CHAPTER-I
INTRODUCTION

1.1 Introduction

Most of the rockets produced today are fuelled by hydroxyl terminated polybutadiene (HTPB)-based composite propellant for propulsion. The composite propellant consists of three major ingredients, i.e. (a) a polymeric binder, (b) an inorganic oxidizer, and (c) a metallic fuel. In the present scenario, HTPB-based composite propellant with ammonium perchlorate (AP) as oxidizer and aluminum powder as metallic fuel has become the state-of-the-art propellant for rocket propulsion [1].

The burning rate of composite rocket propellant is the principal ballistic element that is taken into account while designing the rocket motor for both space and missile applications. On ignition of the rocket motor, the burning surface of the propellant grain regresses in a direction that is perpendicular to the surface. The propellant burns layer by layer. The linear rate of regression of propellant grain expressed in mm/s or inch/s, is termed as the burning rate \( r \). The linear burning rate (BR) is one of the important ballistic requirements of the propellant. It is well established that the linear BR of a solid propellant has strong dependence on chamber pressure \( p_c \) of the rocket motor. The pressure dependence on BR is satisfactorily described by an empirical equation called Saint Robert’s law, i.e. \( r = a p_c^n \), where \( a \) is a constant and \( n \) is known as the pressure index [2]. From this empirical equation, it can be inferred that the BR of the propellant increases with increase of chamber pressure. The BR of a typical HTPB/AP/Al-based composite propellant with 86-88% solid loading is of the order 5-7 mm/s at 35 kgf/cm² chamber pressure. The higher BR, i.e. 8-15 mm/s @ 35 kgf/cm², is a desirable characteristic of many rocket motors to meet various challenges of tactical mission requirement.

The higher BR is often achieved either by increasing the chamber pressure or by adding a chemical, i.e. burn rate modifier which has a potential of catalyzing the
combustion process of the solid fuel [3, 4]. To achieve high BR by increasing the chamber pressure is not desirable as it requires a complex design of the rocket motor and at very high pressure, the rocket may explode leading to the mission failure. The propellant, therefore, must have the BR that is required to deliver the desired ballistics without invoking a complex design or unusually a high pressure. Therefore, the second method of increasing the BR by addition of a catalyst is usually preferred for achieving the required BR of a composite propellant.

The BR is increased by physical addition of transition metal-based BR catalysts, e.g. Fe$_2$O$_3$, Co$_2$O$_3$, MnO$_2$, Cr$_2$O$_3$, and copper chromite (CuCr$_2$O$_4$) [5, 6], mixtures of carbonates of copper and chromium [7, 8], transition metal phthalocyanine complexes [9], and organometallic catalysts, e.g. ferrocene, liquid ferrocene derivatives, 1,3-diferrocenyl-1-butene, n-butylferrocene, pentabutylferrocene, and 2,2-bis(ethyl ferrocenyl) propane [10-12], into the propellant mix. The transition metal oxides (TMO) have got a catalytic effect on the combustion of composite propellant. It reduces the decomposition and burning temperature of HTPB/AP/Al-based composite rocket propellant [14]. However, the exact mechanism of BR enhancement is still ambiguous. It is widely believed by the scientists that TMO lowers the activation energy of AP (oxidizer) decomposition by donating electron to perchloric acid and ammonia molecules which are formed by gas phase decomposition of NH$_4$ClO$_4$ [14-16]. Among various TMO catalysts, Fe$_2$O$_3$ and CuCr$_2$O$_4$ are the most commonly used BR catalysts in HTPB/AP/Al-based composite rocket propellant [17].

The higher BR by physical addition of catalyst can be achieved either by increasing the concentration of the catalyst or by decreasing the particle size of the catalyst [6, 18]. However, the BR does not increase linearly with the concentration of the catalyst. After a certain concentration, it shows a plateau effect, i.e. the BR becomes insensitive to increase in concentration of the catalyst [6]. Additionally, the higher loading level of TMO catalyst imposes poor processing, aging, and mechanical characteristics to the composite propellant [11]. When loaded beyond 2\%, it significantly damages the mechanical properties of the propellant and its processing characteristic because of agglomeration [10]. We have studied
the effect of loading of catalyst (CuCr₂O₄) on BR as well as on the mechanical properties of HTPB/AP/Al-based solid composite propellant with 86 % total solid loading. The profile of BR versus concentration of catalyst is presented in Fig.1.1.

