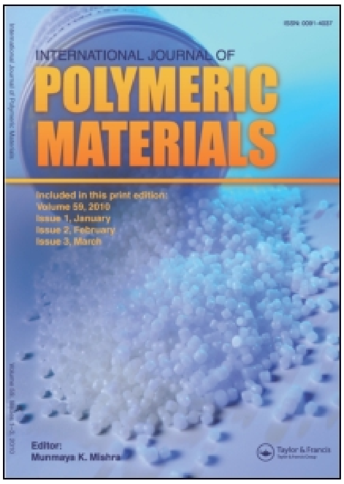

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Amal M. Nassar[a]; Nehal S. Ahmed[a]
[a] Department of Petroleum Applications, Egyptian Petroleum Research Institute, Nasr City, Cairo, Egypt

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The Behavior of α-Olefins Butyl Acrylate Copolymers as Viscosity Index Improvers and Pour Point Depressants for Lube Oil

Amal M. Nassar
Nehal S. Ahmed
Department of Petroleum Applications, Egyptian Petroleum Research Institute, Nasr City, Cairo, Egypt

A lubricant additive may be defined as a material that imparts a new and desirable property not originally present in the oil or reinforces a desirable property already possessed in some degree by the oil. These materials are normally more chemically reactive than the base oil. The additives are being used at various concentrations from a few parts per million to over 30%. A great deal of research is being done at present into the synthesis, technology, and applications of different lube oil additives. In the present work, polymeric additives were prepared by reaction of butyl acrylate with different α-olefins (octene, dodecene, tetradecene, and octadecene). The efficiency of the prepared copolymers as viscosity index improvers and pour point depressants for a base lube oil were studied. It was found that the efficiency as viscosity index improvers increases with increasing the concentration of the prepared copolymers and increasing the chain length of alkyl groups of the α-olefins, and the efficiency as pour point depressants increases with decreasing the concentration and decreasing the molecular weights of the prepared copolymers.

Keywords: acrylate copolymer, lube oil, lube oil additives, pour point depressants, viscosity index improvers

INTRODUCTION

Viscosity index, or VI, is an arbitrary number that indicates the resistance of a lubricant to viscosity change with temperature. The currently accepted viscosity index [1] calculated from the observed viscosities of lubricant at 100° and 210°F gives VT values ranging from

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Address correspondence to Nehal S. Ahmed, Department of Petroleum Applications, Egyptian Petroleum Research Institute, Nasr City, Cairo 11727, Egypt. E-mail: mynehal@yahoo.com

zero or negative values to values of 200 or more. The higher its VI values, the greater the resistance of a lubricant to thicken at low temperatures and thin out at high temperatures. An ideal lubricant for most purposes would possess the same viscosity at all temperatures. Viscosity index improvers are chemical that are added to lubricating oils to make them conform more closely to the ideal lubricant defined earlier. Although a few non-polymeric substances such as metallic soaps exhibit VI improving properties [2], all commercially important VI improvers today are oil soluble organic polymers. Suitable polymers exert a greater thickening effect on oil at high temperatures than they do at lower temperatures [3]. The end result of such selective thickening is that the oil suffers less viscosity change with changing temperature, that is its VI is raised. It has been proposed that selective thickening occurs because the polymer molecule assumes a compact, curled form in a poor solvent such as cold oil and an uncurled, high surface area form in a better solvent such as hot oil [4]. In the latter form, it is more highly solvated and exerts its maximum thickening effect on the oil. In order to constitute a good VI improving additive, a compound must not have only an advantageous effect on the viscosity index of fresh oil, it must also remain stable and satisfy its VI improving in an engine or other device in operation. It is also desirable that VI improving additive has an advantageous effect on the pour point of the lubricating oil into which it is incorporated or at the very least that it has no detrimental effect on the pour point depressors (i.e., the additives that are incorporated in lubricating oils for maintaining them fluid at low temperature).

