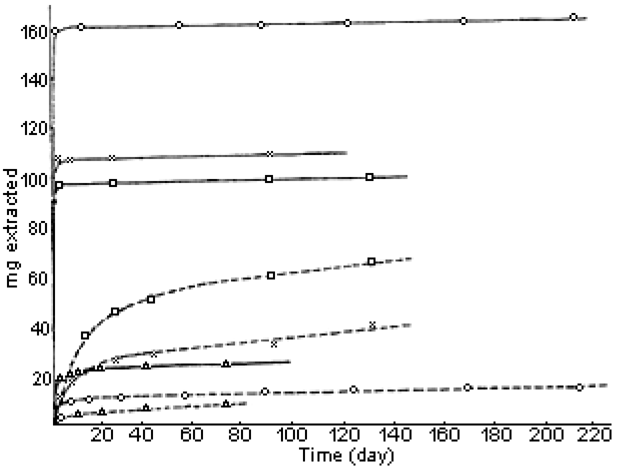


Figure 12: 2,4-Dichlorophenoxyacetic released from 0.2 g of linear, XII_a, and crosslinked, XII_b, homopolymer.

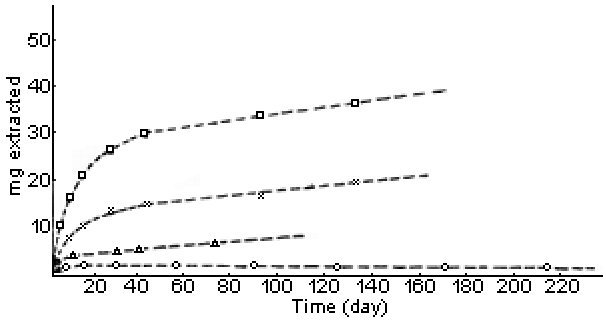


Figure 13: 4-Chloro-2-methylphenoxyacetic acid released from 0.2 g of crosslinked, XII_c, polymer.

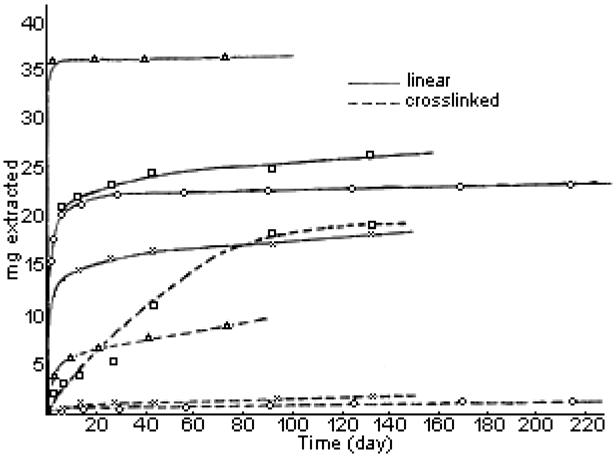


Figure 14: Pentachlorophenol released from 0.2 g of linear, $XIII_a$ and crosslinked, $XIII_b$ polymers.

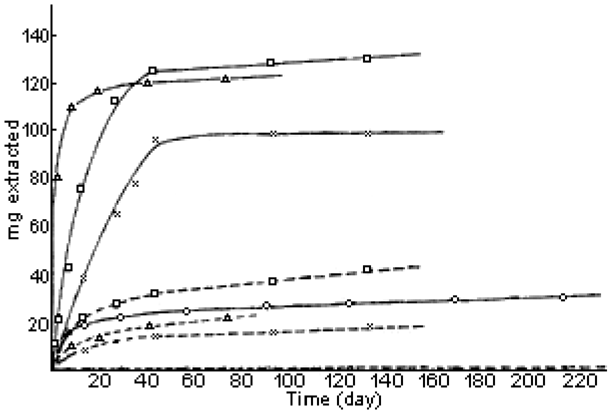


Figure 15: 2,4-Dinito-6-methylphenol released from 0,2 g of linear, $XIII_c$, and crosslinked, $XIII_d$, polymers.