![Graph showing the effect of copper chromite on burn rate of HTPB/AP/Al-based solid composite propellant.](image1)

**Fig.1.1.** Effect of copper chromite on burn rate of HTPB/AP/Al-based solid composite propellant.

![Graph showing the effect of copper chromite on mechanical properties of HTPB/AP/Al-based solid composite propellant.](image2)

**Fig. 1.2.** Effect of copper chromite on mechanical properties of HTPB/AP/Al-based solid composite propellant.

We observed that the BR increased exponentially up to 0.5 % of CuCr₂O₄, and thereafter, it remained nearly constant. Fig.1.2 presents the variation of mechanical properties...
properties, i.e. tensile strength (kgf/cm\(^2\)), elongation (%), initial modulus (kgf/cm\(^2\)), and hardness, of the propellant against concentration of the catalyst. It was observed that tensile strength and modulus of the propellant did not show any clear trend with increase in concentration and were very poor, particularly, at higher level of catalyst loading.

The second method of increasing the BR of propellant by TMO catalyst is by decreasing the particle size of the catalyst. As the particle size of Fe\(_2\)O\(_3\) decreased, its catalytic activity was found to be higher [19]. However, this method of increasing the BR has got inherent disadvantages such as agglomeration, in-homogeneity in the distribution of catalyst in propellant mix, and settling with high level of catalyst loading. Additionally, most of the TMO catalysts are compositionally and morphologically not well defined, and their efficiencies vary from batch to batch from a single manufacturer. Therefore, the method of achieving the higher BR by either increasing the concentration or decreasing the particle size of TMO catalysts makes it difficult to realize a workable propellant.

On the other hand, transition metal phthalocyanine complexes have better catalytic efficiency due to its solubility in the binder phase of solid composite propellant resulting in more consistent and reproducible BR [9]. The transition metal phthalocyanine complexes are well characterized compounds and thermally stable upto 500-600 °C [20]. So, these are considered to be quite suitable as BR catalysts in solid composite propellants. Fong et al. [9] studied the metal phthalocyanine complexes as BR catalysts in HTPB/AP-based composite propellants. The results revealed that the catalytic efficiency for the metal phthalocyanine complexes in a HTPB/AP propellant was in the order: Fe>Cr (F)> Cu>V (O)> Co> Mn> Ni> Zn, Na, Mg. It was observed that the iron and chromium metals were the most effective transition metal catalysts for composite propellant. This was due to the fact that Fe\(^{3+}\) and Cr\(^{3+}\) have got the highest reversible oxidation potential. While the chromium complexes are initially in the (III) oxidation state, the iron complexes are in the (II) oxidation state. Thus, the Fe\(^{2+}\)/Fe\(^{3+}\)/Fe\(^{4+}\) and Cr\(^{3+}\)/Cr\(^{4+}\) reversible redox cycles are possible and can account for the highest observed catalytic BR. However, these complex catalysts also encountered same problems associated with that of TMO catalysts, thus limiting their applications [9].
In the last decades, there had been considerable interest in exploring various ways and means to obtain high BR for composite propellant as the BR obtained with very small particle sized TMO or transition metal phthalocyanine complexes was insufficient for space and defense applications. Therefore, many researchers shifted their attention towards organometallic compounds as BR catalysts. Among various organometallic compounds, bis($\eta^5$-cyclopentadienyl)iron, commonly known as ferrocene, was found to be highly efficient BR catalyst for composite rocket propellant [10]. It can be loaded up to 9% of the propellant composition without much changes in rheological and mechanical properties of the composite propellant [10]. The increase in BR by ferrocene was attributed to its ability to get rapidly oxidized in the burning propellant to iron oxide particles of sub-micron size which act as catalytic sites to accelerate the gas phase decomposition of perchloric acid. The additional advantage of ferrocene catalyst was that it not only increased the BR but also reduced the pressure dependence of BR for fast burning propellants. Unlike the inert solid catalyst such as Fe$_2$O$_3$ which have zero fuel value, the ferrocene catalyst possesses both organic (i.e. bis($\eta^5$-cyclopentadienyl) ring) and inorganic part (i.e. iron) that increase the energy of the propellant via exothermic oxidative reactions[21]. Though a high BR can be achieved by using ferrocene as BR catalyst, it has also got many disadvantages. Being a crystalline solid, it introduced a high degree of in-homogeneity in micro-level distribution throughout the propellant mass. Large amount of this catalyst also generated unfavorable changes in the propellant rheological properties. The negative effects were (a) reduction of pot life, (b) decrease of elongation, and (c) growth of modulus of the propellant [11].

