

PART II

**SYNTHESIS, CHARACTERIZATION, VISCOSITY ANALYSIS OF
HOMOPOLYMER OF METHYL METHACRYLATE AND COPOLYMERS
OF METHYL METHACRYLATE WITH STYRENE AND 1-DECENE AND
COMPARATIVE PERFORMANCE EVALUATION OF THESE POLYMERS
AS POUR POINT DEPRESSANT (PPD) AND VISCOSITY INDEX
IMPROVERS (VII) IN LUBRICATING OILS.**

CHAPTER I

1.1 A BRIEF REVIEW OF THE PRESENT INVESTIGATION

Base fluids mineral oil generally cannot satisfy the requirements of high performance lubricants without using the benefit of modern additive technology. Additives are synthetic chemical substances that can improve lots of different parameters of lubricants. They can boost existing properties; suppress undesirable properties in the base fluids. They can assist each other (synergism) or they can lead to antagonistic effects. Some additives are multifunctional products that decrease the possibility of additives interfering with each other negatively. Additives are used to (a) reduce the oxidative or thermal degradation of an oil, (b) to lessen the deposition of harmful deposits on lubricated parts, (c) to minimize rust and corrosion, (d) to control frictional properties, and (e) to reduce wear. They are also employed to alter purely physical properties of oil such as viscosity / viscosity temperature relationship known as viscosity modifier (VM) or viscosity index improver (VII) and also to improve the low temperature flow properties of the lube oil that is pour point depressant (PPD).

One important feature of an additive is that it should be effective in small quantities. Another important feature is that the additive must not produce unwanted by-products with its use in lubricating oil. An additive should also ideally perform more than one function so that fewer different additives have to be blended into the lubricating oil. Effectiveness in all viscosities and being liquid for ease of use are also desirable attributes in an additive.

A challenge for oil formulators is to find polymers that may improve high temperature viscosity performance as well as low temperature performance such as cold engine starting performance. These attributes, among others, can cause performance tradeoffs with respect to given polymer additives wherein an improvement in one way can be offset by reduced performance in another. Additionally, there is always a commercial incentive to have the polymer be effective at the lowest reasonable concentrations in order to minimize the cost of a given engine oil product or additive.

An enormous research has been devoted to the synthesis, technology and applications of different lube oil additives. Technology has successfully concerned itself with the development of lubricating oil additives which improve the viscosity

index of lubricating oils and additionally have good thickening, dispersing, and detergents effects together with a good protective effect against wear. Further critical points are the effect on the pour point as well as the shear stability of the lubricating oil additives. At the same time, mixtures thereof with mineral oils must give stable systems.

Additives for the future lubricants will be required to maintain oil consumption control over the life of the equipment while providing a high level of thermal stability and enhancing low temperature fluidity. With respect to many applications of lubricating oils, it is desirable that viscosity changes of lubricating oil be relatively small within the temperature change of use and with particular respect to the engine from cold starting up to hot running conditions. Lubricating oil and hydraulic fluids showing smaller changes in viscosity with temperature are desired for many applications. Such oils permit easy starting of cold mechanisms and assure both rapid circulation of the oil to moving parts and an adequate viscosity at maximum operating temperature [1].

A brief introduction of PPD and VII has already been presented in **Chapter I** of **Part I**.

The most extensively used flow improvers (PPD) for fuel oils are ethylene-vinyl acetate copolymers [2-4], the alkyl ester of unsaturated carboxylic acid-olefin copolymers [5-6], and the maleic anhydride alkyl ester of unsaturated carboxylic acid copolymers [7-8].

On the other hand some of the polymers generally used commercially as VII, and known to possess certain inherent advantages and disadvantages in performance, are- (i) Poly isobutylene (PIBs), (ii) Hydro-generated Styrene - isoprene copolymers, (iii) Olefin copolymers (OCP); e.g. Ethylene- propylene copolymer, (IV) Esters of styrene- maleic anhydride copolymers and (v) Poly(alkyl methacrylates) (PAMA).

Polymethacrylate (PMA) viscosity index improvers (VII's) are well known in the lubricating industry. Many attempts have been made to produce PMA VII's that have the desired balance of high temperature and low temperature viscometrics, as well as the required shear stability for a given application.

Polymethacrylates have been known for a long time as lubricating oil additives and are used on a large technical scale. In the last few years the more economical polyolefins have found increasing significance for the same purposes.