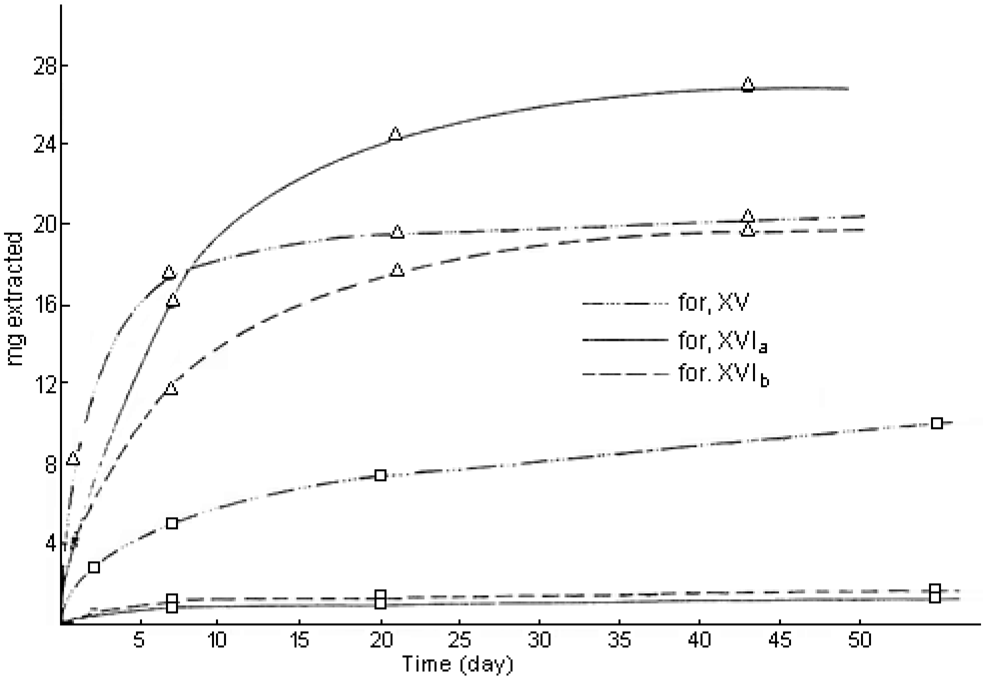


Figure 16: Niclosamide released from 0,1 g of polymers, XV, and $XVI_{a,\,b}$.

trol is inevitable. Furthermore, the hydrophilic and non-crosslinking nature of these polymers lead to a faster rate of hydrolytic cleavage of the pendant pesticide. Another factor is their rapid deterioration in soil by biodegradation and the subsequent destroying of the polymeric matrix within a short period of time, which leads to shorter period of effectiveness of the herbicide.

In order to eliminate or at least to reduce the disadvantage of using excessive amounts of inert polymers as carriers, in addition to the dawbacks of using soluble nitrogen fertilizers, we have recently used the principle of a dual application of controlled release herbicide-fertilizer combination. This principle is based on the use of appropriate polymers as carriers, in which the residual products after the degradation of the polymer become beneficial to the plant growth and the soil by acting as fertilizer. For example, herbicide derivatives of bifunctional compounds have been prepared and polymerized under condensation polymerization conditions. The second attempt is based on the concept of attaching the herbicides to polymeric hydrogels in order to alter the bacis character of sandy soil. In addition to the primary function of these plymers to control the rate of delivery of herbicides, they can play an important role to increase the water retention by sandy soil through avoiding its rapid leaching. Hence, the use of such dual combination of controlled release herbicide-water conservation can contribute positively to change the conventional agricultural irrigation especially for sandy soil.

Polymeric Molluscicides

Bilharzia is one of the most widespread trematode, endemic disease in tropical countries where the spreading of cultivated areas increases. In Egypt, the erection of large areas to perennial irrigation has increased the infection rate since new areas are added as suitable habitates to the snails, which are the intermediate vectors of the parasite.