Further, being a high-melting solid (Mp 172.5 °C), it undergoes sublimation easily at moderate processing temperature of the solid propellant.

Of late, besides the use of solid ferrocene, much of the research work have been focused on the synthesis of ferroceny substituted compounds which have better solubility in the binder phase or exist as liquid or can act as binder-cum-catalyst with specific functional group for reaction with curator. Recently, the liquid ferrocene derivatives, such as 2,2-bis(ethylferroceny1)propane commonly known as catocene, butylferrocene, and 1,3-diferrocenyl-1-butene are being increasingly used as BR catalyst in composite rocket
propellants [11]. In comparison with the commonly used solid catalysts, one of the most important advantages of the liquid catalysts was the possibility of use larger percentage which resulted in high BR [11]. The liquid catalysts were capable of diffusing homogeneously into the composite propellant and showed higher catalytic activity. Liquid ferrocene compounds were as effective as Fe$_2$O$_3$ but acted through a different mechanism. Ferrocene compounds are reported to reduce the activation energy of decomposition, whereas Fe$_2$O$_3$ is known to lower the decomposition temperature of composite propellants [22].

Although ferrocene derivatives were superior as compared to the TMO as BR catalysts, their use had some drawbacks arising from the tendency of migration in propellant and their sensitivity toward oxidation by air. Being liquid, they easily migrated towards the surface of the propellant grain and crystallized on the surface [23]. However, the use of liquid alkyl ferrocene has eliminated the crystallization problem, allowed better dispersion of iron throughout the propellant, and provided better processing qualities by acting as the plasticizer. Most of the alkyl ferrocenes were sufficiently volatile. Catocene is usually hazardous as it becomes volatile at the mixing temperature [22]. So, a significant quantity was lost during propellant processing and increased the risk of fire and explosion hazards due to contact with AP dust in the mixer.

Migration, volatility, and crystallization on the surface of the propellant increased shock sensitivity of the propellant. Further, it destroyed the propellant homogeneity and also gave erratic BR. The surface of the propellant gave higher BR than the rest of the propellant. This made the rocket performances unpredictable. Therefore, migration of unbounded additives between propellant interfaces was considered to be major aging problem in composite propellants [23]. Structural integrity of the composite propellant is of utmost importance for the rocket motor throughout its service life. Migration of liquid catalyst affected motor ballistics due to change in composition, poor structural integrity as a result of changes in mechanical properties, and decreased bonding strength due to dewetting of interfaces. Thus, the liquid ferrocene derivatives are found to be of limited use as BR catalyst in solid composite propellants.
Owing to the various concerns as discussed above, there has been an increasing demand for synthesis of non-migrating, non-volatile, and well compatible BR catalyst to be used in solid composite propellants. Many innovative strategies have been proposed to circumvent the migration and other aging related problems as follows:

(a) Synthesis of large multi-ferrocene molecule [24],
(b) Coating of the ammonium perchlorate oxidizer [25-27],
(c) Incorporation of catalyst into the binder matrix [28], and
(d) Grafting the catalyst into the polymeric backbone of the binder molecule [21,29-32].

Various non-volatile and non-reactive multi-ferrocene bulky molecules, \textit{viz.} 2-ferrocenyl-2-(3-hydroxypropyl)tetrahydrofuran and 1,3-diferrocenyl-1-butene, 2, 2-bis(ethylferrocenyl)polypropane [22,24], have been used as non migrating BR modifiers in composite propellants. These were less likely to migrate through the propellant grain because of greater chain entanglement with the binder. However, aging studies have indicated that migration and oxidation problems still existed but to a lesser extent.

Another approach to arrest the migration towards the propellant surface is by coating AP (oxidizer) with certain tertiary amine derivatives of ferrocene, e.g. aziridinylmethyl ferrocene (AMF) [25], 1-pyrrolidinylmethylferrocene (PMF) [26], and \textit{N,N}-dimethylaminomethylferrocene (DAMF) [27]. The AMF coating were found to be unsuitable and non-effective since the aziridinyl group interfered with cure reaction of the propellant binder. The AMF coated AP was found to be extremely impact, friction, and temperature sensitive, thus limiting their use in solid composite propellant.