Ever since lubricating oils were prepared from crude oils, refiners have experienced difficulty with congelation of these products at low temperatures. Part of the difficulty arises from a natural stiffening at low temperature of the hydrocarbons comprising the bulk of the oil. This type of congelation can be corrected quite easily by the use of a solvent such as kerosene to reduce the viscosity of the oil [5]. The remainder of the difficulty is not as simple to correct and arises from the crystallization at low temperatures of the paraffin wax present in almost all heavy mineral oil fractions. Upon crystallization this wax tends to form interlocking networks that adsorb oil and form a voluminous gel-like structure that restricts the flow or pour of the oil. Even though refining processes known as dewaxing have been developed to remove most of the paraffin from lubricating oil fractions, the small amount of wax remaining after dewaxing can cause serious trouble. Evan a small amount of wax can raise by tens of degrees Fahrenheit the temperature at which an oil will flow freely as measured by suitable “pour point” [6,7]. Because removal of the last traces of wax from oils is a difficult and costly matter other answers were sought by refiners. One of the first satisfactory solutions to the problem was provide by the additive industry in 1931 when a pour point depressant was developed. Since that time many effective pour point depressants have been developed by the additive industry. Certain high molecular weight polymers function by inhibiting the formation of a wax crystal structure that would prevent oil flow at low temperatures. Two general types of pour point depressant are used: (1) Alkyl aromatic polymers that adsorb on the wax crystals as they form, preventing them from growing and adhering to each other and (2) Polymethacrylates that cocrystallize with wax to prevent crystal growth.

The additives do not entirely prevent wax crystal growth, but rather lower the temperature at which a rigid structure is formed. Pour point depressants have found their largest volume use in crankcase oils and in gear oils.

The present work polymerizes butyl acrylate with different, types of α-olefins (octene, dodocene, tetradecene, and octadecene) and tests the products as viscosity index improvers and pour point depressants for lube oil.

EXPERIMENTAL

Preparation of Butyl Acrylate α-Olefin Copolymers

Four polymeric additives were prepared by free radical polymerization of butyl acrylate with four different α-olefins (octene, dodecene, tetradecene, and octadecen). The polymerization was carried out in a four neck found bottom flask equipped with a stirrer, efficient condenser, thermometer, and an inlet for the introduction of nitrogen.

The glass containers with 1 mole of butyl acrylate and 1 mole of α-olefin were thermostated at 70°C, the desired weight of initiator (benzoyl peroxide) was added (1 wt% of the reactant) in presence of toluene and the reaction maintained for 6 h. The copolymers were precipitated by pouring the reaction products into methanol. Thus the copolymers of butyl acrylate with octene (A) with dodecene (B), with tetradecene (c), and with octadecene (D) were prepared.

Determination of the Molecular Weights

The molecular weight of the prepared copolymers were determined by using Gel permeation chromatography (GPC), water 600 E.

Evaluation of the Prepared Compounds as Lube Oil Additives

As Viscosity Index Improvers

The prepared copolymers were evaluated as viscosity index improvers using a base oil (SAE 30) through the viscosity index test (VI) according to the ASTM D-2270-87. The kinematic viscosity of the oil contains the tested copolymer was determined at 40°C and 100°C. Different concentrations ranging between 0.0 and 3.0 wt% were used to study the effect of copolymer concentration on VI.

As Pour Point Depressants

The prepared compounds were evaluated as pour point depressants using a base oil (SAE 30) through the pour point test according to the ASTM D-97-87. The effect of additive concentration was investigated by using different concentrations. The instrument used for measuring the pour point was the Cold filter Plugging Point Automatic Tester (CFPPA-T), model 1sl CPP 97-2.

RESULTS AND DISCUSSION

Polymeric materials are generally considered useful as viscosification agents when dissolved in an appropriate solvent system. The major reason for viscosity enhancement is due to the very large dimensions of the individual polymer chain as compared to the dimension of the single solvent molecules. Any increase in the size of the polymer chain will produce a corresponding enhancement in the viscosity of the solution.

