ORGANOMETALLIC INITIATORS OF FREE-RADICAL POLYMERIZATION:

A thesis submitted by

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SYNOPSIS:

The potentialities of certain organometallic complexes as initiators of free-radical polymerization have been investigated by dilatometric techniques. The systems studied are based on metal(II) acetylacetonates in the absence or presence of a reductant or an oxidizer.

The Bamford initiator, which consists of cupric acetylacetonate and ammonium trichloracetate, does not initiate the polymerization of vinyl acetate at 65°C. Consequently, the kinetics of polymerization of methyl methacrylate previously investigated by Bamford et.al. at 80°C, have been re-examined at 65°C. The kinetics at 65°C were different from that at 80°C. A modified or alternative mechanism at 65°C, which involves a linear termination reaction in addition to the Bamford mechanism, is discussed together with a problem involved in the initiation process.

Certain acetylacetonato complexes initiate the polymerization of certain monomers by themselves. Ferrous acetylacetonate polymerizes styrene and methyl methacrylate, but not vinyl

acetate. The mechanism in these cases probably involves the formation of a complex between monomer and initiator. The important role of the unassociated or associated form of the ferrous acetylacetonate under various experimental conditions is discussed.

The kinetics of the polymerization of methyl methacrylate at 25°C initiated by a mixture of ferrous acetylacetonate and cumene hydroperoxide are discussed.

This thesis contains no material previously submitted for a degree of diploma in any University and, to the best of my knowledge and belief, contains no material previously written by another person, except when due reference is made in the text.

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