Incorporation of ferrocene into the binder matrix \textit{via} the curing agent ensured no migration and complete dispersion of the catalyst. For example, ferrocene derivatives containing hydroxyl and/or isocyanate function groups can be reacted with the HTPB binder network \textit{via} cross linking reaction (if tri-functional) or as chain extender (if bi-functional). However, the quantity of ferrocene incorporated into the propellant formulation
was limited by the stoichiometry of the cross-linking system. These problems restrained the use of these derivatives in composite propellants [28].

From the above discussion, it was clear that though many innovative strategies have been adopted in the recent past, but none could solve the inherent problems of migration, in-homogeneity, and volatility effectively.

The problem of migration can be successfully eliminated by linking the catalyst chemically to the binder instead of adding it physically to the propellant mix. Subramanian et al. [29] synthesized a Fe-linked-HPBP in which iron was coordinately linked to the HTPB backbone using iron carbonyl via a ligand displacement reaction and evaluated its binder-cum-burn rate properties in composite solid propellant. The catalytic efficiency of the Fe-linked-HPBP on the BR of the CSP was found to be superior to that of free iron added as Fe$_2$O$_3$. Bonding of Fe to the extent of 0.8 % did not significantly alter the rheology, molecular weight, and molecular weight distribution of HTPB. Further, synthesis of a co-polymer, i.e. HTPB-grafted-polyvinyl ferrocene from HTPB and vinyl ferrocene in benzene as solvent by free radical technique, was also reported [21]. Grafting was achieved to the extent that the resulting HTPB-grafted-PVF contained about 0.43 wt % of iron. The graft co-polymer was evaluated as a binder-cum-burn-rate modifier in a composite solid propellant using TDI and TMP as curators, and dibutyltindilaurate as the curing catalyst. The results revealed that the HTPB-grafted-PVF had a better catalytic efficiency as compared to the binder-dissolved vinyl ferrocene and also to physically mixed TMO catalysts, i.e. CuO, Cu$_2$O$_3$, and Fe$_2$O$_3$, with same weight percent of the metal.

Of late, efforts have been focused on chemically bonding ferrocene derivatives to the HTPB backbone [31, 32] in order to completely suppress the migration, in-homogeneity, and increase the catalytic efficiency of the iron metal on the thermal decomposition of the HTPB-based PUs propellants.

The primary objective of the present study was to synthesize a binder with a non-migrating, non-volatile, well compatible, effective, and high efficiency BR catalyst to be used in composite solid propellant. The modified binder would ensure that the BR catalyst
remains uniformly distributed throughout the polymeric backbone retaining its catalytic efficiency. We have selected hydroxyl terminated polybutadiene (HTPB) as the substrate polymer for this synthesis, because it has got a number of advantages as detailed below.

(a) HTPB polymer has many advantages over other binder polymers commonly used in composite propellants. It has been reported to be a workhorse resin for modern high-energy solid propellants as it acts both binder as well as fuel. This viscous polymer has excellent physical properties such as low glass transition temperature, high tensile and tear strength, and good chemical resistance [33].

(b) The hydrocarbon nature of HTPB (98.6%) coupled with its low viscosity (5000 mPas at 30 °C) and low specific gravity (0.90 g/cm³), makes it a promising fuel binder for polyurethane propellant. It is capable of taking solid loading up to 86-88% without sacrificing the ease of processibility [34].

(c) It is a major reducing agent and gas producing fuel. It is physically and chemically compatible with the widely used oxidizer like AP and other ingredients at normal storage conditions. As it contains mostly carbon and hydrogen, during combustion, it is decomposed to give large volume of stable molecules like carbon monoxide, carbon dioxide, and water vapors which increases the specific impulse of the rocket motor.

(d) Polyurethane (PU) obtained from HTPB offers many advantages over conventional polyether and polyester based polyurethane systems. Properties exhibited by PUs prepared from HTPB include (a) excellent hydrolytic stability, (b) low water absorption, (c) excellent low temperature flexibility, (d) high compatibility with fillers and extenders, and (e) formulation flexibility [35].

