

**PART – I**

**SYNTHESIS, CHARACTERIZATION AND VISCOSITY STUDIES OF HOMO AND  
COPOLYMER OF METHYL METHACRYLATE AND EVALUATION  
OF THEIR POUR POINT PROPERTIES IN DIFFERENT  
LUBRICATING OILS (BASE STOCKS)**

## CHAPTER-I

### 1.1 A BRIEF REVIEW OF THE PRESENT INVESTIGATION

#### 1.1.1 Introduction

Lubricating oil (lube oil), commonly known as base oil or base stock, is the basic building block of a lubricant. They are complex mixture of paraffinic, aromatic and naphthenic hydrocarbons with molecular weights ranging from medium to high values, which produce oils with desirable viscosities, densities and distillation curves.

The quality of base oils is determined by their olefinic, nitrogenated and sulfured compound contents. This is determined by the refining process which undergoes in its cleaning and removing of impurities. In order to meet composition specifications, these oils are submitted to the hydro treatment (HDT) process before addition of other compounds for commercial production. This process is characterized by the use of operational conditions of low or medium severity so that aromatic distribution is not seriously affected and sulfur compounds are not completely removed.

Wax-bearing lubricating oils are known to set to a semi-plastic mass on cooling below the temperature of the crystallization point of the wax contained in the lubricating oil. At this temperature paraffinic wax forms network of wax crystals and prevents the oil on flowing. The point at which the oil stops flowing is known as pour point of the lube oil which may be defined as the temperature at which the oil sample is no longer considered to flow when subjected to the standardized schedule of quiescent cooling prescribed by ASTM D97-47. The wax networks will also lead to an increase in oil viscosity. The increase in viscosity is generally temporary as a normal internal combustion engine can generate sufficient shear to disrupt the wax networks and allow the oil to flow. However, it should be emphasized that while the physical turning or cranking of the engine is usually unimpeded, the temporary disruption in the oil flow can lead to an increase in bearing wear. Studies have indicated that the amount of wax needed to prevent flow or gel for oil is quite small. Approximately 2% precipitated wax will gel middle distillates, and a similar amount is needed for lubricating oils. This problem presents a substantial disadvantage in the use of lubricating oils by the

petroleum industry. Dewaxing of oil improves the pour point, but this is an expensive procedure. Usually, the procedure is to dewax oil to a certain temperature and then add pour point depressants to improve the low temperature properties. However, at the lower temperature, the same amount of wax will still separate.

The pour point depressants do not make the wax more soluble in oil; they function rather by disrupting or preventing the formation of the waxy network. As little as 0.2 wt. % of a good pour point depressant can lower the pour point of the paraffinic oil or lubricating composition by 30-35<sup>0</sup>C.

Many different types of pour point depressants have been used in the prior art [1]. Previously used pour point depressants are predominantly oligomers having molecular weights of 1,000 to 10,000, or polymers which have molecular weights greater than 10,000. The earlier pour point depressants were either alkylated aromatic polymers or comb polymers. Comb polymers characteristically have long alkyl chains attached to the backbone of the polymer, with the alkyl groups being of different carbon chain lengths. The mechanism of action for pour point depressants has been the subject of much interest. Early indications were that alkylated aromatic compounds function as pour point depressants by coating the surface of the wax crystals and preventing further growth. More recently, however, it appears that the pour point depressants are either absorbed into the face of the wax crystal if the pour point depressant is an alkyl aromatic or co-crystallize with the wax crystal if it is comb polymer. Thus, crystal growth is not prohibited; it is simply directed or channeled along different routes. Light microscopy suggests that wax crystals are typically thin plates or blades, and when a pour point depressant is added to the system, those crystals are smaller and more branched, and thus the pour point depressant may disrupt or redirect crystal growth from different directions into a single direction, and bulkier crystals will be formed. These crystals then can form networks only at much lower temperatures which results in a lower pour point.

The observation of the previous researchers in concord with the present line of investigation is being presented, in a selective manner, in the following paragraphs.

The first formal reports of the action of pour point depressant (PPD) was made by Zimmer, Davis and Frolich [2] following the invention of paraflow by Davis [3]. Ruehrwein [4] reported a certain specificity of action for n-alkyl poly(methacrylate) in the series dodecyl, tetradecyl, hexadecyl and octadecyl. They reported that the longer alkyl polymers are effective in depressing the pour point of the high pour oils while the shorter alkyl polymers are effective on the lower temperature pour oils. Later on, with the development of engine and transmission technologies several types of polymeric products have been prepared and treated as pour point depressant for lube oil and similar oils. Some of them [5-8] are listed below.