Since the use of molluscicides is responsible to combat various molluscs, hence the applications of large quantities of these chemicals are required for combating the bilharzia disease through the control and eradication of the schistosoma snails. As active molluscicide, Niclosamide (5,2'-dichloro-4'-nitrosalicylanilide) has been introduced by Bayer Co., under the trade marks Baylucide or Bayer 73 and applied in Egypt for combating the bilharzia disease. However, the use of great amounts of this

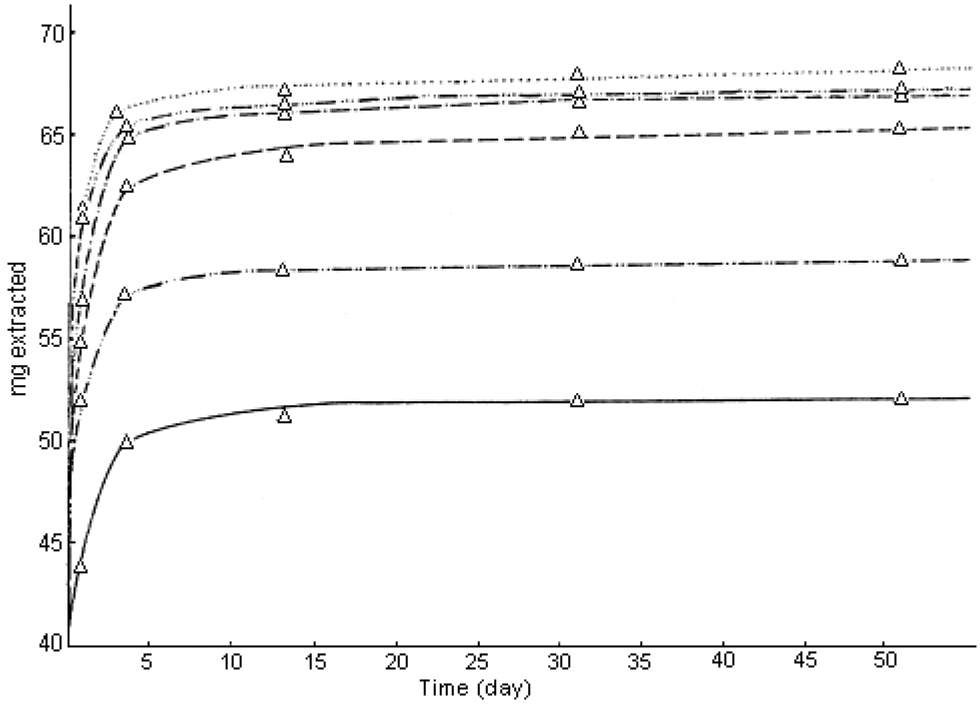


Figure 17: Niclosamide released from 0,2 g of polymers, XIX_{a-e} and XX in dioxan-water (4:1).

compound has offered some economic and environmental toxicity problems.

The chemical combination of molluscicides with the functionalized polymers has been used in an attempt for enhancing the eradication of the snails with the elimination of the side effects associated with the use of a relatively massive Niclosamide dosage. Accordingly, molluscicide polymers containing Niclosamide via covalent and ionic bonds have been prepared by chemical modifications of polymers (13), as shown in Scheme 4. The hydrolytic releases of Niclosamide from the polymers, Figure 16, indicate that: (I) the slower hydrolysis of polymeric molluscicide containing Niclosamide via ester bonds, XV, than that containing the active moiety as counter ion associated with ammonium salt group, XVIa, may be attributed to a) the nature of the covalent ester groups which are more stable toward hydrolysis than the ionic ammonium salt groups, b) the intramolecular interactions of the neighbouring hydrophilic ammonium salt groups which are not modified or generated during the hydrolysis. (ii) The increase in the degree of crosslinking results in a decrease in the rate of exchange, i.e. XVIb has lower rate than XVIa.

However, the main drawback with these polymers is their low loading with the active moieties. For eliminating this disadvantage, polymeric molluscicides have been prepared by polymerization technique of Niclosamide monomers (14). The Niclosamide monomers and their salts have been prepared according to Scheme 5, then homo-and co-polymerized with oliga (oxyethylene) monomers by a solution free radical technique. The attempt for preparation of chain extended Niclosamide monomers through the displacement of the chloride from 2-chloroethanol has been failed, probably because the oxygen of Niclosamide is severaly hindered by the ortho amide function which sterically retard the S_N2 displacement. The hydrolytic release of Niclosamide from the polymers, Figures 17 and 18, confirms the results obtained with the polymeric herbicides, i.e. the release rates are stronghly dependent upon the nature of the medium and the degree of hydrophilicity.