(e) HTPB-based propellants are projected to have lower-cost, improved BR characteristics, higher mechanical properties margins, and increased ballistic performances over the other propellant systems [36].
Owing to the many advantages, it is expected that it will continue to be the most attractive binder in the coming years also. However, to further increase its potential, it is highly desirable to have a HTPB-binder which contains a suitable combustion catalyst as an integral part of the polymer. This would act as a binder as well as combustion catalyst and may obviate various unwanted side reactions which take place during curing process or storage. The solid propellant manufactured from the modified binder is anticipated to be free of combustion instability and give better storage properties. It will influence largely the physico-chemical properties of composite propellants, which would be highly reproducible due to the uniform microscopic distribution of catalyst in the composite propellant system.

1.2 Objectives and Methodology of the Work

The research work described in the thesis aimed at studying the grafting of bis(η⁵-cyclopentadienyl)iron to the hydroxyl terminated polybutadiene via a thiol-ene click reaction and investigating its physico-chemical properties.

The methodology of the present work included the following:

(a) Synthesis of thiol derivative of bis(η⁵-cyclopentadienyl)iron with eco-friendly procedures,

(b) Study of thiol-ene CLICK reaction kinetics of thiol derivative of bis(η⁵-cyclopentadienyl)iron with the double bond of the HTPB pre-polymers,

(c) Characterization of the substrate polymers (HTPB) and their derivative products in terms of primary structure by spectroscopic method such as ¹H NMR, ¹³C NMR, and FTIR spectroscopy, along with viscometry, vapor pressure osmometry (VPO), and gel permeation chromatography (GPC),

(d) Synthesis of polyurethane (PU) elastomers in bulk with toluene diisocyanate (TDI) as the curing agent,

(e) Evaluation of three dimensional network properties of the cured PUs,
(f) Study of cure kinetics and polymer rheology of the pre-PUs by viscometric method, and

(g) Evaluation of catalytic efficiency of the grafted-bis(η⁵-cyclopentadienyl)iron on thermal
decomposition of HTPB pre-polymer by Differential Scanning Calorimeter (DSC).

The total work has been divided into five parts as summarized below.

**Part-I: Synthesis and Characterization of HTPB-grafted-bis(η⁵-cyclopentadienyl)iron Polymers**

In this part, thiol derivative of bis(η⁵-cyclopentadienyl)iron was synthesized from
bis(η⁵-cyclopentadienyl)iron as the starting material and was grafted to the vinylic double
bond of HTPB polymers. The structure and properties of the precursors were investigated
by spectroscopic, viscometry, and other related methods. This part particularly deals with
the study of microstructure and sequence distribution of the HTPB substrate polymers (free
radical and anionic polymers) as well as HTPB-grafted-bis(η⁵-cyclopentadienyl)iron
polymers. High field NMR, [(¹H, ¹³C), HMQC, HBQC, and DEPT], GPC, VPO, and
viscometry were used for analysis of the polymers.

**Part-II: Catalytic Efficiency of HTPB-grafted-bis(η⁵-cyclopentadienyl)iron on
thermo-oxidation of HTPB Polymer**

In this part, the kinetics of thermo-oxidation and decomposition of the substrate
polymers and HTPB-grafted-bis(η⁵-cyclopentadienyl)iron polymers were studied by DSC
using three different isoconversional methods, i.e. (1) Kissinger, (2) Flynn-Wall-Ozawa
(FWO), and (3) Kissinger-Akahira-Sunose (KAS).

**Part-III: Synthesis and Network Properties Evaluation of the Polyurethanes**

In this part, PUs in bulk were synthesized from the substrate as well as HTPB-
grafted-bis(η⁵-cyclopentadienyl)iron polymers by one step technique. The effect of chain
extender/cross linker, NCO/OH, iron content etc on properties of PUs, i.e. tensile strength,
elongation, modulus, hardness, and network properties of PUs, i.e. crosslink density, sol content, and effective chain length, were investigated.

**Part-IV: Cure Kinetics and Rheology of the Polyurethanes**

In this part, cure kinetics of the polymers with toluene diisocyanate (TDI) as the curing agent was investigated by measuring viscosity as a function of time using Brookfield Viscometer.

**Part-V: Thermo-oxidation and Decomposition Kinetics of the Polyurethanes**

In this part, the kinetic analysis of thermo-oxidation and decomposition of the various PU systems were studied by DSC.