Both classes of products show advantages and disadvantages: polymethacrylates are characterized by a good effect from the point of view of the viscosity-temperature relationship of the oil improved therewith, and, when used in sufficiently high concentration, show an outstanding protective effect against wear. Further, they lower the pour point of lubricating oil. On the other hand, the treating costs for these products are comparatively high. This concept is to be understood as meaning the costs required for achieving a desired effect. Polyolefins bring about the same thickening of oil as do polymethacrylates, even already in clearly smaller concentrations, but polyolefins do not improve the pour point. In order to achieve an improvement in the pour point, lubricating oil additives comprising polyolefins must have added there to special pour point improvers such as chlorination products of wax and naphthalene, polyalkylmethacrylates, copolymers of alkylaminoalkylmethacrylates, and polyalkylacrylates. Nevertheless, the decrease in the pour point by the addition of pour point improvers encounters difficulties with certain polyolefins, particularly those which tend to form associates.

Olefin copolymers (or OCP) used as viscosity index improvers: conventionally comprise copolymers of ethylene, propylene and optionally, a diene. Small polymeric side chains do not exert a substantial viscosity modifying effect in oil. Polymerized propylene has one methyl branch for every two backbone carbon atoms. Ethylene polymer is substantially straight chained. Therefore, at a constant amount of polymer in oil (treat rate), an OCP having a higher ethylene content will display an increased high temperature thickening effect (thickening efficiency, or TE). However, polymer chains having long ethylene sequences have a more crystalline polymer structure. Crystalline polymers are less oil soluble than amorphous polymers and as a result, the OCP can drop out of the oil, causing the plugging of engine filters (and the loss of the viscosity modifying effect). Further, OCPs having substantial crystalline segments have been found, again primarily at low temperatures, to interact with waxes in the oil, and other OCP chains, which results in uncontrollable increases in low temperature viscosity and, in extreme cases, the gelling of the lubricating oil. These problems have been found to manifest in Ziegler Natta polymerized OCPs containing greater than about 60 wt. % ethylene (herein after referred to as "high ethylene content OCPs").

Due to their molecular architecture, star polymers are known to provide improved shear stability compared to OCPs. VI improvers that are star polymers made

by hydrogenation of anionically polymerized isoprene are commercially available. Anionic polymerization results in a relatively low molecular weight distribution (M_w/M_n). Hydrogenation results in alternating ethylene/propylene units having a composition comparable to a polymer derived from 40 wt. % ethylene and 60 wt. % propylene. These VI improvers provide excellent shear stability, good solubility and excellent cold temperature properties. However, improvements in the balance between the thickening efficiency and shear stability of star polymers remain possible.

U.S. Patent No. 4,116,917 exemplifies certain star polymers comprising hydrogenated poly(butadiene/isoprene) tapered arms containing about 44.3 wt. % polymer derived from butadiene. Since butadiene initially reacts faster than isoprene when anionic polymerization is initiated with secondary butyllithium (the process described in the patent), a polybutadiene block is first formed. As the butadiene concentration is lowered through polymerization, isoprene begins to add to the living polymer so that, when the polymerization reaction is complete, the chain is made up of a polybutadiene block, a tapered segment containing both butadiene and isoprene addition product, and a polyisoprene block resulting in a living tapered polymer chains that, when coupled with divinylbenzene, produce a star polymer having a polybutadiene block positioned distal from the divinylbenzene-coupled core. The long ethylene sequences of these external hydrogenated polybutadiene blocks were found to cause the same low temperature performance problems associated with high ethylene content OCPs.

To provide an improvement in thickening efficiency while maintaining low temperature performance, U.S. Patent No. 5,460,739 suggests star polymers comprising triblock copolymer arms of hydrogenated polyisoprene/polybutadiene/polyisoprene. The hydrogenated polybutadiene block provides an increased ethylene content, which improves thickening efficiency. The patent suggests that, by placing the hydrogenated polybutadiene block more proximal to the nucleus, the adverse effect on low temperature properties could be minimized. Such polymers were found to provide improved low temperature properties relative to the tapered arm polymers of U.S. Patent No. 4,116,917. However, when such polymers were provided with a hydrogenated polybutadiene block of a size sufficient to provide a credit in thickening efficiency, a debit in low temperature performance remained relative to the pure polyisoprene polymers.

Therefore, among the OCPs, there remains a need for improved VI improvers

that are capable of providing a good viscosity temperature relationship, without the associated reduction in solubility and cold temperature performance.

I. M. El-Gamel [4] has reported the synthesis of methacrylate - C-18 α -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 [9] Rasha has reported a novel PPD based on maleic anhydride -acrylates terpolymers.

N. S. Ahmed et al [10] 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 531556 A disclosed a method for making a lubricating oil multifunctional additive which comprises a polyalkyl methacrylates and hydrogenated block copolymers comprising a conjugated diene having 4 to 6 carbon atoms and styrene.