Wood Preservation

Fouling, as one of the problems in marine environment, is the growth of marine organisms which settle on

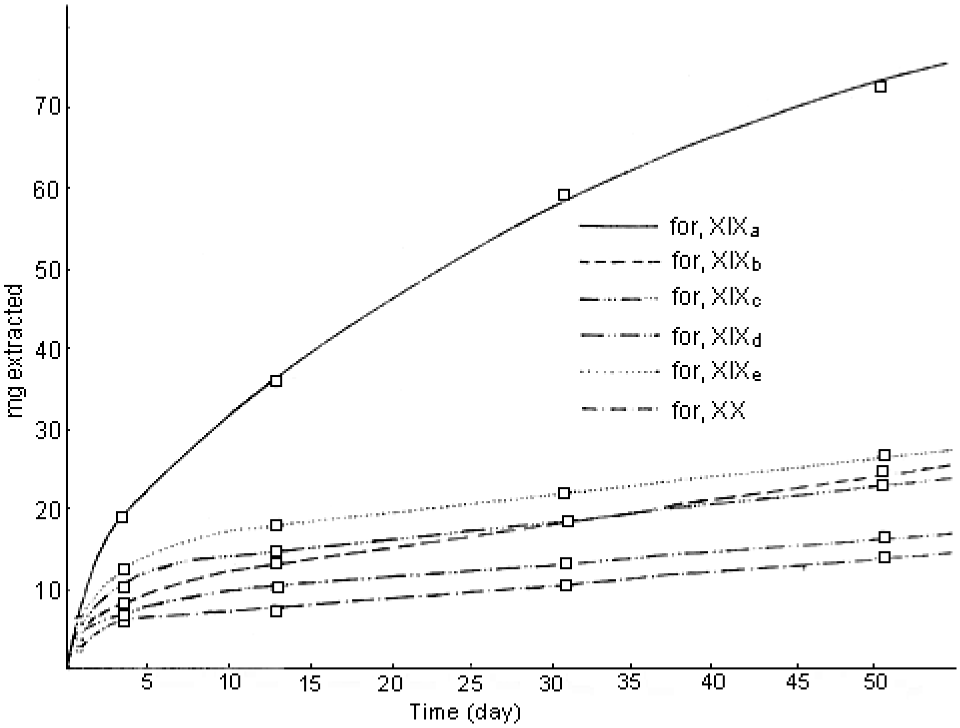


Figure 18: Niclosamide released from 0,2 g of polymers, XIX_{e-e} and XX at pH=10.

submerged surface structures. These organisms destroy the coating and cause an increase in the weight and dimensions of submerged wood structures. In general, antifouling toxicants are applied to wood surfaces to prevent the attachment and growth of all fouling marine organisms. As the toxic agents are simply dispersed into the wood surface in thin films, the rate of water leaching, evaporation, or migration of the biocides demand an amount in excess of that required to control fouling. Hence, large amounts of biocide are wasted to leave the wood empty of toxin in short period of time and becomes susceptible to fouling.

A recent development in this field is the synthesis and uses of active functionalized polymers containing antifouling moieties for the protection of wood against biodegradation. These polymers extend the effective lifetime of antifouling protection because the rate of antifouling decay by the surrounding forces is as relatively low. They are designed to permeate the entire body, thereby protecting the interior as well as the exterior, and hence minimized the environmental hazards and improve other properties of wood at the same time. For example, the wood has been impregnated with a solution of PCP monomers, styrene or methacrylate oligoether comonomers, DVB and initiator, and then heated to initiate the in-situ copolymerization reaction within the wood (15). This impregnation has resulted in filling the accessible voids of the wood with the polymers as measured by the decreased amounts of water and other solvents absorbed by the wood, which has minimized the alternating swelling and shrinking of wood and increased its dimensional stabilities in water. The presence of crosslinker has also decreased the leach rate of the toxic moieties. These conditions of wood treatment can achieve its long term of protection against microbiological decay and hence increases its service life while ensuring minimal impact on the surrounding environment.

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