T H E S I S A B S T R A C T

SYNTHESIS AND EVALUATION OF POLYMERS CONTAINING PENDENTLY ATTACHED METRIBUZIN FOR USE AS CONTROLLED RELEASE HERBICIDES

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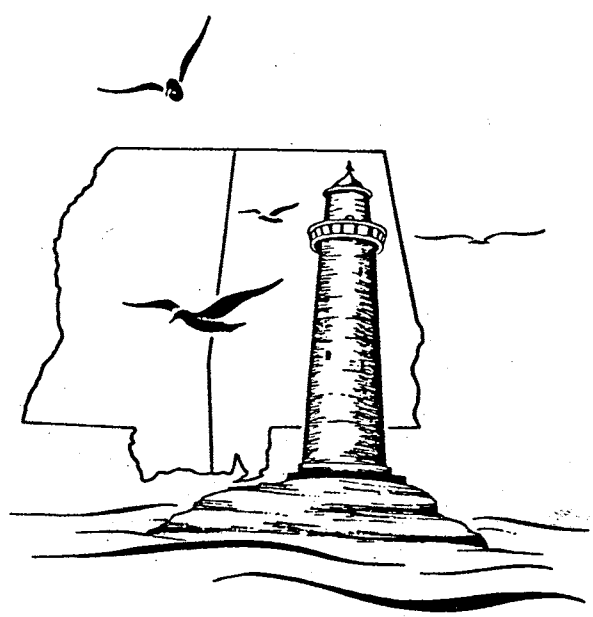

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by

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Metribuzin chloroformamide was reacted with cellulose, chitin, starch, dextran, hydroxyethylcellulose, and PVA in homogeneous solutions to prepare systems with metribuzin attached to the polymer through carbamate linkages. The potential of these polymers as controlled release herbicides which function by bond hydrolysis was evaluated.

The degrees of substitution (DS) were controlled by adjusting the ratio of chloroformamide to hydroxyl groups. Attainable DS ranged from 0.05 to 2.0. Metribuzin chloroformamide was prepared in high yield by reaction of phosgene and metribuzin under mild conditions. Metribuzin isocyanate could not be obtained using the same reagents under more stringent conditions.

New methods based on gel permeation chromatography and dialysis were developed and used to quantitate attached

and residual unattached herbicide. The latter generally amounted to less than 0.5% of the total herbicide content.

Slow hydrolysis of carbamate linkages occurred for dextran and PVA having low DS. The maximum rate observed was 5% release in 40 days for a PVA with DS of 0.06. The appearance of free herbicide did not follow first-order kinetics for the carbamate bond concentration. Hydrolysis was significantly faster at pH 10 than at pH 7, and virtually no hydrolysis took place at pH 4. Samples with higher DS gave low levels of release which could be attributed to unattached material. Hydrophilicity of the high DS materials was too low to permit accessibility of water to the bonds for hydrolysis under heterogeneous conditions. The carbamate bond was too stable to allow reasonable rates of hydrolysis, even for water-soluble materials, where accessibility was high. Use of more labile bonds will be required to achieve faster rates of hydrolysis. Release by enzymatic or photolytic degradation has not been evaluated. Biological processes may be important for the natural polysaccharide systems.