The way in which these additives function can be summarized very briefly. In effect, they perform two functions, that is, thickening, which merely increases fluid viscosity, and viscosity index (VI) improvement, which corresponds to limited thickening at ambient temperatures and a correspondingly greater thickening at elevated temperatures. This can be accomplished by utilizing a polymeric additive that is poorly solvated by the liquid at ambient temperatures. However, at elevated temperatures the polymer is more highly solvated such that the polymer expands and is a relatively more effective thickener [8].

The copolymerization of butyl acrylate with different α-olefins was carried out and the molecular weight of the polymers of butyl acrylate with octene (A), butyl acrylate with dodecene (B), butyl acrylate with tetradecene (c), and butyl acrylate with octadecene (D) were determined and given in Table 1, which indicates that the molecular

TABLE 1 The Mean Molecular Weights of the Prepared Copolymers

Copolymer designation	Mean mol. wt
A	8500
B	13000
C	16000
D	22000

weight increases by increasing the length of alkyl chain length of α-olefin.

Efficiency of the Prepared Copolymers as Viscosity Index Improvers for Lube Oil

The prepared copolymers were tested for their effectiveness as viscosity index improvers for a base oil (SAE 30) according the ASTM D-2270. In this respect, the kinematic viscosity of the oil containing different concentration of the prepared copolymers was determined at 40°C and 100°C.

Effect of Concentration of the Prepared Copolymer on V.I.

Different concentrations of the prepared additives (A–D) ranging between 0.00 and 3.0 wt% were used to study the effect of the additive concentration on VI. The data tabulated in Table 2 indicate that the VI increases with increasing concentration of the prepared additives in solution. Of course, increasing the concentration of the polymer leads to increased total volume of polymer random coils in the oil solution. Consequently a high concentration of polymer will impart a higher viscosity index than a low concentration of the same polymer [9–10].

TABLE 2 Dependence of V.I. on the Concentration of Additives (A–D)

	Viscosity in presence of			
Conc. wt%	A	B	C	D
3.0	99	104	110	128
2.0	92	96	100	114
1.0	92	94	97	102
0.5	90	92	93	95
0.25	88	89	90	90
0	93	93	93	93

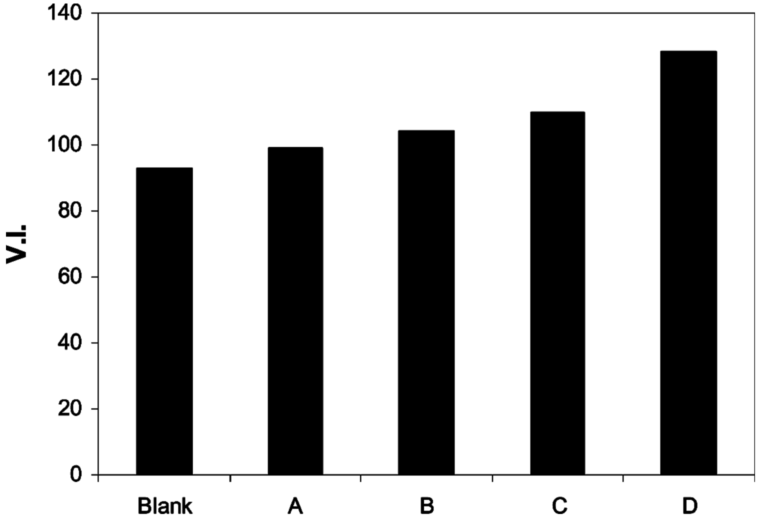

FIGURE 1 Effect of alkyl chain length of additives (A, B, C, and D) on viscosity index.

Effect of Alkyl Chain Length on V.I.

The α-olefin used in preparation are octene C_8, dodecene C_{12}, tetradecene C_{14}, and octadecene C_{18} so the effect change of α-olefin on the efficiency of the prepared copolymer as viscosity index improvers was studied. The results, given in Figure 1, indicate that by increasing the alkyl chain length of α-olefins from C_8 to C_{18} the efficiency of the prepared copolymers as viscosity index improvers increases [10–12]. This may be due to increasing the molecular weight of the polymers.

