

Executive summary (not exceeding 500 words)

In alignment with the "Make in India" wave and based on current and future needs of the Indian petrochemicals and polyolefin industry in general, it is believed to be the right time to develop an indigenous source of catalysts, polymers and processes for metallocene-catalyzed, structurally and rheologically controlled, premium grade, linear low density polyethylene (LLDPE) from linear alpha olefins (LAOs) of higher chain length, such as 1-Hexene or 1-Octene, which has so far been the forte of the likes of multinationals such as Dow, DuPont, and ExxonMobil.

Similarly, there is demand for the catalytic, on-purpose (that is about 100% selective) production of those alpha olefins, by metal complex catalysis, instead of inefficient, fractional distillation from polyolefin oligomeric mixtures derived from conventional processes, to make the resultant LLDPE eventually commercially viable.

Current project proposes to develop innovative and non-infringing design around of the best known, proprietary catalyst motifs for the ethylene-hexene copolymerization catalysts, more specifically the constrained geometry catalyst (CGC) motifs, particularly focusing on the bite angle around the metal centre to provide access to large macro-monomers of growing chain thus introducing long chain branching (LCB) concomitant with high activity and co-monomer incorporation, in order to provide not only desired rheology and processing ease, along with physical & mechanical properties.

Such LLDPE would gain application in the premium packaging, thermoforming, molding etc. grades, vis-à-vis existing low end, 1-butene based LLDPE available across the Indian petrochemical sector, which many a time needs downstream blending of low density polyethylene (LDPE) to attain right rheology.

"TCG Life Sciences Private Limited" ("TCGLS"), operating since 2001 from Kolkata and Pune, India, is a chemistry based research company focused on providing collaborative research services to pharmaceutical, agricultural, animal health industries of United States, Europe, Japan and Australia and, of late, PETROCHEMICAL industries. TCGLS has leading multinationals like Roche, Boehringer Ingelheim, Syngenta, BASF and Dow as its customers and a strong talent pool of 800+ trained scientists, drawn from the best national and international institutes and industry, as the workforce.

TCGLS' parent company, "The Chatterjee Group" ("TCG"), a premiere, global private equity firm headquartered from New York, USA and having investments and operations spanning several continents and industries, has a controlling stake in Haldia Petrochemical Ltd. ("HPL"), India's second largest petrochemical company and TCGLS undertakes research & development work for and on behalf of HPL.

Post successful completion of project, TCGLS envisages scale up, take trials at pilot and commercial scale, develop and transfer the technology to HPL for commercial production in its existing 1-butene LLDPE plant with minimal changes in hardware. Said pilot and commercial trial activity may be conducted in partnership with appropriate consulting and engineering firms, apart from HPL.

Further from HPL, which to TCGLS for all legal and practical purposes is a Customer, TCGLS is open to commercialization of either the catalyst(s) or the polymerization or both with other catalyst and polyolefin producers / licensors keeping in view direct or indirect benefit to the Indian petrochemical and polyolefin industry.

Background and motivation (not exceeding 500 words)

Metallocenes are often termed as single site catalysts (SSC) due to well defined structure of the active site. Metallocene has several advantages such as high productivity, narrow MWD, improved co-monomer efficiency, tailor made properties. We will use these unique properties of metallocenes to develop LLDPE to desired architecture and properties.

Structural superiority of the metallocene catalyzed ethylene copolymers:

Metallocene technology allows for the production of polyolefin copolymers with great precision over the polymer microstructure such as: up to 20% Co-monomer incorporation (giving much higher flexibility in terms of the end properties of the polymer), Uniform co-monomer distribution (sharper melting point (95C) compared to ZN-LLDPEs (120-130C), important for heat seal packaging), Long chain branching (LCB, length of the branch >40 Carbon, better melt rheology of the polymer) [1-12].

Motivation:

Reactor grade LLDPE with LCB microstructure, which currently is the most interesting category within the m-LLD family due to its modified rheology, has been delivered by the Ti based "Insite" constrained geometry catalyst (CGC) platform of Dow Chemical, a silicon-bridged mono-cyclopentadiene (mono-Cp)/amine catalyst, wherein the Bite Angle around the metal centre is large enough to accommodate access of very large macro-monomer.

Current proposal derives direct motivation from the CGC and intends to create innovative and non-infringing design around, to develop indigenous catalyst system and achieve controlled LCB along with high co-monomer incorporation and uniform co-monomer distribution, by replacing the amine ligand, the silicon bridge and the substituents with alternatives, even going beyond metallocene and replacing the Cp. The next critical requirement for the production of such LLDPE is the selective (exclusive) trimerization of ethylene to deliver the co-monomer 1-Hexene. It was first reported way back in 1967 (Union Carbide) during ethylene polymerization using Cr tris(2-ethylhexanoate) with partially hydrolyzed triisobutylaluminum (TIBAL).

However, the real breakthrough came with the discovery of Phillips trimerization catalyst, Cr ligated by a substituted pyrrole. Till date, this is the only catalyst used commercially for the selective trimerization of ethylene, and the first commercial plant for 1-hexene was operationalized (47000 TPA) by Qatar Chemical Company (2003). Other processes such as SHOP, Gulf/CP and Ineos exhibit Poisson/Schulz-Flory distribution of oligomers, which are then fractionated to produce α -olefins, thereby CAPEX and OPEX intensive. Ever since a lot of innovations have taken place wherein several families of ligands were reported for ethylene trimerization, such as Pyrrole, Phosphine, tridentate Phosphine type (P-P-P), Diphosphino amine type (P-N-P), Sulfur, tridentate NNN type, several bidentate ligands such as aminopyridyl, diphenylphosphino and dicyclohexylphosphino pyridyl (BP chemicals), pyridyl-thioether, diphosphine – all for Cr metal complex.