- 1) Copolymer of styrene-maleic anhydride ester containing 20-22 carbons.
- 2) Copolymer of maleic anhydride and vinylmethyl ether esterified with alcohol of different chain lengths.
- 3) Mixed alkyl esters made by reacting two or more certain monohydric alcohols with inter-polymer which contain units derived from  $\alpha$ ,  $\beta$  unsaturated dicarboxylic acids or their derivatives and vinyl aromatic monomers having up to 12 carbon chains .
- 4) Copolymer of alkyl acrylates and 4-vinyl pyridine
- 5) Poly(alkyl acrylates) having C-20 to C-24 alkyl chain.
- 6) Alkyl naphthalenes.

In a recent paper Azim et al [9] have reported the synthesis of some polymeric additive based on styrene- maleic anhydride copolymer as multifunctional [Viscosity Modifier (VM), Pour Point Depressant (PPD), Detergent-dispersant] additives for lube oil.

Copolymers of maleic anhydride and vinyl acetate (VA) with different esters of acrylic acid were found to act as a PPD and VM. It was found that the efficiency of the prepared compounds as PPD increases with decreasing the concentration of the prepared polymers, increasing the chain length of alkyl groups and increases with decreasing the molecular weight. [10]. I.M. El- Gamel [11] has reported the synthesis of methacrylate - C-18  $\alpha$ -olefin copolymer as a potential PPD for waxy residue fuel oil and concluded that polymeric structure with long side chain of average 21 carbons have the potential to decrease the pour point of the oil. In a recent paper [12] Rasha has reported a novel PPD based on maleic anhydride -acrylates terpolymers.

N.S.Ahmed et al [13] has reported the synthesis of multifunctional lubricating oil additives based on polyalkyl polyamines which has PPD properties in lube oil, they claimed.

Commercially a line of poly(methacrylate) based pour point depressants are in use now a days such as, 'Acryloid' from the Rohm and Haas Company, 'TLA' followed by a numerical suffix or 'TC' followed by a numerical suffix from Texaco. There has also been a substantial patent activity concerned with pour point depressants which comprise poly(methacrylate) compositions. Thus U. S. Patent no. 3,607,749 and 4,203,854 disclosed poly(methacrylate) as viscosity index improvers, but without any data as to their low temperature performance.

U.S. Patent no. 3,598,736 disclosed the addition of small amounts of oil soluble copolymers of polymethacrylates (wherein the alkyl side chain contains from 10 to 20 carbon atoms with average of between 13.8 and 14.8 carbon atoms) to lubricating oils to reduce the pour point. Patent No. 3,679,644 (U.S) also reported the similar work.

U.S. Patent no. 4,073,738 has claimed the use of alkyl acrylate or alkyl methacrylate, wherein the alkyl group side chain can have from 8 to 30 carbon atoms and preferably from 8 to 22 carbon atoms, as a pour point depressant in lube oil.

U. S. Patent No. 4,088,589 disclosed a combination of pour point depressants of which one can be an oil soluble polymer of an alkyl acrylate or methacrylate which contains a side chain comprising 10 to 18 carbon atoms in the alkyl group.

U. S. Patent No. 2,655,479 of Munday et al has directed to polyester pour depressants and is particularly concerned with average side chain length of acrylate polymer pour depressants. They have claimed that homopolymers are not good pour point depressants but that copolymers are generally good pour point depressants. U. S. Patent 3,598,737 has disclosed lubricant compositions which contain copolymers of acrylate esters which are said to improve various characteristics including pour point. This patent states that the average number of carbon atoms should be at least 12.5 to 14.3.

U. S. Patent No. 3,897,353 disclosed oil compositions comprising lubricating oil and a pour point depressant which can be an alkyl methacrylate. These acrylates may be made from monomers wherein the alkyl portion of the ester or the side chain has from 12 to 18 carbon atoms and includes mixtures. However, the polymers of this patent are made from nitrogen- containing monomers.

From the above literature work the author has found some discrete work on the methacrylate chemistry functioning as a pour point depressant when added to lube oil and no systematic study in this direction has so far been carried out. Thus it was felt necessary to undertake a systematic study towards the synthesis and characterization of homo and copolymer of methyl methacrylate and evaluation of their pour point properties in different base stocks. Viscometric studies were also included in the investigation with the anticipation that it may put some light towards the morphological features of the additives in a solvent.