U.S. Patent no. 3,598,736 disclosed the addition of small amounts of oil soluble copolymers of poly(methacrylates) (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. 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.

The invention in U.S. patent 3,252,949 relates to highly syndiotactic oil-soluble methacrylate polymers having superior viscosity index improving properties when incorporated in mineral and synthetic oils (functional fluids) and to compositions of these polymers in functional fluids. These polymers also have dispersancy properties by incorporating a minor amount of appropriate co-monomer during polymerisation to give the polymer dispersancy properties or by treatment after the formation of the polymer.

Conventional methacrylate polymers useful as viscosity index improvers in functional fluids are described in U.S. patent 2,091,627. These polymers are made by free radical polymerization at about 70⁰ F or above.

U.S. Patent No. 4,089,794 discloses ethylene copolymers derived from ethylene and one or more C₃ to C₈ alphaolefin solution grafted with an ethylenically-unsaturated carboxylic acid material followed by a reaction with a polyfunctional material reactive with carboxyl groups, such as a polyamine, a polyol, or a hydroxyamine which reaction product is useful as a sludge and varnish control additive in lubricating oils.

U.S. Patent No. 4,357,250 discloses a reaction product of a copolymer and an olefin carboxylic acid via the "ene" reaction followed by a reaction with a monoaminepolyamine mixture

U.S. Patent No. 4,382,007 discloses a dispersant-VI improver prepared by reacting a polyamine-derived dispersant with an oxidized ethylene-propylene polymer or an ethylene-propylene diene terpolymer.

U.S. Patent No. 4,320,019 discloses a multipurpose lubricating additive prepared by the reaction of an interpolymer of ethylene and a C3-C8 alpha-monoolefin with an olefinic carboxylic acid acylating agent to form an acylating reaction intermediate which is then reacted with an amine.

U.S. Patent No. 4,144,181 discloses polymer additives for fuels and lubricants comprising a grafted ethylene copolymer reacted with a polyamine, polyol or hydroxyamine and finally reacted with an alkaryl sulfonic acid.

U.S. Patent No. 5,932,525 teaches multi-grade lubricating oils comprising a low saturate base stock, less than three mass percent of an ash less dispersant and a viscosity modifier.

U.S. Patent No. 5,427,702 discloses mixed ethylene alphaolefin copolymer multifunctional viscosity modifiers.

U.S. Patent No. 4,863,623 teaches multifunctional olefin copolymer VI improvers.

W.O. Patent No. 2007042560 A1 discloses a multifunctional lubricating oil composition having a polymethacrylate additive.

W.O. Patent No. 2013055481 A1 discloses multifunctional polyalphaolefin high efficiency engine oil composition for lube oils.

W.O. Patent No. 2013055483 A1 discloses preparation of mixed polyalphaolefin high efficiency engine oil additive composition for lube oils.

U.S. Patent No. 20100292424 A1 discloses an improved process which employs mixed alpha-olefins as feed over activated metallocene catalyst systems to provide essentially random liquid polymers particularly useful in lubricant components or as functional fluids.

U.S. Patent No. 8293689 B2 provides a lubricating composition containing an oil of lubricating viscosity and methacrylate polymer with pendant groups. The invention further provides for a method of controlling viscosity index by supplying to an oil of lubricating viscosity the polymer with pendant groups.

U.S. Patent No. 8163683 B2 discloses a pour point depressant for lubricants comprising: a mixture of an alkyl(meth)acrylate polymer (A) that is composed of an alkyl(meth)acrylate containing alkyl groups having an average carbon number (C_A) of 12.5 to 13.8, and an alkyl(meth)acrylate polymer (B) that is composed of an alkyl(meth)acrylate containing alkyl groups having an average carbon number (C_B) of 13.9 to 15.5.

Thus from above literature survey it has been observed that either with methacrylate (or acrylate) polymers/copolymers or olefin polymers/copolymers, one could not hold the both PPD and VII properties satisfactorily. So there are still a limitation with the development of multifunctional additives comprising both PPD and VII properties.

The idea of combining products of both classes of polymers, in order thereby to produce lubricating oil additives with improved properties, was obvious. Industry awaits the preparation of lubricating oil additives in a liquid (oil-based) form and with the highest possible absolute polymer content.

In the present work multifunctional additives were prepared via the preparation of methyl methacrylate (MMA) homopolymer, methyl methacrylate - styrene copolymers and methyl methacrylate - 1-decene copolymers with different

percentage. Comparative characterization of these polymers and their evaluation as viscosity index improvers and pour point depressants were also carried out.

These compositions have the advantage of providing a better compromise between the various effects required of a viscosity additive: solubility, thickening power, selectivity, shearing strength and pour point.