The most recent trend in the field of exclusive ethylene trimerization are the Cp/arene type (Hessen and coworkers), Si-bridged Cp/arene (Sumitomo), other bridged and non-bridged Cp/thio, Cp/oxo, phenoxy/imino type, and methoxy/oxo type bidentate ligands – all with the Ti metal centre.

Current project derives direct motivation from these latest motifs with Ti metal centre and seeks to create innovative and non-infringing design arounds, to develop indigenous trimerization catalyst and also, going beyond Ti, test some of the effective designs with Zr, for relative cost effectiveness.

If either the Ti or the Zr metal platform works for both on-purpose 1-Hexene production and the copolymerization, the project would help develop a seamless technology from ethylene to Hexene and LLDPE.

Project outcomes (please list specific objectives): *The project should address a specific need of the industry/industries and there should be clear expected outcomes from the project. It is expected that joint patents will result from this project.*

Firstly the project will develop indigenous catalyst for both on-purpose 1-hexene and LLDPE production, either as know-how or for commercial production. Catalyst developed from this project can be produced by transferring know-how to either known catalyst vendors/licensors or newly developed vendor, depending on the need of the petrochemical entity.

The project, when taken to commercial scale, will help to provide indigenous catalyst and technology for and LLDPE production in the existing 1-butene LLDPE plant with minimal hardware changes, to HPL in particular and the Indian petrochemical and polymer industry in general.

LLDPE developed out of this project would gain application in the premium packaging, thermoforming, molding etc. grades, vis-à-vis existing low end, 1-butene based LLDPE available across the Indian petrochemical sector, which many a time needs downstream blending of low density polyethylene (LDPE) to attain right rheology.

The know-how developed on the catalyst and polymerization should be expected to generate Intellectual Property (IP) jointly/appropriately by the IIT and TCGLS and about 4 to 5 patents are expected with further filing in appropriate jurisdictions. Certain characterization and reaction studies may also constitute manuscripts for quality academic publication, which will be decided after protecting the IP.

Scope (not exceeding 1500 words): *The scope should clearly lay out the contributions of the academic partner and the industry partner.*

Catalyst for Ethylene-Hexene copolymerization to produce LLDPE:

Current proposal derives direct motivation from the Dow's "Insite" CGC platform and intends to create innovative and non-infringing design around, to develop indigenous catalyst system and achieve controlled LCB for advanced rheology, along with high co-monomer incorporation and uniform co-monomer distribution.

After sufficient due diligence on the prior art and background Intellectual Property to understand novelty and encumbrance scenario, the research will investigate the effects on chain microstructure, co-monomer incorporation and distribution in the product LLDPE polymer, by:

- replacing the amine with other ligand centers, including but not limited to oxo, phenoxy and methoxy (subject to prior art, IP analysis and design)
- replacing the silicon bridge with other bridges, including but not limited to phenyl, cyclohexyl, substituted carbonyl, to alter the bite angle around metal centre (subject to prior art, IP analysis and design screening)
- replacing the substituents with alternatives to alter the bulk and angle of the bridge and the bite angle (subject to prior art, IP analysis and design screening)
- going beyond metallocene and replacing the Cp with some of the above-mentioned ligands, to provide post-metallocene catalysts (subject to prior art, IP analysis and design screening)
- investigate effect of hydrolyzed and un-hydrolyzed MAO / boron based co-catalysts as appropriate, on the productivity
- incorporating Zr metal centre in some of the effective structures from above, in place of Ti

Catalyst for exclusive & selective trimerization of ethylene to produce 1-Hexene:

The most recent trend in the field of exclusive ethylene trimerization are the Cp/arene type [13-15], Si-bridged Cp/arene type [16], other bridged and un-bridged Cp/thio, Cp/oxo, phenoxy/imino type, and methoxy/oxo type bidentate ligands – all with the Ti metal centre [17-19].

After sufficient due diligence on the prior art and background Intellectual Property to understand novelty and encumbrance scenario, the research will investigate the effect on yield, selectivity and molecular weight distribution of the product 1-Hexene of similar motifs, by:

- designing bidentate combinations of above few ligand types, with or without Cp (subject to prior art, IP analysis and design screening)
- examining P-P-P, P-N-P and N-N-N tridentate ligand systems with Ti, if required with the help of hydrolyzed or un-hydrolyzed TEAL / TIBAL / MAO / boron based co-catalysts as appropriate for the purpose of productivity (subject to prior art, IP analysis and design screening)
- incorporating Zr metal centre in some of the effective structures from above, in place of Ti

Heterogenization of the LLDPE copolymerization catalyst:

The copolymerization catalyst will be supported primarily on silica and the following effects shall be investigated [20]:

- type of silica support
- slip recipe to enhance fluidization (though activity will be evaluated in slurry polymerization in the lab scale, yet the pilot and commercial production is on fluidized bed)
- binder recipe to arrest attrition, and
- anti-static recipe to minimize static charge generation, which would otherwise promote catalyst sticking and fouling (known to be one of the most critical reason for failure, so far)

Experimental and theoretical studies on process scale up:

Such studies shall be conducted under the guidance and advice of appropriate process consultant entity or organization, preferably at the infrastructure. Both IIT and TCGLS shall be performing a coordinating and assimilating role, depending on bandwidth.