Efficiency of the Prepared Copolymers as Pour Point Depressants

The action of pour point depressants in the crankcase lubricant is very complex. Pour point depressants have no effect on the crystallization temperature or the number of crystals formed. The pour point depressants work by adsorption into the crystals being formed to redirect their crystal formation and by cocrystallization to form smaller more isotropic crystals and a higher solubility wax in the mixed crystals. The effectiveness of a pour point depressant depends on the chemical composition and structural characteristics of the polymer and the length of the alkyl side chain [13–14].

TABLE 3 Dependence of Pour Point on the Concentration of Additives (A–D)

	Pour point (°C) in presence of			
Conc. wt%	A	B	C	D
3.0	−4	−4	−4	−4
2.0	−10	−7	−7	−4
1.0	−16	−13	−10	−7
0.5	−19	−13	−10	−7
0.25	−19	−16	−13	−7
0	−4	−4	−4	−4

The Effect of Concentration

The prepared compounds (A, B, C, and D) were tested as pour point depressants (PPD). The experimental data grouped in Table 3 show that all the prepared compounds are effective as pour point depressants, and it was found that the efficiency of the prepared compounds as pour point depressant increases by decreasing the concentration of additives used. This is explained by the solvation power of the oil [15]. It is well understood that the solvation power of any solvent decreases with a decrease in the temperature and vice versa. This reduction in the solvation power becomes more obvious when the molecular weight of the solute and its concentration increases. As a result of this decrease in solvation power, the copolymer prepared from octadecene (D) has been precipitates or forms a gel and enhance the lateral crystal growth of the precipitated wax. The copolymer based on octene (A) is better PP depressants as compared with the other prepared copolymers.

Effect of Alkyl Chain Length

As the chain length of alkyl groups in α-olefin increases the pour point temperature enlarges (see Figure 2). This figure reveals that the PP temperature decreases as the chain length of alkyl group in α-olefin decreases. This is attributed to the enhanced solubility of the molecules having shorter branches. Thus the order of the efficiency of the prepared additives as pour point depressants is $A > B > C > D$. The data in Figure 2 reveal that the efficiency of the prepared additives as pour point depressants (more negative value) increases with decreasing molecular weight of the prepared compounds. This may be due to the effect of molecular weight of the prepared compounds, which reduces the adsorption of the additive molecule on the wax crystal.

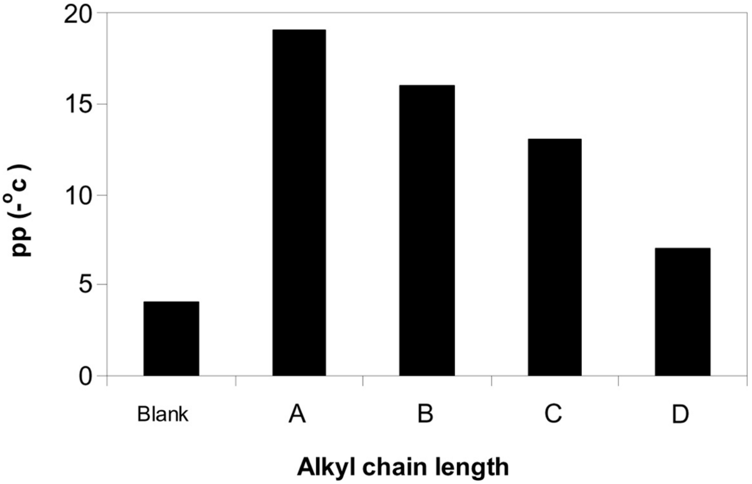

FIGURE 2 Effect of alkyl chain length of additives (A, B, C, and D) on pour point. Additive concentration is 0.25% wt.

CONCLUSIONS

The following conclusions may be derived from the results of this study:

- The efficiency of the prepared copolymers as viscosity index improvers increases with increasing concentration of the additives in the solution.
- The V.I. increases with increasing the chain length of alkyl group of α-olefins.
- The efficiency of the prepared copolymers as pour point depressants increases with decreasing the concentration of the additives and decreasing the chain length of the alkyl groups.

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